TRIPLE OXYGEN ISOTOPES IN LAKE WATERS, LACUSTRINE CARBONATES AND PEDOGENIC CARBONATES: AN INDICATOR FOR EVAPORATION

by
Haoyuan Ji

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Oxygen isotopic compositions of minerals and natural waters have been widely used in paleoclimatology and paleohydrology to infer climate parameters. However, $^{18}$O/$^{16}$O ratios alone are often very complicated to interpret because $^{18}$O/$^{16}$O ratios can be affected by temperature and topography as well as hydrological processes such as evaporation and precipitation. Deviations in $^{17}$O/$^{16}$O relative to $^{18}$O/$^{16}$O [often denoted as $\Delta^{17}$O = $\ln(\delta^{17}$O +1) - $\lambda\ln(\delta^{18}$O +1)] have been shown to be sensitive to evaporation due to the difference in isotopic fractionation exponent [$\theta = \ln(\delta^{17}$O +1) / $\ln(\delta^{18}$O +1)] between water-vapor equilibrium and vapor diffusion in the air. Thus, the triple oxygen isotope systems of minerals and natural waters may provide additional information on hydrologic processes that are not discernable from analysis of $^{18}$O/$^{16}$O ratios alone.

Chapter 2 of the thesis explores the possibility of using $\Delta^{17}$O in lake waters and lacustrine carbonates as an indicator for local evaporation. Samples were collected from salt lakes, freshwater lakes as well as their associated rivers in western USA. Triple oxygen isotope data of all samples were presented to show the variation of $\Delta^{17}$O under different hydrological and climatic scenarios. They are shown to be generally consistent with theoretical models adapted from the Craig-Gordon model. An open pan evaporation experiment was also conducted to study the effect of dissolved salt on triple oxygen isotopes in natural waters. Contrary to salt effect on $\delta^{18}$O, we did not observe significant salt effect on $\Delta^{17}$O.
Chapter 3 examines how triple oxygen isotopes in soil carbonates can be used to distinguish soil carbonate $\delta^{18}O$ which has been modified by significant evaporation. Soil carbonate samples from East Africa, USA and China were measured. Results show that most deep soil carbonates samples (>50cm) do not show significant deviation of $\Delta^{17}O$ from primary precipitation. Meanwhile, some shallow soil carbonates have different $\Delta^{17}O$ compared with primary precipitation due to evaporative modification. This is basically consistent with a theoretical model developed in this chapter which simulates triple oxygen isotopes profiles in drying soil columns.

The overall object of this thesis is to investigate the usage of triple oxygen isotopes in terrestrial environments, especially in soil carbonates and lacustrine carbonates, as an indicator for evaporation. This will be helpful to decouple the $\delta^{18}O$ variation caused by evaporative modification and other climatic factors and therefore to elucidate $\delta^{18}O$ recorded in carbonate minerals.

In addition, in an Appendix of this thesis, results from a series of heating experiments on dolomite samples were conduct to study $^{13}C$-$^{18}O$ bond reordering process in dolomite. The clumped isotope measurements show that the clumped isotope reordering progress within dolomite is much slower compared to previously reported results for calcite.
Primary Advisor:

Benjamin H. Passey, PhD, *Department of Earth and Planetary Sciences*

Second Reader:

Naomi E. Levin, PhD, *Department of Earth and Planetary Sciences*
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1. Introduction

In past decades, oxygen isotopes in natural waters and minerals have emerged to be a powerful tool in the study of both modern and ancient environments. The $^{18}$O/$^{16}$O ratio of natural waters is determined by hydrological cycle processes, recording information about evaporation, transport, mixing, condensation and precipitation (Urey et al. 1951; Clayton 1961; Craig 1961; Dansgaard 1964; Gat 1996). However, interpretations of $^{18}$O/$^{16}$O ratio in many natural systems are complicated because different climatic and hydrologic factors can affect oxygen isotope fractionations. For example, an increase of $^{18}$O/$^{16}$O ratio in benthic sediments throughout Earth’s history can be explained by the increase of $^{18}$O/$^{16}$O ratio in ocean water itself or higher fractionation factor caused by lower temperatures (Muehlenbachs 1998; Veizer et al. 1999; Cummins et al. 2014).

As an important terrestrial water reservoir, lake waters primarily originate from precipitation and then experience many other hydrological processes such as mixing and evaporation. The variation of $^{18}$O/$^{16}$O ratio in lacustrine systems including waters and precipitating carbonate minerals can provide insights into the hydrology and climate of lake basins (e.g. Dincer 1968; Gat 1995; Gibson et al. 2015). However, $^{18}$O/$^{16}$O ratios cannot tell us all information about the extent of evaporation in lake basins. Therefore, it is difficult to use $^{18}$O/$^{16}$O ratios alone to correctly and comprehensively reconstruct environmental and hydrological scenarios of lake basins.
Oxygen isotopic composition in soil carbonates, particularly deep carbonates (< 50 cm), are often used as an approximation of local primary precipitation assuming equilibrium has been reached in many fields such as paleoclimatology and paleoaltimetry (Cerling 1984; Quade et al. 1989; Cerling and Quade 1993). However, potential factors such as strong seasonal bias and evaporative modification recorded make it problematic to immediately consider them as an equivalent to mean annual primary precipitation without other supporting evidence (e.g. Quade et al. 2007; Breecker et al. 2009; Quade et al. 2013).

Therefore, it is necessary to develop a new tool to provide additional information in lacustrine and soil systems to solve problems mentioned above. Compared to the widely used $^{18}\text{O}/^{16}\text{O}$ ratio in terrestrial settings, the $^{17}\text{O}/^{16}\text{O}$ ratio is rarely used, partly due to relatively low concentration of corresponding $^{17}\text{O}$-bearing isotopologues in most natural settings. Therefore, measuring techniques for $^{17}\text{O}/^{16}\text{O}$ ratios in waters and minerals have long been not advanced enough to achieve sufficient precision. Before the 2000s, $^{17}\text{O}/^{16}\text{O}$ ratios were mostly used to investigate non-mass dependent processes, for example, in the stratosphere and in meteorites (e.g. Clayton et al. 1973; Thiemens et al. 1975; Luz and Barkan 1999). On the other hand, $^{17}\text{O}/^{16}\text{O}$ ratios were considered to carry little additional information because almost all terrestrial samples fall on a single line in $^{17}\text{O}$-$^{18}\text{O}$ graph which is defined as Terrestrial Fractionation Line (TFL, Clayton and Mayeda 1982). However, it has been shown that different terrestrial processes have different $^{17}\text{O}$-$^{18}\text{O}$ slopes as both theoretical calculation and laboratory measurements have progressed (Young et al. 2002; Barkan and Luz 2005; Barkan and Luz 2007). Many subsequent
researches therefore investigate the application of triple oxygen isotopes in many natural water systems such as ocean water, primary precipitation, tap water, and leaf water, to distinguish equilibrium and kinetic processes in hydrological processes (e.g. Landais et al. 2006, 2008, 2010, 2012; Luz and Barkan 2010; Li et al. 2015; Surma et al. 2015). These studies have shown that $^{17}\text{O}/^{16}\text{O}$ ratios, combined with traditional $^{18}\text{O}/^{16}\text{O}$ ratios, have great potential to be used as a new tool to indicate oxygen isotopic composition variation caused by kinetic process such as evaporation. However, the application of triple oxygen isotopes in carbonate minerals is still limited partly due to the lack of efficient measurement methods with high precision. This problem hindered the application of triple oxygen isotopes in paleoclimatology and paleohydrology since ancient water is very difficult to be well-preserved.

I started to study triple oxygen isotopes in lacustrine and soil carbonates right after Passey et al. (2014) introduced a new laboratory method with enough precision to determine $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ in carbonate minerals. This method has been successfully used in many terrestrial settings. In the following chapters, I’ll present triple oxygen isotope data from lake waters, lacustrine carbonates and soil carbonates. By providing new datasets, building theoretical models, and conducting laboratory experiments, this thesis aims to lay the foundation work to the application of triple oxygen isotopes in reconstructing paleoenvironmental conditions in terrestrial settings, specifically in lacustrine and soil systems.
1.1 References


2 Triple oxygen isotopes in lake waters and lacustrine carbonates: a proxy for evaporation and basin hydrology

Abstract
Evaporation leads to a deficit in the residual water of $\Delta^{17}\text{O}$, a measure of the departure of $^{17}\text{O}/^{16}\text{O}$ from a characteristic relationship with $^{18}\text{O}/^{16}\text{O}$. We investigate the potential of this property to help resolve local evaporative signatures from regional climatic signatures in the oxygen isotope compositions of lake waters and carbonates. We explore mass balance triple oxygen isotope models for flow-through and closed basin lakes, and we present new triple oxygen isotope data from waters and carbonates of rivers and lakes in the semiarid western United States. The data show a clear lowering of $\Delta^{17}\text{O}$ in closed basin lakes and freshwater lakes relative to their source rivers. There is variable agreement between model-predicted isotopic compositions and observed isotopic compositions when conventional assumptions are made about model parameters (e.g., atmospheric water vapor is in isotopic equilibrium with regional precipitation, diffusive fractionation factors are intermediate between open ocean and strictly non-turbulent conditions, and relative humidity = mean annual relative humidity). This suggests that for some lakes the isotopic composition of atmospheric water vapor is influenced by the lake water itself, the effective diffusive fraction factor is more similar to open-ocean values, relative humidity is more similar to seasonal minima, or a combination of these. We also investigate the effects of water salinity on the triple oxygen isotope evolution of evaporating pans of water in the laboratory, and find no significant effects relative to distilled water for the Na$^+$, K$^+$, Ca$^{++}$, and Mg$^{++}$ chloride solutions that we studied. We demonstrate how $\Delta^{17}\text{O}$ can be used in conjunction with reconstructed lake water $\delta^{18}\text{O}$ to improve estimates of the $\delta^{18}\text{O}$ values of primary (unevaporated) meteoric waters entering
the lake basin. In conclusion, we find that $\delta^{17}$O is a sensitive tracer of lake water evaporation.

2.1 Introduction

Oxygen isotope ratios in lake water are determined by the isotopic mass balance of water inputs (primary precipitation, river and stream inflows, groundwater inflow, and exchange with atmospheric vapor) and outputs (evaporation, river and stream outflows, groundwater infiltration). The ratio $^{18}R = ^{18}$O/$^{16}$O, typically denoted as $\delta^{18}$O, where $\delta^{18}$O = $^{18}$Rsample/$^{18}$Rstandard − 1, has been widely used to infer climatic, hydrological and tectonic information such as lake water balance (Dincer 1968; Gat 1995; Gibson et al. 2015) and paleoelevation (Garzione et al. 2000; Poage and Chamberlain 2001; Rowley and Garzione 2007). Likewise, $\delta^{18}$O values of lacustrine carbonates have been used to infer the $\delta^{18}$O of ambient lake water, given knowledge or estimates of the formation temperature of the carbonate (e.g., Huntington et al. 2010; Hren and Sheldon 2012), and assuming isotopic equilibrium between water and precipitated carbonate minerals (Talbot, 1990; Leng and Marshall, 2004). Inasmuch, $\delta^{18}$O analysis of lacustrine carbonates has been a useful tool to study the paleoclimatology and paleohydrology of lake basins.

However, the precise climatic and hydrological setting of a water body is usually not discernable by a single isotopic signature (Figure 2.1). In particular, $\delta^{18}$O varies widely in source precipitation, being affected by moisture source, temperature history along the moisture transport trajectory, mixing with preexisting atmospheric moisture, and other factors (e.g., Gat, 1996; Gibson and Edwards, 2002; Leng and Marshall, 2004). During
and subsequent to the actual precipitation event, the $\delta^{18}$O value can be further modified by evaporation and exchange with ambient vapor. Therefore, the $\delta^{18}$O value of lake waters reflects a host of factors relating to the pre-precipitation history of the water vapor (primarily a regional- to hemispheric- climatic signature), and to the syn- and post-precipitation history of the condensed water (primarily a local climate and hydrology signature). In the case of extant waters, the $^2$H/$^1$H ratio (or $\delta^2$H) is commonly used in conjunction with $\delta^{18}$O to help parse out these factors (Craig 1961; Dansgaard 1964; Gat, 1996; Gibson et al., 2008; Gibson et al. 2015). A linear correlation exists between $\delta^2$H and $\delta^{18}$O of global precipitation [the Global Meteoric Water Line (GMWL)], where $\delta D \approx 8 \times \delta^{18}$O+10 (Craig, 1961). Kinetic fractionation during evaporation leads to a deviation of the isotopic composition of lake water from the GMWL (defined as d-excess, Dansgaard, 1964), such that evaporated waters can be identified on a plot of $\delta^2$H versus $\delta^{18}$O.

However, the use of the d-excess method in paleoclimatology and paleohydrology is limited because hydrogen and oxygen only co-occur in a subset of authigenic minerals (e.g., clay minerals), because these minerals may have isotopic compositions that reflect sources other than lake waters, and because isotopic compositions of these minerals, particularly $\delta^2$H, can be susceptible to modification by post-depositional reactions (Taylor, 1974; Dilles et. al., 1992). These difficulties motivate the search for a new proxy to reconstruct the paleoclimate and paleohydrology of lake basins.
Figure 2.1 Schematic diagram showing three different hydrological scenarios viewed in oxygen isotope space. Scenario 1: Primary precipitation with $\delta^{18}$O = -5‰; Scenario 2: Closed basin under a relative humidity of 60% and with input water of -15‰; Scenario 3: Through-flow lake under a relative humidity of 80%, with evaporation to input ratio ($X_E$) of 0.5 and with input water of -10‰. (A) These three scenarios are not discernable using $\delta^{18}$O; (B) By introducing $\Delta^{17}$O as an additional variable, these three hydrological scenarios can be distinguished.
The other stable oxygen isotope, $^{17}\text{O}$, is less commonly used, partly because $^{17}\text{O}/^{16}\text{O}$ in Earth surface materials has long been assumed to carry little additional information beyond that provided by $^{18}\text{O}/^{16}\text{O}$, given the principle of mass-dependent fractionation ($\delta^{17}\text{O} = \theta \delta^{18}\text{O}$; notation is described in Section 2). However, improvements in analytical precision and in theoretical calculations have shown that there is a range of mass-dependent behaviors (Young et al., 2002). For example, Barkan and Luz (2007) demonstrated that diffusion of water vapor through air carries a $\theta$ value of 0.5185, while equilibrium isotope exchange between liquid water and water vapor carries a value of 0.529 (Barkan and Luz, 2005). Published data show clear evidence of a negative correlation between the deviation from the equilibrium line and relative humidity for evaporating leaf water (Landais et al., 2006) and evaporating lake, pond, and laboratory waters (Surma et al., 2015). Thus, the extent of deviation of $^{17}\text{O}/^{16}\text{O}$ from the equilibrium fractionation line could be a useful tool to investigate aridity and hydrology in the geological record (Figure 2.1).

Despite many successful applications of the triple oxygen isotope system in natural waters (Luz and Barkan, 2010; Risi et al., 2010; Levin et al., 2014; Passey et al., 2014; Herwartz et al., 2015; Li et al., 2015; Surma et al., 2015), the use of the $\Delta^{17}\text{O}$ method in carbonate minerals has been limited by a lack of analytical methods with high precision [that is, precision of better than ~ 0.015‰ (1σ)]. The difficulty of high-precision $\Delta^{17}\text{O}$ measurements relates to the fact that the nominal mass of the most abundant $^{17}\text{O}$-containing CO$_2$ isotopologue, $^{12}\text{C}^{17}\text{O}^{16}\text{O}$, is the same as that of the most abundant $^{13}\text{C}$-
containing isotopologue, $^{13}$C$^{16}$O$^{16}$O. Thus, the two isotopologues are indistinguishable by conventional stable isotope ratio mass spectrometry.

Recently, several different methods have been presented for high precision triple oxygen isotope analysis of CO$_2$ (including CO$_2$ generated from carbonate by phosphoric acid digestion). These are based on equilibrating CO$_2$ with a phase more amenable to triple oxygen isotope analysis such as H$_2$O (Barkan and Luz, 2012) or O$_2$ (Barkan and Luz (2015); Mahata et al. (2016), or on quantitative conversion of O in CO$_2$ to the more amenable phase (H$_2$O; Passey et al. (2014)). In this study we use the reduction-fluorination method developed by Passey et al. (2014), which achieves an external precision of $\sim0.01\%$ (1\$) for $\Delta^{17}$O as based on repeated analysis of carbonate standards, a level of precision enables meaningful reconstruction of aspects of paleoenvironments such as aridity and evaporation.

In this paper, we develop and explore model predictions for triple oxygen isotope compositions of different kinds of lake systems, ranging from flow-through lakes with little evaporative water loss, to closed-basin lakes where all water outflux is via evaporation, to pan evaporation where there is no influx and only evaporative outflux. The models are based on equations presented in Criss (1999) that account for variations in relative humidity, turbulent versus diffusive transport of water during evaporation, and the fraction of water leaving a lake as evaporation versus outflow or groundwater infiltration. We then present triple oxygen isotope data from five lakes and their associated rivers in semiarid western United States: Bear Lake (Utah-Idaho), a
freshwater flow-through lake; the Great Salt Lake (Utah), a saline closed-basin lake with inlet environments that approximate a flow-through behavior because of poor mixing; Lake Tahoe (California-Nevada), a freshwater flow-through lake, and Mono Lake (California) and Pyramid Lakes (Nevada), both alkaline closed basin lakes. We also present an experimental dataset examining the influence of dissolved chloride salts on triple oxygen isotope trajectories during evaporation.

2.2 Methods and Materials

2.2.1. Notation

The isotopic fractionation factor between two phases A and B is defined as

\[ \alpha_{A-B} = R_A / R_B \] (1)

Where \( R \) is the ratio of heavy isotope to \(^{16}\text{O}\), and the asterisks denote the heavy isotope \((^{17}\text{O} \text{ or } ^{18}\text{O})\). For mass-dependent fractionation processes, the fractionation factor for \(^{17}\text{O} / ^{16}\text{O} \) and \(^{18}\text{O} / ^{16}\text{O} \) will follow a power law (Matsuhisa et al., 1978; Young et al. 2002):

\[ ^{17}\alpha_{A-B} = (^{18}\alpha_{A-B})^\theta \] (2)

Note that \( \lambda \) and \( \beta \) are sometimes used here in place of \( \theta \). The symbol \( \theta \) is generally used for simple chemical processes such as liquid-vapor equilibrium (the symbol \( \beta \) is also used in this sense, e.g., Young et al., 2002, 2014), whereas \( \lambda \) is used for systems involving many processes. For example, the net behavior of the hydrological cycle carries a \( \lambda \) value of 0.528±0.001 (Luz and Barkan, 2010).
To linearize the exponential relationship, \(\delta'\)-notation is adopted and is defined as (Miller 2002)

\[
\delta'^{\text{O}_A} = 1000 \ln\left(\frac{\text{R}_A}{\text{R}_{\text{ref}}}\right) \quad (3)
\]

where \(A\) denotes phase \(A\), \(*\) denotes the mass number of heavy oxygen isotope (17 or 18) and \(\text{ref}\) denotes the reference material such as VSMOW (Vienna Standard Mean Ocean Water). Note that \(\delta'\)-notation is different than the \(\delta\)-notation \([\delta^{\text{O}_A} = 1000 \times (\text{R}_A/\text{R}_{\text{ref}} - 1)]\) widely used in stable isotope studies.

If phase \(B\) in Equation (1) is the reference material, then mass-dependent fractionation law can be rewritten as

\[
\frac{17\text{R}_A}{17\text{R}_{\text{ref}}} = \left(\frac{18\text{R}_A}{18\text{R}_{\text{ref}}}\right)^\theta \quad (4)
\]

The logarithmic form of this equation is

\[
\ln\left(\frac{17\text{R}_A}{17\text{R}_{\text{ref}}}\right) = \theta \ln\left(\frac{18\text{R}_A}{18\text{R}_{\text{ref}}}\right) \quad (5)
\]

Substituting \(\delta'\)-notation into (5), we will see a linear relationship between \(\delta^{17}\text{O}\) and \(\delta^{18}\text{O}\):

\[
\delta^{17}\text{O}_A = \theta \delta^{18}\text{O}_A \quad (6)
\]

The parameter \(\Delta^{17}\text{O}\) quantitatively defines the deviation from a reference relationship between \(^{17}\text{O}/^{16}\text{O}\) and \(^{18}\text{O}/^{16}\text{O}\). It is denoted in this paper as:

\[
\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.528 \times \delta^{18}\text{O} \quad (7)
\]
Here 0.528 is the slope of the triple oxygen isotope GMWL (Meijer and Li 1998; Landais et al., 2008; Luz and Barkan, 2010). Note that different values for the slope of reference line have been used in different studies [e.g., 0.516 (Hoffman and Pack, 2010), 0.517 (Thiemens, 1999), 0.521 (Luz et al., 1999), 0.518 (Nicholson et al., 2014) and 0.5305 (Pack and Herwartz, 2014; Herwartz et al., 2014; Herwartz et al., 2015)]. The slope of 0.528 is based on all published meteoric water observations through about 2010, and is heavily influenced by isotopically-light precipitation from polar latitudes. As discussed by Luz and Barkan (2010), a value of 0.528 is the theoretical prediction for water masses whose isotopic compositions evolve primarily in response to Rayleigh distillation. More recent studies are suggestive of a shallower meteoric water line slope in the tropics (Landais et al., 2010) and warmer regions of the mid-latitudes (Li et al., 2015) that may be related to syn- or post-precipitation evaporation of meteoric water (a process not accounted for in the standard Rayleigh distillation model). Provisionally, we continue to use a value of 0.528, because of its precedence for meteoric waters (e.g., Landais et al., 2006, 2008, 2010; Luz and Barkan, 2010; Li et al., 2015) and because it distinguishes Rayleigh processes versus secondary evaporative effects (the focus of this study).

2.2.2 Materials

2.2.2.1 Lake/River waters and lacustrine carbonates

Lakes in the western US (Figure 2.2, Table 2.1) were chosen for study because there is a high potential for evaporation in arid or semi-arid environments, and because a variety of lakes exist, ranging from freshwater to hypersaline / alkaline. Lake waters and their primary inflow and outflow water samples, as well as associated carbonate samples, were
collected in June 2014 from Bear Lake (Utah/Idaho); Great Salt Lake (Utah); Lake Tahoe (California/Nevada); Pyramid Lake (Nevada); and Mono Lake (California).

Bear Lake is a flow-through lake on the boundary of Utah and Idaho, USA. Water from Bear River is diverted into the lake through a canal and buffered by Mud Lake (Figure 2.2). Water samples 2014BL-001W, 2014BL-002W and 2014BL-003W were collected from outlet canal, inlet canal and Mud Lake respectively. Three water samples (2014BL-005W, 2014BL-008W, 2014BL-009W), two shell samples (2014BL-005shell, 2014BL-008C) and one lake marl sample (2014BL-005C) were collected from Bear Lake.

Great Salt Lake is a hypersaline lake located in Utah, USA. The lake is separated into several different parts owing to the existence of a railroad causeway, the automobile causeway accessing Antelope Island, and emergent salt flats to the south of Antelope Island (Figure 2). The sample 2014GSL-001W2 was collected from northwestern side of Antelope Island along the bank of Gilbert Bay, and 2014GSL-001C is carbonate-rich sediment sample collected from the same location. The samples 2014GSL-002W (Farmington Bay water) and 2014GSL-003W (Gilbert Bay water) were collected adjacent to, but on opposite sides, of the Antelope Island causeway. The sample 2014GSL-JRW was collected from south side of the Gilbert Bay. Two shell samples 2014GSL-003C1 and 2014GSL-003C1 were collected from the ponds on the northeastern side of Antelope Island along the bank of Gilbert Bay. The ponds have distinctly different salinity and oxygen isotopic composition compared with lake water itself, and we surmise that they have significant contributions from precipitation or meteoric-derived groundwater, or
both. In addition, 2014GSL-006W, 2014BearR-001W and 2014JR-W are water samples collected from Weber River, Bear River and Jordan River, respectively, which are the three primary inflows of the Great Salt Lake.

The Lake Tahoe-Truckee River-Pyramid Lake system straddles the eastern Sierra Nevada and northwestern Great Basin (Figure 2). Most of the input water of Lake Tahoe originates from several small creeks and direct precipitation. It is the headwater of Truckee River, which is the only primary inflow of Pyramid Lake. 2014TL002-W is a water sample collected from Lake Tahoe. Sample 2014TrukeeR-0608-002W was collected from Truckee River near its source from Lake Tahoe and 2014TrukeeR-W2 is water sample collected from Truckee River near its entrance to Pyramid Lake. Three lake water samples (2014PL001-W1, 2014PL002-W1, 2014PL004-W1) and two lake shell samples (2014PL-001C, 2014PL-002C) were collected along the west bank of Pyramid Lake.

Mono Lake is a closed basin alkaline lake located in the east side of Sierra Nevada and is fed primarily by creeks originating from these mountains (Figure 2). Water samples are from west side of the lake (2014MonoL-W1, 2014MonoL-002W1), and from Lee Vining Creek (2014LVC-W1) and Mill Creek (2014MillR-W1). Shells were not found in the lake or along the bank but a carbonate sediment sample (2014MonoL-001C) was collected and measured.

All water samples were sealed in 10ml glass vials with PolyCone caps secured with Parafilm M®, and stored in a refrigerator before measurement. Lacustrine carbonate samples include live or recently dead shells, and lake marls collected along the shoreline
beneath the water surface. Lake marls were cleaned by deionized water to remove soluble minerals and treated by 3% H₂O₂ to remove organics prior to stable isotope analysis. Shells were cleaned by deionized water and crushed into powder. All powder samples were dried overnight at 60°C and stored in glass vials before measurement.

2.2.2.2 Open-pan evaporation experiments
Open-pan evaporation experiments were conducted in order to investigate salinity effects on triple oxygen isotope fractionation exponents during evaporation. We used initial solute concentrations of 0.5 M for each of NaCl, KCl, MgCl₂, and CaCl₂, which translates to total dissolved solids (TDS) ranging from 29 to 55 g/L in the initial solutions, and up to ~400 g/L in the most evaporated final solutions. For reference, Great Salt Lake and Mono Lakes have TDS of ca. 250 g/L and 100 g/L, respectively, whereas seawater is ~35 g/L. The deionized water and salt solutions were placed into different Petri dishes and subjected to open-air evaporation in our laboratory, where temperature and relative humidity during the course of evaporation were ~23 °C and ~40 – 50%, respectively. Remaining water samples were collected every 12 hours. Remaining water fractions were determined by weighing the dish + water prior to taking each sample.
<table>
<thead>
<tr>
<th>Name</th>
<th>Type/X_E</th>
<th>Location</th>
<th>Elevation</th>
<th>Lake Area</th>
<th>Volume</th>
<th>Residence Time</th>
<th>Lake Water Oxygen Isotopic Composition</th>
<th>Primary Inflow/Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Tahoe</td>
<td>Throughflow X_E: 0.63&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Nevada/California, USA 39.10N 120.03W&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1899m&lt;sup&gt;a&lt;/sup&gt;</td>
<td>500 km&lt;sup&gt;2&lt;/sup&gt;</td>
<td>124 km&lt;sup&gt;3&lt;/sup&gt;</td>
<td>650yr&lt;sup&gt;e&lt;/sup&gt;</td>
<td>~-5.60‰&lt;sup&gt;f,g&lt;/sup&gt;</td>
<td>Inflow: Many creeks with melting snow water Outflow: Trukee River</td>
</tr>
<tr>
<td>Bear Lake</td>
<td>Throughflow X_E: 0.55&lt;sup&gt;c&lt;/sup&gt;, 0.29&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Utah/Idaho, USA 42.00N 111.33W&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1805m&lt;sup&gt;e&lt;/sup&gt;</td>
<td>282 km&lt;sup&gt;2&lt;/sup&gt;</td>
<td>8 km&lt;sup&gt;3&lt;/sup&gt;</td>
<td>37yr&lt;sup&gt;c&lt;/sup&gt;</td>
<td>~-8.10‰&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Inflow: Inlet Canal Outflow: Outlet Canal</td>
</tr>
<tr>
<td>Pyramid Lake</td>
<td>Closed Basin X_E: 1</td>
<td>Nevada, USA 40.03N 119.83W&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1159m&lt;sup&gt;a&lt;/sup&gt;</td>
<td>453km&lt;sup&gt;2&lt;/sup&gt;</td>
<td>27 km&lt;sup&gt;3&lt;/sup&gt;</td>
<td>50yr&lt;sup&gt;b&lt;/sup&gt;</td>
<td>~-0.50‰&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Inflow: Trukee River Outflow: Evaporation</td>
</tr>
<tr>
<td>Mono Lake</td>
<td>Closed Basin X_E: 1</td>
<td>California, USA 38.00N 119.00W&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1945m&lt;sup&gt;b&lt;/sup&gt;</td>
<td>180 km&lt;sup&gt;2&lt;/sup&gt;</td>
<td>2.97 km&lt;sup&gt;3&lt;/sup&gt;</td>
<td>25yr&lt;sup&gt;d&lt;/sup&gt;</td>
<td>~-0.10‰&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Inflow: Rush Creek Lee Vining Creek Mill Creek Outflow: Evaporation</td>
</tr>
<tr>
<td>Great Salt Lake</td>
<td>Closed Basin/Semi-closed Basin</td>
<td>Utah, USA 41.10N 112.50W&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1280m&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4360 km&lt;sup&gt;2&lt;/sup&gt;</td>
<td>19 km&lt;sup&gt;3&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>Inflow: Bear River Jordan River Weber River Outflow: Evaporation</td>
</tr>
</tbody>
</table>
References:
b. World Lake Database (http://wldb.ilec.or.jp/). International Lake Environment Committee Foundation (ILEC).
Figure 2.2 Map of Western US lakes, associated rivers, and sampling locations. (A) Pyramid Lake in Nevada, USA; (B) Great Salt Lake in Utah, USA; (C) Bear Lake in Idaho/Utah, USA; (D) Mono Lake in California, USA.
2.2.3 Analytical Methods

2.2.3.1 Triple oxygen isotope measurements

Triple oxygen isotopes of carbonate samples were measured at Johns Hopkins University following methods described in Passey et al. (2014). Briefly, carbonates are reacted in 100% H$_3$PO$_4$ (90 °C) to yield CO$_2$. The CO$_2$ is cryogenically purified and then reduced by H$_2$ at 560 °C over Fe powder catalyst to yield H$_2$O. The water is then fluorinated by CoF$_3$ at 350 °C to yield O$_2$, which is analyzed for $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O using a Thermo MAT 253 mass spectrometer. The observed external precision of the method is 0.01‰ (1σ) for δ$^{17}$O as based on repeated analysis of carbonate standards. Water samples were directly injected into the CoF$_3$ reactor to be fluorinated, with the evolved O$_2$ purified and analyzed in exactly the same manner as the CaCO$_3$-derived O$_2$.

All triple oxygen isotope data in this work are normalized to concurrent analyses of VSMOW-SLAP, for which δ$^{18}$O and δ$^{17}$O for VSMOW are defined as 0‰ and 0‰ respectively and δ$^{18}$O for SLAP (Standard Light Antarctic Precipitation) is defined as -55.5‰ (Schoenemann et al., 2013). δ$^{17}$O for SLAP is assumed as 0‰ in this framework, therefore δ$^{17}$O of SLAP is calculated as -29.6986‰ in this reference frame. For reference, during the course of this study and in the context of this VSMOW-SLAP reference frame, we obtained the following values for NBS-19 (n = 4, all ± values are 1σ): δ$^{17}$O = 19.089 ± 0.130‰, δ$^{18}$O = 36.416 ± 0.246 ‰, and δ$^{17}$O = -0.139 ± 0.003 ‰. For NBS-18 (n = 3, all ± values are 1σ), we observed values of δ$^{17}$O = 7.801‰ ± 0.141‰, δ$^{18}$O = 14.942 ± 0.269‰, and δ$^{17}$O = -0.089 ± 0.001 ‰. We note that these values are for the CO$_2$ liberated from carbonate by phosphoric acid digestion at 90 °C.
2.2.3.2 Clumped isotope measurements

Clumped isotope compositions of lake sediments and shells were measured and normalized following methods described in Passey et al. (2010) and Dennis et al. (2011) as detailed for our specific laboratory practices in Henkes et al. (2013). For shell samples, temperatures are calculated from measured Δ47 values using the modern mollusk and brachiopod calibration from Henkes et al. (2013). Temperatures of non-molluscan lake carbonates (i.e., marls) are calculated based on Equation 5 of Passey and Henkes (2012), which is itself based on the theoretical equation for calcite Δ63 temperature sensitivity developed by Schauble et al. (2006), but shifted by 0.280‰ to account for acid fractionation during 90 °C common acid bath acid digestion in our laboratory. For reference, we observed the following values for carbonate standards co-analyzed with our samples: NBS-19: Δ47 = 0.391 ± 0.011 ‰ (1σ, n = 21); 102-GC-AZ01 (an internal standard): Δ47 = 0.697 ± 0.000 ‰ (1σ, n = 35).

2.3 Model Description

The isotopic composition of lake water is controlled by water and isotope mass balance and can be expressed as (Figure 2.3):

$$\frac{\partial v}{\partial t} = I - O = P + I_f - O_f - E$$  \hspace{1cm} (8)

$$\frac{\partial (v R_{iw})}{\partial t} = IR_I^* - OR_O^* = PR_P^* + I_f R_{I_f}^* - O_f R_{O_f}^* - ER_E^*$$  \hspace{1cm} (9)

$I$ in the above equations is the total inflow which includes precipitation $P$ as well as combined surface and subsurface inflow $I_f$. $O$ is the total outflow which includes
combined surface and subsurface outflow $O_f$ as well as the evaporation flux $E$. $R^*$ is the isotope ratio for each component.

For a well-mixed lake with a constant volume (steady-state assumption, Figure 2.3), the equations can be rewritten as

\[ P + I_f = O_f + E \quad (10) \]
\[ PR^*_P + I_f R^*_f = O_f R^*_f + ER^*_E \quad (11) \]

The evaporation flux is enriched in lighter isotopes because of both kinetic and equilibrium isotope effects. Thus, evaporation will lead to progressive enrichment of heavier isotopes in the residual water body. For $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$, this phenomenon has been well studied (e.g., Craig and Gordon, 1965; Brutsaert, 1975; Merlivat and Jouzel, 1979; Cappa et al., 2003). This process is mainly controlled by the extent of evaporation and relative humidity in the atmosphere ($h$). Based on kinetic theory, Criss (1999) derived the fractionation factor during evaporation as

\[ \alpha_{evap} = \frac{R_W}{R_E} = \frac{\alpha_{evap}^0(1-h)}{1-\alpha_{evap}R_V/R_W} \quad (12) \]
Figure 2.3 Schematic diagram showing the three different hydrological scenarios examined in this study. (A) Closed basin lake with surface water inflow but without surface or subsurface water outflow. Water loss is only through evaporation. (B) Throughflow lake with surface or subsurface inflow and outflow. (C) Desiccating pond or open pan without any inflow or outflow, where water loss is only through evaporation.
Here, $R_w$, $R_E$ and $R_v$ are isotope ratio in liquid water, evaporating water vapor and ambient atmospheric water vapor, respectively, $h$ denotes relative humidity, and $\alpha_{eq}$ is the equilibrium fractionation factor between liquid water and water vapor. The parameter $\alpha^0_{evap}$ is a fractionation factor during evaporation in the limit that relative humidity is 0, and is equivalent to the product of the equilibrium fractionation and kinetic fractionation ($\alpha^0_{evap} = \alpha_{eq} \times \alpha_{diff}$). Note that, in Craig and Gordon (1965), $\alpha^0_{evap}$, $\alpha_{eq}$ and $\alpha_{diff}$ are respectively referred as $(1 + \epsilon/10^3)$, $(1 + \epsilon^*/10^3)$ and $(1 + C_k/10^3)$.

Combining (12) with the steady state equations (10) and (11), the isotopic ratio of lake water can be described as (Criss, 1999):

$$R_w = \frac{\alpha^0_{evap}(1-h)R_I + \alpha_{eq}hX_ER_V}{X_E + \alpha^0_{evap}(1-h)R_I(1-X_E)}$$

(13)

where $X_E$ is defined as the volumetric fraction of inflowing water that is lost to evaporation:

$$X_E = \frac{E}{I}$$

(14)

In a simpler closed basin (terminal lake) case (Figure 2.3A), all inflowing water is removed by evaporation ($X_E = 1$) and the above equation simplifies to (Criss, 1999):

$$R_w = \alpha^0_{evap}(1 - h)R_I + \alpha_{eq}hR_V$$

(15)

A third scenario, for pan evaporation (that is, evaporation of a pool of water with no influx of water, as shown in Figure 2.3C) is developed in Section 5 in the context of results for our saline water evaporation experiments.
Equations 13 and 15 permit calculation of steady-state isotopic compositions of well-mixed lakes ranging from 100% flow-through (no evaporation) to 100% closed-basin (no outflowing water). Before these equations can be used, appropriate values must be determined for the six free parameters in the model (Table 2.2). Three of the parameters are descriptions of climate and lake hydrology \( (h, R_I, X_E) \) and we treat these as specified parameters that are varied across their typical ranges. Of the remaining three parameters, \( R_V \) and \( \alpha_{evap} = \alpha_{eq} \times \alpha_{diff} \), only \( \alpha_{eq} \) is well-defined, and we use values of \( ^{18}\alpha_{eq} = 1.0094 \) (Majoube, 1971) and \( \theta_{eq} = 0.529 \) (Barkan and Luz, 2005). For \( R_V \), we provisionally assume equilibrium with water of composition \( R_I \), and for \( \alpha_{diff} \) we use 1.0412, a value commonly used in lake studies (Gonfiantini, 1986; Gat, 1996; Gibson et al., 2002; Gibson et al., 2015). In Section 5 we further discuss the parameter \( \alpha_{diff} \) and explore model sensitivity to variation in both \( R_V \) and \( \alpha_{diff} \).

Figure 2.4 presents the basic model predictions for flow-through and closed basin lakes based on equations 13 and 15 and the parameters listed in Table 2.2. The model predicts that \( \Delta^{17}O \) in closed basin lake water can be as much as \( \sim 0.075\% \) lower than primary precipitation when relative humidity is low. The magnitude of lowering in \( \Delta^{17}O \) increases with decreasing relative humidity. Flow-through lakes should have \( \Delta^{17}O \) values that are similar to or slightly lower than primary precipitation (as much as \( \sim 0.025\% \) lower than precipitation), while low to moderate evaporation throughflow lake waters have intermediate lowering of \( \Delta^{17}O \).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Explanation</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{\text{diff}}$</td>
<td>$^{18}$O fractionation factor for natural lake water diffusion into dry air</td>
<td>1.0142</td>
<td>Discussion in section 5.1</td>
</tr>
<tr>
<td>$\alpha_{\text{eq}}$</td>
<td>$^{18}$O fractionation factor for water–water vapor equilibrium at room temperature</td>
<td>1.0094</td>
<td>Majoube, 1971</td>
</tr>
<tr>
<td>$\theta_{\text{diff}}$</td>
<td>Triple oxygen exponent for lake water diffusion</td>
<td>0.5185</td>
<td>Barkan and Luz, 2007</td>
</tr>
<tr>
<td>$\theta_{\text{eq}}$</td>
<td>Triple oxygen exponent for lake water-water vapor equilibrium</td>
<td>0.529</td>
<td>Barkan and Luz, 2005</td>
</tr>
<tr>
<td>$\alpha_{\text{diff}}, \alpha_{\text{eq}}$</td>
<td>$^{17}$O fractionation factor for lake water diffuse into dry air and water-water vapor equilibrium at room temperature</td>
<td>$^{17}\alpha_{\text{diff}} = (^{18}\alpha_{\text{diff}})^{\theta_{\text{diff}}}$, $^{17}\alpha_{\text{eq}} = (^{18}\alpha_{\text{eq}})^{\theta_{\text{eq}}}$</td>
<td>By their definitions</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Isotope ratio of input water (normalized to VSMOW)</td>
<td>0.98 to 1.00 ($\delta^{18}O$: -20‰ to 0‰)</td>
<td></td>
</tr>
<tr>
<td>$\Delta^{17}O_i$</td>
<td>$\Delta^{17}O$ value for input water</td>
<td>0.033‰ (average value of global mean meteoric water)</td>
<td>Luz and Barkan, 2010</td>
</tr>
<tr>
<td>$R_v$, $R_v$</td>
<td>Isotopic composition of atmospheric vapor</td>
<td>Assume it is in equilibrium with input water</td>
<td>Discussion in section 5.4</td>
</tr>
</tbody>
</table>
Figure 2.4 Modeled triple oxygen isotope compositions of lake waters under different hydrological scenarios. Star symbols show the isotopic compositions of inflowing water, and squares show equilibrium compositions of the lakes under different atmospheric relative humidities (h). See Table 5 for parameters used in model calculation and Section 3 for detailed discussion. (A) Predicted \( \delta^{18}O \) and \( \Delta^{17}O \) for closed basin lakes. (B) Predicted \( \delta^{18}O \) and \( \Delta^{17}O \) for moderate evaporation through-flow lakes. Half of output water is evaporation (evaporation to input ratio \( X_E = 0.5 \)). (C) Predicted \( \delta^{18}O \) and \( \Delta^{17}O \) for moderate low evaporation through-flow lakes. Twenty percent of output water is evaporation (evaporation to input ratio \( X_E = 0.2 \)). (D) Schematic summary for different lake types.
2.4 Data – Model Comparison

2.4.1 Isotopic compositions of western U.S. lakes

The isotopic compositions of lake waters and lacustrine carbonates are reported in Tables 2.3 and 2.4, and are plotted in Figures 2.5. The isotopic compositions of \( \text{O}_2 \) generated from carbonates are plotted along with \( \text{O}_2 \) generated from waters in Figure 2.5A. The gap between the waters and carbonates reflects a combination of the carbonate-water fractionation, acid fractionation, and any isotopic effects arising from our sample reaction and purification procedures (see Passey et al., 2014). Note that with the CoF\(_3\)-based water fluorination method used here, there is no known or detectable fractionation between \( \text{O}_2 \) generated from waters and the O in water itself (Barkan and Luz, 2005). Lacustrine carbonate data are represented as their equivalent water isotopic compositions in Figure 2.5B and in all following discussions, unless otherwise noted, in order to facilitate comparison with lake waters. These equivalent water compositions were calculated using the \( ^{18}\text{O}/^{16}\text{O} \) fractionation factors given in Table 4 combined with the \( \theta \) value for carbonate-water fractionation (0.5245) determined by Passey et al. (2014).

For river samples, \( \delta^{18}\text{O} \) values range from -19.2‰ to -7.7‰ with an average value of -14.8‰. \( \Delta^{17}\text{O} \) values range from 0.010‰ to 0.055‰ with an average value of 0.031‰. For throughflow lake samples, \( \delta^{18}\text{O} \) values range from -10.0‰ to -3.7‰ with an average value of -7.1‰. \( \Delta^{17}\text{O} \) values range from -0.024‰ to 0.017‰, with an average value of
Table 2.3
Lake water sample information and measured isotopic composition (units in ‰)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Water Type</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Elevation</th>
<th>Date of Collection</th>
<th>Salinity</th>
<th>N</th>
<th>$\delta^{18}O_{V SMOW}$ avg</th>
<th>$\delta^{18}O_{V SMOW}$ SD</th>
<th>$\Delta^{17}O_{V SMOW}$ avg</th>
<th>$\Delta^{17}O_{V SMOW}$ SD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lake Tahoe (CA/NV, USA)</strong></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>2014TL002-W</td>
<td>Throughflow Lake</td>
<td>119.93 W</td>
<td>39.21 N</td>
<td>1920 m</td>
<td>8-Jun-2014</td>
<td>0 %</td>
<td>1</td>
<td>-5.53</td>
<td>0.38</td>
<td>0.005</td>
<td>0.012</td>
</tr>
<tr>
<td>2014TrukeyR-0608-002W</td>
<td>Outflow River</td>
<td>120.18 W</td>
<td>39.33 N</td>
<td>1772 m</td>
<td>8-Jun-2014</td>
<td>-</td>
<td>1</td>
<td>-6.98</td>
<td>0.38</td>
<td>0.010</td>
<td>0.012</td>
</tr>
<tr>
<td><strong>Bear Lake (UT/ID, USA)</strong></td>
<td></td>
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</tr>
<tr>
<td>2014BL-001W</td>
<td>Outlet Canal</td>
<td>111.36 W</td>
<td>42.30 N</td>
<td>1803 m</td>
<td>2-Jun-2014</td>
<td>-</td>
<td>1</td>
<td>-15.91</td>
<td>0.38</td>
<td>0.016</td>
<td>0.012</td>
</tr>
<tr>
<td>2014BL-002W</td>
<td>Inlet Canal</td>
<td>111.30 W</td>
<td>42.22 N</td>
<td>1810 m</td>
<td>2-Jun-2014</td>
<td>-</td>
<td>1</td>
<td>-18.55</td>
<td>0.38</td>
<td>0.046</td>
<td>0.012</td>
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<tr>
<td>2014BL-003W</td>
<td>Throughflow Lake (Mud Lake)</td>
<td>111.26 W</td>
<td>42.13 N</td>
<td>1817 m</td>
<td>2-Jun-2014</td>
<td>0 %</td>
<td>1</td>
<td>-19.11</td>
<td>0.38</td>
<td>0.044</td>
<td>0.012</td>
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<tr>
<td>2014BL-005W</td>
<td>Throughflow Lake</td>
<td>111.26 W</td>
<td>42.07 N</td>
<td>1814 m</td>
<td>2-Jun-2014</td>
<td>0 %</td>
<td>2</td>
<td>-9.97</td>
<td>0.38</td>
<td>0.008</td>
<td>0.012</td>
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<tr>
<td>2014BL-008W</td>
<td>Throughflow Lake</td>
<td>111.29 W</td>
<td>41.89 N</td>
<td>1829 m</td>
<td>2-Jun-2014</td>
<td>0 %</td>
<td>2</td>
<td>-9.95</td>
<td>1.40</td>
<td>0.007</td>
<td>0.015</td>
</tr>
<tr>
<td>2014BL-009W</td>
<td>Throughflow Lake</td>
<td>111.36 W</td>
<td>41.86 N</td>
<td>1894 m</td>
<td>2-Jun-2014</td>
<td>0 %</td>
<td>2</td>
<td>-9.35</td>
<td>1.53</td>
<td>0.019</td>
<td>0.027</td>
</tr>
<tr>
<td><strong>Pyramid Lake (NV, USA)</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2014PL001-W1</td>
<td>Closed Basin Lake</td>
<td>119.45 W</td>
<td>39.84 N</td>
<td>1171 m</td>
<td>6-Jun-2014</td>
<td>0.6 %</td>
<td>1</td>
<td>-0.90</td>
<td>0.38</td>
<td>-0.034</td>
<td>0.012</td>
</tr>
<tr>
<td>2014PL002-W1</td>
<td>Closed Basin Lake</td>
<td>119.60 W</td>
<td>39.95 N</td>
<td>1167 m</td>
<td>6-Jun-2014</td>
<td>0.6 %</td>
<td>1</td>
<td>-0.43</td>
<td>0.38</td>
<td>-0.038</td>
<td>0.012</td>
</tr>
<tr>
<td>2014PL004-W1</td>
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<td>119.67 W</td>
<td>40.05 N</td>
<td>1162 m</td>
<td>6-Jun-2014</td>
<td>0.6 %</td>
<td>1</td>
<td>-0.34</td>
<td>0.38</td>
<td>-0.036</td>
<td>0.012</td>
</tr>
<tr>
<td>2014TrukeyR-W1</td>
<td>Inflow River</td>
<td>119.74 W</td>
<td>39.52 N</td>
<td>1342 m</td>
<td>6-Jun-2014</td>
<td>-</td>
<td>1</td>
<td>-9.56</td>
<td>0.38</td>
<td>0.016</td>
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</tr>
<tr>
<td>2014TrukeyR-W2</td>
<td>Inflow River</td>
<td>119.28 W</td>
<td>39.63 N</td>
<td>1249 m</td>
<td>6-Jun-2014</td>
<td>-</td>
<td>1</td>
<td>-9.89</td>
<td>0.38</td>
<td>0.026</td>
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<tr>
<td><strong>Mono Lake (CA, USA)</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014MonoL-W1</td>
<td>Closed Basin Lake</td>
<td>119.14 W</td>
<td>37.98 N</td>
<td>1953 m</td>
<td>7-Jun-2014</td>
<td>7.6 %</td>
<td>2</td>
<td>-3.59</td>
<td>0.38</td>
<td>-0.031</td>
<td>0.012</td>
</tr>
<tr>
<td>2014MonoL-002W1</td>
<td>Closed Basin Lake</td>
<td>119.02 W</td>
<td>37.94 N</td>
<td>1947 m</td>
<td>7-Jun-2014</td>
<td>6.8 %</td>
<td>2</td>
<td>-5.27</td>
<td>0.38</td>
<td>-0.026</td>
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<tr>
<td>2014LVC-W1</td>
<td>Inflow River</td>
<td>119.11 W</td>
<td>37.97 N</td>
<td>1963 m</td>
<td>7-Jun-2014</td>
<td>-</td>
<td>1</td>
<td>-16.19</td>
<td>0.38</td>
<td>0.041</td>
<td>0.012</td>
</tr>
<tr>
<td>2014MillR-W1</td>
<td>Inflow River</td>
<td>119.13 W</td>
<td>38.02 N</td>
<td>1956 m</td>
<td>7-Jun-2014</td>
<td>-</td>
<td>1</td>
<td>-16.68</td>
<td>0.38</td>
<td>0.024</td>
<td>0.012</td>
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<tr>
<td>2014-RushC-W1</td>
<td>Inflow River</td>
<td>119.05 W</td>
<td>37.95 N</td>
<td>1959 m</td>
<td>7-Jun-2014</td>
<td>-</td>
<td>1</td>
<td>-14.42</td>
<td>0.38</td>
<td>0.043</td>
<td>0.012</td>
</tr>
</tbody>
</table>

**Great Salt Lake (UT, USA)**
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Location Description</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth (m)</th>
<th>Date</th>
<th>CO2 (%)</th>
<th>δ18O</th>
<th>Δ17O</th>
<th>CO2 (%)</th>
<th>δ18O</th>
<th>Δ17O</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014GSL-001W2</td>
<td>Semi-closed Basin Lake (Gilbert Bay)</td>
<td>41.03 N</td>
<td>112.27 W</td>
<td>1276 m</td>
<td>1-Jun-2014</td>
<td>14.0 %</td>
<td>-4.73</td>
<td>0.90</td>
<td>-0.016</td>
<td>0.022</td>
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</tr>
<tr>
<td>2014GSL-002W</td>
<td>Semi-closed Basin Lake (Farmington Bay)</td>
<td>41.06 N</td>
<td>112.24 W</td>
<td>1283 m</td>
<td>1-Jun-2014</td>
<td>3.1 %</td>
<td>-6.33</td>
<td>0.38</td>
<td>-0.012</td>
<td>0.012</td>
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</tr>
<tr>
<td>2014GSL-003W</td>
<td>Semi-closed Basin Lake (Gilbert Bay)</td>
<td>41.06 N</td>
<td>112.24 W</td>
<td>1283 m</td>
<td>1-Jun-2014</td>
<td>11.6 %</td>
<td>-4.35</td>
<td>0.38</td>
<td>-0.017</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>2014GSL-JRW</td>
<td>Semi-closed Basin Lake (Gilbert Bay)</td>
<td>40.73 N</td>
<td>112.21 W</td>
<td>1285 m</td>
<td>5-Jun-2014</td>
<td>13.2 %</td>
<td>-14.70</td>
<td>0.68</td>
<td>-0.020</td>
<td>0.012</td>
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<tr>
<td>2014GSL-006W</td>
<td>Inflow River</td>
<td>41.25 N</td>
<td>112.12 W</td>
<td>1289 m</td>
<td>1-Jun-2014</td>
<td>0 %</td>
<td>-15.71</td>
<td>0.38</td>
<td>0.008</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>2014BearR-001W</td>
<td>Inflow River</td>
<td>41.55 N</td>
<td>112.10 W</td>
<td>1290 m</td>
<td>2-Jun-2014</td>
<td>-</td>
<td>-16.58</td>
<td>0.57</td>
<td>0.040</td>
<td>0.012</td>
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<tr>
<td>2014JR-W</td>
<td>Inflow River</td>
<td>40.74 N</td>
<td>112.92 W</td>
<td>1292 m</td>
<td>5-Jun-2014</td>
<td>0 %</td>
<td>-14.70</td>
<td>0.68</td>
<td>0.024</td>
<td>0.012</td>
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</tbody>
</table>

*Note:* For samples measured only once, errors (SD) are reported as 1σ on long-term standard material measurements (0.38‰ for δ18O and 0.012‰ for Δ17O). For samples measured twice or more, errors (SD) are reported as larger value of long-term measurement precision of standard materials and 1σ on n analyses of water samples.
### Table 2.4
Lacustrine carbonate information, measured isotopic composition, and calculated parent water isotopic composition (units in ‰)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Description / Mollusk Taxon</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Elevation (m)</th>
<th>N</th>
<th>Measured T (°C)</th>
<th>( \delta^{18}O )_{VSMOW} \text{avg}</th>
<th>( \delta^{18}O )_{VSMOW} \text{SD}</th>
<th>( \Delta^{17}O )_{VSMOW} \text{avg}</th>
<th>( \Delta^{17}O )_{VSMOW} \text{SD}</th>
<th>Calculated ( \delta^{18}O )_{VSMOW} \text{avg}</th>
<th>Calculated ( \Delta^{17}O )_{VSMOW} \text{avg}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bear Lake(UT/ID, USA) \text{[Mean Annual Temperature = 6°C]}</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014BL-005C</td>
<td>Lake marl</td>
<td>111.25 W</td>
<td>42.07 N</td>
<td>1814 m</td>
<td>3</td>
<td>30.18</td>
<td>0.52</td>
<td>-0.157</td>
<td>0.002</td>
<td>26.9</td>
<td>1.0364</td>
<td>-5.3</td>
</tr>
<tr>
<td>2014BL-005Shell</td>
<td>Valvatidae</td>
<td>111.25 W</td>
<td>42.07 N</td>
<td>1814 m</td>
<td>2</td>
<td>34.98</td>
<td>0.00</td>
<td>-0.160</td>
<td>0.003</td>
<td>12.9</td>
<td>1.0394</td>
<td>-3.7</td>
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<tr>
<td>2014BL-008C</td>
<td>Corbicula</td>
<td>111.29 W</td>
<td>41.89 N</td>
<td>1829 m</td>
<td>2</td>
<td>33.23</td>
<td>0.02</td>
<td>-0.150</td>
<td>0.003</td>
<td>15.8</td>
<td>1.0388</td>
<td>-4.8</td>
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<tr>
<td>Pyramid Lake(NV, USA) \text{[Mean Annual Temperature = 12.5°C]}</td>
<td></td>
<td></td>
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<tr>
<td>2014PL-001C</td>
<td>Planorbidae</td>
<td>119.45 W</td>
<td>39.84 N</td>
<td>1171 m</td>
<td>2</td>
<td>37.81</td>
<td>0.47</td>
<td>-0.160</td>
<td>0.002</td>
<td>13.8</td>
<td>1.0309</td>
<td>-0.67</td>
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<tr>
<td>2014PL-002C</td>
<td>Planorbidae</td>
<td>119.60 W</td>
<td>39.95 N</td>
<td>1167 m</td>
<td>2</td>
<td>38.76</td>
<td>0.36</td>
<td>-0.163</td>
<td>0.000</td>
<td>17.0</td>
<td>1.0301</td>
<td>0.98</td>
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<tr>
<td>Mono Lake(CA, USA) \text{[Mean Annual Temperature = 8.6°C]}</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014MonoL-001C</td>
<td>Lake marl</td>
<td>119.02 W</td>
<td>37.94 N</td>
<td>1947 m</td>
<td>3</td>
<td>40.93</td>
<td>0.68</td>
<td>-0.201</td>
<td>0.010</td>
<td>47.3</td>
<td>1.0324</td>
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</tr>
<tr>
<td>2014GSL-001C</td>
<td>Lake marl</td>
<td>112.27 W</td>
<td>41.03 N</td>
<td>1276 m</td>
<td>2</td>
<td>34.40</td>
<td>0.74</td>
<td>-0.158</td>
<td>0.005</td>
<td>25.1</td>
<td>1.0368</td>
<td>-1.7</td>
</tr>
<tr>
<td>2014GSL-003C1</td>
<td>Planorbiella</td>
<td>112.24 W</td>
<td>41.06 N</td>
<td>1283 m</td>
<td>2</td>
<td>23.78</td>
<td>0.23</td>
<td>-0.099</td>
<td>0.001</td>
<td>23.9</td>
<td>1.037</td>
<td>-12.56</td>
</tr>
<tr>
<td>2014GSL-003C2</td>
<td>Lymnaeidae</td>
<td>112.24 W</td>
<td>41.06 N</td>
<td>1283 m</td>
<td>2</td>
<td>27.29</td>
<td>0.28</td>
<td>-0.108</td>
<td>0.000</td>
<td>30.8</td>
<td>1.0356</td>
<td>-7.68</td>
</tr>
<tr>
<td>2014GSL-JRC</td>
<td>Lake marl</td>
<td>112.21 W</td>
<td>40.73 N</td>
<td>1285 m</td>
<td>2</td>
<td>34.74</td>
<td>0.18</td>
<td>-0.162</td>
<td>0.001</td>
<td>20.3</td>
<td>1.0378</td>
<td>-2.34</td>
</tr>
</tbody>
</table>

**Note:** Errors for measured isotopic composition (SD) are reported as 1σ on n analyses of carbonate samples. Error for calculated isotopic composition of their ambient water (±) are reported from standard error propagation using 95% confidential intervals or 1.96 * S.E.M of parameters reported by Passey *et al.* (2014). Mean annual temperatures data are from Western Regional Climate Center (http://www.wrcc.dri.edu/)
Figure 2.5 Measured triple oxygen isotope compositions of lake and river waters and associated carbonates from the western USA. (A) Measured isotopic compositions waters and carbonates. (B) Same as (A), except now the isotopic compositions for carbonates are reported as values of their parent waters. Temperatures used to calculate fractionation factor between carbonate and ambient water are based on clumped isotope thermometry of the same carbonate samples. Error bars for $\delta^{18}O$ and $\Delta^{17}O$ of water samples are 1σ of repeat analyses. Error bars for $\delta^{18}O$ and $\Delta^{17}O$ of carbonates are calculated based on standard error propagation using 95% confidential intervals or 1.96 * S.E.M of parameters reported by Passey et al. (2014).

0.003‰. For closed basin or semi-closed basin lake samples, $\delta^{18}O$ values range from -5.8‰ to 9.2‰, with an average value of -1.6‰. $\Delta^{17}O$ values range from -0.089‰ to -0.010‰ with an average value of -0.033‰.
In general, river samples have lowest $\delta^{18}\text{O}$ and highest $\Delta^{17}\text{O}$, closed basin lake samples have highest $\delta^{18}\text{O}$ and lowest $\Delta^{17}\text{O}$, and the isotopic compositions of throughflow lake samples are in between those observed for rivers and closed basin lakes. The sample with the lowest $\delta^{18}\text{O}$ and highest $\Delta^{17}\text{O}$ was collected from an inlet canal of Bear lake, which originates from the Bear River, which is fed primarily by snow melt from the nearby Uinta mountains. The highest $\delta^{18}\text{O}$ and lowest $\Delta^{17}\text{O}$ observed in our dataset is for the calculated parent water of a carbonate collected along the shores of Mono Lake.

2.4.2 Comparison with model predictions

Measured isotopic compositions of lake waters and lacustrine sediments from the western United States (Figure 2.6; Table 2.2 and Table 2.3) are generally consistent with the model predictions. In all cases, $\Delta^{17}\text{O}$ in evaporated lake water is significantly different from that of unevaporated water such as precipitation and freshwater rivers. We clearly observe a lowering of $\Delta^{17}\text{O}$ of lake water relative to freshwater inflow. In general, the calculated parent water isotopic compositions of lacustrine carbonates (including mollusks and lake marls) mirror the $^{17}\text{O}$ anomalies of lake water, but in many cases the parent waters have higher $\delta^{18}\text{O}$ and lower $\Delta^{17}\text{O}$ than the actual water samples that we analyzed. In the following text, we discuss each lake system on a case-by-case basis.

Pyramid Lake is a closed basin lake located in the northwestern Great Basin (Figure 2.2). The precipitation in this region is seasonal. During winter, westerlies bring significant moisture from the Pacific Ocean while in summer only limited moisture arrives from the
Figure 2.6 Measured isotopic compositions of lake waters and lacustrine carbonates, shown in the context of model predictions for different lake scenarios (as in Figure 2.4).

Gulf of California. Therefore, the input water of Pyramid lake in summer time is mostly from Trukee river runoff which originates from winter precipitation in the Sierra Nevada (Benson, 1994). Assuming the isotopic composition of Trukee river water as a representative the isotopic composition of overall input water, we use the model developed in Section 3 to predict the triple oxygen isotope composition of Pyramid Lake (Figure 2.7A). The blue shaded area shows predicted values after considering the measurement error of input water. The measured isotopic compositions of the lake water overlap the model prediction for h ~0.6. This h value is not substantially different from the mean annual relative humidity value of 0.52 from the CRU 2.0 climate dataset (New et al., 2002).
Figure 2.7 Comparison of measured isotopic compositions lake waters and lacustrine carbonates for each lake and their model predicted values. Section 4 for details. (A) For Pyramid Lake, the blue shaded area represents model outputs for closed basin after considering the measurement error for input water. The measured data of lake waters and carbonates fall in the region where relative humidity is inferred as ~0.6. (B) For Mono Lake, blue shaded area represents model outputs for the closed basin scenario after considering the measurement error for input water. The difference between measured data and model predicted data may be related to several factors, as discussed in Sections 4 and 5. (C) For Bear Lake, the green shaded area represents model outputs assuming $X_E = 0.2$, the blue shaded area represents model outputs assuming $X_E = 0.5$, and the yellow shaded area represents model outputs assuming $X_E = 0.8$. Isotopic composition of input water is assumed to be the same as collected waters from Bear River and inlet canal. (D) For Great Salt Lake, causeways and roads separate the whole lake basin into different parts. Gilbert Bay samples show lower $\delta^{17}O$ and higher salinity while Farmington Bay samples have higher $\delta^{17}O$ and lower salinity.
Mono Lake is a closed basin lake located on the western side of the Great Basin and eastern edge of the Sierra Nevada (Figure 2.2). Mono Lake is fed by three major tributaries, Mill Creek, Lee Vining Creek and Rush Creek. Similar to Pyramid Lake, the precipitation in the Mono Lake catchment is also very winter-biased. On an annual scale, winter precipitation as well as surface runoff from Sierra Nevada dominates the water input of Mono Lake (Li et al., 1997). Model predictions of isotopic composition of Mono Lake are plotted in Figure 2.7B. The measured water $\Delta^{17}$O is higher but within error of the closed basin model for $h$ of about 0.5, which agrees with the mean annual $h$ value from the CRU 2.0 dataset of 0.53. A possible explanation for the slight deviation could be underground infiltration. The existence of lake water-groundwater exchange through faults and fractures at the bottom of the Mono Lake basin has been indicated (Rogers and Dreiss, 1995a; Rogers and Dreiss, 1995b), and if hydrologically important would undermine the closed basin assumption. In the case of net infiltration of lake water into the subsurface, $\Delta^{17}$O of lake water would be higher than in the purely closed-basin scenario. Values of $\alpha_{\text{diff}}$ and $R_v$ also strongly influence the model predictions, and will be discussed in Section 5. For parent waters calculated from carbonate samples collected along the mineral-encrusted banks of the lake, the closed basin model predicts $\delta^{18}$O and $\Delta^{17}$O values that are significantly lower and higher, respectively, than observed values. One possible explanation is that the waters in which these mineral crusts formed were hydrologically disconnected from the main lake during the course of evaporation and mineral precipitation. For this case, the isotopic composition of the water would continuously evolve and would be better modeled as a pan evaporation scenario (i.e., using the Rayleigh model discussed in section 5.5).
Lake Tahoe is a flow-through lake located within the Sierra Nevada range at a latitude intermediate of Pyramid Lake and Mono Lake. Unfortunately, we do not have measurements of its source water isotopic compositions, which precludes useful modeling of lake water isotopic compositions. If it is assumed that the source waters are isotopically similar to the inputs of Mono Lake (i.e., High Sierra snowmelt), the modeled lake water isotopic composition is lower in $\Delta^{17}$O (for any given $\delta^{18}$O) than the measured $\Delta^{17}$O values of lake water. However, the catchment elevation for Lake Tahoe is substantially lower than the catchment elevation of Mono Lake, and hence the assumption that both basins have similar source water isotopic compositions may not be a good one. We will refrain from further discussion of Lake Tahoe given the lack of necessary isotopic data for this lake system.

Bear Lake is located on eastern margin of the Great Basin and is surrounded by the Bear River Range to the west and the Bear Lake Plateau to the east (Figure 2.2). The Bear River bypasses the north end of the lake, but is hydrologically connected to the lake through human made inlet and outlet canals. Water diverted from Bear River contributes ~60% of the overall input water, with the balance of water input from several small streams and spring-fed streams from the Bear River Range and Bear Lake Plateau, as well as direct precipitation (Bright et al. 2006). The evaporation to input ratio ($X_E$) for Bear Lake is not well known, and estimates vary from 0.55 to 0.29 (Bright et al., 2006; Dean et al., 2009). Figure 2.7C shows that there is a good match between the modeled and measured isotopic compositions of Bear Lake water for models using h between 0.1
and 0.4, and $X_E$ of $\sim 0.5$, whereas for the carbonate-based water isotopic compositions the best match is for $h$ between 0.2 and 0.3 and $X_E$ of 0.8. In both cases, the $h$ values are significantly lower than CRU 2.0-based estimates of mean annual $h$ (0.56), and are lower than (or just overlap) with driest summer month $h$ (0.40). It is possible that $\alpha_{\text{diff}}$ or $R_v$ values (or both) used in the model are inappropriate for Bear Lake, and we further discuss the model sensitivity to these parameters in Section 5. The isotopic compositions of calculated parent waters of Bear Lake carbonates are significantly different from the isotopic compositions of Bear Lake waters. This may partly due to the difference between water collection time and shell growth or marl precipitation season. Model predictions for Bear Lake use the isotopic composition of Bear River and inlet canals to represent the input values. However, this assumption may be undermined because of the lack of data from spring waters and direct precipitation. Thus a more comprehensive survey is needed to have a better understanding of the isotopic hydrology of Bear Lake.

Great Salt Lake is a hypersaline lake without any surface outflow, and is fed by three primary rivers: Jordan River, Weber River and Bear River (Figure 2.2). However, the construction of causeways and roads has divided the lake basin into several parts, and each part has significantly different hydrology which is manifest clearly in differing salinities. Thus the Great Salt Lake is more appropriately considered as “a string of lakes” rather than a single closed basin lake. Water and carbonate samples in this study were collected from Farmington Bay and Gilbert Bay. Farmington Bay is a small water body making up the southeast part of the lake, and is separated from other parts of the lake by Antelope Island Road, and a salt flat in the south of Antelope Island. Jordan River is the
primary source of freshwater into Farmington Bay, and the bay water in turn flows into Gilbert Bay. Therefore, Farmington Bay has lower salinity compared to other parts of the Great Salt Lake. We can observe in Figure 2.7D that the water sample in Farmington Bay has the lowest salinity (3.1%) and highest $\delta^{17}\text{O}$ value, and isotopically falls into the throughflow lake realm. Gilbert Bay is the main part of South Arm of the Great Salt Lake and exchanges water with the North Arm through a causeway. It accepts water from Farmington Bay (itself fed by Jordan River) as well as from Weber River. Water and carbonate samples collected from Gilbert Bay show a higher salinity (13-14%) and lower $\delta^{17}\text{O}$ (Figure 2.7D) than water from Farmington Bay. We do not have samples from North Arm, which has salinities as high as 20-30%. Of all the parts of the Great Salt Lake, the North Arm is hydrologically most similar to a closed basin lake. Therefore we predict that it would have the lowest $\delta^{17}\text{O}$ values of all parts of the lake.

2.5 Discussion

2.5.1 Sensitivity to model parameters

2.5.1.1 Kinetic fractionation ($\alpha_{\text{diff}}$)

Model predicted results are sensitive to the choice of kinetic fractionation factor.

In the Craig and Gordon model, the kinetic fractionation factor is expressed as:

$$\alpha_{\text{diff}} - 1 = \theta \left[ \left( \frac{D}{D^*} \right)^n - 1 \right]$$  \hspace{1cm} (16)

Here, $D$ and $D^*$ are diffusivities of two isotopologues $\text{H}_2^{16}\text{O}$ and $\text{H}_2^{18}\text{O}$ respectively. Merlivat (1978) reported the ratio of these diffusivities as 1.0285. The exponent term $n$
ranges between 0.5 for turbulent flow and 1 for pure molecular diffusion. The coefficient \( \theta \) denotes the relative contribution of diffusive transport and can be assumed to be 1 for small bodies of water. However, according to Gat (1996), \( \theta \) can be higher for larger water bodies, such as North American Great Lakes (0.88) and Mediterranean Sea (0.5).

The range of \( \alpha_{\text{diff}} \) based on the Craig and Gordon model is shown in Figure 2.8A. For most lake studies, it is reasonable to assume that \( n \) is 0.5 and \( \theta \) is 1. Therefore, \( \alpha_{\text{diff}} \) will be calculated as 1.0142 (Gonfiantini, 1986; Gat, 1996; Gibson et al., 2002; Gibson et al., 2015). This value is basically consistent with wind tunnel experiments by Merlivat (1970) and Cappa et al. (2002).

Merlivat and Jouzel (1979) developed another model to estimate kinetic fractionation factors at the reference height over the ocean surface based on the evaporation model by Brutsaert (1975). In this model, different equations are applied for smooth and rough water-atmosphere surfaces based on the surface roughness Reynolds number and therefore wind speed (Figure 8B). However, Luz and Barkan (2010) reported \( \alpha_{\text{diff}} \) calculated from marine vapor as 1.0096 which is higher than Merlivat model prediction. Figure 8B shows that \( \alpha_{\text{diff}} \) has a major impact on model-predicted lake water isotopic compositions. Higher values of \( \alpha_{\text{diff}} \) result in waters with higher \( \Delta^{17}\text{O} \). Inasmuch as
Figure 2.8 (A) The effects of $\alpha_{\text{diff}}$ on model predicted $\delta^{18}O$ and $\Delta^{17}O$ for closed basin lake. (B) Calculated values of $\alpha_{\text{diff}}$ from Craig – Gordon model for different $n$ and $\theta$. Some of values measured and calculated by other investigators are also shown. Star symbol represents the value used in this study. Line 1: 1.0283 [molecular diffusion of water vapor in dry air, Barkan and Luz (2007)]; Line 2:1.0096 [vapor diffusion in air over ocean surface, Luz and Barkan (2010)]; Line 3:1.0062 [calculated value for smooth regime by equation in Merlivat and Jouzel (1979)]; Line 4:1.0035 [calculated value for rough regime by equation in Merlivat and Jouzel (1979)]. See section 5.1 for detailed discussion.
most of our model-data misfit involved data being higher in $\Delta^{17}O$ than model predictions, it is possible that the value of $\alpha_{\text{diff}} = 1.0142$ used in our models is too high for most Western U.S. lakes. A hypothesis that could be further investigated is that western U.S. lakes experience greater atmospheric turbulence due to generally windier conditions (and hence lower values of $\alpha_{\text{diff}}$) compared to the more humid-climate lakes upon which the typical $\alpha_{\text{diff}} = 1.0142$ value is largely based.

2.5.1.2 Sensitivity to the isotopic composition of atmospheric vapor ($R_v$)

As in our model, the isotopic composition of atmospheric moisture is commonly assumed to be in equilibrium with the local precipitation or runoff. This assumption is reasonable for most regions globally (Gibson et al., 2008). However, this assumption could be undermined in arid regions, for two basic reasons: (1) in arid regions with low $h$, the lake represents one of few possible sources of moisture to the atmosphere (in contrast with a humid climate where evapotranspiration on land surrounding the lake can be a major source of moisture to the atmosphere); and (2) in arid regions, the isotopic composition of the lake may depart significantly from the isotopic composition of precipitation due to evaporative enrichment in heavy isotopes. In other words, while all lakes will contribute water vapor to the local atmosphere, for flow-through lakes in humid climates this water vapor will be isotopically similar to vapor in equilibrium with local precipitation, while for arid climate lakes it is more likely to be markedly different from vapor in equilibrium with local precipitation.
Assuming the isotopic composition of atmospheric vapor for this case is a mixture of evaporated lake water and original advected vapor (in equilibrium with local precipitation or runoff) equation (12) can be rearranged as [equation (17) in Benson and White, 1994; equation (20) in Gibson et al., 2015]:

$$R_E = \frac{R_W - h \alpha_{eq} R_V F}{\alpha_{evap}^0 (1-h) + h (1-F) \alpha_{eq}}$$

where $F$ is the fraction of original advected vapor and other parameters are the same as described in Section 3. Therefore the equation for isotopic composition of lake water under steady-state [equation (13)] should be revised to

$$R_W = \frac{\alpha_{evap}^0 (1-h) + h (1-F) \alpha_{eq}}{X_E + \alpha_{evap}^0 (1-h) + h (1-F) \alpha_{eq}}$$

If $F$ is 1, this equation reduces to equation (13) which means all atmospheric vapor comes from advected vapor in equilibrium with local precipitation. Comparisons between this revised model and original model for the closed basin scenario under different relative humidity and different $F$ are shown in Figure 2.9. After considering the contribution of evaporating water, model predictions will have higher $\Delta^{17}$O and higher $\delta^{18}$O, and this effect will be more significant with higher atmospheric water vapor content (relative humidity) and lower fraction of advected vapor ($F$). These patterns are in the direction of the typical offset we observe between measured and modeled isotopic compositions, and
Figure 2.9 The effects of isotopic composition of atmospheric vapor ($R_T$) on model predictions. The revised isotopic composition of atmospheric vapor is a mixture of advected water vapor (equilibrium with local precipitation/runoff) and evaporating water vapor for lake water. The fractions of advected water vapor in final atmospheric vapor are denotes as $F$. Green lines represent revised model predicted values considering the mixture of evaporating water and red lines represent original model predicted values. (A) Models outputs for $F = 0$. (B) Models outputs for $F = 0.5$ (C) Models outputs for $F = 0.8$. See section 5.4 for detailed discussion.
hence it is plausible that the air masses over typical western U.S. lakes contain a substantial fraction of water vapor derived from the lakes themselves.

2.5.1.3 Sensitivity to salinity

Salinity could influence the isotopic enrichment of lake water in two ways. First, relative humidity (h) over salty water will reach higher values because saturated vapor pressure decreases as salt concentration increases. This will limit the extent of evaporation when the moisture content of the atmosphere reaches the saturation point with respect to the saline water. Second, hydration layers will form around ions in solution, and the preferential orientation of different water isotopologues within hydration layer can cause changes in equilibrium isotope fractionation factors.

This phenomenon was first observed by Feder and Taube (1952). Numerous subsequent investigations (e.g., Sofer and Gat, 1972; Sofer and Gat, 1975; Bopp, 1977; Horita, 1989; O’Neil and Truesdell, 1991; Horita 2005) of this “salt effect” for $^{18}O/^{16}O$ in aqueous solution have shown that the magnitude of salt effect depends on salt species and varies approximately linearly with the molarities of solution. In order to better describe the behavior of isotopes in brine water, isotope activity ratios instead of isotopic compositions are often used. However, according to these previous investigations, salinity for most natural waters is not high enough to significantly modify $^{18}O/^{16}O$ fractionation factors. According to Horita (2005), the calculated salinity effect on $^{18}O/^{16}O$ for Dead Sea water, which is among the most saline lakes in the world, is -2.4‰. This value could be considered as an upper limit of the salinity effect on $^{18}O/^{16}O$ in natural
waters. The salinity effect on $^{18}\text{O}/^{16}\text{O}$ fractionation for most natural waters is estimated to be less than 1‰, which is only slightly larger than our measurement precision. However, no data for salinity effects on $^{17}\text{O}/^{16}\text{O}$ have been reported to our knowledge. Hence we conducted the open pan evaporation experiment (described in Section 2) to quantify the salinity effect on both $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ during evaporation.

The results of these open pan evaporation experiments are given in Table 2.5 and illustrated in Figure 2.10. From Figure 2.10B, we can observe that $\delta^{18}\text{O}$ of remaining water increases as remaining water fraction decreases for deionized water, NaCl solution, KCl solution and MgCl$_2$ solution. However, for CaCl$_2$ solution, this trend slows and even reverses when evaporation is closing to the end. $\Delta^{17}\text{O}$ of remaining water (Figure 2.10C) decreases as remaining water fraction decreases for deionized water, NaCl solution, KCl solution and MgCl$_2$ solution. Similarly, for CaCl$_2$ solution, this trend slows and reverses at the final stage of evaporation. A possible explanation is that evaporation process slows and ceases when vapor pressure over the CaCl$_2$ solution surface reaches its saturation point. Therefore, the water will never totally dry up. However, the remaining water is still exchanging with atmospheric vapor and drives the isotopic composition of remaining water down to the equilibrium value with atmospheric vapor.
Table 2.5
Measured isotopic composition (units in ‰), remaining water fraction (Fw) and calculated fractionation factors for open pan evaporation experiments

<table>
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<th>Fw</th>
<th>N</th>
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<th>calculated</th>
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<tr>
<td></td>
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<td>δ¹⁸O VSMOW</td>
<td>Δ¹⁷O VSMOW</td>
</tr>
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<td>avg SD</td>
<td>avg SD</td>
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<td>0.002 0.12</td>
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<td>1.58 0.38</td>
<td>-0.006 0.12</td>
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**0.5M MgCl₂ Solution**

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<td>-0.07</td>
<td>0.45</td>
<td>-0.081</td>
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</tbody>
</table>

**0.5M CaCl₂ Solution**

**Note:** For samples measured only once, errors (SD) are reported as 1σ on long-term standard material measurements (0.38‰ for δ¹⁸O and 0.012‰ for Δ¹⁷O). For samples measured twice or more, errors (SD) are reported as larger value of long-term measurement precision of standard materials and 1σ on n analyses of water samples. $^{18}\alpha_{\text{evap}}$ is calculated as slope from the linear regression of ln($^{18}$R) – ln(F). $^{17}\alpha_{\text{evap}}$ is calculated as slope from the linear regression of ln($^{17}$R) – ln(F). $\lambda_{\text{evap}}$ is calculated as slope from the linear regression of $\delta^{17}$O – $\delta^{18}$O. Errors are reported as standard error (1σ) on regressed slope. Regression analysis are done by Microsoft Excel linest function.
Figure 2.10. Measured isotopic composition of residual water from open pan evaporation experiments. (A) $\delta^{17}$O - $\delta^{18}$O relationship of measurements results are shown. The slope of this line is considered as triple oxygen isotope fractionation component during the evaporation process $\lambda_{evap}$. (B) $\delta^{18}$O – ln($F$) relationship of measurement results are shown. As the remaining water fraction ($F$) decreases, $\delta^{18}$O increases. (C) $\Delta^{17}$O – ln($F$) relationship of measurement results are shown. As the remaining water fraction ($F$) decreases, $\Delta^{17}$O decreases. For samples only measured once, Error bars for $\delta^{18}$O and $\Delta^{17}$O are reported as the value of our long-term precision for standard materials (0.38‰ for $\delta^{18}$O and 0.012‰ for $\Delta^{17}$O). For samples measured twice or more, error bars are reported as the larger value of our long-term precision for standard materials and standard deviation of measurement.
A Rayleigh distillation model may be applied to describe the isotopic composition of remaining water during open pan evaporation:

\[
\frac{d\ln R_w}{d\ln F_w} = \left(\frac{1}{\alpha_{evap}} - 1\right) F_w
\]

(19)

where \(F_w\) is the remaining water fraction and \(\alpha_{evap}\) is apparent fractionation factor during the process of evaporation which is influenced by \(\alpha^0_{evap}, \alpha_{diff}\) and relative humidity.

Therefore \(\ln(R_w)\) and \(\ln(F_w)\) should have a linear relationship during evaporation, and from the slope for \(\ln(R_w) - \ln(F_w)\) line, one can calculate fractionation factors \(\alpha_{evap}\) for deionized water and different solutions. For the CaCl\(_2\) solution, we exclude the final collected sample \((F_w = 0.14)\) because it is apparently off the evaporation line and possibly collected after evaporation had ceased. Calculated values are listed in Table 3.5. The calculated \(^{18}\text{O}/^{16}\text{O}\) fractionation factors for deionized water, NaCl solution, KCl solution, MgCl\(_2\) solution and CaCl\(_2\) solution are 1.0154±0.0016, 1.0155±0.0017, 1.0160±0.0017, 1.0152±0.0021 and 1.0121±0.0015, respectively. There is no significant difference between deionized water and NaCl solution. KCl solution has a slightly higher \(\alpha_{evap}\) while MgCl\(_2\) has a slightly lower value. However, they do not have a significant difference within the precision of the experiment. In contrast, CaCl\(_2\) has a much lower \(\alpha_{evap}\) and that means CaCl\(_2\) could have a relative large salinity effect on \(^{18}\text{O}\) during evaporation. These results are basically consistent with previous investigations of \(^{18}\text{O}/^{16}\text{O}\) salinity effects, except MgCl\(_2\) does not show significant salinity effect in our open pan experiment (O’Neil and Truesdell, 1991; Horita 2005).
Triple oxygen fractionation exponents for the open pan evaporation experiments ($\lambda_{\text{evap}}$) can be calculated from the slope of $\delta^{17}$O - $\delta^{18}$O line (Figure 2.10A). They are calculated as 0.5204±0.0010, 0.5203±0.0016, 0.5198±0.0009, 0.5207±0.0013, 0.5208±0.0011 for deionized water, NaCl solution, KCl solution, MgCl$_2$ solution and CaCl$_2$ solution respectively. There is no significant difference between these values, and the values are typical of mass-dependent fractionation processes. Thus the salinity effect for $\Delta^{17}$O is apparently negligible during evaporation processes, at least under the precision of our experiments.

2.5.1.4 Sensitivity to formation temperature of carbonates

Accurate calculation of $\Delta^{17}$O and $\delta^{18}$O of parent waters of lacustrine carbonates is predicated on knowledge of the formation temperature of the carbonate (or, more precisely, knowledge of the isotopic fractionation factors between carbonate and water during mineral growth). Since the triple oxygen isotope fractionation exponent between carbonate minerals and water used here (0.5245; Passey et al., 2014) is different than the slope of reference line (0.528), errors in formation temperature will lead to errors in calculated $\Delta^{17}$O, as well as calculated $\delta^{18}$O. Using the calcite-water $^{18}$O/$^{16}$O fractionation factor temperature dependence of Kim & O’Neil (1997) and assuming that the triple oxygen isotope exponent is insensitive to temperature, a 10°C error in estimated formation temperature will lead to ~0.01‰ error in calculated water $\Delta^{17}$O, and ~2‰ error in calculated water $\delta^{18}$O. Thus, while these errors are important to consider, they are close to the analytical uncertainty of our methods, and are far smaller than the total isotopic variation that we observe in natural lakes.
2.5.2 Reconstructing paleohydrology and $\delta^{18}$O of unevaporated meteoric waters

A major impetus behind these efforts is the possibility of reconstructing past lake hydrology and $\delta^{18}$O of unevaporated meteoric water based on isotopic analysis of lacustrine carbonates. Here we explore the end member scenario where the only available information is the triple oxygen isotope composition of the lacustrine carbonate. How well can we reconstruct actual environmental conditions based on such data?

Perhaps the most basic approach is to use the measured $\Delta^{17}$O at face value to make statements about whether or not a paleolake was likely to have been significantly evaporated. From studies of present-day meteoric waters, it has been shown that global meteoric water has a mean $\Delta^{17}$O value of about 0.025‰ (Luz and Barkan (2010) report a mean value of 0.033‰ for a global survey, whereas Li et al. (2015) report a mean of 0.017‰ for conterminous United States meteoric waters), with values ranging between about -0.005 and 0.060‰. Therefore reconstructed lake water values lower than about -0.005‰ could be taken as strong evidence that the lake water is evaporated. We note that our measured mean value for flow-through lakes (~ 0.01‰) overlaps with the lower end of the meteoric water range, so it may be difficult to distinguish moderate evaporation from little or no evaporation. If our observations for closed basin lakes are representative, then values of ~ -0.025‰ (the mean value we observe for closed basin lakes) could be taken as evidence of a closed-basin lake, or at least a highly-evaporated lake.
Figure 2.11 Illustration of an approach for estimating $\delta^{18}O$ of meteoric waters based on reconstructed lake water isotopic compositions. (A) the method requires a typical evaporation slope for lakes ($\lambda_{avg}$), which can be calculated by regressing a line through all samples from different lake systems (here using Bear Lake and its input waters as an example). (B) In application to the fossil record, the reconstructed lake water isotopic composition is combined with the characteristic evaporation slope and the characteristic $\Delta^{17}O$ value of the GMWL to reconstruct the $\delta^{18}O$ of unevaporated meteoric water ($\delta^{18}O_{model-GMWL}$).
Figure 2.12 Reconstructed water isotopic compositions versus measured input water isotopic compositions. The model $\delta^{18}O_{\text{model-GMWL}}$ values are a far better approximation of input water isotopic compositions (and hence, meteoric water isotopic compositions) than are the reconstructed lake water $\delta^{18}O$ values.

In terms of reconstructing unevaporated meteoric water $\delta^{18}O$, the system is underconstrained, so strictly unambiguous reconstructions are likely not possible. However, it may be possible to improve significantly upon the lake water $\delta^{18}O$ value calculated from $\delta^{18}O$ and $T(\Delta_{47})$ of carbonate. We observe that the triple oxygen isotope slope of the evaporation trajectory is fairly uniform across the different lakes that we examined; regression of $\delta^{17}O$ versus $\delta^{18}O$ for all samples within a lake basin yield the following values: 0.5229 (Bear Lake), 0.5231 (Mono Lake), 0.5235 (Great Salt Lake), and 0.5220 (Pyramid Lake). This slope clearly varies for different hydrological scenarios (e.g., see the model predictions shown in Figure 2.4), but it may be possible to use a typical slope for purposes of back-calculating the isotopic composition of unevaporated water. Such back-calculation or back-projection (Figure 2.11) would require three
parameters: the measured triple isotopic composition of lacustrine carbonate, the typical evaporation slope, and a characteristic triple oxygen isotope GMWL. For purposes of the present discussion, we can assume that the typical evaporation slope is the average slope observed across the different lakes in our study, $\lambda_{\text{avg}} = 0.5229$. For simplicity, we assume that the GMWL has a slope of $\lambda_{\text{ref}} = 0.528$ and an intercept of $\Delta^{17}\text{O}_{\text{model-GMWL}} = 0.025\%_o$ (i.e., it is a straight line with value of 0.025‰ on a plot of $\Delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ where $\lambda_{\text{ref}} = 0.528$). Thus the reconstructed ‘unevaporated’ meteoric water $\delta^{18}\text{O}$ value is given by the intersection between the GMWL and a line with slope $\lambda_{\text{avg}}$ that passes through the reconstructed values of lake water, $\Delta^{17}\text{O}_{\text{w,meas}}$ and $\delta^{18}\text{O}_{\text{w,meas}}$ (Figure 2.11):

$$\delta^{18}\text{O}_{\text{model-GMWL}} = \frac{\Delta^{17}\text{O}_{\text{model-GMWL}}-\Delta^{17}\text{O}_{\text{w,meas}}+(\lambda_{\text{avg}}-\lambda_{\text{ref}})\delta^{18}\text{O}_{\text{w,meas}}}{\lambda_{\text{avg}}-\lambda_{\text{ref}}}$$

(20)

As a proof of concept, we calculate such model $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{model-GMWL}}$) based on our measured lake water and lacustrine carbonate parent water isotopic compositions, and compare these with the observed values for rivers entering those lakes (we exclude Pyramid Lake from this analysis as its primary source river, the Truckee River, is sourced partly from Lake Tahoe and hence is pre-evaporated). Figure 2.12 shows that there is generally a good correspondence between $\delta^{18}\text{O}_{\text{model-GMWL}}$ and measured river $\delta^{18}\text{O}$ values, and that the $\delta^{18}\text{O}_{\text{model-GMWL}}$ values are a far better approximation of river compositions than the uncorrected lake water $\delta^{18}\text{O}$ values. Clearly more studies will be needed to assess the usefulness of this approach, but it appears to be a promising way of further interpreting measured lacustrine carbonate triple oxygen isotope compositions.
2.6 Conclusions

We developed isotopic mass balance models that predict $\Delta^{17}$O in lake waters and lacustrine carbonates and which can be used to infer hydrological characteristics of present and past lake basins. Measured isotopic compositions of lake waters and lacustrine carbonates from the western US are generally consistent with model predictions. We clearly observe the lowering of $\Delta^{17}$O in closed basins. Model predictions are sensitive to the value of the kinetic fractionation factor ($\alpha_{\text{diff}}$). Higher $\alpha_{\text{diff}}$ results in larger fractionation during the process of evaporation. Therefore, model predicted values of $\Delta^{17}$O will be lower and $\delta^{18}$O will be higher. For many natural lakes, it is commonly assumed the isotopic composition of atmospheric vapor is in equilibrium with local precipitation/ runoff. However, the mixture of evaporating water vapor into atmospheric vapor will lead to higher $\Delta^{17}$O and higher $\delta^{18}$O. Salinity effects on $\Delta^{17}$O do not appear to be significant for NaCl, KCl, MgCl$_2$ and CaCl$_2$ solution from the observation of open pan evaporation experiments. A possible explanation is that the salinity effect on $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O follows a mass-dependent law with similar slope as the typical meteoric waters, and therefore they are canceled during the calculation of $\Delta^{17}$O. Overestimation or underestimation of carbonate formation temperature will lead small errors in calculated $\Delta^{17}$O of their ambient water. Therefore, an accurate estimation of formation temperature is required to have a better calculated $\Delta^{17}$O value and have a better estimation of lake paleoclimate and paleohydrology. Finally, we show that it is possible to estimate $\delta^{18}$O of unevaporated meteoric waters based on lake water triple oxygen isotopic compositions, given knowledge of a typical evaporation slope for lakes, and a characteristic triple oxygen isotope meteoric water line. This approach promises to provide much better
estimates of past meteoric water isotopic compositions than are possible based only on
$\delta^{18}$O analyses of lacustrine carbonates.

2.7 References

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2224.

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Pyramid Lake surface-water system. 1. Data analysis and extraction of paleoclimatic

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Truckee River-Pyramid Lake surface-water system. 3. Source of water vapor


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3 The effect of evaporation on oxygen isotopic compositions of soil carbonates: An examination by triple oxygen isotopes

Abstract

Oxygen isotope compositions ($\delta^{18}O$) of soil carbonates have been widely used to reconstruct $\delta^{18}O$ of local precipitation. However, published datasets show that there can be significant departures between calculated soil water $\delta^{18}O$ and amount-weighted mean annual $\delta^{18}O$ of local precipitation. Explanations for this offset include seasonality of soil carbonate formation and evaporative modification of $\delta^{18}O$ prior to soil carbonate formation. The development of carbonate clumped isotope thermometry has improved the ability to estimate soil carbonate formation temperatures and therefore seasonality. However, estimating the extent of evaporative modification soil water remains difficult. Here we explore the use of triple oxygen isotopes as an indicator of evaporative modification of oxygen isotopes in the parent waters of soil carbonates. We present triple oxygen and clumped isotope data for soil carbonates from East Africa, northern China and the western United States. We compare the reconstructed parent water triple oxygen isotope compositions with previously published triple oxygen isotope data for both unevaporated or slightly evaporated natural waters and significantly evaporated natural waters. The soil water isotopic compositions are most similar to unevaporated to slightly-evaporated meteoric water isotopic compositions, and do not show large evaporative modifications seen in, for example, closed basin lakes and leaf waters. We also explore a numerical model to simulate triple oxygen isotopes profiles in soil columns. The model shows that deep soil layers are much more resistant to evaporative modification.
compared with shallow layers, which is in general agreement with previous studies. Sensitivity tests demonstrate that lower relative humidity, higher potential evaporation as well as higher soil porosity and higher soil tortuosity can enhance evaporation in the soil column and therefore lead to stronger and deeper evaporative modifications on triple oxygen isotopes.

3.1 Introduction

The oxygen isotopic composition of soil carbonate is primarily controlled by the isotopic composition of local precipitation, provided that precipitation is the dominant supply of soil water in well-drained soils (Cerling 1984). Therefore, soil carbonate can be used to reconstruct the isotopic composition of meteoric water and to investigate climatic and topographic conditions, assuming isotopic equilibrium has been reached during the formation of soil carbonate, the temperature of carbonate growth is generally known, and no major post-formation alteration has occurred (e.g., Quade et al. 1989; Cerling and Quade 1993; Quade et al. 2007; Rowley and Garzione 2007).

However, many datasets show significant deviation between the oxygen isotopic compositions of local mean annual precipitation ($\delta^{18}O_{\text{mw}}$) and the oxygen isotopic composition of soil waters inferred from measurements of soil carbonate ($\delta^{18}O_{\text{sw}}$).
Figure 3.1 Data compilation of soil water $\delta^{18}O$ calculated from soil carbonates vs. observed $\delta^{18}O$ of local precipitation (Table S1). (A) Oxygen isotopic compositions of local precipitation is reported as amount-weighted mean annual $\delta^{18}O$. Most samples are above the 1:1 line except those from Tibet, China and East Africa. (B) Oxygen isotopic compositions of local precipitation are reported as mean summer $\delta^{18}O$ (for the northern hemisphere) or warmest three months (for sites near the equator). Most samples are closer to the 1:1 line compared with (A). All temperatures used in calculation of soil water $\delta^{18}O$ are from clumped isotope thermometry. Local precipitation data are extracted from the Online Isotopes in Precipitation Calculator (OIPC) (Bowen and Revenaugh 2003; Bowen 2013).
Figure 3.1 shows compiled data from studies that evaluate soil carbonate formation temperatures and $\delta^{18}O_{sw}$ using clumped isotope thermometry (Passey et al., 2010; Quade et al., 2013; Hough et al., 2014). The reconstructed $\delta^{18}O_{sw}$ values are consistently higher than mean annual $\delta^{18}O_{mw}$ values, and more similar to the $\delta^{18}O_{mw}$ of warm-season precipitation.

Possible explanations for this phenomenon include: (1) the seasonality of soil carbonate formation such that soil carbonate does not record the mean annual soil temperature or mean annual isotopic composition of meteoric water; and (2) evaporative modification of soil water isotopic compositions such that they no longer represent $\delta^{18}O_{mw}$.

Initial studies of the carbonate clumped isotope compositions of recent soil carbonates (Passey et al. 2010; Quade et al. 2013; Hough et al. 2014) along with an earlier monitoring study by Breecker et al. (2009) suggested that soil carbonate formation is strongly biased towards the warm season. If true, this would be consistent with explanation (1), suggesting that the soil waters recorded by soil carbonates primarily reflect warm season precipitation. However, several exceptions to this 'warm season bias' in soil carbonate formation have now been reported, typically for soil carbonates forming in climates with persistently wet warm seasons and dry cool seasons (Peters et al. 2013; Burgener et al. 2016; Gallagher et al., 2016). In terms of the second hypothesis, evaporative enrichment can be mitigated by sampling deep pedogenic carbonates (>50cm), which are commonly considered to be an approximation of unevaporated meteoric water (Quade et al. 1989). However, many studies have also shown that $^{18}O/^{16}O$
enrichment (be it related to evaporation or seasonal bias) is not fully eliminated in deep soil carbonates (e.g., Figure 3.1; Quade et al. 2007; Burgener et al. 2016). Therefore, the lack of quantitative proxies to indicate the extent of evaporative enrichment in soil carbonates still hinders the elucidation of oxygen isotopic composition of soil carbonates.

Fractionation in $^{17}$O/$^{16}$O relative to fractionation of $^{18}$O/$^{16}$O has long been known to follow a mass dependency rule ($\delta^{17}$O = $\theta \delta^{18}$O, notation is described in section 2.2). The triple oxygen isotope fractionation exponent $\theta$ is typically ~0.52 for terrestrial processes. However, these fractionation exponents vary slightly for different processes, leading to non-zero values of the $\Delta^{17}$O parameter, where $\Delta^{17}$O = $\delta^{17}$O - $\lambda \delta^{18}$O, and $\lambda$ is a constant representing a typical fractionation relationship. Luz and Barkan have shown that this triple oxygen isotope fractionation exponent $\theta$ has different values for water-water vapor equilibrium and the diffusion of water vapor in dry air, experimentally determined as 0.529 and 0.5185, respectively (Barkan and Luz 2005; Barkan and Luz 2007). Therefore, evaporation will drive $^{17}$O/$^{16}$O ratios from the equilibrium fractionation line, and the degree of such deviation (represented by $\Delta^{17}$O) can be used as a quantitative indicator of the extent of evaporation (e.g., Landais et al., 2006; Surma et al., 2015).

$\Delta^{17}$O in liquid water has been increasingly studied as a hydrological parameter in the past decade (e.g., Landais et al., 2006, 2008, 2010; Luz and Barkan, 2010; Li et al., 2015; Surma et al., 2015). However, comprehensive investigation of $\Delta^{17}$O variation in carbonates has been limited owing to a lack of high-precision and time-efficient methods for analyzing $\Delta^{17}$O in carbonate minerals. The recently developed method by Passey et al.
(2014) enables high-precision $\Delta^{17}O$ measurements of carbonate minerals and has been successfully used on materials from multiple environmental settings.

In this study, we present triple oxygen isotope data from both recent and fossil soil carbonates from East Africa, China and the United States. Then we discuss how $\Delta^{17}O$ can be used to estimate the extent of evaporative modifications on isotopic compositions recorded in soil carbonate minerals. We also develop a numerical model to simulate triple oxygen isotope profiles in drying soil adapted from equations presented in Mathieu and Bariac (1996). Our goal is to provide a new geochemical proxy in soil carbonates to decouple $\delta^{18}O$ variation driven by evaporation from $\delta^{18}O$ variation related to other climatic factors.

3.2 Materials and Methods

3.2.1 Samples

Recent soil carbonates were collected from China, Ethiopia and United States (Table 3.1; Figure 3.2). CN2008-DM-164-130-1 is a pendant-type soil carbonate and was collected at 130cm depth from Damiao, Inner Mongolia, China. Precipitation in Damiao is strongly summer biased under the influence of East Asian Monsoon. The average temperature for warmest three month is 20.8°C while the mean annual temperature is only 6.0°C,
Figure 3.2 Triple oxygen isotopes for recent soil carbonates as well as paleosols from East Africa, China and USA (Table 1). (A) Isotopic compositions of carbonates reported as values of directly analyzed O₂ liberated from carbonate by the acid digestion / reduction / fluorination procedure. Error bars for δ¹⁸O and Δ¹⁷O are 1σ. For samples measured only once, error bars are reported as 1σ observed for repeated analysis of standards (0.70‰ for δ¹⁸O and 0.010‰ for Δ¹⁷O). (B) Isotopic compositions of carbonates are reported as their corresponding parent waters, calculated using equations described by Passey et al. (2014) assuming isotopic equilibrium has been reached between carbonates and their parent waters. Temperatures used to calculate fractionation factors between carbonate and ambient water are calculated from clumped isotope thermometry. Error bars for δ¹⁸O and Δ¹⁷O are calculated based on standard error propagation using 95% confidential intervals or 1.96 * S.E.M. Parameters used in calculation are reported by Passey et al. (2014).
showing a large seasonal temperature variation in this region. CA08-BHS-005-01 is also a pedant-type soil carbonate and was sampled at 140cm depth. It was collected from Blackhawk Slide, Mojave Desert, California in USA which has a hot and dry climate pattern. Mean annual precipitation in sampling site is only 105.4mm while the average temperature of warmest three months can reach 25.8°C. GONJQ-305-01 and GON07 samples are small nodule carbonates and were collected from Gona, Ethiopia. ET05-AWSH-48 is crack fill carbonates and was collected from Awash, Ethiopia. Gona and Awash are both located within 12 latitudinal degrees of the equator and therefore shows a very small seasonal temperature variation. Detailed descriptions of these samples and climate conditions in sampling sites are provided in Passey et al. (2010). Five vertisol samples including BUR MH 30 Buff, BUR MH 70 White, SHP 80 XTLN, SHP 100 Buff and RCWMA LD 129-140E were collected from Texas, USA. The number in sample labels denote their depth below surface. Two BUR MH samples were collected from high terrace near Snook, TX with an estimated age of 16-18 ky. Two SHP samples were collected from lowest terrace from Texas A&M Experimental Station near College Station, TX with an estimated age of <400-1000 yr. More information of these samples are described in Robinson (2002). RCWMA LD sample was collected from Richland Creek Wildlife Management Area near Fairfield, TX and detailed descriptions is provided in Michel et al. (2013).
### Table 3.1
Fossil and modern soil carbonate information, measured isotopic composition, and calculated parent water isotopic composition

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Description</th>
<th>Depth</th>
<th>N</th>
<th>Measured</th>
<th>T (°C)</th>
<th>δ^18O_VSMOW avg</th>
<th>Δ^17O_VSMOW avg</th>
<th>Calculated δ^18O_VSMOW avg ±</th>
<th>Calculated Δ^17O_VSMOW avg ±</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>East Africa Fossil Soil Carbonate (paleosol)</strong></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KN07WT-429</td>
<td>Nachukui Formation 3.42 Ma</td>
<td>618 m</td>
<td>2</td>
<td>34.729</td>
<td>40.8</td>
<td>0.287</td>
<td>-0.119</td>
<td>1.0336</td>
<td>1.652 ± 1.25</td>
</tr>
<tr>
<td>KN07WT-436</td>
<td>Nachukui Formation 3.63 Ma</td>
<td>652 m</td>
<td>3</td>
<td>33.552</td>
<td>28.0</td>
<td>0.570</td>
<td>-0.119</td>
<td>1.0362</td>
<td>-1.966 ± 1.11</td>
</tr>
<tr>
<td>KN07WT-475</td>
<td>Nachukui Formation 1.32 Ma</td>
<td>112 m</td>
<td>2</td>
<td>35.019</td>
<td>36.1</td>
<td>0.541</td>
<td>-0.131</td>
<td>1.0345</td>
<td>1.069 ± 1.25</td>
</tr>
<tr>
<td>KN07WT-488</td>
<td>Nachukui Formation 1.46 Ma</td>
<td>187 m</td>
<td>2</td>
<td>33.585</td>
<td>36.1</td>
<td>0.355</td>
<td>-0.128</td>
<td>1.0345</td>
<td>4.014 ± 1.24</td>
</tr>
<tr>
<td>KN07WT-502</td>
<td>Nachukui Formation 1.02 Ma</td>
<td>85 m</td>
<td>3</td>
<td>41.987</td>
<td>36.5</td>
<td>0.427</td>
<td>-0.133</td>
<td>1.0345</td>
<td>8.112 ± 1.11</td>
</tr>
<tr>
<td>ET04-OMO-303</td>
<td>Shungura Formation 2.51 Ma</td>
<td>511 m</td>
<td>2</td>
<td>34.574</td>
<td>32.7</td>
<td>0.022</td>
<td>-0.124</td>
<td>1.0352</td>
<td>0.492 ± 1.25</td>
</tr>
<tr>
<td>ET04-OMO-307</td>
<td>Shungura Formation 2.45 Ma</td>
<td>504 m</td>
<td>2</td>
<td>33.585</td>
<td>35.9</td>
<td>0.471</td>
<td>-0.125</td>
<td>1.0346</td>
<td>-0.403 ± 1.25</td>
</tr>
<tr>
<td>ET04-OMO-323</td>
<td>Shungura Formation 2.77 Ma</td>
<td>573 m</td>
<td>2</td>
<td>33.807</td>
<td>35.9</td>
<td>0.709</td>
<td>-0.115</td>
<td>1.0346</td>
<td>-0.791 ± 1.25</td>
</tr>
<tr>
<td><strong>East Africa Modern Soil Carbonate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>GONJQ-305-1</td>
<td>Nodule</td>
<td>50 cm</td>
<td>2</td>
<td>33.684</td>
<td>29.1</td>
<td>0.156</td>
<td>-0.117</td>
<td>1.0359</td>
<td>-1.616 ± 1.25</td>
</tr>
<tr>
<td>GON07-4.3-1</td>
<td>Nodule</td>
<td>13 cm</td>
<td>2</td>
<td>37.080</td>
<td>35.9</td>
<td>0.759</td>
<td>-0.135</td>
<td>1.0346</td>
<td>3.092 ± 1.24</td>
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<tr>
<td>GON07-4.6-2</td>
<td>Nodule</td>
<td>35 cm</td>
<td>1</td>
<td>36.600</td>
<td>39.3</td>
<td>0.700</td>
<td>-0.139</td>
<td>1.0337</td>
<td>3.432 ± 1.58</td>
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<tr>
<td>GON07-4.7-1</td>
<td>Nodule</td>
<td>45 cm</td>
<td>2</td>
<td>34.695</td>
<td>28.9</td>
<td>0.532</td>
<td>-0.123</td>
<td>1.0360</td>
<td>-0.644 ± 1.25</td>
</tr>
<tr>
<td>ET05-AWSH-48-1</td>
<td>Crack fill</td>
<td>130 cm</td>
<td>2</td>
<td>34.169</td>
<td>25.2</td>
<td>0.190</td>
<td>-0.119</td>
<td>1.0367</td>
<td>-1.911 ± 1.25</td>
</tr>
<tr>
<td><strong>California, USA Modern Soil Carbonate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA08-BHS-005-1</td>
<td>Pendant</td>
<td>140 cm</td>
<td>2</td>
<td>27.388</td>
<td>24.9</td>
<td>0.383</td>
<td>-0.121</td>
<td>1.0368</td>
<td>-8.754 ± 1.25</td>
</tr>
<tr>
<td><strong>Inner Mongolia, China Modern Soil Carbonate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN2008-DM-164-130-1</td>
<td>Pendant</td>
<td>130 cm</td>
<td>1</td>
<td>29.497</td>
<td>23.4</td>
<td>0.700</td>
<td>-0.137</td>
<td>1.0371</td>
<td>-6.950 ± 1.59</td>
</tr>
<tr>
<td><strong>Texas, USA Modern Soil (Vertisol) Carbonate</strong></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

78
<table>
<thead>
<tr>
<th>Location</th>
<th>Depth</th>
<th>Sample</th>
<th>Isotope</th>
<th>δ₁⁸O</th>
<th>Δ₁⁷O</th>
<th>δ₁₁₂</th>
<th>Temperature</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>BUR MH 30 Buff</td>
<td>30 cm</td>
<td>1</td>
<td>34.516</td>
<td>0.700</td>
<td>-0.122</td>
<td>0.010</td>
<td>25.6</td>
<td>1.0366</td>
</tr>
<tr>
<td>SHP 80 XTLN</td>
<td>80 cm</td>
<td>2</td>
<td>35.076</td>
<td>0.144</td>
<td>-0.122</td>
<td>0.003</td>
<td>32.0</td>
<td>1.0353</td>
</tr>
<tr>
<td>RCWMA LD 129-140E</td>
<td>129-140 cm</td>
<td>2</td>
<td>33.900</td>
<td>0.011</td>
<td>-0.117</td>
<td>0.000</td>
<td>31.1</td>
<td>1.0355</td>
</tr>
<tr>
<td>BUR MH 70 White</td>
<td>70 cm</td>
<td>2</td>
<td>35.440</td>
<td>0.447</td>
<td>-0.111</td>
<td>0.018</td>
<td>24.2</td>
<td>1.0369</td>
</tr>
<tr>
<td>SHP 100 Buff</td>
<td>100 cm</td>
<td>1</td>
<td>35.611</td>
<td>0.700</td>
<td>-0.112</td>
<td>0.010</td>
<td>25.8</td>
<td>1.0366</td>
</tr>
</tbody>
</table>

Note: Unit for isotopic compositions is ‰. For samples measured only once, errors (SD) are reported as 1σ on long-term standard material measurements (0.70‰ for δ¹⁸O and 0.010‰ for Δ¹⁷O). For samples measured twice or more, errors (SD) are reported as 1σ on n analyses of carbonate samples. Errors for calculated isotopic composition of their ambient water (±) are reported from standard error propagation using 95% confidential intervals or 1.96 * S.E.M of parameters reported by Passey et al. (2014). Temperatures are calculated by clumped isotope thermometry. For Texas vertisol samples, clumped isotope temperatures are measured in this study. All the other temperatures are provided by Passey et al. (2010).

a. For the East Africa fossil soil carbonate samples, this depth corresponds to the maximum burial depth of the samples. For all other samples, this depth corresponds to depth below the soil surface from which the carbonate was collected.
In addition to modern soil carbonates, fossil soil carbonates (paleosols) were also measured in this study. ET04-OMO and KN07-WT samples were paleosols collected from the Shungura Formation and Nachukui Formation, respectively, in East Africa. All samples formed within the past 4 Ma, with age uncertainties of ~40ka (Passey et al. 2010). A brief description and burial depth of paleosol samples are provided in Table 1.

3.2.2 Notation and Laboratory measurements of triple oxygen isotopes

The isotopic fractionation factor for $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O between phase A and phase B follows an exponential relationship for mass-dependent processes and can be described as:

$$^{17}\alpha_{A-B} = (^{18}\alpha_{A-B})^\theta$$  \hspace{1cm} (1)

where $\alpha$ denotes the isotope fractionation factor (defined as $^*\alpha_{A,B} = ^*R_A / ^*R_B$ and $R$ is the ratio of heavy isotope to $^{16}$O). The triple oxygen fractionation exponent symbol $\theta$ is generally used for simple chemical or physical process while $\lambda$ is used for complicated systems involving multiple processes such as the net behavior of the hydrological cycle.

Triple oxygen isotope fractionation exponents vary among different processes. As mentioned in the introduction, $\theta$ for water-water vapor equilibrium and the diffusion of water vapor in dry air are experimentally determined as 0.529±0.001 and 0.5185±0.0002 respectively (Barkan and Luz 2005; Barkan and Luz 2007). For the overall net behavior of global hydrological processes, a fractionation exponent $\lambda$ has been determined as 0.528 based on published data of meteoric waters (Luz and Barkan 2010). This value is generally consistent with theoretical predictions of Rayleigh processes and has been
widely chosen as the slope of reference line to study hydrology problems (e.g., Luz and Barkan, 2010; Passey et al., 2014; Li et al., 2015; Surma et al. 2015). Therefore, in this paper the parameter $\Delta^{17}$O, which denotes the extent of $^{17}$O/$^{16}$O deviating from reference line, is defined as:

$$\Delta^{17}$O = $\delta^{17}$O - 0.528 $\times$ $\delta^{18}$O \quad (2)$$

where the delta-prime notation ($\delta'$) is defined as:

$$\delta'^{18}O_A = 1000 \ln(^{18}R_A / ^{18}R_{ref}) \quad (3)$$

All triple oxygen isotope measurements of soil carbonates were conducted at Johns Hopkins University during summer 2013 and summer 2015. Detailed descriptions of analytical conditions and normalization methods are described in Passey et al. (2014). In short, there are three phases before samples are finally sent into the mass spectrometer. First, carbonate samples are reacted with 100% H$_3$PO$_4$ at 90°C to release CO$_2$ in a vacuum line. Second, the purified CO$_2$ is introduced into a reduction line to react with H$_2$ at 560°C to yield H$_2$O, and this reaction is catalyzed by Fe powder. Third, released H$_2$O is fluorinated by CoF$_3$ at 350°C to yield O$_2$. Finally, the released O$_2$ is analyzed by a Thermo MAT 253 mass spectrometer for $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O ratios. All measured data are then normalized to the VSMOW-SLAP scale as introduced by Schoenemann et al. (2013). Under this normalization framework, $\delta^{18}$O and $\delta^{17}$O as well as $\Delta^{17}$O for VSMOW are all defined as 0‰. For the SLAP standard (Standard Light Antarctic Precipitation), $\delta^{18}$O and $\Delta^{17}$O are defined as -55.5‰ and 0‰, respectively. Therefore $\delta^{17}$O of SLAP is calculated as -29.6986‰.
During the course of measurements, we obtained values for NBS-19 as (n = 9, all ± values are 1σ): \( \delta^{18}O = 36.372 \pm 0.550 \%o \), and \( \Delta^{17}O = -0.139 \pm 0.005 \%o \). For NBS-18, the measured values are (n = 4, all ± values are 1σ): \( \delta^{18}O = 15.237 \pm 0.705 \%o \), and \( \Delta^{17}O = -0.099 \pm 0.002 \%o \).

3.2.3 Formation temperatures for soil carbonates and clumped isotope measurements

All formation temperatures of soil carbonates are estimated based on clumped isotope thermometry. Clumped isotope temperatures of the recent soil carbonates from East Africa, Inner Mongolia, China and California, USA as well as paleosols from East Africa are taken from Passey et al. (2010). Clumped isotope compositions of Texas vertisols were measured at Johns Hopkins University in summer 2015 following methods described in Henkes et al. (2013). Temperatures were calculated based on Equation 5 of Passey and Henkes (2012). For reference, this equation is developed by shifting theoretical equations in Shauble et al. (2006) since we used 90°C acid bath digestion method in our lab. We observed the following values for carbonate standards analyzed during the course of our study: NBS-19: \( \Delta_{47} = 0.392 \pm 0.018 \%o \) (1σ, n = 15); 102-GC-AZ01: \( \Delta_{47} = 0.693 \pm 0.013 \%o \) (1σ, n = 21) (an internal standard).

3.3 Results

Isotopic compositions of all soil carbonates are presented in Table 3.1 and plotted in Figure 3.2. Figure 3.2A shows the isotopic compositions of the soil carbonates (as the \( O_2 \) generated from the acid digestion / reduction / fluorination method), whereas Figure 3.2B
shows the equivalent soil water isotopic compositions calculated from measured values of soil carbonates. The isotopic fractionation factors used in this calculation are based on the equation for temperature dependency of the calcite-water $^{18}$O/$^{16}$O fractionation presented in Kim and O’Neil (1997). Triple oxygen isotope fractionation exponent (0.5245) is from Passey et al. (2014). As discussed in section 2.3, all formation temperatures are estimated by clumped isotope thermometry.

For recent soil carbonates from East Africa, China and USA, $\delta^{18}$O values range from 27.4‰ to 37.1‰. For their corresponding soil waters, calculated $\delta^{18}$O values range from -8.8‰ to 3.4‰. The sample with lowest $\delta^{18}$O was collected from Inner Mongolia, China while the highest $\delta^{18}$O value was observed from sample collected from East Africa. Excluding two shallow carbonate samples GON07-4.3-1 and GON07-4.6-2 which were collecte from 13cm and 35cm depth, respectively, $\delta^{18}$O values for all deep carbonates range from 27.4‰ to 35.6‰ and corresponding soil waters $\delta^{18}$O values range from -8.8‰ to -0.3‰.

In contrast to the large range of observed $\delta^{18}$O value (>8‰) within our dataset, $\Delta^{17}$O values of recent soil carbonates range from -0.023‰ to 0.008‰. Moreover, when excluding shallow carbonates, $\Delta^{17}$O values range between -0.009‰ to 0.008‰, which is a range that is similar the propagated error (~0.017‰) for calculated soil water $\Delta^{17}$O values. The highest $\Delta^{17}$O value was observed from shallow soil carbonates in Ethiopia while the lowest $\Delta^{17}$O value obtained from deep soil carbonates from another sampling sites in Ethiopia. In terms of deep soil carbonates (>50 cm), the sample with lowest $\Delta^{17}$O
was collected from Inner Mongolia, China.

For paleosols collected from East Africa, $\delta^{18}O$ values range from 33.6‰ to 42.0‰. Their corresponding soil waters have $\delta^{18}O$ values that range from -1.9‰ to 8.1‰. Similar to the pattern shown in recent soil carbonates, $\Delta^{17}O$ for all paleosol samples also has a small range from -0.014‰ to 0.006‰.

3.4. Discussion

3.4.1 $\delta^{18}O$ of soil waters calculated from soil carbonates ($\delta^{18}O_{sw}$) vs. $\delta^{18}O$ of local precipitation ($\delta^{18}O_{mw}$)

Understanding the relationship between observed $\delta^{18}O$ of local precipitation and calculated $\delta^{18}O$ of soil waters from soil carbonates is crucial for the usage of isotopic composition of soil carbonates as a proxy to local primary precipitation. Many datasets have been presented since early studies such as Solomans et al. (1978) and Cerling (1984) first demonstrated positive relationships between $\delta^{18}O_{mw}$ and $\delta^{18}O_{sw}$. However, formation temperatures of soil carbonates used to calculate isotopic fractionation factors in these published data are often estimated based on local mean, minimum, or maximum annual air temperatures (e.g. Quade et al. 1989; Cerling and Quade 1993; Quade et al. 2007; Rowley and Garzione 2007). Recent developments in clumped isotope thermometry provide independent constraints on soil carbonate formation temperature (e.g., Passey et al. 2010; Quade et al. 2013; Peters et al. 2013; Hough et al. 2014). Therefore, it is worthwhile to revisit this relationship based on new data.
As discussed in the introduction, we compiled three datasets published in recent years. Sampling sites in these datasets include East Africa (Passey et al., 2014); Inner Mongolia, China (Passey et al., 2014); Tibet, China (Quade et al., 2013); India (Quade et al., 2013) and California (Passey et al., 2014), Nebraska, Wyoming (Hough et al., 2014), Arizona, Nevada (Quade et al., 2013), USA. These sampling sites encompass a broad range of latitude, rainfall and temperature. Formation temperatures of soil carbonates used to calculate isotopic fractionation factors are obtained from clumped isotope thermometry. Isotopic compositions of soil waters (δ\(^{18}\)O\(_{sw}\)) were calculated based on the equation for carbonate-water temperature-dependent isotopic fractionation presented in Kim and O’Neil (1997). Oxygen isotopic composition of local precipitation (δ\(^{18}\)O\(_{mw}\)) were obtained from Online Isotopes in Precipitation Calculator (OIPC) (Bowen and Revenaugh 2003; Bowen 2013).

We therefore plot calculated δ\(^{18}\)O\(_{sw}\) against observed δ\(^{18}\)O\(_{mw}\) in Figure 3.1. In Figure 3.1A, δ\(^{18}\)O\(_{mw}\) (ma) are precipitation-weighted average annual values. Meanwhile in Figure 3.1B, δ\(^{18}\)O\(_{mw}\) (ms) are average values for warmest three months (For low latitude locations such as East Africa) or summer months (June, July, August; For mid latitude locations in northern hemisphere).

Two observations can be obtained from the compiled dataset: (1) There is an obvious positive departure of δ\(^{18}\)O\(_{sw}\) from 1:1 line of precipitation-weighted average annual δ\(^{18}\)O\(_{mw}\) (ma) in most sampling sites except Tibet, China and East Africa. The average value for this departure [δ\(^{18}\)O\(_{sw}\) - δ\(^{18}\)O\(_{mw}\) (ma)] is calculated as 2.6‰ for all samples. This
result is generally consistent with previous studies (e.g., Quade et al. 1989; Quade et al. 2007) but has a slightly lower value. The average departure of $\delta^{18}O_{sw}$ from $\delta^{18}O_{mw\text{(ma)}}$ for all deep carbonates (>50 cm) is 2.4‰ while shallow soil carbonates have a higher value of 3.4‰. Small seasonal variation of temperature and precipitation in low latitude East Africa possibly explains the small deviation of $\delta^{18}O_{sw}$ over $\delta^{18}O_{mw\text{(ma)}}$ in East African samples. In Tibet, $\delta^{18}O_{mw\text{(ma)}}$ is coincidently similar with $\delta^{18}O_{mw\text{(ms)}}$. (2) This departure can be reduced when comparing $\delta^{18}O_{sw}$ against summer months or warmest three months $\delta^{18}O_{mw\text{(ms)}}$ (Figure 3.1B). The average value for the difference between $\delta^{18}O_{sw}$ and $\delta^{18}O_{mw\text{(ms)}}$ is only 0.8‰ for all samples. Similarly, shallow soil carbonates preserve a higher average departure value (1.4‰) compared to deep soil carbonates (0.7‰).

Therefore, calculated $\delta^{18}O_{sw}$ should be interpreted cautiously. Sampling deep soil carbonates can mitigate the departure of $\delta^{18}O_{sw}$ from $\delta^{18}O_{mw}$ but cannot fully eliminate it. This departure can be partly attributed to the seasonality of soil carbonate formation but we cannot rule out the effect of evaporation modification with only $\delta^{18}O$ data from soil carbonates.

### 3.4.2 Estimating the extent of evaporation from soil carbonate $\Delta^{17}O$

We demonstrate triple oxygen isotope compositions of evaporating waters predicted by a conceptual Rayleigh fractionation model in Figure 3.3.
This conceptual model assumes water in a reservoir is evaporating into infinite and humid atmosphere. Oxygen isotopic composition of atmospheric vapor is constant and is in equilibrium with primary precipitation. Based on the theoretical framework in Criss (1999), the oxygen isotopic composition of evaporating water can be calculated by:

$$d\ln R_w = (\frac{1}{\alpha_{evap}} - 1)d\ln F$$  \hspace{1cm} (4)$$

where the star denotes the mass number of heavy isotopes (17 or 18). The remaining water fraction is denoted as $F$. The isotope ratio of remaining water and isotopic fractionation factor during evaporation are denoted as $R_w$ and $\alpha_{evap}$ respectively. The effective isotopic fractionation factor during evaporation ($\alpha_{evap}$) is determined by relative humidity ($h$), isotopic composition of atmospheric vapor ($R_V$) and remaining water ($R_W$), isotopic fractionation factors for water-vapor equilibrium ($\alpha_{eq}$) and molecular diffusion of water vapor in dry air ($\alpha_{diff}$). It can be calculated by Equation 4.31 in Criss (1999) as:

$$\alpha_{evap} = \frac{\alpha_{evap}^0(1-h)}{1-\alpha_{eq}hR_V/R_W}$$  \hspace{1cm} (5)$$

where $\alpha_{evap}^0$ is effective isotopic fractionation factor for evaporation when relative humidity is 0 and can be calculated as:

$$\alpha_{evap}^0 = \alpha_{eq} \times \alpha_{diff}$$  \hspace{1cm} (6)$$

As shown by schematic diagram (Figure 3.3), evaporation can drive $\delta^{18}O$ in remaining water toward higher values. However, there is significant overlap in $\delta^{18}O$ given the broad range of $\delta^{18}O$ in primary precipitation. Therefore, it is very difficult to use $\delta^{18}O$ alone to distinguish evaporated waters from their original precipitation. On the other hand, $\Delta^{17}O$ will become lower as evaporation proceeds. This is due to lower triple oxygen isotope fractionation exponent value for diffusion of water vapor through air ($\theta_{diff} = 0.5185$)
compared with the reference line ($\lambda = 0.528$). As shown in the figure, evaporated waters should have lower $\Delta^{17}$O values than primary precipitation, with some but significantly less overlap than is the case with $\delta^{18}$O. The extent of $\Delta^{17}$O lowering is also affected by relative humidity. Lower relative humidity tends to enhance the fraction of kinetic process during evaporation and increase the deviation of $^{17}$O from the reference line.

Therefore, $\Delta^{17}$O can be used to distinguish unevaporated or slightly evaporated primary precipitation against significant evaporated water body. A significant lowering of $\Delta^{17}$O compared with local primary precipitation in water body and their associated carbonate could be considered as an indicator for significant evaporation.

To estimate the evaporation signal preserved in our soil carbonate samples, we plot measured $\Delta^{17}$O vs. $\delta^{18}$O (represented by their corresponding soil waters) in Figure 3.4 and compare them with previously published data for natural waters from low- or mid-latitude regions. These data include unevaporated or slightly evaporated primary precipitation (Luz and Barkan 2010), tap waters (Li et al. 2015), sea waters (Luz and Barkan 2010) and surface runoff (Luz and Barkan 2010; Surma et al. 2015; Ji and Passey unpublished data) as well as significantly evaporated water reservoirs such as closed basin lakes and ponds in arid regions (Surma et al. 2015; Ji and Passey unpublished data).
Figure 3.3 Schematic diagram showing simulated $\delta^{18}O$ and $\Delta^{17}O$ of evaporating waters predicted by a conceptual Rayleigh distillation model. This model assumes water in a reservoir is freely evaporating into atmosphere following a Rayleigh distillation process. Initial $\delta^{18}O$ of water ranges between -20%o and 0%o, while initial $\Delta^{17}O$ ranges from 0%o to 0.040%o. $F$ denotes the fraction of remaining water. (A) Relative humidity is set as 0.8. (B) Relative humidity is 0.4. Both subplots demonstrate that $\Delta^{17}O$ differs for unevaporated waters versus significantly-evaporated waters, while $\delta^{18}O$ values show considerable overlap for the two types of waters.
Figure 3.4 Comparison of our measured triple oxygen isotopes of soil carbonates (reported as their ambient waters) with previously published data for natural waters. Plus markers represent unevaporated or slightly evaporated waters including rainfall, tap waters, rivers, and throughflow lakes [Luz and Barkan 2010; Li et al. 2015 Surma et al. 2015; Ji and Passey (unpublished)]. Cross markers represent sea waters (Luz and Brakan 2010). Grey soild circles represent significantly evaporated waters such as closed basin lakes and desiccating ponds [Ji and Passey (unpublished); Surma et al. 2015]. Error bars are the same as Figure 2.
As shown in Figure 3.4, most soil carbonates fall in the realm of unevaporated or slightly evaporated waters. They are generally within the range of primary meteoric waters, but are consistently lower than average $\Delta^{17}O$ values for global meteoric water and US continental tap waters, which are 0.033‰ (Luz and Barkan 2010) and 0.017‰ (Li et al. 2015), respectively (however, we note that the former value includes a significant fraction of meteoric water data collected from high latitude regions as snow and ice and may not be representative of the low and mid-latitude settings in our study). The propagated error for reconstructed parent water $\Delta^{17}O$ values, ~0.017‰, however, places nearly all samples within error of mean meteoric water $\Delta^{17}O$ values. Two shallow recent soil carbonates, GON07-4.3-1 and GON07-4.6-2, have lower $\Delta^{17}O$ values than primary precipitation and indicate probable occurrence of evaporation before or during carbonate formation. One deep recent soil carbonate (CN2008-DM-164-130-1) from Inner Mongolia, China also shows a slightly lower $\Delta^{17}O$. And this is consistent with higher $\delta^{18}O$ departure recorded in soil carbonate against both mean annual precipitation $\delta^{18}O$ and summer months precipitation $\delta^{18}O$ in this region.

In general, we do not observe a universal and significant $\Delta^{17}O$ lowering recorded in deep soil carbonates from our dataset. However, the one-box Rayleigh distillation model described above is only an approximation of isotope modification during soil water evaporation. Evaporation in the soil column cannot be modeled as water freely evaporating into atmosphere. Actually, the Rayleigh distillation model requires the water reservoir to be isotoipcally homogeneous. Soil water moves slowly through connected
pore space within and between soil particles and this limits homogenization in soil column. Therefore, it is worthwhile to explore a more specific model to simulate triple oxygen isotopes in evaporating soil water columns.

3.4.3 One-dimensional numerical model for simulation of triple oxygen isotopes profile in drying soil

We present a numerical model to study the behavior of triple oxygen isotopes profile in drying soil column in this section. This model is adapted from a numerical model developed by Mathieu and Bariac (1996) which has been validated to be generally consistent with previous theoretical and experimental research on $\delta^{18}O$ profiles in drying vertical soil columns (e.g., Barnes and Allison 1983a, 1983b, 1984; Walker et al. 1988).

3.4.3.1 Model framework

This numerical model is implemented under a few key assumptions and limitations. First, the soil column in the model is assumed as “bare soil”, that is, biological activity such as evapotranspiration and photosynthesis is not considered. Second, water transfer in the soil column includes both the liquid phase and vapor phase. Only vertical water transfers are included in the model. That means this model is a one-dimensional model. Third, the liquid phase and vapor phase in each layer (~1cm) are isotopic equilibrium anywhere and anytime. This requires water and water vapor to reach isotopic equilibrium “instantly” (within unit time step, ~1s). This assumption is reasonable according to diffusion experiments conducted by Thoma et al. (1978). Fourth, the soil column in the model is homogeneous and perfectly packed, i.e., soil features such as porosity and tortuosity are
set as constant values everywhere in the soil column. There are also no macrostructures such as root channels.

In addition, to simplify the model, we assume temperature is constant in the soil column. Therefore, this model is an isothermal model which is different from the original model in Mathieu and Bariac (1996). As discussed by Barnes and Allison (1984) and Mathieu and Bariac (1996), thermally-driven vapor transport is basically against diffusion-driven vapor transport because of negative temperature gradient, therefore modeled non-isothermal $\delta^{18}$O profiles have a smaller $\delta^{18}$O enrichment peak that occurs at a slightly deeper depth.

In the model, a meter-long soil column is divided into 100 layers (boxes). Each layer represents 1cm thick of soil with unit surface area (1 m$^2$). Mass conservation law applies within each layer (box) in terms of water and triple oxygen isotopes flux as:

$$\frac{dM_{\text{water}}}{dt} = -\frac{dF_{\text{liquid}} + dF_{\text{vapor}}}{dz}$$  

$$\frac{d(M_{\text{water}} R_{\text{liquid}} + M_{\text{vapor}} R_{\text{vapor}})}{dt} = -\frac{d^* F_{\text{liquid}} + d^* F_{\text{vapor}}}{dz}$$

Equation (7) is mass conservation law for water movement. Liquid water flux $F_{\text{liquid}}$ consists of two components, matric flux $F_{lm}$ and gravitational flux $F_{lg}$. According to Darcy’s law, they can be expressed as:

$$F_{lm} = -K \frac{d\psi}{dz}$$

$$F_{lg} = Kg$$

\[93\]
where $K$ is hydraulic conductivity and $g$ is gravitational acceleration. Hydraulic conductivity is calculated from water content ($\theta$) through hydraulic conductivity function. Water matric potential is denoted as $\psi$ and is related with water content ($\theta$) through soil water retention curve (soil water characteristic function) (Table 2). Water content $\theta$ in this model is gravimetric based and is expressed as the percentage of water mass per unit soil mass.

We do not consider thermally-driven vapor flux in this isothermal model, therefore $F_{vapor}$ only includes mass flux and is expressed as:

$$F_{vapor} = F_{v\theta} = -D^V \rho^s \frac{Mh}{RT} \frac{d\psi}{dz}$$ (11)

Here, $M$ is water molar mass, $R$ is the gas constant, $T$ is temperature and $\rho^s$ is the density for water vapor. The effective diffusivity of water vapor in soil $D^v$ is determined by water diffusivity in air $d^v$, soil tortuosity $\tau$ and porosity $p$ and soil water content. According to Phillip (1955) and Barnes and Allison (1983), it can be calculated by

$$D^V = d^V (p - \theta) \tau$$ (12)

The equation to estimate effective soil relative humidity $h$ in equation (11) is derived from the Kelvin equation as follows:

$$h = \exp \left( \frac{Mh}{RT} \right)$$ (13)

Parameters in equation (12) are the same as above equations.

The star notation in the isotopic mass conservation equation (8) denotes the mass number for heavy isotopes (17 or 18). There are two separate mass conservation equations for $^{18}$O and $^{17}$O respectively in this model. Isotopic flux in the liquid phase and vapor phase
are represented as \( *F_{\text{liquid}} \) and \( *F_{\text{vapor}} \). In addition to isotopic flux associated with matric flux and gravitational flux, there exists diffusional isotopic flux driven by concentration gradient of heavy isotopes \(^{18}\text{O}\) and \(^{17}\text{O}\) in vertical profile. Equations to quantify isotopic flux are shown below

\[
*F_{\text{l}} = F_{\text{l}} *R_l \\
*F_{\text{lg}} = F_{\text{lg}} *R_l \\
*F_{\text{ld}} = -*D^l \rho \frac{d^*R_l}{dz} \\
*F_{\text{v}} = F_{\text{v}} *R_v \\
*F_{\text{vd}} = -*D^v \rho^v h \frac{d^*R_v}{dz}
\]

The effective diffusivity of liquid water \( \text{H}_2^{16}\text{O} \) in soil \( D^l \) can be calculated from water self-diffusion coefficient \( d^l \) as

\[
D^l = \tau \theta d^l
\]

As stated before, the isotope ratio for water vapor \( (R_v) \) and liquid water \( (R_l) \) are assumed to be equilibrium within one layer. Therefore \( R_v = R_l / \alpha_{l-v} \) holds true at any time step. The diffusivities of heavy isotopologues \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \) are calculated from the diffusivity of normal water molecules \( \text{H}_2^{16}\text{O} \) based on kinetic theory.

A full drainage scenario is adopted in the model. Therefore there is no water replenishment from the bottom boundary layer, \textit{i.e.}, there is no upward flux flowing into the bottom layer. However, this can be easily changed by reconfiguring the bottom
boundary layer. At the surface boundary layer, the evaporation flux to the atmosphere is modeled following Campbell (1985) and Shimojima et al. (1990) as:

\[ F_{\text{evap}} = -E_p \frac{h_a - h_0}{1 - h_a} \quad (20) \]

\[ F^*_{\text{evap}} = -E_p \frac{h_0 R_{\text{av}}^p - h_a R_{\text{av}}^a}{a_{\text{diff}}(1 - h_a)} \quad (21) \]

Here, \( E_p \) denotes the potential evaporation which represents the evaporation flux when soil is saturated with water. Relative humidity of atmosphere and soil surficial layer are denoted as \( h_a \) and \( h_0 \), respectively. There are other theoretical approaches to simulate the surface evaporation flux (e.g., Brutsaert 1975; Merlivat and Jouzel 1979). These methods introduce many additional parameters and increase the complexity of the model beyond the first-order predictions we seek here, and hence we use the Cambell (1985) and Shimojima et al., (1990) approximations here.

The initial status is set as a soil column saturated with water. Combining all the equations above, the model will then simulate evolution of triple oxygen isotopes profile as the soil gradually dries.

### 3.4.3.2 Model output

We ran the numerical model with parameters listed in Table 3.2. Model outputs are shown in Figure 3.5. In Figure 3.5A, \( \delta^{18}\text{O} \) profiles are shown for 30 days, 120 days and 173 days while Figure 3.5B shows corresponding \( \Delta^{17}\text{O} \) profiles.

We can observe from Figure 3.5 that even when there is strong \( \delta^{18}\text{O} \) enrichment and \( \Delta^{17}\text{O} \) lowering in shallow soil layers (\(< 30\text{cm}\)), deep layers of soil column only show slight
isotopic evaporative modification after more than 170 days drying period. This result is consistent with interpretations of triple oxygen isotope data from our collection of soil carbonates as we discussed in previous sections. Therefore, we argue that deep soil carbonate is much more resistant to evaporative enrichment. However, model predictions should be interpreted cautiously given the ideality of the model. In the real world, all assumptions can be breached. For example, macrostructures such as soil cracks and root channels may increase water-air surface area and enhance evaporation flux. Vegetation may increase water loss without isotopic fractionation by evapotranspiration. Other factors such as ground water recharge, soil thermal expansion/shrinkage, soil vertical mixing and soil heterogeniety may also further complicate isotope vertical distributions and cause large variability in real soil profiles (e.g., vertical $\delta^{18}$O profiles in Quade et al. 1989 and Breecker et al. 2009).

In addition, shallow layers of soil column experience two phases of evaporation in the model, which is consistent with previous research. During the first phase, liquid water transfer dominates and leads to a continuous $\delta^{18}$O enrichment and $\Delta^{17}$O lowering in
Figure 3.5 Output of numerical models described in Section 4.3. (A) Simulated vertical $\Delta^{17}$O profile after continuous drying for 30 days, 120 days and 173 days. (B) Simulated vertical $\delta^{18}$O profile after continuous drying for 30 days, 120 days and 173 days.

Surficial soil layers. In the second phase, surface layers have lost most of their liquid water, and water transfer in those layers become vapor-dominated. Now soil water is strongly influenced by isotopic composition of atmospheric vapor and an “evaporating
front” with $\delta^{18}$O enrichment peak and $\Delta^{17}$O lowering peak will be formed on the boundary of vapor-dominated layers and liquid-dominated layers.

### 3.4.3.3 Sensitivity test on key model parameters

The choice of parameters can influence $\delta^{18}$O and $\Delta^{17}$O profiles in model outputs. Among all parameters in the model, variation of initial isotopic composition of soil water will parallel-shift the predicted vertical profiles. Some physical parameters such as density, diffusivity and molar mass of water and water vapor are mostly well-constrained based on decades of experiments. Therefore, we will do sensitivity test for soil texture parameters such as porosity $p$, tortuosity $\tau$ as well as climatic parameters including atmospheric relative humidity $h$ and potential evaporation flux $E_p$. Results are shown in Figure 3.6.

In general, evaporation flux from soil column will be enhanced in drier climate with low relative humidity. Therefore, soil column under low relative humidity ($h=0.2$) demonstrates a significantly higher $\delta^{18}$O peak and lower $\Delta^{17}$O peak after drying 120 days (Figure 3.6A and 3.6B). On the other hand, the soil column under high relative humidity ($h=0.8$) only has a slight $\delta^{18}$O enrichment and $\Delta^{17}$O lowering. Potential evaporation flux...
Table 3.2  
Parameters used in the model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>explanation</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>Soil porosity</td>
<td>0.35&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Soil tortuosity</td>
<td>0.67&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>$h_a$</td>
<td>Atmosphere relative humidity</td>
<td>0.5</td>
</tr>
<tr>
<td>$E_p$</td>
<td>Potential evaporation ($\text{kg} , \text{s}^{-1} , \text{m}^{-2}$)</td>
<td>$7.5 \times 10^{-5}$ ($\approx 2365 , \text{mm yr}^{-1}$)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature ($^\circ\text{C}$)</td>
<td>30</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Water density ($\text{kg} , \text{m}^{-3}$)</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Water density ($\text{kg} , \text{m}^{-3}$)</td>
<td>0.03</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Water content ($\text{kg/kg}$)</td>
<td>c</td>
</tr>
<tr>
<td>$K$</td>
<td>Hydraulic conductivity ($\text{kg} , \text{s}^{-1} , \text{m}^{-3}$)</td>
<td>d</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass of water ($\text{kg} , \text{mol}^{-2}$)</td>
<td>$1.8 \times 10^2$</td>
</tr>
<tr>
<td>$d^v$</td>
<td>Water vapor diffusion coefficient ($\text{m}^2 , \text{s}^{-1}$)</td>
<td>$2.58 \times 10^{-5}$&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>$d^l$</td>
<td>Liquid water self-diffusion coefficient ($\text{m}^2 , \text{s}^{-1}$)</td>
<td>$2.3 \times 10^{-9}$&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>$^{18}\alpha_{eq}$</td>
<td>Equilibrium $^{18}$O fractionation factor for water–water vapor</td>
<td>1.0090&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>$\theta_{\text{diff}}$</td>
<td>Triple oxygen exponent for water diffusion</td>
<td>0.5185&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>$\theta_{eq}$</td>
<td>Triple oxygen exponent for water-water vapor equilibrium</td>
<td>0.529&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
<tr>
<td>$^{17}\alpha_{\text{diff}}, ,^{17}\alpha_{eq}$</td>
<td>$^{17}$O fractionation factor for water diffusion in dry air and water-water vapor equilibrium</td>
<td>$^{17}\alpha_{\text{diff}} = (^{18}\alpha_{\text{diff}})^{\theta_{\text{diff}}}$, $^{17}\alpha_{eq} = (^{18}\alpha_{eq})^{\theta_{eq}}$</td>
</tr>
<tr>
<td>$^{18}R_1$</td>
<td>Isotope ratio of input water (normalized to VSMOW)</td>
<td>1.00 ($\delta^{18}\text{O}: 0%o$)</td>
</tr>
<tr>
<td>$\Delta^{17}\text{O}_1$</td>
<td>$\Delta^{17}\text{O}$ value for input water</td>
<td>0.000</td>
</tr>
<tr>
<td>$^{17}R_v, ,^{18}R_v$</td>
<td>Isotopic composition of atmospheric vapor</td>
<td>Assume it is in equilibrium with input water</td>
</tr>
</tbody>
</table>

Note:

a. Soil porosity is defined as percentage of void spaces within soil column and ranges from 0 to 1. Basically, porosity for sandy soil is 0.3-0.5 while clay has higher porosity. The value 0.35 used here is the same as Barnes and Allison (1984).

b. Soil tortuosity is defined as ratio of straight molecule transport path against effective transport path. It ranges from 0 to 1. The value 0.67 used here is suggested by Penman (1940) for uniform sand and used in Barnes and Allison (1985).

c. Water content in this study is gravimetric based. Saturated water content ($\theta_{\text{sat}}$) is considered as the same value as porosity, i.e., all void spaces are filled with water in soil column. Residue water content ($\theta_{\text{res}}$) is defined as the minimum water content in soil column and can be calculated assuming corresponding effective soil relative humidity equals atmosphere relative humidity.

d. Hydraulic conductivity in this study is calculated from water content by $K=0.0056\theta^3$. This function is used in Mathieu and Bariac (1996) by fitting the data provided by Phillip (1957). Note that Different soil columns can have very different hydraulic conductivity functions.

$E_p$ is defined as the evaporation flux when soil water is saturated and is determined by local temperature and day length. Variation of $E_p$ is large among different locations and different seasons. From Figure 3.6C and 3.6D, we observe that higher potential evaporation flux ($E_p = 10^{-4}$ kg s$^{-1}$ m$^{-2}$ $\approx$ 3153 mm yr$^{-1}$) will enhance the evaporative modification in soil profile compared with lower potential evaporation flux ($E_p = 10^{-5}$ kg s$^{-1}$ m$^{-2}$ $\approx$ 315.3 mm yr$^{-1}$). However, potential evaporation does not have a significant effect after the surficial layer is mostly dried up when evaporation flux is far less than potential evaporation. Therefore we choose 30 days for comparison. Soil porosity determines the available space for water and vapor movements. Higher soil porosity means it is easier for water and vapor to flow along the vertical profile. Soil tortuosity is defined as the ratio of the apparent or straight path versus the effective water transport path within the soil column. Tortuosity ratio is always between 0 and 1 because of the curvature of soil particles. Barnes and Allison (1983) estimated that the tortuosity for a perfectly packed sandy soil column is 0.67. Similar with porosity, higher tortuosity means it is more straightforward for water or water vapor to transport throughout the soil column and therefore enhance the evaporation flux. Figure 3.7 shows sensitivity test on soil porosity and tortuosity. $\delta^{18}$O enrichment and $\Delta^{17}$O lowering in soil column are higher and deeper with higher tortuosity or porosity which is consistent with discussion above.
Figure 3.6 Sensitivity tests on key climatic parameters. (A) (B) Simulated vertical $\Delta^{17}$O and $\delta^{18}$O profiles assuming atmosphere relative humidity is 0.2, 0.5 and 0.8 after continuous drying for 120 days. (C)(D) Simulated vertical $\Delta^{17}$O and $\delta^{18}$O profiles assuming potential evaporation is $10^{-4}$ kg s$^{-1}$ m$^{-2}$, $5 \times 10^{-5}$ kg s$^{-1}$ m$^{-2}$, $10^{-5}$ kg s$^{-1}$ m$^{-2}$ after continuous drying for 30 days.
Figure 3.7 Sensitivity tests on key soil character parameters. (A), (B) Simulated vertical $\Delta^{17}O$ and $\delta^{18}O$ profiles assuming soil porosity is 0.3, 0.5 and 0.7 after continuous drying for 120 days. (C), (D) Simulated vertical $\Delta^{17}O$ and $\delta^{18}O$ profiles assuming soil tortuosity is 0.3, 0.5 and 0.7 after continuous drying for 120 days.
3.5 Conclusions

Our compiled dataset demonstrates that soil water $\delta^{18}$O calculated from soil carbonate can deviate from predicted $\delta^{18}$O of local mean annual precipitation. However, deviations of calculated soil water $\delta^{18}$O against $\delta^{18}$O of summer or warmest three months precipitation are much smaller. Partly due to large variation of $\delta^{18}$O in global precipitation, soil carbonate $\delta^{18}$O alone cannot estimate the extent of evaporative enrichment of soil water $\delta^{18}$O.

Triple oxygen isotopes in soil carbonate can be used to estimate the extent of evaporation since unevaporated primary precipitation and evaporated water body have different $\Delta^{17}$O values. Significant lowering of $\Delta^{17}$O compared with unevaporated primary precipitation implies occurrence of evaporation before or during the formation of soil carbonates. Our dataset of triple oxygen isotopes in soil carbonates from USA, China and East Africa demonstrates that most deep soil carbonates do not show drastic $\Delta^{17}$O lowering, considering the propagated calculation error, and therefore imply at most only minor evaporation has occurred before or during the formation of soil carbonates.

Our numerical model confirms this indication that $\Delta^{17}$O in deep soil water is resistant to evaporative modification. However, the complexity of soil conditions in the natural world will increase the variability of vertical distributions of oxygen isotopes. This again highlights the significance of using $\Delta^{17}$O together with traditional $\delta^{18}$O in soil carbonates to interpret their oxygen isotopic compositions more comprehensively and correctly.
Table 3.S1
Compiled dataset of soil water δ¹⁸O calculated from soil carbonate (δ¹⁸O_sw) vs. local precipitation δ¹⁸O (δ¹⁸O_ms)

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**Avg:**

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| India           | -10.6    | -14.2     | 3.6      | -9.8        | -0.8     |
| Tibet, China    | -1.5     | -5.0      | 3.4      | -3.7        | 2.1      |</p>
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*Note:*

δ¹⁸O (ma) is δ¹⁸O of amount-weighted local mean annual precipitation. δ¹⁸O (ms) is δ¹⁸O of mean summer or warmest three months precipitation. diff_sw-ma is δ¹⁸O difference between δ¹⁸O (sw) and δ¹⁸O (ma) while diff_sw-ms is δ¹⁸O difference between δ¹⁸O (sw) and δ¹⁸O (ms).
3.6 References


of relief in the western Andes (30°S) revealed by clumped isotope thermometry.


Landais A., Barkan E. and Luz B. (2008) Record of $\delta^{18}$O and $\delta^{17}$O-excess in ice from Antarctica during the last 150,000 years. Geophys. Res. Lett. 35, L02709.


4. Conclusion

This thesis investigates the distribution of triple oxygen isotopes in lake waters and lacustrine carbonates as well as soil carbonates. We explore the possibility of using $\Delta^{17}$O combined with traditional $\delta^{18}$O to provide more information to reconstruct terrestrial paleoclimate and paleohydrology, particularly the effect of evaporation on oxygen isotopic composition of lacustrine carbonates and soil carbonates. To achieve this goal, triple oxygen isotopes of carbonate samples from western USA, China and East Africa were measured and compared with theoretical model outputs developed in this thesis.

Chapter 2 reports $\Delta^{17}$O data in different types of lakes and their associated input/output rives from western USA. We can observe from these data that the lowering of $\Delta^{17}$O is related to the extent of evaporation of lake basins. Meanwhile, it is also affected by hydrological scenarios of lake basins, water salinity, isotope fractionation factors during evaporation, and the isotopic composition of ambient air vapor over lake surface. We also examine how do these factors affect triple oxygen isotopes of lake waters and lacustrine carbonates by laboratory open-pan evaporation experiments and theoretical model. This project lays the foundation work for using triple oxygen isotopes as an evaporation indicator in lacustrine system.

Chapter 3 presents triple oxygen isotope data in soil carbonates from western USA, China and East Africa including both modern soil carbonates and paleosols. Most deep soil carbonates do not show significant lowering of $\Delta^{17}$O, implying that these samples did not experience significant evaporation. This is generally consistent with our theoretical
model simulating triple oxygen isotopes in one-dimension drying soil profile. Therefore, $\Delta^{17}$O in soil carbonates can be used to estimate the extent of evaporative modification on oxygen isotopic composition.

In summary, the studies of triple oxygen isotopes in lake waters, lacustrine carbonates and soil carbonates in this thesis are among a series of pioneering and foundational work to investigate the usage of $\Delta^{17}$O in carbonate minerals to reconstruct terrestrial paleoclimate and paleohydrology. Our measured data from natural samples, theoretical modeling output, and laboratory experiments have shown the potential and significance of using triple oxygen isotopes as an evaporation indicator in paleoclimatology and paleohydrology. Meanwhile, our study also demonstrates the complexity of triple oxygen isotopes system in lacustrine and soil carbonates. Many climatic and hydrologic factors should be taken into consideration in order to correctly and comprehensively understand triple oxygen isotopes data. These results highlight the necessity of further investigation in this emerging and promising field.
APPENDIX

Clumped isotope reordering in dolomite: Heating experiments and data

A1. Introduction

Carbonate clumped isotope thermometry has been widely used in many fields of paleoclimatology (e.g. Ghosh et al. 2006; Came et al. 2007; Eiler 2007; Eiler 2011; Huntington et al. 2015). This geothermometer is based on measuring abundances of $^{13}$C-$^{18}$O bonds in carbonate minerals such as calcite, aragonite and dolomite. The temperature information obtained by using this method is considered to be independent of the isotopic compositions of ambient waters of carbonate minerals. Therefore, clumped isotope analysis of carbonate minerals are very promising to provide independent estimates of growth temperatures.

However, for carbonate minerals formed in high temperature environments such as carbonatites, temperatures calculated from clumped isotope thermometry have shown different values in samples with different cooling rates (Dennis and Schrag, 2010). This has been attributed to $^{13}$C-$^{18}$O bond reordering process during cooling or burial process of carbonate minerals. It complicates our interpretation of temperatures obtained from the carbonate clumped isotope geothermometer. Therefore, it is necessary to investigate the relationship between cooling rate and apparent equilibrium temperature calculated from clumped isotope thermometry in carbonate minerals.

Some studies have been done on carbonate clumped isotope reordering process in both abiogenic and biogenic calcites (e.g. Passey and Henkes 2012; Henkes et al. 2014;
Shenton et al. 2015). By doing heating experiments on carbonate minerals, Arrhenius parameters of solid-state reordering of $^{13}\text{C}-^{18}\text{O}$ bond have been determined, allowing for modeling and estimating cooling rates of these minerals. Therefore, carbonate clumped isotopes could also be used as a geospeedometer to reconstruct thermal history of minerals.

However, samples used in these studies do not include dolomites which are among most common carbonate minerals on Earth’s surface. Therefore, the main objective of this project is to determine Arrhenius parameters of solid-state reordering of $^{13}\text{C}-^{18}\text{O}$ bond in dolomite by conducting heating experiments described in previous studies and exploring the potential of using dolomite as a geospeedometer.

A2. Notations and methods

Clumped isotope thermometry measures the abundance of $^{13}\text{C}-^{18}\text{O}$ bonds in carbonate minerals. The basic exchange reaction in dolomite is:

$$\text{CaMg}(^{13}\text{C}^{16}\text{O}_3)_2 + \text{CaMg}(^{12}\text{C}^{18}\text{O}_4)_2 \leftrightarrow \text{CaMg}(^{13}\text{C}^{18}\text{O}_4)_2 + \text{CaMg}(^{12}\text{C}^{16}\text{O}_3)_2 \quad (A1)$$

The measure of the degree of $^{13}\text{C}-^{18}\text{O}$ clumping in carbonate are calculated from corresponding CO$_2$ which is generated by acid digestion and is denoted as $\Delta_{47}$. It can be calculated as:

$$\Delta_{47} = \left[ \frac{R^{47}}{R^{47}} - 1 \right] - \left[ \frac{R^{46}}{R^{46}} - 1 \right] - \left[ \frac{R^{45}}{R^{45}} - 1 \right] \quad (A2)$$

where $R^i$ is the abundance ratio of mass $i$ relative to mass 44 and asteroid mark means the corresponding ratio that would occur in the sample if it had a stochastic distribution.
As derived in Passey and Henkes (2012), reaction progress can be calculated by:

\[
\ln \left( \frac{\Delta_{47}^t - \Delta_{47}^q}{\Delta_{47}^e - \Delta_{47}^q} \right) = \ln [1 - F] = -kt
\]  

where \( \Delta_{47}^t \), \( \Delta_{47}^q \) and \( \Delta_{47}^{\text{init}} \) are \( \Delta_{47} \) values for samples after heating the time duration of \( t \), equilibrium values under given temperature \( T \) and initial values, respectively. \( F \) is the fraction of reaction toward equilibrium and \( k \) is reaction rate constant.

Samples with known \( \Delta_{47} \) values were heated in furnace for different time durations under different temperatures. The equilibrium \( \Delta_{47} \) values under given temperatures can be calculated based on Equation (5) in Passey and Henkes (2012). Therefore, reaction rate constants \( k \) under different temperatures \( T \) can be determined by a series of heating experiments. From this information, Arrhenius parameters (activation energy \( E_a \) and frequency factor \( K_0 \) ) can be calculated by simple regression (or a curve stripping approach for multi component minerals). Finally, with Arrhenius parameters obtained from heating experiments, the cooling rate can be calculated by Equation (14) in Passey and Henkes (2012) which is:

\[
- \frac{dT}{dt} = \frac{\gamma RT_c^2 k_T}{E_a} 
\]  

where \( dT/dt \) is cooling rate. Activation energy \( E_a \) and frequency factors \( k_T \) under given temperature \( T_c \) are calculated from heating experiments. \( R \) is gas constant and \( \gamma \) is another constant which 1.78 here.

A3. Materials, heating experiments and measurements
A dolomite sample collected from the Latemar carbonate buildup, Dolomites, Italy, is proposed to have formed during the Triassic by relatively low temperature (<100°C) dolomitization (Ferry et al., 2011). Sample preparation follows the procedure described by Passey and Henkes (2012). Rock samples were first cleaned and then crushed. The crushed powders were then sieved to uniform size (60-120 mesh) and rinsed in a sonicator. Samples were all dried in a 60°C oven overnight.

Aliquots (~35mg) of the dolomite sand were then loaded and sealed into quartz tubes under vacuum. CO₂ gas with distinctive carbon and oxygen isotopic composition was also loaded into quartz tubes. This CO₂ gas could be used as an indicator for some undesirable reactions occurred during heating such as decarbonation of carbonate samples.

The dolomite samples were heated in a tube furnace under 425°C, 475°C, 525°C, 575°C and 625°C for time durations ranging from 30 minutes to more than 20 days (Table A1). They were quenched rapidly after heating using a compressed air gun.

All clumped isotope measurements were conducted and calibrated during 2012 summer in the Johns Hopkins University Stable Isotope Lab following methods described by Henkes et al. (2014). Δ47 values for carbonate standards during the course of measurements are: 102-GC-AZ01: Δ47 = 0.707 ± 0.010 ‰ (1σ, n = 8); UU Carrara: Δ47 = 0.402 ± 0.013 ‰ (1σ, n = 5).
A4. Results and discussions

All clumped isotope data are presented in Figure A1 and Table A1. Figure A1 shows the evolution of $\Delta_{47}$ as a function of time for heating experiments under different temperatures. We can observe from the data that $\Delta_{47}$ values of dolomite samples gradually approach to equilibrium as heating time increases.

However, $\Delta_{47}$ values did not reach equilibrium values in any of the experiments, including those which has been heated for more than 20 days. This is different with heating experiments for calcite minerals conducted by Passey and Henkes (2012). Figure A2 demonstrates the evolution of $\Delta_{47}$ as a function of time for dolomite (this study) and calcite (Passey and Henkes, 2012) under 425°C and 475°C. For a given temperature, isotopic reordering is faster in calcite compared to dolomite. Therefore, dolomite samples in this study are more resistant to $^{13}$C-$^{18}$O bond reordering process. The reason for this is still unknown to us. It could be related to the alternating Mg$^{++}$ and Ca$^{++}$ layers and different crystal structure of dolomite minerals. Further investigation is needed to solve this problem. For example, a series of heating experiment could be conducted on a series of carbonate minerals with different Mg concentration. Magnesite (MgCO$_3$) could be used as an end member component in this kind of study.
### Table A1 Results for dolomite heating experiments

<table>
<thead>
<tr>
<th>Reaction ID</th>
<th>T (°C)</th>
<th>Time (minutes)</th>
<th>$\delta^{13}$C (PDB, ‰)</th>
<th>$\delta^{18}$O (PDB, ‰)</th>
<th>$\Delta_{47}$ (CDES, ‰)</th>
</tr>
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<tr>
<td>unreacted</td>
<td>-</td>
<td>-</td>
<td>3.283</td>
<td>-3.848</td>
<td>0.586</td>
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<tr>
<td></td>
<td>±1σ</td>
<td></td>
<td>0.024</td>
<td>0.067</td>
<td>0.004</td>
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<td>RDX-201</td>
<td>425</td>
<td>32</td>
<td>3.244</td>
<td>-3.959</td>
<td>0.578</td>
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<td>RDX-202</td>
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<td>RDX-204</td>
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<tr>
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<td>720</td>
<td>3.230</td>
<td>-3.920</td>
<td>0.564</td>
</tr>
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<td>RDX-203</td>
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<td>3.227</td>
<td>-4.001</td>
<td>0.545</td>
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<tr>
<td>RDX-207</td>
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<td>3.201</td>
<td>-3.996</td>
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<tr>
<td>RDX-206</td>
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<td>10080</td>
<td>3.295</td>
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</tr>
<tr>
<td>RDX-199</td>
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<td>30</td>
<td>3.311</td>
<td>-3.826</td>
<td>0.553</td>
</tr>
<tr>
<td>RDX-192</td>
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<td>60</td>
<td>3.326</td>
<td>-3.857</td>
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<tr>
<td>RDX-194</td>
<td>475</td>
<td>240</td>
<td>3.272</td>
<td>-3.800</td>
<td>0.558</td>
</tr>
<tr>
<td>RDX-197</td>
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<td>720</td>
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<td>-3.815</td>
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</tr>
<tr>
<td>RDX-191</td>
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<tr>
<td>RDX-193</td>
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<td>2880</td>
<td>3.311</td>
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<tr>
<td>RDX-193</td>
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<td>3.267</td>
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<td>RDX-200</td>
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<td>RDX-195</td>
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<td>RDX-215</td>
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<tr>
<td>RDX-212</td>
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<td>3.256</td>
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<td>RDX-211</td>
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<tr>
<td>RDX-213</td>
<td>525</td>
<td>4432</td>
<td>3.211</td>
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<tr>
<td>RDX-208</td>
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<td>3.278</td>
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<tr>
<td>RDX-209</td>
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<td>3.212</td>
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<tr>
<td>RDX-228</td>
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<td>33</td>
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<td>RDX-229</td>
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<td>RDX-227</td>
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<tr>
<td>RDX-222</td>
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<td>2.770</td>
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<td>RDX-219</td>
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<td>31727</td>
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<td>RDX-220</td>
<td>625</td>
<td>5992</td>
<td>-8.198</td>
<td>-9.083</td>
<td>0.323</td>
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</table>
Note: Long-term analytical precision (1σ) for Δ47, δ13C and δ18O are 0.013‰, 0.1‰ and 0.1‰, respectively. Δ47 values in this table are reported based on ‘carbon dioxide equilibrium scale’ described by Dennis et al. (2010).
Figure A1 Clumped isotope results of dolomite heating experiments under 425°C, 475°C, 525°C and 575°C. Error bars are reported as long-term analytical precision (1σ) in our lab which is 0.013‰ for Δ47. The equilibrium Δ47 value under 425°C (0.321‰) is plotted as dashed line in the figure which is calculated by Passey and Henkes (2012). Clumped isotope values in dolomite samples in this study didn’t reach the equilibrium value until the end of the heating experiments.
Figure A2 Clumped isotope results for dolomite heating experiments (this study) and Optical calcite heating experiments (MGB-CC-1 in Passey and Henkes, 2012). Error bars are reported as long-term analytical precision (1σ) in our lab which is 0.013‰ for $\Delta_{47}$. The equilibrium $\Delta_{47}$ value under 425°C (0.321‰) is plotted as dashed line in the figure which is calculated by Passey and Henkes (2012). Dolomite samples in this study are more resistant to $^{13}$C-$^{18}$O bond reordering compared with optical calcite samples.
Figure A3 $\delta^3$C and $\delta^{18}$O of dolomite heating experiments. Error bars are reported as long-term analytical precisions (1σ) in our lab which are 0.100‰ for both $\delta^3$C and $\delta^{18}$O.
Figure A3 (A) and (B) show $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of all dolomite samples. For heating experiments under 425°C, 475°C and 525°C, both carbon and oxygen isotopic compositions of samples remain unchanged throughout heating experiments. That means there is no significant isotopic exchange between loaded CO$_2$ and dolomite samples. However, $\delta^{3}\text{C}$ and $\delta^{8}\text{O}$ of dolomite samples changed with time under 575°C as shown by figures. This could be related to thermal decomposition of dolomite under high temperature. More detailed analysis of end products is needed to have more comprehensive understanding of this phenomenon.

Our heating experiments show that dolomite samples are (1) more resistant to solid-state $^{13}\text{C}$-$^{18}\text{O}$ bond reordering under 425°C, 475°C and 525°C and (2) will possibly thermally decompose under high temperatures and therefore their bulk carbon and oxygen isotopic compositions will be changed. In order to further investigate clumped isotope reordering behavior in dolomite, we need to design new apparatus to prevent thermal decomposition of dolomite. A possible solution could be adding silver oxalate to the sample capsules, which will decompose under high temperature and release CO$_2$. Therefore, partial pressure of CO$_2$ will be much higher and prevent thermal decomposition of dolomite samples.
A5. References


Haoyuan Ji

40 Newport Pkwy., Apt 2902, Jersey City NJ 07310 • (443) 676-4452 • haoyuanjijhu@gmail.com
Location of birth: Baoji, Shaanxi, P.R.China • Date of birth: 06/14/1989 • Citizenship: P.R.China

RESEARCH INTERESTS
• Stable isotope geochemistry: triple oxygen isotopes in lake and soil systems, clumped isotope in carbonate minerals
• Paleoclimatology

EDUCATION
Johns Hopkins University, Baltimore, MD, USA 2011-2016
Ph.D. in Earth and Planetary Sciences
Advisor: Benjamin H. Passey
Thesis Title: Triple oxygen isotopes in lake waters, lacustrine carbonates and soil carbonates: An indicator for evaporation.

University of Science & Technology of China, Hefei, China 2007-2011
B.S. in Earth and Space Science
Advisor: Liguang Sun

GRANTS & AWARDS
David Elliott Memorial Field Fund Grant (EPS, JHU) 2014
Ernst Cloos Memorial Fellowship (EPS, JHU) 2011-2012
Zhao Jiuzhang Scholarship (USTC) 2010
USTC Overseas Alumni Scholarship (USTC) 2010
Chinese National Undergraduate Scholarship (Ministry of Education, China) 2009
"Climbing in Geoscience" Scholarship (USTC) 2008

FIELD EXPERIENCE
Sample collections in western USA: Pyramid Lake (NV), Bear Lake (UT/ID), Great Salt Lake (UT), Lake Tahoe (CA/NV) and Mono Lake (CA) 2014
Paleozoic stratigraphy in western Maryland, USA 2011
Metamorphic petrology intern in Dabie Mountains, Anhui, China 2010
Structural geology and tectonics intern in Yanshan Mountains, Beijing, China 2009
Physical geology intern in Nanjing, Jiangsu, China 2008

LABORATORY EXPERIENCE
Graduate Research Assistantship 09/2011 - 08/2016
Dept. of Earth and Planetary Sciences, Johns Hopkins University
• Helped in calibration, maintenance, optimization of the water fluorination and CO₂ reduction line coupled to a MAT253 isotope ratio mass spectrometer (IRMS) for triple oxygen isotopes in waters and carbonates.
• Analyzed triple oxygen isotopes in CO₂ gas, primary precipitation, lake waters, river waters, sea waters, leaf waters, sea shells, lacustrine carbonates and soil carbonates.
• Simulated and implemented the isotope behavior and carbon cycle in Neoproterozoic (“snowball Earth” dynamic model) atmosphere.
• Conduct heating experiments to study C-O clumped isotope reordering behavior in carbonate minerals including calcite and dolomite.
Undergraduate Research Assistantship
Institute of Polar Environments, University of Science and Technology of China 09/2009 - 06/2011
• Analyzed strontium isotope ratio in sediments columns from East China Sea.

TEACHING EXPERIENCE
I have been teaching assistantship for following classes in JHU and USTC.

Population and Community Ecology (JHU) 2015 Fall
Guided Tour of the Planets (JHU) 2015 Spring
Introduction to Global Environmental Change (JHU) 2014 Fall
Climate Change: Science and Policy (JHU) 2014 Spring
Conversation with the Earth (JHU) 2013 Fall
Environmental Field Methods (JHU) 2013 Spring
Conversation with the Earth (JHU) 2012 Fall
Introduction to Earth Science (USTC) 2009 Fall

PUBLICATIONS AND PUBLISHED ABSTRACTS


4. Levin N.E., DeLuca N.M., Passey B.H., Ji H., Abbott M.B., Polissar P. and Rodbell D.T. Constraining hydroclimate change in the tropical Andes during the late Quaternary using $\Delta^{18}$O and $\Delta^{17}$O in lacustrine carbonates. (Submitted to 2016 AGU Fall Meeting)


