1 **Evaporation induced ^{18}O and ^{13}C enrichment in lake systems: a**
2 **global perspective on hydrologic balance effects**

4 Travis W. Horton^{a*}, William F. Defliese^b, Aradhna K. Tripathi^{b,c} and Christopher Oze^a

6 ^a *Department of Geological Sciences, Private Bag 4800, University of Canterbury,*
7 *Christchurch 8140, New Zealand*

8 ^b Department of Earth, Planetary, and Space Sciences, 595 Charles Young Drive, Box
9 951567, Los Angeles, California, 90095-1567, U.S.A.

10 ^c Department of Atmospheric and Oceanic Sciences, Institute of the Environment and
11 Sustainability, 595 Charles Young Drive, Box 951567, Los Angeles, California, 90095-
12 1567, U.S.A.

14 * Corresponding author: *Department of Geological Sciences, Private Bag 4800,*
15 *University of Canterbury, Christchurch 8140, New Zealand*
16 *E-mail address: travis.horton@canterbury.ac.nz*

18 **Keywords:** evaporation; hydrologic balance; lakes; lacustrine; stable isotopes;
19 oxygen isotopes; carbon isotopes; clumped isotopes; hydrology; paleohydrology;
20 isotope hydrology; hydroclimate; climate change; paleoclimate; paleoelevation;
21 paleothermometry; carbonate; soil carbonate; continental; terrestrial; western U.S.;
22 Great Basin; Sierra Nevada; Southern Alps New Zealand

ABSTRACT

Growing pressure on sustainable water resource allocation in the context of global development and rapid environmental change demands rigorous knowledge of how regional water cycles change through time. One of the most attractive and widely utilized approaches for gaining this knowledge is the analysis of lake carbonate stable isotopic compositions. However, endogenic carbonate archives are sensitive to a variety of natural processes and conditions leaving isotopic datasets largely underdetermined. As a consequence, isotopic researchers are often required to assume values for multiple parameters, including temperature of carbonate formation or lake water $\delta^{18}\text{O}$, in order to interpret changes in hydrologic conditions. Here, we review and analyze a global compilation of 57 lacustrine dual carbon and oxygen stable isotope records with a topical focus on the effects of shifting hydrologic balance on endogenic carbonate isotopic compositions.

Through integration of multiple large datasets we show that lake carbonate $\delta^{18}\text{O}$ values and the lake waters from which they are derived are often shifted by $>+10\text{‰}$ relative to source waters discharging into the lake. The global pattern of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ covariation observed in $>70\%$ of the records studied and in several evaporation experiments demonstrates that isotopic fractionations associated with lake water evaporation cause the heavy carbon and oxygen isotope enrichments observed in most lakes and lake carbonate records. Modeled endogenic calcite compositions in isotopic equilibrium with lake source waters further demonstrate that evaporation

effects can be extreme even in lake records where $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ covariation is absent. Aridisol pedogenic carbonates show similar isotopic responses to evaporation, and the relevance of evaporative modification to paleoclimatic and paleotopographic research using endogenic carbonate proxies are discussed.

Recent advances in stable isotope research techniques present unprecedented opportunities to overcome the underdetermined nature of stable isotopic data through integration of multiple isotopic proxies, including dual element ^{13}C -excess values and clumped isotope temperature estimates. We demonstrate the utility of applying these multi-proxy approaches to the interpretation of paleohydroclimatic conditions in ancient lake systems. Understanding past, present, and future hydroclimatic systems is a global imperative. Significant progress should be expected as these modern research techniques become more widely applied and integrated with traditional stable isotopic proxies.

1. Introduction

Ongoing climate change induced shifts in water balance will be exacerbated by the increased demand for food, energy resources, and fresh water in many parts of the world in coming decades (IPCC, 2014). Our ability to anticipate how regional hydrologic systems will respond to modern era climate change is largely informed by our understanding of how similar systems have responded in the past. In the context of these globally significant challenges, paleohydroclimate research remains one of the most relevant sub-disciplines of modern geoscience.

Endogenic lacustrine minerals are particularly attractive recorders of paleohydroclimate due to the fact that changes in mineral chemistry are directly linked to changes in water balance in many settings. Stable oxygen isotope proxies are the most widely applied proxies in this regard due to their large kinetic fractionations during evaporation (Leng and Marshall, 2004): it has long been known that as a liquid evaporates, the residual fluid becomes enriched in the less abundant heavy isotope(s) (Urey et al., 1932). However, lakes are complex systems and it can be challenging to isolate the effects of evaporation and changing water balance from other effects based on oxygen (or hydrogen) isotopes alone. Thus, there is an urgent need to develop and apply multi-proxy approaches to interpreting terrestrial paleohydroclimate, particularly in areas where water resource scarcity is a looming problem.

Using western U.S. water isotope and global Quaternary lake carbonate datasets compiled from the literature, we show that evaporation induced isotopic

fractionations in lake systems are often $>+10\text{‰}$ from unmodified meteoric waters for $\delta^{18}\text{O}$. Such large shifts in isotopic composition challenge the basic assumptions regarding temperature of mineral formation or source water composition applied in many stable isotopic studies underscoring the underdetermined nature of single element isotopic records. Most of the lake carbonate records included in the global dataset we present show significant positive covariation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ highlighting the need to take into account all possible controls on stable isotopic proxies, including evaporation effects, for both the Quaternary climate change and paleotopographic research.

In an effort to improve our understanding of what happens to water when it evaporates, we performed a simple experiment: we allowed natural water samples to evaporate and we analyzed their evolving stable carbon and oxygen isotopic compositions. Over the course of our six-day long evaporation experiment, isotopic compositions changed by $>+10\text{‰}$ in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ -dissolved inorganic carbon (DIC), consistent with the thermodynamics of kinetic fractionation, empirical evidence from endogenic carbonate archives, isotopic monitoring of modern hydrologic systems, and similar evaporation experiments performed under a variety of environmental conditions. The observed positive linear covariation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ follows the same narrow range in slope (ca. 0.7 to 1.2) as is present in a global compilation of Quaternary lacustrine carbonate isotopic archives ($n=57$) and laminated lacustrine carbonates reported here providing a quantitative basis for recognizing evaporative effects in endogenic carbonate isotopic records.

2. Materials and analytical methods

2.1 Global Lake Carbonate Stable Isotope Compilation

The global database of published Quaternary lake carbonate records we compiled includes more than 11,200 dual C and O stable isotopic analyses on endogenic lake carbonate samples spanning a >100° latitude range and >4800m altitude range (Table 1). Modern aridity index values (i.e. precipitation:evaporation) were extracted for each location (Table 1) from a global aridity index raster (Trabucco and Zomer, 2009) using ArcGIS. Many of the stable isotopic records were downloaded from the open access NCDC on-line database while other records were sourced from the primary literature. Please refer to the primary references listed in Table 1 for detailed information on all of these previously published dual element stable isotopic records.

2.2 Western U.S. Modern Water Stable Isotope Compilation

We compiled modern meteoric, river, and lake water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values from a variety of published sources (Friedman, 2000; Coplen and Kendall, 2000; Friedman et al., 2002; Henderson and Shuman, 2009). This compilation includes 799 individual meteoric water analyses, 3875 river water analyses, and 247 lake water analyses predominantly from the western U.S. (Fig. 1). Aridity index values

were extracted for each location as described above. For more information regarding these data, please refer to the primary sources.

2.3 Evaporation Experiments

In an effort to document the stable isotopic response to evaporation, we determined $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ -DIC values for three 250ml natural water samples allowed to evaporate in 500ml open-top beakers on a laboratory bench in the climate-controlled (21°C) stable isotope analytical facility at the University of Canterbury (Christchurch, New Zealand). All three samples were collected in Southland, New Zealand (one upland river sample, one groundwater sample, one coastal lowland stream sample) as part of a larger regional isotope hydrology investigation. Threaded 250ml sample collection bottles were over-filled in the field and stored at 4°C prior to analysis. Hydrogen and oxygen stable isotopic compositions were determined using a Picarro, Inc. Liquid Water Isotope Analyzer and two-point (i.e. stretch-and-shift) normalized to the SMOW-SLAP scale based on replicate analysis of International Atomic Energy Agency (IAEA) certified reference waters SMOW2 and SLAP. GISP, IAEA-TEL1, IAEA-TEL2, IAEA-TEL3, IAEA-TEL4 check standards were also analyzed at regular intervals across the analytical sequence for quality control and quality assurance purposes. $\delta^2\text{H}$ values are precise to $<1.0\text{‰}$ and $\delta^{18}\text{O}$ values are precise to $<0.1\text{‰}$.

$\delta^{13}\text{C}$ -DIC values were determined using the Spötl (2005) method. In brief, 1ml sub-samples were injected into ultra-high purity ($>99.999\%$) helium flushed

10ml borosilicate exetainer vials pre-loaded with 103% phosphoric acid. Dissolved inorganic carbon (DIC) derived CO₂, liberated by the acid-water reaction, was analyzed using a ThermoFinnigan GasBench II coupled to a ThermoFinnigan DeltaV⁺ isotope ratio mass spectrometer operating under a continuous flow of ultra-high purity helium. $\delta^{13}\text{C}$ -DIC values were two-point normalized to the VPDB scale based on replicate analysis of IAEA certified reference materials NBS18 and NBS19. All $\delta^{13}\text{C}$ -DIC values are precise to <0.10‰.

Each water sample was analyzed and massed at least once daily over the duration of the six-day evaporation experiment. Approximately 65% of the initial water volume evaporated over the course of the experiment for all three samples.

2.4 Stable Isotopic Analysis of lake carbonates

Quaternary (Mono Lake tufa) and middle Miocene laminated lacustrine carbonates (Barstow Fm. tufa, California, U.S.A.; Bannockburn Fm. oncholite, Otago, New Zealand) were analyzed for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the stable isotope analytical facility at the University of Canterbury. Hand samples were cut into flat slabs and milled at 0.5mm resolution using a diamond-coated Dremel tool parallel to the growth axis. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of acidified (103% phosphoric acid) sample powders were determined using a ThermoFinnigan GasBench II coupled to a ThermoFinnigan DeltaV⁺ isotope ratio mass spectrometer operating under continuous ultra-high purity He flow conditions. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values were two-point normalized to the VPDB scale based on replicate analysis of IAEA certified

reference materials NBS18 and NBS19. A MERCK carbonate internal lab standard was also analyzed at regular intervals throughout each analytical sequence. All laminated lacustrine carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are precise to $<0.10\text{‰}$.

Δ_{47} values for the middle Miocene Barstow Fm. Tufa, middle Miocene Bannockburn Fm. oncholite and Quaternary Mono Lake tufa samples were determined using a Thermo Finnigan MAT 253 dual inlet gas source mass spectrometer (“Chewbacca”) in the Triпати Lab at the University of California, Los Angeles, which has been modified to simultaneously measure masses 44-49 and is equipped with a custom built extraction device (Passey et al., 2010). For each analysis, 5 mg of sample powder was digested with 105 wt. percent H_3PO_4 using a common acid bath apparatus held at 90 °C. The resulting CO_2 was cryogenically isolated and further purified by a gas chromatograph. Purified CO_2 was transferred to the mass spectrometer, and simultaneously analyzed for $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Δ_{47} . Δ_{47} values were corrected for acid fractionation using an empirically derived acid fractionation offset of 0.092‰ (Henkes et al., 2013; Defliese et al., 2015), and are reported on the absolute reference frame (Dennis et al., 2011). Δ_{47} values were converted to temperatures (see Supplementary Information) using a variety of calibrations, (Ghosh et al., 2006; Eagle et al., 2013; Zaarur et al., 2013; Tang et al., 2014; Defliese et al., 2015), which have been adjusted to a common acid fractionation reference frame (Defliese et al. 2015). Water $\delta^{18}\text{O}$ values were calculated by using the measured carbonate $\delta^{18}\text{O}$ value in conjunction with the measured Δ_{47} -based temperature according to the carbonate-water oxygen isotope equilibrium fraction equation of Kim and O’Neil (1997).

The water and lake carbonate data we report is a combination of primary data original to this study and previously published datasets. The reader is referred to the original sources for all previously published data in both the text and figure captions.

3. Results

3.1 Western North America Water Isotopes

Meteoric waters from western North America closely approximate the global meteoric water line (GMWL) and span an $\sim 35\text{‰}$ range in $\delta^{18}\text{O}$ (Fig. 2a; Friedman, 2000; Coplen and Kendall, 2000; Friedman et al., 2002; Henderson and Shuman, 2009). Yet, some of these meteoric water samples, specifically those at the more positive end of the dataset, plot significantly to the right of the GMWL reflecting the effects of evaporation during rainout and resulting in a more negative regional meteoric water line y-intercept value (2.38) than is generally assigned to the GMWL (~ 10).

River waters from western North America show a similar pattern, albeit with a dampened range in $\delta^{18}\text{O}$ ($\sim 30\text{‰}$ versus $\sim 35\text{‰}$). Such signal dampening is easily explained by source water mixing along hydrological flow paths. The more negative y-intercept value of western North America river water (1.59) in comparison to meteoric water from the same region (2.38) is almost certainly the result of

220 additional surface water evaporation (Fig. 2b) either in through-flowing lakes or the
221 rivers themselves.

222 Although originating from meteoric and riverine sources, modern lake
223 waters in western North America clearly depart from the GMWL (Fig. 2c). Lakes
224 from less arid environments generally plot closer to the GMWL, although some
225 humid and sub-humid environment lakes are shifted to the right of the GMWL along
226 a regional evaporation line of slope ~ 5.2 (dark blue and blue triangles in Fig. 2c). In
227 contrast, most lakes in semi-arid to arid environments plot well to the right of the
228 GMWL unequivocally due to the effects of lake water evaporation.

229 The more pronounced effect of evaporation on lake water isotopic
230 compositions is best demonstrated through quantification of the positive $\delta^{18}\text{O}$ shift
231 away from the GMWL recognized in most western North America lakes (Fig. 2d). We
232 determined the evaporation induced $\delta^{18}\text{O}$ shift (i.e. change in $\delta^{18}\text{O}$ value) for
233 individual meteoric, river and lake water samples by subtracting the observed $\delta^{18}\text{O}$
234 value from the corresponding $\delta^{18}\text{O}$ value at the intersection of the GMWL ($\delta^2\text{H} =$
235 $8 \times \delta^{18}\text{O} + 10$) and an intermediate and representative slope 4.5 evaporation line. The
236 median $\delta^{18}\text{O}$ shift for the 248 lake water samples we compiled is $+4.6\text{‰}$, with a
237 minimum of -1.3‰ at Bonneville Salt Flat (January, 1993) and a maximum of
238 $+23.5\text{‰}$, also at Bonneville Salt Flat and in the same calendar year (July, 1993).

239 These results demonstrate the extreme isotopic sensitivity of lake systems to
240 evaporation induced kinetic fractionation effects, particularly in arid and semi-arid
241 environments. A statistical comparison of meteoric, river and lake water $\delta^{18}\text{O}$ shift
242 values indicates that, on average, meteoric waters are not significantly different

243 than river waters ($p=0.34$; two-tailed t-test), yet lake waters are highly significantly
244 different than both meteoric and river waters ($p=10^{-36}$ and $p=10^{-41}$, respectively;
245 two-tailed student's t-test).

246 The fact that lake water isotopic compositions do not reflect meteoric water
247 isotopic compositions is further demonstrated by a comparison of observed lake
248 water $\delta^{18}\text{O}$ values and modeled meteoric water $\delta^{18}\text{O}$ values (Online Isotopes in
249 Precipitation Calculator; Bowen, 2014) at each lake's location (Fig. 3). Surprisingly,
250 relatively few lakes exhibit more negative $\delta^{18}\text{O}$ values than local meteoric water
251 despite the cordilleran physiography of western North America: lakes should be
252 recharged by higher altitude meteoric water sources that are ^{18}O depleted relative
253 to local meteoric recharge. Yet, the empirical pattern present in the data we
254 compiled is quite the opposite (Fig. 3): the by far majority of lakes are ^{18}O enriched
255 relative to local meteoric water. Interestingly, even lakes in humid environments
256 can be enriched in ^{18}O by up to $\sim 12\text{‰}$ in comparison to local meteoric water, and
257 lakes in semi-arid to arid environments can exhibit ^{18}O enrichments on the order of
258 $+15\text{‰}$ (Fig. 3).

259 The results presented above provide important context to our discussion of
260 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ covariation in the following sections. The unequivocal and potentially
261 extreme effects of evaporation on surface water isotopic compositions present
262 major challenges to single element (i.e. O or H) proxies of temperature, elevation,
263 water source apportionment, atmospheric circulation conditions and any
264 combination of these environmental conditions. However, these same results

confirm that stable isotopic lacustrine archives are potentially powerful recorders of hydrologic balance.

3.2 Evaporation Experiment

The stable isotope community has long known of the potentially extreme effects of evaporation on the isotopic composition of liquids. After all, Urey himself applied this knowledge when he demonstrated the existence of deuterium through evaporative enrichment of liquid hydrogen (Urey et al., 1932). Yet, the liquid itself is not the only phase affected by the chemical consequences of evaporation.

As water evaporates its chemistry changes: concentrating dissolved phases, increasing alkalinity and forcing changes in equilibrium conditions. One of the most obvious consequences of evaporation is the formation of sedimentary evaporites including some lacustrine carbonates (e.g. trona and tufa). The isotopic effects of evaporation on endogenic carbonates have been a research focus of the terrestrial paleoclimate community for many years (e.g. Stuiver, 1970), and one of the most commonly reported observations is O and C stable isotopic covariation.

Coupled ^{18}O and ^{13}C enrichment in endogenic carbonates has been documented and discussed at some length in the limnological (Stuiver, 1970; Talbot, 1990; Li and Ku, 1997; Huang et al., 2014), pedological (Cerling and Quade, 1993; Quade et al., 2007; Ding et al., 2014), and speleological communities (Hendy, 1971; Mickler et al., 2006; Dreybrodt and Deininger, 2014). Oxygen and carbon stable isotopic covariation has also been documented in evaporating Dead Sea brines

(Stiller et al., 1985), degassing epithermal systems (Zheng, 1990) and laboratory experiments (Ufnar et al., 2008; Abongwa and Atekwana, 2013). Although several hydrological models incorporate evaporative effects in their isotopic determinations (Appelo, 2002; Benson and Paillet, 2002; Cappa et al., 2003; Jones et al., 2005; Jones and Imbers, 2010), only one of these models explicitly addresses the coupled effects of evaporation on oxygen and carbon isotope fractionation (Deininger et al., 2012). However, the model of Deininger and others (2012) specifically applies to thin-film evaporation associated with stalagmite formation in caves rather than surface water evaporation in lakes. Although evaporative effects on lake water and lake carbonate isotopic compositions have been highly studied, an integrated understanding of how evaporation influences the coupled carbon and oxygen isotope compositions of surface waters remains elusive.

In fact, the general lack of dual O and C stable isotopic data for evaporating solutions in the primary literature is somewhat surprising given the widespread empirical demonstration of isotopic covariation in many carbonate lakes and soil environments. Although we do not intend to fill this gap in the literature here, the evaporation experiment data we report reinforce what many have inferred from empirical results and isotopic theory: evaporation causes ^{18}O enrichment in water and ^{13}C enrichment in DIC.

All three water samples that we allowed to evaporate showed ^{18}O and ^2H enrichment according to well-known kinetic fractionation processes (Cappa et al., 2003). Over the six-day evaporation period, all three samples lost ~65% of their mass to evaporation at near constant evaporation rates (Fig. 4a). The stable O and H

isotopic response to evaporation increased residual water $\delta^{18}\text{O}$ values by $\sim 11\text{-}13\text{‰}$ and $\delta^2\text{H}$ values by $\sim 45\text{-}55\text{‰}$ over the course of the experiment. All three samples followed similar linear evaporation trends away from the GMWL (Fig. 4b).

As each of the samples evaporated, clear progressive ^{13}C enrichments in DIC, on the order of $1\text{-}2\text{‰}$ per day, occurred over the six-day experiment. From these data and the corresponding water $\delta^{18}\text{O}$ values, we calculated the equilibrium fractionation (Kim and O'Neil, 1997) O and C stable isotopic compositions of calcite that would have formed from these evaporating waters at 21°C (Fig. 4c). Although not as strongly linear as the O and H isotopic response, statistically significant ($p < 0.05$; t-test) positive covariation was observed in all three samples. The relatively constant linear covariation slope ($m = 0.7$ to $m = 1.2$) is notably similar to what has been observed in the lacustrine carbonate rock record (Horton and Oze, 2012) suggesting systematic isotopic fractionations occur as excess CO_2 degasses from the water body, ^{13}C enriched bicarbonate ions (and carbonate ions above $\text{pH} > 8.3$) further dominate the DIC pool as alkalinity increases in response to evaporation, and the water molecules themselves become ^{18}O enriched as they evaporate (Zheng, 1990; Valero-Garcés et al., 1999; Cappa et al., 2003; Dreybrodt and Deininger, 2014).

A number of different processes can cause ^{13}C enrichment of the DIC pool, including carbon isotope fractionation caused by an increased rate of aquatic photosynthesis relative to respiration and decomposition, equilibrium exchange with atmospheric carbon dioxide, and inputs of carbon derived from magmatic or marine limestone sources. Of these processes, only equilibrium exchange with

atmospheric carbon dioxide is a possible factor influencing our experimental results. Thus, our findings suggest that evaporation induced increases in alkalinity (i.e. increased bicarbonate concentration) drives DIC ^{13}C enrichment through isotopic equilibrium exchange with CO_2 (ca. 8‰ at 25°C in the HCO_3^- – CO_2 system; Mook et al., 1974). This interpretation and our results are consistent with mechanistic models of the isotopic response of DIC during evaporation (Abongwa and Atekwana, 2013; Dreybrodt and Deininger, 2014).

3.3 Global Pattern of O and C isotopic covariation

Tens if not hundreds of research investigations into lake carbonate isotope variability have been conducted in the twenty-five years since Talbot (1990) published his review of the paleohydrological interpretation of lake carbonate stable isotopic records. In an effort to further explore and update the paleohydrological interpretation of lacustrine isotopic archives, we compiled 57 lake carbonate dual element (i.e. O and C) stable isotopic records (Table 1) representing 38 different globally distributed lake systems published in 46 different primary sources, of which 42 were published between 1990 and 2015. These 57 records were selected because they span a broad range of geographic, physiographic, climatic and hydrologic conditions including high and low latitude environments, closed and open basin hydrologies, low and high altitudes, and humid to arid hydroclimates. The most salient pattern that emerges from the analysis of this compilation is O and C stable isotopic covariation.

Of the 57 lake records analyzed, 41 show a statistically significant ($p < 0.05$, t-test) positive covariation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, 3 show a statistically significant ($p < 0.05$, t-test) negative covariation (Medicine Lake, Valero-Garcés et al., 1995; Wallywash Pond, Holmes et al., 2007; Seven Mile Lake; Anderson et al., 2011), and 13 show no significant isotopic covariation (Fig. 5). The average linear regression slope of the 41 records with a significant positive covariation trend is 0.62, across slope values ranging between 1.67 and 0.1. The average range in $\delta^{18}\text{O}$ values spanned by these 41 records is 6.9‰, with a maximum range of 13.5‰ and minimum range of 1.2‰. Nearly three-quarters (i.e. 72%) of the lake records we compiled show statistically significant positive covariation trends spanning isotopic compositional ranges that are difficult to explain in the absence of extreme isotopic modification by evaporative enrichment of lake waters in both ^{18}O and ^{13}C .

4. Discussion

4.1 From source to sink: O and C isotopes in Quaternary lake systems

Oxygen and carbon stable isotopic covariation in endogenic lacustrine carbonates is not uncommon (Talbot, 1990). Yet, relatively few studies have analyzed the oxygen and carbon isotopic composition of both modern lake water samples and lake source (i.e. inflow) water samples, making it difficult to quantify the extent to which lacustrine processes, including evaporation, modify source water O and C chemistries. In an effort to quantify these source water modification

effects on the stable isotopic composition of lake carbonates, we modeled individual lake carbonate isotopic compositions using two different approaches and compared these results to observed isotopic records.

In our first analysis we only consider oxygen isotope compositions. As part of this analysis, we modeled the oxygen isotope composition of calcite that would have formed from mean summertime precipitation (Bowen, 2014) at mean summer month air temperatures (Hijmans et al., 2005) according to temperature dependent oxygen isotope equilibrium fractionation (Kim and O'Neil, 1997):

$$1000\ln\alpha(\text{Calcite-H}_2\text{O}) = 18.03(10^3T^{-1}) - 32.42 \quad (1)$$

where T is temperature in kelvins and α is the temperature dependent calcite-water fractionation factor. We then compared these model $\delta^{18}\text{O}$ values to the average $\delta^{18}\text{O}$ observed in all 57 of the global lake carbonate records we compiled (Fig. 6). In this model, the calculated $\delta^{18}\text{O}$ values assume that lake calcite formed from unmodified local meteoric water. Although this analysis represents an overly simplified model of oxygen isotope equilibrium fractionation in lake carbonates, it is similar to the approach used in 27 of the 45 (i.e. 60%) of the published sources (see Table 1) we used in our data compilation.

Similar to what was observed in our comparison of modern meteoric water and lake water $\delta^{18}\text{O}$ (Fig. 3), the observed average lake carbonate $\delta^{18}\text{O}$ values are more positive than the modeled summer month meteoric water derived calcite $\delta^{18}\text{O}$ values (Fig. 6). Lakes in humid environments generally plot closer to the 1:1 line,

suggesting lakes in these environments are less impacted by evaporative modification, yet 46 of the 57 lake records analyzed (i.e. 81%) plot to the right of the 1:1 line consistent with evaporative modification of lake water $\delta^{18}\text{O}$. Forty-two percent of the lake carbonate $\delta^{18}\text{O}$ records are $>5\text{‰}$ shifted towards more positive $\delta^{18}\text{O}$ than would be expected for summer month carbonate precipitates derived from unmodified local meteoric water. Although many lakes with vastly different modern aridity index values show similar offsets between modeled and observed $\delta^{18}\text{O}$, lakes from currently arid and semi-arid environments have a much larger average $\delta^{18}\text{O}$ offset (5.4‰) than sub-humid and humid environment lakes (2.0‰).

This model analysis of 57 global Quaternary lake carbonate $\delta^{18}\text{O}$ records demonstrates the challenges of working with underdetermined stable isotopic systems. By assuming temperatures of carbonate formation or source water oxygen isotope composition, or any other environmental parameters (e.g. atmospheric circulation; seasonally variable recharge sources; etc.) that may similarly influence these two unknowns in carbonate mineral-water oxygen isotope equilibrium fractionation equations, researchers effectively pre-determine the primary control on carbonate $\delta^{18}\text{O}$ values. For example, had we assumed winter month (or pre-interglacial) temperatures of formation in our analysis rather than modern summer month temperatures we would have generated more positive modeled carbonate $\delta^{18}\text{O}$ values. Conversely, had we used mean annual or weighted mean annual precipitation stable isotopic compositions rather than summer month precipitation values, we would have generated more negative modeled carbonate $\delta^{18}\text{O}$ values. In either instance the likely interpretations rely heavily on the assumptions that

underlie the analysis. Such overly simplistic approaches reinforce the challenges associated with traditional single element stable isotopic investigations of complex hydrologic and climatic systems.

In our second analysis, we examined a subset of Quaternary lacustrine carbonate isotopic records where complementary modern lake and source water oxygen and carbon isotope data were also available in the literature. From these data, we were able to separately calculate the O and C stable isotopic compositions of calcite forming in isotopic equilibrium with both source water and lake water. Because Quaternary lake carbonate dual element isotopic records were also available for these lake systems, we were able to graphically present each lake's complete stable isotopic profile, including modeled source water derived calcite, modeled lake water derived calcite, and observed lake carbonate compositions, on individual bivariate plots (Fig. 7). There are several key insights to be gained from these isotopic profiles.

First, modeled source water derived calcite compositions (green stars, Fig. 7) are several permil more negative than modeled lake water derived calcite compositions (red stars, Fig. 7) in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. In the context of the evaporation experiment results we present above, the $\sim 8\text{‰}$ to $\sim 15\text{‰}$ differences between source water calcite and lake water calcite isotopic compositions is best explained by high levels of evaporation (i.e. the equivalent of the isotopic response to $>50\%$ losses to evaporation). Determining the extent to which source water O and C isotopic compositions are modified by evaporation can now be determined with relative ease. Triple-oxygen isotope analysis of water, an excellent indicator of

evaporation effects (Passey et al., 2014), is becoming more common as researchers begin utilizing current generation off-axis integrated cavity output spectrometers (Berman et al., 2013) and high sensitivity isotope ratio mass spectrometers (Barkan and Luz, 2005), and $\delta^{13}\text{C}$ -DIC analyses are similarly more accessible to the geochemical research community (e.g. Bass et al., 2014). We encourage researchers interested in both modern and ancient lake systems to pursue these multi-proxy approaches to advancing our understanding of source water modification during lacustrine residence. A crucial aspect of such endeavors will be to study both the source water, lake water and carbonate precipitation as an integrated and temporally dynamic system, rather than discrete hydrologic components suitable for study in isolation.

Second, measured Quaternary carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values generally plot along a slope ~ 1 positive linear covariation trend that also includes the modeled source and lake calcite compositions (i.e. the line connecting green stars to red stars shown in Fig. 7). The general agreement between measured paleolake carbonate compositions and modeled modern lake calcite compositions demonstrates that this approach provides a reasonably accurate first-order approximation of endogenic lake carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. The lack of overlap between modeled source water derived calcite compositions and observed paleolake compositions reinforces the fact that meteoric derived source waters are modified by in-lake processes. Just as we have shown above for modern lakes, paleolake carbonates do not reflect meteoric derived source water isotopic compositions. Based on the results of our evaporation experiments, we argue that the relatively systematic slope ~ 1 positive

linear covariation trends, linking both modeled calcite and measured paleolake carbonate isotopic compositions, is further evidence that evaporation during lake residence is the primary driver of these individual lake isotope profiles.

Third, lake carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values show severe isotopic modification due to lake water evaporation regardless of whether or not they exhibit isotopic covariation (Fig. 7). Strong positive covariation between lake carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values has been associated with closed-basin hydrology or lakes with very long residence times, implying that evaporative effects are the primary driver of these covariant trends (e.g. Talbot, 1990).

Our analysis reinforces these interpretations, yet it also demonstrates that even lake carbonate records lacking significant positive covariation trends can also be severely impacted by the effects of evaporation. Several Quaternary lake carbonate records, notably those from arid environment closed-basins including Mono Lake cores MLB-003D (Benson et al., 2003), MLC-001T (Benson et al., 2003), ML91-FC3 (Li et al., 1997) and Pyramid Lake core PLC-97.3 (Benson et al., 2002), do not show significant covariation trends. Yet, according to our analysis, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values measured in these cores are $\sim 10\text{‰}$ to $\sim 15\text{‰}$ enriched in both ^{18}O and ^{13}C along a slope ~ 1 trend relative to modeled modern source water derived calcite compositions (Fig. 7). These extreme isotopic enrichments relative to less evolved inflow water isotopic compositions is demonstrated by the positions of the green stars (i.e. inflow water derived carbonate compositions) shown in Fig. 7 relative to the positions of the red stars (i.e. lake water derived carbonate compositions). The Mono Lake data presented in Fig. 7e provide an excellent example.

Several of the Mono Lake carbonate records we compiled (Fig. 7e) do not exhibit statistically significant positive covariation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Slopes of these statistically not significant linear regressions fit to these records range between -0.02 and +0.77. Applying the logic presented in Talbot's seminal review of carbonate lake paleohydrology (Talbot, 1990), it would be tempting to interpret that Mono Lake was not hydrologically closed during these intervals due to a shift in hydrologic balance towards relatively wetter conditions. However, the lack of isotopic covariation and associated variability in regression line slopes are the consequence of the fact that these metrics are determined by comparing the lake carbonate values to themselves. By comparing these same data to the isotopic compositions expected from inflow waters (Fig. 7e) and other records from Mono Lake that do exhibit significant covariation (Fig. 7a), our analysis reveals that these intervals instead represent some of the most isotopically enriched periods captured by any of the Mono Lake archives.

The most plausible mechanism of such severe heavy isotope enrichments is evaporation. Given the overlap between the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values observed in these Mono (Fig. 7e) and Pyramid Lake (Fig. 7f) records and other records from the same lakes (Fig. 7a, b), we suggest that a stable, yet highly arid, climatic condition was present during deposition of these lake carbonates. The possibility that extreme isotopic modification by evaporation fails to impart significant positive O and C covariation trends on lake carbonate archives is problematic in that it increases the probability that isotopic evaporation effects may pass unrecognized by the researcher.

4.2 Relevance to other research topics

The data and interpretations we present above are not restricted to the lacustrine Quaternary paleoclimate community. The underlying hydrochemical processes and conditions at the core of our review and analysis are key topics in modern research on regional hydrologic cycles and water resource management, as well as the broader limnology, biogeochemistry and aquatic ecology communities. In the context of stable isotopic proxies, however, the data and analysis we present is particularly relevant to both the pedogenic carbonate and paleotopographic research communities.

Pedogenic carbonate formation is most commonly associated with arid to semi-arid environments (Jenny, 1994). Thus, it is reasonable to assume that if evaporation is the dominant process controlling stable O and C isotopic compositions in endogenic lacustrine carbonates, then similar effects should be expected in pedogenic carbonates. To explore this possibility, we plotted the seminal western U.S. aridisol pedogenic carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values reported by Cerling and Quade (1993) and classified each value by its site-specific modern aridity index (Fig. 8a). The stable isotopic data reported by Cerling and Quade (1993) correspond with average soil carbonate isotopic compositions observed below 30cm depth in modern soils.

As would be expected from isotopic enrichment due to evaporation, modern soil carbonates from the western U.S. describe a statistically significant positive

covariation trend ($p=4.7^{-10}$, t-test) with a slope very close to 1 ($m=1.03$; Fig. 8a). The observation that pedogenic carbonates from hyper-arid and arid environments exhibit the most positive $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, while semi-arid to humid environment soils show the most negative values, further suggests that evaporation is the dominant control on both the oxygen and carbon isotope composition of these soil carbonate samples at >30 cm depth (Fig. 8a). More recent research on the stable isotopic composition of arid environment soil carbonates support this interpretation (Quade et al., 2007). Future research based on the stable isotopic composition of pedogenic soil carbonates, whether for paleoclimatic or paleotopographic purposes, will benefit significantly from multi-proxy research approaches that provide quantitative constraints on the effects of soil water evaporation (e.g. Horton and Oze, 2012; Ji et al., 2014; Passey et al., 2014).

The stable isotope paleotopography community will almost certainly benefit from similar approaches for similar reasons. Just as the Quaternary paleoclimate community must address the underdetermined nature of stable isotopic proxies available from terrestrial archives, the stable isotope paleotopography community must also take care to accurately interpret authigenic mineral isotopic records sensitive to changing water balance in evolving orographic rain shadows. Failing to account for the isotopic effects of evaporation and uplift induced shifts in regional hydroclimatic conditions, could lead to erroneous paleoelevation interpretations on the order of kilometers (Horton and Oze, 2012).

As recognized in a smaller lake carbonate compilation (Horton and Oze, 2012), both the Quaternary lake carbonate and modern soil carbonate records we

investigated here indicate there is an apparent quantitative relationship between hypsometric altitude and positive linear covariant trend y-intercept value (i.e. ^{13}C -excess; Fig. 7; Fig. 8). The dual element ^{13}C -excess paleoelevation approach takes advantage of the systematic nature of the empirically and experimentally observed positive covariation slope $m \approx 1$ and combines this relationship with the well-known altitude effect on meteoric water $\delta^{18}\text{O}$ values to estimate hypsometric altitudes within ± 500 m errors (Horton and Oze, 2012). Application of this proxy to modern soil carbonates from the Mojave Desert-Great Basin region (Fig. 8a), as well as middle Miocene laminated lacustrine carbonates from the modern Sierra Nevada (Fig. 8b; Barstow Fm. tufa; Mud Hills, California) and Southern Alps (Fig 8b; Bannockburn Fm. oncholite; Otago, New Zealand) orographic rain shadows, yields hypsometric elevations on the order of 1.5 km for all three records. These ^{13}C -excess elevations agree well with modern elevations across the Great Basin (~ 1700 m mean elevation in the north; ~ 900 m mean elevation in the south; Saltus and Thompson, 1995) and published paleotopographic interpretations for the Sierra Nevada (Mulch et al., 2006; Cassel et al., 2009). However, a ~ 1.5 km high 'proto' Southern Alps at ~ 15 Ma is an entirely new interpretation that provides important detail otherwise lacking in the only other paleoelevation study on the mountain range (Chamberlain et al., 1999).

The ^{13}C -excess approach to determining paleoelevations represents one way future researchers can overcome the stable isotopic evaporation problem. Yet, the most robust interpretations of paleoelevation are likely to result from combining the ^{13}C -excess approach with complementary proxies of both evaporation (e.g. triple

oxygen stable isotope analysis; Passey et al., 2014) and temperature (e.g. clumped isotope analysis; Petryshyn et al., 2015).

4.3 Multi-proxy methods

The research we present demonstrates that the underdetermined nature of stable isotopic systems is a key challenge in paleoenvironmental research. The sensitivity of terrestrial systems to a number of environmental variables is both a strength and weakness of stable isotope proxy methods. However, recent advances in stable isotope analytical techniques create unprecedented opportunities to determine multiple independent proxy datasets for the same suite of samples. Using some of the same lake carbonate samples discussed above, we below demonstrate the utility of applying coupled $\delta^{18}\text{O}$ and Δ_{47} temperature estimates to assessments of paleohydroclimatic conditions.

We determined $\delta^{18}\text{O}$ and Δ_{47} values for a previously toppled modern era Mono Lake tufa tower collected near the South Tufa visitor's area (U.S. Department of Agriculture, Special Use Permit: LVD050047T issued to Horton). $\delta^{18}\text{O}$ values determined on individual carbonate laminations present in this tufa are $\sim 13\text{‰}$ more positive than would be expected for Mono Lake inflow water derived carbonate (Fig. 7a). Paleotemperature estimates for two Δ_{47} analyses of this same sample (Table 2) are 15.8°C ($\pm 4.3^{\circ}\text{C}$) and 15.4°C ($\pm 3.3^{\circ}\text{C}$). Inputting the $\delta^{18}\text{O}$ values and Δ_{47} paleotemperature estimates to the Kim and O'Neil (1997) oxygen isotope equilibrium fractionation equation yields lake water $\delta^{18}\text{O}$ values of -2.3‰ ($\pm 0.9\text{‰}$).

and -1.4‰ (± 0.7 ‰) VSMOW (Table 2). These values are 13‰ to 14‰ more positive than published Mono Lake inflow water $\delta^{18}\text{O}$ values and 1‰ to 2‰ more negative than present day Mono Lake water (Li et al., 1997). By combining traditional carbonate $\delta^{18}\text{O}$ data with more recently developed Δ_{47} clumped isotope analytical methods we were able to isolate and solve for a single variable ($\delta^{18}\text{O}_{\text{water}}$) in the calcite-water equilibrium fractionation equation. Our multi-proxy approach demonstrates that Mono Lake water was highly modified by evaporation at the time of tufa formation, consistent with the interpretations published by others (Li and Ku, 1997; Li et al., 1997; Benson et al., 2003) and the basin's arid hydroclimatic setting in the rain shadow of the Sierra Nevada.

Application of this multi-proxy method is similarly instructive for middle Miocene laminated lacustrine carbonates exposed in the central Mojave Desert (Barstow Formation tufa) and central Otago in Aotearoa/New Zealand's South Island (Bannockburn Formation oncholite). $\delta^{18}\text{O}$ values determined for carbonate powders drilled at 0.5 mm spacing across a 100mm wide section of the Barstow Formation tufa do not covary with $\delta^{13}\text{C}$ ($r^2=0.03$; $n=201$; Fig. 8b) suggesting evaporative effects may not have been a primary control on the isotopic composition on the water filling this 15 million year-old lake basin. However, Δ_{47} paleotemperature estimates for the Barstow tufa are relatively warm (48.3°C; Table 2), yielding lake water $\delta^{18}\text{O}$ values of -0.4‰ (± 0.3 ‰) VSMOW (Table 2) under equilibrium calcite-water fractionation conditions. In this case, combining $\delta^{18}\text{O}$ and Δ_{47} paleotemperature estimates suggests that the Barstow Formation tufa may have

632 been fed by hot springs generated by local magmatic systems present in the central
633 Mojave during the middle Miocene (Glazner et al., 2002).

634 In a third example, multi-proxy $\delta^{18}\text{O}$ and Δ_{47} values determined for an
635 oncholite preserved in central Otago's ~17 million year-old Bannockburn Formation
636 are consistent with paleontologic, palynologic and sedimentologic interpretations of
637 paleolake Manuherikia's natural environment, climate and physiography. The
638 occurrence of mekosuchine crocodile bones and subtropical casuarinas and palm
639 pollen in Manuherikia sediments suggest a relatively warm subtropical climate not
640 unlike that of modern northern New Zealand (Schwarzshans et al., 2012). The Δ_{47}
641 paleotemperature estimates we determined (Table 2) reinforce this interpretation
642 returning values that range between 17.7°C ($\pm 3.9^\circ\text{C}$) and 24.6°C ($\pm 2.6^\circ\text{C}$), similar to
643 the range in modern-era monthly average air temperatures in Northland, New
644 Zealand, and several degrees warmer than the modern-era mean annual air
645 temperature of central Otago.

646 Bannockburn Formation oncholite sedimentary structures and textures
647 suggest these laminated lacustrine carbonates formed in the shallow littoral zone of
648 an ephemeral sub-basin in the paleolake Manuherikia system (Lindqvist, 1994). If
649 true, we would expect Manuherikia oncholites to exhibit isotopic compositions
650 consistent with evaporative modification of lake water. The significant ($p < 0.05$; t-
651 test) positive covariation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the Bannockburn Formation
652 sample (Fig. 8b) and the equilibrium fractionation lake water $\delta^{18}\text{O}$ values (-0.1‰
653 $\pm 0.8\text{‰}$ to $+2.6\text{‰} \pm 0.6\text{‰}$ VSMOW; Table 2) determined using the above Δ_{47}
654 paleotemperature estimates and associated oncholite $\delta^{18}\text{O}$ values provide strong

empirical evidence that these samples indeed formed in the presence of evaporated lake water. Integrating these findings with the ^{13}C -excess paleoelevation proxy results which suggest the presence of a ~ 1.5 km high catchment hinterland in the Manuherikia system (see section 4.3, above) provides further paleoenvironmental detail that cannot be achieved through application of traditional single element stable isotopic proxy methods.

5. Conclusions

A review of globally distributed Quaternary lake carbonate stable isotopic records and modern water isotopic compositions from western North America reinforces what the scientific community has known for decades: evaporation enriches surface waters and associated authigenic minerals in both ^{18}O and ^{13}C . This empirical pattern of O and C heavy isotope enrichment is corroborated by simple evaporation experiment results, and is consistent with the thermodynamics of kinetic fractionation of evaporating water, degassing of dissolved CO_2 , and ^{13}C enrichment of DIC as alkalinity increases at Earth surface temperatures. Of utmost importance is the recognition that the isotopic effects of evaporation can be extreme, often in excess of 10‰ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Traditional single-element isotopic records fail to record the full extent of these evaporative effects due to their sensitivity to myriad environmental conditions and the difficulty in determining unmodified source water compositions from terrestrial archives.

However, the systematic nature of evaporation induced positive covariation in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for both lacustrine and pedogenic carbonates presents opportunities to apply dual element and multi-proxy methods to this isotopic evaporation problem even in systems where covariation is not immediately apparent. Integration of traditional O and C isotopic compositions with clumped isotope and triple-oxygen proxies has the potential to produce detailed empirical data-based interpretations of hydroclimatic and paleoenvironmental conditions in terrestrial settings on a variety of spatial and temporal scales. Our research demonstrates that the integration of multiple stable isotopic proxy methods not only improves paleoclimate research outcomes but also paleotopographic interpretations of geological archives (e.g. Chamberlain and Poage, 2000; Horton et al., 2004; Horton and Chamberlain, 2006; Sjostrom et al., 2006). As they become more widely applied, we anticipate that similar multi-proxy research approaches will help improve our understanding of modern hydrological responses to rapidly changing environmental conditions.

Acknowledgements

We thank the U.S. Department of Agriculture – Forest Service for granting TWH a special use permit (authorization ID: LVD050047T) allowing for the collection of previously broken (i.e. toppled) laminated carbonate deposits/tufas at Mono Lake, Inyo National Forest, California, U.S.A. We thank Dave Eiriksson for his University of Puget Sound senior thesis research and fieldwork on the California laminated lacustrine carbonates, and Clinton Rissmann and Michael Killick of Environment Southland (Invercargill, New Zealand) for providing the water samples used in our evaporation experiments. We would also like to thank Matt Jones for his invitation to submit this manuscript and his contribution to the scientific community as editor of this Water Isotope Systematics special issue of Quaternary Science Reviews. We acknowledge support from DOE grant DE-FG0213ER16402 and NSF grants EAR-1352212, EAR-1325054, and EAR-0949191. The original manuscript was improved by thoughtful and constructive reviews provided by two anonymous referees.

References

- Abell, P.I., Awramik, S.M., Osborne, R.H., Tomellini, S., 1982. Plio-pleistocene lacustrine stromatolites from lake Turkana, Kenya: Morphology, stratigraphy and stable isotopes. *Sed. Geol.* 32, 1-26.
- Abongwa, P.T., Atekwana, E.A., 2013. Assessing the temporal evolution of dissolved inorganic carbon in waters exposed to atmospheric CO_{2(g)}: A laboratory approach. *J. Hydrol.* 505, 250-265.
<http://dx.doi.org/10.1016.j.hydrol.2013.09.045>.
- Anderson, L., Abbott, M.B., Finney, B.P., Burns, S.J., 2005. Regional atmospheric circulation change in the North Pacific during the Holocene inferred from lacustrine carbonate oxygen isotopes, Yukon Territory, Canada. *Quat. Res.* 64, 21-35.
- Anderson, L., Finney, B.P., Shapley, M.D., 2011. Lake carbonate- $\delta^{18}\text{O}$ records from the Yukon Territory, Canada: Little Ice Age moisture variability and patterns. *Quat. Sci. Rev.* 30, 997-898.
- Andrews, J.E., Pedley, M., Dennis, P.F., 2000. Palaeoenvironmental records in Holocene Spanish tufas: a stable isotope approach in search of reliable climatic archives. *Sedimentol.* 47, 961-978.

729

730 Appelo, C.A.J., 2002. Calculating the fractionation of isotopes in hydrochemical
731 (transport) processes with PHREEQC-2, in: Schulz, H.D., Hader, A. (Eds.),
732 Geochemical processes in soil and groundwater. Wiley-VCH, Weinheim, pp. 383-
733 398.

734

735 Barkan, E., Luz, B., 2005. High precision measurements of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios
736 in H_2O . Rapid Commun. Mass Spectrom. 19, 3737-3742.

737

738 Bass, A.M., Munksgaard, N.C., O'Grady, D., Williams, M.J.M., Bostock, H.C., Rintoul,
739 S.R., Bird, M.I., 2014. Continuous shipboard measurements of oceanic $\delta^{18}\text{O}$, δD
740 and $\delta^{13}\text{C}_{\text{DIC}}$ along a transect from New Zealand to Antarctica using cavity ring-
741 down isotope spectrometry. J. Marine Syst. 137, 21-27.
742 <http://dx.doi.org/10.1016/j.jmarsys.2014.04.003>.

743

744 Benson, L., White, L.D., Rye, R., 1996. Carbonate deposition, Pyramid Lake Subbasin,
745 Nevada: 4) Comparison of the stable isotope values of carbonate deposits
746 (tufas) and the Lahontan lake-level record. Palaeogeogr. Palaeoclimatol.
747 Palaeoecol. 122, 45-76.

748

749 Benson, L.V., Paillet, F., 2002. HIBAL: a hydrologic-isotopic-balance model for
750 application to paleolake systems. Quat. Sci. Rev. 21, 1521-1539.

751

Benson, L.V., Kashgarian, M., Rye, R., Lund, S.P., Paillet, F., Smoot, J.P., Kester, C.,
Mensing, S., Meko, D., Lindström, S., 2002. Holocene multidecadal and
multicentennial droughts affecting Northern California and Nevada. *Quat. Sci.*
Rev. 21, 659-682.

Benson, L.V., Linsley, B.K., Smoot, J.P., Mensing, S., Lund, S.P., Stine, S., 2003.
Influence of the Pacific Decadal Oscillation on the climate of the Sierra Nevada,
California and Nevada. *Quat. Res.* 59, 151-159.

Benson, L.V., Lund, S.P., Smoot, J.P., Rhode, D.E., Spencer, R.J., Verosub, K.L.,
Louderback, L.A., Johnson, C.A., Rye, R.O., Negrini, R.M., 2011. The rise and fall of
Lake Bonneville between 45 and 10.5 ka. *Quat. Int.* 235, 57-69.
<http://dx.doi.org/10.1016/j.quaint.2010.12.014>.

Benson, L.V., Smoot, J.P., Lund, S.P., Mensing, S.A., Foit Jr., F.F., Rye, R.O., 2013.
Insights from a synthesis of old and new climate-proxy data from the Pyramid
and Winnemucca lake basins for the period 48 to 11.5 cal ka. *Quat. Int.*, 310, 62-
82. <http://dx.doi.org/10.1016/j.quaint.2012.02.040>.

Berman, E.S.F., Levin, N.E., Landais, A., Li, S., Owano, T., 2013. Measurement of $\delta^{18}\text{O}$,
 $\delta^{17}\text{O}$, and ^{17}O -excess in Water by Off-Axis Integrated Cavity Output Spectroscopy
and Isotope Ratio Mass Spectrometry. *Anal. Chem.* 85, 10392-10398.

- Bird, B.W., Abbott, M.A., Rodbell, D.T., Vuille, M., 2011. Holocene tropical South American hydroclimate revealed from a decadal resolved lake sediment $\delta^{18}\text{O}$ record. *Earth Planet. Sci. Lett.* 310, 192-202.
<http://dx.doi.org/10.1016/j.epsl.2011.08.040>.
- Bowen, G.J., 2014. The Online Isotopes in Precipitation Calculator, version 2.2.
<http://www.waterisotopes.org>.
- Cappa, C.D., Hendricks, M.B., DePaolo, D.J., Cohen, R.C., 2003. Isotopic fractionation of water during evaporation. *J. Geophys. Res.* 108, 1-10.
<http://dx.doi.org/10.1029/2003JD003597>.
- Cassel, E.J., Graham, S.A., Chamberlain, C.P., 2009. Cenozoic tectonic and topographic evolution of the northern Sierra Nevada, California, through stable isotope paleoaltimetry in volcanic glass. *Geology* 37, 547-550.
- Cerling, T.E., Quade, J., 1993. Stable carbon and oxygen isotopes in soil carbonates, in: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records*. Geophysical Monograph 78, American Geophysical Union, Washington, D.C., pp. 217-232.

796 Chamberlain, C.P., Poage, M.A., Craw, D., Reynolds, R.C., 1999. Topographic
797 development of the Southern Alps recorded by the isotopic composition of
798 authigenic clay minerals, South Island, New Zealand. *Chem. Geol.* 155, 279-294.
799

800 Chamberlain, C.P., Poage, M.A., 2000. Reconstructing the paleotopography of
801 mountain belts from the isotopic composition of authigenic minerals. *Geology*
802 28, 115-118.
803

804 Chipman, M.L., Clegg, B.F., Hu, F.S., 2012. Variation in the moisture regime of
805 northeastern interior Alaska and possible linkages to the Aleutian Low:
806 inferences from a late-Holocene $\delta^{18}\text{O}$ record. *J. Paleolimnol.* 48, 69-81.
807 <http://dx.doi.org/10.1007/s10933-012-9599-0>.
808

809 Coplen, T.B., Kendall, C., 2000. Stable hydrogen and oxygen isotope ratios for
810 selected sites of the U.S. Geological Survey's NASQAN and benchmark surface-
811 water networks. U.S. Geol. Surv. Open File Rep., 00-160, 424pp.
812

813 Dean, W.E., Forester, R.M., Bright, J., Anderson, R.Y., 2007. Influence of the diversion
814 of Bear River into Bear Lake (Utah and Idaho) on the environment of deposition
815 of carbonate minerals. *Limnol.* 52, 1094-1111.
816

817 Defliese, W.F., Hren, M.T., Lohmann, K.C., 2015. Compositional and temperature
818 effects of phosphoric acid fractionations on Δ_{47} analysis and implications for

819 discrepant calibrations. *Chem. Geol.* 396, 51-60.

820 <http://dx.doi.org/10.1016/j.chemgeo.2014.12.018>.

821
822 Deininger, M., Fohlmeister, J., Scholz, D., Mangini, A., 2012. Isotope disequilibrium
823 effects: The influence of evaporation and ventilation effects on the carbon and
824 oxygen isotope composition of speleothems – A model approach. *Geochimica et*
825 *Cosmochimica Acta* 96, 57-79. <http://dx.doi.org/10.1016/j.gca.2012.08.013>.

826
827 Ding, L., Xu, Q., Yue, Y., Wang, H., Cai, F., Li, S., 2014. The Andean-type Gangdese
828 Mountains: Paleoelevation record from the Paleocene–Eocene Linzhou Basin.
829 *Earth Planet. Sci. Lett.* 392, 250-264.

830
831 Dreybrodt, W., Deininger, M., 2014. The impact of evaporation to the isotope
832 composition of DIC in calcite precipitating water films in equilibrium and kinetic
833 fractionation models. *Geochimica et Cosmochimica Acta* 125, 433-439.
834 <http://dx.doi.org/10.1016/j.gca.2013.10.004>.

835
836 Eagle, R.A., Eiler, J.M., Tripathi, A.K., Ries, J.B., Freitas, P.S., Hiebenthal, C.,
837 Wanamaker, A.D., Taviani, M., Elliot, M., Marensi, S., Nakamura, K., Ramirez, P.,
838 Roy, K., 2013. The influence of temperature and seawater carbonate saturation on
839 ^{13}C - ^{18}O bond ordering in bivalve mollusks. *Biogeosciences* 10, 4591-4606.
840 <http://dx.doi.org/10.5194/bg-10-4591-2013>.

842 Fontes, J., Gasse, F., Gilbert, E., 1996. Holocene environmental changes in Lake
843 Bangong basin (Western Tibet). Part 1: Chronology and stable isotopes of
844 carbonates of a Holocene lacustrine core. *Palaeogeogr. Palaeoclimat. Palaeoecol.*
845 120, 25-47.

846

847 Friedman, I., 2000. Database of surface and ground water samples analyzed for
848 deuterium and oxygen-18 from the western states of Arizona, California,
849 Colorado, Idaho, Montana, Nevada, New Mexico, Oregon, Utah, Washington, and
850 Wyoming. U.S. Geol. Surv. Open File Rep., 00-388.

851

852 Friedman, I., Smith, G.I., Johnson, C.A., Moscati, R.J., 2002. Stable isotope
853 compositions of waters in the Great Basin, United States 2. Modern
854 precipitation. *J. Geophys. Res.* 107, 1-22.
855 <http://dx.doi.org/10.1029/2001JD000566>.

856

857 Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E.A., Schrag, D., Eiler,
858 J.M., 2006. ^{13}C - ^{18}O bonds in carbonate minerals: A new kind of paleothermometer.
859 *Geochimica et Cosmochimica Acta* 70, 1439-1456.
860 <http://dx.doi.org/10.1016/j.gca.2005.11.014>.

861

862 Glazner, A.F., Walker, J.D., Bartley, J.M., Fletcher, J.M., 2002. Cenozoic evolution of the
863 Mojave block of southern California, in: Glazner, A.F., Walker, J.D., Bartley, J.M.

(Eds.), *Geologic Evolution of the Mojave Desert and Southwestern Basin and Range*. Geological Society of America Memoir 195, Boulder, Colorado, pp. 19-41.

Gonyo, A.W., Yu, Z., Bebout, G.E., 2012. Late Holocene change in climate and atmospheric circulation inferred from geochemical records at Kepler Lake, south-central Alaska. *J. Paleolimnol.* 48, 55-67.
<http://dx.doi.org/10.1007/s10933-012-9603-8>.

Henderson, A.K., Shuman, B.N., 2009. Hydrogen and oxygen isotopic compositions of lake water in the western United States. *Geol. Soc. Am. Bull.* 121, 1179–1189.
<http://dx.doi.org/10.1130/B26441.1>.

Hendy, C.H., 1971. The isotopic geochemistry of speleothems-I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochimica et Cosmochimica Acta* 35, 801-824.

Henkes, G.A., Passey, B.H., Wanamaker, A.D., Grossman, E.L., Ambrose, W.G., Carroll, M.L., 2013. Carbonate clumped isotope compositions of modern marine mollusk and brachiopod shells. *Geochimica et Cosmochimica Acta* 106, 307-325.
<http://dx.doi.org/10.1016/j.gca.2012.12.020>.

886 Hijmans, R.J., Cameron, S.E., Parra, J.L., Jones, P.G., Jarvis, A., 2005. Very high
887 resolution interpolated climate surfaces for global land areas. *Int. J. Climatol.* 25:
888 1965-1978.

889

890 Hillaire-Marcel, C., Casanova, J., 1987. Isotopic hydrology and paleohydrology of the
891 Magadi (Kenya)-Natron (Tanzania) basin during the Late Quaternary.
892 *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 58, 155-181.

893

894 Holmes, J.A., Darbyshire, D.P.F., Heaton, T.H.E., 2007. Palaeohydrological significance
895 of late Quaternary strontium isotope ratios in a tropical lake. *Chem. Geol.*, 236,
896 281-290. <http://dx.doi.org/10.1016/j.chemgeo.2006.10.002>.

897

898 Horton, T.W., Sjostrom, D.J., Abruzzese, M.J., Poage, M.A., Waldbauer, J.R., Hren, M.,
899 Wooden, J., Chamberlain, C.P., 2004. Spatial and temporal variation of Cenozoic
900 surface elevation in the Great Basin and Sierra Nevada. *Am. J. Sci.* 304, 862-888.
901 <http://dx.doi.org/10.2475/ajs.304.10.862>.

902

903 Horton, T.W., Chamberlain, C.P., 2006. Stable isotopic evidence for Neogene surface
904 downdrop in the central Basin and Range Province. *Geol. Soc. Am. Bull.* 118,
905 475-490. <http://dx.doi.org/10.1130/B25808>.

906

907 Horton, T.W., Oze, C., 2012. Are two elements better than one? Dual isotope-ratio
908 detrending of evaporative effects on lake carbonate paleoelevation proxies.

909 Geochem. Geophys. Geosyst. 13, 1-15.

910 <http://dx.doi.org/10.1029/2012GC004132>.

911
912 Hu, F.S., Slawinski, D., Wright, H.E., Ito, E., Johnson, R.G., Kelts, K.R., McEwan, R.F.,
913 Boedigheimer, A., 1999. Abrupt changes in North American climate during early
914 Holocene times. *Nature* 400, 437-440.

915
916 Hu, F.S., Ito, E., Brown, T.A., Curry, B.B., Engstrom, D.R., 2001. Pronounced Climatic
917 Variations in Alaska during the Last Two Millennia. *Proc. Natl. Acad. Sci.* 98,
918 10552-10556. <http://dx.doi.org/10.1073/pnas.181333798>.

919
920 Huang, X., Oberhänsli, H., von Suchodoletz, H., Prasad, S., Sorrel, P., Plessen, B.,
921 Mathis, M., Usabaliev, R., 2014. Hydrological changes in western Central Asia
922 (Kyrgyzstan) during the Holocene as inferred from a palaeolimnological study
923 in lake Son Kul. *Quat. Sci. Rev.* 103, 134-152.
924 <http://dx.doi.org/10.1016/j.quatscirev.2014.09.012>.

925
926 IPCC, 2014. Climate Change 2014: Synthesis Report. Contribution of Working
927 Groups I, II and III to the Fifth Assessment Report of the Intergovernmental
928 Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer
929 (eds.)]. IPCC, Geneva, Switzerland, 151 pp.

931 Jenny, H., 1994. Factors of Soil Formation: A System of Quantitative Pedology. Dover,
 932 New York.
 933
 934 Ji, H., Passey, B.H., Li, S., Levin, N.E., 2014. Triple oxygen isotopes in soils and lakes.
 935 In: 2014 GSA Annual Meeting (Vancouver, British Columbia).
 936
 937 Jones, M.D., Leng, M.J., Roberts, C.N., Türkeş, M., Moyeed, R., 2005. A coupled
 938 calibration and modelling approach to the understanding of dry-land lake
 939 oxygen isotope records. *J. Paleolimnol.* 34, 391-411.
 940 <http://dx.doi.org/10.1007/s10933-005-6743-0>.
 941
 942 Jones, M.D., Imbers, J., 2010. Modeling Mediterranean lake isotope variability. *Global*
 943 *Planet. Change* 71, 193-200.
 944 <http://dx.doi.org/10.1016/j.globplacha.2009.10.001>.
 945
 946 Katz, A., Kolodny, Y., Nissenbaum, A., 1977. The geochemical evolution of the
 947 Pleistocene Lake Lisan-Dead Sea system. *Geochimica et Cosmochimica Acta* 41,
 948 1609-1626.
 949
 950 Kim, S.T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects
 951 in synthetic carbonates. *Geochimica et Cosmochimica Acta* 61, 3461-3475.
 952 [http://dx.doi.org/10.1016/S0016-7037\(97\)00169-5](http://dx.doi.org/10.1016/S0016-7037(97)00169-5).
 953

954 Kirby, M.E., Mullins, H.T., Patterson, W.P., Burnett, A.W., 2002. Late glacial-Holocene
 955 atmospheric circulation and precipitation in the northeast United States
 956 inferred from modern calibrated stable oxygen and carbon isotopes. *Geol. Soc.*
 957 *Am. Bull.* 114, 1326-1340.
 958
 959 Kronfeld, J., Vogel, J.C., Rosenthal, E., Weinstein-Evron, M., 1988. Age and
 960 paleoclimatic implications of the Bet Shean travertines. *Quat. Res.* 30, 298-303.
 961
 962 Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data
 963 from lake sediment archives. *Quat. Sci. Rev.* 23, 811-831.
 964 <http://dx.doi.org/10.1016/j.quatascirev.2003.06.012>.
 965
 966 Li, H., Ku, T., 1997. $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariance as a paleohydrological indicator for closed-
 967 basin lakes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 133, 69-80.
 968
 969 Li, H., Ku, T., Stott, L.D., Anderson, R.F., 1997. Stable isotope studies on Mono Lake
 970 (California). 1. $\delta^{18}\text{O}$ in lake sediments as proxy for climatic change during the
 971 last 150 years. *Limnol. Oceanogr.* 42, 230-238.
 972
 973 Li, H., Xu, X.M., Ku, T.L., You, C.F., Buchheim, H.P., Peters, R., 2008. Isotopic and
 974 geochemical evidence of palaeoclimate changes in Salton Basin, California,
 975 during the past 20 kyr: 1. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records in lake tufa deposits.
 976 *Palaeogeogr. Palaeoclimat. Palaeoecol.* 259, 182-197.

977

978 Lindqvist, J.K., 1994. Lacustrine stromatolites and oncoids: Manuherikia Group
979 (Miocene), New Zealand, in: Bertrand-Sarfati, J., Monty, C. (Eds.), Phanerozoic
980 Stromatolites II. Springer Netherlands, pp. 227-254.

981

982 Liu, Z., Sun, H., Li, H., Wan, N., 2011. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and deposition rate of tufa in
983 Xiangshui River, SW China: implications for land-cover change caused by
984 climate and human impact during the late Holocene. Geol. Soc. London Spec.
985 Pub. 352, 85-96.

986

987 Mayer, B. Schwark, L.A., 1999. 15,000-year stable isotope record from sediments of
988 Lake Steisslingen, Southwest Germany. Chem. Geol. 161, 315-337.

989

990 Menking, K.M., Bischoff, J.L., Fitzpatrick, J.A., Burdette, J.W., Rye, R.O., 1997.
991 Climatic/Hydrologic oscillations since 155,000 yr B.P. at Owens Lake, California,
992 Reflected in abundance and stable isotope composition of sediment carbonate.
993 Quat. Res. 48, 58-68.

994

995 Mickler, P.J., Stern, L.A., Banner, J.L., 2006. Large kinetic isotope effects in modern
996 speleothems. Geol. Soc. Am. Bull. 118, 65-81.

997 <http://dx.doi.org/10.1130/B25698.1>.

998

999 Mook, W.G., Bommerson, J.C., Staverman, W.H., 1974. Carbon isotope fractionation
 1000 between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet. Sci.*
 1001 *Lett.* 22, 169-176. [http://dx.doi.org/10.1016/0012-821X\(74\)90078-8](http://dx.doi.org/10.1016/0012-821X(74)90078-8).
 1002
 1003 Morinaga, H., Itota, C., Isezaki, N., Goto, H., Yaskawa, K., Kusakabe, M., Liu, J., Gu, Z.,
 1004 Yuan, B., Cong, S., 1993. Oxygen-18 and carbon-13 records for the last 14,000
 1005 years from lacustrine carbonates of Siling-Co (Lake) in the Qinghai-Tibetan
 1006 Plateau. *Geophys. Res. Lett.* 20, 2909-2912.
 1007
 1008 Morrill, C., Overpeck, J.T., Cole, J.E., Liu, K.B., Shen, C., Tang, L., 2006. Holocene
 1009 variations in the Asian monsoon inferred from the geochemistry of lake
 1010 sediments in central Tibet. *Quat. Res.* 65, 232-243.
 1011 <http://dx.doi.org/10.1016/j.yqres.2005.02.014>.
 1012
 1013 Mulch, A., Graham, S.A., Chamberlain, C.P., 2006. Hydrogen isotopes in Eocene river
 1014 gravels and paleoelevation of the Sierra Nevada. *Science* 313, 87-89.
 1015
 1016 Nelson, D.B., Abbott, M.B., Steinman, B., Polissar, P.J., Stansell, N.D., Ortiz, J.D.,
 1017 Rosenmeier, M.F., Finney, B.P., Riedel, J., 2011. Drought variability in the Pacific
 1018 Northwest from a 6,000-yr lake sediment record. *Proc. Natl. Acad. Sci.* 108, 1-6.
 1019
 1020 Nelson, S.T., Wood, M.J., Mayo, A.L., Tingey, D.G., Eggett, D., 2005. Shoreline tufa and
 1021 tufaglomerate from Pleistocene Lake Bonneville, Utah, USA: stable isotopic and

1022 mineralogical records of lake conditions, processes, and climate. *J. Quat. Sci.* 20,
 1023 3-19.
 1024
 1025 Passey, B.H., Levin, N.E., Cerling, T.E., Brown, F.H., Eiler, J.M., 2010. High-
 1026 temperature environments of human evolution in East Africa based on bond ordering
 1027 in paleosol carbonates. *Proc. Natl. Acad. Sci.* 107, 11245-11249.
 1028 <http://dx.doi.org/10.1073/pnas.1001824107>.
 1029
 1030 Passey, B.H., Hu, H., Ji, H., Montanari, S., Li, S., Henkes, G.A., Levin, N.E., 2014. Triple
 1031 oxygen isotopes in biogenic and sedimentary carbonates. *Geochimica et*
 1032 *Cosmochimica Acta* 141, 1-25. <http://dx.doi.org/10.1016/j.gca.2014.06.006>.
 1033
 1034 Petryshyn, V.A., Lim, D., Laval, B.L., Brady, A., Slater, G., Tripathi, A.K., 2015.
 1035 Reconstruction of limnology and microbialite formation conditions from
 1036 carbonate clumped isotope thermometry. *Geobiol.* 13, 53-67.
 1037
 1038 Piovano, E.L., Ariztegui, D., Bernasconi, S.M., McKenzie, J.A., 2004. Stable isotopic
 1039 record of hydrological changes in subtropical Laguna Mar Chiquita (Argentina)
 1040 over the last 230 years. *Holocene* 14, 525-535.
 1041
 1042 Quade, J., Rech, J.A., Latorre, C., Betancourt, J.L., Gleeson, E., Kalin, M.T.K., 2007. Soils
 1043 at the hyperarid margin: The isotopic composition of soil carbonate from the

1044 Atacama Desert, Northern Chile. *Geochimica et Cosmochimica Acta* 71, 3772-
 1045 3795. <http://dx.doi.org/10.1016/j.gca.2007.02.016>.
 1046
 1047 Rosen, M. R., Arehart, G.B., Lico, M.S., 2004. Exceptionally fast growth rate of <100-
 1048 yr-old tufa, Big Soda Lake, Nevada: Implications for using tufa as a paleoclimate
 1049 proxy. *Geology* 32, 409-412.
 1050
 1051 Saltus, R.W., Thompson, G.A., 1995. Why is it downhill from Tonopah to Las Vegas?:
 1052 A case for mantle plume support of the high northern Basin and Range.
 1053 *Tectonics* 14, 1235-1244.
 1054
 1055 Schwarzhans, W., Scofield, R.P., Tennyson, A.J.D., Worthy, J.P., Worthy, T.H., 2012.
 1056 Fish remains, mostly otoliths, from the non-marine early Miocene of Otago, New
 1057 Zealand. *Acta Palaeontol. Pol.* 57, 319-350.
 1058 <http://dx.doi.org/10.4202/app.2010.0127>.
 1059
 1060 Seltzer, G., Rodbell, D., Burns, S., 2000. Isotopic evidence for late Quaternary climatic
 1061 change in tropical South America. *Geology* 28, 35-38.
 1062
 1063 Sjostrom, D.J., Hren, M.T., Horton, T.W., Waldbauer, J.R., Chamberlain, C.P., 2006.
 1064 Stable isotopic evidence for a pre-late Miocene elevation gradient in the Great
 1065 Plains–Rocky Mountain region, USA. *Geol. Soc. Am. Special Paper* 398, 309-319.
 1066 [http://dx.doi.org/10.1130.2006.2398\(19\)](http://dx.doi.org/10.1130.2006.2398(19)).

1067

1068 Smith, A.J., Donovan, J.J., Ito, E., Engstrom, D.R., 1997. Ground-water processes
 1069 controlling a prairie lake's response to middle Holocene drought. *Geology* 25,
 1070 391-394.

1071

1072 Spötl, C., 2005. A robust and fast method of sampling and analysis of $\delta^{13}\text{C}$ of
 1073 dissolved inorganic carbon in ground waters. *Isot. Environ. Health Stud.* 41,
 1074 217-221. <http://dx.doi.org/10.1080/10256010500230023>.

1075

1076 Stevens, L.R., Stone, J.R., Campbell, J., Fritz, S.C., 2006. A 2200-yr record of hydrologic
 1077 variability from Foy Lake, Montana, USA, inferred from diatom and geochemical
 1078 data. *Quat. Res.* 65, 264-274.

1079

1080 Stiller, M., Rounick, J.S., Shasha, S., 1985. Extreme carbon-isotope enrichments in
 1081 evaporating brines. *Nature* 316, 434-435.

1082

1083 Stuiver, M., 1970. Oxygen and carbon isotope ratios of fresh-water carbonates as
 1084 climatic indicators. *J. Geophys. Res.* 75, 5247-5257.

1085

1086 Talbot, M.R., 1990. A review of the palaeohydrological interpretation of carbon and
 1087 oxygen isotopic ratios in primary lacustrine carbonates. *Chem. Geol.* 80, 261-
 1088 279.

1089

1090 Trabucco, A., Zomer, R.J., 2009. Global Aridity Index (Global-Aridity) and Global
 1091 Potential Evapo-Transpiration (Global-PET) Geospatial Database. CGIAR
 1092 Consortium for Spatial Information. Published online, available from the CGIAR-
 1093 CSI GeoPortal at: <http://www.csi.cgiar.org/>
 1094
 1095 Ufnar, D.F., Gröcke, D.R., Beddows, P.A., 2008. Assessing pedogenic calcite stable-
 1096 isotope values: Can positive linear co-variant trends be used to quantify palaeo-
 1097 evaporation rates? *Chem. Geol.* 256, 46-51.
 1098 <http://dx.doi.org/10.1016/j.chemgeo.2008.07.022>.
 1099
 1100 Urey, H.C., Brickwedde, F.G., Murphy, G.M., 1932. A hydrogen isotope of mass 2.
 1101 *Phys. Rev.* 39, 164-165.
 1102
 1103 Valero-Garcés, B.L., Kelts, K., Ito, E., 1995. Oxygen and carbon isotope trends and
 1104 sedimentological evolution of a meromictic and saline lacustrine system: the
 1105 Holocene Medicine Lake basin, North American Great Plains, USA. *Palaeogeogr.*
 1106 *Palaeoclimatol. Palaeoecol.* 117, 253-278.
 1107
 1108 Valero-Garcés, B.L., Delgado-Huertas, A., Ratto, N., Navas, A., 1999. Large ^{13}C
 1109 enrichment in primary carbonates from Andean Altiplano lakes, northwest
 1110 Argentina. *Earth Planet. Sci. Lett.* 171, 253-266.
 1111

1112 Valero-Garcés, B.L., Moreno, A., Navas, A., Mata, P., Machín, J., Huertas, A.D.,
 1113 Sampériz, P.G., Schwalbe, A., Morellón, M., Cheng, H., Edwards, R.L., 2008. The
 1114 Taravilla lake and tufa deposits (Central Iberian Range, Spain) as
 1115 palaeohydrological and palaeoclimatic indicators. *Palaeogeogr. Palaeoclimat.*
 1116 *Palaeoecol.* 259, 136-156.
 1117
 1118 Wang, R.L., Scarpitta, S.C., Zhang, S.C., Zheng, M.P., 2002. Later Pleistocene/Holocene
 1119 climate conditions of Qinghai-Xizhang Plateau (Tibet) based on carbon and
 1120 oxygen stable isotopes of Zabuye Lake sediments. *Earth Planet. Sci. Lett.* 203,
 1121 461-477.
 1122
 1123 Wu, J., 1997. Compositions of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in various carbonates of core RM in the
 1124 Zoigê Basin and climatic significance. *Chinese Geogr. Sci.* 7, 229-235.
 1125
 1126 Xu, H., Ai, L., Tan, L., An, Z., 2006. Stable isotopes in bulk carbonates and organic
 1127 matter in recent sediments of Lake Qinghai and their climatic implications.
 1128 *Chem. Geol.* 235, 262-275.
 1129
 1130 Yu, Z., Eicher, U., 1998. Abrupt climate oscillations during the last deglaciation in
 1131 central North America. *Science* 282, 2235-2238.
 1132
 1133 Yuan, F., Koran, M.R., Valdez, A., 2013. Late Glacial and Holocene record of climatic
 1134 change in the southern Rocky Mountains from sediments in San Luis Lake,

1135 Colorado, USA. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 392, 146-160.

1136 <http://dx.doi.org/10.1016/j.palaeo.2013.09.016>.

1137

1138 Zaarur, S., Affek, H.P., Brandon, M.T., 2013. A revised calibration of the clumped

1139 isotope thermometer. *Earth Planet. Sci. Lett.* 382, 47-57.

1140 <http://dx.doi.org/10.1016/j.epsl.2013.07.026>.

1141

1142 Zheng, Y.F., 1990. Carbon-oxygen isotopic covariation in hydrothermal calcite

1143 during degassing of CO₂. *Mineral. Deposita* 25, 246-250.

1144

1145

1146

1147

1148

1149

1150

1151

1152

1153

1154

1155

1156

1157

1158

Figure Captions

Fig. 1. Aridity index (P:E) map of western North America (equidistant conic projection) showing modern meteoric (white snowflakes), river (blue circles) and lake (light blue triangles) water sample collection sites (Friedman, 2000; Coplen and Kendall, 2000; Friedman et al., 2002; Henderson and Shuman, 2009). 10 of the 38 globally distributed Quaternary paleolake systems, comprising 24 of the 57 dual element stable isotopic records compiled as part of this review, are also shown (red stars).

Fig. 2. Compiled western North America meteoric (a), river (b) and lake (c) water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ compositions reported in Friedman (2000), Coplen and Kendall (2000), Friedman and others (2002), and Henderson and Shuman (2009). Regional stable isotopic water line equations represent the least-squares linear regression fits through all data points plotted in each panel. Black star (a-c) represents standard mean ocean water (SMOW) and thick black line (a-c) represents the global meteoric water line (GMWL). Lake water symbols (c) are color coded according to the modern aridity index at each sampling site. Panel (d) shows frequency distributions and whisker-box plots of the $\delta^{18}\text{O}$ shift away from the global meteoric water line along an evaporation line of slope 4.5 for each sample type. Vertical lines in the whisker-box plots (d) represent, minimum, lower quartile, median, upper quartile, and maximum $\delta^{18}\text{O}$ shift values observed.

Fig. 3. Comparison of modeled meteoric water $\delta^{18}\text{O}$ values (Bowen, 2014) and observed lake water $\delta^{18}\text{O}$ values reported in Friedman (2000), Coplen and Kendall (2000), Friedman and others (2002), and Henderson and Shuman (2009). Meteoric water values were calculated for the same month in which each lake water sample was collected. Symbols are color coded according to the modern aridity index at each lake water sampling site. Solid line represents a 1:1 (i.e. no difference) relationship. Labeled dashed lines represent +10‰ and +20‰ ^{18}O lake water enrichments relative to local temporally matched meteoric water.

Fig. 4. Evaporation experiment results for three South Island, New Zealand, water samples, including one upland river (circles), one groundwater sample (inverted triangles) and one coastal lowland stream (upright triangles). Symbols in all panels are color coded by %-water evaporated. Panel (a) shows the near constant evaporation rate of all three samples, panel (b) shows the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopic response to evaporation, and panel (c) shows the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ -DIC response. Thick black line and black star in (b) represent the GMWL and SMOW, respectively. Thin black lines in all panels

represent least-squares linear regression fits. Each sample was allowed to evaporate for ~6 days in a 500ml beaker at 21°C.

Fig. 5. Global aridity index map (a) showing location (red stars) of the fifty-seven Quaternary lake carbonate dual element $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records (>11,200 total data points), from thirty-eight discrete lake systems, compiled as part of this review. Panel (b) presents the least-squares linear regression fits to these isotopic records. Black regression lines correspond with records exhibiting a statistically significant correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Red regression lines correspond with records exhibiting no significant correlation. Dashed line represents a 1:1 (i.e. $m=1$) relationship. All data were normalized to the mean isotopic composition of each record using an additive shift.

Fig. 6. Modeled isotopic equilibrium summer month lake calcite $\delta^{18}\text{O}$ values (see text for details) plotted against the average lake carbonate $\delta^{18}\text{O}$ value in each of the fifty-seven Quaternary records we compiled. Symbols are color coded according to modern aridity index values with whiskers showing $\pm 1\sigma$. Solid black line represents a 1:1 (i.e. no difference) relationship. Labeled dashed lines correspond with -5‰, +5‰, +10‰ and +15‰ ^{18}O depletion/enrichments in observed lake carbonate isotopic composition relative to modeled summer lake calcite compositions.

Fig. 7. $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ bivariate plots for Quaternary lake carbonate records where modern source (i.e. inflow) water and lake water $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ -DIC values were available from the literature. Green stars represent the isotopic equilibrium composition of calcite forming in equilibrium with source water at each site's mean annual air temperature. Red stars represent the isotopic equilibrium composition of calcite forming in equilibrium with lake water at each site's mean annual air temperature. Quaternary lake carbonate data symbols as indicated in panel legends. Solid black line represents a 1:1 relationship; dashed lines represent $\pm 5\text{‰}$ differences between lake carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Mono Lake tufa data are original to this study. See Table 1 for all other primary data sources. Modern hypsometric altitudes (z_{hyp}) are shown in (a-d).

Fig. 8. $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ bivariate plots for Cerling and Quade's (1993) modern aridisol soil carbonates from the western U.S. Great Basin/Mojave Desert region (a), and middle Miocene (~15Ma) laminated lacustrine carbonates from the Mojave Desert's Mud Hills area Barstow Formation and Otago New Zealand's Lake Manuherikia sequence Bannockburn Formation at Vinegar Hill (b). Pedogenic soil carbonate symbols in (a) are color-coded based on modern aridity index. Solid

1225 black line represents a 1:1 relationship; dashed lines represent $\pm 5\text{‰}$ differences between lake
1226 carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Modern regional hypsometric altitude (z_{hyp}) is shown in (a). Middle Miocene
1227 lacustrine carbonate data in (b) are original to this study.

Table 1

Compiled Quaternary lake carbonate stable isotopic record information including primary published sources.

Lake	Number of Records	Latitude (°)	Longitude (°)	Lake Elevation (m.a.s.l.)	Modern Aridity Index (P:E)	Age (yrs)	Source(s)
Ahung	1	31.62	92.06	4575	0.570	<9,000	Morrill et al., 2006
Bangong	1	33.70	79.00	4241	0.130	<11,000	Fontes et al., 1996
Bear	1	42.00	-111.33	1805	0.324	modern	Dean et al., 2007
Big Soda	1	39.52	-118.88	1216	0.096	<100 yrs	Rosen et al., 2004
Bonneville	2	41.00	-114.00	1570	0.162	<45,000	Nelson et al., 2005; Benson et al., 2011
Cahuilla	1	33.40	-116.05	-24	0.042	<20,000	Li et al., 2008
Castor	1	48.53	-119.55	596	0.328	<6,000	Nelson et al., 2011
Chiquita	1	-30.90	-62.85	67	0.565	<250	Piovano et al., 2004
Crawford	3	43.47	-79.95	~150	1.022	<13,000	Yu and Eicher, 1998
Deep	1	47.68	-95.37	411	0.730	<12,000	Hu et al., 1999
Elk	2	45.87	-95.80	366	0.673	<12,000	Smith et al., 1997
Farewell	1	62.55	-153.63	320	0.819	<2,059	Hu et al., 2001
Fayetteville Green	1	43.03	-75.97	70	1.148	<3,186	Kirby et al., 2002
Foy	1	48.17	-114.36	1004	0.587	<2,500	Stevens et al., 2006
Jellybean	1	60.35	-134.80	730	0.491	<7,556	Anderson et al., 2005
Junin	1	-11.02	-76.12	4082	0.935	<18,000	Seltzer et al., 2000
Keché	1	68.02	-146.92	740	0.496	<3,450	Chipman et al., 2012
Kepler	2	61.55	-149.21	26	0.731	<792	Gonyo et al., 2012
Lisan	2	31.50	35.00	-200	0.280	<60,000	Katz et al., 1977; Kronfeld et al., 1988
Medicine	1	44.82	-97.35	519	0.599	<10,600	Valero-Garcés et al., 1995
Mono	6	38.00	-119.00	1945	0.296	<300	Li and Ku, 1997; Li et al., 1997; Benson et al., 2003;
Natron/Magadi	1	-2.42	36.00	538	0.231	>200,000	Hillaire-Marcel and Casanova, 1987 (P3)
Owens	4	36.43	-117.95	1084	0.170	<155,000	Menking et al., 1997; Benson et al., 2002
Pumacocha	1	-11.89	-75.05	4635	1.147	<2,300	Bird et al., 2011
Pyramid/Lahontan	6	40.00	-119.50	1250	0.126	<30,000	Benson et al., 1996; Benson et al., 2002; Benson et al., 2013
Qinghai	1	37.06	100.30	3192	0.479	<18,000	Xu et al., 2006
Ruidera/Alcaraz	1	38.93	-2.90	950	0.392	<5000	Andrews et al., 2000
San Luis	1	37.68	-105.72	2300	0.198	<17,000	Yuan et al., 2013
Seven Mile	1	62.18	-136.38	520	0.454	<1,100	Anderson et al., 2011
Siling	1	31.75	89.00	4500	0.399	<15,000	Morinaga et al., 1993
Steisslingen	1	47.80	8.92	446	1.205	<15,000	Mayer and Schwark, 1999
Taravilla	1	40.65	-1.97	1100	0.525	<11,000	Valero-Garcés et al., 2008
Turkana	1	3.58	36.12	360	0.097	<105	Abell et al., 1982
Twiss	1	43.45	-79.95	~150	1.009	<13,000	Yu and Eicher, 1998
Wallywash	1	17.97	-77.81	7	0.989	<120,000	Holmes et al., 2007
Xiangshui	1	25.42	107.88	310	1.086	<4,280	Liu et al., 2011
Zabuye	1	31.35	84.07	4421	0.347	<30,000	Wang et al., 2002
Zoige	1	33.95	102.35	3400	0.774	<140,000	Wu, 1997
Total	57						

Table 2: Stable isotope data ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Δ_{47}), Δ_{47} -temperature estimates and reconstructed $\delta^{18}\text{O}_{\text{water}}$.

Sample (Age)	Number of Analyses	$\delta^{13}\text{C}$ (‰) ¹	$\delta^{18}\text{O}$ (‰) ¹	Δ_{47} (‰) ²	Δ_{47} -Temperature (°C) ³	$\delta^{18}\text{O}_{\text{water}}$ (‰) ⁴
Mono Lake tufa interior (modern)	3	7.77±0.06	-2.78±0.04	0.734±0.013	15.8±4.3	-2.3±0.9
Mono Lake tufa outer laminations (modern)	4	8.84±0.01	-1.76±0.02	0.735±0.010	15.4±3.3	-1.4±0.7
Barstow Fm. tufa (Middle Miocene)	4	-0.50±0.05	-7.16±0.02	0.648±0.004	48.3±1.8	-0.4±0.3
Bannockburn Fm. oncholite interior laminations (Middle Miocene)	4	3.50±0.04	0.30±0.02	0.708±0.008	24.6±2.8	2.6±0.6
Bannockburn Fm. oncholite outer laminations (Middle Miocene)	4	9.95±0.05	0.89±0.04	0.721±0.005	19.7±1.8	2.2±0.4
Bannockburn Fm. oncholite bulk homogenate (Middle Miocene)	4	3.64±0.05	-0.94±0.06	0.728±0.012	17.7±3.9	-0.1±0.8

¹ Relative to V-PDB² On absolute reference frame³ Determined using the calibration of Defliese and others (2015)⁴ Relative to V-SMOW

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8