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

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A B S T R A C T

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 $\delta^{18}O$, 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 $\delta^{18}O$ values and the lake waters from which they are derived are often shifted by $>+10‰$ relative to source waters discharging into the lake. The global pattern of $\delta^{18}O$ and $\delta^{13}C$ 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 $\delta^{18}O$ and $\delta^{13}C$ 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.

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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

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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‰ from unmodified meteoric waters for $\delta^{18}O$. 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 $\delta^{18}O$ and $\delta^{13}C$ 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‰ in both $\delta^{18}O$ and $\delta^{13}C$-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 $\delta^{18}O$ and $\delta^{13}C$ 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 >4800 m 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 δ^2H and $\delta^{18}O$ 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 δ^2H, $\delta^{18}O$, and $\delta^{13}C$-DIC values for three 250 ml natural water samples allowed to evaporate in 500 ml 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 250 ml 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. δ^2H values are precise to <1.0‰ and $\delta^{18}O$ values are precise to <0.1‰.

$\delta^{13}C$-DIC values were determined using the Spötl (2005) method. In brief, 1 ml sub-samples were injected into ultra-high purity (>99.999%) helium flushed 10 ml borosilicate exetainer vials pre-loaded with 103% phosphoric acid. Dissolved inorganic carbon (DIC) derived CO_2, 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. $\delta^{13}C$-DIC values were two-point normalized to the VPDB scale based on replicate analysis of IAEA certified reference materials NBS18 and NBS19. All $\delta^{13}C$-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 $\delta^{18}O$ and $\delta^{13}C$ in the stable isotope analytical facility at the University of Canterbury. Hand samples were cut into flat slabs and milled at 0.5 mm resolution using a diamond-coated Dremel tool parallel to the growth axis. $\delta^{18}O$ and $\delta^{13}C$ of acidified (103% phosphoric acid) sample powders were determined using a Thermo-Finnigan GasBench II coupled to a ThermoFinnigan DeltaV$^+$ isotope ratio mass spectrometer operating under continuous ultra-high purity He flow conditions. $\delta^{18}O$ and $\delta^{13}C$ 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 $\delta^{18}O$ and $\delta^{13}C$ values are precise to <0.10‰.

Δ_{47} values for the middle Miocene Barstow Fm. Tufa, middle

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	<9000	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	<6000	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	<2059	Hu et al., 2001
Fayetteville Green	1	43.03	−75.97	70	1.148	<3186	Kirby et al., 2002
Foy	1	48.17	−114.36	1004	0.587	<2500	Stevens et al., 2006
Jellybean	1	60.35	−134.80	730	0.491	<7556	Anderson et al., 2005
Junin	1	−11.02	−76.12	4082	0.935	<18,000	Seltzer et al., 2000
Keche	1	68.02	−146.92	740	0.496	<3450	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	<2300	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	<1100	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	<4280	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						

Miocene Bannockburn Fm. oncholite and Quaternary Mono Lake tufa samples were determined using a ThermoFinnigan MAT 253 dual inlet gas source mass spectrometer ("Chewbacca") in the Tripati 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 $\delta^{18}O$, $\delta^{13}C$, 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 $\delta^{18}O$ values were calculated by using the measured carbonate $\delta^{18}O$ 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 ~35‰ range in $\delta^{18}O$ (Fig. 2a; Friedman, 2000; Coplen and Kendall, 2000; Freidman 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 $\delta^{18}O$ (~30‰ versus ~35‰). 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 additional surface water evaporation (Fig. 2b) either in
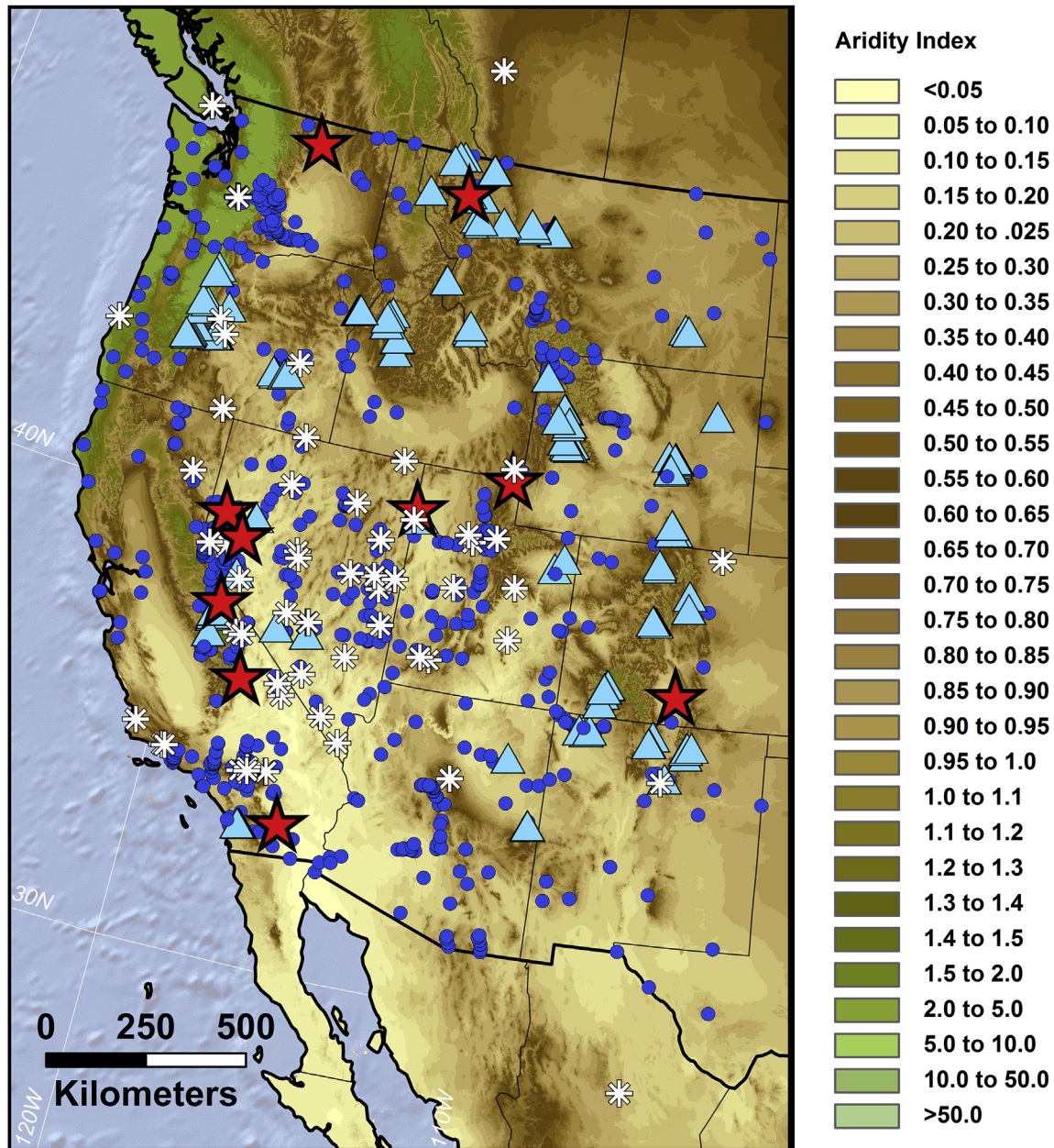
Fig. 1. Aridity index (P:E) map of western North America (equidistant conic projection) showing modern meteoric (white snowflakes), river (blue circles) and lake (light blue triangles) water sample collection sites (Friedman, 2000; Coplen and Kendall, 2000; Friedman et al., 2002; Henderson and Shuman, 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).

through-flowing lakes or the rivers themselves.

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

The more pronounced effect of evaporation on lake water isotopic compositions is best demonstrated through quantification of the positive $\delta^{18}O$ shift away from the GMWL recognized in most western North America lakes (Fig. 2d). We determined the

evaporation induced $\delta^{18}O$ shift (i.e. change in $\delta^{18}O$ value) for individual meteoric, river and lake water samples by subtracting the observed $\delta^{18}O$ value from the corresponding $\delta^{18}O$ value at the intersection of the GMWL ($\delta^2H = 8 \times \delta^{18}O + 10$) and an intermediate and representative slope 4.5 evaporation line. The median $\delta^{18}O$ shift for the 248 lake water samples we compiled is +4.6‰, with a minimum of −1.3‰ at Bonneville Salt Flat (January, 1993) and a maximum of +23.5‰, also at Bonneville Salt Flat and in the same calendar year (July, 1993).

These results demonstrate the extreme isotopic sensitivity of lake systems to evaporation induced kinetic fractionation effects, particularly in arid and semi-arid environments. A statistical comparison of meteoric, river and lake water $\delta^{18}O$ shift values indicates that, on average, meteoric waters are not significantly
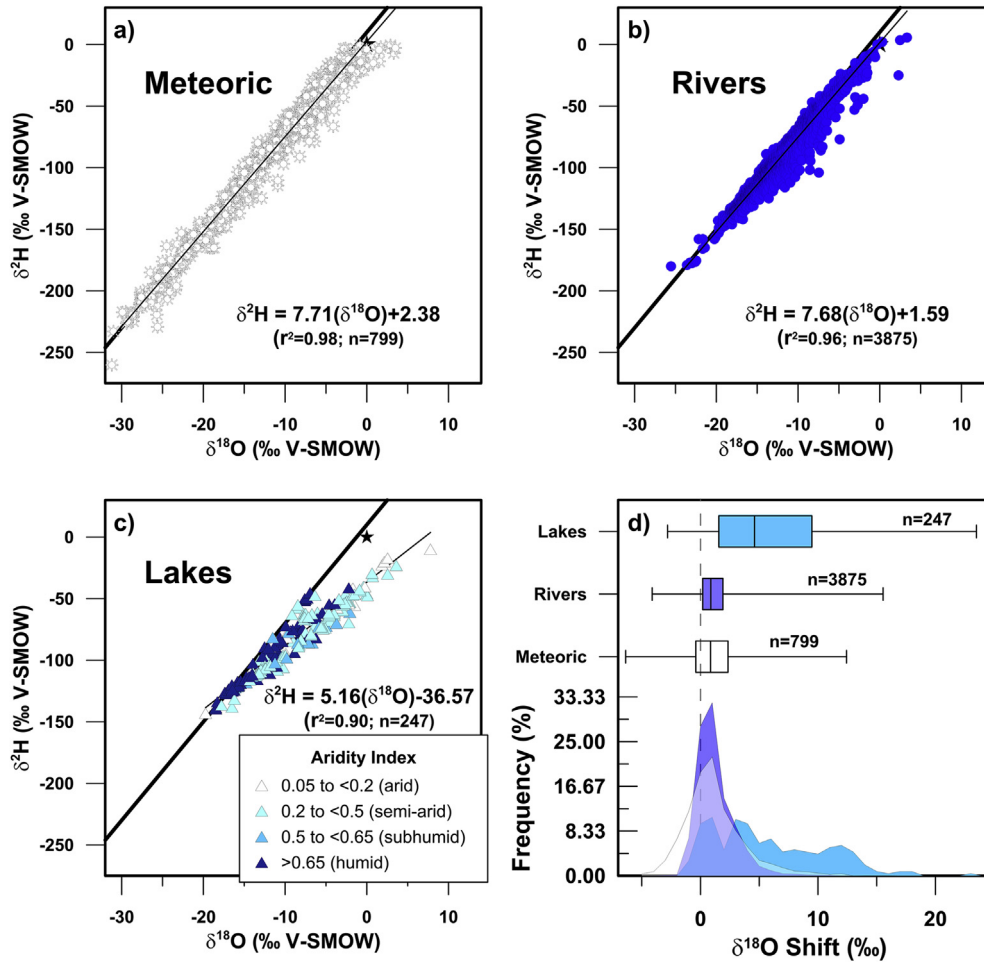
**Fig. 2.** Compiled western North America meteoric (a), river (b) and lake (c) water δ^2H and $\delta^{18}O$ compositions reported in Friedman (2000), Coplen and Kendall (2000), Friedman et al. (2002), and Henderson and Shuman (2009). Regional stable isotopic water line equations represent the least-squares 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 $\delta^{18}O$ 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 $\delta^{18}O$ shift values observed.

different than river waters (p = 0.34; two-tailed t-test), yet lake waters are highly significantly different than both meteoric and river waters (p = 10^{-36} and p = 10^{-41}, respectively; two-tailed t-test).

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

The results presented above provide important context to our discussion of $\delta^{18}O$ and $\delta^{13}C$ covariation in the following sections. The unequivocal and potentially extreme effects of evaporation on
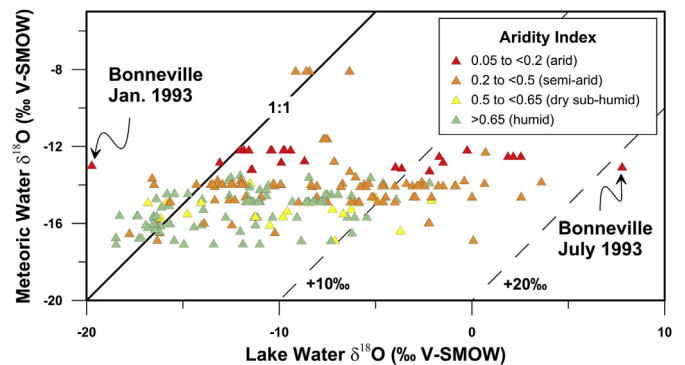
Fig. 3. Comparison of modeled meteoric water $\delta^{18}O$ values (Bowen, 2014) and observed lake water $\delta^{18}O$ values reported in Friedman (2000), Coplen and Kendall (2000), Friedman et al. (2002), and Henderson and Shuman (2009). Meteoric water values were calculated for the same month in which 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.

surface water isotopic compositions present major challenges to single element (i.e. O or H) proxies of temperature, elevation, water source apportionment, atmospheric circulation conditions and any 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 et al. (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 ^{2}H 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 $\delta^{18}O$ values by ~11–13‰ and $\delta^{2}H$ values by ~45–55‰ over the course of the experiment. All three samples followed similar linear evaporation trends away from the GMWL (Fig. 4b).

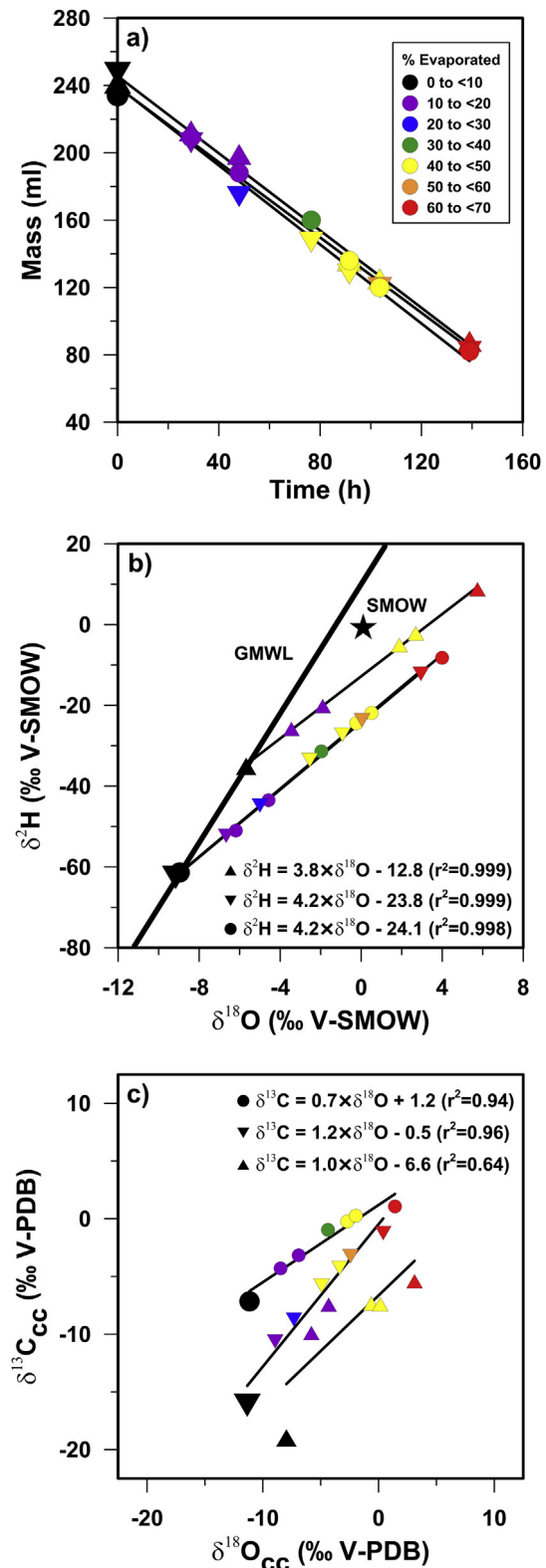As each of the samples evaporated, clear progressive ^{13}C

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 $\delta^{2}H$ and $\delta^{18}O$ isotopic response to evaporation, and panel (c) shows the $\delta^{18}O$ and $\delta^{13}C$-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 500 ml beaker at 21 °C.

enrichments in DIC, on the order of 1–2‰ per day, occurred over the six-day experiment. From these data and the corresponding water $\delta^{18}O$ 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 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 $\delta^{18}O$ and $\delta^{13}C$, 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 $\delta^{18}O$ 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):

$$1000\ln\alpha(\text{Calcite-}H_2O) = 18.03(10^3T^{-1}) - 32.42 \tag{1}$$

where T is temperature in kelvins and α is the temperature dependent calcite-water fractionation factor. We then compared these model $\delta^{18}O$ values to the average $\delta^{18}O$ observed in all 57 of the global lake carbonate records we compiled (Fig. 6). In this model, the calculated $\delta^{18}O$ 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 $\delta^{18}O$ (Fig. 3), the observed average lake carbonate $\delta^{18}O$ values are more positive than the modeled summer month meteoric water derived calcite $\delta^{18}O$ 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 $\delta^{18}O$. Forty-two percent of the lake carbonate $\delta^{18}O$ records are >5‰ shifted towards more positive $\delta^{18}O$ 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 $\delta^{18}O$, lakes from currently arid and semi-arid environments have a much larger average $\delta^{18}O$ offset (5.4‰) than sub-humid and humid environment lakes (2.0‰).

This model analysis of 57 global Quaternary lake carbonate $\delta^{18}O$ 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 $\delta^{18}O$ values. For example, had we assumed winter month (or pre-interglacial)
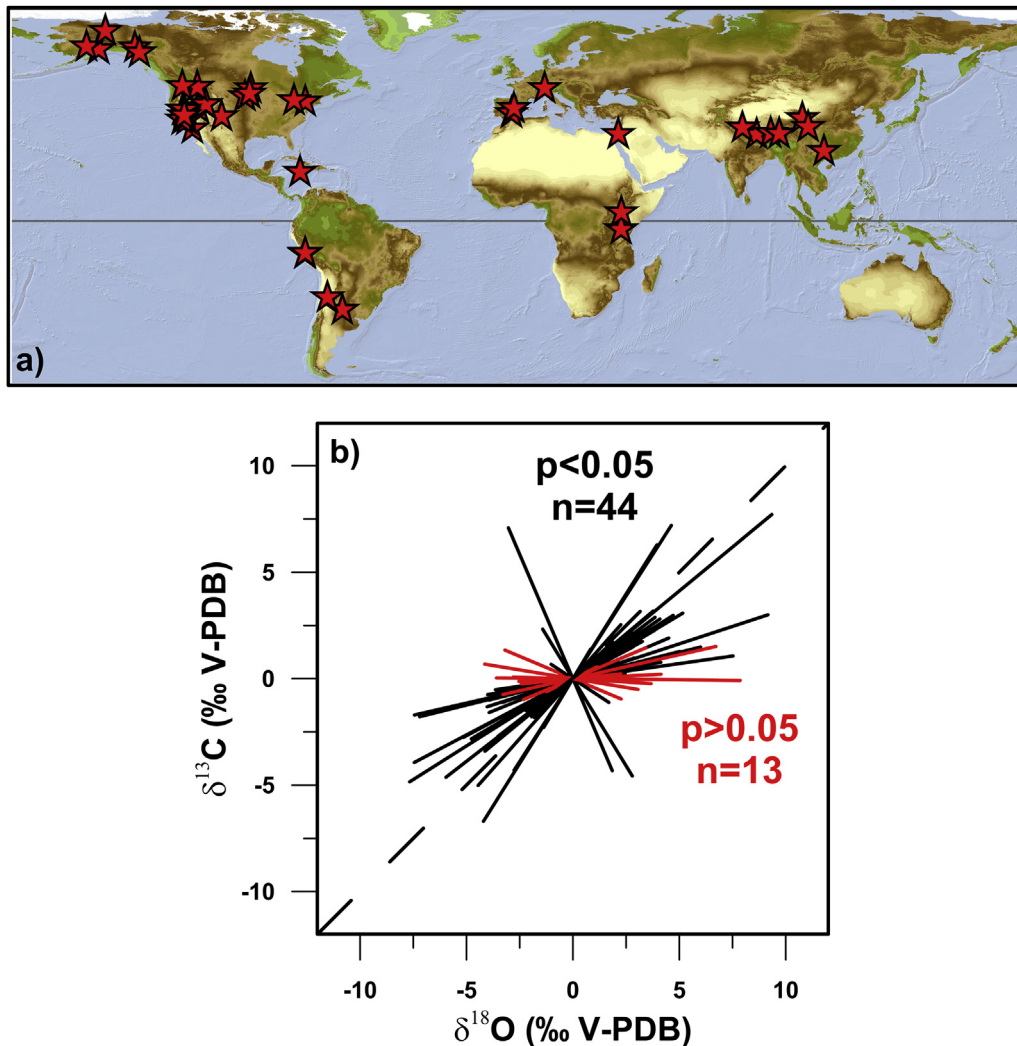
Fig. 5. Global aridity index map (a) showing location (red stars) of the fifty-seven Quaternary lake carbonate dual element $\delta^{18}O$ and $\delta^{13}C$ records (>11,200 total data points), from thirty-eight discrete lake systems, compiled as part of this review. Panel (b) presents the least-squares linear regression fits to these isotopic records. Black regression lines correspond with records exhibiting a statistically significant correlation between $\delta^{18}O$ and $\delta^{13}C$. 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.

temperatures of formation in our analysis rather than modern summer month temperatures we would have generated more positive modeled carbonate $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ and $\delta^{13}C$. In the context of the evaporation experiment results we present above, the ~8‰–~15‰ 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 $\delta^{13}C$-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
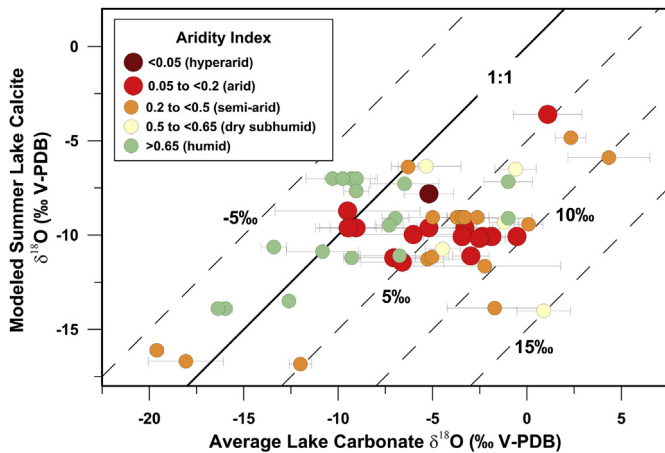
Fig. 6. Modeled isotopic equilibrium summer month lake calcite $\delta^{18}O$ values (see text for details) plotted against the average lake carbonate $\delta^{18}O$ value in each of the fifty-seven Quaternary records we compiled. Symbols are color coded according to modern aridity index values with whiskers showing $\pm 1\sigma$. Solid black line represents a 1:1 (i.e. no difference) relationship. Labeled dashed lines correspond with -5‰, $+5\text{‰}$, $+10\text{‰}$ and $+15\text{‰}$ ^{18}O depletion/enrichments in observed lake carbonate isotopic composition relative to modeled summer lake calcite compositions.

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 $\delta^{18}O$ and $\delta^{13}C$ 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 $\delta^{18}O$ and $\delta^{13}C$ 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 $\delta^{18}O$ and $\delta^{13}C$ 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 $\delta^{18}O$ and $\delta^{13}C$ 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 $\delta^{18}O$ and $\delta^{13}C$ values measured in these cores are ~10‰−~15‰ 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 $\delta^{18}O$ and $\delta^{13}C$. 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 $\delta^{18}O$ and $\delta^{13}C$ 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 $\delta^{18}O$ and $\delta^{13}C$ 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 30 cm 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)
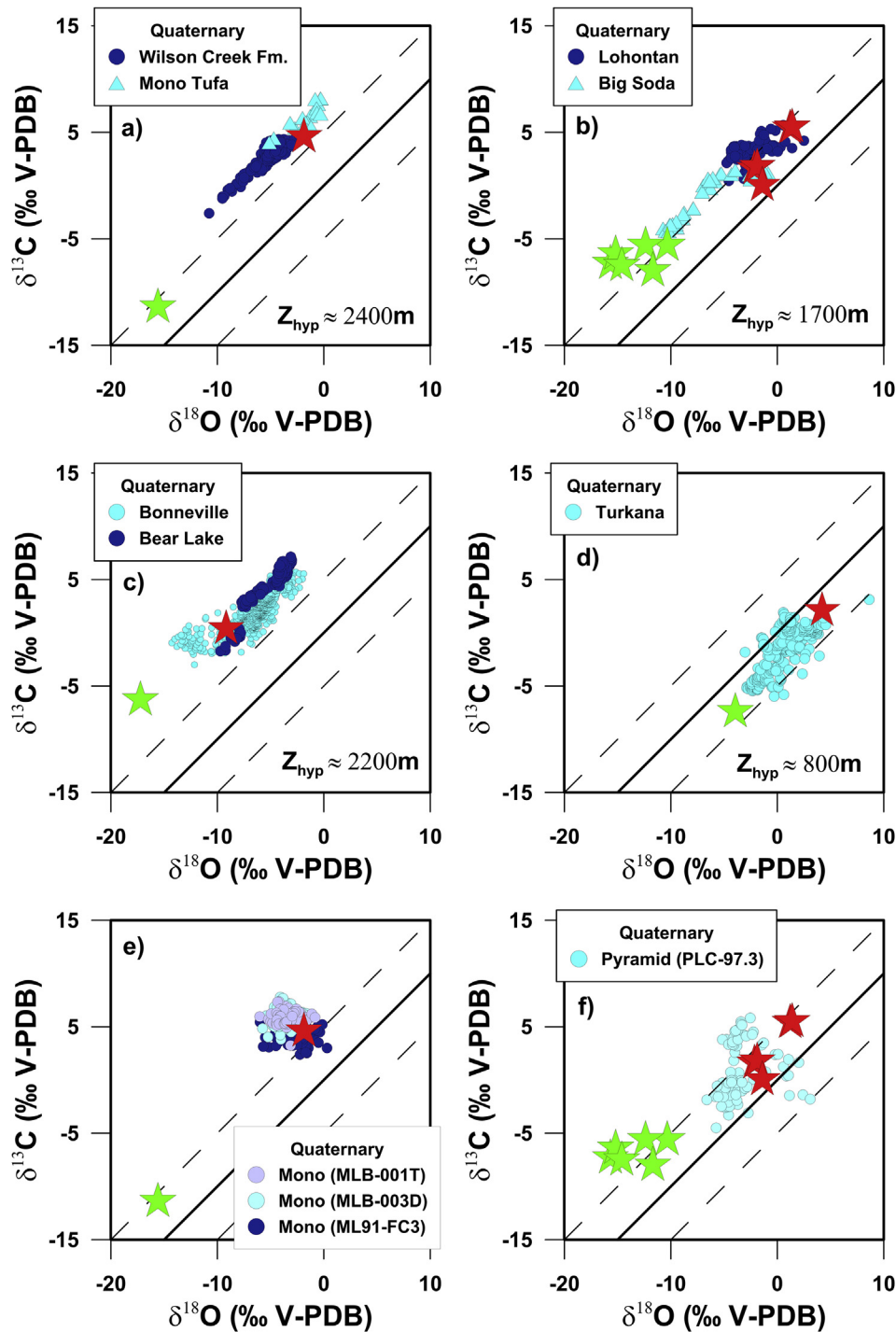
Fig. 7. δ^{13}C versus δ^{18}O bivariate plots for Quaternary lake carbonate records where modern source (i.e. inflow) water and lake water δ^{18}O and δ^{13}C-DIC values were available from the literature. Green stars represent the isotopic equilibrium composition of calcite forming in equilibrium with 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 ±5‰ differences between lake carbonate δ^{18}O and δ^{13}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–f).

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 δ^{18}O and δ^{13}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).
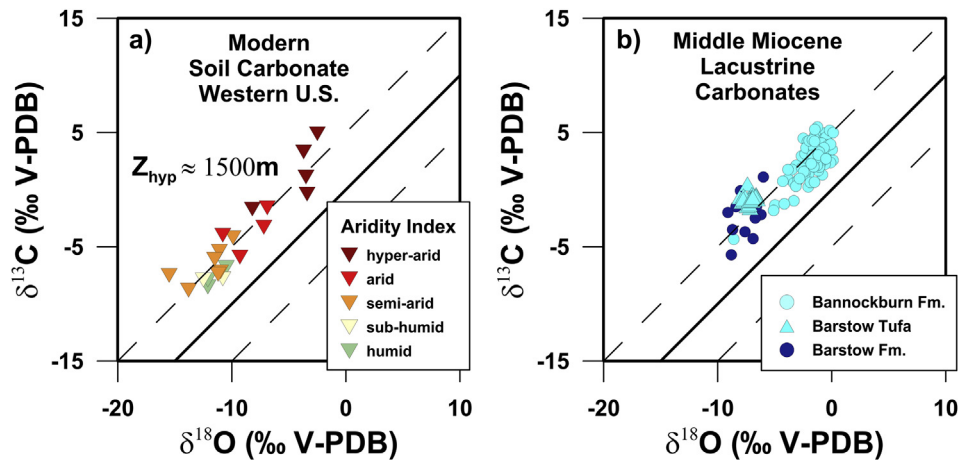
Fig. 8. δ^{13}C versus δ^{18}O bivariate plots for Cerling and Quade's (1993) modern aridisol soil carbonates from the western U.S. Great Basin/Mojave Desert region (a), and middle Miocene (~15Ma) laminated lacustrine carbonates from the Mojave Desert's Mud Hills area Barstow Formation and Otago New 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 black line represents a 1:1 relationship; dashed lines represent ±5‰ differences between lake carbonate δ^{18}O and δ^{13}C. Modern regional hypsometric altitude (z_{hyp}) is shown in (a). Middle Miocene lacustrine carbonate data in (b) are original to this study.

The stable isotope paleotopography community will almost certainly benefit from similar approaches for similar reasons. Just as the Quaternary paleoclimate community must address the under-determined 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 δ^{18}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 under-determined 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 δ^{18}O and Δ_{47} temperature estimates to assessments of paleohydroclimatic conditions.

We determined δ^{18}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). δ^{18}O values determined on individual carbonate laminations present in this tufa are ~13‰ 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 (±4.3 °C) and 15.4 °C (±3.3 °C). Inputting the δ^{18}O values and Δ_{47} paleotemperature estimates to the Kim and O'Neil (1997) oxygen isotope equilibrium fractionation equation yields lake water δ^{18}O values of -2.3‰ (±0.9‰). and -1.4‰ (±0.7‰) VSMOW (Table 2). These values are 13‰–14‰ more positive than published Mono Lake inflow water δ^{18}O values and 1‰–2‰ more negative than present day Mono Lake water (Li et al., 1997). By combining traditional carbonate δ^{18}O data with more recently developed Δ_{47} clumped isotope analytical methods we were able to isolate and solve for a single variable (δ^{18}O$_{water}$) 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.

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

Sample (Age)	Number of analyses	$\delta^{13}C$ (‰)[a]	$\delta^{18}O$ (‰)[a]	Δ_{47} (‰)[b]	Δ_{47}-temperature (°C)[c]	$\delta^{18}O_{water}$ (‰)[d]
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

[a] Relative to V-PDB.
[b] On absolute reference frame.
[c] Determined using the calibration of Defliese et al. (2015).
[d] Relative to V-SMOW.

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). $\delta^{18}O$ values determined for carbonate powders drilled at 0.5 mm spacing across a 100 mm wide section of the Barstow Formation tufa do not covary with $\delta^{13}C$ ($r^2 = 0.03$; 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 $\delta^{18}O$ values of −0.4‰ (±0.3‰) VSMOW (Table 2) under equilibrium calcite-water fractionation conditions. In this case, combining $\delta^{18}O$ and Δ_{47} paleotemperature estimates suggests that the Barstow Formation tufa may have been fed by hot springs generated by local magmatic systems present in the central Mojave during the middle Miocene (Glazner et al., 2002).

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

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

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Appendix A. Supplementary information

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.quascirev.2015.06.030.

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