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 δ^{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 δ^{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 δ^{18}O and δ^{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 isotopic 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 δ^{18}O and δ^{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.
June 21, 2015

To: Colin V. Murray-Wallace (Editor-in-Chief, Quaternary Science Reviews)
From: Dr. Travis Horton (U. Canterbury, Geological Sciences)
Re: JQSR-D-15-0005R1

Thank you for inviting us to submit a revised version of our article JQSR-D-15-0005R1, “Evaporation induced $^{18}O$ and $^{13}C$ enrichment in lake systems: a global perspective on hydrologic balance effects on terrestrial stable isotopic proxy records,” submitted to QSR’s Water Isotope Systematics special issue. We have carefully considered the thoughtful and constructive reviews provided by Matt Jones, and we have made extensive revisions to the manuscript in response to his review. Our revised submission (JQSR-D-15-0005R2) now titled, “Evaporation induced $^{18}O$ and $^{13}C$ enrichment in lake systems: a global perspective on hydrologic balance effects,” is much stronger, better organized and more concise as a result. We are pleased to submit our revised manuscript to Quaternary Science Reviews for your consideration.

Our revisions address Matt’s forty-two comments, enumerated and described in detail in the attached document.

Thank you for considering our revised manuscript for publication in Quaternary Science Review’s Water Isotope Systematics special issue. We look forward to hearing from you.

Sincerely,

Travis W. Horton
Geological Sciences, University of Canterbury
Christchurch 8140, New Zealand
Travis.horton@canterbury.ac.nz
Reviewers' comments:

Thank you for submitting this revised manuscript and for the careful responses to the reviewers' comments.

I've been through the paper a couple of times and think it still needs a little bit of tidying up before we send it for publication and I'd be grateful if you could look through my comments below.

Some of these are more general comments, which might be worth bearing in mind as you go through the paper again, some are clearly quite specific, but I've listed them in the order they come in the paper.

Title: I think this could be shortened to 'Evaporation induced $^{18}$O and $^{13}$C enrichment in lakes: a global perspective on hydrological balance effects'

1) We have changed the title to read, "Evaporation induced $^{18}$O and $^{13}$C enrichment in lake systems: a global perspective on hydrologic balance effects." (Lines 1-2)

We retained 'lake systems' in our revised title as one of the key findings of our review is that the isotopic effects of in-lake evaporation are best demonstrated by comparing in-flow water compositions to lake water compositions: by analyzing only lake archives, researchers may fail to recognize the potential severe effects of lake water evaporation as our Mono Lake examples demonstrate. Future research should consider the whole hydrologic system and not only the lakes themselves.

Abstract line 54 suggest '…integration of multiple isotope proxies....'

2) Changed to read, “…integration of multiple isotopic proxies...” (Line 53)

I think it's important to qualify that these multiple proxies are all isotopic. Here and elsewhere you use this phrase, but multi-proxy approaches are now quite common in palaelimnological work and might not include isotopic proxies. These other proxies can however aid the interpretation of isotope data, including the degree of evaporation e.g. using carbonate mineralogy.

Introduction line 66 your opening sentence could use a reference e.g. one of the recent IPCC reports.

3) We have added a reference to the IPCC 5th Assessment Report “Climate Change 2014:Synthesis Report.” (Line 65)

Line 85 suggest '…fractionations in lake systems are often >+10ppt from meteoric waters for $d^{18}$O' [forgive the lack of symbols here]
4) Changed to read, “fractionations in lake systems are often >+10‰ from unmodified meteoric waters for $\delta^{18}O$.” (Lines 84-85)

I think the rest of this section, through to line 101, needs toning down a bit. I understand your response to reviewers in relation to some of these records and interpretation of data, however, many of your studies cited in Table 1 are at least 10 years old, and I think the community has moved on a bit, such that most (certainly not all, but most) interpretations of lake oxygen isotope data now take into account the evaporative, or not, setting of the lake under investigation. One of the other papers in the special issue states that 'Stable isotopic methods have been widely used to study lake evaporation...', and the Gibson et al contribution already online (http://www.sciencedirect.com/science/article/pii/S0277379115001559) uses this as the basis of their paper.

Later in the manuscript you use the word 'quantify' on a few occasions, and I think there is an important difference between authors trying to quantify past change in climate and those just reporting qualitatively, relative changes in environmental or climatic states. If we are to improve our interpretations we need to be more quantitative, as you suggest and show in the paper, but this doesn't undermine everything that has gone before, it builds on the collective knowledge gained.

Given that some specific suggestions about this section...

Line 85 - 89 I would suggest something along the lines of 'Such large shifts in isotopic composition remind us of the challenges involved in the interpretation of lake isotopic studies, where systems have multiple controls (such as evaporation, temperature of mineral formation, and changes in source water composition) which need to be carefully determined on a case by case basis.'

5) We appreciate the suggested revision for these lines of our manuscript, but we strongly believe our phrasing is more powerful, clearer and better aligned to the key point of our manuscript: single element stable isotopic investigations of lake carbonates are underdetermined. Improving future interpretations of lake carbonate isotopic records must include acceptance of the fact that single element isotopic proxies are not really proxies at all given their sensitivity to so many unconstrained variables.

Line 91 and 92 it reads as though you are suggesting that only presenting stable oxygen isotope compositions is a problem? If so, I think you need to qualify why and be careful with the examples you choose to make this point. The von Grafenstein et al., 1999 paper for example builds on work in a preceding 1996 paper in GCA where they present both d18O and d13C of ostracods, and show multiple years of monitoring data showing the relationship between d18O and temperature or rainfall isotope values. The Anderson 2011 paper uses oxygen and hydrogen isotope values to shown that the lake waters are not evaporating before going on to use the
oxygen isotopes in the palaeoreconstruction.

**6) We have removed these lines from the revised manuscript (R2). The topic is explored later in the manuscript.**

Line 97-99 suggest changing to something like 'The work we present here again highlights, for both Quaternary climate change research and paleotopographic research over tectonic time-scales, the need to take into account all possible controls on stable isotope proxies, including evaporation.'

**7) Changed to read, “Most of the lake carbonate records included in the global dataset we present show significant positive covariation between δ¹⁸O and δ¹³C 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.”** (Lines 88-92)

Line 102-115 suggest changing the order of this paragraph such that your evaporation experiment follows (as support to) your compilation of archive data.

**8) The preceding paragraph has been significantly revised (new lines 82-92) with a clearer focus on our compilation of archive data.**

Line 111 these slope values seem different to those given on line 376?

**9) Changed to read, “the same narrow range in slope (ca. 0.7 to 1.2) as is present…”** (Line 102)

Line 222 suggest '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 probably reflecting...' I use the word significantly here to differentiate from the noise around the MWL plotted, some of which are to the right of the GMWL.

**10) Line changed as suggested. (Lines 209-210)**

Line 229 wasn't sure where the value of 0.5 came from - the intercept value is 1.59 on the figure?

**11) Changed to 1.59, as shown in Fig.2b. (Line 217)**

Line 230 suggest '...result of additional surface...'

**12) Text changed as suggested. (Lines 218-219)**
Lines 232-234 I would suggest removing these lines. These data are already published and this is not a new result - the point made is also laid out in the following paragraph.

13) Lines have been removed.

Line 238 suggest ‘...sub-humid lakes, [presumably] those with more 'closed' hydrological settings, are shifted...’

14) Most of these humid and sub-humid environment lakes have open/through-flowing hydrologies. Thus, we have not added the suggested modifying text, “those with more closed hydrological settings.” We have removed the word ‘clearly’ from, “are [clearly] shifted...” (Line 224)

In general it would be worth mentioning different lake hydrological settings somewhere. Lakes without surface outflow have to loose water from evaporation and/or groundwater (another often under-discussed issue) and therefore it’s not a surprise that some lakes plot to the right of the MWL and are evaporating.

15) Unfortunately the regional DEM we used does not have sufficient resolution to allow for a detailed assessment of each lake’s hydrologic context. We searched through the multiple references used in our compilation and none of these articles include detailed information about each lake’s hydrology. We agree, this would be very worthwhile discussing in some detail. Unfortunately, we are not in a position to do this for the current manuscript.

Fig. 2d this is a nice, and unusual way of presenting this data, and makes the point nicely. I just wondered why you used the GMWL, rather than the regional meteoric water line defined in 2a, and a evaporation line slope of 4.5 rather than the slope of 5.16 defined in c? The latter needs justifying in the text, the former is less important given the similarities in the numbers.

16) We have changed the text to read, “...an intermediate and representative slope 4.5 evaporation line.” We chose this value for several reasons. The empirically observed ‘lake water’ slope of 5.16 shown in Fig. 2c includes many hundreds of data points from lakes spread across western North America with variable and site-specific hydrologies and climatic settings. Thus, this value of 5.16 will be a maximum evaporation line slope as it will include both highly evaporated and less evaporated waters across a wide range in unmodified meteoric water isotopic compositions. Individual lakes show local evaporation lines with slopes that range between ~4 and ~5. Thus, the evaporation line slope we have used, 4.5 is ‘intermediate and representative’
of the true evaporation line slopes recognized across western North America. Our evaporation experiments show slightly less positive evaporation line of slopes ranging between 3.8 and 4.2, but these samples were evaporated in a climate controlled lab rather than field settings in western North America. (Line 234)

Line 272-273 suggest changing this sentence to 'The results presented above provide important context to our discussion of d18O and d13C co-variation in the following sections.' This will help tie all your 'work packages' together.

17) Text changed as suggested. (Lines 258-259)

Lines 277-279 suggest 'However, these same results confirm that...' given what you have discussed in the introduction.

18) Text changed as suggested. (Lines 263-264)

Line 302 - 309 It's not clear what this list of hydrological models adds to this section. Are you just showing that proxy system models of this co-variation are rare compared to oxygen and hydrogen systems? If so this section of text could be shortened considerably.

19) We have added the sentence, “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 an effort to provide clarity around the point this list of hydrological models contributes to our manuscript. (Lines 295-298)

Lines 324-325. The first sentence of this paragraph is not needed, and it's slightly contradictory as it stands.

20) This sentence has been removed as suggested.

Paragraph beginning line 340 suggest starting this paragraph 'A number of in lake processes can cause $^{13}$C enrichment of the TDIC pool, including...' as you give the references later in the paragraph.

21) We have changed the sentence to read, “A number of different processes can cause $^{13}$C enrichment, including...” We have left-out the suggested 'in-lake' modifier as these processes can occur up gradient from the lakes themselves in addition to in the lakes themselves. (Line 328)
Line 357 suggest 'Tens if not hundreds of research investigations into lake carbonate isotope variability have been conducted…'

22) Text changed as suggested. (Line 343)

Line 359-360 I would remove the sentence beginning 'Unfortunately...unless you can quantify 'relatively few'.

23) Text changed as suggested. This sentence has been removed.

Line 388 'relatively few studies' but an increasing number are doing this, it's becoming the norm, especially for oxygen, maybe less so for carbon.

24) Sentence revised to read, “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…” (Lines 374-376)

Line 391 suggest '...modify source water chemistries for both O and C.'

25) Text revised as suggested. (Lines 377-378)

Line 396 - 406 Although I fully accept this is a very basic model to aid discussion, and that is a valid approach, I would suggest using a) annual mean, or ideally annually weighted mean, water values as source water - this is more realistic than just summer values for most lakes, although summer temperatures are probably a good basis for carbonate precipitation (Dean et al., in press; http://www.sciencedirect.com/science/article/pii/S0022169414008890) and b) comparing only to core top or recent (say last 1000 yeas at most) carbonate data. These would be fair assumptions to compare.

If you want to show the full core dataset in figure 6 please add error bars to the points shown.

26) The R1 version of Fig. 6 includes 1 standard deviation whiskers on each data point. Some are not visible as the whiskers are smaller than the data symbol/circle.

Another approach for the figure would be to plot potential present day calcite values i.e. the full range from summer to winter waters and temperatures against the full range of the lake carbonates - so plot envelopes instead of points. This may be difficult given the number of sites, but may be informative.
27) We considered these possibilities when preparing the initial manuscript. Our feeling at the time was that it was best to present matched summer precipitation/temperature data only as this is when lake carbonates will form in most lakes. Annual precipitation isotope values will only serve to increase the difference between observed and modeled values (i.e. all data points will simply shift down by a permil or two) as inclusion of winter month precipitation isotopic compositions will force the modeled results towards more negative values. Thus, we felt our approach was appropriate as it is conservative – these are the minimum differences between modeled and observed values. In addition, we felt that such a detailed comparative analysis was not well aligned to the key points of the manuscript, and that by including such an analysis, we would be further diluting the focus of an already broad scope manuscript. We've included this Figure 6 and overly simplistic model analysis simply to show that Quaternary lake carbonate isotope archives are poorly matched to conservative estimates of modern values and (more importantly) that the by far majority of Quaternary records are isotopically enriched (i.e. the data plot to the right of the 1:1 line). We are reluctant to expand on this simplistic analysis in the revised version of the manuscript.

We have addressed your above points by revising this section of the text (See lines 420-426 or revised version).

Please give the Kim and O'Neil equation in the paper.

28) The Kim and O'Neil equation has been added to the manuscript. (Lines 386-390)

Line 421 suggest removing the word 'undetermined'

29) We have kept the word ‘undetermined’ in this sentence as it captures and reinforces the key contribution of our manuscript.

Line 429 generate rather than generated

30) Text changed as suggested. (Line 420)

435 suggest removing the word 'model'

31) Text changed as suggested.

Line 462 - 464 I would add carbonate precipitation into this list - and many studies are now doing this or trying to do this as much as is possible e.g. Dean et al., in press
32) Text changed as suggested. (Line 456)

Lines 469-470 suggest replacing 'our model' with 'this'

33) Text changed as suggested. (Line 463)

Lines 465 - 468 interestingly this suggests that source waters have changed relatively little, compared to evaporative state, over the timescale of these records.

34) You are correct. It is difficult to envision processes other than evaporation that can cause the very large ranges in both $\delta^{18}$O and $\delta^{13}$C observed in most lake carbonate records.

Line 471 remove the word 'yet'

35) Text changed as suggested.

Lines 481-483 this is a very important point. Our archives are complex systems and each one behaves differently - so we need to build up a picture of each site to the best of our ability for the present situation and in the past, using multiple proxies, isotopic and otherwise.

In general in this section it would be interesting to see some discussion of why some sites don't co-vary, and if you can get from your list of sites an idea of what controls the slope of the co-variation in the sites that do.

36) We strongly believe that this is a very worthwhile topic for detailed exploration in a separate manuscript/study. The current MS is intended to be a global review of the topic that is supplemented by original data and multi-proxy stable isotopic approaches to solving 'the evaporation problem'.

Line 525 Relevance to other archives or research questions? Just to qualify, as the proxy is the same, even though it may be a proxy for something else!

37) Section sub-heading changed to, “Relevance to other research topics,” as suggested. (Line 518)

Line 550 etc Do you think your soil data is regionally specific? Where is the Quade et al data from? I would have thought that local TDIC pools are even more important in
soils than in lakes - if not this is really interesting!

38) The soil data are exclusively from Cerling and Quade (1993) and the dataset includes pedogenic carbonates from across the western United States. It’s a fairly large regional coverage, thus there will be differences in local soil systems. We included these data because the pattern of isotopic covariation is remarkably similar to our experimental results and the global empirical lake carbonate records. All three lines of evidence point to the simplest interpretation that evaporation is the common driver of the observed covariation along similar m=1 slopes. We agree that this is a very interesting and telling empirical result that strengthens the theme/topic of our manuscript.

Line 574 Is using a slope of 1 valid given the range you shown earlier? How much difference does it make to your elevation calculations if you use a slope of 0.6, the average from your earlier data, for example - or is this included in the ±500m error?

39) The ±500m error is based on a range in covariation slopes ranging between ~0.5 to 1.5. Readers can refer to Horton and Oze (2012) for details if they are interested in exploring this topic further.

Line 618 suggest '...negative than present day Mono Lake water...'

40) Text changed as suggested. (Line 611)

Line 640 - 650 In general this section of the discussion, highlighting how new analyses can add to, and better, our interpretations is really useful. But this particularly paragraph I think you could remove - as it's implicit in the previous paragraph and goes beyond what is needed for your discussion in this paper.

41) We have removed this paragraph from the revised (R2) manuscript.

Line 690 related to a comment above; do these records, or their authors, try to 'quantitatively' record the full extent of anything?

42) We have removed the word ‘quantitatively’ from the sentence as suggested.

Matt Jones 18/06/15
Solving the Isotopic Evaporation Problem
- Evaporation induced fractionation significantly modifies lake source water $\delta^{18}$O.
- Evaporation causes $^{13}$C enrichment in the dissolved inorganic carbon pool.
- Significant O and C isotopic covariation occurs in >70% of lake carbonate records.
- Evaporation impacts isotope proxy records even when covariation is absent.
- Multi-proxy methods reveal detail not achievable with traditional approaches.
Evaporation induced $^{18}\text{O}$ and $^{13}\text{C}$ enrichment in lake systems: a global perspective on hydrologic balance effects

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Keywords: evaporation; hydrologic balance; lakes; lacustrine; stable isotopes; oxygen isotopes; carbon isotopes; clumped isotopes; hydrology; paleohydrology; isotope hydrology; hydroclimate; climate change; paleoclimate; paleoelevation; paleothemometry; carbonate; soil carbonate; continental; terrestrial; western U.S.; 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 $\delta^{18}O$, 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 $>+10\%_0$ 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.
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 $>+10\%o$ 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 $>+10\%o$ 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 >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 δ²H and δ¹⁸O 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 $\delta^2$H, $\delta^{18}$O, and $\delta^{13}$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. $\delta^2$H 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, 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 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 0.5mm 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 ThermoFinnigan 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‰.

$\Delta_{47}$ values for the middle Miocene Barstow Fm. Tufa, middle Miocene Bannockburn Fm. oncolite and Quaternary Mono Lake tufa samples were determined using a Thermo Finnigan 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 $\Delta_{47}$. $\Delta_{47}$ 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). $\Delta_{47}$ 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 $\Delta_{47}$-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 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 ($\delta^2$H = 8\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 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 student’s 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 $\sim$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 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 \(^{18}\text{O}\) and \(^{13}\text{C}\) 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 $\delta^{18}O$ values by $\sim11\text{-}13\%$ and $\delta^2H$ values by $\sim45\text{-}55\%$ 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 $^{13}C$ enrichments in DIC, on the order of $1\text{-}2\%$ 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 $21^\circ C$ (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 δ^{18}O and δ^{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 δ^{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):

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

where \( T \) is temperature in kelvins and \( \alpha \) 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) 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 $\sim8\%$ to $\sim15\%$ 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 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 $\sim$10‰ to $\sim$15‰ enriched in both $^{18}$O and $^{13}$C along a slope $\sim$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 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 \((p=4.7 \times 10^{-10}, t\text{-test})\) with a slope very close to 1 \((m=1.03; \text{Fig. 8a})\). The observation that pedogenic carbonates from hyper-arid and arid environments exhibit the most positive \(\delta^{18}O\) and \(\delta^{13}C\) 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).

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 \(\delta^{18}\)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 (\(\sim 1700\) m mean elevation in the north; \(\sim 900\) 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 \(\sim 1.5\) km high ‘proto’ Southern Alps at \(\sim 15\) 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 $\delta^{18}$O and $\Delta$47 temperature estimates to assessments of paleohydroclimatic conditions.

We determined $\delta^{18}$O and $\Delta$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). $\delta^{18}$O values determined on individual carbonate laminations present in this tufa are $\sim$13‰ more positive than would be expected for Mono Lake inflow water derived carbonate (Fig. 7a). Paleotemperature estimates for two $\Delta$47 analyses of this same sample (Table 2) are 15.8°C (±4.3°C) and 15.4°C (±3.3°C). Inputting the $\delta^{18}$O values and $\Delta$47 paleotemperature estimates to the Kim and O’Neil (1997) oxygen isotope equilibrium fractionation equation yields lake water $\delta^{18}$O values of -2.3‰ (±0.9‰).
and -1.4‰ (±0.7‰) VSMOW (Table 2). These values are 13‰ to 14‰ more positive than published Mono Lake inflow water δ18O values and 1‰ to 2‰ more negative than present day Mono Lake water (Li et al., 1997). By combining traditional carbonate δ18O data with more recently developed Δ47 clumped isotope analytical methods we were able to isolate and solve for a single variable (δ18Owater) 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). δ18O values determined for carbonate powders drilled at 0.5 mm spacing across a 100mm wide section of the Barstrow Formation tufa do not covary with δ13C (r²=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, Δ47 paleotemperature estimates for the Barstow tufa are relatively warm (48.3°C; Table 2), yielding lake water δ18O values of -0.4‰ (±0.3‰) VSMOW (Table 2) under equilibrium calcite-water fractionation conditions. In this case, combining δ18O and Δ47 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 $\Delta_{47}$ 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 $\Delta_{47}$
paleotemperature estimates we determined (Table 2) reinforce this interpretation
returning values that range between $17.7^\circ C \pm 3.9^\circ C$ and $24.6^\circ C \pm 2.6^\circ C$, 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‰
$\pm 0.8‰$ to $+2.6‰ \pm 0.6‰$ VSMOW; Table 2) determined using the above $\Delta_{47}$
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.
Acknowledgements

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**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 $\delta^2$H and $\delta^{18}$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 $\delta^{18}$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.

**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 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 $\delta^2$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 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 $\delta^{18}O$ 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.

**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 ±1σ. 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.** $\delta^{13}C$ versus $\delta^{18}O$ bivariate plots for Quaternary lake carbonate records where modern source (i.e. inflow) water and lake water $\delta^{18}O$ and $\delta^{13}C$-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 $\delta^{18}O$ and $\delta^{13}C$. 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-d).

**Fig. 8.** $\delta^{13}C$ versus $\delta^{18}O$ 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 δ¹⁸O and δ¹³C. Modern regional hypsometric altitude ($z_{hyp}$) is shown in (a). Middle Miocene lacustrine carbonate data in (b) are original to this study.
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<tr>
<th>Lake</th>
<th>Number of Records</th>
<th>Latitude (°)</th>
<th>Longitude (°)</th>
<th>Lake Elevation (m.a.s.l.)</th>
<th>Modern Aridity Index (P: E)</th>
<th>Age (yrs)</th>
<th>Source(s)</th>
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**Total**: 57
### Table 2: Stable isotope data ($^{\delta^{13}}$C, $^{\delta^{18}}$O, $\Delta_{47}$), $\Delta_{47}$-temperature estimates and reconstructed $^{\delta^{18}}$O$_{water}$.

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<th>Sample (Age)</th>
<th>Number of Analyses</th>
<th>$^{\delta^{13}}$C (‰)$^1$</th>
<th>$^{\delta^{18}}$O (‰)$^1$</th>
<th>$\Delta_{47}$ (‰)$^1$</th>
<th>$\Delta_{47}$-Temperature (ºC)$^1$</th>
<th>$^{\delta^{18}}$O$_{water}$ (‰)$^4$</th>
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<td>0.735±0.010</td>
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<td>0.648±0.004</td>
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<td>-0.4±0.3</td>
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<td>Bannockburn Fm. oncholite interior laminations (Middle Miocene)</td>
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$^1$ Relative to V-PDB
$^2$ On absolute reference frame
$^3$ Determined using the calibration of Defliese and others (2015)
$^4$ Relative to V-SMOW
Figure 7

Click here to download high resolution image
Supplementary Data

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