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Title: Evaporation induced  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  enrichment in lake systems: a global perspective on hydrologic balance effects

Article Type: SI: Water Isotope Systematics

Keywords: evaporation; hydrologic balance; lakes; lacustrine; stable isotopes; oxygen isotopes; carbon isotopes; clumped isotopes; hydrology; paleohydrology; isotope hydrology; hydroclimate; climate change; paleoclimate; paleoelevation; paleothermometry; carbonate; soil carbonate; continental; terrestrial; western U.S.; Great Basin; Barstow Formation; Mono Lake tufa; Sierra Nevada; Manuherikia Group; Southern Alps New Zealand

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

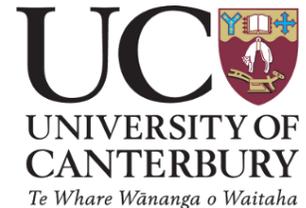
Through integration of multiple large datasets we show that lake carbonate  $\delta^{18}\text{O}$  values and the lake waters from which they are derived are often shifted by  $>+10\text{‰}$  relative to source waters discharging into the lake. The global pattern of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  covariation observed in  $>70\%$  of the records studied and in several evaporation experiments demonstrates that isotopic fractionations associated with lake water evaporation cause the heavy carbon and oxygen isotope enrichments observed in most lakes and lake carbonate records. Modeled endogenic calcite compositions in isotopic equilibrium with lake source waters further demonstrate that evaporation effects can be extreme even in lake records where  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  covariation is absent. Aridisol pedogenic carbonates show similar isotopic responses to evaporation, and the relevance of evaporative modification to paleoclimatic and paleotopographic research using endogenic carbonate proxies are discussed.

Recent advances in stable isotope research techniques present unprecedented opportunities to overcome the underdetermined nature of stable isotopic data through integration of multiple isotopic

proxies, including dual element  $^{13}\text{C}$ -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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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  $^{18}\text{O}$  and  $^{13}\text{C}$  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  $^{18}\text{O}$  and  $^{13}\text{C}$  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,

A handwritten signature in black ink, appearing to read 'Travis W. Horton'.

Travis W. Horton  
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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  $^{18}\text{O}$  and  $^{13}\text{C}$  enrichment in lakes: a global perspective on hydrological balance effects'

**1) We have changed the title to read, "Evaporation induced  $^{18}\text{O}$  and  $^{13}\text{C}$  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 palaeolimnological 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 5<sup>th</sup> Assessment Report "Climate Change 2014: Synthesis Report." (Line 65)**

Line 85 suggest '...fractionations in lake systems are often  $>+10\text{ppt}$  from meteoric waters for  $\text{d}^{18}\text{O}$ ' [forgive the lack of symbols here]

**4) Changed to read, “fractionations in lake systems are often >+10‰ from unmodified meteoric waters for  $\delta^{18}\text{O}$ .” (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  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of ostracods, and show multiple years of monitoring data showing the relationship between  $\delta^{18}\text{O}$  and temperature or rainfall isotope values. The Anderson 2011 paper uses oxygen and hydrogen isotope values to show 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  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  highlighting the need to take into account all possible controls on stable isotopic proxies, including evaporation effects, for both the Quaternary climate change and paleotopographic research." (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. 2 d 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 <sup>13</sup>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 <sup>13</sup>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 years 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 ‘underdetermined’ 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  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  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  $\pm 500\text{m}$  error?

**39) The  $\pm 500\text{m}$  error is based on a range in covariation slopes ranging between  $\sim 0.5$  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)**

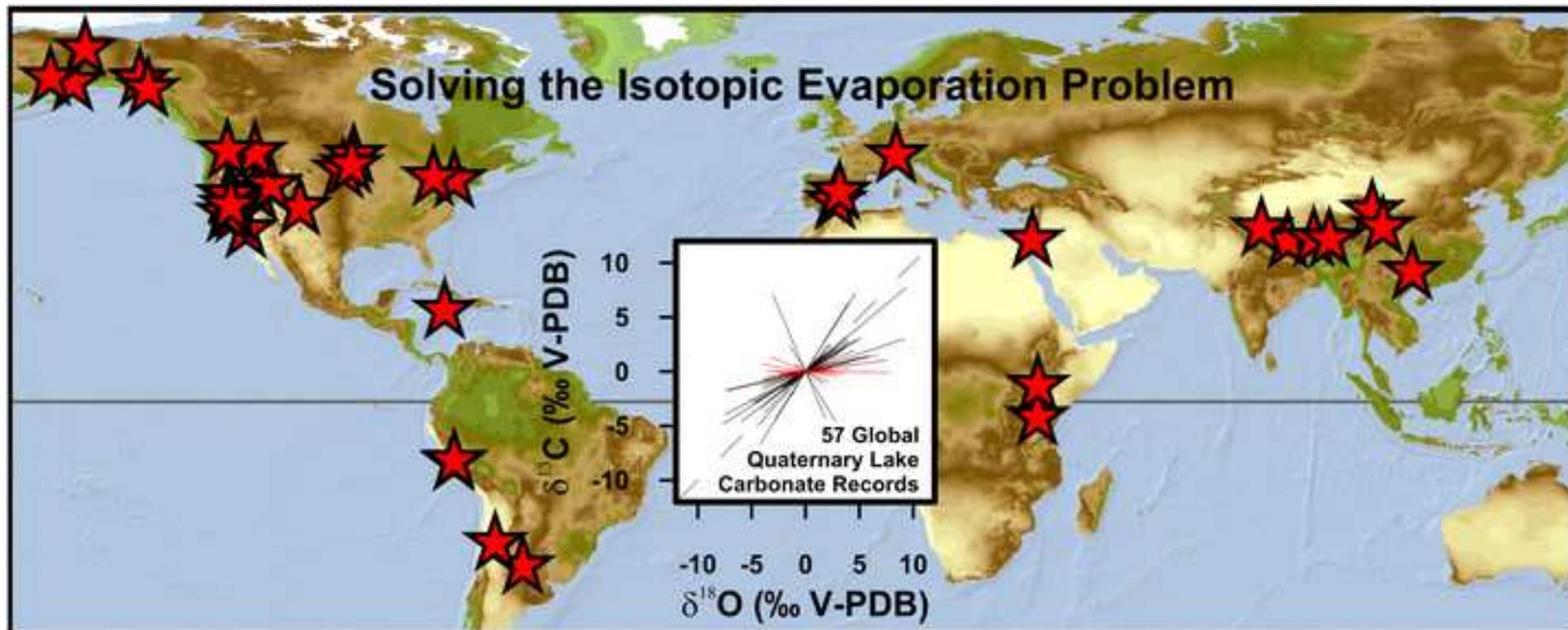
Line 640 - 650 In general this section of the discussion, highlighting how new analyses can add to, and better, our interpretations is really useful. But this particularly paragraph I think you could remove - as it's implicit in the previous paragraph and goes beyond what is needed for your discussion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



## \*Highlights (for review)

- Evaporation induced fractionation significantly modifies lake source water  $\delta^{18}\text{O}$ .
- Evaporation causes  $^{13}\text{C}$  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.

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

3

4 Travis W. Horton<sup>a\*</sup>, William F. Defliese<sup>b</sup>, Aradhna K. Tripathi<sup>b,c</sup> and Christopher Oze<sup>a</sup>

5

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17

18 **Keywords:** evaporation; hydrologic balance; lakes; lacustrine; stable isotopes;

19 oxygen isotopes; carbon isotopes; clumped isotopes; hydrology; paleohydrology;

20 isotope hydrology; hydroclimate; climate change; paleoclimate; paleoelevation;

21 paleothermometry; carbonate; soil carbonate; continental; terrestrial; western U.S.;

22 Great Basin; Sierra Nevada; Southern Alps New Zealand

23 **ABSTRACT**

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

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

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

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

61 **1. Introduction**

62

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

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

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

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

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

106

107 **2. Materials and analytical methods**

108

109 *2.1 Global Lake Carbonate Stable Isotope Compilation*

110

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

121

122 *2.2 Western U.S. Modern Water Stable Isotope Compilation*

123

124 We compiled modern meteoric, river, and lake water  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values  
125 from a variety of published sources (Friedman, 2000; Coplen and Kendall, 2000;  
126 Friedman et al., 2002; Henderson and Shuman, 2009). This compilation includes  
127 799 individual meteoric water analyses, 3875 river water analyses, and 247 lake  
128 water analyses predominantly from the western U.S. (Fig. 1). Aridity index values

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

131

### 132 *2.3 Evaporation Experiments*

133

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

150  $\delta^{13}\text{C}$ -DIC values were determined using the Spötl (2005) method. In brief,  
151 1ml sub-samples were injected into ultra-high purity (>99.999%) helium flushed

152 10ml borosilicate exetainer vials pre-loaded with 103% phosphoric acid. Dissolved  
153 inorganic carbon (DIC) derived CO<sub>2</sub>, liberated by the acid-water reaction, was  
154 analyzed using a ThermoFinnigan GasBench II coupled to a ThermoFinnigan DeltaV+  
155 isotope ratio mass spectrometer operating under a continuous flow of ultra-high  
156 purity helium.  $\delta^{13}\text{C}$ -DIC values were two-point normalized to the VPDB scale based  
157 on replicate analysis of IAEA certified reference materials NBS18 and NBS19. All  
158  $\delta^{13}\text{C}$ -DIC values are precise to <0.10‰.

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

162

#### 163 *2.4 Stable Isotopic Analysis of lake carbonates*

164

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

175 reference materials NBS18 and NBS19. A MERCK carbonate internal lab standard  
176 was also analyzed at regular intervals throughout each analytical sequence. All  
177 laminated lacustrine carbonate  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are precise to  $<0.10\text{‰}$ .  
178  $\Delta_{47}$  values for the middle Miocene Barstow Fm. Tufa, middle Miocene  
179 Bannockburn Fm. oncholite and Quaternary Mono Lake tufa samples were  
180 determined using a Thermo Finnigan MAT 253 dual inlet gas source mass  
181 spectrometer (“Chewbacca”) in the Tripati Lab at the University of California, Los  
182 Angeles, which has been modified to simultaneously measure masses 44-49 and is  
183 equipped with a custom built extraction device (Passey et al., 2010). For each  
184 analysis, 5 mg of sample powder was digested with 105 wt. percent  $\text{H}_3\text{PO}_4$  using a  
185 common acid bath apparatus held at  $90\text{ °C}$ . The resulting  $\text{CO}_2$  was cryogenically  
186 isolated and further purified by a gas chromatograph. Purified  $\text{CO}_2$  was transferred  
187 to the mass spectrometer, and simultaneously analyzed for  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , and  $\Delta_{47}$ .  $\Delta_{47}$   
188 values were corrected for acid fractionation using an empirically derived acid  
189 fractionation offset of  $0.092\text{‰}$  (Henkes et al., 2013; Defliese et al., 2015), and are  
190 reported on the absolute reference frame (Dennis et al., 2011).  $\Delta_{47}$  values were  
191 converted to temperatures (see Supplementary Information) using a variety of  
192 calibrations, (Ghosh et al., 2006; Eagle et al., 2013; Zaarur et al., 2013; Tang et al.,  
193 2014; Defliese et al., 2015), which have been adjusted to a common acid  
194 fractionation reference frame (Defliese et al. 2015). Water  $\delta^{18}\text{O}$  values were  
195 calculated by using the measured carbonate  $\delta^{18}\text{O}$  value in conjunction with the  
196 measured  $\Delta_{47}$ -based temperature according to the carbonate-water oxygen isotope  
197 equilibrium fraction equation of Kim and O’Neil (1997).

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

202

### 203 **3. Results**

204

#### 205 *3.1 Western North America Water Isotopes*

206

207           Meteoric waters from western North America closely approximate the global  
208 meteoric water line (GMWL) and span an  $\sim 35\text{‰}$  range in  $\delta^{18}\text{O}$  (Fig. 2a; Friedman,  
209 2000; Coplen and Kendall, 2000; Freidman et al., 2002; Henderson and Shuman,  
210 2009). Yet, some of these meteoric water samples, specifically those at the more  
211 positive end of the dataset, plot significantly to the right of the GMWL reflecting the  
212 effects of evaporation during rainout and resulting in a more negative regional  
213 meteoric water line y-intercept value (2.38) than is generally assigned to the GMWL  
214 ( $\sim 10$ ).

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

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

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

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

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

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

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

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

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

267

### 268 *3.2 Evaporation Experiment*

269

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

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

282 Coupled  $^{18}\text{O}$  and  $^{13}\text{C}$  enrichment in endogenic carbonates has been  
283 documented and discussed at some length in the limnological (Stuiver, 1970; Talbot,  
284 1990; Li and Ku, 1997; Huang et al., 2014), pedological (Cerling and Quade, 1993;  
285 Quade et al., 2007; Ding et al., 2014), and speleological communities (Hendy, 1971;  
286 Mickler et al., 2006; Dreybrodt and Deininger, 2014). Oxygen and carbon stable  
287 isotopic covariation has also been documented in evaporating Dead Sea brines

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

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

307         All three water samples that we allowed to evaporate showed  $^{18}\text{O}$  and  $^2\text{H}$   
308 enrichment according to well-known kinetic fractionation processes (Cappa et al.,  
309 2003). Over the six-day evaporation period, all three samples lost ~65% of their  
310 mass to evaporation at near constant evaporation rates (Fig. 4a). The stable O and H

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

314 As each of the samples evaporated, clear progressive  $^{13}\text{C}$  enrichments in DIC,  
315 on the order of  $1\text{-}2\text{‰}$  per day, occurred over the six-day experiment. From these  
316 data and the corresponding water  $\delta^{18}\text{O}$  values, we calculated the equilibrium  
317 fractionation (Kim and O'Neil, 1997) O and C stable isotopic compositions of calcite  
318 that would have formed from these evaporating waters at  $21^\circ\text{C}$  (Fig. 4c). Although  
319 not as strongly linear as the O and H isotopic response, statistically significant  
320 ( $p < 0.05$ ; t-test) positive covariation was observed in all three samples. The  
321 relatively constant linear covariation slope ( $m = 0.7$  to  $m = 1.2$ ) is notably similar to  
322 what has been observed in the lacustrine carbonate rock record (Horton and Oze,  
323 2012) suggesting systematic isotopic fractionations occur as excess  $\text{CO}_2$  degasses  
324 from the water body,  $^{13}\text{C}$  enriched bicarbonate ions (and carbonate ions above  
325  $\text{pH} > 8.3$ ) further dominate the DIC pool as alkalinity increases in response to  
326 evaporation, and the water molecules themselves become  $^{18}\text{O}$  enriched as they  
327 evaporate (Zheng, 1990; Valero-Garcés et al., 1999; Cappa et al., 2003; Dreybrodt  
328 and Deininger, 2014).

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

334 atmospheric carbon dioxide is a possible factor influencing our experimental results.  
335 Thus, our findings suggest that evaporation induced increases in alkalinity (i.e.  
336 increased bicarbonate concentration) drives DIC  $^{13}\text{C}$  enrichment through isotopic  
337 equilibrium exchange with  $\text{CO}_2$  (ca. 8‰ at 25°C in the  $\text{HCO}_3^-$ – $\text{CO}_2$  system; Mook et  
338 al., 1974). This interpretation and our results are consistent with mechanistic  
339 models of the isotopic response of DIC during evaporation (Abongwa and Atekwana,  
340 2013; Dreybrodt and Deininger, 2014).

341

### 342 *3.3 Global Pattern of O and C isotopic covariation*

343

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

357 Of the 57 lake records analyzed, 41 show a statistically significant ( $p < 0.05$ , t-  
358 test) positive covariation between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , 3 show a statistically significant  
359 ( $p < 0.05$ , t-test) negative covariation (Medicine Lake, Valero-Garcés et al., 1995;  
360 Wallywash Pond, Holmes et al., 2007; Seven Mile Lake; Anderson et al., 2011), and  
361 13 show no significant isotopic covariation (Fig. 5). The average linear regression  
362 slope of the 41 records with a significant positive covariation trend is 0.62, across  
363 slope values ranging between 1.67 and 0.1. The average range in  $\delta^{18}\text{O}$  values  
364 spanned by these 41 records is 6.9‰, with a maximum range of 13.5‰ and  
365 minimum range of 1.2‰. Nearly three-quarters (i.e. 72%) of the lake records we  
366 compiled show statistically significant positive covariation trends spanning isotopic  
367 compositional ranges that are difficult to explain in the absence of extreme isotopic  
368 modification by evaporative enrichment of lake waters in both  $^{18}\text{O}$  and  $^{13}\text{C}$ .

369

#### 370 4. Discussion

371

##### 372 4.1 From source to sink: O and C isotopes in Quaternary lake systems

373

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

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

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

388

$$389 \quad 1000\ln\alpha(\text{Calcite-H}_2\text{O}) = 18.03(10^3T^{-1}) - 32.42 \quad (1)$$

390

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

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

403 suggesting lakes in these environments are less impacted by evaporative  
404 modification, yet 46 of the 57 lake records analyzed (i.e. 81%) plot to the right of the  
405 1:1 line consistent with evaporative modification of lake water  $\delta^{18}\text{O}$ . Forty-two  
406 percent of the lake carbonate  $\delta^{18}\text{O}$  records are  $>5\text{‰}$  shifted towards more positive  
407  $\delta^{18}\text{O}$  than would be expected for summer month carbonate precipitates derived  
408 from unmodified local meteoric water. Although many lakes with vastly different  
409 modern aridity index values show similar offsets between modeled and observed  
410  $\delta^{18}\text{O}$ , lakes from currently arid and semi-arid environments have a much larger  
411 average  $\delta^{18}\text{O}$  offset ( $5.4\text{‰}$ ) than sub-humid and humid environment lakes ( $2.0\text{‰}$ ).

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

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

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

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

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

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

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

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

481 Our analysis reinforces these interpretations, yet it also demonstrates that  
482 even lake carbonate records lacking significant positive covariation trends can also  
483 be severely impacted by the effects of evaporation. Several Quaternary lake  
484 carbonate records, notably those from arid environment closed-basins including  
485 Mono Lake cores MLB-003D (Benson et al., 2003), MLC-001T (Benson et al., 2003),  
486 ML91-FC3 (Li et al., 1997) and Pyramid Lake core PLC-97.3 (Benson et al., 2002), do  
487 not show significant covariation trends. Yet, according to our analysis, the  $\delta^{18}\text{O}$  and  
488  $\delta^{13}\text{C}$  values measured in these cores are  $\sim 10\text{‰}$  to  $\sim 15\text{‰}$  enriched in both  $^{18}\text{O}$  and  
489  $^{13}\text{C}$  along a slope  $\sim 1$  trend relative to modeled modern source water derived calcite  
490 compositions (Fig. 7). These extreme isotopic enrichments relative to less evolved  
491 inflow water isotopic compositions is demonstrated by the positions of the green  
492 stars (i.e. inflow water derived carbonate compositions) shown in Fig. 7 relative to  
493 the positions of the red stars (i.e. lake water derived carbonate compositions). The  
494 Mono Lake data presented in Fig. 7e provide an excellent example.

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

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

518

519 *4.2 Relevance to other research topics*

520

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

529         Pedogenic carbonate formation is most commonly associated with arid to  
530 semi-arid environments (Jenny, 1994). Thus, it is reasonable to assume that if  
531 evaporation is the dominant process controlling stable O and C isotopic  
532 compositions in endogenic lacustrine carbonates, then similar effects should be  
533 expected in pedogenic carbonates. To explore this possibility, we plotted the  
534 seminal western U.S. aridisol pedogenic carbonate  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values reported by  
535 Cerling and Quade (1993) and classified each value by its site-specific modern  
536 aridity index (Fig. 8a). The stable isotopic data reported by Cerling and Quade  
537 (1993) correspond with average soil carbonate isotopic compositions observed  
538 below 30cm depth in modern soils.

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

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

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

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

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

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

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

589

#### 590 *4.3 Multi-proxy methods*

591

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

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

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

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

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

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

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

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

661

## 662 **5. Conclusions**

663

664 A review of globally distributed Quaternary lake carbonate stable isotopic  
665 records and modern water isotopic compositions from western North America  
666 reinforces what the scientific community has known for decades: evaporation  
667 enriches surface waters and associated authigenic minerals in both  $^{18}\text{O}$  and  $^{13}\text{C}$ . This  
668 empirical pattern of O and C heavy isotope enrichment is corroborated by simple  
669 evaporation experiment results, and is consistent with the thermodynamics of  
670 kinetic fractionation of evaporating water, degassing of dissolved  $\text{CO}_2$ , and  $^{13}\text{C}$   
671 enrichment of DIC as alkalinity increases at Earth surface temperatures. Of utmost  
672 importance is the recognition that the isotopic effects of evaporation can be  
673 extreme, often in excess of 10‰ for both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . Traditional single-element  
674 isotopic records fail to record the full extent of these evaporative effects due to their  
675 sensitivity to myriad environmental conditions and the difficulty in determining  
676 unmodified source water compositions from terrestrial archives.

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

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706 **References**

707

708 Abell, P.I., Awramik, S.M., Osborne, R.H., Tomellini, S., 1982. Plio-pleistocene  
709 lacustrine stromatolites from lake Turkana, Kenya: Morphology, stratigraphy  
710 and stable isotopes. *Sed. Geol.* 32, 1-26.

711

712 Abongwa, P.T., Atekwana, E.A., 2013. Assessing the temporal evolution of dissolved  
713 inorganic carbon in waters exposed to atmospheric CO<sub>2(g)</sub>: A laboratory  
714 approach. *J. Hydrol.* 505, 250-265.  
715 <http://dx.doi.org/10.1016.j.hydrol.2013.09.045>.

716

717 Anderson, L., Abbott, M.B., Finney, B.P., Burns, S.J., 2005. Regional atmospheric  
718 circulation change in the North Pacific during the Holocene inferred from  
719 lacustrine carbonate oxygen isotopes, Yukon Territory, Canada. *Quat. Res.* 64,  
720 21-35.

721

722 Anderson, L., Finney, B.P., Shapley, M.D., 2011. Lake carbonate- $\delta^{18}\text{O}$  records from the  
723 Yukon Territory, Canada: Little Ice Age moisture variability and patterns. *Quat.*  
724 *Sci. Rev.* 30, 997-898.

725

726 Andrews, J.E., Pedley, M., Dennis, P.F., 2000. Palaeoenvironmental records in  
727 Holocene Spanish tufas: a stable isotope approach in search of reliable climatic  
728 archives. *Sedimentol.* 47, 961-978.

729

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

734

735 Barkan, E., Luz, B., 2005. High precision measurements of  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios  
736 in  $\text{H}_2\text{O}$ . Rapid Commun. Mass Spectrom. 19, 3737-3742.

737

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

743

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

748

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

751

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

756

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

760

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

765

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

770

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

774

775 Bird, B.W., Abbott, M.A., Rodbell, D.T., Vuille, M., 2011. Holocene tropical South  
776 American hydroclimate revealed from a decadal resolved lake sediment  $\delta^{18}\text{O}$   
777 record. *Earth Planet. Sci. Lett.* 310, 192-202.  
778 <http://dx.doi.org/10.1016/j.epsl.2011.08.040>.  
779

780 Bowen, G.J., 2014. The Online Isotopes in Precipitation Calculator, version 2.2.  
781 <http://www.waterisotopes.org>.  
782

783 Cappa, C.D., Hendricks, M.B., DePaolo, D.J., Cohen, R.C., 2003. Isotopic fractionation of  
784 water during evaporation. *J. Geophys. Res.* 108, 1-10.  
785 <http://dx.doi.org/10.1029/2003JD003597>.  
786

787 Cassel, E.J., Graham, S.A., Chamberlain, C.P., 2009. Cenozoic tectonic and topographic  
788 evolution of the northern Sierra Nevada, California, through stable isotope  
789 paleoaltimetry in volcanic glass. *Geology* 37, 547-550.  
790

791 Cerling, T.E., Quade, J., 1993. Stable carbon and oxygen isotopes in soil carbonates,  
792 in: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in*  
793 *Continental Isotopic Records*. Geophysical Monograph 78, American  
794 Geophysical Union, Washington, D.C., pp. 217-232.  
795

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

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

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

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

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

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

819       discrepant calibrations. *Chem. Geol.* 396, 51-60.  
820       <http://dx.doi.org/10.1016/j.chemgeo.2014.12.018>.  
821  
822       Deininger, M., Fohlmeister, J., Scholz, D., Mangini, A., 2012. Isotope disequilibrium  
823       effects: The influence of evaporation and ventilation effects on the carbon and  
824       oxygen isotope composition of speleothems – A model approach. *Geochimica et*  
825       *Cosmochimica Acta* 96, 57-79. <http://dx.doi.org/10.1016/j.gca.2012.08.013>.  
826  
827       Ding, L., Xu, Q., Yue, Y., Wang, H., Cai, F., Li, S., 2014. The Andean-type Gangdese  
828       Mountains: Paleoelevation record from the Paleocene–Eocene Linzhou Basin.  
829       *Earth Planet. Sci. Lett.* 392, 250-264.  
830  
831       Dreybrodt, W., Deininger, M., 2014. The impact of evaporation to the isotope  
832       composition of DIC in calcite precipitating water films in equilibrium and kinetic  
833       fractionation models. *Geochimica et Cosmochimica Acta* 125, 433-439.  
834       <http://dx.doi.org/10.1016/j.gca.2013.10.004>.  
835  
836       Eagle, R.A., Eiler, J.M., Tripathi, A.K., Ries, J.B., Freitas, P.S., Hiebenthal, C.,  
837       Wanamaker, A.D., Taviani, M., Elliot, M., Marensi, S., Nakamura, K., Ramirez, P.,  
838       Roy, K., 2013. The influence of temperature and seawater carbonate saturation on  
839        $^{13}\text{C}$ - $^{18}\text{O}$  bond ordering in bivalve mollusks. *Biogeosciences* 10, 4591-4606.  
840       <http://dx.doi.org/10.5194/bg-10-4591-2013>.  
841

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

846

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

851

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

856

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

861

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

864 (Eds.), *Geologic Evolution of the Mojave Desert and Southwestern Basin and*  
865 *Range*. Geological Society of America Memoir 195, Boulder, Colorado, pp. 19-41.  
866

867 Gonyo, A.W., Yu, Z., Bebout, G.E., 2012. Late Holocene change in climate and  
868 atmospheric circulation inferred from geochemical records at Kepler Lake,  
869 south-central Alaska. *J. Paleolimnol.* 48, 55-67.  
870 <http://dx.doi.org/10.1007/s10933-012-9603-8>.  
871

872 Henderson, A.K., Shuman, B.N., 2009. Hydrogen and oxygen isotopic compositions of  
873 lake water in the western United States. *Geol. Soc. Am. Bull.* 121, 1179–1189.  
874 <http://dx.doi.org/10.1130/B26441.1>.  
875

876 Hendy, C.H., 1971. The isotopic geochemistry of speleothems-I. The calculation of  
877 the effects of different modes of formation on the isotopic composition of  
878 speleothems and their applicability as palaeoclimatic indicators. *Geochimica et*  
879 *Cosmochimica Acta* 35, 801-824.  
880

881 Henkes, G.A., Passey, B.H., Wanamaker, A.D., Grossman, E.L., Ambrose, W.G., Carroll,  
882 M.L., 2013. Carbonate clumped isotope compositions of modern marine mollusk and  
883 brachiopod shells. *Geochimica et Cosmochimica Acta* 106, 307-325.  
884 <http://dx.doi.org/10.1016/j.gca.2012.12.020>.  
885

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

889

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

893

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

897

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

902

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

906

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

909 Geochem. Geophys. Geosyst. 13, 1-15.  
910 <http://dx.doi.org/10.1029/2012GC004132>.  
911  
912 Hu, F.S., Slawinski, D., Wright, H.E., Ito, E., Johnson, R.G., Kelts, K.R., McEwan, R.F.,  
913 Boedigheimer, A., 1999. Abrupt changes in North American climate during early  
914 Holocene times. *Nature* 400, 437-440.  
915  
916 Hu, F.S., Ito, E., Brown, T.A., Curry, B.B., Engstrom, D.R., 2001. Pronounced Climatic  
917 Variations in Alaska during the Last Two Millennia. *Proc. Natl. Acad. Sci.* 98,  
918 10552-10556. <http://dx.doi.org/10.1073/pnas.181333798>.  
919  
920 Huang, X., Oberhänsli, H., von Suchodoletz, H., Prasad, S., Sorrel, P., Plessen, B.,  
921 Mathis, M., Usabaliev, R., 2014. Hydrological changes in western Central Asia  
922 (Kyrgyzstan) during the Holocene as inferred from a palaeolimnological study  
923 in lake Son Kul. *Quat. Sci. Rev.* 103, 134-152.  
924 <http://dx.doi.org/10.1016/j.quatscirev.2014.09.012>.  
925  
926 IPCC, 2014. *Climate Change 2014: Synthesis Report. Contribution of Working*  
927 *Groups I, II and III to the Fifth Assessment Report of the Intergovernmental*  
928 *Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer*  
929 *(eds.)]. IPCC, Geneva, Switzerland, 151 pp.*  
930

931 Jenny, H., 1994. Factors of Soil Formation: A System of Quantitative Pedology. Dover,  
932 New York.  
933

934 Ji, H., Passey, B.H., Li, S., Levin, N.E., 2014. Triple oxygen isotopes in soils and lakes.  
935 In: 2014 GSA Annual Meeting (Vancouver, British Columbia).  
936

937 Jones, M.D., Leng, M.J., Roberts, C.N., Türkeş, M., Moyeed, R., 2005. A coupled  
938 calibration and modelling approach to the understanding of dry-land lake  
939 oxygen isotope records. *J. Paleolimnol.* 34, 391-411.  
940 <http://dx.doi.org/10.1007/s10933-005-6743-0>.  
941

942 Jones, M.D., Imbers, J., 2010. Modeling Mediterranean lake isotope variability. *Global*  
943 *Planet. Change* 71, 193-200.  
944 <http://dx.doi.org/10.1016/j.globplacha.2009.10.001>.  
945

946 Katz, A., Kolodny, Y., Nissenbaum, A., 1977. The geochemical evolution of the  
947 Pleistocene Lake Lisan-Dead Sea system. *Geochimica et Cosmochimica Acta* 41,  
948 1609-1626.  
949

950 Kim, S.T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects  
951 in synthetic carbonates. *Geochimica et Cosmochimica Acta* 61, 3461-3475.  
952 [http://dx.doi.org/10.1016/S0016-7037\(97\)00169-5](http://dx.doi.org/10.1016/S0016-7037(97)00169-5).  
953

954 Kirby, M.E., Mullins, H.T., Patterson, W.P., Burnett, A.W., 2002. Late glacial-Holocene  
955 atmospheric circulation and precipitation in the northeast United States  
956 inferred from modern calibrated stable oxygen and carbon isotopes. *Geol. Soc.  
957 Am. Bull.* 114, 1326-1340.  
958

959 Kronfeld, J., Vogel, J.C., Rosenthal, E., Weinstein-Evron, M., 1988. Age and  
960 paleoclimatic implications of the Bet Shean travertines. *Quat. Res.* 30, 298-303.  
961

962 Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data  
963 from lake sediment archives. *Quat. Sci. Rev.* 23, 811-831.  
964 <http://dx.doi.org/10.1016/j.quatscirev.2003.06.012>.  
965

966 Li, H., Ku, T., 1997.  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  covariance as a paleohydrological indicator for closed-  
967 basin lakes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 133, 69-80.  
968

969 Li, H., Ku, T., Stott, L.D., Anderson, R.F., 1997. Stable isotope studies on Mono Lake  
970 (California). 1.  $\delta^{18}\text{O}$  in lake sediments as proxy for climatic change during the  
971 last 150 years. *Limnol. Oceanogr.* 42, 230-238.  
972

973 Li, H., Xu, X.M., Ku, T.L., You, C.F., Buchheim, H.P., Peters, R., 2008. Isotopic and  
974 geochemical evidence of palaeoclimate changes in Salton Basin, California,  
975 during the past 20 kyr: 1.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  records in lake tufa deposits.  
976 *Palaeogeogr. Palaeoclimat. Palaeoecol.* 259, 182-197.

977

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

981

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

986

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

989

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

994

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

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

998

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

1022 mineralogical records of lake conditions, processes, and climate. *J. Quat. Sci.* 20,  
1023 3-19.

1024

1025 Passey, B.H., Levin, N.E., Cerling, T.E., Brown, F.H., Eiler, J.M., 2010. High-  
1026 temperature environments of human evolution in East Africa based on bond ordering  
1027 in paleosol carbonates. *Proc. Natl. Acad. Sci.* 107, 11245-11249.  
1028 <http://dx.doi.org/10.1073/pnas.1001824107>.

1029

1030 Passey, B.H., Hu, H., Ji, H., Montanari, S., Li, S., Henkes, G.A., Levin, N.E., 2014. Triple  
1031 oxygen isotopes in biogenic and sedimentary carbonates. *Geochimica et*  
1032 *Cosmochimica Acta* 141, 1-25. <http://dx.doi.org/10.1016/j.gca.2014.06.006>.

1033

1034 Petryshyn, V.A., Lim, D., Laval, B.L., Brady, A., Slater, G., Tripathi, A.K., 2015.  
1035 Reconstruction of limnology and microbialite formation conditions from  
1036 carbonate clumped isotope thermometry. *Geobiol.* 13, 53-67.

1037

1038 Piovano, E.L., Ariztegui, D., Bernasconi, S.M., McKenzie, J.A., 2004. Stable isotopic  
1039 record of hydrological changes in subtropical Laguna Mar Chiquita (Argentina)  
1040 over the last 230 years. *Holocene* 14, 525-535.

1041

1042 Quade, J., Rech, J.A., Latorre, C., Betancourt, J.L., Gleeson, E., Kalin, M.T.K., 2007. Soils  
1043 at the hyperarid margin: The isotopic composition of soil carbonate from the

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

1067

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

1071

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

1075

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

1079

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

1082

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

1085

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

1089

1090 Trabucco, A., Zomer, R.J., 2009. Global Aridity Index (Global-Aridity) and Global  
1091 Potential Evapo-Transpiration (Global-PET) Geospatial Database. CGIAR  
1092 Consortium for Spatial Information. Published online, available from the CGIAR-  
1093 CSI GeoPortal at: <http://www.csi.cgiar.org/>  
1094

1095 Ufnar, D.F., Gröcke, D.R., Beddows, P.A., 2008. Assessing pedogenic calcite stable-  
1096 isotope values: Can positive linear co-variant trends be used to quantify palaeo-  
1097 evaporation rates? *Chem. Geol.* 256, 46-51.  
1098 <http://dx.doi.org/10.1016/j.chemgeo.2008.07.022>.  
1099

1100 Urey, H.C., Brickwedde, F.G., Murphy, G.M., 1932. A hydrogen isotope of mass 2.  
1101 *Phys. Rev.* 39, 164-165.  
1102

1103 Valero-Garcés, B.L., Kelts, K., Ito, E., 1995. Oxygen and carbon isotope trends and  
1104 sedimentological evolution of a meromictic and saline lacustrine system: the  
1105 Holocene Medicine Lake basin, North American Great Plains, USA. *Palaeogeogr.*  
1106 *Palaeoclimatol. Palaeoecol.* 117, 253-278.  
1107

1108 Valero-Garcés, B.L., Delgado-Huertas, A., Ratto, N., Navas, A., 1999. Large <sup>13</sup>C  
1109 enrichment in primary carbonates from Andean Altiplano lakes, northwest  
1110 Argentina. *Earth Planet. Sci. Lett.* 171, 253-266.  
1111

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

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

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

1137

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

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

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

1141

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

1143 during degassing of CO<sub>2</sub>. *Mineral. Deposita* 25, 246-250.

1144

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1147

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1159 **Figure Captions**

1160

1161 **Fig. 1.** Aridity index (P:E) map of western North America (equidistant conic projection) showing  
1162 modern meteoric (white snowflakes), river (blue circles) and lake (light blue triangles) water sample  
1163 collection sites (Friedman, 2000; Coplen and Kendall, 2000; Friedman et al., 2002; Henderson and  
1164 Shuman, 2009). 10 of the 38 globally distributed Quaternary paleolake systems, comprising 24 of the  
1165 57 dual element stable isotopic records compiled as part of this review, are also shown (red stars).

1166

1167 **Fig. 2.** Compiled western North America meteoric (a), river (b) and lake (c) water  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$   
1168 compositions reported in Friedman (2000), Coplen and Kendall (2000), Friedman and others (2002),  
1169 and Henderson and Shuman (2009). Regional stable isotopic water line equations represent the  
1170 least-squares linear regression fits through all data points plotted in each panel. Black star (a-c)  
1171 represents standard mean ocean water (SMOW) and thick black line (a-c) represents the global  
1172 meteoric water line (GMWL). Lake water symbols (c) are color coded according to the modern aridity  
1173 index at each sampling site. Panel (d) shows frequency distributions and whisker-box plots of the  
1174  $\delta^{18}\text{O}$  shift away from the global meteoric water line along an evaporation line of slope 4.5 for each  
1175 sample type. Vertical lines in the whisker-box plots (d) represent, minimum, lower quartile, median,  
1176 upper quartile, and maximum  $\delta^{18}\text{O}$  shift values observed.

1177

1178 **Fig. 3.** Comparison of modeled meteoric water  $\delta^{18}\text{O}$  values (Bowen, 2014) and observed lake water  
1179  $\delta^{18}\text{O}$  values reported in Friedman (2000), Coplen and Kendall (2000), Friedman and others (2002),  
1180 and Henderson and Shuman (2009). Meteoric water values were calculated for the same month in  
1181 which each lake water sample was collected. Symbols are color coded according to the modern  
1182 aridity index at each lake water sampling site. Solid line represents a 1:1 (i.e. no difference)  
1183 relationship. Labeled dashed lines represent +10‰ and +20‰  $^{18}\text{O}$  lake water enrichments relative  
1184 to local temporally matched meteoric water.

1185

1186 **Fig. 4.** Evaporation experiment results for three South Island, New Zealand, water samples, including  
1187 one upland river (circles), one groundwater sample (inverted triangles) and one coastal lowland  
1188 stream (upright triangles). Symbols in all panels are color coded by %-water evaporated. Panel (a)  
1189 shows the near constant evaporation rate of all three samples, panel (b) shows the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$   
1190 isotopic response to evaporation, and panel (c) shows the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ -DIC response. Thick black  
1191 line and black star in (b) represent the GMWL and SMOW, respectively. Thin black lines in all panels

1192 represent least-squares linear regression fits. Each sample was allowed to evaporate for ~6 days in a  
1193 500ml beaker at 21°C.

1194

1195 **Fig. 5.** Global aridity index map (a) showing location (red stars) of the fifty-seven Quaternary lake  
1196 carbonate dual element  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  records (>11,200 total data points), from thirty-eight discrete  
1197 lake systems, compiled as part of this review. Panel (b) presents the least-squares linear regression  
1198 fits to these isotopic records. Black regression lines correspond with records exhibiting a statistically  
1199 significant correlation between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . Red regression lines correspond with records  
1200 exhibiting no significant correlation. Dashed line represents a 1:1 (i.e.  $m=1$ ) relationship. All data  
1201 were normalized to the mean isotopic composition of each record using an additive shift.

1202

1203 **Fig. 6.** Modeled isotopic equilibrium summer month lake calcite  $\delta^{18}\text{O}$  values (see text for details)  
1204 plotted against the average lake carbonate  $\delta^{18}\text{O}$  value in each of the fifty-seven Quaternary records  
1205 we compiled. Symbols are color coded according to modern aridity index values with whiskers  
1206 showing  $\pm 1\sigma$ . Solid black line represents a 1:1 (i.e. no difference) relationship. Labeled dashed lines  
1207 correspond with -5‰, +5‰, +10‰ and +15‰  $^{18}\text{O}$  depletion/enrichments in observed lake  
1208 carbonate isotopic composition relative to modeled summer lake calcite compositions.

1209

1210 **Fig. 7.**  $\delta^{13}\text{C}$  versus  $\delta^{18}\text{O}$  bivariate plots for Quaternary lake carbonate records where modern source  
1211 (i.e. inflow) water and lake water  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ -DIC values were available from the literature. Green  
1212 stars represent the isotopic equilibrium composition of calcite forming in equilibrium with source  
1213 water at each site's mean annual air temperature. Red stars represent the isotopic equilibrium  
1214 composition of calcite forming in equilibrium with lake water at each site's mean annual air  
1215 temperature. Quaternary lake carbonate data symbols as indicated in panel legends. Solid black line  
1216 represents a 1:1 relationship; dashed lines represent  $\pm 5\%$  differences between lake carbonate  $\delta^{18}\text{O}$   
1217 and  $\delta^{13}\text{C}$ . Mono Lake tufa data are original to this study. See Table 1 for all other primary data  
1218 sources. Modern hypsometric altitudes ( $z_{\text{hyp}}$ ) are shown in (a-d).

1219

1220 **Fig. 8.**  $\delta^{13}\text{C}$  versus  $\delta^{18}\text{O}$  bivariate plots for Cerling and Quade's (1993) modern aridisol soil  
1221 carbonates from the western U.S. Great Basin/Mojave Desert region (a), and middle Miocene  
1222 (~15Ma) laminated lacustrine carbonates from the Mojave Desert's Mud Hills area Barstow  
1223 Formation and Otago New Zealand's Lake Manuherikia sequence Bannockburn Formation at Vinegar  
1224 Hill (b). Pedogenic soil carbonate symbols in (a) are color-coded based on modern aridity index. Solid

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

Table 1

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

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

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

Sample (Age)	Number of Analyses	$\delta^{13}\text{C}$ (‰) <sup>1</sup>	$\delta^{18}\text{O}$ (‰) <sup>1</sup>	$\Delta_{47}$ (‰) <sup>2</sup>	$\Delta_{47}$ -Temperature (°C) <sup>3</sup>	$\delta^{18}\text{O}_{\text{water}}$ (‰) <sup>4</sup>
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

<sup>1</sup> Relative to V-PDB<sup>2</sup> On absolute reference frame<sup>3</sup> Determined using the calibration of Defliese and others (2015)<sup>4</sup> Relative to V-SMOW

Figure 1  
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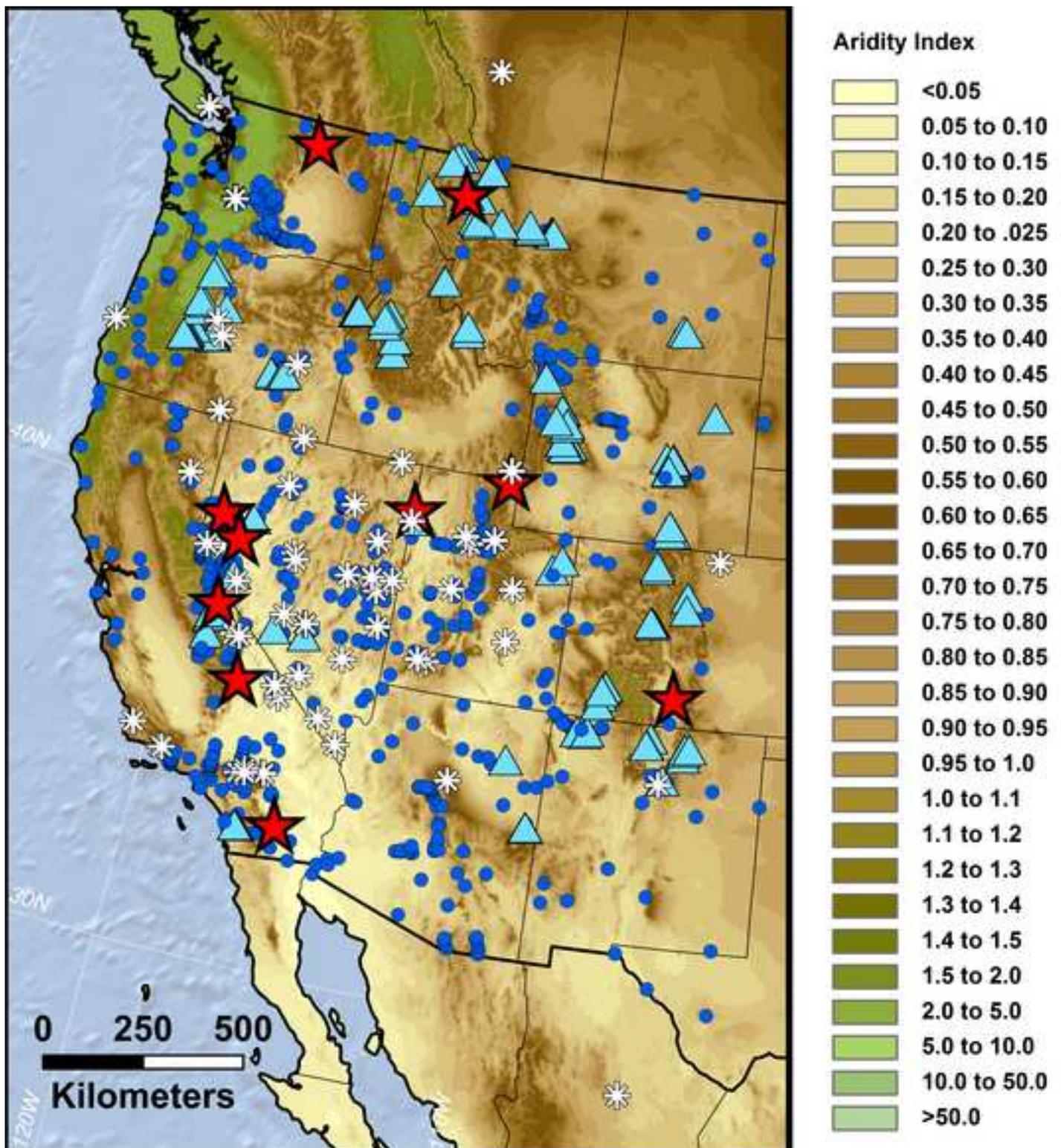


Figure 2

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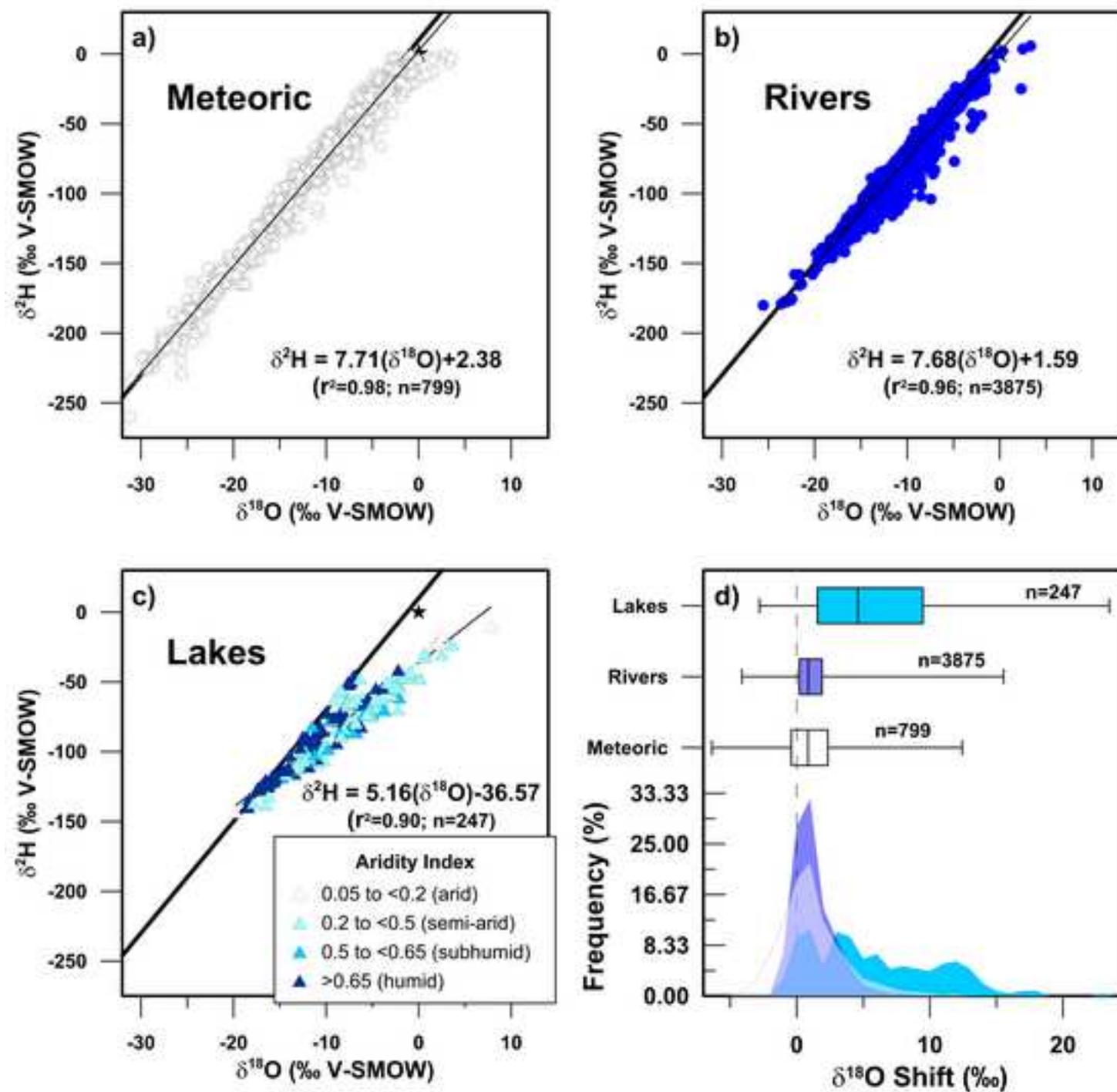


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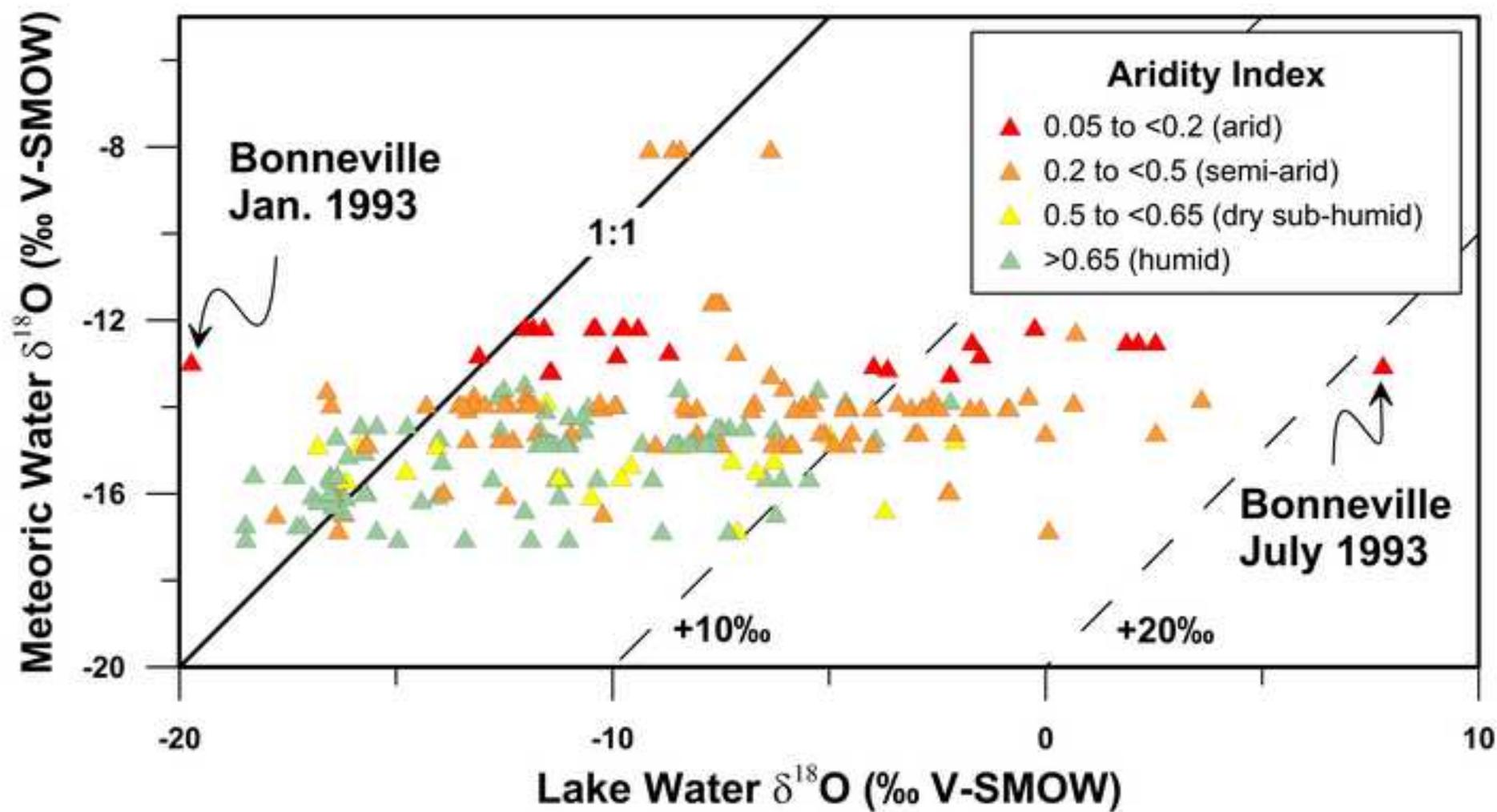


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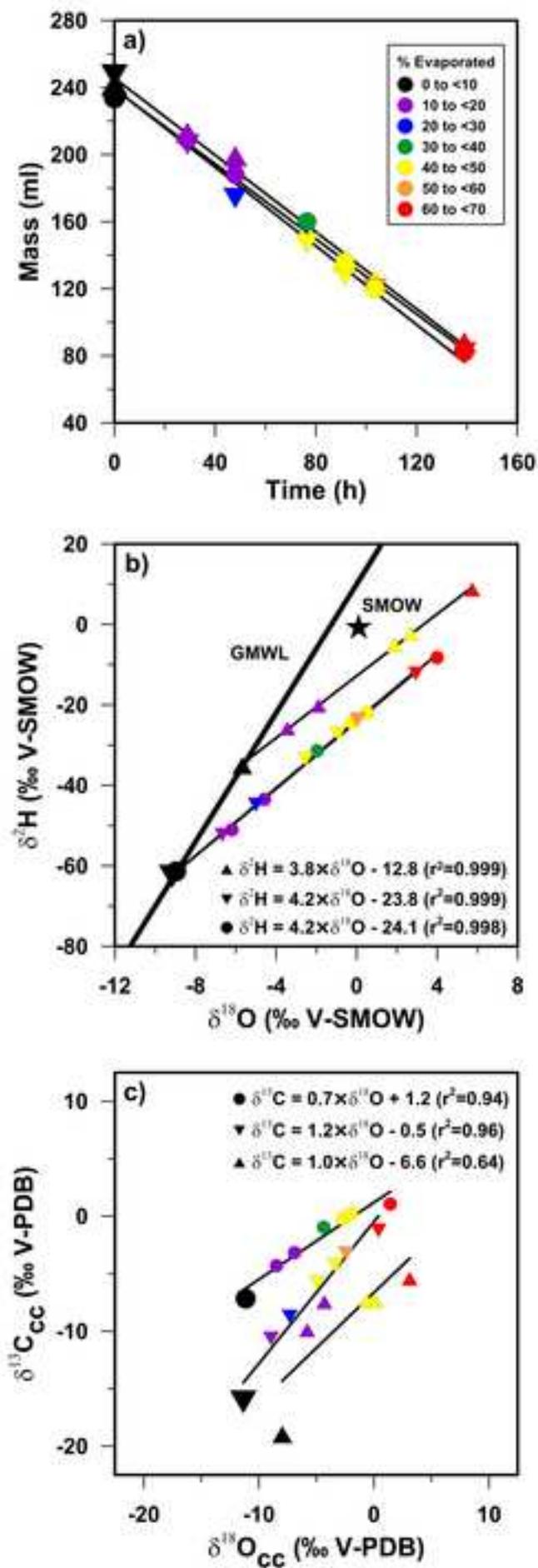


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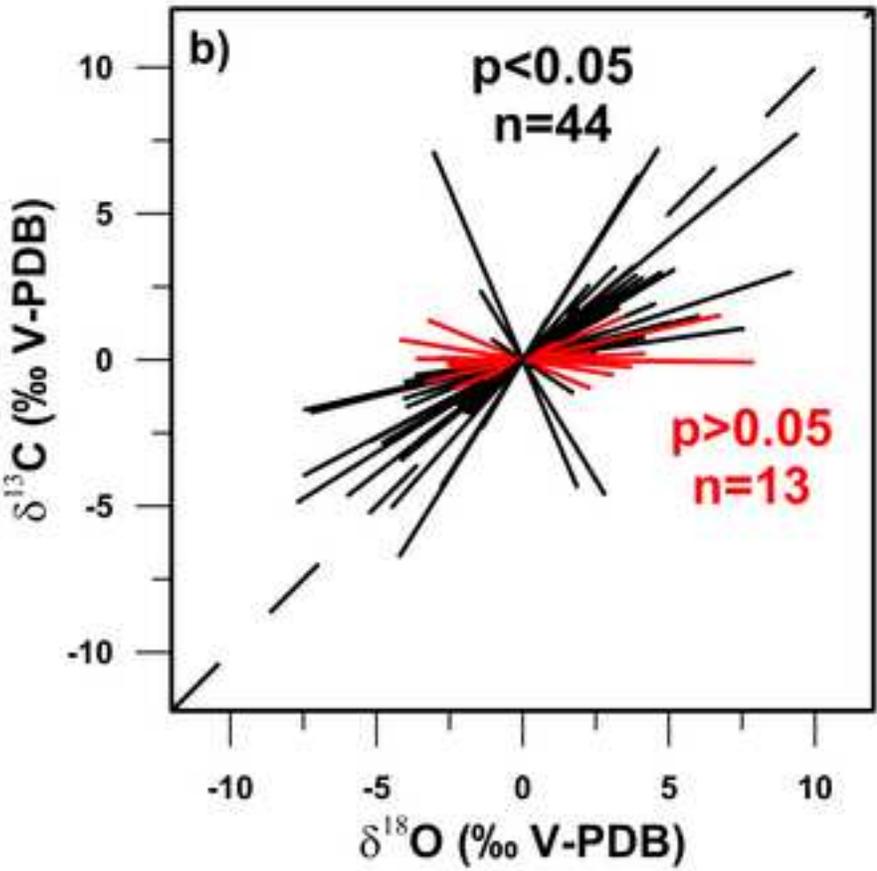


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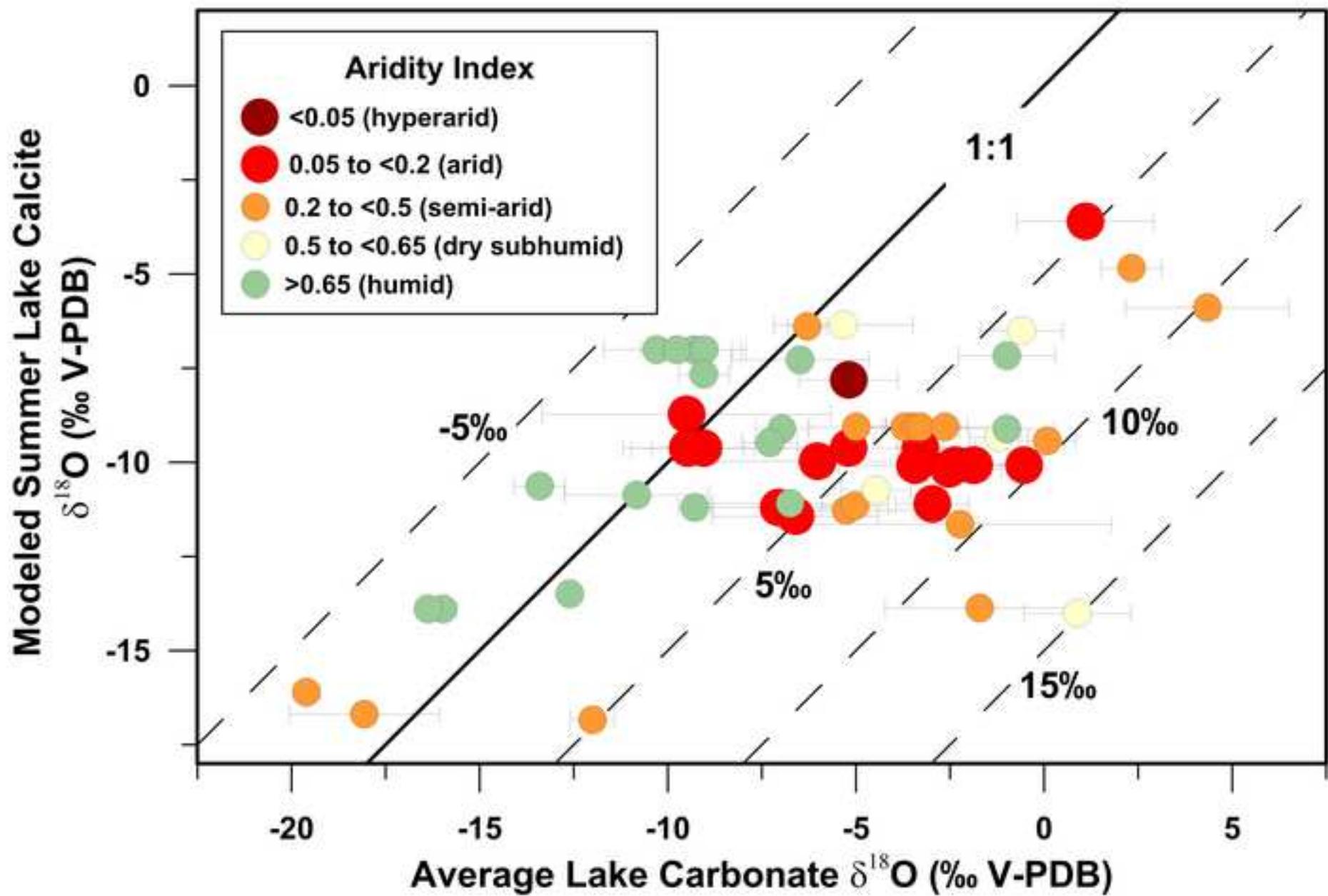


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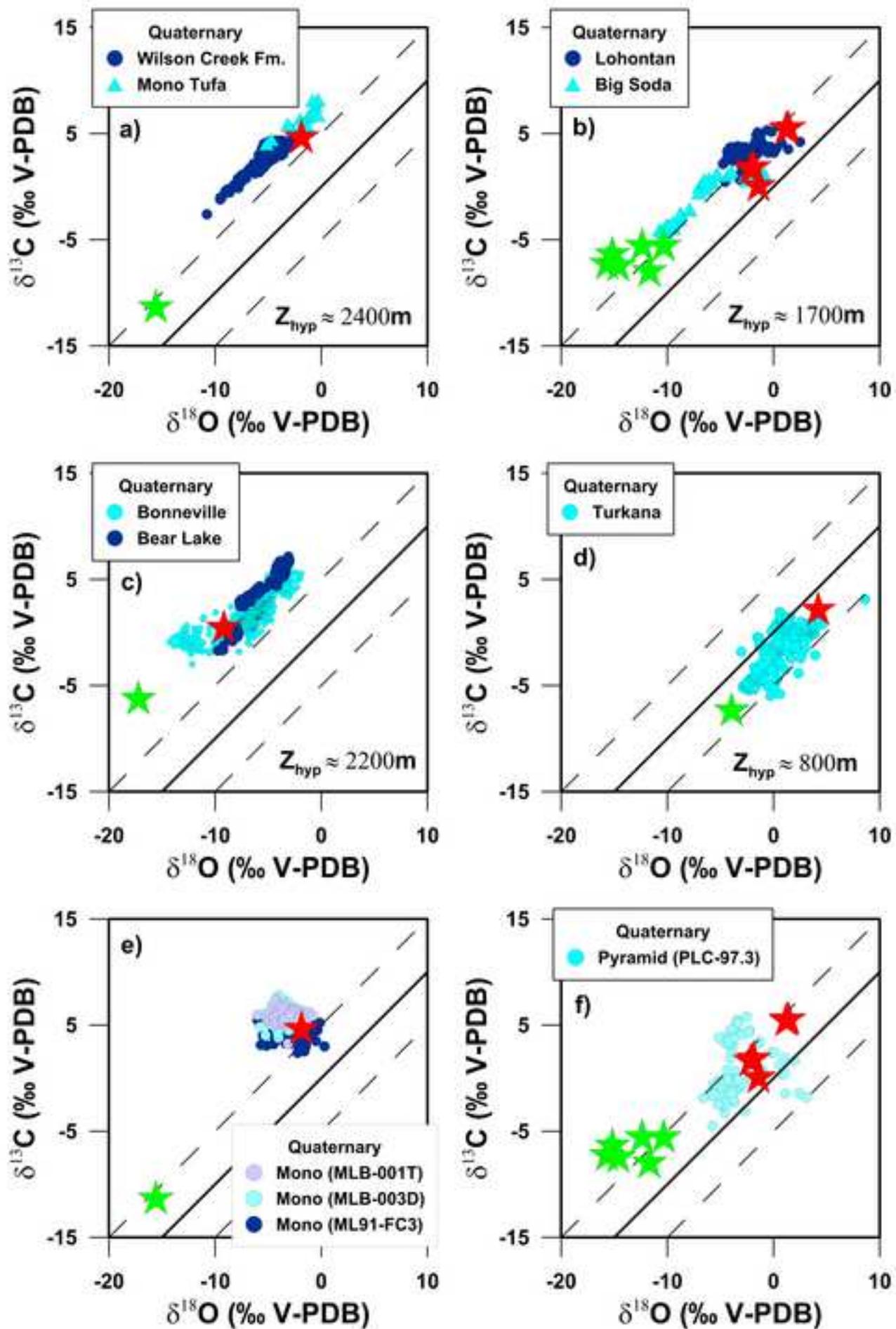
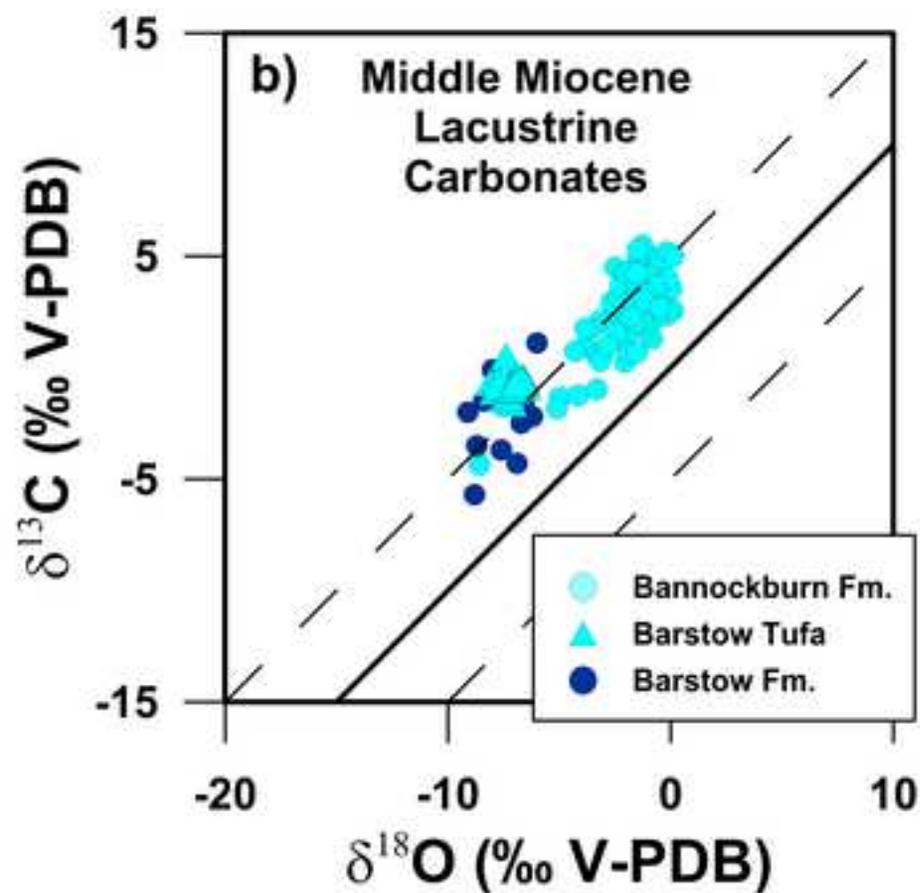
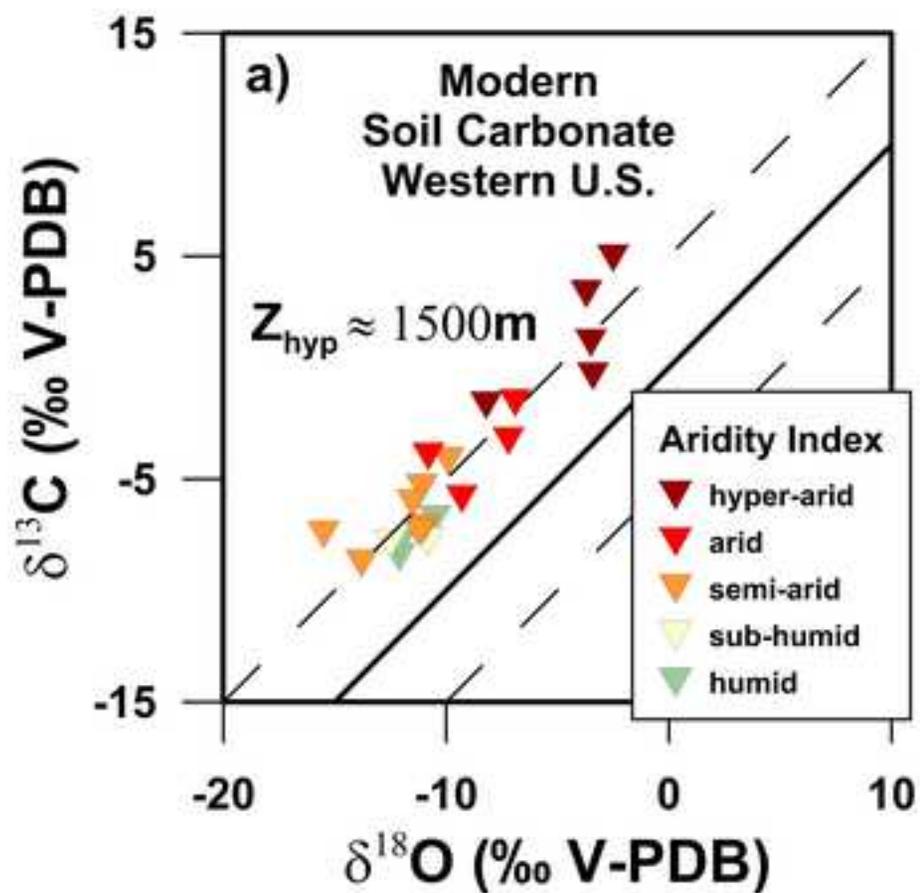


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