Quaternary Science Reviews xxx (2015) 1–15

Contents lists available at ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

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

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ARTICLE INFO

*Article history:*
Received 3 January 2015
Received in revised form
23 June 2015
Accepted 29 June 2015
Available online xxx

*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
Western U.S.
Sierra Nevada
Southern Alps New Zealand

ABSTRACT

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

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

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

## 1. Introduction

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

Endogenic lacustrine minerals are particularly attractive

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http://dx.doi.org/10.1016/j.quascirev.2015.06.030
0277-3791/© 2015 Published by Elsevier Ltd.

Please cite this article in press as: Horton, T.W., et al., Evaporation induced $^{18}O$ and $^{13}C$ enrichment in lake systems: A global perspective on hydrologic balance effects, Quaternary Science Reviews (2015), http://dx.doi.org/10.1016/j.quascirev.2015.06.030

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

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

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

## 2. Materials and analytical methods

### 2.1. Global lake carbonate stable isotope compilation

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

### 2.2. Western U.S. modern water stable isotope compilation

We compiled modern meteoric, river, and lake water $\delta^{2}$H and $\delta^{18}$O values from a variety of published sources (Friedman, 2000; Coplen and Kendall, 2000; Friedman et al., 2002; Henderson and Shuman, 2009). This compilation includes 799 individual meteoric water analyses, 3875 river water analyses, and 247 lake water analyses predominantly from the western U.S. (Fig. 1). Aridity index values were extracted for each location as described above. For more information regarding these data, please refer to the primary sources.

### 2.3. Evaporation experiments

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

$\delta^{13}$C-DIC values were determined using the Spötl (2005) method. In brief, 1 ml sub-samples were injected into ultra-high purity (>99.999%) helium flushed 10 ml borosilicate exetainer vials pre-loaded with 103% phosphoric acid. Dissolved inorganic carbon (DIC) derived $CO_2$, liberated by the acid–water reaction, was analyzed using a ThermoFinnigan GasBench II coupled to a ThermoFinnigan DeltaV$^{+}$ isotope ratio mass spectrometer operating under a continuous flow of ultra-high purity helium. $\delta^{13}$C-DIC values were two-point normalized to the VPDB scale based on replicate analysis of IAEA certified reference materials NBS18 and NBS19. All $\delta^{13}$C-DIC values are precise to <0.10‰.

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

### 2.4. Stable isotopic analysis of lake carbonates

Quaternary (Mono Lake tufa) and middle Miocene laminated lacustrine carbonates (Barstow Fm. tufa, California, U.S.A.; Bannockburn Fm. oncholite, Otago, New Zealand) were analyzed for $\delta^{18}$O and $\delta^{13}$C in the stable isotope analytical facility at the University of Canterbury. Hand samples were cut into flat slabs and milled at 0.5 mm resolution using a diamond-coated Dremel tool parallel to the growth axis. $\delta^{18}$O and $\delta^{13}$C of acidified (103% phosphoric acid) sample powders were determined using a ThermoFinnigan GasBench II coupled to a ThermoFinnigan DeltaV$^{+}$ isotope ratio mass spectrometer operating under continuous ultra-high purity He flow conditions. $\delta^{18}$O and $\delta^{13}$C values were two-point normalized to the VPDB scale based on replicate analysis of IAEA certified reference materials NBS18 and NBS19. A MERCK carbonate internal lab standard was also analyzed at regular intervals throughout each analytical sequence. All laminated lacustrine carbonate $\delta^{18}$O and $\delta^{13}$C values are precise to <0.10‰.

$\Delta_{47}$ values for the middle Miocene Barstow Fm. Tufa, middle

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