Triple oxygen and hydrogen isotopes of gypsum hydration water for quantitative paleo-humidity reconstruction

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A R T I C L E   I N F O

A B S T R A C T

Atmospheric relative humidity is an important parameter affecting vegetation yet paleo-humidity proxies are scarce and difficult to calibrate. Here we use triple oxygen ($\delta^{17}O$ and $\delta^{18}O$) and hydrogen (δD) isotopes of structurally-bound gypsum hydration water (GHW) extracted from lacustrine gypsum to quantify past changes in atmospheric relative humidity. An evaporation isotope-mass-balance model is used together with Monte Carlo simulations to determine the range of climatological conditions that simultaneously satisfy the stable isotope results of GHW, and with statistically robust estimates of uncertainty. We apply this method to reconstruct the isotopic composition of paleo-waters of Lake Estanya (NE Spain) and changes in normalized atmospheric relative humidity (RH_n) over the last glacial termination and Holocene (from ~15 to 0.6 cal. kyrs BP). The isotopic record indicates the driest conditions occurred during the Younger Dryas (YD; ~12–13 cal. kyrs BP). We estimate a RH_n of ~40–45% during the YD, which is ~30–35% lower than today. Because of the southward displacement of the Polar Front to ~42°N, it was both windier and drier during the YD than the Bølling–Allerød period and Holocene. Mean atmospheric moisture gradually increased from the Preboreal to Early Holocene (~11 to 8 cal. kyrs BP, 50–60%), reaching 70–75% RH_n from ~7.5 cal. kyrs BP until present-day. We demonstrate that combining hydrogen and triple oxygen isotopes in GHW provides a powerful tool for quantitative estimates of past changes in relative humidity.

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1. Introduction

The presence of gypsum ($CaSO_4 \cdot 2H_2O$) in lacustrine sediments is commonly interpreted as evidence of dry climatic conditions in the past (Hodell et al., 1995, 2005, 2012; Torfstein et al., 2008; Morellón et al., 2009a; Escobar et al., 2012, amongst many others). Evaporation of Ca^{2+}–SO_4^{2-}-rich lake waters can lead to gypsum supersaturation under conditions of high evaporation relative to inflow (surficial and/or subterranean water intakes). These conditions are generally accompanied by decreased input of fine-grained allochthonous sediments as a result of decreasing runoff, resulting in sediments that are dominantly composed of gypsum. Interbedded layers of gypsum and other non-evaporitic facies (e.g. clay minerals) in lakes are often attributed to alternating wet and dry conditions (e.g. Hodell et al., 1995; Ortiz et al., 2006; Morellón et al., 2009a; Escobar et al., 2012; Valero-Garcés et al., 2014; Li et al., 2017).

The isotopic composition of lake waters is sensitive to long-term changes in the Evaporation/Inflow (E/I) regime and normalized atmospheric relative humidity (RH_n), defined as water vapor concentration in the air divided by the saturated vapor concentration at lake surface temperature (e.g. Uemera et al., 2010; Gibson et al., 2016). In addition to E/I and RH_n, climatic variations recorded in lacustrine carbonates (i.e. $\delta^{18}O$ of authigenic carbonates) can be masked by the effect of temperature on the

oxygen isotopic value during carbonate precipitation (Hodell et al., 2012). In contrast, structurally-bound gypsum hydration water (GHW) can be used to reconstruct the isotopic value of paleo-lake waters with little to no effect of temperature. The fractionation factors for oxygen and hydrogen isotopes between the free solution and GHW are largely independent of temperature in the range of most lakes (e.g. 10–35 °C; Gázquez et al., 2017a). Thus, the oxygen and hydrogen isotopes ($\delta^{18}O$ and δD) of GHW can be used to infer the isotopic composition of paleo-lake waters at the time of gypsum precipitation (Hodell et al., 2012; Grauel et al., 2016; Li et al., 2017). GHW retains the isotopic values of the parent solution provided that it has not been altered by post-depositional processes (e.g. exposure to temperature >50 °C after deposition, solution-reprecipitation, etc.). Whether the original isotopic composition of GHW has been preserved or not must be evaluated on a case-by-case basis (Hodell et al., 2012; Evans et al., 2015; Gázquez et al., 2017a).

Recent analytical developments permit precise measurements of triple oxygen isotopes ($^{17}O/^{18}O/^{16}O$), and the derived parameter ^{17}O-excess (also called $\Delta^{17}O$), in natural waters (Luz and Barkan, 2010; Steig et al., 2014) and GHW (Gázquez et al., 2015) with precision better than $\pm 0.01\permil$ (i.e. 10 per meg; $\pm 1\sigma$). This parameter is defined as:

$$^{17}O\text{-excess} = \ln(\delta^{17}O + 1) - 0.528\ln(\delta^{18}O + 1) \qquad (1)$$

where: $\delta^{17}O$ and $\delta^{18}O$ denote the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ in water standardized to the VSMOW-SLAP scale (Barkan and Luz, 2005; Luz and Barkan, 2010; Schoenemann et al., 2013). The value of 0.528 describes the $\delta^{17}O$ and $\delta^{18}O$ relationship in rainwater worldwide (Luz and Barkan, 2010). The ^{17}O-excess averages ~37 per meg with respect to V-SMOW in modern meteoric waters and shows lower values in evaporated water (Luz and Barkan, 2010; Steig et al., 2014; Li et al., 2015; Surma et al., 2015; Gázquez et al., 2017b). The trajectory of $\delta^{18}O$ and ^{17}O-excess in evaporated water is relatively insensitive to temperature and salinities below 100 g/l (Luz and Barkan, 2010; Passey et al., 2014); however, it is significantly affected by other parameters such as the hydrological balance of the water body and atmospheric relative humidity (Surma et al., 2015; Gázquez et al., 2017b; Herwartz et al., 2017; see Fig. 1).

Despite the potential of lake sediments as palaeoclimatic archives, stable isotopes in inorganic and organic proxies often allow only qualitative interpretation of past hydrological changes. Quantitative reconstructions from isotope proxy data, including changes in atmospheric relative humidity, have been difficult to achieve and calibrate. Here we evaluate the potential of using triple oxygen and hydrogen isotopes in lacustrine GHW to quantify changes in atmospheric relative humidity in the past. We use a Raleigh evaporation isotope-mass-balance (IMB) to quantitatively determine climatic conditions at the time of gypsum precipitation. Monte Carlo simulations are used to find the most probable solution to the model and evaluate uncertainties in RH_n. We apply this method to isotopic data ($\delta^{17}O$, $\delta^{18}O$ and δD, and derived d-excess and ^{17}O-excess) of GHW from Lake Estanya (Southern Pre-Pyrenees, NE Spain) to infer climate during the Late Glacial and Holocene periods (ca. 15 cal. kyrs BP to 0.6 cal. kyrs BP). We model the isotopic values of paleo-lake Estanya under different environmental/geochemical scenarios. We compare the isotopic results and derived RH_n values with previous sedimentological and geochemical proxies in the lake sequence (Morellón et al., 2009b), as well as other biological indicators such as pollen, diatoms and chironomids (Morellón et al., 2011; Vegas-Vilarrúbia et al., 2013; González-Sampériz et al., 2017). Lastly, we discuss more generally the potential application of the method to other lakes.

2. Approach and model

The oxygen ($\delta^{17}O$ and $\delta^{18}O$) and hydrogen (δD) isotopic composition of lake waters increase with more arid conditions and higher evaporation relative to inflow (E/I). Each isotope ratio follows a slightly different fractionation leading to variability in d-excess and ^{17}O-excess parameters (Surma et al., 2015; Gibson et al., 2016; Herwartz et al., 2017; and references therein). The isotopic evolution of water during evaporation (e.g. $\delta^{18}O$ vs ^{17}O-excess and $\delta^{18}O$ vs d-excess) depends on the isotopic composition of the initial water (inflow), temperature and RH_n, the isotopic composition of the water vapor in equilibrium with the liquid water and the ratio of water loss by evaporation (E) with respect to the inflow (I), with the remainder lost as outflow. The process is described by the expression (Criss, 1999):

$$^*R_{WS} = \frac{^*\alpha^0_{evap} \cdot (1 - h_n) \cdot {}^*R_{WI} + {}^*\alpha^0_{eq} \cdot h_n \cdot E/I \cdot R_v}{E/I + {}^*\alpha^0_{evap} \cdot (1 - h_n) \cdot (1 - E/I)} \qquad (2)$$

where $^*R_{WS}$ is the isotopic ratio of the evaporated water. $^*\alpha^0_{evap}$ is the effective fractionation factor, calculated as a product of the equilibrium fractionation factor ($^*\alpha^0_{eq}$) and the diffusive fractionation factor ($^*\alpha^0_{diff}$) between the liquid water and vapor. The parameter h_n is the normalized relative humidity of air (0 to 1). Note that h_n is not necessarily the same as RH in the open atmosphere because the temperature at the lake surface can differ from the air temperature at the boundary layer. R_{WI} is the isotopic ratio of the input prior to evaporation (i.e., the inflow to the lake). R_v is the isotopic ratio of the vapor and depends on the degree to which the atmospheric water vapor (v_{eq}) is in equilibrium with R_{WI} (Gibson et al., 2016), where:

$$R_v = R_{WI} * (\alpha^0_{eq} * v_{eq}) \qquad (3)$$

E/I represents the fraction of water loss by evaporation with respect to the inflow from the system (e.g. $E/I = 0$ means no evaporation whereas $E/I = 1$ means all the water is lost to evaporation; i.e. there is no outflow). This model assumes homogeneous isotopic composition of both the liquid and vapor phases.

Equilibrium fractionation factors for $\delta^{18}O$ and δD are well known and calculated here as a function of temperature using the equations of Horita and Wesolowski (1994). $\alpha^{17}O^0_{eq}$ is calculated as $\alpha^{17}O^0_{eq} = \alpha^{18}O^0_{eq}{}^\theta$, where θ is 0.529 ± 0.001 (Barkan and Luz, 2005). Kinetic fractionation during evaporation under natural conditions is not as strongly constrained as equilibrium fractionation. Here we use a combination of natural and laboratory experiments to calculate α^0_{diff} (Landais et al., 2006; Barkan and Luz, 2007, Luz et al., 2009). First, $\alpha^{18}O^0_{diff}$ varies as a function wind driven turbulence (Dongmann et al., 1974; Uemura et al., 2010; Haese et al., 2013) (see discussion section) and is calculated as:

$$\alpha^{18}O^0_{diff} = 1.0283^w \qquad (4)$$

where w varies between 0.5 (pure turbulent mixing; $\alpha^{18}O^0_{diff} = 1.0141$) and 1.0 (pure diffusion; $\alpha^{18}O^0_{diff} = 1.0283$). $\alpha^{17}O^0_{diff}$ is calculated as $\alpha^{17}O^0_{diff} = \alpha^{18}O^0_{diff}{}^\theta$, where θ is 0.5185 (Landais et al., 2006; Barkan and Luz, 2007).

αD^0_{diff} varies as a function of $\alpha^{18}O^0_{diff}$ and temperature (T, in °C) based on experiments by Luz et al. (2009), where:

$$\alpha D^0_{diff} = (1.25 - 0.02T)(\alpha^{18}O^0_{diff} - 1) + 1 \qquad (5)$$

In $\delta^{18}O$–^{17}O-excess and $\delta^{18}O$–d-excess space (Fig. 1), the predicted trends of waters undergoing evaporation in partial equilibrium with atmospheric vapor take the form of curves. We see that both ^{17}O-excess and d-excess are largely sensitive to RH_n during