

Polissar & Freeman (2010)

Effects of Aridity and Vegetation on Plant-wax δD in Modern Lake Sediments

Electronic annex EA-1

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1. PRECIPITATION ISOTOPES FROM LAKEWATERS

The lakes in this study are mostly located in remote and topographically complex regions where little information is available on precipitation isotope values. In these locations, stream, spring and lake waters (hereafter termed lake water for brevity) were used to calculate precipitation values.

1.1. Calculation of Precipitation Isotope Values

Precipitation values were calculated for a lake as the intersection between the local evaporation line (LEL) passing through the lake isotope composition and the global meteoric waterline (GMWL). The slope of the LEL was calculated from lake, spring and groundwater isotope values in each region. For regions with large elevation differences for these samples, their isotope values were adjusted to a common reference altitude prior to determining the slope of the LEL:

$$(1) \quad \delta_{z_{ref}} = \delta_z + (z - z_{ref}) \Gamma_{d\delta/dz}$$

The isotopic lapse rate ($\Gamma_{d\delta/dz}$) was determined from published precipitation isotope vs. elevation data for each region (Gonfiantini et al., 2001; Vimeux et al., 2005; Polissar et al., 2006). This adjustment was generally small, but necessary to obtain the best estimate of the LEL (raw and adjusted lakewater values available in the electronic annex EA-4). Evaporation lines were fit to the elevation adjusted $\delta^{18}O$ and δD values using an algorithm that calculates uncertainties in the fitting parameters that include uncertainties in both x - and y -values as well as the dispersion of the data (Press et al., 1994). The slope of the LEL for an individual lake was taken as the slope of the regional LEL while the intercept of the line was calculated from the $\delta^{18}O$ and δD values for that lake (not adjusted for altitude differences):

$$(2) \quad b_{LEL} = \delta D_{LW} - m_{LEL} \delta^{18}O_{LW}$$

The intersection of a lake's LEL with the GMWL (slope of 8 and intercept of 10, Rozanski et al., 1993) was calculated as:

$$(3) \quad \delta^{18}O_{ppt} = \frac{b_{LEL} - b_{GMWL}}{m_{GMWL} - m_{LEL}}$$

Lakewaters, LELs and the GMWL are shown in Figure S1 for each study region.

1.2. Comparison with the Online Isotopes in Precipitation Calculator

One dataset for comparison with the lakewater approach is provided by precipitation isotope values calculated with the Online Isotopes in Precipitation Calculator (OIPC, accessible at wateriso.eas.purdue.edu/waterisotopes/). OIPC values reflect global statistical relations between latitude, elevation and the $\delta^{18}O$ and δD values of precipitation with an empirical spatial correction based upon sites with measured precipitation values (Bowen and Revenaugh, 2003). Most of our study lakes lie far from these sites, often with significant intervening topography that can change air mass isotopic compositions and lead to diverging OIPC and lakewater-derived precipitation values. Therefore, the OIPC comparison provides a general test of the overall range of the data (reflecting the large latitudinal extent of our sites) but is expected to differ in detail within any particular region.

The $\delta^{18}O$ and δD values of precipitation calculated from lakewater and those calculated from the OIPC lie along a 1:1 line (Fig. S2) indicating they both reflect continent-scale spatial patterns of isotopes in precipitation. In detail there are differences between the lakewater and OIPC-derived values, as expected from the data coverage used in the empirical correction to OIPC values. Additional differences could result from watershed hypsometry. OIPC values were calculated at the elevation of each lake while watershed precipitation integrates a range of

elevations above the lake with more negative isotope values. This process would yield lakewater-derived values more negative than the OIPC, as seen at several sites in Fig. S2.

1.3. Comparison with Published Values

In several of our study regions there are published data on meteoric-derived waters (precipitation, stream, lake and groundwater) to compare with our precipitation $\delta^{18}O$ and δD values calculated from surface waters. In Venezuela, the lakewater-derived precipitation isotope values plot along the isotope-elevation relationship determined from lower elevation GNIP and groundwater values (summarized in Polissar et al., 2006). In Nicaragua, Payne and Yurtsever (1974) measured isotope values on precipitation and groundwaters north of Lake Nicaragua. These measurements suggest a range of -5.9 to -7.3 for the $\delta^{18}O$ value of low elevation precipitation, with the more positive value derived from groundwater and thus likely representative of long-term precipitation means. This value is very close to the -5.7 ± 0.4 ‰ value in this study, determined from unevaporated lake waters located west of Lake Nicaragua. In Pennsylvania, O'Driscoll et al. (2005) measured precipitation, soil, stream and groundwaters from two catchments near the Bear Meadows bog area. The $\delta^{18}O$ value for Bear Meadows water (-9.9 ‰ calculated from a δD value of -69 ‰ using the GMWL) is identical to the isotope value of -9.9 ‰ calculated for the elevation of Bear Meadows from the isotope-elevation relationship determined from the data in O'Driscoll et al. ($\delta^{18}O = z * 3.0363 * 10^{-3} - 8.175$).

2. LAKEWATER ISOTOPE ENRICHMENT AND CLIMATE

Our goal is to use the isotopic enrichment of lake water as a measure for isotopic effects of aridity on plant wax δD values. The isotopic enrichment of lake water depends upon the ratio of inflow/evaporation (I/E), atmospheric relative humidity normalized to surface water temperature (h) and the isotopic composition of atmospheric moisture (δ_A):

$$(4) \quad \Delta\delta_L^{SS} = \delta_L - \delta_I = \frac{\delta_I(\epsilon_k - h + \epsilon^*/\alpha^*) + (h\delta_A + \epsilon_k + \epsilon^*/\alpha^*)}{\left(\frac{I}{E} - 1\right)(\epsilon_k + 1 - h) + 1/\alpha^*}$$

where α^* is the equilibrium liquid/vapor isotopic fractionation ($\epsilon = \alpha - 1$) and ϵ_k describes kinetic fractionation during evaporation (modified from Eq. 21 in Gonfiantini, 1986).

During evaporation, the equilibrium and kinetic fractionations, relative humidity and the isotopic composition of atmospheric moisture have an effect on soil and plant waters analogous to that in lakes. Therefore, lakewater isotopic enrichment due to these factors is, to first-order, a useful indicator for the isotopic consequences of evaporation on soil and leaf water (and by inference plant-wax δD). Differences between soil/leafwater and lakewater enrichment should occur due to the inflow/evaporation ratio. In lakes, this ratio is determined by the precipitation/evaporation ratio (P/E), efficiency of watershed runoff vs. evapotranspiration and the watershed and lake areas (c.f. Gibson and Edwards, 2002). The P/E ratio will also affect soil evaporation and potentially leaf evaporation (through water stress and regulation of stomatal conductance), therefore the fundamental non-climatic difference between lake and soil/leaf evaporation is the influence of watershed runoff and lake size on lake evaporation.

We evaluate the effect of watershed runoff and lake size on lakewater enrichment by examining the relationship between lakewater isotopic enrichment and the lake/watershed area ratio (L/W). The L/W ratio correlates with the runoff/evaporation ratio under similar climatic

regimes. Positive correlations between these variables would be expected in systems where L/W rather than climate is the primary determinant of lakewater enrichment, however we find that for most regions and lakes there is not a strong relationship between L/W ratio and isotopic enrichment (Fig. S3). This indicates that for the majority of the lakes climate—not watershed/lake area—is the primary determinant of lakewater enrichment. The exceptions are five lakes with no surface outflow that presumably lose most of their water by evaporation (Laguna Grande de Los Patos, Laguna Verdes Baja, Laguna Verdes Medio, Laguna de la Pata and Laguna Zapatera). Relative to other lakes in a region, these lakes occupy the portion of Fig. S3 where lake/watershed area ratios likely influence isotopic enrichment. The isotopic enrichment of these terminal lakes continues to be sensitive to relative humidity and the isotopic composition of atmospheric moisture but should be insensitive to the inflow/evaporation ratio. We continue to include these lakes in our analysis because their enrichment, while reflecting higher lake/watershed areas, also reflects drier conditions in these regions as indicated by climate data and the slope of the evaporation line (see below). Their inclusion reduces the slope of any relationship between lake isotopic enrichment and plant-wax apparent fractionation because their evaporative enrichment is magnified compared to a lake in the same climatic regime but with a larger watershed.

The observation that climate is a determining factor of lakewater enrichment in our study is supported by climatic data and a negative relationship between the slope of the local evaporation line (LEL) and the magnitude of lakewater enrichment. Precipitation, evaporation and relative humidity from stations across Washington, Utah and Colorado (Fig. S4 and S5) illustrate trends in the evaporative potential of lakes that correlate with differences in the isotopic enrichment of lake waters in our study. Minimal lakewater enrichment occurs in the Cascade

Mountains of Washington State where humidity is higher and the P/E balance is positive. In contrast, lakewater enrichment is large on the Wasatch plateau in central Utah where humidity and P/E are low, and is lower and decreases eastward in the Colorado Rocky Mountains, tracking increases in relative humidity and the P/E ratio.

In Venezuela there are strong east-west climate gradients (Weingarten et al., 1991) that are reflected in lakewater isotope enrichments. Precipitation is 1.4 to 2 times higher in the western slopes of the eastern cordillera (east of the Rio Chama) that includes the Páramo de Mucubají and eastern cordillera regions in our study (EA-4) relative to the western cordillera that includes the Páramo de los Piedras Blancas and Páramo el Banco (Pulwarty et al., 1998). Reduced precipitation in the western cordillera is accompanied by greatly reduced cloud cover and solar radiation. This strong east-west decrease in precipitation and cloudiness is also present in lakewater enrichment, with greater enrichment in the western cordillera (EA-1 and EA-4).

Further evidence that climatic factors are an important component of differences in lakewater enrichment is a negative relationship between the slope of the local evaporation line (LEL) and lakewater enrichment. The LEL slope depends upon the isotopic difference between lake inflow (δ_I) and atmospheric water vapor (δ_A) and relative humidity. If δ_I and δ_A are in isotopic equilibrium, the LEL slope is ~ 4 and is insensitive to relative humidity (Gat, 1995). However, if δ_A is enriched compared to equilibrium with δ_I , the slope of the LEL is responsive and increases with relative humidity. In the strongly seasonal climates that define our study locations, δ_A is very likely enriched relative to equilibrium with δ_I during the seasons where evaporation is strongest (dry season in the tropics, summer in the mid-latitudes). This should impart a negative relationship between the slope of the LEL and lakewater enrichment if relative humidity and δ_A are important determinants of evaporative enrichment. Overall we find that the

slope of the LEL is lower where lake enrichment is greater (Fig. S6), supporting our inference that lakewater enrichment is a useful measure of the evaporative signal in plant-wax δD .

(It is important to note that any errors in the determination of the LEL would in all cases yield positive covariation of enrichment and LEL slope, rather than the negative relationship we observe. The positive correlation is a consequence of positive deviations of the LEL slope yielding negative deviations in precipitation isotope values and larger isotopic enrichments.)

3. ESTIMATION OF UNCERTAINTIES IN REGRESSION PARAMETERS

The dataset used to regress plant-wax apparent fractionation ($\epsilon_{nC_{29}/ppt}$) against lakewater evaporative enrichment ($\epsilon_{LW/ppt}$) contains correlated errors in $\epsilon_{nC_{29}/ppt}$ and $\epsilon_{LW/ppt}$ because both are affected by uncertainty in precipitation isotope values. In the manuscript, we calculated uncertainties in the regression fitting parameters assuming independent errors in x and y values. Here, we determine whether possible correlated errors in x and y lead to different values and uncertainties for these parameters.

When calculating the apparent fractionation of lipids from precipitation and the evaporative enrichment of lakewater over precipitation, we propagated the uncertainties in lakewater, precipitation and lipid isotope values. For sites where we defined precipitation values by lakewater compositions, we also included uncertainties in the slope of the local evaporation line and the covariance between errors in the $\delta^{18}O$ and δD of precipitation that results from constraining these values to the global meteoric water line.

We calculated local evaporation lines for subregions in Bolivia and Venezuela (see EA-1 Section 1, Table S1). In each subregion, water isotope data define a local evaporation line for each of several lakes located near (and sometimes including) the study lakes. The slope of this line was calculated by linear regression of lakewater $\delta^{18}O$ and δD values and the uncertainty in the slope includes the dispersion of the data and uncertainties in lakewater $\delta^{18}O$ and δD values (Press et al., 1994). In a number of cases, uncertainties in lakewater $\delta^{18}O$ and δD values were calculated from the standard deviation of 2 to 3 samples collected between 1997 and 2008. In other cases, the uncertainty was estimated based upon variability at nearby lakes.

We used a Monte-Carlo approach to develop uncertainties in estimates for lipid/precipitation and lakewater/precipitation isotopic differences because of the covariance of

errors in precipitation $\delta^{18}O$ and δD at sites where lakewater was used to define these values. For each Monte-Carlo iteration, the Gaussian probability distribution function (pdf) of the LEL, lakewater $\delta^{18}O/\delta D$, precipitation $\delta^{18}O/\delta D$ (when not calculated from lakewater) and *n*-alkane δD were randomly sampled and these values used to calculate apparent *n*-alkane/precipitation δD (ϵ_a) and lakewater/precipitation $\delta^{18}O$ ($\epsilon_{LW/ppi}$) fractionations. For each simulated dataset, the slope and intercept of regression lines for each ecosystem were then determined. The Monte-Carlo simulation was run for 30,000 iterations and the bivariate frequency distribution of slope and intercepts was used to calculate confidence ranges for the joint distribution of these parameters (Fig. S7). The Monte-Carlo approach yields uncertainties for the fitting parameters that are equal to or less than those in the manuscript (compare Fig. S7 with Table 4) suggesting the manuscript values are conservative estimates. In the manuscript data tables we provide univariate uncertainties although covariance exists in the uncertainties of some of these values (Fig. S7).

4. DERIVATION OF LAKE-LEAF EVAPORATION LINES

The meteoric water line is defined as:

$$(5) \quad \delta D_{ppt} = m_{ppt} \delta^{18}O_{ppt} + d_{ppt}$$

where $m = 8$ and $d = 10$ for the global meteoric water line. The apparent fractionation of lakewater (LW) and the n -C₂₉ alkane relative to precipitation is given by:

$$(6a) \quad \alpha_{nC_{29}/ppt} = \frac{\delta D_{nC_{29}} + 1}{\delta D_{ppt} + 1}$$

$$(6b) \quad \alpha_{LW/ppt} = \frac{\delta^{18}O_{LW} + 1}{\delta^{18}O_{ppt} + 1}$$

The empirical relationship between $\alpha_{LW/ppt}$ and $\alpha_{nC_{29}/ppt}$ determined in our work is described by:

$$(7a) \quad \varepsilon_{nC_{29}/ppt} = m_{\varepsilon} \varepsilon_{LW/ppt} + \varepsilon_o$$

which, using $\varepsilon \equiv \alpha - 1$, can be re-written as:

$$(7b) \quad \alpha_{nC_{29}/ppt} = m_{\varepsilon} (\alpha_{LW/ppt} - 1) + \alpha_o$$

Values for m_{ε} and ε_o are found in Table 4 of the manuscript. When the lake water $\delta^{18}O$ value and n -C₂₉ δD values are known, setting Eq. 6a equal to 7b and, substituting with Eqs. 5 and 6b, multiplying through and simplifying, writes an equation of quadratic form $Ax^2 + Bx + C = 0$, where:

$$(8a) \quad x = \delta^{18}O_{ppt}$$

$$(8b) \quad A = m_{ppt} (m_{\varepsilon} - \alpha_o)$$

$$(8c) \quad B = (\delta D_{nC_{29}} + 1) - m_{ppt} m_{\varepsilon} (\delta^{18}O_{LW} + 1) + (m_{ppt} + d_{ppt} + 1) (m_{\varepsilon} - \alpha_o)$$

$$(8d) \quad C = -(d_{ppt} + 1) [m_{\varepsilon} \delta^{18}O_{LW} + \alpha_o] + (\delta D_{nC_{29}} + 1)$$

The $\delta^{18}O$ of precipitation can be solved using the quadratic formula:

$$(9) \quad x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

and the δD of precipitation calculated with Eq. 5.

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6. SUPPLEMENTAL FIGURES

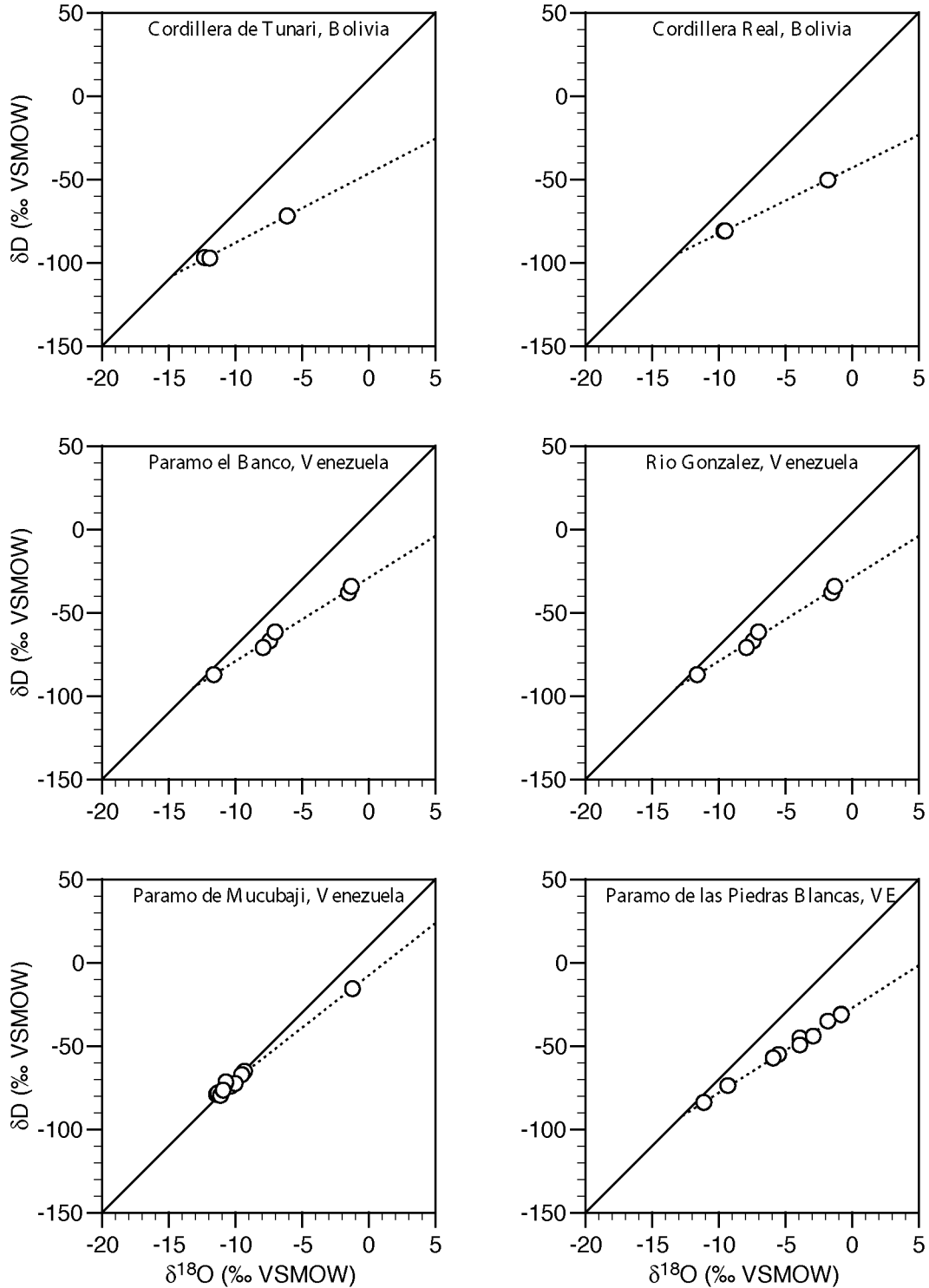


Figure S1 – Lakewater isotope values, local evaporation lines and the global meteoric waterline for every study region.

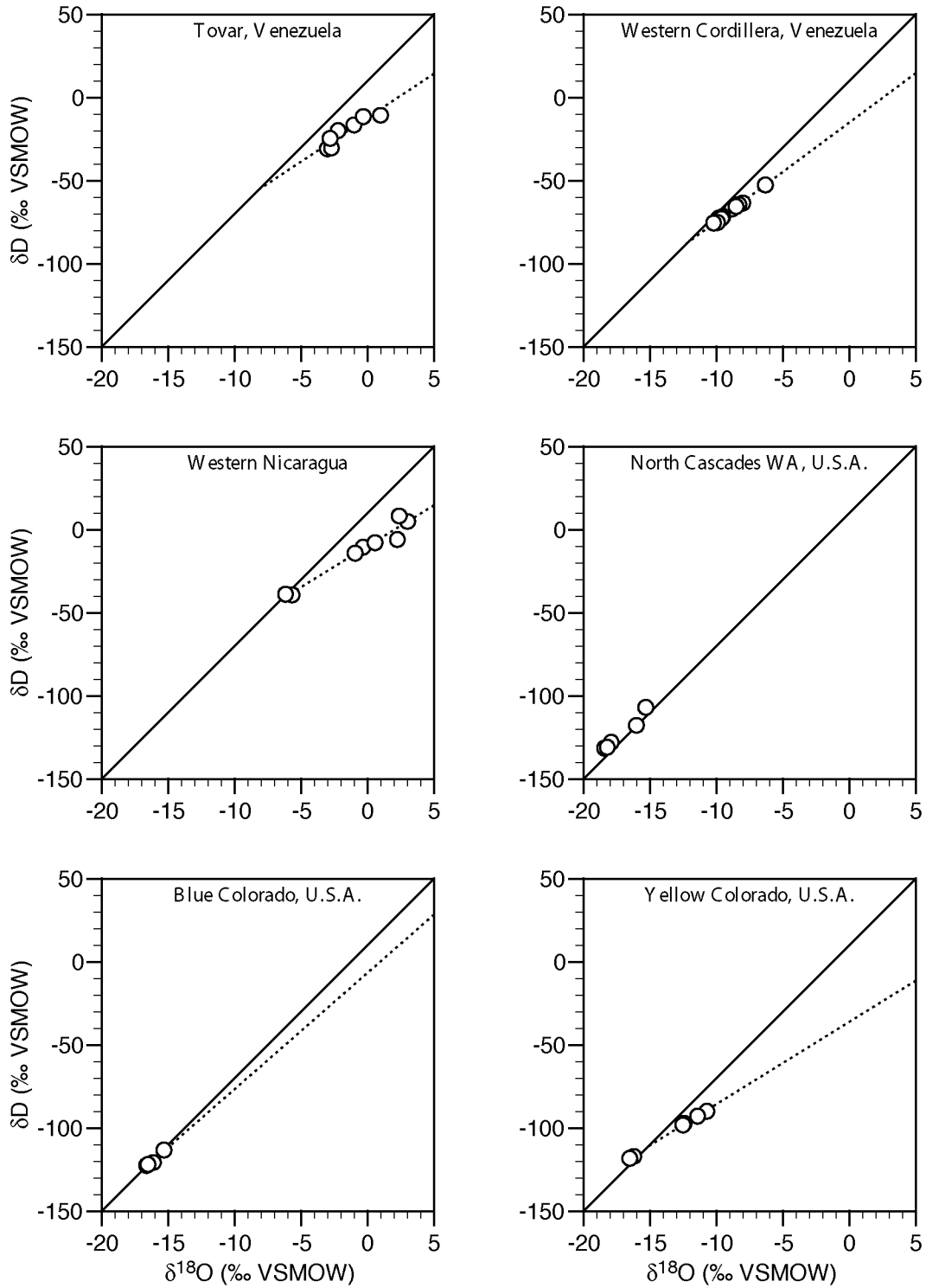


Figure S1 – continued.

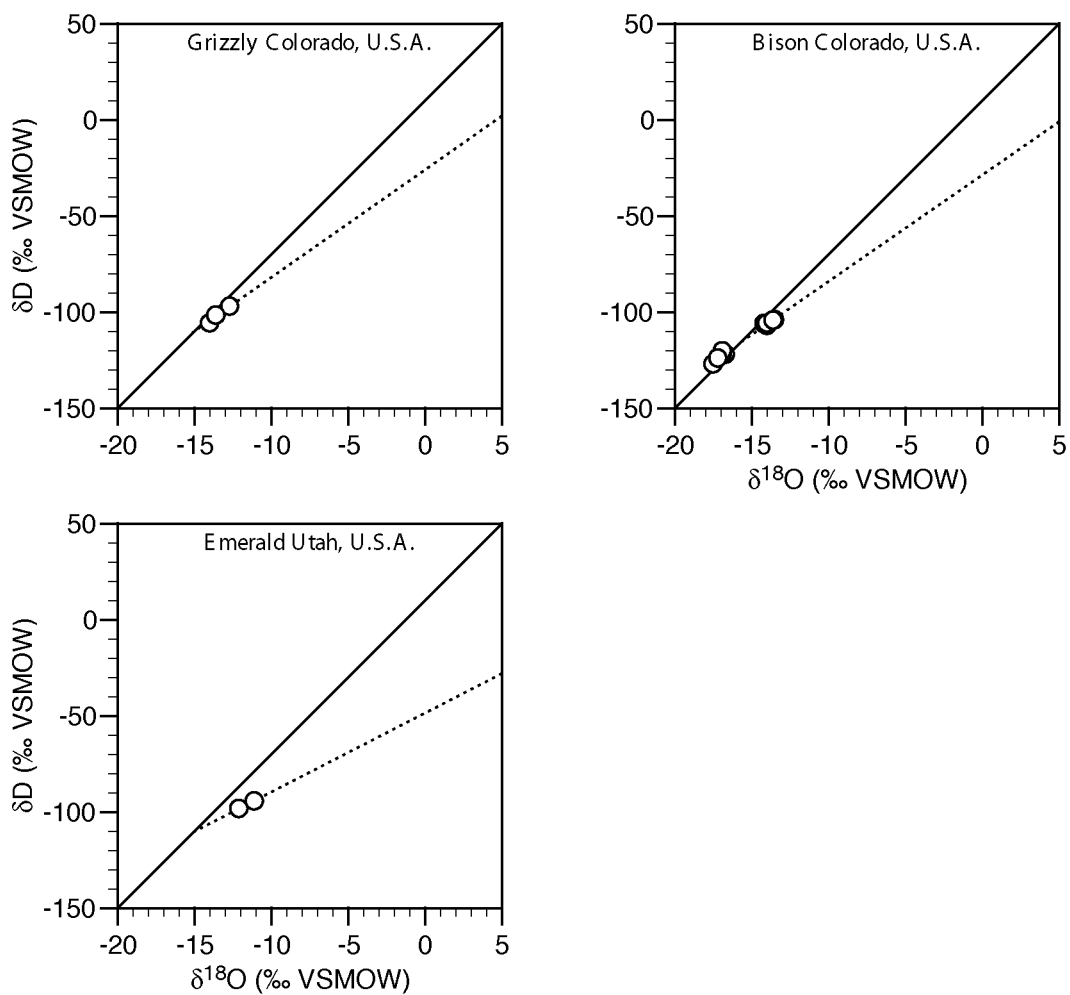


Figure S1 – continued.

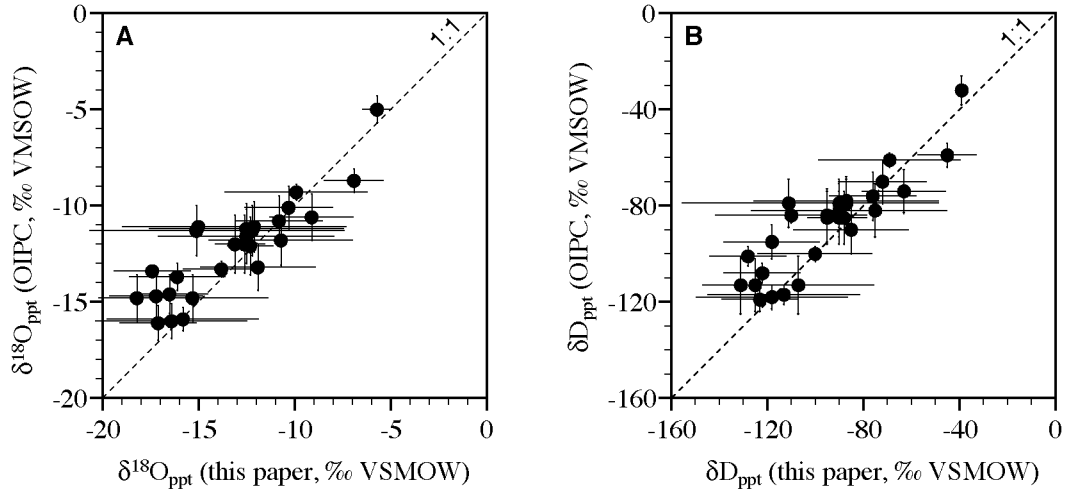


Figure S2 – Precipitation isotope values used in this study compared with values calculated from the OIPC. Error bars show 95% confidence intervals calculated as described in the main text and from the OIPC.

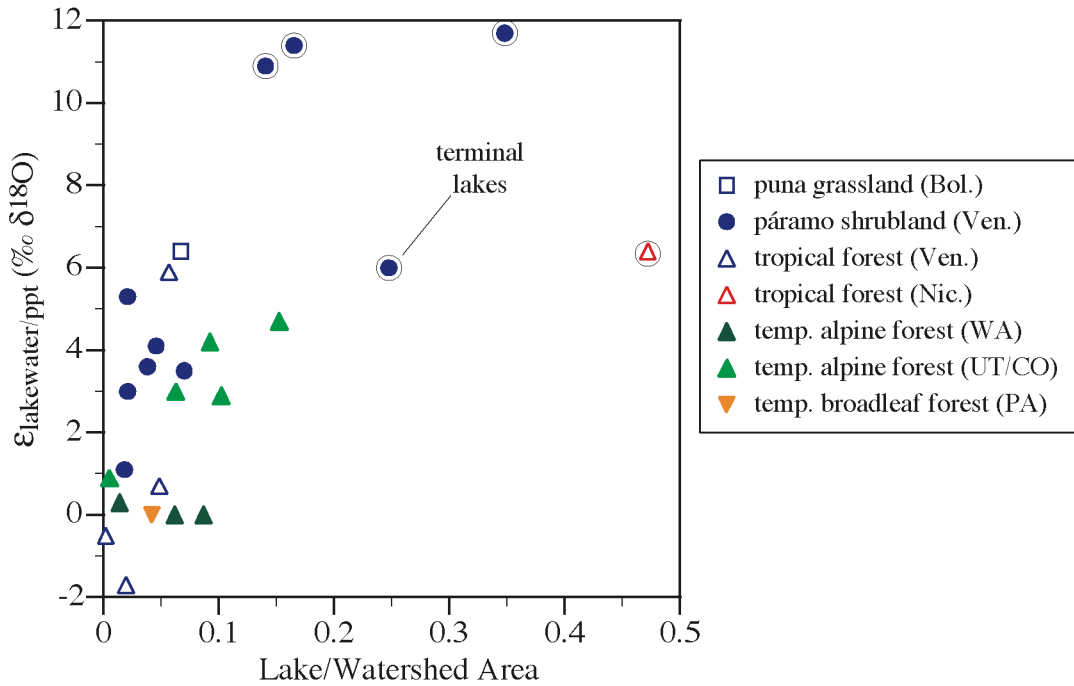


Figure S3 – Relationship between watershed/lake area ratio and the isotopic enrichment of lake water. Terminal lakes whose isotopic enrichment is influenced by the lake/watershed area are circled.

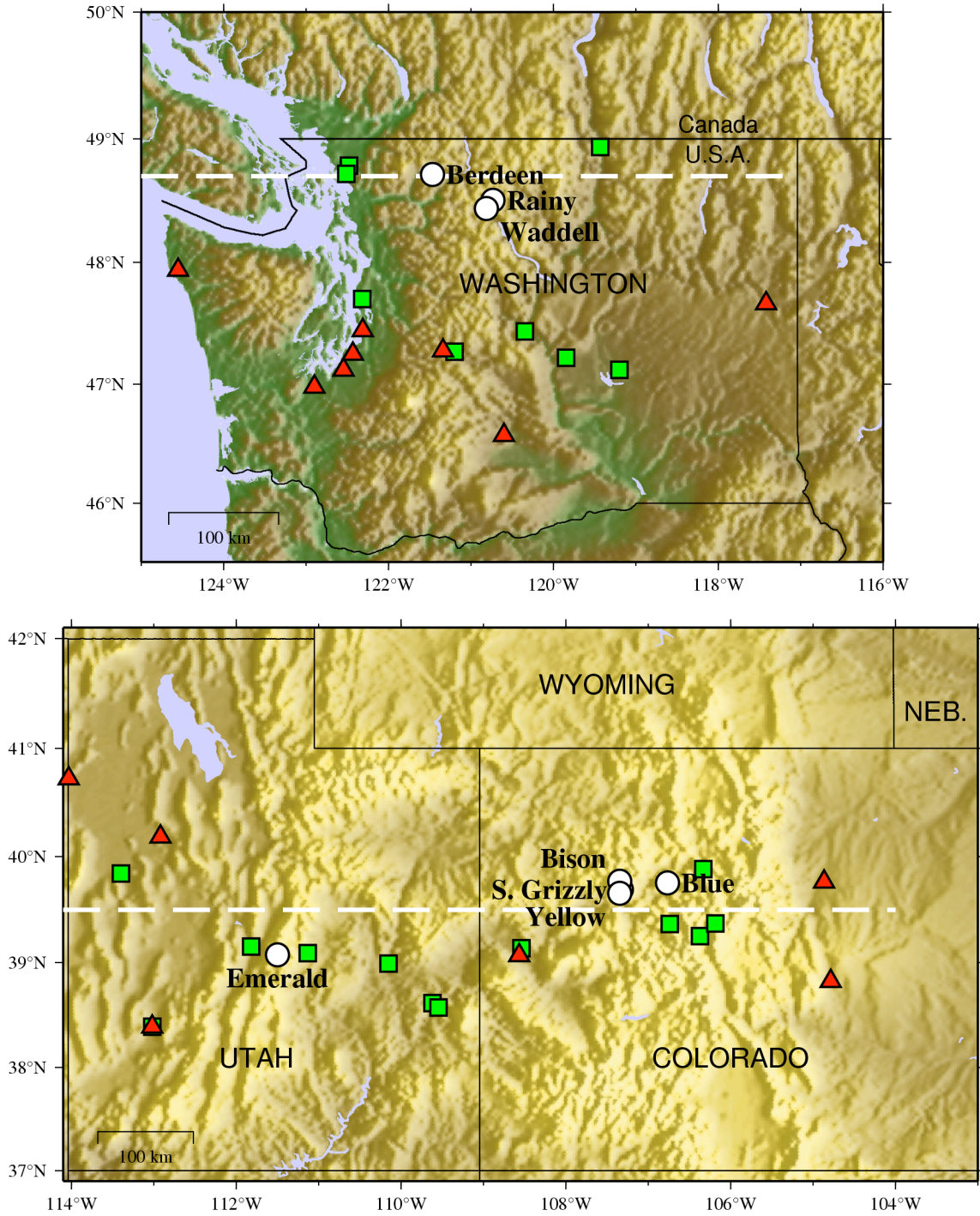


Figure S4 – Location of lakes from gymnosperm-dominated alpine watersheds (Data in Table 1 and EA-1 and EA-4) and climate stations (triangles, relative humidity; squares, precipitation/evaporation). Dashed white lines show the locations of climate and lakewater isotope profiles in Fig. S5.

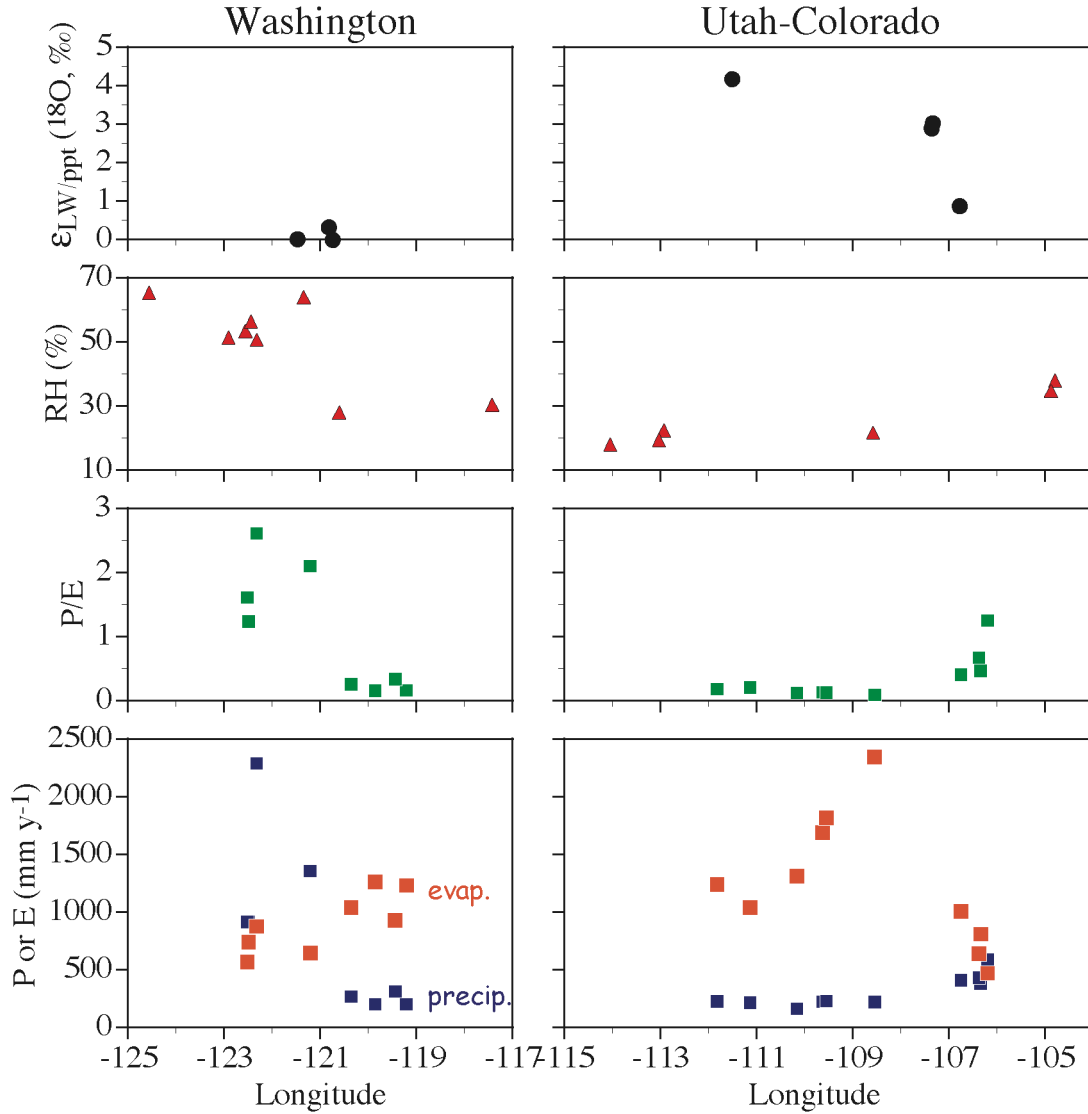


Figure S5 – Longitudinal profiles of long-term average precipitation, pan evaporation, P/E ratio, relative humidity (summer afternoon average) and lakewater isotope enrichment for gymnosperm dominated alpine watersheds. The geographic location of profiles is shown in Fig. S4. Climate data are from the Western Regional Climate Center (www.wrcc.dri.edu).

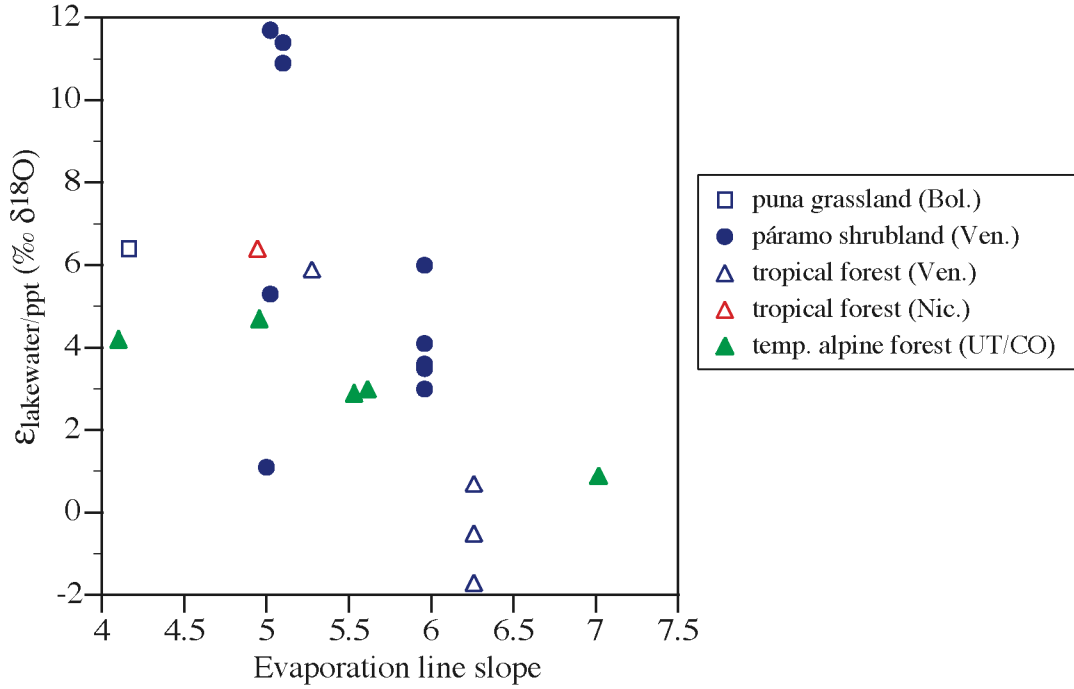


Figure S6 – Relationship between the slope of the local evaporation line and the isotopic enrichment of lake water.

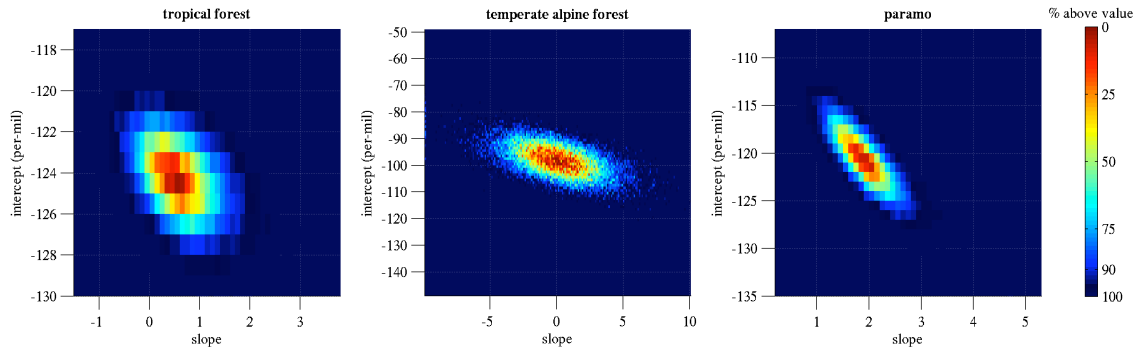


Figure S7 – Bivariate frequency distribution of slope/intercept pairs of ϵ_a , $\epsilon_{LW/ppt}$ regression calculated from Monte-Carlo uncertainties. Colors indicate the fraction of the Monte-Carlo datasets with the same or fewer counts. Thus, all colors greater than 90 % defines the region that includes 90 % of the simulations.