JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 115, D09109, doi:10.1029/2009JD013345, 2010

Variations of $\delta^{18}O$ in rainwater from southwestern Oregon

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Received 8 October 2009; revised 16 December 2009; accepted 4 January 2010; published 13 May 2010.

[1] We examine the relation between $\delta^{18}O$ in rainwater collected in southwestern Oregon and climate variables including temperature, parcel trajectory, precipitation amount, and specific humidity. Local surface air temperature at the time of sample collection explains a large proportion of $\delta^{18}O$ variability, suggesting that paleoclimatic archives that are related to rainfall $\delta^{18}O$ should be useful for qualitative temperature reconstructions. Models of Rayleigh distillation of air masses originating in the North Pacific can broadly constrain the observed isotopic variability in southwestern Oregon. Results from a Hybrid Single-Particle Lagrangian Integrated Trajectory Model suggest that recent parcel pathways have little influence on the isotopic composition of precipitation collected at our site. We also find no significant relation between rainfall $\delta^{18}O$ and precipitation amount. Changes in specific humidity along the parcel tracks, however, indicate that the water vapor exchange of the air mass with the underlying ocean influenced the isotopic composition of the most enriched samples.

Citation: Ersek, V., A. C. Mix, and P. U. Clark (2010), Variations of $\delta^{18}O$ in rainwater from southwestern Oregon, *J. Geophys. Res.*, *115*, D09109, doi:10.1029/2009JD013345.

1. Introduction

[2] Oxygen isotope ratios preserved in ice cores, speleothems, lake sediments and other geological archives are commonly used as a proxy of past climate changes, but require regional understanding of the relation between climate and $\delta^{18}O$ of the source precipitation (where $\delta^{18}O = 1000*(^{18}O/^{16}O_{sample} - ^{18}O/^{16}O_{reference}) / ^{18}O/^{16}O_{reference}$). Earlier studies showed that at high latitudes both $\delta^{18}O$ in precipitation and air temperature are very low, implying some spatial correlation (and not necessarily a temporal one) between air temperature and $\delta^{18}O$ [*Dansgaard*, 1964; *Peel et al.*, 1988]. More recent modeling studies [*Brown and Simmonds*, 2004] suggest that the modern correlation between $\delta^{18}O$ and temperature is not constant and depends on the moisture transport and distribution of landmasses. For paleoclimate archives preserved in carbonate mineral phases (e.g., speleothems), this relation is important because precipitation-temperature correlation may otherwise be masked by local calcite temperature equilibrium effects, in which temperature and $\delta^{18}O_{calcite\text{-}water}$ are negatively correlated [*Kim and O'Neil*, 1997].

[3] In contrast, the observed isotopic composition of rainfall at low latitudes is inversely correlated with rainfall rate, the so-called "amount effect" [*Dansgaard*, 1964]. The amount effect also occurs at midlatitudes, especially during intense convective storms in the summer [*Dansgaard*, 1964], although $\delta^{18}O$ in midlatitude winter precipitation is more likely to correlate with temperature. Studies of individual midlatitude precipitation events reveal a strong negative correlation of $\delta^{18}O$ with precipitation amount [*Gedzelman et al.*, 1987; *Lawrence et al.*, 1982; *Treble et al.*, 2005], while long-term climatologic studies suggest a closer correspondence between $\delta^{18}O$ and surface temperature, with a slope of ~0.5‰/°C for many midlatitude locations [*Rozanski et al.*, 1993]. The range of variability for this slope at different midlatitude and high-latitude locations is significantly reduced if one considers temperature during precipitation events rather then mean surface temperature over the time of precipitation collection [*Kohn and Welker*, 2005].

[4] Despite these well-established effects, a large portion of the variance in rainwater $\delta^{18}O$ at a given location still remains unexplained by temperature and precipitation amount [*Noone and Simmonds*, 2002]. Additional contributors to observed isotopic variability include changes in source regions, vapor transport pathways, seasonality, the balance of precipitation and evaporation, and hemispheric-scale influences on export of water vapor from tropical systems [*Araguás-Araguás et al.*, 2000; *Lee et al.*, 2007; *Schmidt et al.*, 2007].

[5] The degree to which these changes affect the isotopic composition of rainfall in the western U.S. is not well known because of the low density and short record of the Global Network of Isotopes in Precipitation (GNIP) stations [*Welker*, 2000]. However, a sensitivity study of seasonally changing $\delta^{18}O$ in rainfall from North America [*Vachon et al.*, 2007] indicates that western Oregon has one of the lowest seasonal $\delta^{18}O$ ranges in the United States (1–2.5‰). In northern California, studies of D/H ratios in rainwater

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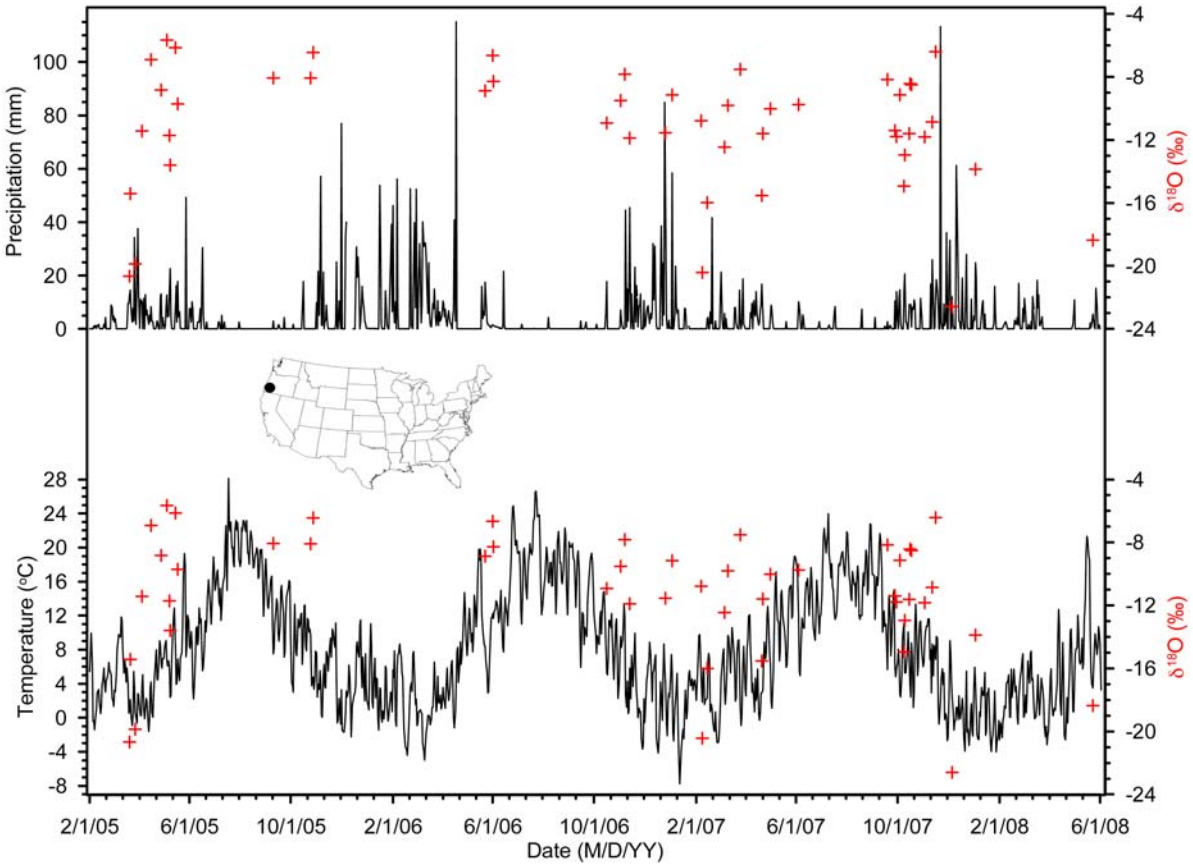


Figure 1. Time series (lines) of precipitation and temperature plotted together with rainwater δ^{18}O of samples collected at OCNM (pluses). Inset map shows the position of OCNM in the western United States.

found that in coastal proximal settings, D/H variability follows an open-system behavior in which precipitation is not recycled by evapotranspiration, and the isotopic fractionation is compatible with a Rayleigh distillation process as the air rises and cools over the coastal mountains [*Ingraham and Taylor*, 1986, 1991].

[6] Here we investigate the effects of rainfall amount, temperature and changes in parcel trajectory and specific humidity on δ^{18}O of rain events sampled at Oregon Caves National Monument (OCNM) in western United States (42°N, 123°W). The study site is located at an altitude of 1200 m in the Klamath Mountains, approximately 75 km east of the Pacific coast (Figure 1), a zone where major Pacific storms enter North America. The Klamath Mountains are very rugged and the higher peaks that characterize the region to the south and west of OCNM may elevate air masses approaching OCNM.

[7] The mean annual temperature at OCNM is 8°C, and the mean annual precipitation is 1600 mm. Approximately 85% of precipitation falls between November and April (PRISM Group, Oregon State University, http://www.prismclimate.org). This strong seasonal cycle is driven by the migration of the Pacific subtropical high-pressure cell, which is displaced southward during winter months by the Aleutian low-pressure system, resulting in primarily southwesterly winds and abundant precipitation. During this time the North Pacific has a high density of storms particularly north of 40°N where cyclone densities exceed 2×10^{-3} (deg. lat.)$^{-2}$ with corresponding mean pressure deficits of 8–9 hPa [*Simmonds and Keay*, 2002]. The opposite situation occurs during summer months when the Aleutian low is weakened and the northward migration of the subtropical high drives predominantly northeasterly winds and dry conditions at OCNM [*Taylor and Hannan*, 1999].

2. Methods

[8] We collected 48 rainfall samples between 2005 and 2008. The water was collected in glass bottles with airtight screw-cap seals and plastic vapor barriers, which were subsequently stored in a refrigerator for periods of 1 to 12 months before measurement. δ^{18}O of the rainfall was measured at Oregon State University using established H_2O–CO_2 equilibration methods [*Epstein and Mayeda*, 1953] on a ThermoQuest Finigan DeltaPlusXL mass spectrometer equipped with an automated equilibrator of local design. The isotopic composition of waters is reported relative to VSMOW and the reproducibility of local reference waters run on the same day and in the same way as the samples was ± 0.03‰ (n = 23) on this system.

[9] The trajectories of air masses that delivered precipitation to our study site were derived using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT)

Model, version 4 [*Draxler and Hess*, 1997] from the NOAA Air Resources Laboratory. This model provides insight into the history of the air masses that were sampled in our study and has been used in other similar studies that related air parcel trajectories with the isotopic composition of rainfall [*Burnett et al.*, 2004; *Lee et al.*, 2003; *Pfahl and Wernli*, 2008; *Sjostrom and Welker*, 2009; *Strong et al.*, 2007]. HYSPLIT relies on gridded meteorological data sets and uses a predictor-corrector method for calculating particle trajectories. The errors in the trajectories are estimated to be around 15–30% of trajectory length and are associated with how well the numerical fields estimate the true flow field, and the representation of a continuous atmospheric flow field with gridded data points limited in time and space. We therefore visually checked each parcel trajectory against satellite imagery obtained from NOAA's Geostationary Operational Environmental Satellites (GOES).

[10] All trajectories were started at 500 m above the ground and were traced back 48 h before arrival. Temperature, precipitation, altitude, pressure and humidity were calculated hourly for each trajectory using information from the EDAS 40 km meteorological data set.

3. Results

[11] The values for rainwater δ^{18}O range from −22‰ to −5‰, have a mean of −11‰ ± 4‰ (1σ), and are negatively skewed. Because of the strong precipitation seasonality in SW Oregon, our sampling is biased toward the cool-rainy season when most of precipitation falls at our site. Skewness is associated with a small population of highly depleted values with δ^{18}O of less than −18‰, a surprising level of depletion in this midlatitude site near the ocean. These highly depleted values were analyzed in replicate and confirmed. At least one such value was measured in each of four winters.

3.1. Effect of Parcel Trajectories and Temperatures

[12] Studies that assessed the influence of parcel trajectories on rainfall δ^{18}O found a strong connection between the path of the storm and the isotopic composition of precipitation [*Barras and Simmonds*, 2008; *Burnett et al.*, 2004; *Gedzelman and Lawrence*, 1982]. Our analysis of back trajectories shows that parcel tracks span an area from 26°N to 55°N and from ~130°W to 150°W (Figure 2 and auxiliary material Figure S1).[1] Because of this large spatial spread in parcel tracks, we focus our discussion on the end-members of the rainwater samples.

[13] Back trajectories for high δ^{18}O events (values ≥ −8‰) span over ~20 degrees of latitude, from 26°N to 46°N (Figure 2b). Seawater δ^{18}O over this latitude band ranges from −1.0 to +0.2‰ [*LeGrande and Schmidt*, 2006]. Back trajectories for low δ^{18}O events (values ≤ −18‰) span over ~10 degrees of latitude of the same latitude band as the high δ^{18}O events (32°N to 42°N) (Figure 2a), with correspondingly similar seawater δ^{18}O values (−1 to 0‰). Overall, the trajectory analysis thus indicates that, at least on the synoptic timescales analyzed here, the large differences in δ^{18}O of rainwater collected at our site cannot be attributed to systematic changes in air mass trajectory.

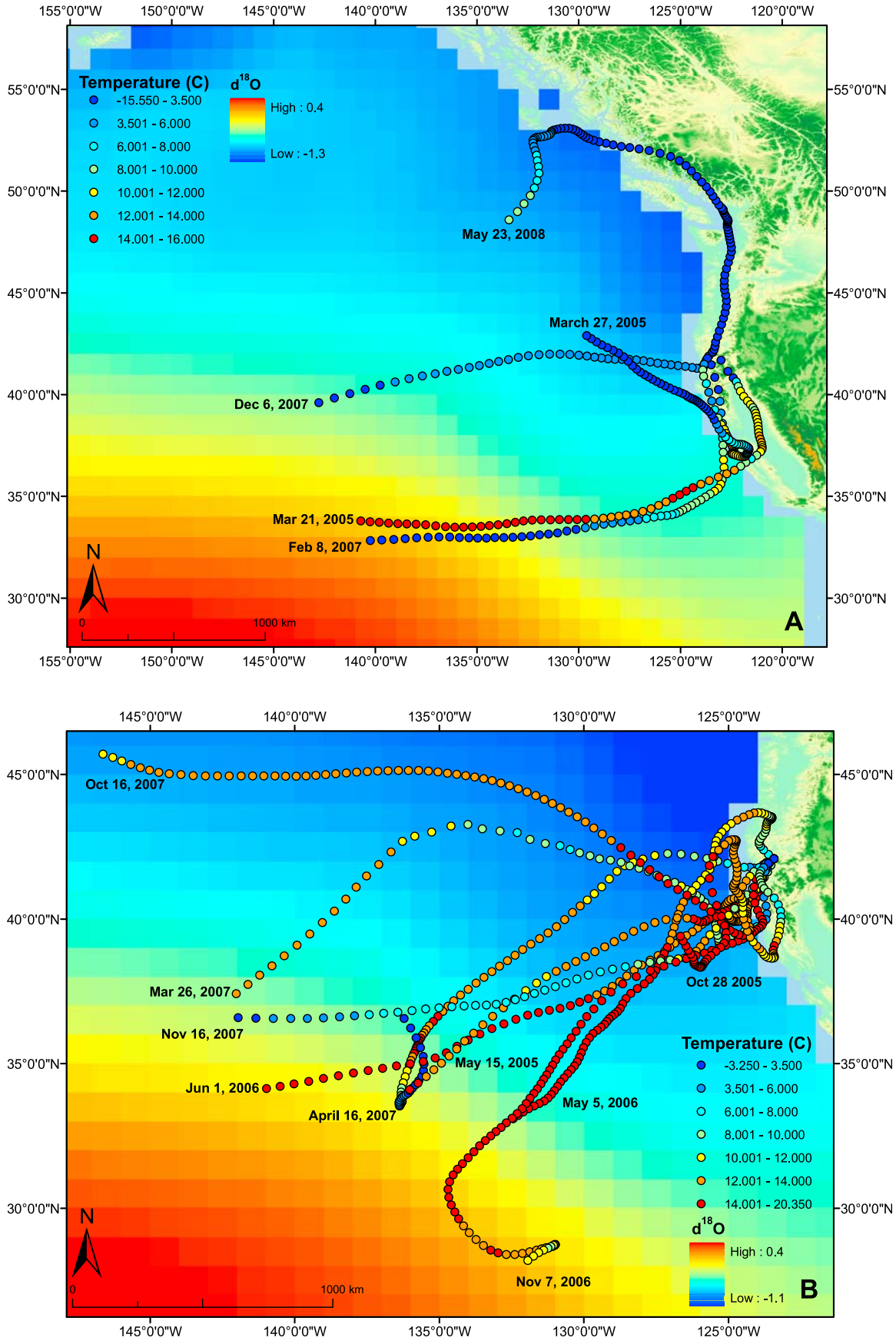
[14] Local surface temperature explains 29% of the variability in the raw rainwater δ^{18}O (r = 0.54, P value = 0.0001), with a T: δ^{18}O slope of 0.7‰/°C (Figure 3a). The isotopic composition of rain within an individual storm can vary greatly due to continual depletion of the air mass or changes in the degree of isotopic exchange between raindrops and the surrounding air [*McDonnell et al.*, 1990; *Pionke and DeWalle*, 1992]. To remove some of these meteorological effects and gain insight into the underlying climatology that influences the isotopic composition of rainfall, we average all values within a calendar month and perform a linear regression of average δ^{18}O against the corresponding monthly averaged temperatures. Each monthly data point is weighted in the regression analysis by the monthly average precipitation. In this case, monthly temperature explains 65% of the variance in amount-weighted monthly δ^{18}O (P value = 0.005), and the T: δ^{18}O slope increases to 0.9‰/°C (Figure 3b). In this analysis the average leverage of a single data point is 0.2 while the leverage for June is more than three times larger than the average value. June rainfall represents only ~1% of total annual precipitation at OCNM, however, indicating that this leverage is unjustified in evaluating the temperature influence on precipitation δ^{18}O. Accordingly, if we exclude the values for June, monthly surface temperature explains 80% of monthly averaged δ^{18}O variability.

[15] A logarithmic fit explains a higher percentage of variance in δ^{18}O values than a linear fit, both in the case of raw (r^2 = 0.39) and monthly averaged data (including June, r^2 = 0.74). This is not surprising since both the Rayleigh distillation equation, which expresses changes in isotopes as a function of fraction of vapor remaining, and the equations for water vapor saturation as a function of temperature would predict a curvilinear relationship between oxygen isotopes and temperature.

[16] Most of the measured δ^{18}O values fall within the range predicted by Rayleigh distillation for reasonable oceanic moisture sources in the North Pacific. Figures 3a and 3b include the field of Rayleigh-predicted rainfall δ^{18}O from air masses initially equilibrated with the seawater in the tropical Pacific (T = 28°C) and in the north Pacific (T = 10°C) then cooled during transport. In both scenarios we set the seawater δ^{18}O at 0‰ and the relative humidity at 85%. Most points fall between the two Rayleigh curves suggesting that a Rayleigh process with a combination of low and high-latitude moisture sources could approximate the isotopic fractionation at our location. Some of the most depleted samples fall outside the two Rayleigh curves suggesting that these depleted samples could have formed at high levels in the clouds. Similarly, *Friedman et al.* [2002] found the dominance of Rayleigh processes on rainfall δ^{18}O in the Great Basin area with varying moisture sources.

[17] While OCNM is in a near-coastal setting where slopes are generally lower [*Rozanski et al.*, 1993], the T: δ^{18}O slopes that we observe at our site are higher than the average slope of 0.5 commonly observed for the midlatitudes [*Dansgaard*, 1964]. In general, lower T: δ^{18}O slopes are characteristic of precipitation falling during warmer seasons due to a combination of lower fractionation coefficients for the liquid-water transition versus solid-vapor

[1] Auxiliary materials are available in the HTML. doi:10.1029/2009JD013345.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Temperature (C)
-15.550 - 3.500
3.501 - 6.000
6.001 - 8.000
8.001 - 10.000
10.001 - 12.000
12.001 - 14.000
14.001 - 16.000
d18O
High : 0.4
Low : -1.3
May 23, 2008
March 27, 2005
Dec 6, 2007
Mar 21, 2005
Feb 8, 2007
N
0
1000 km
A
Oct 16, 2007
Mar 26, 2007
Nov 16, 2007
Jun 1, 2006
April 16, 2007
May 15, 2005
May 5, 2006
Oct 28 2005
Nov 7, 2006
Temperature (C)
-3.250 - 3.500
3.501 - 6.000
6.001 - 8.000
8.001 - 10.000
10.001 - 12.000
12.001 - 14.000
14.001 - 20.350
d18O
High : 0.4
Low : -1.1
B

Figure 2

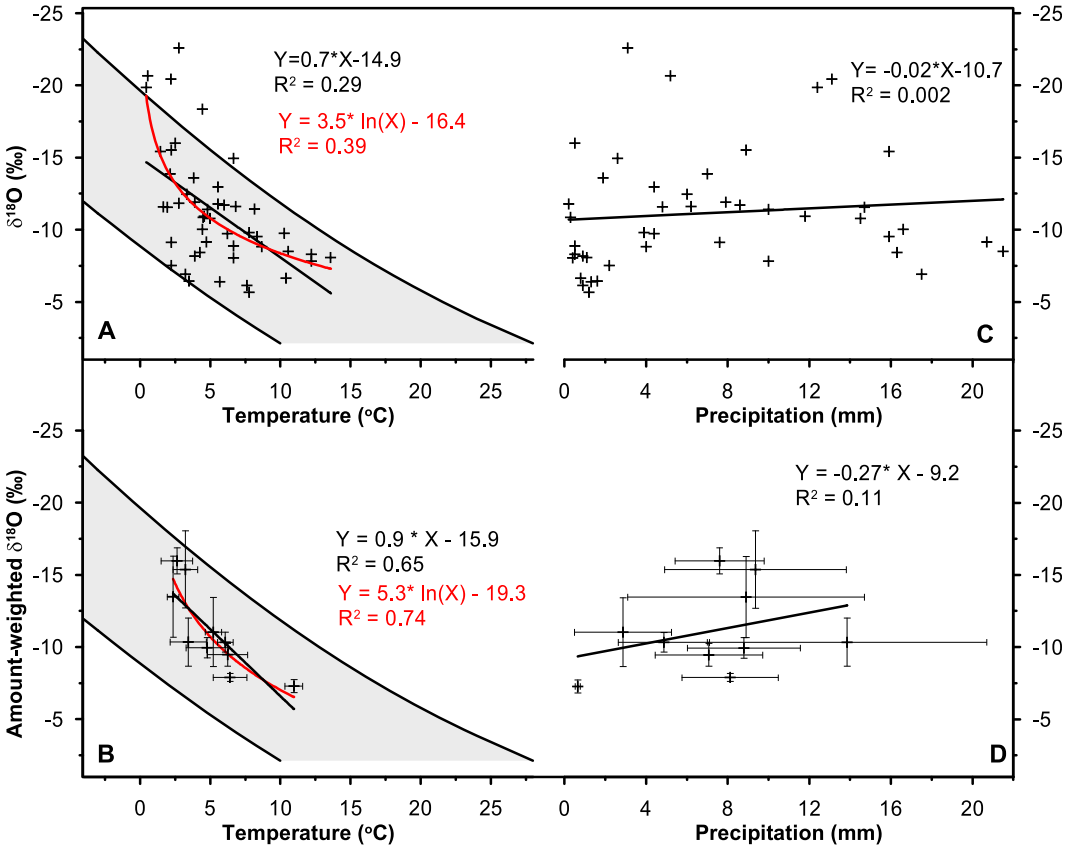

Figure 3. (a) Temperature versus precipitation δ^{18}O and (c) precipitation amount versus δ^{18}O on synoptic timescales and (b and d) the corresponding monthly averaged values and the standard error of the mean for the monthly averages. Black regression lines and text show the linear regressions and the corresponding statistics while the red line and text in Figures 3a and 3b indicate the logarithmic fit and the related regression statistics. Shaded regions in Figures 3a and 3b indicate the area bounded by Rayleigh distillation curves of air masses originating in the tropical Pacific (source temperature 28°C) and North Pacific (source temperature 10°C). The most depleted samples in winter are best explained by distillation of water vapor that originated at relatively high temperatures, consistent with a low-latitude source of water vapor reaching western Oregon.

phase change, the mixing of both temperature and mixing ratios during convection [*Jouzel*, 1986] and higher evapotranspiration during the plant growing season [*Rozanski et al.*, 1993]. These effects are less important in Oregon, where the summers are generally dry, and we therefore infer that the high T: δ^{18}O slope in the Klamath Mountains reflects the predominance of winter precipitation. Further, OCNM is situated at high altitude and models using Rayleigh adiabatic condensation processes show that the δ^{18}O: altitude slope increases with altitude due to lower temperatures and the associated increase of the condensation rate [*Gonfiantini et al.*, 2001]. To obtain additional insight into this issue we use rainfall δ^{18}O data from Vancouver Island (British Columbia), the nearest GNIP station that has both δ^{18}O and temperature information. This station has data collected from 1975 to 1982. The GNIP Database, 2006, from IAEA/WMO (available at http://isohis.iaea.org) and the monthly precipitation δ^{18}O is well correlated with monthly temperature (r = 0.8), but with a low slope of 0.2 ‰/°C. However, if the Vancouver Island data from the cool half of the year (October–March) are considered, the slope increases to 0.5 ‰/°C (r = 0.9) while during the warm season (April–September) the slope is 0.1 ‰/°C (r = 0.5).

[18] In Figure 4 we consider the temporal relationship between temperature changes along the parcel track and rainwater δ^{18}O. Although there is some overlap in distributions, three out of the five isotopically depleted events clearly have colder storm temperatures than the enriched events for most of the 48 h prior to rainfall collection. In

Figure 2. Back trajectories for (a) low δ^{18}O and (b) high δ^{18}O rain events arriving at OCNM at an altitude of 500 m above ground level. The color scale of the parcel trajectories represents the hourly temperature as extracted from the HYSPLIT model, and the colored background represents the gridded sea surface δ^{18}O from *LeGrande and Schmidt* [2006]. The rest of the trajectories are shown in auxiliary material Figure S1.

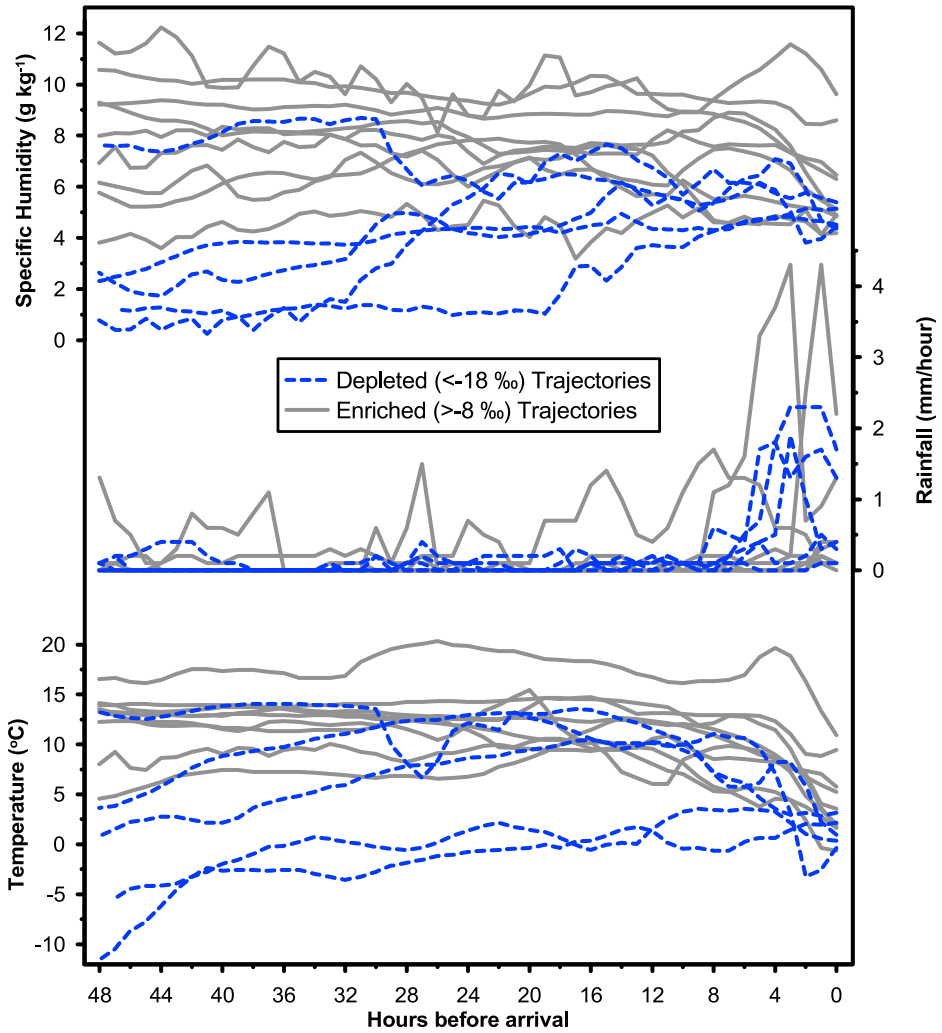

Figure 4. Calculated (top) specific humidity, (middle) rainfall rate, and (bottom) temperatures for the last 48 h before arrival at OCNM for depleted and enriched trajectories.

most cases, temperatures associated with depleted trajectories are rising in the period between 48 and 8 h before arrival, while for enriched trajectories temperatures tend to remain approximately constant or vary within a narrow range over the same time interval. Both enriched and depleted trajectories show a sharp decrease in temperature during the last 8–4 h before arrival as the air masses rise over the Klamath Mountains. The cooling of air masses shortly before precipitation collection was also calculated for parcel trajectories arriving in Melbourne, Australia [*Barras and Simmonds*, 2009].

3.2. Effect of Rainfall Amount

[19] The amount of precipitation can influence the isotopic composition of rainfall due to a high degree of removal of ^{18}O from the cloud layer during intense precipitation events, incomplete equilibration of large raindrops with water vapor near the ground, evaporation below the cloud base during less intense storms [*Dansgaard*, 1964], and continuous isotopic exchange of the water vapor with raindrops below the cloud base [*Miyake et al.*, 1968; *Rozanski et al.*, 1993].

[20] We find no statistical significant relation between rainfall amount integrated 24 h prior to sample collection and δ^{18}O at 95% confidence (r = −0.05, P value = 0.7) (Figure 3c). This lack of correlation is also true regardless of the time interval for which precipitation amount is considered (ranging between 1 and 48 h prior to collection). To assess whether the low correlation is caused by competing factors that act in opposite directions, we performed a linear regression between the residuals of T versus δ^{18}O and precipitation amount, but also find no significant correlation between the residuals and precipitation amount. If we remove the weather noise by averaging precipitation and δ^{18}O into monthly values, the R-squared statistic indicates that the model explains 11% of the variability in δ^{18}O (Figure 3d), but the P value (0.34) indicates that there is not a statistically significant relationship between precipitation amount and δ^{18}O at the 95.0% or higher confidence level.

[21] Large or rapid changes in specific humidity along the storm tracks can indicate condensation or entrainment of moisture, which in turn will modify the isotope ratios in the air mass [*Barras and Simmonds*, 2008]. The calculated specific humidities along the trajectories suggest that

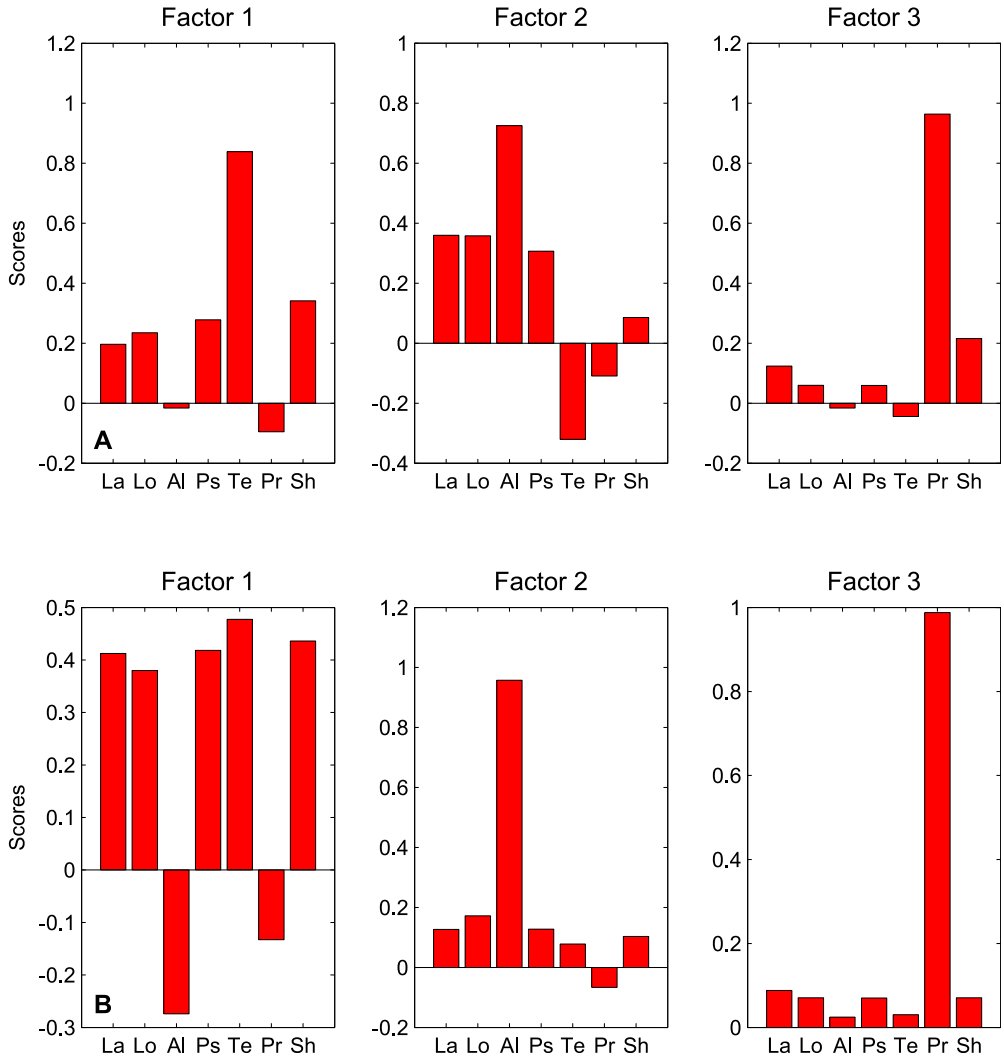

Figure 5. Score loading for the first three varimax factors from Q-mode factor analysis. (a) Factor scores for depleted events. (b) Factor scores for enriched events. The labels for the *x* axes are: La, latitude; Lo, longitude; Al, altitude; Ps, pressure; Te, temperature; Pr, precipitation; and Sh, specific humidity.

isotopically depleted trajectories start entraining moisture 30–16 h before the rainfall was collected, while enriched trajectories have relatively constant humidities, indicating water vapor exchange of the air mass for the much of the 48 h before arrival (Figure 4). This phenomenon may partly counteract the continuous isotopic depletion of air masses through Rayleigh distillation and contributes to the higher δ^{18}O values measured in rainwater.

3.3. Multivariate Analysis

[22] To obtain a semiquantitative distinction between the factors that influenced the most depleted and most enriched rainwater samples, we conducted a Q-mode factor analysis [*Klovan and Imbrie*, 1971; *Miesch*, 1980] using the parameters obtained for parcel trajectories in the HYSPLIT model. Included in this analysis are latitude, longitude, altitude, pressure, temperature, precipitation and specific humidity. The first three extracted varimax factors in the Q-mode analysis for depleted storms explain 98% of the variance in rainfall δ^{18}O. Factor 1 explains 64% of the variance and is dominated by temperature (Figure 5a), factor 2 has the highest scores for altitude and explains 24% of the variance, while factor 3 explains 10% of the variance and is clearly dominated by precipitation. In the case of enriched storms the first three factors explain 98% of the rainfall δ^{18}O variance. Factor 1 has 76% of the total variance and shows similar factor scores for all of the variables, except rainfall and altitude, factor 2, which explains 12% of the variance, is dominated by altitude, and factor 3 is clearly dominated by precipitation, explaining 10% of the variance (Figure 5b). It would therefore appear that while storm temperature is the dominant control over δ^{18}O values in depleted storms, the situation is more complex in warmer storms, although temperature still plays a major role in determining the isotopic composition of rainfall.

4. Conclusions

[23] Analysis of event-based rainfall δ^{18}O variability in SW Oregon reveals that temperature is an important factor

in explaining the isotopic variability and suggests that proxy records that are related to past changes of rainwater δ^{18}O in this area have the potential to capture temperature variability on annual timescales or longer. It is unclear, however, if this is also the case for other places along the west coast of North America, given that our site is situated in an area with unusually low seasonal δ^{18}O variability. Analyses of parcel trajectories that delivered moisture to our location indicate that parcel path does not have a large control on rainfall δ^{18}O, highlighting the importance of atmospheric processes in determining the isotopic signature of rainfall in SW Oregon. Similarly, there is no significant association between rainfall amount and rainfall δ^{18}O values.

[24] Changes in specific humidity along the parcel trajectory suggest that continuous condensation and entrainment of moisture along the storm path, particularly in the case of storms with high δ^{18}O values, may also influence the δ^{18}O composition of rainfall events in Oregon. However, the range of isotopic variability can be broadly constrained by models of Rayleigh distillation for air masses originating between the tropical and North Pacific Ocean.

[25] **Acknowledgments.** We thank John Roth, Elizabeth Hale, and the staff at OCNM for collecting water samples and for providing the local temperature and precipitation data. We also thank Jeremy Shakun for helping with the initial setup of the trajectory model. The authors gratefully acknowledge the NOAA Air Resources Laboratory for the provision of the HYSPLIT model. Comments from three anonymous reviewers improved this manuscript. The NSF Paleoclimate Program funded this research.

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