

Geography and Vintage Predicted by a Novel GIS Model of
Wine $\delta^{18}\text{O}$ JASON B. WEST,^{*,†} JAMES R. EHLENGER,[‡] AND THURE E. CERLING[‡]Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, Utah 84112, and
IsoForensics, 423 Wakara Way, Salt Lake City, Utah 84108

Wine hydrogen and oxygen stable isotopes record the climatic conditions experienced by the grape vine and the isotopic composition of the vine's source water during berry development. As such, stable isotopes have been explored extensively for use in detecting wine adulteration or for independently verifying claims of origin. We present the results of a study designed to evaluate the relationships between wine water $\delta^{18}\text{O}$ and spatial climate and precipitation $\delta^{18}\text{O}$ patterns across the winegrape-growing regions of Washington, Oregon, and California. Retail wines produced from typically small vineyards across these regions were obtained from the 2002 vintage, and the $\delta^{18}\text{O}$ of wine water was analyzed using a CO_2 equilibration method. Significant correlations were observed between the measured wine water $\delta^{18}\text{O}$ from 2002 and the long-term average precipitation $\delta^{18}\text{O}$ and late season 2002 climate, based on a spatial join with continuous geographic information system (GIS) maps of these drivers. We then developed a regression model that was implemented spatially in a GIS. The GIS model is the first of its kind and allows spatially explicit predictions of wine $\delta^{18}\text{O}$ across the region. Because high spatial resolution monthly climate layers are now available for many years, wine $\delta^{18}\text{O}$ could be modeled for previous years. We therefore tested the model by executing it for specific years and comparing the model predictions with previously published results for wine $\delta^{18}\text{O}$ from seven vintages from Napa and Livermore Valleys, California. With the exception of one year, an anomaly potentially related to the effects of El Niño on precipitation isotopic composition, the model predicted well the wine $\delta^{18}\text{O}$ for both locations for all vintages and generally reflected the consistent enrichment of wine from Napa relative to Livermore. Our results suggest that wine water $\delta^{18}\text{O}$ records both source water $\delta^{18}\text{O}$ and climate during the late stages of winegrape ripening and that GIS models of wine water $\delta^{18}\text{O}$ are useful tools for independently verifying claims of regional origin and vintage.

KEYWORDS: Stable isotope ratio; oxygen; water; spatial modeling; database; fraud; label

INTRODUCTION

Wine is an agricultural product that derives much of its commercial value from the geographic location and year of winegrape production (1). Recognition of this has led to regulations in most wine-producing regions and the pursuit of many different independent methods of verifying claims of provenance and vintage (2–6). Stable isotope ratios have been particularly useful in making these verifications, especially in the European market (7). The stable isotope ratios of water (oxygen and hydrogen) yield unique geographic information (8, 9), primarily because of the predictable spatial variation of precipitation stable isotope ratios over the Earth's surface (10, 11). This spatial variation in precipitation is recorded in plant material since plants take up soil water that is derived generally

from local precipitation and incorporate hydrogen and oxygen atoms into the products of photosynthesis (12–14). For crops that are irrigated, this additional water can differ isotopically from local precipitation inputs, especially if that water is transported over long distances, and can therefore affect plant isotopic composition. Stable oxygen and hydrogen isotope ratios of wine have therefore commonly been used to detect adulteration of wines (3, 15, 16), to identify or verify claims of winegrape source locations (8–9, 17), and as recorders of climate (18, 19).

Although it is true that stable isotopes have been used for years in this way, there has not been a strong effort to try to model wine isotopes to explicitly predict source regions, nor have potentially powerful tools such as geographic information systems (GISs) been utilized. We were interested in evaluating the potential for wine oxygen stable isotope ratios ($\delta^{18}\text{O}$) to integrate and record precipitation stable isotope ratios and the climatic conditions during winegrape growth. We were further interested in developing a model of wine $\delta^{18}\text{O}$ that could be

* To whom correspondence should be addressed. Phone: (801) 587-3404. E-mail: jwest@biology.utah.edu.

[†] University of Utah.

[‡] IsoForensics.

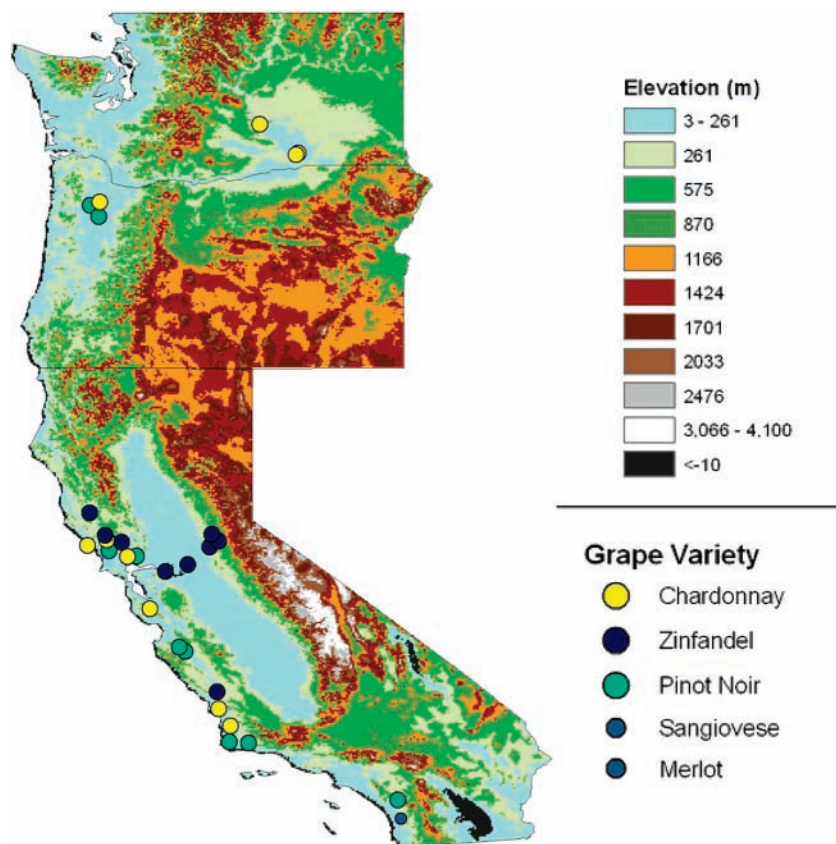


Figure 1. Geographical distribution of wine samples shown over a digital elevation map. All samples were obtained from bottles purchased at retail outlets labeled with either “estate bottled” or some other indication of locally sourced grapes (e.g., identification of the source vineyard) and were 2002 vintages. Grape varieties are as indicated in the legend. Smaller symbols are for varieties with only one sample.

executed in a GIS to allow spatially and temporally explicit predictions of wine stable isotope ratios for winegrape-growing regions in the coastal western United States. Wine $\delta^{18}\text{O}$ values have been explicitly linked to source water $\delta^{18}\text{O}$ (20–22), although in at least one paper it has been claimed that temperature and humidity have a dominant control on wine $\delta^{18}\text{O}$ values, essentially eliminating the source water signal (19). Grape water should primarily reflect the evaporative conditions of the grape water prior to harvest (20, 21, 23). Therefore, it should incorporate an isotopic “signal” both from the water accessed by the grapevine roots and from the evaporative conditions experienced by the grape. If a more detailed understanding of the controls on wine stable isotope ratios can be obtained, especially in a spatial context, the utility of wine stable isotope ratios in forensics and as archives of past conditions would be significantly improved.

Our approach to the development of a spatially and temporally explicit model of wine $\delta^{18}\text{O}$ was to sample industrial wines (produced commercially and purchased from retail stores) from the 2002 vintage that were derived from grapes grown in vineyards located along a primarily north to south transect along the western coast of the United States and analyze the wine water $\delta^{18}\text{O}$ for all samples. The wine water $\delta^{18}\text{O}$ of these wines was then compared to spatially continuous GIS map layers of source water $\delta^{18}\text{O}$ and climate to evaluate the impacts of these two large-scale drivers on wine water $\delta^{18}\text{O}$. Following a determination of the relevant climatic drivers, a model was developed that predicted wine water $\delta^{18}\text{O}$ values from long-term average source water $\delta^{18}\text{O}$ (precipitation) and climatic conditions for specific years. This model was then implemented as a raster overlay in a GIS and run using continuous raster grids as drivers. The model outputs for appropriate years were

then compared to previously published results for two locations in California reported by Ingraham and Caldwell (19).

MATERIALS AND METHODS

Wine samples were obtained from retail outlets and conformed to the following specifications: (1) 2002 vintage, (2) estate bottled or other identification that made an explicit claim of a discrete source of the grapes (e.g., a single vineyard identified on the bottle), and (3) Pinot Noir ($n = 12$), Zinfandel ($n = 12$), or Chardonnay ($n = 15$) varieties, and including one sample each of two other varieties (Merlot and Sangiovese). Although this approach introduces some uncertainty related to the accuracy of the label information, we believe that those U.S. producers that make claims of estate bottling or specific identifications of vineyards generally provide accurate label information, especially wines from smaller producers (the majority of samples acquired). The sample geographic and elevation distribution is shown in **Figure 1**. Samples were obtained from a significant north–south gradient of wine-producing regions along the western coast of the United States, as well as an east–west transect across the Central Valley of California. The wine samples were then analyzed for wine water $\delta^{18}\text{O}$. A subset of these samples ($n = 22$) was also analyzed for wine distillate $\delta^{18}\text{O}$.

Wine water $\delta^{18}\text{O}$ was obtained by first quantitatively vacuum distilling a 1 mL wine sample to remove wine solids and to allow complementary analysis of the complete distillate $\delta^{18}\text{O}$ of the same sample (see below). The 1 mL wine sample was distributed across clean glass wool, frozen to liquid nitrogen temperatures, placed under vacuum, and then heated to approximately 100 °C under vacuum in a closed system with a cold finger at liquid nitrogen temperatures. Distillation continued to completion. Following distillation, a 500 μL aliquot was then taken from each of these distillates and equilibrated for 48 h with 10% CO_2 gas at approximately 21 °C (room temperature of a climate-controlled building). The $\delta^{18}\text{O}$ of the equilibrated CO_2 gas was then analyzed with an elemental analyzer coupled to a Finnigan MAT Delta

Plus mass spectrometer (Thermo Electron Co., Waltham, MA). CO_2 rapidly equilibrates with water and has been shown to reflect accurately the $\delta^{18}\text{O}$ of water in water/ethanol mixtures (22, 24). Laboratory standard water samples calibrated on the V-SMOW scale were included with each set to allow the empirical calculation of the equilibrium offset between water $\delta^{18}\text{O}$ and equilibrated CO_2 $\delta^{18}\text{O}$, eliminating the need to carefully control the temperature during equilibration (25, 26). We conducted several evaluations of the accuracy and precision of quantifying wine water $\delta^{18}\text{O}$ using this method. The range of variation in $\delta^{18}\text{O}$ of the CO_2 from the same known water sample was $1\sigma = 0.2\text{‰}$, that of replicate injections from a single vial was $1\sigma = 0.1\text{‰}$, and that of replicate samples from a given bottle of wine carried through the entire process was $1\sigma = 0.2\text{‰}$. In addition to the water $\delta^{18}\text{O}$, the complete distillate (primarily water and ethanol) was also analyzed for $\delta^{18}\text{O}$ with a high-temperature conversion/elemental analyzer (TC/EA) coupled to a Finnigan Delta Plus XL mass spectrometer for a subset of samples ($n = 18$; $\delta^2\text{H}$ was obtained as well from this analysis, but will be discussed only briefly).

All results were incorporated into a wine stable isotope database that included the location of the vineyard, as well as other information about the sample. These data were then imported to ArcGIS as a point vector (shape) file. This vector data layer was intersected with raster data layers of long-term annual average expected precipitation $\delta^{18}\text{O}$ (from <http://waterisotopes.org>) and modeled monthly means of daily minimum and maximum air temperatures and mean daily dew point temperatures (from <http://www.ocs.orst.edu/prism/>) to yield long-term average precipitation $\delta^{18}\text{O}$ and monthly climate data for each wine sample location. The long-term annual average precipitation $\delta^{18}\text{O}$ map was selected for two primary reasons. First, the utilization of a continuous data layer such as this map provides estimated long-term average precipitation values for any location, and second, once the model is developed, wine water $\delta^{18}\text{O}$ can be predicted for locations not sampled directly by executing the model for all grid cells in the input layers. It therefore represents a compromise between source water accuracy and achieving the modeling goals.

Although the precipitation map cannot specifically identify plant source water, since it is based on long-term precipitation averages, it should represent the isotopic composition of the long-term average soil moisture available to plants, with some important caveats for irrigated crops such as some winegrapes. The map cannot account for any significant input of isotopically distinct irrigation water (e.g., water transported over long distances), nor does it account for any other potential isotopic changes, such as evaporation from soil surfaces. The degree of error introduced by irrigation water depends on the isotopic divergence of irrigation water from local precipitation and the volume of water applied. It is not currently possible to quantitatively evaluate this error in detail; however, some discussion of the likely degree of error is justified. The source of irrigation water is important. If, for example, river water is utilized, then the isotopic composition of irrigation water has the potential to be somewhat depleted relative to that predicted by the precipitation map in the western United States, especially in high topographic relief areas (27). If, however, there is long-distance transport, or the source is a relatively shallow reservoir, then the source water has the potential to be enriched relative to long-term average precipitation. Groundwater has been shown to be similar to long-term average local precipitation especially if recharge rates are relatively high (28, 29), but relatively complex interactions have been observed among precipitation, surface water, and groundwater (30), and fossil water can differ significantly from the mean isotopic composition of precipitation for recent decades.

A semiquantitative estimate of the potential divergence between precipitation and irrigation water can be made by comparing the difference between the mapped precipitation $\delta^{18}\text{O}$ and the $\delta^{18}\text{O}$ of local municipal waters for the region under study. In a recent paper the isotopic composition of municipal waters collected in many locations across the United States has been reported, as well as an interpolated map similar to that produced for precipitation for the surface of the Earth (31). Local municipal water should approximate irrigation water since municipal water can draw on multiple sources that should be similar to those utilized by agriculture. In addition, some winegrape growers irrigate with "recycled" municipal wastewater (32). According

to Bowen et al. (31), the differences observed between measured tap water $\delta^{18}\text{O}$ and the mapped annual precipitation $\delta^{18}\text{O}$ (tap minus precipitation) for the states of Washington, California, and Oregon ranged from approximately -2‰ to as high as 6‰ for the regions of interest, with most observations showing a range of less than $\pm 2\text{‰}$. These potential divergences need to be considered relative to their proportional contribution to vine water, especially after veraison when deficit irrigation is often utilized. Of course, individual vineyards in individual years have the potential to differ, even dramatically, from these generalizations. In this context, it is also important to recognize that significant interannual variation in the isotopic composition of precipitation itself could also result in error in our attempts to relate measured wine water $\delta^{18}\text{O}$ to modeled wine water $\delta^{18}\text{O}$ since the current model does not incorporate interannual variability in precipitation $\delta^{18}\text{O}$. Because higher density maps with greater annual resolution are not currently available, we believe that this annual map represents the best current proxy for plant available water $\delta^{18}\text{O}$ at the scale of regions such as the western United States. We therefore utilize this approach primarily to evaluate its potential to improve understanding of wine isotopic variation, recognizing the uncertainties in estimating the isotopic composition of vine source water discussed here. Future efforts will subsequently be directed at quantifying these errors and improving the models and model products.

There are several potential sources of continuous, gridded climate data for this area (33); however, we selected the PRISM dataset produced by the Oregon Climate Service (34) because of its specific focus on the climate of the United States and the explicit incorporation of terrain effects in addition to elevation. These climate datasets are available at a relatively high spatial resolution (0.042° grid cells) and for all years and months necessary for this analysis. Recent analyses suggest that reanalysis and common interpolation methods generally agree, yielding high confidence in the use of these interpolated datasets (33).

Following intersection with the precipitation $\delta^{18}\text{O}$ and 2002 climate data layers, correlation analyses were performed to evaluate the potential roles of both source water $\delta^{18}\text{O}$ and climate (derived from these raster data layers) in controlling geographic variation in wine water $\delta^{18}\text{O}$. In addition to the correlation analyses, a multiple-linear-regression model was fitted to the data that incorporated as drivers the precipitation $\delta^{18}\text{O}$ and the climate immediately preceding and during grape harvest for most winegrapes (means of September and October). This fitted multiple regression was then explored as a potential mechanistic explanation of the spatial variation in wine water $\delta^{18}\text{O}$. This was done by developing a raster overlay model from this regression model. The raster overlay simply involves executing the multiple-regression model at each grid cell using precipitation $\delta^{18}\text{O}$ and the climate layers as the input variables and producing a new raster containing the results of that calculation for each corresponding grid cell (more detail on these GIS approaches may be found at <http://isoscap.es.org>). The model was then executed using the appropriate climate layers for the years for which a previously published longitudinal survey of wine $\delta^{18}\text{O}$ was conducted for two locations in California (Napa and Livermore Valleys). A shape file containing the locations of Napa and Livermore cities was then intersected with each year's model predictions. A graphical comparison of these model predictions was then made with the published results.

RESULTS

Wine samples were obtained from the major wine-producing regions of the western coast of the United States, including Washington, Oregon, and northern and southern California (see **Figure 1**). There was a relatively large range of water $\delta^{18}\text{O}$ values obtained from these wines (**Figure 2**). Wines from Washington and Oregon, although less numerous, were clearly distinguishable from those from California, with $\delta^{18}\text{O}$ values ranging from near zero to almost 3‰ . Although consistently higher than those from Washington and Oregon, there was also a large range of $\delta^{18}\text{O}$ values obtained for the California wines. This is especially evident in the wines from the Central Coast, with wine water $\delta^{18}\text{O}$ values ranging from 3.9‰ to 10.7‰ in

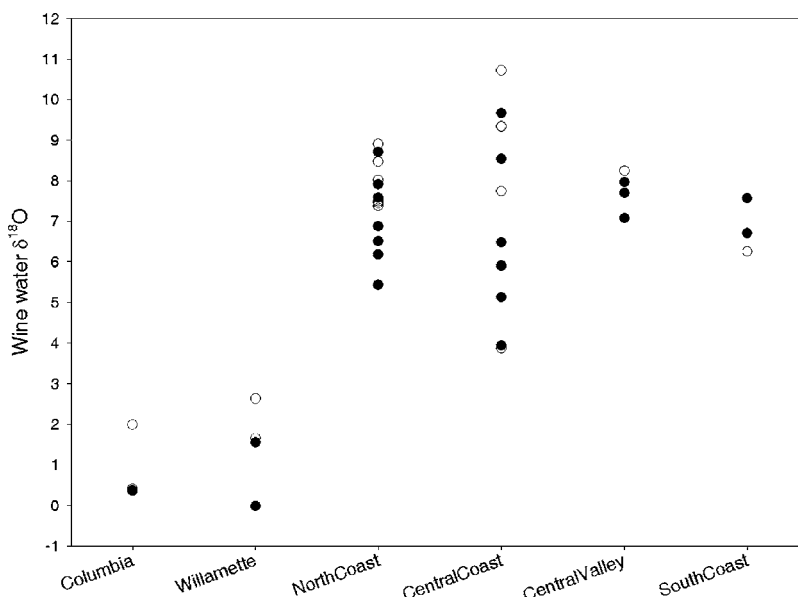


Figure 2. Wine water $\delta^{18}\text{O}$ results plotted by geographical regions. Open circles represent samples from bottles labeled as “estate bottled” ($n = 19$), and filled circles represent bottles labeled with some other indication of source vineyard location ($n = 23$).

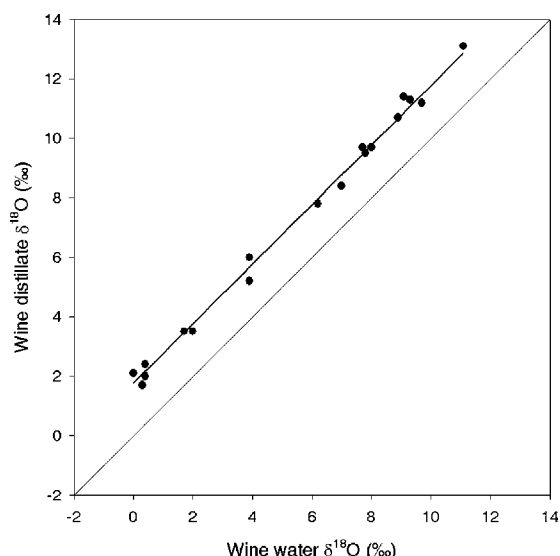


Figure 3. Wine distillate $\delta^{18}\text{O}$ versus wine water $\delta^{18}\text{O}$. The fitted line has a slope of 1.0, and the intercept is 1.7 ($n = 18$, $R^2 = 0.997$, $P < 0.0001$).

that region. Even comparing North Coast to South Coast wines, there was considerable overlap in measured wine water $\delta^{18}\text{O}$ values. In addition to the wine water samples analyzed, a subset of wine distillates were analyzed, and the results of this analysis and comparison are shown in **Figure 3**. The slope of the fitted line relating wine distillate $\delta^{18}\text{O}$ to wine water $\delta^{18}\text{O}$ was not different from 1, and the y intercept was 1.7‰. The wine distillate $\delta^2\text{H}$ was also compared to the wine distillate $\delta^{18}\text{O}$ and yielded a linear regression slope of 5.7 and an intercept of -48.6 ($R^2 = 0.74$, $P < 0.0001$).

As expected, a positive correlation was observed between wine water $\delta^{18}\text{O}$ and predicted precipitation $\delta^{18}\text{O}$ ($R = 0.45$, $P = 0.004$; see **Figure 4**). This is in spite of the relatively poor data density on the coast and the known uncertainties associated with predicting precipitation $\delta^{18}\text{O}$ in coastal regions (see ref 35). In addition, the comparison with modeled climate for wine sample locations in 2002 revealed strong correlations both at the beginning of the growing season and at the end of the season (see **Table 1**). Wine water $\delta^{18}\text{O}$ was not, however, correlated

with climate variation for months during the middle, relatively hot part of the growing season.

On the basis of these results and those previously published showing strong correlations between wine water $\delta^{18}\text{O}$ and climate at the end of the growing season (36), a multiple-regression model was developed to permit the prediction of wine water $\delta^{18}\text{O}$ from both expected source water $\delta^{18}\text{O}$ and climatic variation. A stepwise multiple-regression analysis showed strong predictive power for both September and October maximum and dew point temperatures (results not shown). However, since September and October climates are also correlated, climate values for these two months were averaged, and this end of season climate average was then used in the multiple-regression model. The final model had the form

$$\text{wine water } \delta^{18}\text{O} = 8.70 + 0.588T_{\text{maxSO}} - 0.568T_{\text{dnnSO}} + 1.37\delta^{18}\text{O}_{\text{precip}}$$

with T_{maxSO} being the mean of the monthly mean maximum daily temperatures for September and October, T_{dnnSO} being the mean of the monthly mean daily dew point temperatures for September and October (see the PRISM Group, Oregon State University, <http://www.prismclimate.org>, date created Aug 2, 2004; 34), and $\delta^{18}\text{O}_{\text{precip}}$ being the modeled long-term average precipitation $\delta^{18}\text{O}$ (see ref 38). The adjusted R^2 for this model was 0.57 ($P < 0.0001$). To illustrate the explanatory power of the model and the variation between the varieties and states of the origin, the data are shown plotted against model predictions, separated by grape variety, in **Figure 5** (although included in the model, the Sangiovese and Merlot data are not plotted because only one sample each was obtained). The distribution of $\delta^{18}\text{O}$ values was widest for Chardonnay and lowest for Zinfandel, primarily due to the relatively large geographic distribution of Chardonnay grapes and the restricted distribution of Zinfandel grapes.

To further evaluate the utility of this model, and to allow comparisons with other data collected from known locations, the model was implemented in ArcGIS using the raster overlay feature in Model Builder (see <http://isoscapes.org>). The model results for 2002 are shown in **Figure 6**, with the wine sample origin locations and county outlines also shown. The distinction

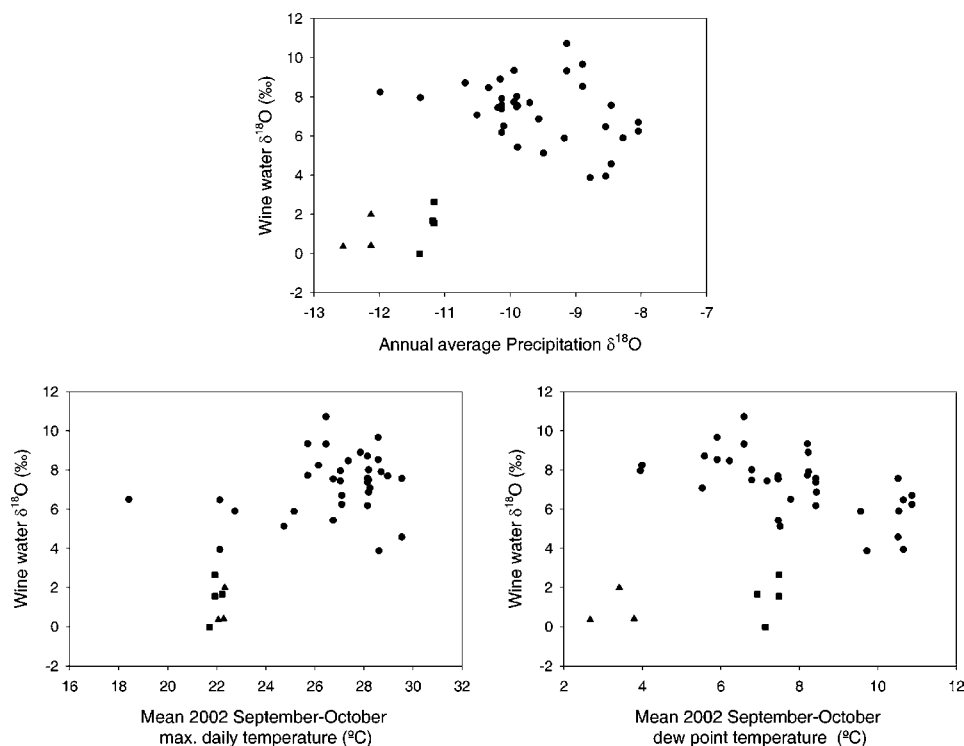


Figure 4. Wine water $\delta^{18}\text{O}$ plotted against climate and precipitation $\delta^{18}\text{O}$ drivers used in the fitted multiple-linear-regression model (see **Figure 1**). California samples ($n = 35$) are shown as circles, Oregon samples ($n = 4$) as squares, and Washington samples ($n = 3$) as triangles.

Table 1. Correlation Coefficients for Pairwise Correlations between Wine Water $\delta^{18}\text{O}$ and Climate Parameters Derived from a GIS Intersection between Wine Sample Locations and Expected Climate Layers Produced by the PRISM Group^a

month	min temp (°C)	max temp (°C)	mean dew point temp (°C)
March	0.51	0.70	0.46
April	0.47	0.54	0.48
May	0.14	0.53	0.14
June	-0.02	0.34	-0.37
July	-0.17	0.10	-0.14
August	-0.09	0.16	0.13
September	0.21	0.47	-0.01
October	0.46	0.77	0.23

^a Oregon State University, <http://www.prismclimate.org>, date created Aug 2, 2004.

between the wines produced in the more northern Washington and Oregon regions and those produced in California is clearly evident, with much lower isotope ratios predicted in the northern regions. Also worth noting is the relatively wide range of expected values along the coastal regions of California. This variation is driven primarily by differences in climate, since the expected variation in precipitation $\delta^{18}\text{O}$ is not as variable (see <http://waterisotopes.org>). Also overlaid on the predicted map are the locations of the Napa and Livermore Valleys (actual locations were Napa and Livermore cities). In addition to the model results shown in **Figure 6**, the model was run for the same vintage years analyzed by Ingraham and Caldwell (19). Since Ingraham and Caldwell (19) analyzed total wine $\delta^{18}\text{O}$, the model results for wine water were converted to expected total wine $\delta^{18}\text{O}$ by adding 1.7‰ to the wine water prediction. This is based on the results shown in **Figure 3** comparing the wine water $\delta^{18}\text{O}$ values to the $\delta^{18}\text{O}$ values obtained for wine distillate. Although the wine distillate does not include wine solids, it is likely that the distillates compare well with total bulk wine given the relatively small proportion of total wine

mass attributable to solids. The results of the model executions for the Napa and Livermore locations are shown in **Figure 7**, as are the results for those locations reported by Ingraham and Caldwell (19). With the exception of a strong divergence between the model predictions and data in 1992, the model predictions and data agree quite well. The interannual changes in wine, previously attributed to climatic differences, are well predicted by this model. In addition to the correct prediction of interannual changes in wine $\delta^{18}\text{O}$, the model also generally predicts higher $\delta^{18}\text{O}$ values for Napa Valley wines compared to Livermore Valley wines, consistent with the results from Ingraham and Caldwell (19). Although the model performed quite well relative to the data, it should be noted that the model both under- and overpredicts wine $\delta^{18}\text{O}$ values for individual years.

DISCUSSION

Consistent with our expectations based on the geographic distributions of precipitation $\delta^{18}\text{O}$ variation, wine water $\delta^{18}\text{O}$ values from Washington and Oregon wines were considerably lower than those from all wines from California. Wines from different regions in California also showed significant amounts of variability, but could not readily be differentiated on the basis of $\delta^{18}\text{O}$ values alone. Measured wine water $\delta^{18}\text{O}$ derived from wines that came from California-, Washington-, and Oregon-grown grapes were positively correlated with source water $\delta^{18}\text{O}$ values and with air temperatures derived from spatially continuous geospatial climate data layers for each vineyard location. The patterns of correlation between wine water $\delta^{18}\text{O}$ and source water $\delta^{18}\text{O}$ and climate illustrate some important points. First, although the vapor content of the atmosphere should reduce the degree of isotopic enrichment in the grape water (20), there

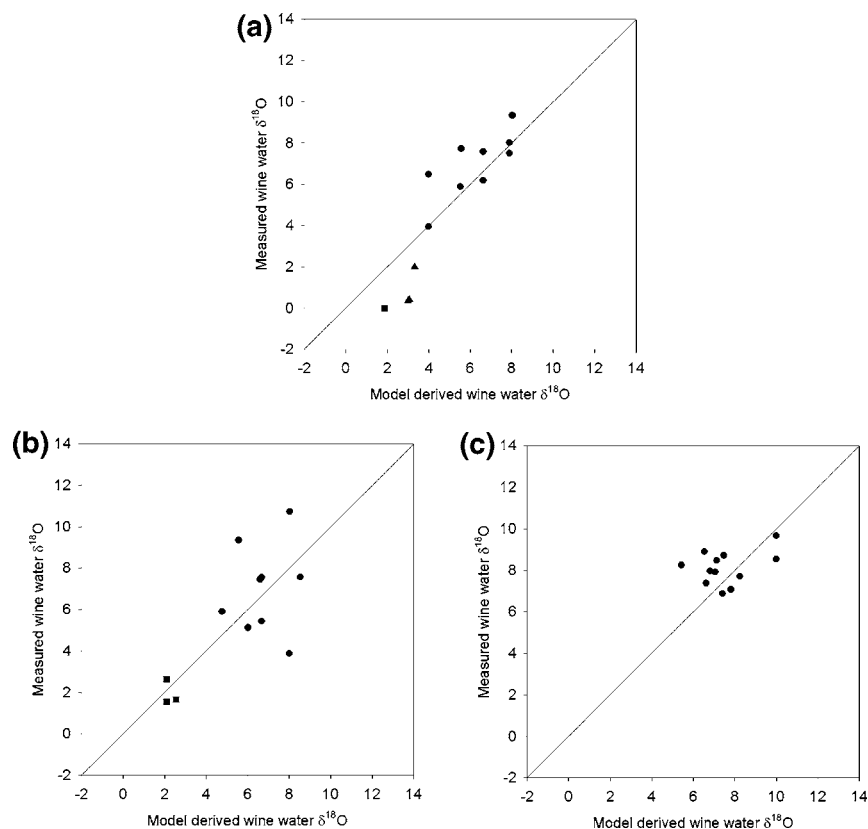


Figure 5. Wine water $\delta^{18}\text{O}$ data versus multiple-regression model predicted wine water $\delta^{18}\text{O}$ for (a) Chardonnay, (b) Pinot Noir, and (c) Zinfandel grape varieties from the 2002 vintage. California samples are shown as circles, Oregon samples as squares, and Washington samples as triangles. The model is based on the 2002 climate and long-term annual average precipitation $\delta^{18}\text{O}$ and fitted to the measured wine water $\delta^{18}\text{O}$ data (see Figure 4).

is not a consistent pattern of declines in wine water $\delta^{18}\text{O}$ with increasing dew point temperature across the complete dataset. The observed patterns in wine water $\delta^{18}\text{O}$ values are consistent with a multivariate control on wine water $\delta^{18}\text{O}$ and in part disagree with the conclusions of Ingraham and Caldwell (19) that source water does not play an important role in wine $\delta^{18}\text{O}$ variability. Climate is clearly important in controlling wine water $\delta^{18}\text{O}$. However, the isotopically depleted precipitation that falls on vineyards in Washington and Oregon results in wines that are also relatively depleted isotopically in spite of the relatively large vapor pressure deficit in the atmosphere there.

In agreement with previously reported results (15, 18–20, 39), we did observe good correlations between wine water $\delta^{18}\text{O}$ and climatic patterns. Strong correlations between wine $\delta^{18}\text{O}$ and climate immediately prior to harvest have been reported (39, 40), whereas others find stronger correlations by including the midsummer warmer months (19). The extreme temperatures and evaporative demands during the middle of the growing season were not reflected in the wine $\delta^{18}\text{O}$ values in this study, consistent with expected relatively high grape water turnover rates. It is worth noting that although we did find correlations with the climatic conditions at the beginning of the growing season as well as at the end, the climatic conditions at the beginning and end of the growing season were correlated. This likely explains the correlations between wine water $\delta^{18}\text{O}$ and the early season climate and does not suggest a mechanistic link between them.

Although there were differences observed between varieties, these differences were generally small and were also confounded with differences in the climates of the different regions. Zinfandel grapes tended to have higher $\delta^{18}\text{O}$ values than the other varieties. However, Zinfandel grapes tend to be grown, and in our sampling were generally restricted, to warmer, drier

climates. As such it cannot be determined from these results whether varieties differ inherently in wine water $\delta^{18}\text{O}$ values. Previous authors have concluded that the differences in wine stable isotope ratios observed among varieties were due to differences in their time of harvest and not to any inherent differences among varieties, although both increases (19) and decreases (39) in wine $\delta^{18}\text{O}$ have been observed as the harvest date occurs later in the season. Future work could attempt to resolve these issues by sampling multiple varieties over time and in regions that differ significantly in both climate and precipitation $\delta^{18}\text{O}$. Understanding water flow into and out of grape berries could be critical to understanding the expected isotopic composition of grapes and wine. Recent studies (41, 42) contradict previous reports (43) of postveraison cessation of xylem water flow. If there are differences among varieties in how phloem and xylem water or solute transport change during berry development, this could significantly affect the grape water stable isotope composition. The measured wine water $\delta^{18}\text{O}$ values reported here are quite high. Phloem water would be expected to be partially enriched through evaporation in the leaves, potentially explaining the highly enriched wine water values observed here.

A multiple-linear-regression model that incorporated long-term average precipitation $\delta^{18}\text{O}$ and mean maximum and dew point temperatures for September and October was fitted to the 2002 vintage wine water $\delta^{18}\text{O}$ results. When this model was driven with the relevant spatially continuous raster layers for the years sampled by Ingraham and Caldwell (19) for wines from Napa and Livermore, there was good agreement between model predictions and the reported data across years. There was also good agreement between the model predictions and a temporally extended dataset for Napa Valley only (19; results not shown). These results suggest that, as expected, wine water

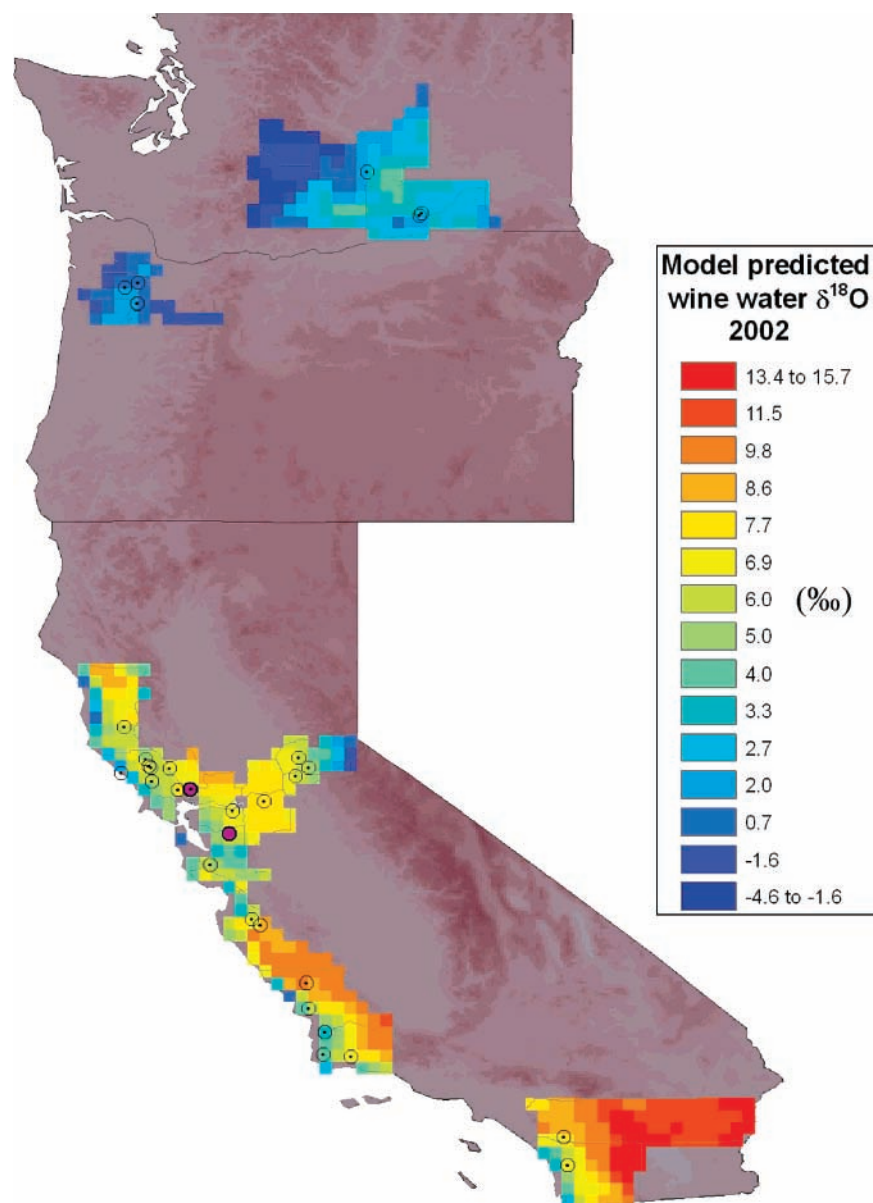


Figure 6. Model output for 2002 for the counties containing or near the locations of the source vineyards for all wine samples (over digital elevation for reference). Also shown are the locations of Napa (northern) and Livermore (southern) Valleys in purple.

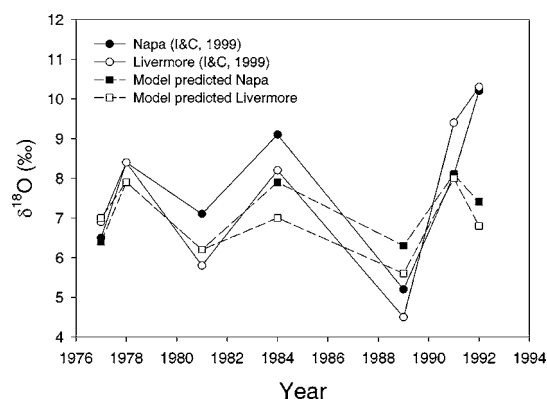


Figure 7. Geographic information system model output for Napa and Livermore (see locations in **Figure 6**) and results published by Ingraham and Caldwell (19) for those locations. Years lacking data are those years for which no data were reported by Ingraham and Caldwell (19).

$\delta^{18}\text{O}$ may be predicted for a range of conditions and across multiple vintages using simple models that relate wine water

$\delta^{18}\text{O}$ to climate and precipitation $\delta^{18}\text{O}$. Although vinification processes may change from vineyard to vineyard, and from year to year, it appears that this model accurately predicts the large interannual changes for a given vineyard, as well as maintains the relative differences across years between vineyards. There was one significant exception to this in the Napa/Livermore dataset in 1992. The model predicted a decline in wine $\delta^{18}\text{O}$, whereas the reported results show an increase relative to the value for the previous year. Although we cannot directly account for this discrepancy, it is possible that it is related to the El Niño/Southern Oscillation (ENSO) event of 1991/1992 that dramatically affected rainfall patterns and amounts (45, 46). It may be that this event was sufficient to cause the precipitation $\delta^{18}\text{O}$ to deviate significantly from long-term averages, resulting in wine $\delta^{18}\text{O}$ not well predicted by our model. Unfortunately, we do not have precipitation records for these locations and years. However, of the vintages analyzed, the lowest Southern Oscillation Index was recorded in 1992 (data not shown; <http://www.cgd.ucar.edu/cas/catalog/climind/soi.html>).

These results strongly suggest that wine water $\delta^{18}\text{O}$ may indeed serve as a useful recorder of past climates. Although our results suggest that source water $\delta^{18}\text{O}$ is important in controlling large-scale variation in wine water $\delta^{18}\text{O}$, the available data did not permit us to evaluate the effects of interannual variation in precipitation $\delta^{18}\text{O}$. Future model improvements could include an explicit consideration of interannual variation in precipitation $\delta^{18}\text{O}$, as well as import of irrigation water. In addition to the potential utility of wine water $\delta^{18}\text{O}$ in reconstructing the climate, these results suggest that, as the uncertainties we have discussed are better understood and the model sophistication grows, GIS models such as this one may be useful for the detection of adulterations of wine, as well as for identifying wines that may not be consistent with the year and location claimed on wine labels (see, e.g., ref 39), further strengthening the utility of single isotopes in making these determinations.

ACKNOWLEDGMENT

J.B.W. thanks Jerry and Linda Johnston and Jill West for help with wine sampling. Craig Cook and Mike Lott provided assistance with the isotope analyses. Gabe Bowen supplied the precipitation isotope map.

LITERATURE CITED

- Beverland, M.; Luxton, S. Managing integrated marketing communication (IMC) through strategic decoupling - How luxury wine firms retain brand leadership while appearing to be wedded to the past. *J. Advertising* **2005**, *34* (4), 103–116.
- Almeida, C. M.; Vasconcelos, M. T. S. D. ICP-MS determination of strontium isotope ratio in wine in order to be used as a fingerprint of its regional origin. *J. Anal. At. Spectrom.* **2001**, *16* (6), 607–611.
- Kosir, I. J.; Kocjancic, M.; Ogrinc, N.; Kidric, J. Use of SNIF-NMR and IRMS in combination with chemometric methods for the determination of chaptalisation and geographical origin of wines (the example of Slovenian wines). *Anal. Chim. Acta* **2001**, *429* (2), 195–206.
- Boscaini, E.; Mikoviny, T.; Wisthaler, A.; von Hartungen, E.; Mark, T. D. Characterization of wine with PTR-MS. *Int. J. Mass Spectrom.* **2004**, *239* (2–3), 215–219.
- Brescia, M. A.; Kosir, I. J.; Caldarola, V.; Kidric, J.; Sacco, A. Chemometric classification of Apulian and Slovenian wines using H-1 NMR and ICP-OES together with HPICE data. *J. Agric. Food Chem.* **2003**, *51* (1), 21–26.
- Coetzee, P. P.; Steffens, F. E.; Eiselen, R. J.; Augustyn, O. P.; Balcaen, L.; Vanhaecke, F. Multi-element analysis of South African wines by ICP-MS and their classification according to geographical origin. *J. Agric. Food Chem.* **2005**, *53* (13), 5060–5066.
- Rossmann, A. Determination of stable isotope ratios in food analysis. *Food Rev. Int.* **2001**, *17* (3), 347–381.
- Asche, S.; Michaud, A. L.; Brenna, J. T. Sourcing organic compounds based on natural isotopic variations measured by high precision isotope ratio mass spectrometry. *Curr. Org. Chem.* **2003**, *7* (15), 1527–1543.
- Martin, M. L.; Martin, G. J. Site-specific isotope effects and origin inference. *Analysis* **1999**, *27* (3), 209–213.
- Gat, J. R.; Airey, P. L. Stable water isotopes in the atmosphere/biosphere/lithosphere interface: Scaling-up from the local to continental scale, under humid and dry conditions. *Global Planet. Change* **2006**, *51*, 25–33.
- Dutton, A.; Wilkinson, B. H.; Welker, J. M.; Bowen, G. J.; Lohmann, K. C. Spatial distribution and seasonal variation in O-18/O-16 of modern precipitation and river water across the conterminous USA. *Hydrol. Processes* **2005**, *19* (20), 4121–4146.
- Dawson, T. E.; Mambelli, S.; Plamboeck, A. H.; Templer, P. H.; Tu, K. P. Stable isotopes in plant ecology. *Annu. Rev. Ecol. Syst.* **2002**, *33*, 507–559.
- Roden, J. S.; Lin, G. G.; Ehleringer, J. R. A mechanistic model for interpretation of hydrogen and oxygen isotope ratios in tree-ring cellulose. *Geochim. Cosmochim. Acta* **2000**, *64* (1), 21–35.
- West, J. B.; Bowen, G. J.; Cerling, T. E.; Ehleringer, J. R. Stable isotopes as one of nature's ecological recorders. *Trends Ecol. Evol.* **2006**, *21* (7), 408–414.
- Ogrinc, N.; Kosir, I. J.; Spangenberg, J. E.; Kidric, J. The application of NMR and MS methods for detection of adulteration of wine, fruit juices, and olive oil. A review. *Anal. Bioanal. Chem.* **2003**, *376* (4), 424–430.
- Martinelli, L. A.; Moreira, M. Z.; Ometto, J. P. H. B.; Alcarde, A. R.; Rizzon, L. A.; Stange, E.; Ehleringer, J. R. Stable carbon isotopic composition of the wine and CO₂ bubbles of sparkling wines: Detecting C-4 sugar additions. *J. Agric. Food Chem.* **2003**, *51* (9), 2625–2631.
- Zhang, B. L.; Buddrus, S.; Trierweiler, M.; Martin, G. J. Characterization of glycerol from different origins by H-2- and C-13-NMR studies of site-specific natural isotope fractionation. *J. Agric. Food Chem.* **1998**, *46* (4), 1374–1380.
- Martin, G. J.; Martin, M. L. Climatic significance of isotope ratios. *Phytochem. Rev.* **2003**, *2* (1–2), 179.
- Ingraham, N. L.; Caldwell, E. A. Influence of weather on the stable isotopic ratios of wines: Tools for weather/climate reconstruction? *J. Geophys. Res., [Atmos.]* **1999**, *104* (D2), 2185–2194.
- Martin, G. J.; Odier, D.; Godineau, V.; Naudet, N. Natural isotope tracers and water filiation in the vine ecosystem. *Appl. Geochem.* **1989**, *4*, 1–11.
- Martin, G. J.; Guillou, C.; Martin, M. L.; Cabanis, M. T.; Tep, Y.; Aerny, J. Natural factors of isotope fractionation and the characterization of wines. *J. Agric. Food Chem.* **1988**, *36*, 316–322.
- Gremaud, G.; Pfammatter, E.; Piantini, U.; Quaile, S. Classification of Swiss wines on a regional scale by means of a multi-isotopic analysis combined with chemometric methods. *Mitt. Lebensmittelunter. Hyg.* **2002**, *93*, 44–56.
- Tardaguila, J.; Bertamini, M.; Reniero, F.; Versini, G. Oxygen isotope composition of must-water in grapevine: effects of water deficit and rootstock. *Aust. J. Grape Wine Res.* **1997**, *3*, 84–89.
- Bréas, O.; Reniero, F.; Serrini, G. Isotope ratio mass spectrometry: Analysis of wines from different European countries. *Rapid Commun. Mass Spectrom.* **1994**, *8*, 967–970.
- Epstein, S.; Mayeda, T. Variation in the O¹⁸ content of waters from natural sources. *Geochim. Cosmochim. Acta* **1953**, *4*, 213–224.
- Mills, G. A.; Urey, H. C. The kinetics of isotopic exchange between carbon dioxide, bicarbonate ion, carbonate ion and water. *J. Am. Chem. Soc.* **1940**, *62*, 1019–1026.
- Dutton, A.; Wilkinson, B. H.; Welker, J. M.; Bowen, G. J.; Lohmann, K. C. Spatial distribution and seasonal variation in O-18/O-16 of modern precipitation and river water across the conterminous USA. *Hydrol. Processes* **2005**, *19* (20), 4121–4146.
- Aquilina, L.; Ladouche, B.; Dorfliger, N. Water storage and transfer in the epikarst of karstic systems during high flow periods. *J. Hydrol.* **2006**, *327* (3–4), 472–485.
- Ofterdinger, U. S.; Balderer, W.; Loew, S.; Renard, P. Environmental isotopes as indicators for ground water recharge to fractured granite. *Ground Water* **2004**, *42* (6–7), 868–879.
- Palmer, P. C.; Gannett, M. W.; Hinkle, S. R. Isotopic characterization of three groundwater recharge sources and inferences for selected aquifers in the upper Klamath Basin of Oregon and California, USA. *J. Hydrol.* **2007**, *336* (1–2), 17–29.

- (31) Bowen, G. J.; Ehleringer, J. R.; Chesson, L. A.; Stange, E.; Cerling, T. E. Stable isotope ratios of tap water in the contiguous United States. *Water Resour. Res.* **2007**, *43* (3).
- (32) Page, A. L.; Ayanaba, A.; Baram, M. S.; Barrett, G. W.; Boggess, W. G.; Chang, A.; Cooper, R. C.; Dick, R. I.; Graef, S. P.; Long, T. E.; St. Hilaire, C.; Silverstein, J.; Stuart, S. C.; Waggoner, P. E. *Use of reclaimed water and sludge in food crop production*; National Academy Press: Washington, DC, 1996; pp 178.
- (33) Betts, A. K.; Zhao, M.; Dirmeyer, P. A.; Beljaars, A. C. M. Comparison of ERA40 and NCEP/DOE near-surface data sets with other ISLSCP-II data sets. *J. Geophys. Res.* **2006**, *111* (D22SO4).
- (34) Daly, C.; Neilson, R. P.; Phillips, D. L. A Statistical-Topographic Model for Mapping Climatological Precipitation over Mountainous Terrain. *J. Appl. Meteorol.* **1994**, *33* (2), 140–158.
- (35) Bowen, G. J.; Wassenaar, L. I.; Hobson, K. A. Global application of stable hydrogen and oxygen isotopes to wildlife forensics. *Oecologia* **2005**, *143* (3), 337–348.
- (36) Smart, R. E.; Dry, P. R. A climate classification for Australian viticultural regions. *Aust. Grapegrower Winemaker* **1980**, *17*, 8–16.
- (37) Daly, C. Guidelines for assessing the suitability of spatial climate data sets. *Int. J. Climatol.* **2006**, *26*, 707–721.
- (38) Bowen, G. J.; Revenaugh, J. Interpolating the isotopic composition of modern meteoric precipitation. *Water Resour. Res.* **2003**, *39* (10), 1299.
- (39) Rossmann, A.; Reniero, F.; Moussa, I.; Schmidt, H. L.; Versini, G.; Merle, M. H. Stable oxygen isotope content of water of EU data-bank wines from Italy, France, and Germany. *Z. Lebensm.-Unter.-Forsch. A: Food Res. Technol.* **1999**, *208*, 400–407.
- (40) Christoph, N.; Rossmann, A.; Voerkelius, S. Possibilities and limitations of wine authentication using stable isotope and meteorological data, data banks and statistical tests. Part 1: Wines from Franconia and Lake Constance 1992 to 2001. *Mitt. Klosterneuburg* **2003**, *53*, 23–40.
- (41) Keller, M.; Smith, J. P.; Bondada, B. R. Ripening grape berries remain hydraulically connected to the shoot. *J. Exp. Bot.* **2006**, *57* (11), 2577–2587.
- (42) Rogiers, S. Y.; Greer, D. H.; Hatfield, J. M.; Orchard, B. A.; Keller, M. Solute transport into Shiraz berries during development and late-ripening shrinkage. *Am. J. Enol. Vitic.* **2006**, *57* (1), 73–80.
- (43) Düring, H.; Lang, A.; Oggionni, F. Patterns of water flow in Riesling berries in relation to developmental changes in their xylem morphology. *Vitis* **1987**, *26*, 123–131.
- (44) Findlay, N.; Oliver, K. J.; Nil, N.; Coombe, B. G. Solute Accumulation by Grape Pericarp Cells: IV. Perfusion of pericarp apoplast via the pedicel and evidence for xylem malfunction in ripening berries. *J. Exp. Bot.* **1987**, *38* (4), 668–679.
- (45) Ramp, S. R.; McClean, J. L.; Collins, C. A.; Semtner, A. J.; Hays, K. A. S. Observations and modeling of the 1991–1992 El Nino signal off central California. *J. Geophys. Res., [Oceans]* **1997**, *102* (C3), 5553–5582.
- (46) Polis, G. A.; Hurd, S. D.; Jackson, C. T.; Pinero, F. S. El Niño effects on the dynamics and control of an island ecosystem in the Gulf of California. *Ecology* **1997**, *78* (6), 1884–1897.

Received for review April 24, 2007. Revised manuscript received June 7, 2007. Accepted June 11, 2007. Financial support was provided by IsoForensics, Inc., Salt Lake City, UT.

JF071211R