Oxygen isotope ratios in Holocene carbonates across a climatic gradient, eastern Washington State, USA: Evidence for seasonal effects on pedogenic mineral isotopic composition

B.A. Stevenson,1 E.F. Kelly,1 E.V. McDonald,2 A.J. Busacca3 and J.M. Welker4

Abstract
Oxygen isotope ratios of pedogenic carbonates were analyzed along a climatic gradient in the Palouse region of eastern Washington State to evaluate changes in their isotopic composition with changing climate. A modern analog approach was used to assess the relationship between the isotope ratios in the pedogenic carbonates with those in soil water (measured in June when we anticipated carbonate formation might occur because of low soil water content), and meteoric water from two National Atmospheric Deposition Program (NADP) sites adjacent to our sequence. Mean annual meteoric water δ18O values (wrt VSMOW) from the two NADP sites varied slightly with elevation, −13.9‰ at the Starkey site (elevation 1253 m) and −13.0‰ at the Palouse site (elevation 766 m) but showed distinct seasonal trends with weighted means ranging from −11.9‰ during autumn to −15.0‰ during the winter. Carbonate δ18O (wrt VPDB) varied significantly with MAP, ranging from −14.1‰ at the most arid site to −11.4‰ at the wettest site but displayed a trend opposite to that of soil water δ18O (−4 to −12‰ VSMOW for the 70 cm depth). Neither measured soil water δ18O values nor mean meteoric water δ18O values generated realistic temperatures of formation for the observed trend in carbonate δ18O values. When mean annual temperatures across the gradient were used for temperature of formation, calculated soil water δ18O in equilibrium with carbonate δ18O was similar to winter precipitation δ18O at the most arid sites but became increasingly similar to mean annual meteoric δ18O as MAP increased. We suggest that the unexpected trend in carbonate δ18O is largely due to the diminishing influence of winter precipitation/snowmelt on soil moisture as MAP increases across the climatic gradient and that seasonal effects of meteoric water may need to be considered in pedogenic mineral isotopic equilibrium in temperate regions.

Keywords
meteoric water, modern analogs, oxygen isotopes, Palouse loess, pedogenic carbonates, soil water

Introduction
Oxygen isotope data from ice cores and marine sediments have played a key role in reconstructing global scale climate change (Fricke and O’Neil, 1999). The isotopic composition of pedogenic minerals has shown potential as an equivalent proxy in terrestrial ecosystems, however, the pedologic system is complex, and it is often difficult to determine which of several environmental variables exert the greatest influence over mineral isotopic composition (Savin and Epstein, 1970). The factors that affect pedogenic mineral oxygen isotope composition include the isotopic composition of soil water and temperature (Lawrence and Taylor, 1971; Savin and Epstein, 1970). In studies of paleosols, however, both the isotopic composition of soil water and temperature of formation values are unknown. Thus either soil water isotopic composition or temperature of formation must be constrained in order to estimate the other from mineral isotopic composition.

Soil water isotopic composition reflects the isotopic composition of meteoric water and processes or interactions that alter the isotopic composition of meteoric water once within the soil. On a global scale, average annual isotopic composition of meteoric water varies predictably with latitude, but at a particular location can vary dramatically over the course of storms, seasonally, and on longer timescales reflecting changing climatic regimes (Bowen and Revenaugh, 2003; Dansgaard, 1964; Gat, 1980). The isotopic composition of meteoric water can be modified in the soil by evaporative soil water loss (which leaves the residual soil water enriched in 18O) or interaction with groundwater or immobile water (e.g. water adsorbed to clays). The mode of water loss from soil is important as transpiration or downward percolation of soil water out of the pedogenic zone is generally thought to occur without isotopic fractionation (Hsieh et al., 1998a; Zimmerman et al., 1967). Temperature also affects the degree of isotopic fractionation...
between substances (O’Neil, 1986) and the isotopic signature of a specific mineral is dependent not only on the isotopic composition of soil water from which it equilibrates, but upon the temperature of formation as well.

Changes in oxygen isotope ratios observed in paleosol soil minerals (primarily pedogenic carbonate) have been used to infer global-scale changes in atmospheric weather patterns (Amundson et al., 1996; Gregory et al., 1989; Mack et al., 1991; Quade et al., 1989a). Dworkin et al. (2005) found that a spatial model of annual meteoric δ18O (in contrast to a temporal model) was the most accurate predictor of carbonate 18O in modern soils found in Texas USA, but suggested the model might prove inadequate in continental interior basins where meteoric δ18O does not follow typical latitudinal patterns (which they note comprises many arid climates of the world).

The use of pedogenic carbonates as a stand-alone paleotemperature indicator has been less successful as even in modern systems it has often been difficult to relate mineral isotopic values with meteoric water at temperatures of formation reasonable for that location (see for instance Quade et al., 1989b). In part this may be because of variation in seasonal patterns of precipitation or alteration of meteoric water values in the soil, but few intensive studies of soil water (let alone the relationship between soil water and pedogenic minerals) exist.

Hsieh et al. (1998a) demonstrated that in a Hawaiian climosequence, soil water δ18O can vary along a sequence depending on seasonal meteoric water inputs and the balance between evaporative and transpirative soil water loss. Soil water was always more depleted in δ18O (more positive) than meteoric water at their most arid site (180 mm MAP), but approached meteoric water values at higher precipitation sites, particularly when soil moisture content was high. Ferretti et al. (2003) measured soil water values over a 3 year period in the eastern Colorado plains and found that winter and early spring soil water was generally much more enriched (positive) than meteoric water (particularly during the winter months), and soil water only approached meteoric water values after heavy summer thunderstorms when soil moisture was high. They note, however, that during the period of measurement, winter precipitation had very little effect on soil moisture and that any snowpack was largely sublimated.

Robertson and Gazis (2006) measured soil water δ18O values over a year-long period at two sites within the same region as our study (on the eastern slope of the Cascade Mountains). They also noted that soil water was more enriched than meteoric water, but in contrast to Ferretti et al. (2003) found that deep (>60 cm depth) soil water at the arid site (225 mm MAP) was only recharged in the spring by snowmelt, and the soil water retained an isotopic signature throughout the year that appeared to be dominated by snowmelt and spring precipitation. The effect of winter and spring precipitation were diminished at the wetter site (580 mm MAP) because of increased meteoric inputs and mixing with a larger pool of immobile water.

Thus, it is uncertain whether pedogenic carbonate δ18O can be best described by annual meteoric water δ18O values or whether more complex changes in soil water also need to be considered. Breeker et al. (2009) argue that there is likely to be a seasonal component to carbonate formation and that oxygen isotope equilibrium occurs at minimum calcite solubility during hot, dry conditions but others (Quade et al., 1989b) have suggested that carbonates may be deposited at the time of the deepest wetting front penetration into the soil.

Despite the debate and uncertainty surrounding oxygen isotope equilibrium in carbonates, few studies have assessed the relationships among the environmental variables that determine carbonate δ18O values (meteoric water, soil water, and temperature) to determine how they interact on an ecosystem scale (e.g. Amundson et al., 1989; Quade et al., 1989b). Even fewer of these studies have occurred in temperate regions where seasonal difference in temperature and isotopic composition of meteoric water are large. The extent to which these factors interact in modern systems may prove useful in inferring past climate change in paleosols and the mechanisms of carbonate formation and their movement in soils. Oxygen isotope ratios of pedogenic carbonates were analyzed along a climatic gradient in eastern Washington State USA to evaluate changes in their isotopic composition across the gradient. A modern analog approach was used to compare the relationships between the δ18O values in the carbonates and the trends in isotopic measurements of meteoric water and soil water over the gradient.

Methodology

Site description and field sampling

The study site was located in the Palouse loess region of southeastern Washington State, USA (Figure 1). The Palouse region is an area of long-term loess deposition where numerous soil profiles have been formed and subsequently buried under the episodically aggrading landscape (Busacca and McDonald, 1994; McDonald and Busacca, 1992). The most recent loess deposit across the region (L1) sits above Mount Saint Helens set S tephra and is Late Pleistocene to Holocene in origin with a maximum thermaluminescence date of ~14 ka (just above the MSH set S tephra) and a date of ~8.2 ka at 1 m depth from the soil surface at the CHR-1 site (Richardson et al., 1997, 1999). Surface soil horizons (above calcic horizons) were non-calcareous so it was assumed carbonates in the calcic horizon were pedogenic and not lithogenic in origin.

As part of a larger project investigating the paleoclimatology and paleoecology of the Palouse region (e.g. Blinnikov et al., 2001, 2002; O’Geen and Busacca, 2001), modern soils (i.e. modern analogs) along a climatic gradient were used to determine how the isotopic composition of soil carbonates reflect changes in climate (e.g. Stevenson et al., 2005). These modern relationships could then be used to infer climatic shifts from changes in the isotopic composition of a sequence of buried paleosols.

The climatic gradient of study extended from the rainshadow of the Cascade Range in the west, mean annual precipitation (MAP) of 200 mm, to the Blue Mountains in the east, MAP greater than 1000 mm (pedogenic carbonates were present in sites up to 580 mm MAP). Precipitation is largely derived from frontal storms originating from north Pacific high pressure zones and entering the region from the northwest during the late fall, winter and spring (Phillips, 1965, 1970). Convective thunderstorms provide localized, intense rains during the summer months but total precipitation during the summer is much less than that during the late fall, winter and spring.

Dominated vegetation along the sequence include: shrub (Artemisia tridentata), perennial bunchgrass (Festuca idahoensis, Agropyron spicatum), and coniferous communities (Pinus ponderosa, Pseudotsuga menziesii, Abies grandis, Abies lasiocarpa and Picea engelmannii). Soils along the sequence were all derived from the L1 loess parent material, and sites were chosen to minimize topographic and other variations (e.g. a bioclimatic sequence
in the sense of Jenny, 1941). Table 1 includes relevant site information. Although elevation generally increases over the climatic gradient, the sequence is not a true elevational gradient nor a simple transect.

As previously mentioned, this study was in conjunction with a larger project investigating the paleoclimatology of the interior Pacific Northwest. Sites for carbonate sampling were chosen to facilitate soil sampling of buried paleosols (some sites were sampled to depths in excess of 10 m). Most of these sites were roadside cuts or supported agricultural activity and were not suitable for evaluation of soil water. Undisturbed native vegetation reference sites were selected across the climatic gradient to monitor soil water. The trend in carbonate $\delta^{18}O$ across sites had been established by the time we sampled for soil water, therefore carbonates were not sampled at soil water sites. We were constrained by the dates of NADP samples available for analysis and collecting detailed meteoric water data across all sites was not feasible within the project. Sampling dates for soil water and meteoric water did not overlap and we acknowledge this as a shortcoming, but our main intent was to compare/contrast the trends in oxygen isotope values of soil and meteoric water values across the gradient with that of the pedogenic carbonates, not necessarily to fully characterize these values at each site.

For consistency, disseminated or weakly cemented pedogenic carbonates, at the first indication of effervescence with 10% HCl, were sampled from the top millimeters of the Bk horizon (carbonate nodules or filaments were not present as all sites along the gradient). Samples were sealed in airtight plastic bags and stored in a chilled cooler until return to the laboratory where they were air dried. Three subsamples per site were taken, except the most arid site where five subsamples were taken as it was expected that isotopic variation would be higher because of increased evaporative demand. Soil water was sampled by extracting approximately 100 g soil at two depths, near-surface (15 cm) and deep (70 cm), from a hand-dug soil pit during two sampling periods (early June and mid August, 1995). The sample dates were chosen because we anticipated decreased soil moisture levels during the summer months would be conducive to carbonate formation. Triplicate subsamples were taken at each depth, placed in Qorpak™ bottles, sealed, and taped with Parafilm™ to prevent evaporative loss of

<table>
<thead>
<tr>
<th>Site</th>
<th>MAP (mm)</th>
<th>Elevation (m)</th>
<th>MAT (ºC)</th>
<th>Dominant Vegetation</th>
<th>Depth to carbonate zone (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SW1)</td>
<td>200</td>
<td>230</td>
<td>13</td>
<td>a</td>
<td>NA</td>
</tr>
<tr>
<td>KPI</td>
<td>220</td>
<td>410</td>
<td>12</td>
<td>a,b</td>
<td>0.54</td>
</tr>
<tr>
<td>UI</td>
<td>330</td>
<td>450</td>
<td>11</td>
<td>b</td>
<td>NA</td>
</tr>
<tr>
<td>(SW2)</td>
<td>330</td>
<td>450</td>
<td>11</td>
<td>b</td>
<td>NA</td>
</tr>
<tr>
<td>WIN1</td>
<td>430</td>
<td>520</td>
<td>11</td>
<td>b,c</td>
<td>1.23</td>
</tr>
<tr>
<td>CHR1</td>
<td>485</td>
<td>758</td>
<td>11</td>
<td>b,c</td>
<td>1.71</td>
</tr>
<tr>
<td>SAP2</td>
<td>495</td>
<td>400</td>
<td>11</td>
<td>b,c</td>
<td>2.41</td>
</tr>
<tr>
<td>CH1</td>
<td>580</td>
<td>945</td>
<td>10</td>
<td>c,b,d</td>
<td>1.58</td>
</tr>
<tr>
<td>(SW3)</td>
<td>660</td>
<td>640</td>
<td>10</td>
<td>c,d</td>
<td>NA</td>
</tr>
<tr>
<td>(SW4)</td>
<td>870</td>
<td>1050</td>
<td>7</td>
<td>d,c</td>
<td>NA</td>
</tr>
<tr>
<td>(SW5)</td>
<td>1100</td>
<td>1550</td>
<td>6</td>
<td>e</td>
<td>NA</td>
</tr>
</tbody>
</table>

*a*Mean annual precipitation.  
*b*Mean annual temperature.  
*c*Dominant plant species: (a) Artemisia tridentata; (b) Agropyron spicatum; (c) Festuca idahoensis; (d) Pinus ponderosa; (e) Pseudotsuga menziesii.  
*d*Carbonates not sampled at soil water sites.
water. Samples were then placed in a chilled cooler and later refrigerated until analyses were performed.

**Laboratory methodology**

Carbonate samples were pretreated to remove organic carbon (baked under vacuum at 400°C) then reacted with 100% phosphoric acid at 90°C and the resulting CO₂ gas cryogenically purified (adapted from Bowen, 1966). Carbon dioxide was analyzed on a VG Isochrom™ isotope ratio mass spectrometer in dual inlet mode. Precision of the procedure for standards run on line was 0.11‰. isotopic measurements are presented in the delta (δ) notation:

\[
\delta = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000
\]

where \( R \) is the \(^{18}\text{O}/^{16}\text{O} \) ratio in the sample and \( R_{\text{standard}} \) is the \(^{18}\text{O}/^{16}\text{O} \) ratio of the standard. Values for carbonates are expressed as per mil (‰) and are referenced to the VPDB (Vienna Pee Dee Belemnite) standard. For comparison of carbonate δ\(^{18}\text{O} \) to soil water δ\(^{18}\text{O} \), the VPDB standard was converted to VSMOW (Vienna Standard Mean Ocean Water) using the equation: \( \delta^{18}\text{O}_{\text{VSMOW}} = 1.03091 \times \delta^{18}\text{O}_{\text{VPDB}} + 30.91 \) (Friedman and O’Neil, 1977).

Soil water δ\(^{18}\text{O} \) analyses were performed after the method of Hsieh et al. (1998b). Soil samples were gamma-irradiated to sterilize the soil and placed in sampling vessels on a vacuum line. Soil water was frozen using a dry ice-ethanol slush, and non-condensable gas was then thawed. This freeze-thaw procedure was repeated several times to ensure complete degassing of soil and soil water. A known volume of CO₂ gas was then injected into the container and allowed to equilibrate with soil water for approximately 48 h; the CO₂ gas was then purged and non-condensable gas was cryogenically purified then analyzed via mass spectrometry and referenced to the VSMOW standard. Precision for the procedure was 0.3‰.

Meteoric water samples were obtained from two National Atmospheric Deposition Program (NADP) sites, the Palouse Conservation Farm (Site #WA24, elevation 766 m, lat./long. 46°45′38″/117°11′05″) and the Starkey Experimental Forest (Site #OR18, elevation 1253 m, lat./long. 45°26′52″/118°30′41″), adjacent to our study area (Vachon et al., 2007; Welker, 2000). Available NADP samples (collected on a weekly basis) for a period of approximately 2.5 years (May 1989–December 1991) were analyzed by the CO₂ equilibration method (adapted from Epstein and Mayeda, 1953; Ehleringer and Osmod, 1989) on a VG Multirep™ inlet system. Precision for the procedure was 0.2‰. Mean δ\(^{18}\text{O} \) values of meteoric water were calculated by weighting the measured δ\(^{18}\text{O} \) values by precipitation amount over the indicated time period. Weighted mean annual averages for each site were calculated using data from May 1989 to April 1991 as inclusion of the additional 6 months data may have skewed the annual average because of changes in seasonal isotopic composition of the precipitation. Soil water and meteoric water values are reported as per mil (‰) and referenced to the VSMOW standard.

Temperatures of carbonate formation were calculated using the fractionation factors between calcite and water as described in the equation by Kim and O’Neal (1997):

\[
10^\Delta T = 18.03(10^\Delta T^{-1}) - 32.42
\]

where \( \alpha \) is equal to the CO₂–H₂O fractionation factor, and \( T \) is temperature of formation in degrees K. The term \( 10^\Delta T \) is approximated by \( \Delta^{18}\text{O} \) (carbonate–soil water), the per mil difference in oxygen isotope values between carbonate and soil water under equilibrium conditions. Soil water δ\(^{18}\text{O} \) values from the 70 cm depth were used in these calculations as carbonates at all sites except the most arid were below this depth (and at the most arid site closer to 70 cm than the shallow depth).

**Statistical analysis**

Regression analysis was used to determine the relationships between MAP and soil water and carbonate δ\(^{18}\text{O} \) across the gradient (GenStat Release 10.1, Copyright 2007, Lawes Agricultural Trust, Rothamsted Experimental Station). The standard deviation of the subsamples for each measurement are reported, but were not considered as replicates for statistical analysis. The regression equation for MAP and soil water δ\(^{18}\text{O} \) (70 cm depth) was used to interpolate soil water values across carbonate sampling sites. Elevation was used for meteoric water interolation across sites as the relationship between elevation and meteoric water has been better documented (e.g. Bowen and Revenaugh, 2003; Dutton et al., 2005) than that for MAP and meteoric water.

**Results**

Mean annual meteoric water δ\(^{18}\text{O} \) values were more depleted at the high elevation Starkey site (−13.9‰, elevation 1253 m) in comparison to the Palouse site (−13.0‰, elevation 766 m). Individual samples ranged from −5.6‰ to −20.9‰ at the Starkey site and from −7.2‰ to −18.7‰ at the Palouse site. Quarterly means were less variable and showed distinct differences by season and site (Figure 2). Though total precipitation increased over the gradient, the quarterly percentage of total precipitation was similar across sites. Winter (January–March) values were most negative at both sites (−15.0‰ at the Palouse site and −15.4‰ at the Starkey site), whereas autumn (October–December) precipitation was most enriched (−11.8‰) at the Palouse site and the July–September period most enriched (−12.5‰) at the Starkey site.

Soil water δ\(^{18}\text{O} \) became depleted with increasing depth and MAP, ranging from 2.6‰ at 15 cm (near surface) in the most arid site to −13.2‰ at the 70 cm depth at the highest precipitation site (Figure 3). Date of sampling overall was not significant (e.g. there was no overall difference between the sampling dates), but August data was more variable than June data, and for simplicity, data from the June sampling period were used throughout the paper. Regression analysis indicated that near surface (15 cm) soil water δ\(^{18}\text{O} \) values were highly correlated with an inverse (hyperbolic) function of MAP (\( r^2=0.98, p=0.002 \)). The relationship between deep soil water δ\(^{18}\text{O} \) (70 cm depth) and MAP was strongly correlated with a linear function of MAP (\( r^2=0.89, p=0.01 \)).

Pedogenic carbonate δ\(^{18}\text{O} \) values became more positive with increasing MAP and ranged from −14.1 to −11.4 (‰ PDB) over the gradient. Carbonate δ\(^{18}\text{O} \) showed a significant relationship with MAP (\( r^2 = 0.71, p = 0.02 \)) but the trend was opposite to that of soil water (Figure 3). Calculated temperatures of formation for carbonates, assuming equilibrium between measured soil water (70 cm depth) and carbonate δ\(^{18}\text{O} \) values, ranged from approximately 26 to 59°C (Table 2).
Discussion

Pedogenic carbonates along the Palouse climatic gradient showed an opposite trend to soil water values, becoming more enriched as MAP increased. Calculated temperatures of carbonate formation using June soil water data from the 70 cm depth (collected during the growing season when we anticipated soil moisture levels to be rapidly decreasing and carbonate precipitation likely to occur) were also unrealistic, indicating that the carbonates were not in isotopic equilibrium with measured soil water values. In contrast to this study, both Quade et al. (1989b) and Amundson et al. (1989) found that carbonate δ18O values became more depleted with increasing elevation (and MAP) in a Great Basin desert environment because of the depletion of meteoric water with elevation.

In the Palouse, we found that near surface soil water δ18O values were enriched compared to the deep soil water δ18O values and soil water δ18O became more depleted (more negative) as MAP increased. Deep soil water δ18O values (70 cm depth) at the highest precipitation and elevation site (−12.6‰) approached the mean annual meteoric water value (−13.9‰) at the high-elevation Starkey site. These results are similar to trends obtained by Hsieh et al. (1998a), for a bioclimatic sequence in Hawaii. At high rainfall sites, transpirative water loss (associated with greater biomass) as well as high recharge from meteoric water, result in soil water δ18O values that were more depleted whereas in arid sites, evaporative soil water loss predominates (particularly at shallow depths) with little meteoric recharge, resulting in more enriched soil water δ18O values.

In comparison with data from the same region (the eastern Cascades of interior Washington State), deep soil water δ18O values at high precipitation Palouse sites were similar to those observed by Robertson and Gazis (2006), but Palouse sites of similar MAP (200–500 mm) were more enriched (more positive) by approximately 5–7‰. Whether deep soil water at Palouse arid sites was subjected to a greater degree of evaporative soil water loss than deep soil water at the sites of Robertson and Gazis (2006) or whether soil water δ18O values within a region can vary significantly based on soil type or other edaphic factors would need further study.

The major driving variables behind the δ18O values in carbonates are the δ18O values of soil water and the temperature of carbonate formation. In Kyle Canyon, Nevada (Amundson et al., 1989), the carbonate δ18O values follow the same pattern as meteoric water

Figure 2. Quarterly percentage of precipitation across the Palouse climatic gradient and seasonal mean meteoric δ18O values for NADP sites adjacent to the study area. The Palouse Conservation Farm NADP site is at an elevation of 766 m, and the Starkey Experimental Forest site is at 1253 m. The mean weighted annual average (and standard deviation) for each site shown in the legend. Numbers below bars indicate number of samples and (standard deviation of the seasonal mean).

Figure 3. Soil water δ18O by depth (June sampling date) and carbonate δ18O as a function of MAP. Error bars represent the standard deviation of subsamples collected at each site (and the site average indicated in parentheses). Soil water sampling extended over the entire sequence (200–1100 mm MAP) whereas carbonates were only present in sites less than ~600 mm MAP.
Table 2. Calculated temperatures of carbonate (CO$_3$) formation assuming equilibrium with soil water $\delta^{18}$O (70 cm depth) measured during June

<table>
<thead>
<tr>
<th>Site</th>
<th>MAP (mm)</th>
<th>$CO_3-\delta^{18}$O (PDB)*</th>
<th>$CO_3-\delta^{18}$O (SMOW)*</th>
<th>$SW-\delta^{18}$O (SMOW)*</th>
<th>$\Delta^{18}$O(CO$_3$-H$_2$O)$^c$</th>
<th>Calculated temp$^d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KPI</td>
<td>220</td>
<td>-14.3</td>
<td>16.1</td>
<td>-5.9</td>
<td>22.0</td>
<td>58.5</td>
</tr>
<tr>
<td>U1</td>
<td>330</td>
<td>-12.4</td>
<td>18.1</td>
<td>-6.8</td>
<td>24.9</td>
<td>41.8</td>
</tr>
<tr>
<td>WIN1</td>
<td>430</td>
<td>-13.0</td>
<td>17.5</td>
<td>-7.6</td>
<td>25.1</td>
<td>40.7</td>
</tr>
<tr>
<td>CHR1</td>
<td>485</td>
<td>-11.9</td>
<td>18.6</td>
<td>-8.1</td>
<td>26.7</td>
<td>32.1</td>
</tr>
<tr>
<td>SAP2</td>
<td>495</td>
<td>-11.2</td>
<td>19.4</td>
<td>-8.1</td>
<td>27.5</td>
<td>27.9</td>
</tr>
<tr>
<td>CH1</td>
<td>580</td>
<td>-11.4</td>
<td>19.2</td>
<td>-8.8</td>
<td>28.0</td>
<td>25.5</td>
</tr>
</tbody>
</table>

$^*$Carbonate $\delta^{18}$O$_{CO_3}$ = 1.03091 x $\delta^{18}$O$_{PDB}$ + 30.91 (Friedman and O’Neil, 1977).
$^*$Soil water $\delta^{18}$O (% SMOW) from regression equation (70 cm depth), Figure 3.
$^*$Carbonate $\delta^{18}$O (% SMOW) – Soil water $\delta^{18}$O (% SMOW).
$^*$Temperature calculated from: 10$^\Delta$O = 18.03 (10$^T$) – 32.42 where $\delta^{18}$O (carbonate-water) approximates (10$^\Delta$O), and $T$ = temperature in Kelvin (Kim and O’Neil, 1997).

Figure 4. Carbonate $\delta^{18}$O values from the Palouse region of Washington State. Also shown are the trend in carbonate $\delta^{18}$O values that would result from equilibrium with measured soil water $\delta^{18}$O (70 cm depth) at mean annual temperature, and the relationship between carbonate $\delta^{18}$O values and MAP from Kyle Canyon, Nevada (adapted from Amundson et al., 1989)

Deriving the temperature of formations using the modern analog approach assumes that current conditions represent conditions under which the carbonates were formed and that the variation in current conditions has been adequately measured (see for instance Vachon et al., 2007). A further assumption is that the carbonates at the different sites were formed over the same time periods (i.e. the same climatic conditions). The earliest date for the beginning of loess deposition is approximately 14 ka, and the thermolixinescence date at CHR-1 (8.2 ka) is clearly Holocene. We sampled the uppermost surface of the Bk horizon at all sites and assume the carbonates to be relatively recent (mid to late Holocene), but can be no older than the date of the soil profile (8.2 ka using the CHR-1 date). Both meteoric water and soil water $\delta^{18}$O values follow established trends from previous studies (Amundson et al., 1989; Hsieh et al., 1998a; Quade et al., 1996). Shifting circulation patterns over the northwest US during the last glacial maximum (Late Pleistocene) appear to have resulted in anticyclonic easterly winds in the Palouse (Sweeney et al., 2004), that probably would have affected the oxygen isotope composition of meteoric water (and more importantly, may have affected the trend in isotopic values of meteoric water over the gradient), but given the geographic location of the study area it seems unlikely that major changes in circulation or climate would have occurred during the Holocene.

As previously noted, measured soil water oxygen isotope values in equilibrium with carbonate values yielded temperatures of formation that were unrealistic (Table 2). Substituting meteoric water values for soil water (Table 3), temperatures of formation are somewhat more realistic (~5 to 23°C) but are still too high and the range between sites too great. Cerling (1984) suggested that seasonal changes in the wetting front may affect carbonate oxygen isotope values. In the vicinity of our study, Robertson and Gazis (2006) noted that soil wetting to the greatest depth can occur during the winter snowmelt or spring period. If winter precipitation values are used instead of observed summer soil water values, calculated temperatures of carbonate formation range from 12 to –3°C. These temperature values are much more realistic but still require a much larger range in temperatures of formation than is indicated by the difference in MAT between sites.

Table 3 contains the calculated soil water $\delta^{18}$O values that would be in equilibrium with measured carbonate $\delta^{18}$O assuming MAT as temperature of formation across the gradient. These values are more negative than our measured soil water values. The
Table 3. Temperature of carbonate formation calculations (a) using mean annual meteoric $\delta^{18}O$, (b) using mean winter meteoric $\delta^{18}O$, and (c) calculated soil water (SW) values in equilibrium with measured carbonate $\delta^{18}O$ assuming MAT as temperature of formation (see Table 2 for full explanation of temperature of formation calculations)

<table>
<thead>
<tr>
<th>Site</th>
<th>$\text{CO}_2$-18O (SMOW)</th>
<th>SW 18O (SMOW)</th>
<th>$\Delta^{18}O$(CO$_2$-H$_2$O)</th>
<th>Calc temp (°C)</th>
<th>SW 18O (SMOW)</th>
<th>$\Delta^{18}O$(CO$_2$-H$_2$O)</th>
<th>Calc temp (°C)</th>
<th>SW 18O (SMOW)</th>
<th>$\Delta^{18}O$(CO$_2$-H$_2$O)</th>
<th>Calc temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KPI</td>
<td>16.1</td>
<td>-12.3</td>
<td>28.4</td>
<td>23.4</td>
<td>-14.7</td>
<td>30.8</td>
<td>3.4</td>
<td>-12.5</td>
<td>31.1</td>
<td>11.0</td>
</tr>
<tr>
<td>U1</td>
<td>18.1</td>
<td>-12.4</td>
<td>30.5</td>
<td>13.8</td>
<td>-14.7</td>
<td>32.8</td>
<td>5.8</td>
<td>-13.6</td>
<td>31.1</td>
<td>11.0</td>
</tr>
<tr>
<td>Win1</td>
<td>17.5</td>
<td>-12.5</td>
<td>30.0</td>
<td>16.0</td>
<td>-14.8</td>
<td>32.2</td>
<td>0.0</td>
<td>-12.5</td>
<td>31.1</td>
<td>10.7</td>
</tr>
<tr>
<td>CHR1</td>
<td>18.6</td>
<td>-12.9</td>
<td>31.6</td>
<td>8.7</td>
<td>-15.0</td>
<td>33.6</td>
<td>0.0</td>
<td>-12.5</td>
<td>31.1</td>
<td>10.7</td>
</tr>
<tr>
<td>SAP2</td>
<td>19.4</td>
<td>-12.3</td>
<td>31.6</td>
<td>8.5</td>
<td>-14.7</td>
<td>34.1</td>
<td>-1.8</td>
<td>-11.8</td>
<td>31.2</td>
<td>10.5</td>
</tr>
<tr>
<td>CH1</td>
<td>19.2</td>
<td>-13.3</td>
<td>32.5</td>
<td>4.9</td>
<td>-15.1</td>
<td>34.3</td>
<td>-2.8</td>
<td>-12.1</td>
<td>31.3</td>
<td>10.1</td>
</tr>
</tbody>
</table>

$^1$Meteoric precipitation adjusted by elevation for each site from regression of elevation and mean annual meteoric precipitation (or mean winter meteoric precipitation) for the two NAPD sites.

$^2$The equation: $\Delta^{18}O$(carbonate-water) = 18.03 (10$^{-T}$)–32.42 [where $\Delta^{18}O$(carbonate-water) approximates (10$^{10}$lnx)] was solved for soil water $\delta^{18}O$, using MAT as temperature of formation and carbonate $\delta^{18}O$ as shown in their study in Texas USA. However, a similar model (that appears to include the same changes in meteoric water isotope values) was not used in this study. Meteoric precipitation was added as potential water to the model by addition of 100 m to each precipitation event. The model was run for 1000 years. The isotopic composition of the resulting soil water was then calculated using the temperature of formation value for each site.

Conclusions

Carbonate $\delta^{18}O$ values in the Panola system are highest in their study in Texas USA. However, a similar model (that appears to include the same changes in meteoric water isotope values) was not used in this study. Meteoric precipitation was added as potential water to the model by addition of 100 m to each precipitation event. The model was run for 1000 years. The isotopic composition of the resulting soil water was then calculated using the temperature of formation value for each site.
water values across the gradient were unrealistic. Several factors may affect pedogenic carbonate $\delta^{18}O$ values, but differential effects of winter/spring precipitation on soil water oxygen isotope values appears to be the most likely driver affecting carbonate $\delta^{18}O$ values across the Palouse region of eastern Washington State.

For paleoclimatic reconstruction using carbonate $\delta^{18}O$ values, seasonal fluctuations in meteoric water $\delta^{18}O$ values may need to be considered, particularly in temperate climates where seasonal fluctuations in both meteoric and soil water isotopic composition can be large. The modern analog approach can be useful in interpreting $\delta^{18}O$ values of pedogenic minerals, but our data suggest that evaluation of the different driving variables must be carefully considered, particularly when comparing results from different climatic regimes.

**Acknowledgments**

This work was funded through NSF Grants #EAR92-19148 and #EAR92-20012 to A.J. Busacca and E.F. Kelly, and NSF equipment Grant #9413903 to Colorado State University. Thank you to Jean Hsieh for analyzing soil water samples at Cal Tech and David Hunter for assisting with figures. Dr Carey Gazis and an anonymous reviewer provided valuable comments on the manuscript.

**References**


