Calibration of the clumped isotope geothermometer in soil carbonate in Wyoming and Nebraska, USA: Implications for paleoelevation and paleoclimate reconstruction

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A B S T R A C T

Recent work has shown that soil carbonates typically form as the soil dries after seasonal rainfall, and therefore record seasonal aspects of climate rather than mean annual conditions. Because soil carbonate formation is closely related to the timing of local rainfall and drying, it is necessary to understand the formation seasonality and temperature, and soil water δ18O values recorded in modern soil carbonate before accurate estimates of stable isotope-based paleoelevation and paleoclimate can be made. Here we study carbonate clumped-isotope (Δ47) and oxygen isotopes (Δ18O) compositions of modern soil carbonates and seasonal variations of soil moisture and temperature of nearby climate stations in Wyoming and western Nebraska, USA, to understand the seasonality of soil carbonate formation in semi-arid to arid temperate montane settings. We find that soil carbonate clumped-isotope temperatures (T(Δ47)) are 3–5°C higher than mean summer air temperature and are similar to or higher than average summer soil temperature. At depths >40 cm, soil moisture dramatically decreases in early summer following the cessation of spring rains and snowmelt and shows only brief increases after major mid–late summer rain events. Soil water δ18O values calculated using carbonate Δ18O and T(Δ47) values are similar to the δ18O values of local mean summer precipitation. These lines of evidence suggest that soil carbonates in our study area formed during times of soil dewatering in early summer and after major summer rain events in mid–late summer, and in or near equilibrium with mean summer precipitation δ18O values.

T(Δ47) values of modern soil carbonates are inversely correlated with elevation, with a lapse rate, −4.0°C/km, similar to the modern air and soil temperature lapse rates. Calculated soil water δ18O values also are inversely correlated with elevation, with a lapse rate of −3.7‰/km. Sample elevations can be reconstructed using both T(Δ47) values and calculated soil water δ18O values between 900 m and 2600 m in our studied area, with an accuracy of ±0.5 km or less. However, δ18O values of precipitation and soil water reflect the complex interaction of climatic, environmental, and topographic conditions prior to carbonate formation, whereas T(Δ47) values may be influenced by site-specific conditions. We suggest that both soil carbonate T(Δ47) values and calculated soil water δ18O values should be used to corroborate paleoelevation reconstruction, and the seasonal nature of soil carbonate formation should be considered when soil carbonate T(Δ47) values and δ18O values are applied for paleoclimate reconstruction.

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1. Introduction

The oxygen isotope composition of soil carbonate is a powerful tool for the reconstruction of paleoclimate, paleoenvironment, and paleoelevation because meteoric water δ18O values are influenced by climatic, environmental and topographic conditions, and because ancient meteoric water δ18O values are recorded by soil carbonate δ18O values (e.g. Quade et al., 1989, 2007, 2011; Cerling and Quade, 1993; Quade and Cerling, 1995; Chamberlain et al., 1999; Rowley and Garzione, 2007). Some major complications of this type of work include: (1) the potential that soil carbonates form in equilibrium with soil water that is not representative of meteoric water because of evaporative enrichment in 18O (e.g. Quade et al., 2007); (2) the temperature dependence of oxygen isotope fractionation between soil water and soil carbonate, in that the δ18O value of soil water can only be accurately calculated from the δ18O value of soil carbonate when the mineralization temperature is well constrained; and (3) the potential for seasonal bias in
the timing of soil carbonate mineralization such that the isotopic composition of soil carbonate reflects the environmental conditions of a particular season and not annual average conditions (Breecker et al., 2009; Passey et al., 2010; Peters et al., 2013; Quade et al., 2013). Therefore, the seasonality of soil carbonate formation must be identified in order to correctly interpret stable isotope proxies.

Carbonate clumped isotope thermometry uses the temperature-dependent enrichment of “clumped” isotopologues in carbonate (i.e., molecules with more than one rare isotope such as $^{13}$C$^{18}$O$^{16}$O$_2$) with respect to a stochastic distribution to determine carbonate mineralization temperature (Ghosh et al., 2006a, 2006b; Eiler, 2007; Huntington, 2009). The carbonate clumped isotope (Δ47) method also involves determination of $\delta^{13}$C and $\delta^{18}$O values of carbonate, and the latter can be combined with the clumped-isotope temperature to determine the $\delta^{18}$O value of soil water during carbonate mineralization using a carbonate–water oxygen isotope paleothermometry equation (e.g., Kim and O’Neil, 1997). Therefore, clumped isotope thermometry provides unambiguous estimates of mineralization temperature (T(Δ47)) and fluid isotopic composition (e.g., $\delta^{18}$Osw), and both kinds of information can help elucidate the seasonal timing of soil carbonate mineralization.

Our purpose here is to calibrate the soil carbonate clumped isotope geothermometer in the temperate, semi-arid climate of Wyoming and western Nebraska, USA. We investigate the formation temperature of soil carbonate by applying carbonate clumped isotope thermometry to modern soil carbonates and by investigating the seasonal variation of soil moisture and temperature. We find that soil carbonate formation is not only biased to warm season temperatures, consistent with earlier studies (Breecker et al., 2009; Passey et al., 2010; Peters et al., 2013; Quade et al., 2013), but is also particularly biased to the periods of soil dewatering in early summer, and after major rainstorms in mid–late summer. By comparing calculated soil water $\delta^{18}$O (Δ47 values with seasonal precipitation $\delta^{18}$O values, we find that soil carbonate in our study area formed in (or near) equilibrium with summer precipitation $\delta^{18}$O values. These findings improve the application of clumped isotope geothermometry and oxygen isotope composition in paleoelavation and paleoclimate reconstruction.

2. Study area

The modern landscape of Wyoming is characterized by basement-cored ranges and intermontane basins formed during late Cretaceous – early Eocene thick-skinned Laramide deformation (e.g., Dickinson and Snyder, 1978; Dickinson et al., 1988). Mountain ranges in Wyoming are up to 4 km high, and current basin floor elevations decrease from 2200 m in western Wyoming to 900 m in the Great Plains of western Nebraska. The study area is generally situated along the Sweetwater and North Platte River systems that cross Wyoming and western Nebraska (Fig. 1).

The climate of the study area is dominated by the Westernies and local topographic conditions (Bryson and Hare, 1975; Whitlock and Bartlein, 1993; Mock, 1996). Vapor masses are derived from the Pacific in winter with contributions from the Gulf of Mexico that become increasingly important toward the south-east corner of the study area (Bryson and Hare, 1975; Mock, 1996; Liu et al., 2010). Within the study area today, the annual precipitation amount ranges between 15 and 60 cm with the mean of ∼35 cm based on 30-year normals (decadally updated mean values measured over a 30 year period – the current period is 1981–2011) and mostly occurs in late spring to early summer (NCDC, 2012) (Fig. 2). Mean annual precipitation amount increases gradually eastward to ∼55 cm in the western Great Plains (Mullen, NE; NCDC, 2012). Mean monthly air temperatures range from −10 °C to 22 °C with mean annual air temperature of 7 °C and a mean summer (JJA) air temperature of 19 °C (Fig. 2; NCDC, 2012). Low rainfall amounts, low relative humidity, and strong winds lead to semi-arid to arid conditions in Wyoming and western Nebraska.

While we attempted to collect and sample “recent” soil carbonate, it is likely that the carbonate samples integrate carbonate mineralization over the past several thousand years and therefore Holocene paleoclimate is relevant to this study. During the Holocene, the climate of the study area was characterized by winter wet/summer dry conditions similar to today (Whitlock and Bartlein, 1993). Climate models (Thompson et al., 1993; Shin et al., 2003), pollen (Whitlock and Bartlein, 1993; Whitlock et al., 1995), and stable isotopes from fossil teeth (Kohn and McKay, 2010), goethite (Stjostrom et al., 2004) and paleosols (Takeuchi and Larson, 2005) suggest that summer climate conditions at 9 ka were warmer and drier than present due to increased summer insolation and the subsequent intensification of the east Pacific subtropical high and northward shift of the polar jet stream. The climate model of Thompson et al. (1993) shows that paleoclimate at 9 ka was only ∼2 °C higher than today. However, other studies based on oxygen isotopes of paleosols (Amundson et al., 1996) and from plant macrofossils (Lyford et al., 2003) suggest that warmer summers in Wyoming may have been accompanied by periods of relatively wetter conditions especially in the mid-Holocene (5.5–3 ka), presumably due to the increased influence of the North American summer monsoon. Although Holocene climate has varied throughout the last 10 ka, the variation of temperature (∼2 °C) is small (e.g. Thompson et al., 1993; Whitlock et al., 1995) compared to the elevation dependent clumped isotope temperature signal (∼10 °C) we will discuss in this paper. Moreover, precipitation was seasonal with amounts and sources consistent with modern conditions.

Both soil moisture and temperature are important factors controlling the stable isotopic composition of soil carbonate and the timing of its mineralization. We compile the soil moisture and temperature data over a six-year period (2006–2011) in order to understand the seasonality of soil carbonate formation. Although a six-year average is brief compared to the integrated climate signals recorded in soil carbonate, the six-year average air temperature is not statistically different from the 30 year normals of the closest meteorological stations. Furthermore, both the six-year and 30 year averages integrate climate anomalies like El-Nino and La Nina. Based on the similarities among data sets we assume that the six-year average soil moisture and soil temperature data are representative of longer duration records.

Based on the six-year averages of monthly soil moisture and soil temperature recorded at 50 cm below the surface as well as air temperature and precipitation amount (Tables A1 and A2), the seasonal variation of soil moisture in Wyoming and western Nebraska appears to depend on the timing and amount of rainfall and snowmelt (Fig. 2). Because precipitation amount is generally high during April–June, overlapping with and immediately following snowmelt, soil moisture remains high during spring and early summer, but decreases to a baseline by the end of June or early July when rainfall amount dramatically decreases (Fig. 2). Summertime soil moisture content at 50 cm depth increases only after major rainfall events (amount >1.5 cm). Soil moisture increases within 1 day of the rain event and generally returns to baseline values within ∼21 days suggesting that soil water is only briefly retained in the soil profile and is quickly removed by evaporation, evapotranspiration, and runoff/percolation (Fig. 2). The correlation between long-term monthly soil moisture and rainfall amount in Wyoming ($r = 0.70$) suggests that in areas with no soil moisture data, precipitation amount may be qualitatively used as a proxy for soil moisture. Also, seasonal variation of soil temperature generally follows air temperature ($r ≥ 0.87$; Fig. 2). Mean monthly soil temperature exceeds the mean annual air temperature from late spring to early fall and, at low elevations (<2100 m), soil temper-
Fig. 1. Map of the study area showing locations of soil temperature stations (stars; S – Big Sandy opening, W – Windy Peak, T – Torrington, L – Laramie), precipitation stations (diamonds; P – Pinedale, Y – Yellowstone, B – Brooklyn Lake, N – Newcastle, NP – North Platte), soil carbonate samples (filled triangles = samples with $\Delta^{13}C$ and $\delta^{18}O$ results; open triangles = samples with $\delta^{18}O$ results only). Note that samples and climate station data are not co-located. Elevation transect (A–A') shows an eastward decrease in surface elevation. Black line in profile represents mean elevation along 10 km-wide swath and grey area indicates range of elevations within the swath. 2X and 5X represent locations where multiple (2 and 5 samples, respectively) were obtained.

Fig. 2. A) Climate data from 2006–2011 for two selected climate stations in Wyoming (Windy Peak and Torrington; see Fig. 1 for locations) showing seasonal patterns of precipitation, air temperature, soil temperature and soil moisture at 50 cm depth. B) Daily climate data (June–September, 2007) for the same climate stations as in A, showing relationship of soil moisture at 20 cm and 50 cm depths to precipitation amount. Data sources: NWCC (2012), NCDC (2012), WRDS (2012).

3. Materials and methods

We collected 24 stage I–II soil carbonates (e.g., Table 1 of Gile et al., 1966) as rinds formed on the undersides of conglomerate clasts and as filaments and cements collected from outcrop or by using a soil auger. Samples were collected from late Pleistocene and Holocene river terraces and therefore may record an integrated climate signal over potentially several thousands of years. To limit the age uncertainty and the influence of climate variability from the Pleistocene, only the outer-most rind coatings were analyzed. Samples were collected at various depths below erosion surfaces (Tables 1 and 2), but wherever possible we collected samples from $\geq$40 cm below the erosion surface. Though soil carbonates may form at any depth in the soil profile, we focused on samples from $\geq$40 cm to limit potential effects from diffusion of atmospheric CO$_2$ and to reduce the potential evaporation of soil water during the formation of the soil carbonate (Quade et al., 1989, 2013; Passey et al., 2010). Carbonate clumped-
Table 1
Summary of stable isotope data for soil carbonates analyzed for clumped isotope composition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Elevation (m)</th>
<th>Depth (cm)</th>
<th>N</th>
<th>δ¹⁸O (‰) (VPDB)</th>
<th>Δ₁₈O (‰)</th>
<th>Temperature°(°C)</th>
<th>Δ₁₈O (‰)</th>
<th>Temperature°(°C)</th>
<th>Δ₁₈O (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE11-C2</td>
<td>41.93</td>
<td>−103.63</td>
<td>1236</td>
<td>0</td>
<td>2</td>
<td>−9.1</td>
<td>0.640 (0.017)</td>
<td>26.3 (3.9)</td>
<td>0.796 (0.018)</td>
<td>26.2 (3.9)</td>
<td>0.024</td>
</tr>
<tr>
<td>WY11-C5</td>
<td>42.65</td>
<td>−106.84</td>
<td>1941</td>
<td>55</td>
<td>2</td>
<td>−12.6</td>
<td>0.660 (0.009)</td>
<td>21.9 (2.0)</td>
<td>0.727 (0.009)</td>
<td>21.8 (1.8)</td>
<td>−0.20</td>
</tr>
<tr>
<td>WY11-C9</td>
<td>43.73</td>
<td>−105.87</td>
<td>1815</td>
<td>40</td>
<td>2</td>
<td>−12.8</td>
<td>0.663 (0.009)</td>
<td>21.4 (2.0)</td>
<td>0.729 (0.010)</td>
<td>21.3 (2.0)</td>
<td>−0.035</td>
</tr>
<tr>
<td>WY11-C10</td>
<td>44.21</td>
<td>−107.30</td>
<td>2638</td>
<td>0</td>
<td>2</td>
<td>−15.0</td>
<td>0.680 (0.009)</td>
<td>17.6 (1.9)</td>
<td>0.748 (0.009)</td>
<td>17.6 (1.8)</td>
<td>−0.099</td>
</tr>
<tr>
<td>WY11-C12</td>
<td>43.24</td>
<td>−108.17</td>
<td>1448</td>
<td>0</td>
<td>2</td>
<td>−7.2</td>
<td>0.646 (0.009)</td>
<td>25.1 (2.0)</td>
<td>0.712 (0.009)</td>
<td>24.7 (1.9)</td>
<td>0.009</td>
</tr>
<tr>
<td>WY11-C13</td>
<td>42.87</td>
<td>−108.87</td>
<td>1812</td>
<td>50</td>
<td>1</td>
<td>−14.2</td>
<td>0.636</td>
<td>27.4 (3.0)</td>
<td>0.700</td>
<td>27.2 (2.8)</td>
<td>0.023</td>
</tr>
<tr>
<td>WY11-C18</td>
<td>42.88</td>
<td>−108.51</td>
<td>1728</td>
<td>70</td>
<td>1</td>
<td>−12.0</td>
<td>0.664</td>
<td>21.2 (2.8)</td>
<td>0.730</td>
<td>21.1 (2.6)</td>
<td>0.066</td>
</tr>
<tr>
<td>WY11-C19</td>
<td>42.81</td>
<td>−108.89</td>
<td>2288</td>
<td>30</td>
<td>2</td>
<td>−12.7</td>
<td>0.668 (0.009)</td>
<td>20.1 (2.8)</td>
<td>0.735 (0.009)</td>
<td>20.0 (1.8)</td>
<td>0.050</td>
</tr>
<tr>
<td>WY11-C20</td>
<td>41.89</td>
<td>−105.73</td>
<td>2131</td>
<td>30</td>
<td>2</td>
<td>−8.5</td>
<td>0.663 (0.018)</td>
<td>21.3 (2.0)</td>
<td>0.730 (0.019)</td>
<td>21.1 (3.9)</td>
<td>−0.013</td>
</tr>
<tr>
<td>WY11-C23</td>
<td>42.15</td>
<td>−105.18</td>
<td>1419</td>
<td>60</td>
<td>1</td>
<td>−10.2</td>
<td>0.657</td>
<td>22.6 (4.0)</td>
<td>0.724</td>
<td>22.3 (2.7)</td>
<td>−0.014</td>
</tr>
<tr>
<td>NE11-C24</td>
<td>42.21</td>
<td>−101.65</td>
<td>954</td>
<td>50</td>
<td>2</td>
<td>−8.7</td>
<td>0.642 (0.009)</td>
<td>25.9 (3.0)</td>
<td>0.708 (0.009)</td>
<td>25.6 (1.9)</td>
<td>0.037</td>
</tr>
<tr>
<td>WY11-C26</td>
<td>42.25</td>
<td>−108.85</td>
<td>2550</td>
<td>0</td>
<td>1</td>
<td>−11.5</td>
<td>0.662 (0.016)</td>
<td>21.5 (2.0)</td>
<td>0.729 (0.016)</td>
<td>21.3 (3.3)</td>
<td>0.014</td>
</tr>
<tr>
<td>WY11-S8</td>
<td>42.88</td>
<td>−108.18</td>
<td>1728</td>
<td>75</td>
<td>1</td>
<td>−12.1</td>
<td>0.666</td>
<td>20.7 (3.5)</td>
<td>0.733</td>
<td>20.6 (2.6)</td>
<td>−0.028</td>
</tr>
<tr>
<td>WY11-S9</td>
<td>42.26</td>
<td>−108.80</td>
<td>2315</td>
<td>45</td>
<td>1</td>
<td>−14.1</td>
<td>0.594</td>
<td>37.3 (3.3)</td>
<td>0.657</td>
<td>36.8 (3.1)</td>
<td>−0.010</td>
</tr>
</tbody>
</table>

a Number of unique analyses of CO₂ from carbonate.

b VPDB = Vienna Pee Dee Belemnite. Uncertainties on δ¹³C and δ¹⁸O are < 0.07‰ and 0.06‰ respectively.

c HG = heated gas. Uncertainty calculations follow our method defined in Section 3.

d Ghosh et al. (2006a); $T = \sqrt{\text{SQRT}(59200/\Delta \alpha) + 0.0047}$. Uncertainty is reported in parentheses.

e Dennis et al. (2011): $T = \sqrt{\text{SQRT}(63600/\Delta \alpha) + 0.0047})$ – 273.15. Uncertainty is reported in parentheses.

f Refer to Table A3 for Δ₁₈O data from the carbonate standards.

g Subscript “sw” denotes soil water. δ¹⁸Osw is calculated based on the inferred temperature from clumped isotopes and the measured δ¹⁸Osw using the equation of Kim and O’Neil (1997). VSMOW = Vienna Standard Mean Ocean Water.

Table 2
Summary of stable isotope data for soil carbonates without clumped isotope analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Elevation (m)</th>
<th>Depth (cm)</th>
<th>δ¹⁸O (‰) (VPDB)</th>
<th>Soil temperature (calculated)°(°C)</th>
<th>δ¹⁸Osw (‰) (VSMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE11-C3</td>
<td>42.7</td>
<td>−103.9</td>
<td>1464</td>
<td>50</td>
<td>−10.8</td>
<td>23.5</td>
<td>−8.7</td>
</tr>
<tr>
<td>WY11-C17</td>
<td>42.9</td>
<td>−108.9</td>
<td>1967</td>
<td>50</td>
<td>−12.8</td>
<td>21.2</td>
<td>−11.2</td>
</tr>
<tr>
<td>WY11-C21</td>
<td>42.1</td>
<td>−105.6</td>
<td>2146</td>
<td>40</td>
<td>−10.1</td>
<td>20.4</td>
<td>−8.7</td>
</tr>
<tr>
<td>WY11-S3</td>
<td>42.6</td>
<td>−106.8</td>
<td>1941</td>
<td>55</td>
<td>−13.6</td>
<td>21.3</td>
<td>−12.0</td>
</tr>
<tr>
<td>WY11-S5</td>
<td>43.7</td>
<td>−105.9</td>
<td>1815</td>
<td>55</td>
<td>−11.8</td>
<td>21.9</td>
<td>−10.1</td>
</tr>
<tr>
<td>WY11-S6</td>
<td>42.6</td>
<td>−108.3</td>
<td>1985</td>
<td>40</td>
<td>−12.5</td>
<td>21.1</td>
<td>−10.9</td>
</tr>
<tr>
<td>WY11-S7</td>
<td>42.9</td>
<td>−108.9</td>
<td>1812</td>
<td>50</td>
<td>−10.7</td>
<td>21.9</td>
<td>−9.0</td>
</tr>
<tr>
<td>WY11-S11</td>
<td>42.1</td>
<td>−105.2</td>
<td>1419</td>
<td>50</td>
<td>−9.3</td>
<td>23.7</td>
<td>−7.2</td>
</tr>
<tr>
<td>NE11-S12</td>
<td>42.2</td>
<td>−101.6</td>
<td>954</td>
<td>50</td>
<td>−9.5</td>
<td>25.8</td>
<td>−7.0</td>
</tr>
<tr>
<td>CO11-S16</td>
<td>40.6</td>
<td>−108.3</td>
<td>1758</td>
<td>50</td>
<td>−14.2</td>
<td>22.1</td>
<td>−12.4</td>
</tr>
</tbody>
</table>

a Soil temperature was calculated using the clumped-isotope temperature vs. elevation regression equation ($T = -0.0046 \times \text{Elev.} + 30.222$) shown in Fig. 3.

b δ¹⁸Osw is calculated from the calculated soil T and δ¹⁸Osw using Kim and O’Neil (1997).
isotope analyses were conducted on 14 samples at Johns Hopkins University following the methods of Passey et al. (2010). Equilibrium CO₂ prepared at 1000 °C and 30°C was analyzed concurrently with the unknowns, and clumped-isotope data are reported relative to the “equilibrium CO₂” scale unless explicitly noted otherwise. The data interpretation and graphing of results are presented in Section 5.3.1 below). 

4. Results

All isotope data are presented in Tables 1 and 2. Supporting data for clumped isotope analyses are presented in Table A3. Temperatures calculated from the carbonate clumped-isotope thermometer \( T(\Delta_{47}) \) range from 17.6 °C to 36.8 °C (mean = 22.4 °C) (Fig. 3). Only one value exceeds 27.2 °C, which is outside the 95% confidence interval of the regression between temperature and elevation (Fig. 3). This sample was also only analyzed once (i.e. no replicates). For these reasons, this sample was excluded from further consideration, including figures and statistical analyses. The soil carbonate \( T(\Delta_{47}) \) values are \( \sim 16^\circ\text{C} \) higher than mean annual air temperatures, 3–5°C higher than mean summer (June–July–August) air temperatures, and \( \sim 3^\circ\text{C} \) higher than mean July (hottest month) air temperatures (Fig. 3), but are \( \sim 6.5^\circ\text{C} \) lower than mean July maximum air temperatures and thus are within the range of modern surface temperatures (Fig. 3). Our soil carbonate \( T(\Delta_{47}) \) values are \( \sim 3^\circ\text{C} \) higher than mean summer soil temperatures measured at meteorological stations (Table A1). They are equal to July maximum soil temperatures when elevation is \( < 2 \) km. The difference between carbonate \( T(\Delta_{47}) \) values and soil temperatures appears to become progressively larger when elevation is \( > 2 \) km (Fig. 3), but may also be related to differences between locations of the sample sites and climate stations (see Section 5.3.1 below).

The clumped-isotope temperatures are inversely related to elevation, with a lapse rate of \(-4.0^\circ\text{C/km}\) (Fig. 3). The \( \delta^{18}\text{O} \) values of soil carbonate from \(-7.2\%\) to \(-15.0\%\), and are inversely related to elevation. Oxygen isotope values of soil water \( (\delta^{18}\text{O}_{w}) \) were calculated using clumped-isotope temperatures, soil carbonate \( \delta^{18}\text{O} \) values, and the calcite–water oxygen isotope paleotemperature equation of Kim and O’Neil (1997): When a sample was not analyzed for \( \Delta_{47} \), we used the temperature derived from the \( T(\Delta_{47}) \)-elevation relationship to estimate the carbonate formation temperature to calculate \( \delta^{18}\text{O}_{w} \). Calculated \( \delta^{18}\text{O}_{w} \) values range from \(-14.2\%\) to \(-4.9\%\) (VSMOW; Tables 1 and 2), and decrease with increasing elevation (Fig. 4).

5. Discussion

5.1. Summer formation of soil carbonate in Wyoming and Western Nebraska

We compare \( T(\Delta_{47}) \) values to soil and air temperatures to understand the timing of soil carbonate formation in our study area. Because the carbonate clumped-isotope temperature reflects the temperature of carbonate mineralization (Eiler, 2007), soil carbonate formation temperatures that equal soil temperature, and equal or exceed mean summer air temperature by a few degrees suggest that soil carbonates in Wyoming and western Nebraska form during the summer season, consistent with observations in other...
semi-arid to arid temperate environments (Breecker et al., 2009; Passey et al., 2010; Peters et al., 2013; Quade et al., 2007, 2013). Soil carbonate formation temperatures that are higher than mean summer air temperatures are explained by solar heating of the soil surface (e.g. Breshears et al., 1998; Wu and Nofziger, 1999; Bartlett et al., 2006).

Soil carbonate formation is favored under conditions of increased concentration of \( \text{Ca}^{2+} \) in soil water, increased soil temperature, decreased soil \( \text{pCO}_2 \), and decreased soil water (Cerling and Quade, 1993; Breecker et al., 2009). In the study area, soil moisture is high in April–June, and drops sharply in June and July, then remains low during the rest of the year unless major rain events occur (Fig. 2). Soil temperature reaches its peak in July (Fig. 2A). Both high temperature and the loss of soil moisture in summer may increase \( \text{CaCO}_3 \) activity in soil water and favor the precipitation of soil carbonate in the hot and dry summers in Wyoming and western Nebraska.

Soil carbonate formation temperatures higher than mean summer soil temperatures and equal to or higher than July (hottest month) mean soil temperature (Fig. 3; data from localities \( \geq 2000 \text{ m} \)) indicate that soil carbonate formation may not be biased only to formation during the summer, but potentially to extreme warm or dry events that may not occur every year (Passey et al., 2010; Peters et al., 2013). A caveat however is that the clumped isotope geothermometer has yielded temperatures consistent with mean annual air temperatures in Bolivia (Ghosh et al., 2006b) and Argentina (Peters et al., 2013). These locations have seasonally wet conditions in either winter or summer and as such the soil dries in spring or fall. \( T(\Delta_{47}) \) values then reflect spring or autumn soil temperatures, which are generally closer to mean annual conditions than those observed in Wyoming and Nebraska. These observations suggest that the timing of soil drying may be more important than soil temperature in dictating when soil carbonates form.

5.2. Formation of soil carbonate in equilibrium with summer precipitation after major summer rains

Soil water \( \delta^{18} \text{O}_{\text{sw}} \) values can be used as additional evidence in the determination of seasonality of soil carbonate formation and as a proxy for paleoelevation and paleoclimate (e.g. Rowley et al., 2001; Rowley and Garzione, 2007). Our calculated \( \delta^{18} \text{O}_{\text{sw}} \) values are \( \sim 5.5\% \) higher than modern mean annual precipitation \( \delta^{18} \text{O} \) values from within the study area, but generally agree with modern mean summer precipitation \( \delta^{18} \text{O} \) values (Vachon et al., 2010) (Fig. 4). The similarity between the calculated \( \delta^{18} \text{O}_{\text{sw}} \) values and mean summer precipitation \( \delta^{18} \text{O} \) values may indicate that soil carbonates formed in or near equilibrium with summer rain in Wyoming and western Nebraska. Alternatively, soil carbonates may form in equilibrium with an evaporated mixture of snowmelt, spring rain, and summer rain. Soil moisture at 50 cm in our study area is recharged significantly by snowmelt and rain during the spring (primarily in May) and declines dramatically in early summer (Fig. 2A). The major drying event in early summer overlaps with the growing season, which further decreases soil moisture due to high transpiration rates and may facilitate soil carbonate formation in our study area.

The degree that evaporation has altered \( \delta^{18} \text{O}_{\text{sw}} \) values provides a way to differentiate between these two possible sources of soil water. Soil moisture at shallow depths (20 cm) in the study area is very low. Though frequent rains wet the shallow soil layers quickly, only major rain events increase soil moisture below 50 cm (Fig. 2B). Soil moisture data in Fig. 2B also shows that in the mid–late summer, soil moisture at both 20 and 50 cm increases very rapidly after larger summer storms and suggests that rainwater spends very little time at the surface for potential evaporation prior to infiltrating the soil profile. Rapid infiltration of precipitation is typical of semi-arid to arid environments (Ferretti et al., 2003). Once in the soil profile, soil water can be evaporated, but the percent of soil moisture removed by evaporation decreases with soil depth (Lauenroth and Bradford, 2006). This is also supported by experimental and theoretical studies, which show that evaporation has a minimal effect on the \( \delta^{18} \text{O} \) values of soil water in most soils below 30–50 cm (e.g. Allison et al., 1983; Barnes and Allison, 1983; Ferretti et al., 2003; Xiao et al., 2011). Because soil moisture at 50 cm increases only after large rains and not after smaller ones (Fig. 2B), it suggests that potentially evaporated soil water located at shallow depths does not infiltrate to depths greater than 50 cm, but rather is removed at shallow depths by evaporation and/or transpiration. Therefore, we argue that evaporated soil water at shallow depth does not contribute significantly to soil carbonate mineralization at \( >50 \text{ cm depth} \).

Major rivers in Wyoming and Nebraska have an average \( \delta^{18} \text{O} \) value of \( \sim −17\% \) in spring and early summer (Kendall and Coplen, 2001), representing the \( \delta^{18} \text{O} \) value of the mixture of snowmelt from high mountains and local spring rain. If soil carbonates form in equilibrium with this mixture of snowmelt and spring rain in early summer (rather than summer rainfall), it would require 3–12\% enrichment in \( \delta^{18} \text{O} \) (8\% on average). Though the kinetic effect of evaporation at relative humidities similar to that of Wyoming summer months \((\sim 55\%) \) could lead to a \( \sim 7\% \) increase of water \( \delta^{18} \text{O} \) values (Confiantini et al., 1986), the influence of this effect would be reduced in early summer when relative humidity is higher, and would only occur at or near the surface (e.g. Allison et al., 1983; Ferretti et al., 2003; Lauenroth and Bradford, 2006).

Because evaporation of soil water near the surface has little effect on the soil water at depth, equilibrium evaporation would need to remove \( \sim 60\% \) of the soil water reservoir to achieve the 8\% enrichment. However, Lauenroth and Bradford (2006) show that evaporation removes \(<40\% \) in short-grass steppe environments like those in Wyoming and western Nebraska, and even less in woodlands or at greater soil depths. The evidence discussed above suggests that soil water \( \sim 50 \text{ cm} \) deep in the soil profile should not be highly evaporated. Therefore, soil carbonates form in summer as the soil dries during the major growth season in early summer and following rewatering from large mid–late summer rains, and in (or near) equilibrium with summer precipitation that is not substantially enriched by evaporation. Though we suggest that a significantly evaporated mixture of snowmelt and spring rain is not the dominant soil water composition at the depth we studied, a small degree of evaporation of soil water may cause the variation of calculated \( \delta^{18} \text{O}_{\text{sw}} \) values. This finding highlights the importance of major summer rain events in soil carbonate formation.

5.3. Temperature-elevation relationships

5.3.1. Observed trends of air, soil temperature and \( T(\Delta_{47}) \) versus elevation

Air and soil temperatures are best approximated by a second order polynomial regression (Fig. 3). The observed trends of progressively increasing regression slope with higher elevations (lapse rate increases) for the regression of mean air/soil temperature and elevation may occur in response to increased ground shading with elevation. In Wyoming, flat lying, sparsely vegetated surfaces dominate lower elevations \((<1800 \text{ m}) \), whereas higher elevations \((>2200 \text{ m}) \) are characterized by higher slope angles and greater abundance of leafy vegetation (Driese et al., 1997). Flat, open landscapes receive direct solar radiation over a greater portion of the day than do higher elevation landscapes, which may be shaded by adjacent topography, vegetation, or due to slope aspect over much of the day. In addition, more frequent afternoon rain show-
ters (Fig. 2B) or prolonged snow cover can also lead to lower air and soil temperatures at higher elevations in semi-arid to arid environments such as those in Wyoming. These factors cool the air and soil and lead to the nonlinear nature of the station-based air and soil temperature data with elevation.

Soil carbonate $T(\Delta T)$ values are correlated with elevation in our study area (Fig. 3). Because $T(\Delta T)$ values should follow soil temperature (Eiler, 2007; Ghosh et al., 2006a), the decrease in $T(\Delta T)$ values with elevation should be expected to display a similar second order polynomial regression, but $T(\Delta T)$ values are equally well approximated by a simple linear regression ($T(\Delta T) = −0.004(\text{Elev.}) + 29.7$ ($r^2 = 0.53$)). Scatter of data in this regression may be caused by sample depth, analytical uncertainty, latitude, age uncertainties, degree of solar heating depending on local slope aspect (Quade et al., 2013), vegetation cover (Passey et al., 2010), albedo, and soil/rock type (Bartlett et al., 2006). For example, sample WY-C13 (Elev. = 1812 m) is an outlier with an anomalously high $T(\Delta T)$ value and exerts large leverage on the regression. If removed from the regression, the $T(\Delta T)$-elevation relationship becomes $T(\Delta T) = −0.004(\text{Elev.}) + 29.303$ ($r^2 = 0.72$).

The difference between soil carbonate $T(\Delta T)$ values and station-based soil temperatures becomes progressively larger at higher elevations (Fig. 3). However, the relatively high $T(\Delta T)$ values measured for the highest elevation samples may be due to local climate conditions at the sample site. For instance, sample WY-C26 (Elev. = 2550 m) was obtained from a location with little vegetation and flat, open topography similar to that found at lower elevations, but the air and soil temperature data from this elevation were obtained from stations typically located in more vegetated mountainous regions. The high $T(\Delta T)$ value thus represents a formation temperature that may appear anomalously high when compared to the station data, but more likely represents soil temperatures in locations more amenable to soil carbonate formation and highlights the inherent variability in site-specific conditions possible at any given elevation. Conversely, our low elevation samples were collected from sites similar to the low elevation climate stations (Table A4) and yield similar results for $T(\Delta T)$ and soil temperature (Fig. 3).

5.3.2. Can soil carbonate $T(\Delta T)$ values be used to reconstruct elevation?

Because our data show that soil carbonate $T(\Delta T)$ values linearly decrease as elevation increases between ~950 m and ~2650 m (Fig. 5A), we evaluate the accuracy of using $T(\Delta T)$ values to reconstruct elevations using a linear regression of $T(\Delta T)$ values versus elevation. We reconstruct elevations of the sampling sites by applying this linear regression to the $T(\Delta T)$ values and find that the model predicts the sample elevations reasonably well (Fig. 5B). Propagation of error on this model produces elevation estimates with a mean error of ±450 m. The root mean square error (RMSE) of the predicted versus expected regression is 336 m.

We compared our results to those of other recent studies that have used the clumped isotope geothermometer as a proxy for paleo-elevation (e.g. Huntington et al., 2010; Peters et al., 2013; Quade et al., 2013). Because samples from these studies were obtained at various soil depths, we restricted our comparison to only those samples obtained from 40–85 cm depth (and chose 50 cm as the ideal depth) in order to reduce errors associated with the depth dependence of soil temperature. We further restricted our comparison only to sites with seasonally arid conditions from which a vertical transect of samples were available. Only one sample was chosen per site to avoid bias from pseudoreplication. We find that all, but the Peters et al. (2013) study show a negative trend in $T(\Delta T)$ with elevation with similar lapse rates ($\sim −4 ^\circ C/km$) (Fig. 6). An expected temperature offset exists between the data sets. Modern lacustrine carbonate samples from the Colorado Plateau (Huntington et al., 2010) have lower carbonate formation temperatures (~4–6 °C) than our soil carbonate data (Fig. 6). This is because lake carbonate $T(\Delta T)$ values reflect lake temperatures which are cooler than air temperature. Soil carbonate samples from India and the southern Tibetan Plateau (Quade et al., 2013) show higher carbonate formation temperatures (7–8 °C) than our data (Fig. 6). However, their data was from a lower latitude than our study and as a result had higher $T(\Delta T)$ values that are consistent with local air/soil temperature conditions. $T(\Delta T)$ values of soil carbonate samples from the elevation transect of the Rio Mendoza in west central Argentina (Peters et al., 2013) do not show a consistent trend with elevation, a pattern Peters et al. (2013) attributed to a shift in the seasonal timing of rainfall along their elevation transect. The differences in temperature for sites spanning similar elevations underscore the need for site-specific calibration.

Our study, Huntington et al. (2010), and Quade et al. (2013) all yield similar $T(\Delta T)$ lapse rates, suggesting that, once fully calibrated, paleo-altimetry using the clumped isotope geothermometer may be broadly applicable. Because local climate appears to affect the intercept of the $T(\Delta T)$-elevation regression, the $T(\Delta T)$-elevation relationship can yield the relief between two
sites (when the sites are located at a similar latitude and are influenced by similar climate conditions), but cannot yet be used to compare elevations of sites that fail to meet these criteria. Direct reconstruction of paleoelevation requires a reference site of known elevation. Such a reference site may be shallow marine limestone, soil carbonate formed in marginal marine environment, which represents elevation near sea level. It is also possible that paleoelevation may be constrained from the local modern $T(A_{47})$-elevation relationship, if the timing of soil carbonate formation and paleoclimate during the studied period are consistent with modern soil carbonate used for calibration or if these parameters are constrained through use of climate models.

5.3.3. Comparison to $\delta^{18}O$-elevation relationship

The constraints on soil carbonate formation temperature also improve the accuracy of oxygen isotopes as a paleoaltimeter because soil temperatures and soil carbonate $\delta^{18}O$ values are both measured to unambiguously determine $\delta^{18}O_{\text{sw}}$ values (e.g. Quade et al., 2007; Peters et al., 2013). Linear regression of the calculated $\delta^{18}O_{\text{sw}}$ values and elevation ($\delta^{18}O_{\text{sw}} = -0.004(Elev.) – 2.55 (r^2 = 0.50; n = 12)$) shows an expected decrease in $\delta^{18}O$ values with increasing elevation (Fig. 7A) with $\delta^{18}O$ values similar to that observed for sites collected at depths shallower than 40 cm and have possibly been influenced by evaporation (Fig. 7A). If these samples are not included in the $\delta^{18}O_{\text{sw}}$-elevation regression the relationship becomes $\delta^{18}O_{\text{sw}} = -0.05(Elev.) – 1.1 (r^2 = 0.97, n = 23)$. The $\delta^{18}O_{\text{sw}}$ values ($n = 23$) show large variance ($\sigma^2$), up to 5.4‰, with a maximum difference ($\delta^{18}O_{\text{sw}}\text{max} - \delta^{18}O_{\text{sw}}\text{min}$) of 9.3‰. Forty percent of the variance and one third of the range is induced by samples collected at shallow (<40 cm) depths. We suggest that the remaining variability is mainly induced by precipitation $\delta^{18}O$ values, which are influenced by many other factors including air temperature at condensation, sub-cloud evaporation (e.g. Froehlich et al., 2008), recycling of continental vapors (e.g. Salati et al., 1979; Gat and Airy, 2006; Kurita and Yamada, 2008), changes in vapor source (e.g. Gat and Carmi, 1970) and local topography (Hough et al., 2011). Large variation of summer precipitation $\delta^{18}O$ values is also observed in the Sierra Nevada region (Lechler and Niemi, 2011), on the Tibetan Plateau (Quade et al., 2011) and in Argentina (Hoke et al., 2013). Additional variability can be caused by the degree of evaporation during soil carbonate formation when the sample is collected at <50 cm depth, the relative abundance of snowmelt, spring rain, and summer rain in soil water, the depth in the soil profile at which the carbonate formed, or the relative abundance of soil carbonate formed in early summer versus mid–late summer. Because many factors can cause the variation of precipitation $\delta^{18}O$ values, we suggest the accuracy of
predicted elevation using $\delta^{18}$O values should be no better than using $T(\Delta_{A7})$ values.

Notwithstanding the potential errors outlined above, the reconstructed sample elevations using the $\delta^{18}$O-elevation regression are well matched with the actual sample elevations (Fig. 7B). The error on calculated values of $\delta^{18}$O resulting from uncertainty on $\Delta_{A7}$ is relatively low (<0.5%). The RMSE of the predicted versus expected regression is 376 m, but decreases to 166 m if the samples from soil depths <40 cm are not included in the regression.

5.4. Implications for paleoelevation and paleoenvironment reconstruction

The formation of soil carbonate in summer months, in or near equilibrium with summer precipitation, has significance to paleoelevation and paleoenvironment reconstruction. Paleoclimatic and paleoelevation studies have often assumed that soil carbonates form at a temperature equivalent to mean annual air temperature (e.g. Cerling and Quade, 1993). However, because mean summer air temperature is commonly up to 20°C higher than mean annual air temperature in temperate climates, soil water $\delta^{18}$O values calculated using mean annual air temperature could be as much as 4‰ lower than their true values. Paleoclimatic and paleoelevation studies also commonly compare calculated soil water $\delta^{18}$O values with mean annual precipitation $\delta^{18}$O values. However, in many regions the mean value of summer precipitation $\delta^{18}$O exceeds that of mean annual precipitation by several per mil, as in the southern Tibetan Plateau, where mean summer precipitation $\delta^{18}$O values exceed that of mean annual precipitation by 6–8‰ (Tian et al., 2003) and again may result in anomalously low paleoelevation estimates. In such settings it is critical to consider that reconstructed $\delta^{18}$O values may reflect seasonal precipitation rather than mean annual precipitation.

A seasonal bias in the formation of soil carbonates (timing and temperature) can be useful in characterizing the seasonality of terrestrial environments of the past (e.g. Snell et al., 2013) over periods longer than traditional isotopic analysis of fossil teeth (e.g. Higgins and MacFadden, 2004) and may help us better understand the ramifications that changes in global to local scale climate have on climate dynamics and on climate-erosion teleconnections (e.g. Zhang et al., 2001). However, caution should be given when interpreting soil carbonate $T(\Delta_{A7})$ values and their seasonal climate significance. This is because 1) soil carbonate $T(\Delta_{A7})$ values represent soil temperature during the timing of soil carbonate formation, which is controlled by air temperature and the degree of surface heating depending on local relief and surface shading; 2) soil carbonate $T(\Delta_{A7})$ values can be higher than measured mean hottest month soil temperatures such as in Wyoming and western Nebraska, and may record temperatures that are biased toward extreme temperature (or dry) periods rather than monthly, seasonally, or annually averaged soil temperatures; 3) the seasonal bias of soil temperature varies at different locations depending on the time of soil drying. Locations with winter or summer wet seasons have $T(\Delta_{A7})$ values that reflect spring or autumn soil temperatures, which are generally closer to mean annual conditions than those observed in Wyoming and Nebraska. A change in the seasonality of rainfall (or more directly, soil dewatering) can alter the temperature of soil carbonate formation and complicates any simple relationship between climate data and $T(\Delta_{A7})$ values.

Caution must be exercised when assessing paleoelevation to assure that no such shift in climate has occurred during the period of interest lest it be interpreted incorrectly as a change in surface elevation. Additionally, soil carbonate tends to form in open landscapes and stable soil profiles. In high elevation mountain settings, this could lead to soil carbonate $T(\Delta_{A7})$ values that are higher than average soil temperature at the same elevation, which would result in underestimates of paleoelevation. Therefore, we suggest that both soil carbonate $T(\Delta_{A7})$ and $\delta^{18}$O values should be used to corroborate paleoelevation reconstruction.

Soil carbonates also occur in settings with higher mean annual precipitation (up to ~150 cm/yr). They are common in soil types such as Mollisols and Vertisols that have not yet been thoroughly investigated. These soil types are most commonly preserved in the fossil record. Therefore, it will be important to study the seasonality of carbonate precipitation in these kinds of soils.

This study joins others in establishing the seasonal nature of soil carbonate formation (Breecker et al., 2009; Passey et al., 2010; Peters et al., 2013; Quade et al., 2013). Our research, however, is the first effort to find that soil carbonate $T(\Delta_{A7})$ values correspond to periods when soil moisture dramatically decreases after major summer rain events, and provides evidence that soil carbonates are formed in (or near) equilibrium with summer precipitation $\delta^{18}$O values. We infer that the formation of soil carbonate in Wyoming and western Nebraska occurs as the soil dries and is therefore dependent on the timing of soil dewatering more than on high summertime air/soil temperatures (although high temperatures may promote soil dewatering through transpiration and evaporation). This explains observations from regions where seasonal rainfall occurs during either the summer or winter resulting in soil carbonate $T(\Delta_{A7})$ values that tend to correspond with MAT (Chosh et al., 2006a, 2006b; Peters et al., 2013). We also show that large storms during the dry season are the main source of soil moisture to depths ~40 cm where evaporation of soil water becomes negligible. It is from these waters that soil carbonates form. Furthermore, the similarity in slope for the $T(\Delta_{A7})$-elevation regression among recent studies at regional spatial scales (Huntington et al., 2010; Quade et al., 2013; this study) compared to that at the local scale (Peters et al., 2013) highlights the large role that seasonality of precipitation can exert on paleoelevation estimations. We suggest more data sets covering diverse climate settings should be collected to understand how local climate may change the $T(\Delta_{A7})$-elevation regression in order to promote the application of such a relationship for paleoclimate and paleoelevation reconstructions.

6. Conclusions

This study calibrates the soil carbonate clumped isotope geothermometer in the temperate, semi-arid climate of Wyoming and western Nebraska, USA. Soil carbonate $T(\Delta_{A7})$ values in the studied area are ~16°C higher than mean annual air temperature and 3–5°C higher than mean summer air temperature, suggesting that soil carbonates are formed in summer and that their formation temperatures are influenced by soil heating by solar radiation. Our study also shows that soil carbonate $T(\Delta_{A7})$ values are equal to or higher than maximum soil temperature, suggesting soil carbonates may also be biased to warmest periods or extreme warm/dry events during the summertime. In high elevation mountain settings, soil carbonate $T(\Delta_{A7})$ values may only represent the temperature of areas amenable to soil carbonate formation (open and/or flat), which tend to be warmer than soil temperatures collected at climate stations located in forest-covered, hilly sites.

Soil water $\delta^{18}$O values calculated using carbonate $\delta^{18}$O values and clumped-isotope temperatures are similar to the $\delta^{18}$O values of local mean summer precipitation suggesting that soil carbonates in the studied area are either formed in equilibrium with evaporated soil water during the major soil dewatering in early summer, or near equilibrium with summer precipitation. Because soil ~40 cm are only wet by major rain events, and the infiltration of rain water to deep soil is very rapid, enrichment of $^{18}$O caused by evaporation at soil depth ~40 cm is very limited. We suggest soil carbonates in Wyoming and western Nebraska are formed.
during summer, particularly during the soil drying period in early summers and after major rainstorms in mid–late summers. These conditions thus represent a significant seasonal and drying event bias in the timing and temperature of carbonate formation.

Both soil carbonate $T_{\Delta 47}$ values and calculated $\delta^{18}O_{\text{sw}}$ values decrease as elevation increases and the relationships can be applied to reconstruct paleorelief, and paleoelevation when a reference site with known elevation can be determined. The soil temperature-elevation relationship can be represented by a simple linear equation ($r^2 = 0.72$) over the studied elevation range (900–2600 m). Elevations predicted using the empirically derived linear temperature-elevation relationship and the $\delta^{18}O_{\text{sw}}$ values are within 0.5 km of their actual elevations. Because calculated $\delta^{18}O_{\text{sw}}$ values from soil carbonates with constrained growth temperatures reflect the variation of precipitation $\delta^{18}O$ values albeit as influenced by many climate factors (e.g. sub-cloud evaporation, vapor recycling), and because soil carbonate clumped isotope thermometry is susceptible to site specific climate conditions, we suggest that the use of both soil carbonate $T_{\Delta 47}$ values and calculated soil water $\delta^{18}O$ values can reduce the limitations of the individual techniques and both should be used to corroborate paleoelevation reconstruction.

Finally, we demonstrate that soil carbonate formation is biased to periods of soil water draining following the major precipitation season or large dry season rainfall events, the timing of which varies depending on local climate. Thus it will be important to calibrate the soil carbonate clumped isotope geothermometer in diverse climate settings and soil types, and to remember that, when applying the soil carbonate clumped isotope geothermometer and oxygen isotope values for paleoclimate and paleoelevation reconstructions, soil formation temperature and soil water $\delta^{18}O$ values reflect seasonal soil temperature and seasonal precipitation $\delta^{18}O$ values.

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Appendix A. Supplementary material

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References


