Combining soil water balance and clumped isotopes to understand the nature and timing of pedogenic carbonate formation

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ABSTRACT

Pedogenic carbonate is an important archive for paleoclimate, paleoecology, and paleoelevation studies. However, it can form under seasonal environmental conditions that differ significantly from the mean growing season environment or mean annual conditions, potentially complicating its use for proxy reconstructions. The observed seasonal temperature is typically, but not always, biased high relative to mean annual air temperature (MAT). To evaluate the annual timing of pedogenic carbonate formation, ten different soils were sampled across the western United States. Sites were selected to span a variety of precipitation regimes and soil orders. Precipitation regimes ranged from arid sites (mean annual precipitation (MAP) < 20 cm) that receive the majority of precipitation during the winter to wetter sites (MAP > 50 cm) dominated by summer precipitation. Pedogenic carbonate formation temperatures derived from clumped isotope measurements ranged between 6 and 22 °C, with most samples falling at or below MAT. Clumped isotope temperatures were compared to monthly precipitation normals and modeled monthly values of evapotranspiration and soil water content. Results show that carbonate formation temperatures agree with the annual timing of soil water depletion,

suggesting soil moisture content is a primary control on the timing of pedogenic carbonate formation. Although the seasonal bias is a function of environmental factors that are difficult to reconstruct in paleo-studies, the use of other paleosol proxies can help to assess if changes in clumped isotope temperatures are a function of changes in air temperature or hydrology. These results have important implications for the production of accurate paleoclimate and paleoelevation estimates.

Keywords: paleosol, seasonality, paleoclimate, evapotranspiration

1. INTRODUCTION

Many soils in semi-arid to arid environments exhibit a distinct calcic horizon identifiable by an accumulation of authigenically precipitated pedogenic carbonate. Depending on the age and texture of the soil, pedogenic carbonate can precipitate as thin filaments, clast undercoatings, root casts, nodules, or continuous indurated horizons (Gile et al., 1966). Pedogenic carbonate preserved in paleosols is of particular interest in paleoclimate research. The occurrence of pedogenic carbonate provides a paleoprecipitation limit, as it tends only to form when mean annual precipitation (MAP) is less than 100 cm (Cerling and Quade, 1993; Royer, 1999; Retallack, 2005). Proxies based on the physical nature of pedogenic carbonate, such as depth in soil profile or horizon thickness, have been developed to reconstruct variables such as MAP and degree of seasonality (Retallack, 1994; Retallack, 2005). Widespread interest in the geochemistry of pedogenic carbonate expanded since it was demonstrated that the oxygen and carbon isotopic composition of the carbonate was a reflection of the environment in which it formed (Cerling, 1984; Cerling and Quade, 1993). Subsequently, the oxygen isotope composition of pedogenic carbonate has been used to reconstruct paleohydrology (e.g. Amundson et al., 1996; Deutz et al., 2001; Fox and Koch, 2004), paleotemperature (e.g. Dworkin

et al., 2005; Cleveland et al., 2008), and paleoelevation (e.g. Garzione et al., 2000; DeCelles et al., 2007). The carbon isotope composition of pedogenic carbonate has been used to reconstruct relative abundances of C₃ and C₄ vegetation (e.g. Quade and Cerling, 1995; Deutz et al., 2001; Fox and Koch, 2003; Levin et al., 2004) as well as atmospheric *p*CO₂ (e.g. Cerling, 1991; Ekart et al., 1999; Cotton and Sheldon, 2012; Montañez, 2013).

However, complications exist when using pedogenic carbonate as a paleoclimate proxy. The traditional assumption was that pedogenic carbonates form during conditions reflective of the mean growing season environment, which would typically imply soil temperature conditions between average and maximum annual soil temperature (Cerling and Quade, 1993). However, the growing season occurs at different times of the year under different climate regimes. For example, the growing season in the central plains of North America extends from spring to early autumn (Ode et al., 1980), whereas the growing season in the eastern Mojave Desert extends from late autumn to early spring (Beatley, 1974). It has also been documented in modern soils that carbonate can precipitate at times of excessive dryness when climatic conditions differ strongly from the mean growing season conditions (Breecker et al., 2009). These findings suggest that, in some cases, a complicated seasonal bias may strongly affect the formation and isotopic composition of pedogenic carbonate.

Carbonate clumped isotope thermometry is an attractive tool to apply to the study of pedogenic carbonate, as the abundance of doubly substituted rare isotopes in carbonate is predominantly a function of temperature (Ghosh et al., 2006a; Quade et al., 2007; Passey et al., 2010; Eiler, 2011). The carbonate clumped isotope proxy has featured prominently in recent continental paleoclimate (e.g. Passey et al., 2010; Snell et al., 2013; VanDeVelde et al., 2013) and paleoelevation studies (e.g. Ghosh et al., 2006b; Quade et al., 2011; Lechler et al., 2013;

Leier et al., 2013; Fan et al., 2014; Garzzone et al., 2014; Huntington et al., 2015). However, relating the temperature of pedogenic carbonate formation to climatic variables such as mean annual temperature (MAT) has proven complicated when analyzing modern samples. For example, clumped isotope studies of pedogenic carbonate in East Africa, Tibet, and the Western United States revealed temperatures reflective of a warm season bias rather than MAT (Passey et al., 2010; Quade et al., 2013; Hough et al., 2014). Quade et al. (2013) highlighted many factors that could complicate the relationship between the temperature of soil carbonate formation and air temperature, including excessive ground heating, damping of temperature variation with depth, slope aspect, and vegetative shading. Despite these factors, Quade et al. (2013) were able to relate many modern carbonate-bearing soils to MAT and warmest average monthly temperature, using a depth-based ground heating model that reflected the generally observed warm-season temperature bias. However, pedogenic carbonates collected along an elevation transect in the Andes showed that clumped isotope derived temperatures can be affected by the timing of seasonal rainfall (Peters et al., 2013). Sites that received the majority of annual rainfall during the summer produced results reflective of mean annual soil temperature, whereas sites dominated by winter rainfall were biased towards warm summer temperatures (Peters et al., 2013). These results demonstrate that studies of pedogenic carbonate cannot always assume a warm-season formation bias.

This paper examines the annual timing of pedogenic carbonate formation under different climate regimes, including sites with different annual precipitation regimes and different growing seasons. This study specifically focuses on carbonate-nodule bearing soils ranging from fine to a relatively coarse texture. By comparing clumped isotope derived temperatures of carbonate formation to modelled seasonal soil temperature fluctuations, we assess the relative roles of

normal climate patterns and other environmental factors. Monthly precipitation normals are considered alongside evapotranspiration in order to determine a monthly soil water balance and to assess its control on the timing of pedogenic carbonate formation. The clumped isotope temperatures will also be used to calculate a $\delta^{18}\text{O}$ value for the soil water, allowing for comparison with annual fluctuations in the $\delta^{18}\text{O}$ of precipitation.

1.2. Site Distribution

Sites in this study were selected in order to span a range of soil types as well as different temperature and precipitation regimes (Fig. 1; Table 1). The soils analyzed herein represent three different soil taxonomic orders: Aridisols, Mollisols, and Alfisols. Of these three soil orders, Aridisols tend to be the least developed. They are characteristically dry soils that form in arid environments and are capable of supporting only a limited amount of plant growth. Due to a lack of moisture and productivity, chemical weathering and soil development tend to be very slow in these soils (Knight, 1991). As compared to Aridisols, Mollisols are generally more developed. They typically underlie temperate grasslands, such as the North American Great Plains and the Eurasian Steppe. The defining characteristic of a Mollisol is a thick (generally >25 cm), organic-rich A-horizon known as the mollic epipedon, which is largely a product of the extensive root system of prairie grasses (Soil Survey Staff, 2014). Of the soil orders examined in this study, Alfisols tend to be the most developed, and they are typically found under temperate deciduous forests (Buol et al., 2011). Soils analyzed as part of this study were generally of a finer-grained texture, allowing for greater water holding capacity and a slower drainage rate than coarse-grained, gravelly soils. With time, fine-grained soils will also tend to form carbonate nodules as opposed to clast undercoatings due, in part, to the lack of coarse fragments that serve to nucleate carbonate precipitation.

The sites examined in this study can be divided into four distinct precipitation regimes (Table 1). The two Southern California sites receive the least amount of rainfall, with both sites having a MAP value of less than 20 cm. The little precipitation that these two sites receive tends to fall during the winter months (December-March). At the wet end of the spectrum, the two South Dakota soils receive the most precipitation with MAP values around 60 cm. These two sites experience a typical continental climate with cold winters, hot summers, and peak precipitation falling during June and July. The remaining Arizona, New Mexico, and Colorado sites have MAP values that fall between these two end-members; and these sites can be subdivided into two distinct groups based on the timing of precipitation. In New Mexico and Colorado, the winters are generally dry with precipitation peaking in late summer (July/August). The three Arizona sites on the other hand are strongly affected by the Arizona monsoon and are driest between April and June before precipitation peaks in August.

2. MATERIALS AND METHODS

All of the pedogenic carbonate samples were collected in the field from calcic soil horizons (Cotton and Sheldon, 2012), and only carbonate nodules measuring at least 1 cm in diameter were analyzed, which equates to formation times of at least 2–6 ka (using the transfer function of Retallack, 2005). Where possible, samples were collected below 30 cm depth in order to minimize the effect of diurnal temperature variations and the relative input of atmospheric CO₂. The only exceptions were the two California soils, Muroc and Lavic. These samples were sourced from the California “Soil Series Pedolarium” (see Tabor et al., 2013), and carbonate nodules were slightly shallower than 30 cm depth. Both of these samples had indurated carbonate nodules, however, the nodules from the Lavic soil were approximately 5 mm in diameter.

2.1. Climate data and evapotranspiration

Climate data used in this study were taken from two separate sources, the 1981–2010 United States climate normal (Arguez et al., 2012) and the NCEP North American Regional Reanalysis (NARR) dataset (Mesinger et al., 2006). The motivation behind using these data sources is twofold. They (1) offer the opportunity to compare instrumental climate data that were collected and analyzed using the same methodology across our widely dispersed study sites and (2) provide a long-term record that is less weighted toward anomalous weather events. Monthly temperature and precipitation data were sourced from the 1981–2010 normals (NCDC, 2012). For each site, the climate normals were taken from the closest NOAA weather station that sits at a similar elevation (Table A.1). In order to calculate monthly estimates of reference evapotranspiration (ET_0), the Penman-Monteith equation was used following the methodology of the United Nations FAO-56 paper (Monteith 1981; Allen et al. 1998). The Penman-Monteith equation is defined as follows:

$$ET_0 = \frac{0.408 \Delta (R_n - G) + \gamma \frac{900}{T + 273} u_2 (e_s - e_a)}{\Delta + \gamma (1 + 0.36 u_2)} \quad (1)$$

where Δ is the slope of the saturation vapor pressure relationship, R_n is the net radiation, G is the soil heat flux density, γ is the psychrometric constant, T ($^{\circ}\text{C}$) is the 2 m air temperature, u_2 is the 2 m wind speed, and $e_s - e_a$ is the saturation vapor pressure deficit. According to the FAO-56 methodology, Δ , G , γ , and $e_s - e_a$ can be calculated if the atmospheric pressure, relative humidity and temperature variability are known. The Penman-Monteith equation was used rather than an empirical equation, because it is a physically based model that combines energy balance with mass transfer (Allen et al., 1998).

For the ET_0 calculations, average, maximum, and minimum monthly temperature data from the 1981–2010 climate normals were used as input variables. Because instrumental data is

lacking in spatial and temporal coverage, the remaining climate variables required for the Penman-Monteith equation (pressure, relative humidity, short and longwave radiation, wind speed, and 2 m air temperature) were sourced from the NARR dataset (ESRL-PSD, 2014). This long-term, high-resolution dataset (0.3 degrees at the lowest latitude) was produced by assimilation of a number of observed climate variables including precipitation, using the very high resolution NCEP Eta model (Mesinger et al., 2006). NARR data compares favorably when analyzed alongside observational data (Mesinger et al., 2006). Monthly means for all input variables were taken from the grid cell containing each respective soil site and averaged over the years 1981 to 2010. These 30-year monthly average values were then entered into the Penman-Monteith equation (Eq. (1)) to calculate an average daily ET_0 value in $mm\ day^{-1}$ for each month. The average daily ET_0 value was then multiplied by the number of days in the month to give a 30-year average monthly ET_0 value ($cm\ month^{-1}$).

2.2. Soil temperature and soil water balance

Annual variations in air temperature result in similar temperature variations in soils. However, when considering progressive depths in the soil profile, the amplitude of temperature variation is damped and the phase lag increases (Hillel, 1980). For each soil, annual temperature variation was modeled at the pedogenic carbonate sampling depth. The annual soil temperature variability at depth can be modeled using the equation:

$$T(z, t) = T_{avg} + \frac{A_0 \left| \sin\left(\omega t - \frac{z}{d}\right) \right|}{e^{z/d}} \quad (2)$$

where T_{avg} is equal to MAT, A_0 is the amplitude of annual surface temperature variation, z is depth in the soil, ω is the radial frequency ($2\pi/365$), and d is the damping depth (Hillel, 1980; Quade et al., 2013). At each site, different climate data inputs were used to create two different soil temperature models (Models A and B). For model A, T_{avg} was set to MAT, and A_0 was

calculated as the difference between the warmest and coldest average monthly temperatures. For model B, T_{avg} was set to mean monthly maximum temperature, and A_0 was calculated as the difference between the coldest average monthly temperature and the warmest maximum monthly temperature. The damping depth is defined for all sites as:

$$d = \sqrt{\frac{2\kappa}{C_v \omega}} \quad (3)$$

where κ is the thermal conductivity and C_v is the volumetric heat capacity of the soil. Because κ and C_v change as a function of soil texture (grain size distribution) and water content, we used values measured from soils of a similar texture and at the lowest water content assessed in order to calculate damping depths for each site (Table A.2; Shukla, 2014).

Soil water balance was calculated by comparing the monthly gains (precipitation) and losses (evapotranspiration and percolation below the B-horizon) of water in the soil (Arkley, 1963; Birkeland, 1974). The soil was considered as a single compartment, and the field capacity (maximum water holding capacity) of the soil was calculated based on textural characteristics of the soil series, similar to Tabor et al. (2013). To calculate if there was net storage during a particular month, the monthly ET_0 value was subtracted from the normal monthly precipitation total. There is net storage during a month if precipitation is greater than ET_0 , and conversely there is net loss or no accumulation of soil water if ET_0 is greater than precipitation. The total soil water is never allowed to rise above the field capacity of the soil. Also, because actual evapotranspiration is negligible during cold periods of the year due to frost, ET_0 was set to zero when the daily normal minimum temperature is lower than -4°C (Allen et al., 1998). For months that included days below this threshold, the monthly ET_0 value was multiplied by the fraction of days where daily normal minimum temperatures are above -4°C .

2.3. Geochemistry

Analytical methods for Δ_{47} analyses are described in detail in Defliese et al. (2015), but will be briefly outlined here. Carbonate nodules were microdrilled at low speed, and between 5 and 10 mg of drilled sample was reacted in anhydrous phosphoric acid at 75°C. The resulting CO₂ was purified off-line using cryogenic separation on a vacuum line and a Porapak-Q filled column held at -25°C. The Δ_{47} of the purified gas was then measured on a Thermo Scientific MAT 253 dual inlet stable isotope ratio mass spectrometer outfitted to collect masses 44–49 in the Stable Isotope Laboratory at the University of Michigan. At least three replicates were analyzed for each sample; data are summarized in Table 2.

In order to correct for scale compression and nonlinearity, reference gasses of varying bulk isotopic composition were analyzed after being heated to 1000°C in order to attain a stochastic distribution of isotopes among isotopologues (Huntington et al., 2009). CO₂ standards equilibrated with H₂O at 25°C and the Carrara Marble interlaboratory standard were also measured to allow normalization of Δ_{47} values to the absolute reference frame of Dennis et al. (2011). Long-term laboratory analyses of the Carrara Marble standard yield average values of 0.418‰ with a standard deviation of 0.020‰. An empirically derived acid fractionation correction of 0.067‰ was applied to Δ_{47} measurements to account for the digestion temperature of 75°C (Hren et al., 2013; Defliese et al., 2015).

Conventional carbonate stable isotope data ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) were simultaneously measured during Δ_{47} measurement. Empirically derived corrections of +0.36‰ and +0.10‰ were applied to raw $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, respectively, to account for temperature dependent–fractionation resulting from the transfer of samples through the Porapak-Q column held at -25°C (Petersen et al., 2016). Reference gasses were also passed through the Porapak-Q column held at -25°C, so a further correction to Δ_{47} values was not required. The $\delta^{18}\text{O}$ values were then

corrected using acid fractionation factor of 1.00830 for calcite reacted at 75°C (Swart et al., 1991). The corrected carbonate $\delta^{18}\text{O}$ value and the Δ_{47} temperature were used to calculate the $\delta^{18}\text{O}$ value of the precipitating soil water ($\delta^{18}\text{O}_{\text{sw}}$) using the fractionation factor of Friedman and O'Neil (1977).

$$1000 \ln \alpha_{\text{calcite-water}} = 2.78 \times 10^6 T^{-2} - 2.89 \quad (4)$$

3. RESULTS

Complete results of ET_0 and soil water balance calculations are presented in Table A.3. As an example, the soil temperature and water balance model results for two Soil Climate Analysis Network (SCAN) sites, *Eros* and *Adams Ranch*, are shown in Fig. 2 and Fig. 3. Modelled soil temperatures peak during mid to late July, and reach their nadir between mid-January and early February (Fig 2). Soil temperature model B consistently produces higher temperature results than model A, with the difference most pronounced at peak soil temperatures. Monthly precipitation is greater than ET_0 between October and April at the *Eros* station (Fig. 3B) and between December and February at the *Adams Ranch* station (Fig. 3E), causing water to accumulate in the soils. As ET_0 becomes greater than monthly precipitation, soil water storage declines until the soil effectively “dries out” during April at the *Adams Ranch* site (Fig. 3F). The soil water balance never reaches zero at the *Eros* site, instead sitting at approximately 2 cm between August and October (Fig. 3C). Soil water balance results for all of the sites are summarized in Fig. 4 by highlighting the months for which there is effectively no net soil water storage.

Complete clumped isotope geochemistry data are presented in Tables A.4 and A.5. Average Δ_{47} values for soil carbonate samples range from 0.756 to 0.705‰, with an average standard deviation for replicate analyses of 0.011‰ (Table 2). For all samples, the laboratory

long-term standard deviation of replicate standard analyses (0.020‰) exceeded that of replicate sample analyses (Petersen et al., 2016). Therefore the standard error was calculated for each sample using the long-term standard deviation of the Carrara marble divided by the square root of the number of replicates. Due to uncertainties based on discrepancies among carbonate temperature calibrations, Δ_{47} results are converted to temperatures using the multiple empirical calibrations in Table 2. To date, numerous carbonate clumped isotope temperature calibrations have been developed using a wide range of materials including synthetic calcite and aragonite (Ghosh et al., 2006; Dennis and Schrag, 2010; Zaarur et al., 2013; Grauel et al., 2013; Petrizzo et al., 2014; Wacker et al., 2014; Tang et al., 2014; Defliese et al., 2015), biogenic calcite and aragonite (Ghosh et al., 2006; Ghosh et al., 2007; Tripathi et al., 2010; Thiagarajan et al., 2011; Henkes et al., 2013; Eagle et al., 2013), and siderite (Fernandez et al., 2014). It has been observed that these calibrations can be grouped into two broad categories according to the temperature of the phosphoric acid during sample digestion, where studies that digest samples at temperatures $> 70^{\circ}\text{C}$ tend to produce shallower calibration slopes than those that react samples at 25°C (Fernandez et al., 2014). Exceptions to this observation include the Grauel et al. (2013) calibration, which produced a steep slope from samples reacted at 70°C , and the Petrizzo et al. (2014) calibration, which produced a shallow slope from samples reacted at 25°C . Samples in this study were digested in phosphoric acid held at 75°C , and analysis of synthetic calcite at the University of Michigan produces results within error of other $> 70^{\circ}\text{C}$ calibrations (Defliese et al., 2015). Due to the ongoing uncertainty involving carbonate temperature calibrations, this paper will focus on temperature results using a composite calibration that combines results from multiple studies that reacted samples in phosphoric acid $> 70^{\circ}\text{C}$, excluding siderite (Defliese et al., 2015).

Using the composite calibration, the measured Δ_{47} values correspond to a temperature range of 6 to 22°C. Carbonate nodules from two separate sampling pits were analyzed for the Plughat site. The calculated temperatures of $6 \pm 3^\circ\text{C}$ and $9 \pm 3^\circ\text{C}$ from the two Plughat pits are within error of each other. The final Plughat site temperature ($7 \pm 2^\circ\text{C}$) is determined by combining all of the data from both pits. The Clamo site from South Dakota produced the highest Δ_{47} temperature of $22 \pm 4^\circ\text{C}$, while the Montecito site in New Mexico produced the lowest temperature of $6 \pm 3^\circ\text{C}$.

Measured $\delta^{18}\text{O}$ values of soil carbonate ($\delta^{18}\text{O}_{\text{carb}}$) ranged between -10.5 and -5.3‰ VPDB, while $\delta^{13}\text{C}$ values ranged between -6.4 to -0.5‰ VPDB. The $\delta^{18}\text{O}_{\text{carb}}$ values are relatively well dispersed across the $\sim 5\%$ range, whereas the $\delta^{13}\text{C}$ values cluster in two separate groups. The carbonate from the Kranzburg, Clamo, and Cornville soils all had $\delta^{13}\text{C}$ values of 0.5–0.6‰, while the remaining seven soils had pedogenic carbonate with a $\delta^{13}\text{C}$ value $< -3.3\%$.

The $\delta^{18}\text{O}$ values for the precipitating soil waters ($\delta^{18}\text{O}_{\text{sw}}$) were calculated using the Δ_{47} temperatures and the calcite-water fractionation factor of Friedman and O’Neil (1977), and the calculations are summarized in Table A.6. Calculated $\delta^{18}\text{O}_{\text{sw}}$ values ranged between -3.9 and -11.2‰ VSMOW (Table 2). The two South Dakota sites had $\delta^{18}\text{O}_{\text{sw}}$ values of -3.9 and -6.6‰, whereas the remaining sites all had $\delta^{18}\text{O}_{\text{sw}}$ values below -8.7‰. The only exception was the Guvo soil from Arizona, which had a $\delta^{18}\text{O}_{\text{sw}}$ value of -5.3‰. Of note, the carbonate sampled from two separate soil pits at the Plughat site produced $\delta^{18}\text{O}_{\text{carb}}$ values that differed by 0.9‰. However, individually calculated $\delta^{18}\text{O}_{\text{sw}}$ values of -10.6 and -10.7‰ for each pit were well within error.

4. DISCUSSION

4.1 Data-model comparison

Given that long-term instrumental soil records are unavailable near our study sites, the effectiveness of the soil temperature and moisture models can be assessed using instrumental data for the *Eros* and *Adams Ranch* SCAN stations. Soil temperature and moisture data is available at the *Eros* station since 2003, while the same data is available for the *Adams Ranch* station since 1997 (NRCS, 2016). The *Eros* station is located relatively close to the Kranzburg site (~80 km) and experiences similar temperatures throughout the year, yet it receives nearly 9 cm more annual precipitation. The *Adams Ranch* station is located ~100 km SE of the Witt site, while sitting ~200 m lower in elevation and receiving about 7 cm more annual precipitation.

In Fig. 2, the soil temperature model results at depths of 20 and 51 are compared to instrumental data from both SCAN sites. Model A compares favorably with the observed average soil temperature record between March and October at the *Eros* station, but it underpredicts temperatures between November and February. This discrepancy likely arises because the temperature model does not take into account the effects of freezing and snowpack insulation under extremely cold air temperatures. Poor model performance during very cold points during the year will not affect the overall conclusions of this study, as snowpack and freezing is primarily an issue at the two South Dakota sites and carbonate formation is extremely unlikely at these temperatures. At the *Adams Ranch* station, model B compares favorably with the average observed soil temperature between February and June. The better performance of model B is likely a result of reduced vegetative cover as compared to the South Dakota sites, which would allow for greater ground heating. Taken together, the temperature data from the SCAN sites suggests that model A produces a more accurate picture of annual soil temperature variation for the South Dakota grassland sites, while model B is likely more valid at the remaining semi-arid to arid sites during late winter to early summer. Some uncertainty remains, but at the very least,

the two models together form a range of likely soil temperatures for the majority of the year under a variety of precipitation regimes. More importantly for the purposes of this study, the temperature model performance is best during the times of the year that the soil water balance models indicate soils are likely drying out.

Soil moisture data from the SCAN sites is compared to evapotranspiration and soil water balance results in Fig. 3. Observed soil moisture data is calculated by relating the soil dielectric permittivity to soil-water content using a general multi-soil ‘loam’ calibration equation (Seyfried et al., 2005). The soil water balance results should also not be taken at face value to mean that the soil moisture is completely depleted, but rather the soil effectively begins to dry out. Plants are generally unable to deplete soil water completely, because the adhesive forces to soil particles increase relative to matric water potential forces when soil water content falls. The annual trend of precipitation–ET₀ results compare favorably to the trend in observed soil moisture, especially at 20 cm where the soil moisture will be more readily affected by changes in evapotranspiration. The main discrepancy occurs during the winter at the *Eros* station at 20 cm depth (shaded regions in Fig. 3A), which can be explained by freezing soil temperatures during the winter months (Fig. 2A). The soil water balance compare more favorably with the 51 cm soil moisture results. Data from the *Eros* station shows that it is not until late summer-early fall that soil moisture reaches its growing season minimum, whereas April marks the inflection point at the *Adams Ranch* station. Generally the *Eros* soil is much wetter than the *Adams Ranch*, which may imply that it is only during drought years that the soil effectively dries out

4.2 Timing of pedogenic carbonate formation

The majority of published clumped isotope measurements on modern pedogenic carbonate have produced formation temperatures that tend to fall between warmest monthly

temperature and MAT (e.g. Passey et al., 2010; Quade et al., 2013; Hough et al., 2014). However, soils examined as part of this study tend to be substantially colder than these earlier studies, with all but three of the Δ_{47} temperatures falling at or below MAT (Fig. 5). The long formation time of pedogenic carbonate complicates comparisons to short-term instrumental records of climate and soil conditions. While the concern surrounding short term anomalous weather events (e.g. droughts) is reduced by use of 30 year normal climate data to model typical soil conditions, uncertainty persists regarding regional climate change that occurred while the carbonate nodules formed (2–6 kyrs using the transfer function of Retallack, 2005). Proxy-based climate reconstructions and model simulations indicate that between the Mid-Holocene (~6000 cal years BP) and the preindustrial period (AD ~1700) the North American continental interior generally became more humid and summer temperatures declined slightly (0.5–2°C), while the monsoon-affected North American southwest became drier (Wanner et al., 2008). A small decrease in temperature over this timeframe would serve to increase the extent to which Δ_{47} derived temperatures in the present study fall below MAT. Greater uncertainty surrounds seasonal hydrologic patterns throughout this period, but in the absence of more detailed paleoclimate data we assume that patterns similar to modern were predominant.

It is important to note that choice of clumped isotope temperature calibration can drastically affect the calculated temperatures, especially for the range of Δ_{47} values measured as part of this study. For example, use of the Ghosh (2006a) calibration would result in temperatures at or above MAT for all of our sites (Table 2) and fall more in line with previous studies of pedogenic carbonate that observed Δ_{47} -derived reflecting a warm-season bias (Passey et al. 2010; Quade et al. 2013; Hough et al. 2014). However, the Ghosh (2006a) calibration is not thought to be the appropriate choice for our study, based on the analytical methods used in the

University of Michigan Stable Isotope Laboratory and the current understanding of calibration issues related to clumped isotopes (Defliese et al., 2015).

Uncertainties about calibration choice do not confound earlier work that observed a warm-season bias primarily using the Ghosh et al. (2006a) calibration. For example, if reaction temperature is indeed the primary control underlying the calibration discrepancies (Fernandez et al., 2014; Defliese et al., 2015), use of the Ghosh et al. (2006a) calibration was appropriate in the study of Quade et al. (2013), as their samples were reacted at 25°C. In contrast, samples from Hough et al. (2014) study were reacted at 90°C, and most of the calculated temperatures are reduced (average reduction = 6°C) using the composite calibration of Defliese et al. (2015) rather than the Ghosh et al. (2006a) calibration. However, the recalculated temperatures for all but one site still fall above the range of MAT values included in their study. Therefore, while calibration uncertainties do not contradict the documented warm-season bias for some sites, the colder nature of the results presented herein do underscore that a warm-season temperature bias cannot be presumed for pedogenic carbonate in all settings.

As would be expected from the cold nature of the temperature results in this study, only a few of the soils can be explained using the depth-based ground heating model of Quade et al. (2013). Relatively cold pedogenic carbonate formation temperatures are expected to be less common, in part because calcite tends to be more soluble under colder temperatures (Breecker et al. 2009). However, clumped isotope derived temperatures that fall closer to MAT may occur in some settings due to the mediating effect of precipitation on the timing of pedogenic carbonate formation (Peters et al., 2013). As discussed by Breecker et al. (2009), pedogenic carbonate formation can be driven not only by an increase in temperature, but also by a decline in soil $p\text{CO}_2$ or increased Ca^{2+} activity in the soil solution, both of which are tied to precipitation and

soil water. Soil $p\text{CO}_2$ at depth is primarily sourced from soil respiration, which is a combination of respiration by roots, microbial decomposition of soil organic matter, and respiration by other fauna in the soil (Luo and Zhou, 2006). In arid and semi-arid environments, overall productivity is controlled by the availability of water (Noy-Meir, 1973). Small pulses of water to these ecosystems trigger microbial respiration primarily near the soil surface, and it is not until a larger threshold of water is provided to the soil system that vascular plant productivity will increase, thereby increasing plant water uptake and root respiration and driving a build-up of soil $p\text{CO}_2$ at depth (Huxman et al., 2004). Then, as the soil begins to dry out, soil $p\text{CO}_2$ will fall as productivity and microbial respiration of soil organic matter slows (Liu et al., 2002).

The activity and availability of Ca^{2+} is also tied to precipitation in arid and semi-arid environments. Due to the lack of moisture and biological activity, chemical weathering tends to proceed at a much slower rate under arid and semi-arid climate regimes (Knight, 1991; Cotton et al., 2013), thereby limiting the in-situ supply of Ca^{2+} ions to the soil solution. It has long been suggested that dust sourced Ca^{2+} is important under these climate regimes (e.g. Gile et al., 1966; Machette, 1985). In arid settings, as much as 98% of the Ca^{2+} in the soil can be attributed to dust deposition rather than weathering of bedrock derived silicate minerals (Capo and Chadwick, 1999). If the majority of Ca^{2+} is delivered to the surface during dry months, precipitation is required to translocate dust sourced Ca^{2+} into the soil profile to the depth of carbonate formation. Subsequently, as the soil dries out, the activity of Ca^{2+} will increase, promoting the formation of pedogenic carbonate (Breecker et al., 2009). Therefore, a thorough evaluation of annual fluctuations in precipitation and soil water content is necessary to assess the annual timing and formation temperature of pedogenic carbonate.

4.2.1. Soil water control

As discussed above, the timing of annual precipitation can influence the timing of pedogenic carbonate formation through its effect on Ca^{2+} and soil $p\text{CO}_2$. In addition to monthly precipitation totals, soil water storage and fluctuations in evapotranspiration need to be considered when assessing the timing of soil moisture depletion. For example, antecedent water that accumulates at cooler times of the year (e.g. winter) can be an important source of water to sustain productivity even when monthly precipitation levels are low (Reynolds et al., 2004). The soil water balance can be driven to zero either by a sizeable decrease in precipitation, or by sustained high evapotranspiration.

Water inputs into the soil are limited under arid climate regimes. Therefore, soil water will likely be exhausted soon after a sizable drop in precipitation. The two California soils, Muroc and Lavic, demonstrate this scenario, as they are the driest sites examined in this study. Both of these sites receive the bulk of their precipitation during the winter months, before experiencing a sharp drop in rainfall during April (Fig. 6). Yet these soils are likely drying out ahead of the decline in precipitation due to evapotranspiration losses, with water balance results indicating that the Lavic soil begins to dry out during February and the Muroc soil begins to dry out in March. Clumped isotope temperatures within error of the modeled soil temperature support formation of pedogenic carbonate at these sites during February and March, respectively (Fig 6).

Although the three Arizona soils receive more precipitation on an annual basis than the California soils, the three Arizona soils experience a severe drop in precipitation beginning in April that is driven by the monsoonal climate regime (Fig. 6). Soil water balance results indicate that the Cross-Apache and Cornville sites dry out in April, coincident with the decline in rainfall, whereas the hotter Guvo site dries out a month earlier. The clumped isotope temperatures agree

with the modeled soil temperatures during April and March for the Cornville and the Guvo sites, respectively (Fig 6). This agreement further supports the idea that the timing of carbonate formation is biased by a sharp decline in precipitation that coincides with the annual rise in soil temperature and evapotranspiration. However, the third Arizona soil, Cross-Apache, does not follow this explanation as clearly. The clumped isotope temperature from the Cross-Apache site would better agree with the modelled soil temperatures if the soil water balance predicted that the soil began to dry out a month earlier (March). A possible explanation for this discrepancy is the abundance of coarse fragments in the Cross-Apache soil, with the soil series containing up to 35 percent pebbles and cobbles. Coarse fragments were not accounted for when calculating maximum water holding capacity for each soil, and abundant coarse fragments will likely facilitate flow through and reduce the soil's ability to retain water during the cool winter months. Therefore, it is likely that the Cross-Apache soil dries out earlier than the soil water balance model would suggest.

Unlike the California and Arizona soils, the remaining soils analyzed in this study all lack an excessively dry period during the spring/early-summer. At these sites, the driest months are during the winter when temperatures drop below freezing, inhibiting productivity and likely carbonate formation as well. Soil water balance results for Plughat, Montecito, and Witt indicate that these sites all dry out in April (Fig. 6). The clumped isotope temperatures from all of these sites fall generally agree with the modelled soil temperature range for April. The clumped isotope temperature window for both of the South Dakota soils is distinct from the other sites examined in this study, as it sits at or near the maximum modeled soil temperature at Bk horizon depth. These two sites also receive the most precipitation and experience the widest annual temperature variation (Fig. 6). The soil temperatures peak during July and August, which, for the

Clamo soil at least, suggests mid-summer carbonate formation. At first, it may seem counterintuitive that soil carbonate forms when there is still 6 to 8 cm of monthly precipitation on average; however, according to the soil water balance results this is precisely the time when water storage at this site is exhausted (Fig. 4). At the Kranzburg site, the clumped isotope window overlaps during both late spring and early autumn. Carbonate formation during late August and September is considered more likely due to lower precipitation totals and because a sizeable increase in soil water balance does not occur until October (Fig. 4).

It is important to note that there is a level of uncertainty in the evapotranspiration derived from soil water estimates, attributable to necessary model assumptions. First, ET_0 is distinct from ‘real’ evapotranspiration because it represents the theoretical evapotranspiration from a uniform grass cover assuming peak growth conditions (Lhomme, 1997). When applied to agricultural crops, calculated Penman-Monteith ET_0 values are subsequently modified by a crop coefficient depending on the particular species. Adequate data necessary to create a more precise estimate of evapotranspiration were unavailable for vegetation at sites examined in this study. Therefore, the monthly ET_0 values should be considered as an upper limit of actual evapotranspiration (Lhomme, 1997). The use of monthly precipitation totals as soil infiltration totals should also be considered a maximum value, because some fraction may be lost to runoff or interception by vegetation (Huxman et al., 2004). Despite these necessary assumptions, the calculated soil water estimates allow for a detailed evaluation of soil water limitation and help explain variations in Δ_{47} -derived temperatures.

Pedogenic carbonate, which typically forms on timescales of hundreds to thousands of years, can preserve an integrated signal of past environmental conditions. Its integrative nature depends on, in part, if overprinting (precipitation of younger crystal overgrowths) or

recrystallization is the dominant process in the soil (Deutz et al., 2002). It should also be noted that pedogenic carbonate does not necessarily form every year or always during a certain month, potentially forming during shorter-term, anomalous events that deviate from normal patterns, such as droughts (Breecker et al. 2009; Hough et al., 2014). These factors may contribute to some of the uncertainty in the clumped isotope derived temperatures. However, the general agreement between the Δ_{47} -temperatures and the model results suggests that normal climate factors were the primary control on carbonate formation at our sites. As with other paleosol-based paleoclimate proxies, the integrative nature of paleosol Δ_{47} values can be seen as an advantage because the influence of short-lived climatic events are reduced to some degree and do not dominate the signal (Sheldon and Tabor, 2009).

4.2.2. *Vegetation and excessive ground heating*

Additional factors, including vegetation composition and excessive ground heating can affect the annual timing of pedogenic carbonate formation. When other environmental variables are equal, model results suggest that soils under C₃ vegetation may dry out earlier in the year than soils under C₄ vegetation (Meyer et al., 2014). While we do not possess comprehensive vegetation data for all of the sites examined in this study, the sites range from predominantly C₃ to a mixture of C₃ and C₄ plants based on the bulk $\delta^{13}\text{C}_{\text{org}}$ from the soil surface and A horizons. The fact that most of the sites described herein dry out early in the year lends some credence to their findings. However, recent work from Central Argentina did not identify evidence for different seasons of carbonate formation between predominantly C₃ and mixed (C₃/C₄) vegetation sites (Ringham et al., 2016).

Excess ground heating has been shown to affect the Δ_{47} values of pedogenic carbonate forming in both the southwestern United States and the vegetation-poor Tibetan Plateau (Quade

et al., 2013); however, the generally colder nature of the Δ_{47} temperatures suggests that excess ground heating is not as significant of a factor in sites described herein. The reduced impact of excessive ground heating could be because the sites with the least amount of vegetative cover tend to become water limited at an early point in the year when total radiation values are still relatively low. The South Dakota soils do not dry out until the middle of the year; however, these sites also have the thickest vegetative cover, potentially limiting ground heating.

4.3. Δ_{47} temperature and the $\delta^{18}\text{O}$ of precipitation

Another product of measuring the Δ_{47} values of pedogenic carbonate is that the calculated formation temperature can be used along with the measured $\delta^{18}\text{O}_{\text{carb}}$ to calculate the isotopic composition of the soil water ($\delta^{18}\text{O}_{\text{sw}}$) at the time of formation (Ghosh et al., 2006b; Quade et al., 2007; Hough et al. 2014). Relating $\delta^{18}\text{O}_{\text{sw}}$ to the $\delta^{18}\text{O}$ of precipitation ($\delta^{18}\text{O}_{\text{precip}}$) is complicated by sizable seasonal variation in $\delta^{18}\text{O}_{\text{precip}}$. According to the Online Isotopes in Precipitation Calculator (OIPC), which interpolates a global dataset of precipitation stable isotope data, seasonal $\delta^{18}\text{O}_{\text{precip}}$ variability at these sites can be as much as 13.8‰ (Bowen and Revenaugh, 2003; Bowen, 2014). As meteoric water moves through a soil, it can mix with soil water held near the surface that has been evaporatively enriched in ^{18}O ; but, it can also move relatively rapidly to depth with less mixing due to the existence of coarse fragments or macropores (Mathieu and Bariac, 1996).

Calculating $\delta^{18}\text{O}_{\text{sw}}$ offers an opportunity to assess changes in hydrology, even when local environmental factors (e.g. vegetative shading) can cause soil temperature variations. As the results from the separate pits at the Plughat site suggest (Table 2), $\delta^{18}\text{O}_{\text{sw}}$ can be faithfully recorded even if there are local variations in soil carbonate formation temperature. However, it remains unclear whether $\delta^{18}\text{O}_{\text{sw}}$ values record an integrated signal of precipitation received year-

round, or if they are biased towards certain seasonal contributions. To assess this point, $\delta^{18}\text{O}_{\text{sw}}$ values can be compared to OIPC sourced monthly $\delta^{18}\text{O}_{\text{precip}}$ values. The calculated $\delta^{18}\text{O}_{\text{sw}}$ values are plotted against a weighted average of monthly $\delta^{18}\text{O}_{\text{precip}}$ values in Fig. 7, where each monthly OIPC $\delta^{18}\text{O}$ value was weighted according to the fraction of total precipitation received during that month. The three precipitation scenarios plotted in Fig. 7 exhibit the best agreement with the calculated $\delta^{18}\text{O}_{\text{sw}}$ values. Fig. 7A includes all precipitation received year-round, Fig. 7B considers only the first month without soil water storage, and Fig. 7C plots a weighted average of the three wettest months. A number of additional scenarios were explored (e.g. driest month, months when $P > ET_0$, etc.) and are shown in Fig. A.1. To assess how well the data compare to the 1:1 line, a modified standard error was calculated for Fig. 7, using the 1:1 line instead of a best-fit regression line.

In addition to complications introduced by seasonal variations in $\delta^{18}\text{O}_{\text{precip}}$, the isotopic composition of soil water can deviate significantly from meteoric water, becoming higher with evaporative loss before the water percolates deeper into the soil, especially in finer-textured soils (Cerling and Quade, 1993). It is important to note that scenarios where $\delta^{18}\text{O}_{\text{sw}} > \delta^{18}\text{O}_{\text{precip}}$ are much easier to explain (via evaporative loss) than scenarios where $\delta^{18}\text{O}_{\text{sw}} < \delta^{18}\text{O}_{\text{precip}}$. Two sites, Witt and Clamo, consistently appear excessively ^{18}O -enriched, as compared to the remaining sites (Fig. 7). The Witt and Clamo soil series are unique amongst our sites in that they are described as having a moderately-slow to slow permeability. Slow permeability in these two soils would explain the observed ^{18}O -enrichment as precipitation will percolate slowly into the soil, thereby increasing the time available for evaporative loss near the soil surface.

Of the many scenarios examined, annually integrated $\delta^{18}\text{O}_{\text{precip}}$ values produce one of the better relationships with calculated $\delta^{18}\text{O}_{\text{sw}}$ values, with a S.E. of 2.7‰ (Fig. 7A). However

stronger relationships are observed when only the first month with no soil water storage (Fig. 7B; S.E = 2.1‰) or the three wettest months are considered (Fig. 7C; S.E = 1.8‰). Although the latter scenario has a slightly smaller S.E., a number of the $\delta^{18}\text{O}_{\text{sw}}$ values are more negative than $\delta^{18}\text{O}_{\text{precip}}$, which is difficult to explain. In contrast, all of the $\delta^{18}\text{O}_{\text{sw}}$ values exceed $\delta^{18}\text{O}_{\text{precip}}$ when only precipitation from the month where the soil water balance is considered, with the one exception being the Muroc site (although it is within error of the 1:1 line). Furthermore, a linear regression through the data that excludes the strongly ^{18}O -enriched Clamo and Witt sites has a slope subparallel to the 1:1 line with a fairly strong coefficient of determination ($r^2 = 0.78$). These results suggest that the $\delta^{18}\text{O}_{\text{carb}}$ value of pedogenic carbonate will most directly reflect the $\delta^{18}\text{O}$ composition of seasonal precipitation falling close to the time of carbonate formation

It is important to note that mixing of soil water under seasonally variable precipitation regimes is a complex process. For example, it has been shown in wet environments characterized by strong seasonal variation in precipitation that tightly bound water can remain isolated in small pores and not mix with subsequent precipitation (Brooks et al., 2010). However in water-limited environments, our results suggest that soil water is less likely to remain unutilized in sizeable quantities across seasons. Although the soils likely do not dry out completely, the water content remains low enough that the $\delta^{18}\text{O}_{\text{sw}}$ value will be set by recent precipitation. Soil hydrology can be further complicated by overlying vegetation. Variations in rooting depths suggest that woody and herbaceous plants may rely on water uptake from different soil depths in drier environments, and individual plants have been shown to access pools of water at varying depths during different seasons (Dawson and Pate, 1996; Schenk and Jackson, 2002). Variation in vegetation between the sites as well as fluctuations in soil pH may explain some of the variability observed in the calculated $\delta^{18}\text{O}_{\text{sw}}$ data.

Considering all of the complicating factors, it is encouraging that such a strong relationship exists between the calculated $\delta^{18}\text{O}_{\text{sw}}$ values and the $\delta^{18}\text{O}$ of precipitation that falls during the modeled month of soil water depletion. This overall agreement lends further support to the effectiveness of the soil water balance model results and the conclusion that seasonal fluctuations in soil water balance are controlling the timing of carbonate formation. Additional detailed studies are required from a wider array of sites (across a range of moisture regimes) to examine thoroughly the integration of $\delta^{18}\text{O}_{\text{sw}}$ and $\delta^{18}\text{O}_{\text{precip}}$ during pedogenic carbonate formation. Caution should be taken when interpreting changes in $\delta^{18}\text{O}_{\text{carb}}$ values for they may be reflective of shifts in local hydrology rather than temperature.

4.4. Implications for clumped isotope studies of paleosol carbonates and future directions

It is evident that annual fluctuations in soil water content can control the annual timing of pedogenic carbonate formation. As outlined above, variations in precipitation, evapotranspiration and antecedent water storage control soil water content, and in turn, the timing of pedogenic carbonate formation. Therefore, when interpreting clumped isotope temperature results from a stacked sequence of paleosols, it should be considered whether recorded temperature variations are driven primarily by change in air temperature or a shift in soil hydrology, which may be independent of climate. However, these variables are difficult to constrain directly when evaluating clumped isotope results of paleosol carbonate. An in-depth characterization of paleosols can help to elucidate the primary driver of changes in a particular paleosol clumped isotope record. For example, changes in paleosol texture (grain size) throughout a sequence should be evaluated, as this will partially control water storage outside of the growing season. Reconstructions of paleovegetation from phytolith assemblages, organic matter $\delta^{13}\text{C}$, or pedogenic carbonate $\delta^{13}\text{C}$ are important, as different plant phenotypes will have different water-

uptake strategies and provide variable amounts of shade (e.g. Cerling, 1984; Strömberg and McInerney, 2011). Paleosol climate proxies that reconstruct MAT and MAP independent of pedogenic carbonate can also be used to suggest if a change in air temperature or precipitation regime is more likely (e.g. Sheldon et al., 2002; Sheldon and Tabor, 2009; Nordt and Driese, 2010; Hyland et al., 2015).

Further work is needed on modern pedogenic carbonates, specifically to consider the effects of soil texture and vegetation. Most clumped isotope studies of modern soils have focused on sandy soils or those with coarse clasts capable of developing carbonate undercoatings. However, the majority of paleosols used for paleoclimatic reconstructions tend to be more developed, with nodular carbonate that represents both longer formation times and potentially different modes of carbonate formation. Most of the soils examined as part of this study were fine-grained and capable of storing sizable volumes of antecedent water, and future work should directly assess the different soil textures under similar climate regimes. The predominantly cooler-nature of our Δ_{47} results may be, in part, attributable to differences in how pedogenic carbonate nodules versus clast undercoatings form over time. Soils examined herein all included nodular horizons that may preserve a longer, more time integrative climate signal of regular seasonal patterns than previous studies that focus on carbonate undercoatings. Importantly, the majority of pedogenic carbonates preserved in the geologic record and those used in paleo-reconstructions are well-formed nodules rather than undercoatings. Thus, the new results herein may reflect a better interpretive structure for understanding Δ_{47} results going forward. The effect different vegetation phenotypes have on pedogenic carbonate formation temperatures still needs to be tested directly. For example, C_3 and C_4 plant productivity can be favored at different

points during the year, which may, in turn, affect the seasonality of pedogenic carbonate formation (Ode, et al., 1980; Meyer, et al. 2014).

Considering soil hydrology when discussing clumped isotope results of pedogenic carbonate is especially relevant to paleoelevation studies, because regional uplift can drive changes in regional climate that affect paleoelevation proxies (Ehlers and Poulsen, 2009; Fiorella et al., 2015). As noted above, Δ_{47} temperatures of pedogenic carbonate were notably affected along an elevation transect in the Andes where the seasonality of rainfall varies as a function of elevation. We agree with findings of Peters et al (2013) that the annual timing of precipitation needs to be considered, because it is the primary input of water into a soil. We also stress that other factors should also be considered including other climatic variables that affect evapotranspiration (e.g. temperature variability and humidity), soil texture, and plant water uptake strategies. The fine-grained nature of most of the soils examined herein highlights the importance of considering soil water storage, because it could allow carbonate formation to lag well-behind precipitation events.

5. Conclusions

Our results provide additional credence to the observation that carbonate sourced from modern soils is not always biased towards warm-season temperatures. Clumped isotope temperatures that fall at or below MAT may be less of an exception than published results of modern pedogenic carbonate have documented. When considering clumped isotope derived temperatures of carbonate preserved in paleosols, it is necessary to consider that reconstructed changes in temperature may be indicative of changes in hydrology and vegetation rather than exclusively changes in air temperature.

Clumped isotope temperature variability in modern pedogenic carbonate can be explained by considering a monthly soil water model that accounts for precipitation, evapotranspiration, and soil water storage. Results from this study agree with previous research that suggested the timing of annual precipitation can bias the timing and temperature of pedogenic carbonate formation. The effects of water loss via plant water uptake need to be considered in order to explain all of the sites examined in this study, especially those that lack an excessively dry period during the spring or summer (e.g. the South Dakota sites).

Systematic differences in Δ_{47} results between different soil taxonomic orders were not observed, as it appears that precipitation, evapotranspiration, and antecedent soil water storage are primary controls on the timing of pedogenic carbonate formation. Whereas most previously published clumped isotope studies demonstrated a warm season bias in pedogenic carbonate, the majority of our sites fall at or slightly below MAT. Only the two South Dakota soils that developed under a continental climate were biased well above MAT. The seasonal timing of soil water depletion explains the differences in formation temperatures recorded at our sites. Additionally, the Δ_{47} derived $\delta^{18}\text{O}_{\text{sw}}$ results suggest that the $\delta^{18}\text{O}$ value of the pedogenic carbonate will be seasonally biased towards seasonal precipitation $\delta^{18}\text{O}$ values when soil water content is depleted. Future research should investigate the possibility that differences exist in seasonal formation patterns of pedogenic nodules and clast undercoatings, and therefore the environmental data they record. This point is particularly important because most studies of the geologic record rely on nodular carbonate (as examined herein), rather than undercoatings, which have been the focus of most modern clumped isotope calibration studies. The remaining uncertainty does not preclude the use of this approach on paleosol carbonates in order to assess

664 relative changes in local hydrology, but caution must be taken when interpreting the results in
665 light of climatic or tectonic changes.

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673

674 **Figure Captions**

675 Fig. 1. Map showing sample localities for pedogenic carbonate nodules analyzed in this study
676 along with a 4 km gridded mean annual precipitation (MAP) dataset interpolated from 1981–
677 2010 climate normals (Prism Climate Group, 2015). Soil orders sampled include Mollisols
678 (circles), Alfisols (triangles), and Aridisols (squares). Soil Climate Analysis Network (SCAN)
679 sites used for data-model comparisons are shown as stars.

680

681 Fig. 2. Observed and modeled temperatures for the *Eros* and *Adams Ranch* SCAN sites at soil
682 depths of 20 cm (A and C) and 51 cm (B and D). Temperature data was available and compiled
683 between the years 2003–2015 for the *Eros* station and 1997–2015 for the *Adams Ranch* station
684 (NRCS, 2016). The grey window highlights the absolute range of observed temperatures, while
685 the solid gray line shows the mean temperature during the observation period. Daily soil
686 temperatures were recorded at midnight each night. Model A (dotted line) uses the monthly
687 mean, minimum and maximum 1981–2010 monthly normal average temperatures. Model B uses
688 the minimum monthly normal average temperature and the mean and maximum normal
689 maximum average temperatures.

690

691 Fig. 3. Observed soil moisture data and water balance model results for the *Eros* and *Adams*
692 *Ranch* SCAN sites. Soil moisture data was available and compiled between the years 2003–2015
693 for the *Eros* station (A) and 1997–2015 for the *Adams Ranch* station (D; NRCS, 2016). Solid
694 lines represent the mean daily soil moisture averaged over the observation period, while the
695 symbols represent average monthly soil moisture content. The area shaded gray for the *Eros*

station highlight winter months when soil temperature is below freezing. The difference between normal monthly precipitation and modelled reference evapotranspiration (ET_0) is plotted below (B and E) as well as the modeled soil water storage for each site (C and F).

Fig. 4. Summary of soil water balance calculations for all sites. Months with a positive water balance are shown by the black bar for each site. Months highlighted by a gray bar represent months when the net water balance is less than $0.5 \text{ cm month}^{-1}$.

Fig. 5. Average clumped isotope derived temperatures of pedogenic carbonate formation plotted against mean annual air temperature for each site. The broadly-defined climate regime is indicated by the symbols. The two California sites (triangles) are the driest sites examined in this study (MAP 10-20 cm). The three Arizona sites (diamonds) receive 25–40 cm of annual rainfall, with an exceptionally dry period between April and June. The New Mexico and Colorado sites (squares) receive between 30 and 40 cm of annual rainfall. The South Dakota sites (circles) are the wettest, with MAP in excess of 50 cm. Error bars display a ± 1 S.E. window.

Fig. 6. Plots for each site showing monthly precipitation totals and mean annual temperature values taken from the 1981–2010 climate normals. Annual variation in soil temperature was modeled for the depth at which the pedogenic carbonate was sampled. Model A (dotted line) uses the monthly mean, minimum and maximum 1981–2010 monthly normal average temperatures. Model B uses the minimum monthly normal average temperature and the mean and maximum normal maximum temperatures. The Δ_{47} derived temperature is shown as a

dashed horizontal line with solid lines highlighting a ± 1 S.E. window. The light gray vertical bar highlights the first month when soil water storage equal 0.

Fig. 7. Calculated $\delta^{18}\text{O}$ values of the soil water ($\delta^{18}\text{O}_{\text{sw}}$) at the time of pedogenic carbonate formation plotted against OIPC-derived $\delta^{18}\text{O}$ values of precipitation ($\delta^{18}\text{O}_{\text{precip}}$). Fig. 7A plots a weighted average of OIPC values from all months. Fig. 7B includes only the precipitation that falls during the first month where the soil water storage model goes to 0. Fig 7C plots the weighted average of the three wettest months. For Figs. 7A and 7C the monthly $\delta^{18}\text{O}_{\text{precip}}$ were weighted according to the fraction of annual precipitation received that month. A modified standard error (S.E.) is calculated based on deviation from the 1:1 line considering all 10 sites. The two sites (Clamo and Witt) that are consistently the most ^{18}O -enriched relative to the 1:1 line are shown as white symbols, and a separate standard error (*S.E.) is shown considering only the 8 remaining sites. Also plotted as a solid black line, is a linear regression that excludes the Clamo and Witt sites along with its slope (m) and coefficient of determination (r^2).

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Figure 1

Figure 1

Figure 2

Figure 2.

Figure 3

Figure 3.

Figure 4

Figure 4.

Figure 5

Figure 5.

Figure 6

Figure 6.

Arid - Winter Precipitation (MAP 10-20 cm), California

Semi-Arid Monsoonal (MAP 25-40 cm), Arizona

Semi-Arid (MAP 30-40 cm), New Mexico and Colorado

Continental (MAP > 50 cm), South Dakota

Figure 7

Figure 7

Table 1
Site Information

Site/Soil	Location		Elevation (m)	Soil Order	Nodule Depth (cm)	MAT (°C)	MAP (cm)
	N (°)	W (°)					
<i>Arid – Winter Precipitation (MAP 10-20 cm)</i>							
Muroc	34.918	-118.152	781	Aridisol	21	17.0	16.9
Lavic	34.604	-117.454	859	Aridisol	25	15.8	14.0
<i>Semi-Arid Monsoonal (MAP 20-40 cm)</i>							
Guvo	32.752	-111.962	481	Aridisol	30	21.6	25.0
Cross-Apache	35.331	-112.805	1646	Mollisol	33	12.7	32.5
Cornville	34.603	-111.854	962	Aridisol	35	16.8	36.4
<i>Semi-Arid (MAP 30-50 cm)</i>							
Plughat	37.023	-103.908	1856	Alfisol	60	10.4	45.8
Montecito	36.392	-105.903	2261	Alfisol	35	8.9	32.4
Witt	34.649	-106.343	2097	Aridisol	70	10.6	38.2
<i>Continental (MAP > 50 cm)</i>							
Kranzburg	44.428	-96.784	521	Mollisol	40	6.2	61.7
Clamo	43.834	-97.993	394	Mollisol	40	8.5	54.7

Table 2
Geochemical results from pedogenic carbonate.

Site/Soil	n ^a	$\delta^{13}\text{C}$ (‰) VPDB	$\delta^{18}\text{O}_{\text{carb}}$ (‰) VPDB	Δ_{47} (‰) ARF ^b	StDev (‰) ^c	± 1 S.E (‰) ^d	Δ_{47} Temp. (°C) 'Ghosh' ^e	Temp (°C) 'Dennis' ^f	Temp (°C) 'Composite' ^g	± 1 S.E (°C) ^h	$\delta^{18}\text{O}_{\text{sw}}$ (‰) VSMOW ⁱ
Muroc	3	-5.6	-9.3	0.736	0.013	0.012	20	12	12	4	-10.3
Lavic	3	-3.4	-10.4	0.726	0.015	0.012	22	16	15	4	-10.6
Guvo	3	-3.7	-5.4	0.721	0.010	0.012	23	17	16	4	-5.3
Cross-Apache	3	-6.5	-8.5	0.752	0.009	0.012	17	7	7	3	-10.6
Cornville	3	-0.6	-9.9	0.709	0.008	0.012	25	22	21	4	-8.7
Plughat ^j				0.751	0.013	0.008	17	8	7	2	
<i>Pit 1</i>	3	-6.4	-8.2	0.756	0.014	0.012	16	6	6	3	-10.6
<i>Pit 2</i>	3	-6.5	-9.1	0.745	0.012	0.012	18	9	9	3	-10.7
Montecito	3	-4.5	-8.8	0.755	0.009	0.012	16	6	6	3	-11.2
Witt	3	-5.0	-6.6	0.745	0.008	0.012	18	10	9	3	-8.2
Kranzburg	3	-0.7	-6.0	0.732	0.008	0.012	21	14	13	4	-6.6
Clamo	3	-0.6	-5.2	0.705	0.009	0.012	26	23	22	4	-3.9

^aNumber of replicate analyses

^b Δ_{47} values normalized to the Absolute Reference Frame of Dennis, et al. (2011)

^cStandard deviation of replicate analyses

^dStandard error calculated using the long-term σ of standards (0.020‰) divided by the square root of n

^eTemperature calibration of Ghosh, et al. (2006a), modified for use in the absolute reference frame by Dennis et al. (2011)

^fTemperature calibration of Dennis and Schrag (2010), modified for use in the absolute reference frame by Dennis et al. (2011)

^gComposite calibration of studies which analyzed samples at >70°C, excluding siderite (Defliese et al. 2015)

^hStandard error of calculated temperatures using the 'Composite' calibration

ⁱCalculated $\delta^{18}\text{O}$ of soil water using the $\delta^{18}\text{O}_{\text{carb}}$ value and the temperature from the composite calibration

^jAverage values calculated by combining data from both Plughat soil pits