# Seasonal bias in the formation and stable isotopic composition of pedogenic carbonate in modern soils from central New Mexico, USA

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## ABSTRACT

In order to better calibrate pedogenic carbonate as a proxy for past environments, we compared the stable isotopic composition of soil $CO_2$, soil water, and pedogenic carbonate in young soils from central New Mexico, USA. Seasonal changes in the $\delta^{13}C$ value of soil $CO_2$, the $\delta^{18}O$ value of soil water, and the soil temperature were monitored to establish the timing of isotopic equilibrium with the carbonate. Calcite solubility was calculated from measured temperatures and $CO_2$ concentrations in the soil. This approach allowed us to determine the conditions associated with pedogenic carbonate formation. Carbon isotope equilibrium, oxygen isotope equilibrium, and minimum calcite solubility all occurred simultaneously during warm, dry conditions in May 2008 when soil $CO_2$ concentrations were low. It is therefore concluded that pedogenic carbonate forms during warm, dry periods and does not record mean growing season conditions as typically assumed. The seasonal bias in pedogenic carbonate formation may explain the occurrence of pedogenic carbonate in monsoon climates and its absence in regions where annual precipitation is more uniformly distributed. The implications of the seasonal bias for stable isotope–based paleoenvironmental reconstructions are that paleoelevations may have been previously over- or underestimated, paleoatmospheric $CO_2$ concentrations likely have been significantly overestimated, and pedogenic carbonate provides a $C_4$-biased record of paleovegetation, especially in dry soils.

## INTRODUCTION

Pedogenic carbonate is widely used in the study of paleoenvironments to address questions concerning topics as diverse as human evolu-

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tion, the history of civilizations, the evolution and spread of $C_4$ plants, the elevation history of large plateaus, Quaternary climate and ecologic change, and the relationships among atmospheric $pCO_2$, climate, and the geologic carbon cycle. The most useful pedogenic carbonate paleoenvironmental proxies developed thus far involve stable isotope geochemistry, although morphological and physical observations can be used as qualitative geochronometers (e.g., Gile et al., 1966; Machette, 1985) and indicators of paleoprecipitation (e.g., Retallack, 2005). Quantifications of the conditions that pedogenic carbonate records (especially soil temperature, soil $CO_2$ concentration, and the stable isotopic composition of soil $CO_2$ and soil water) are required for making accurate stable isotope–based paleoenvironmental reconstructions. Soil conditions, however, are known to change dramatically on a seasonal basis (e.g., Parada et al., 1983; Wood and Petraitis, 1984; Hesterberg and Siegenthaler, 1991; Flerchinger and Pierson, 1997), and the results of previous reconstructions have considerable uncertainty because the portion of seasonal variability that pedogenic carbonate records is poorly constrained. In this study the question of whether pedogenic carbonate records mean growing season conditions, as typically assumed in paleoenvironmental work, or seasonally extreme conditions was investigated by monitoring young soils from central New Mexico to investigate when soil $CO_2$ and soil water attain isotopic equilibrium with pedogenic carbonate.

## BACKGROUND

The term *pedogenic carbonate* refers to calcite nodules, filaments, clast coatings, and cemented carbonate horizons that form in soils of subhumid to arid regions worldwide. It is thought that Ca ions, released primarily during dissolution of Ca-bearing minerals in dust, are transported in downward percolating soil water and eventually reprecipitate as pedogenic carbonate at depth (Birkeland, 1999). Therefore, to

understand pedogenic carbonate formation, it is useful to consider the controls on calcite solubility. The following equation illustrates changes in the soil environment that can drive calcite precipitation:

$$a_{CaCO_3} = \frac{4m_{Ca^{2+}}^3}{pCO_2}\left(\frac{K_2}{K_1 K_{cal} K_{CO_2}}\right) \qquad (1)$$

where $a_{CaCO_3}$ is the activity of calcite (which varies between 0 and 1), $m_{Ca^{2+}}$ is the concentration of calcium ions in aqueous solution, $pCO_2$ is the partial pressure of $CO_2$ in the soil gas, and $K_1$, $K_2$, $K_{cal}$, and $K_{CO_2}$ are temperature-sensitive equilibrium constants for the dissociation of carbonic acid, the dissociation of bicarbonate, the dissociation of calcite, and the hydration of $CO_2$, respectively (Drever, 1982). Equation 1 is valid for the system $CaCO_3$-$H_2O$-$CO_2$, assuming that activities equal concentrations and pH < 9. At thermodynamic equilibrium, calcite will precipitate when $a_{CaCO_3}$ = 1. The product of the K terms increases with temperature, meaning that calcite is less soluble at higher temperatures. Therefore, the formation of pedogenic carbonate can be driven by an increase in the concentration of $Ca^{2+}$ in soil solution, a decrease in soil $pCO_2$, or an increase in soil temperature.

Theoretically, the sluggish rates of changes that occur at depth in soils result in the slow precipitation of calcite, allowing isotopic exchange between water, $CO_2$, and carbonate to proceed to equilibrium (Cerling and Quade, 1993). If this is the case, measured $\delta^{13}C$ and $\delta^{18}O$ values of pedogenic carbonate can be used to calculate the $\delta^{13}C$ value of soil $CO_2$ and the $\delta^{18}O$ value of soil water, which in turn record characteristics of the environment in which a soil forms (Cerling, 1984). These relationships are the basis for reconstructing paleoenvironments using the stable isotope composition of pedogenic carbonate preserved in paleosols. It is useful to review the processes that control the stable isotopic composition of soil water and soil $CO_2$ to fully understand the records provided by pedogenic carbonate.

## Soil Water

Precipitation is the primary source of water in unirrigated soils. Water that infiltrates across the soil-air interface either evaporates and returns to the atmosphere or percolates downward through the soil. The $\delta^{18}O$ value of infiltrating water is controlled by the $\delta^{18}O$ value of precipitation and is subsequently modified by evaporation and mixing in the soil. Evaporation is known to enrich residual soil water in $^{18}O$ (Allison, 1982), which explains the high $\delta^{18}O$ value of shallow soil water observed in many studies (e.g., Hsieh et al., 1998; Liu et al., 1995; Mathieu and Bariac, 1996; Gazis and Feng, 2004). Even deep soil water (below 40 cm) is influenced by evaporation in arid Hawaiian soils (Hsieh et al., 1998). However, empirical (Mathieu and Bariac, 1996; Gehrels et al., 1998), experimental (Allison et al., 1983), and theoretical (Barnes and Allison, 1983) studies suggest that in most soils evaporation has a minimal effect on the $\delta^{18}O$ value of water below 30–50 cm. The specific depth likely varies with soil texture, structure, and moisture content along with the evaporation rate, the diffusivity of water vapor through the soil, and the relative humidity in the overlying atmosphere (Barnes and Allison, 1983). Finally, mixing during percolation results in $\delta^{18}O$ values of soil water that are intermediate between the $\delta^{18}O$ values of precipitation from individual events or seasons.

## Soil $CO_2$

$CO_2$ is produced in soils primarily by the roots of plants (autotrophic respiration) and the microbial oxidation of organic matter (heterotrophic respiration). Carbon assimilated by plants ultimately forms the substrates respired in the soil, and thus the $\delta^{13}C$ value of assimilated carbon controls the $\delta^{13}C$ value soil-respired $CO_2$ ($\delta^{13}C_r$). $\delta^{13}C_r$ is particularly sensitive to the relative abundance of $C_3$ versus $C_4$ plants because $C_3$ photosynthesis involves substantially larger carbon isotope fractionation than $C_4$ photosynthesis (i.e., $C_3$ plants have lower $\delta^{13}C$ values than $C_4$ plants). $\delta^{13}C_r$ is also influenced by photosynthetic discrimination in $C_3$ plants, the magnitude of which varies with meteorological conditions (e.g., Ekblad and Högberg, 2001; Fessenden and Ehleringer, 2003; McDowell et al., 2004; Steinmann et al., 2004).

Biologically produced $CO_2$ released into the soil mixes with a relatively constant component of atmospheric $CO_2$ in the soil pore spaces. The resulting increase in soil $CO_2$ concentrations causes net diffusion into the overlying atmosphere. Therefore the concentration and $\delta^{13}C$ value of $CO_2$ in soil pores are controlled by both

diffusion through the soil and mixing between biogenic soil-respired $CO_2$ (modern $\delta^{13}C \approx -12$ to $-30‰$) and atmospheric $CO_2$ (modern $\delta^{13}C \approx -8.5‰$). The more rapid diffusion of $^{12}CO_2$ relative to $^{13}CO_2$ causes soil $CO_2$ to be enriched in $^{13}C$ relative to soil-respired $CO_2$. Low respiration rates, which result in low ratios of biogenic to atmospheric $CO_2$, result in further $^{13}C$ enrichment of soil $CO_2$. The $\delta^{13}C$ value (concentration) of soil $CO_2$ decreases (increases) abruptly with depth in the top 10–30 cm of most soils and typically does not change with depth below ~50 cm. These concepts have been quantified in steady-state production (or respiration)–diffusion models that describe the concentration and isotopic composition of soil $CO_2$ (Cerling, 1984; Cerling and Quade, 1993).

The oxygen isotopic composition of soil $CO_2$ is controlled by oxygen isotope exchange between soil $CO_2$ and soil water in addition to the production and diffusion of $CO_2$ (Hesterberg and Siegenthaler, 1991). The degree of oxygen isotope equilibrium between soil $CO_2$ and soil water is important to consider when using measured $\delta^{18}O$ values of soil $CO_2$ to calculate $\delta^{18}O$ values of soil water, as discussed later. Abrupt spatial heterogeneities in the oxygen isotopic composition of soil water, slow rates of oxygen isotope exchange, and rapid diffusion of $CO_2$ through the soil can cause deviations from oxygen isotope equilibrium (Stern et al., 1999). In the shallow subsurface all three of these factors, along with the invasion of atmospheric $CO_2$ into the soil (Tans, 1998), may result in disequilibrium between $CO_2$ and water. However, empirical studies conclude that below ~30 cm soil $CO_2$ is typically within 1‰ (Amundson and Wang, 1996) or 2‰ (Hesterberg and Siegenthaler, 1991) of isotopic equilibrium with soil water. Mathematical simulations that incorporate empirically derived rate constants for oxygen isotope exchange also suggest that soil $CO_2$ below 10–30 cm closely approaches oxygen isotope equilibrium with soil water (Tans, 1998; Stern et al., 1999).

## Pedogenic Carbonate as a Paleoenvironmental Proxy

Using the fractionation factor determined by Romanek et al. (1992), the carbon isotopic composition of soil $CO_2$ can be calculated from the carbon isotopic composition of pedogenic carbonate using the temperature at which $CO_2$ and calcite are in equilibrium:

$$\delta^{13}C_s = \frac{\delta^{13}C_{pc} + 1000}{\dfrac{11.98 - 0.12T}{1000} + 1} - 1000 \quad (2)$$

where $T$ is temperature (°C), and the subscripts pc and s refer to pedogenic carbonate and soil $CO_2$, respectively. The $\delta^{13}C$ value of soil $CO_2$ is controlled by many variables:

$$\delta^{13}C_S = f\left(\varepsilon, \kappa, J, z_{avg}, \delta^{13}C_r, C_a, \delta^{13}C_a\right) \quad (3)$$

where $\varepsilon$ is the air-filled porosity of the soil, $\kappa$ is the tortuosity of the soil pore spaces, $J$ is the respiration rate in the soil, $z_{avg}$ is the average depth at which respiration occurs in the soil, $C_a$ is the concentration of $CO_2$ in atmospheric air, and the subscripts r and a refer to $CO_2$ respired in the soil and $CO_2$ in atmospheric air, respectively (Cerling, 1984). Equations 2 and 3 can be used to calculate the value of either $\delta^{13}C_r$ or $C_a$ from measurements of $\delta^{13}C_{pc}$. Estimates of $\delta^{13}C_r$ can be used to identify the photosynthetic pathway of local paleovegetation, and estimates of $C_a$ are important for answering questions regarding the evolution of organisms and climate change.

The calculation of $\delta^{13}C_r$ is straightforward only in soils with high respiration rates where uncertainty in $\varepsilon$, $\kappa$, $J$, $z_{avg}$, $C_a$, and $\delta^{13}C_a$ have a minor effect on calculated $\delta^{13}C_r$ values (Cerling, 1984). In this case, $\delta^{13}C_r$ is typically calculated by subtracting ~15‰ from measured $\delta^{13}C_{pc}$ values to account for both diffusion-induced isotope fractionation (~4.4‰, Cerling, 1984) and equilibrium temperature–dependent isotope fractionation. This simple relationship can be used to estimate the relative abundance of $C_3$ and $C_4$ biomass. In soils with respiration rates lower than ~2 mmol/m²/h, both $\delta^{13}C_r$ and respiration rate affect $\delta^{13}C_s$, and therefore $\delta^{13}C_r$ cannot be accurately calculated unless the respiration rate is quantified.

The concentration of $CO_2$ in the atmosphere can be calculated from measured $\delta^{13}C_{pc}$ values using a simplified version of equation 3 known as the $CO_2$ paleobarometer (Cerling, 1999). This calculation requires accurate estimates of soil temperature, $\delta^{13}C_a$, $\delta^{13}C_r$, and the biogenic contribution to soil $CO_2$, $S(z)$, at the time the carbonate formed. $S(z)$ is related to the concentration of $CO_2$ in the soil ($C_s$) by (Cerling, 1984)

$$C_s = S(z) + C_a$$

and is approximately equal to $C_s$ when $C_s \gg C_a$, which is the case in most modern soils. The calculation of atmospheric $CO_2$ concentration is particularly sensitive to $S(z)$ and $\delta^{13}C_r$ and is least uncertain in soils where the value of $\delta^{13}C_r$ is very different from the value of $\delta^{13}C_a$. Therefore the $CO_2$ paleobarometer is typically applied to paleosols that formed before the widespread expansion of $C_4$ vegetation in the late Miocene (e.g., Quade et al., 1989a), so that pure $C_3$ vegetation can be assumed.

The oxygen isotopic composition of soil water can be calculated from the oxygen isotopic composition of pedogenic carbonate using the calibration of Friedman and O'Neil (1977) and the temperature of equilibrium between calcite and water:

$$\delta^{18}O_w = \frac{\delta^{18}O_{pc} + 1000}{e^{\frac{\frac{2.78 \times 10^6}{T^2} - 2.89}{1000}}} - 1000 \qquad (4)$$

where $T$ is temperature (K), and the subscripts w and pc represent water and pedogenic carbonate, respectively. Equation 4 can be used to calculate the $\delta^{18}O$ value of soil water in ancient environments if temperatures are assumed. The $\delta^{18}O$ value of soil water can then be used to estimate the $\delta^{18}O$ value of precipitation, which yields insight into atmospheric circulation patterns (e.g., Amundson et al., 1996) and the paleoelevation of high plateaus (e.g., Garzione et al., 2000).

Pedogenic carbonates collected from >50 cm below the paleosurface are typically used in paleoenvironmental reconstructions to avoid surface artifacts such as extreme evaporation and strong atmospheric $CO_2$ contamination. Sampling at this depth does not, however, avoid seasonal variations. Large seasonal variations in the carbon isotopic composition of soil $CO_2$ (Parada et al., 1983; Hesterberg and Siegenthaler, 1991) and the oxygen isotopic composition of soil water (Hsieh et al., 1998; Hesterberg and Siegenthaler, 1991; Liu et al., 1995; Mathieu and Bariac, 1996; Ferretti et al., 2003) have been observed below 50 cm. In addition, several studies report large seasonal variations in the concentration of $CO_2$ below 50 cm in calcic soils (de Jong, 1981; Parada et al., 1983; Wood and Petraitis, 1984; Amundson et al., 1989). What portion of this seasonal variability does pedogenic carbonate record? In most paleoenvironmental reconstructions, mean annual temperature is assumed in equations 2 and 4. Estimates of mean growing season soil $CO_2$ concentrations in modern soils (~5000 ppm) are typically used in the $CO_2$ paleobarometer (Cerling, 1999). It is assumed that soil water in equilibrium with pedogenic carbonate has a $\delta^{18}O$ value approximately equal to mean annual precipitation and that calculated $\delta^{13}C_r$ values represent the average composition of vegetation. These assumptions, however, have never been verified by careful calibration using modern soils. The measurements made in this study were intended to test for potential seasonal biases in pedogenic carbonate formation and thereby improve the interpretation of measured $\delta^{13}C_{pc}$ and $\delta^{18}O_{pc}$ values.

## SETTING

The soils studied are in the Sevilleta National Wildlife Refuge (NWR) in central New Mexico, USA. New Mexico has a semiarid, monsoon climate in which spring is typically the driest season and almost half the annual precipitation occurs in July, August, and September during intense thunderstorms (Douglas et al., 1993). Total annual precipitation in New Mexico depends strongly on elevation and ranges from ~100 to >1000 mm/yr (Western Regional Climate Center Web site, www.wrcc.dri.edu). The winter of 2006–2007, during the interval of study, was unusually wet, and a record-breaking storm in late December dropped half a meter of snow at the study sites.

We studied four Holocene soils, each in a different biome of the Sevilleta NWR. Four regionally extensive biomes converge on the Sevilleta NWR, allowing the effects of different vegetation on pedogenic carbonate to be studied. The biomes investigated in this study were Plains Grassland, Piñon-Juniper Woodland, Great Basin Shrubland, and Chihuahuan Desert Shrubland. Characteristics of each site are listed in Table 1. The vegetation consists primarily of $C_4$ grasses at the grassland site; $C_3$ trees and $C_4$ grasses at the Piñon-Juniper Woodland site; a mixture of $C_3$ shrubs, $C_4$ shrubs, and $C_4$ grasses at the Great Basin Shrubland site; and almost entirely of *Larrea tridentata* (creosotebush), a $C_3$ shrub, at the Chihuahuan Desert Shrubland site. The Sevilleta Long Term Ecological Research (LTER) project (http://sev.lternet.edu/) at the Sevilleta NWR provides detailed meteorological records useful for monitoring soils. Precipitation records covering the past 15 yr from meteorological stations near the Piñon-Juniper Woodland site and the Great Basin Shrubland site indicate that mean annual precipitation is 375 and 210 mm, respectively (Table 1). Mean annual temperatures are 12 and 15 °C, respectively.

We chose to study young soils in floodplain deposits that flank active, seasonal drainages to maximize the likelihood that peodogenic carbonate formed under the influence of the current vegetation and climate. All four soils studied are developed in gravelly parent material and have ochric A horizons and weak Ck horizons with thin coatings of pedogenic carbonate on the underside of limestone and silicate clasts. Three of the soils are Orthents with <5-cm-thick A horizons. The soil at the Piñon-Juniper site is an Ochrept and has a thicker (~20 cm) and darker A horizon. Pedogenic carbonate was observed only below 20 cm in this soil. No evidence for buried soils was found in any of the soils. When compared with the morphology of dated Holocene soils elsewhere in New Mexico (e.g., Gile, 1977; Wells et al., 1990) the morphology of the soils in this study indicate that they formed in late Holocene alluvium and are probably <1000 yr old.

## METHODS

The stable isotope composition of soil $CO_2$ and soil water were compared with the stable isotope composition of pedogenic carbonate to evaluate when isotopic equilibrium occurs between these phases and therefore what season is recorded by the stable isotopic composition of the carbonate. Samples of pedogenic carbonate were collected once at the beginning of the study, and it was assumed that the stable isotopic composition of pedogenic carbonate in these soils did not change during the interval of investigation. Samples of soil $CO_2$ were collected from permanently installed soil-gas wells approximately once per month for a period of 20 months. The oxygen isotopic composition of soil water was calculated from the measured oxygen isotopic composition of soil $CO_2$ after the two were demonstrated to be close to isotopic equilibrium (see below).

TABLE 1. CHARACTERISTICS OF STUDY SITES

| Site name | Grassland | P.J. Woodland | G.B. Shrubland | C.D. Shrubland |
|---|---|---|---|---|
| Latitude (°N) | 34°17'56.9" | 34°23'06.5" | 34°21'25.6" | 34°16'37.5" |
| Longitude (°W) | 106°37'52.7" | 106°31'34.6" | 106°52'09.7" | 106°54'03.8" |
| Elevation (m) | 1750 | 1900 | 1475 | 1450 |
| Vegetation | $C_4$ grasses | $C_3$ trees, $C_4$ grasses | $C_3$ and $C_4$ shrubs, $C_4$ grasses | $C_3$ shrubs |
| MAT (°C) | | 12 | 15 | 15 |
| MAP (mm) | | 375 | 210 | |
| $\delta^{18}O$ MAP (‰ vs. VSMOW) | | −8 | −7 | |

*Note:* P.J.—Piñon-Juniper; G.B.—Great Basin; C.D.—Chihuahuan Desert; MAT—mean annual temperature; MAP—mean annual precipitation; VSMOW—Vienna Standard Mean Ocean Water.

## Pedogenic Carbonate

One trench (~1 m³) was excavated in one soil in each of the biomes discussed above during July 2006. Between 30 and 50 clasts bearing pedogenic carbonate coatings were collected from each soil trench at depths ranging from 0 to 100 cm. Pedogenic carbonate was sampled from the shallow subsurface to test for the exponentially decaying decrease in $\delta^{13}C$ values that should be expressed in intact pedogenic carbonate profiles (e.g., Quade et al., 1989b). Carbonate below ~50 cm is, however, of primary interest for paleoenvironmental reconstruction because little variation in either the $\delta^{13}C$ or the $\delta^{18}O$ values of pedogenic carbonate is typically observed below this depth.

To minimize contamination by detrital carbonate, coatings were inspected under a binocular microscope for evidence of reworking. Pristine coatings are likely to have formed in situ because the coatings are fragile (either powdery or thin and brittle) and generally poorly fixed to the clast. Therefore, only coatings that appeared unbroken and undisturbed were chosen for analysis. Coatings filling only recesses in the underside of clasts were avoided, as these are clear evidence of reworking. Carbonate coatings were scraped off the clasts with a razor blade, with care not to remove clast material itself. The carbonate samples were then powdered and reacted with 30% $H_2O_2$ to oxidize any organic material prior to stable isotopic analysis (Spötl and Vennemann, 2003). To measure the $\delta^{13}C$ value of soil organic matter, soil samples were reacted with 10% HCl to remove carbonate and were combusted in an elemental analyzer coupled to a Delta Plus mass spectrometer.

## Soil CO₂

Soil-gas wells were installed into one wall of each trench, as described by Breecker and Sharp (2008). Briefly, a soil-gas well consists of a 1 m length of internally electropolished, ¼-in. stainless-steel tubing that is installed horizontally into the soil. The ¼-in. tubing is connected to a 1/16-in. stainless-steel capillary that runs vertically to the surface, where it is sealed by a rubber septum. The septum can be punctured with a syringe to withdraw a gas sample. Thermocouples were installed at three or four different depths, and the pits then were backfilled.

Beginning in September 2006, and continuing through May 2008, samples of the soil atmosphere (0.3–2 mL) were collected from the soil-gas wells approximately once per month. Samples of air were also collected with a syringe at each site every time soil gas was collected. The concentration and stable isotopic composi-

tion of $CO_2$ in these samples were measured in the stable isotope laboratory at the University of New Mexico using the continuous-flow isotope ratio mass-spectrometry method described by Breecker and Sharp (2008). An unprecedented number of small-volume samples can be processed using these rapid sampling and analytical techniques, allowing higher spatial and temporal resolution of seasonal changes in soil $CO_2$ than previously feasible. Approximately 100 samples can be collected and analyzed in 24 h using this technique. The reproducibility ($1\sigma$) of this technique is better than 0.1‰ for carbon and oxygen isotopic compositions and better than 2% for $CO_2$ concentrations. Further details concerning the soil-gas sampling and analytical technique are available in Breecker and Sharp (2008).

## Soil Water

To test whether the $\delta^{18}O$ value of soil $CO_2$ is in equilibrium with water (and therefore can be used to calculate the $\delta^{18}O$ value of soil water) in the relatively dry soils studied, we collected soil $CO_2$ and soil water from the same site on 4 October 2007 for comparison. Soil $CO_2$ samples were collected from gas wells installed as a pilot project to test the gas sampling technique in a sandy soil with only incipient development near Albuquerque, New Mexico. Immediately following gas sampling, samples for soil water were collected by excavating a soil pit ~1 m from the wells. Excavation was periodically halted to allow the collection of ~25 cm³ soil samples from the bottom of the pit. This sampling technique was intended to minimize evaporation from newly exposed soil. The soil samples were immediately sealed in 50 mL plastic centrifuge tubes, and the soil temperature at each sampling depth was then measured before excavation continued. Soil water was extracted from the samples by vacuum distillation and was equilibrated with $CO_2$ for 24 h at 25 °C in Labco exetainers® for oxygen isotopic analysis by continuous-flow mass spectrometry. The fractionation factor determined by Brenninkmeijer et al. (1983) was used to calculate $\delta^{18}O$ values of $CO_2$ in equilibrium with measured $\delta^{18}O$ values of soil water. These calculated equilibrium $CO_2$ $\delta^{18}O$ values were then compared with measured soil $CO_2$ $\delta^{18}O$ values to assess the degree of equilibrium. Once equilibrium was demonstrated, $\delta^{18}O$ values of water were determined from measured $\delta^{18}O$ values of soil $CO_2$, resulting in high spatial and temporal resolution estimates of the $\delta^{18}O$ value of soil water.

Precipitation was collected at the Piñon-Juniper Woodland and Chihuahuan Desert Shrubland sites in plastic separation funnels partly filled with mineral oil to minimize evapora-

tion. The valve at the bottom of the funnel was opened to retrieve a sample every time soil gas was collected, preventing the need to collect the water from below the mineral oil with a syringe. The $\delta^{18}O$ value of precipitation was measured with the same technique used for soil water.

## Data Analysis

The carbon and oxygen isotopic compositions of pedogenic carbonate in equilibrium with measured values of soil $CO_2$ and soil water were calculated for each soil $CO_2$ profile using measured soil temperature in equations 2 and 4, respectively. These calculated values are hereafter referred to as *predicted* values. It was assumed, when calculating the predicted values, that most pedogenic carbonate formed prior to 1900 A.D., when the $\delta^{13}C$ value of atmospheric $CO_2$ began to decrease significantly (Francey et al., 1999). A comparison of predicted and measured values requires consideration that the soil $CO_2$ samples represent the instantaneous, modern environment, whereas the pedogenic carbonate samples probably accumulated over hundreds to perhaps a thousand years. We therefore added 2‰, which is the difference between the preindustrial and the modern atmospheric $CO_2$ values (e.g., Indermühle et al., 1999), to the measured $\delta^{13}C$ values of soil $CO_2$ before calculating predicted carbonate $\delta^{13}C$ values. Differences between the measured and predicted isotopic compositions of pedogenic carbonate ($\Delta^{13}C_{measured-predicted}$ and $\Delta^{18}O_{measured-predicted}$) were calculated for each soil $CO_2$ sampling depth below ~50 cm and for each time samples were collected. The mean of all measured values within ±5 cm of the depth corresponding to each predicted value was used for this calculation. The $\delta^{13}C$ value of soil-respired $CO_2$ was calculated from measured $\delta^{13}C$ and $pCO_2$ values of both soil and atmospheric $CO_2$ (Davidson, 1995). One $\delta^{13}C_r$ value was calculated for each depth at which soil $CO_2$ was collected, and the $\delta^{13}C_r$ values reported in this study represent the mean of the bottom four wells at each site. The concentration of $Ca^{2+}$ in the soil solution at calcite saturation was calculated using an iterative procedure (Drever, 1982) and measured values of soil $pCO_2$ and soil temperature. The presence of other dissolved salts in the soil solution was ignored, a simplification that is justified by the lack of morphological evidence for salt accumulation in the actual profiles. The $\delta^{18}O$ value of mean annual precipitaton at the Piñon-Juniper Woodland and Chihuahuan Desert Shrubland sites was estimated by first calculating the mean $\delta^{18}O$ value of precipitation collected during the cold half (October–March) and warm half of the year. Sevilleta LTER precipitation records indi-
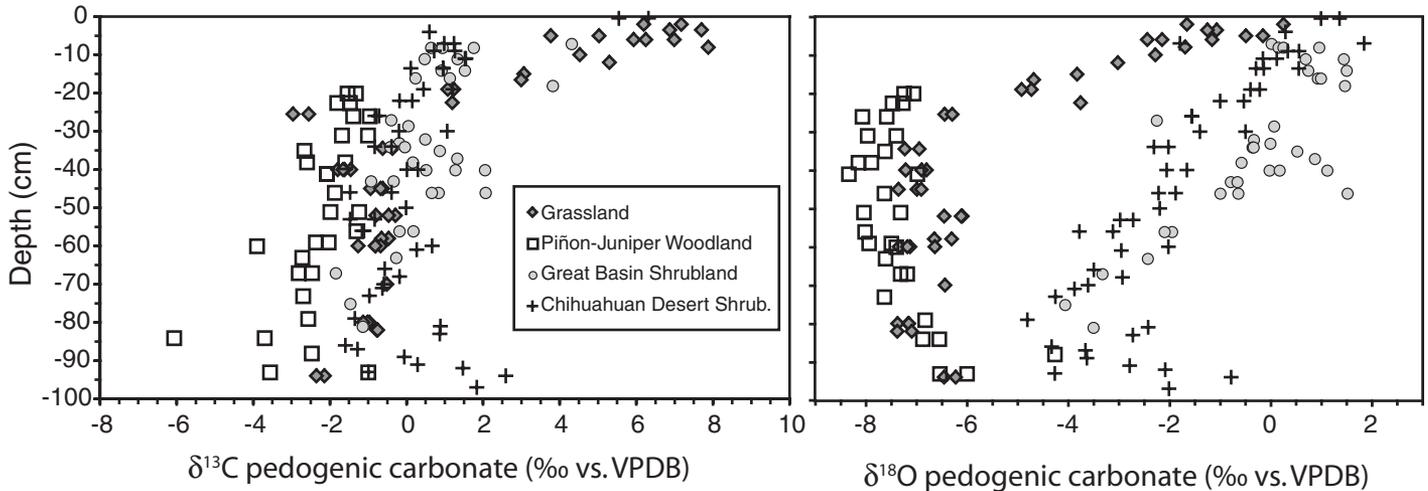
**Figure 1. Measured carbon and oxygen isotopic compositions of pedogenic carbonate. Each data point represents the coating on a single clast. Profiles from each site are shown. VPDB—Vienna Peedee Belemnite.**

cate that the amount of precipitation is approximately equally divided between these time periods and occurs primarily during the winter and summer. Therefore the mean $\delta^{18}O$ value of the winter and summer means was taken to estimate mean annual precipitation.

## RESULTS

Profiles of soil temperature, the concentration of soil $CO_2$, and the $\delta^{13}C$ and $\delta^{18}O$ values of soil $CO_2$ from each biome are included in Table DR1.[1] Soil temperature generally decreases with depth during the warmer half of the year and increases with depth during the colder half of the year. The mean annual soil temperature at 100 cm is ~18 °C at the grassland and shrubland sites and ~15 °C at the Piñon-Juniper Woodland site, which is ~3 °C higher than mean annual air temperature. The seasonal variation in soil temperature at 100 cm is ~20 °C in all the soils studied, consistent with previous observations in a semiarid region (Flerchinger and Pierson, 1997). The concentration of $CO_2$ in the soil atmosphere increases with depth, and the $\delta^{13}C$ value of $CO_2$ in soil air decreases with depth, consistent with the steady-state, concave-down profiles predicted by production-diffusion models (Cerling, 1984; Cerling and Quade, 1993). $CO_2$ concentrations are highest during the wet parts of the summer and lowest in the winter and during the dry parts of the spring and summer. Soil $CO_2$ concentrations range

from 2000 to 7000 ppm at the Piñon-Juniper Woodland site, 700–3500 ppm at the grassland site, 900–3000 ppm at the Chihuahuan Desert Shrubland site, and 700–2000 ppm at the Great Basin Shrubland site. $CO_2$ $\delta^{13}C$ profiles range in shape from nearly invariant with depth to gradually decreasing through the entire top meter of the soil. At 100 cm depth, $\delta^{13}C$ values of soil $CO_2$ are lowest in the winter and highest during the dry parts of the spring and summer. Seasonal variations up to ~20‰ were observed in the $\delta^{18}O$ value of shallow $CO_2$ (5 cm depth), whereas seasonal variations of ~5‰ were observed below 50 cm. Soil $CO_2$ $\delta^{18}O$ profiles are irregularly shaped and have no consistent trend with depth, although the $\delta^{18}O$ values are largely controlled by the $\delta^{18}O$ value of soil water and soil temperature, as discussed below.

Profiles of the measured $\delta^{13}C$ and $\delta^{18}O$ values of incipient pedogenic carbonate are compared in Figure 1. There is considerably more scatter in the carbonate profiles than in the $CO_2$ profiles, but the basic form of each is similar, especially when comparing $CO_2$ profiles for the late spring and the dry parts of the summer. The exponentially decaying decrease with depth in the $\delta^{13}C$ values of pedogenic carbonate agrees with the shape of theoretical and empirical pedogenic carbonate profiles (Quade et al., 1989b). Measured $\delta^{18}O$ values of precipitation are listed in Table 2. The difference between the mean annual $\delta^{18}O$ values at the Piñon-Juniper Woodland and Chihuahuan Desert Shrubland sites agrees well with a lapse rate of –2.8‰/km (Poage and Chamberlain, 2001). The results of the experiment to test for oxygen isotope equilibrium between soil $CO_2$ and soil water are shown in Figure 2. The agreement below

~30 cm between measured soil $CO_2$ $\delta^{18}O$ values and those predicted to be in equilibrium with soil water at soil temperature (Brennink-meijer et al., 1983) demonstrates that $CO_2$ and water are near isotopic equilibrium in the coarse sandy soil used for this experiment. The similarity among calculated $\delta^{18}O$ values of soil water during all times of year at the Chihuahuan Desert Shrubland site is further evidence for $CO_2$-water oxygen isotopic equilibrium below 30 cm (Fig. 2). The $\delta^{18}O$ value of soil $CO_2$ is therefore used to estimate the $\delta^{18}O$ of soil water.

The predicted isotopic compositions of pedogenic carbonate (in equilibrium with soil $CO_2$ and soil water) are compared with the measured carbonate values in Figure 3. In general, the predicted carbonate $\delta^{13}C$ values are lower than the measured values. Predicted carbonate $\delta^{18}O$

TABLE 2. $\delta^{18}O$ VALUES
(‰ VS. VSMOW) OF PRECIPITATION

| Collection date | P.J. Woodland | C.D. Shrubland |
|---|---|---|
| 4 February 2007 | | –9.9 |
| 13 February 2007 | –9.8 | |
| 16 February 2007 | –12.6 | –9.1 |
| 28 March 2007 | –11.1 | –7.0 |
| 11 April 2007 | –10.0 | –7.5 |
| 28 April 2007 | –2.8 | –5.5 |
| 9 June 2007 | –2.4 | –5.1 |
| 26 June 2007 | –1.4 | |
| 26 July 2007 | –6.2 | |
| 2 August 2007 | –6.9 | |
| 11 September 2007 | –7.4 | –7.2 |
| 12 October 2007 | –9.3 | –5.0 |
| | | |
| Mean summer | –5.3 | –6.3 |
| Mean winter | –10.7 | –7.8 |
| Mean annual | –8.0 | –7.0 |

*Note:* P.J.—Piñon-Juniper; C.D.—Chihuahuan Desert; VSMOW—Vienna Standard Mean Ocean Water.

values below ~30 cm are in general higher than the measured values during the fall and winter, lower than the measured values in the summer, and closest to equilibrium with the measured values during the spring. The apparently anomalous relationship between the predicted and measured values of pedogenic carbonate at the grassland site is discussed below.

Time series of soil variables measured at or calculated for depths below 50 cm, including $\Delta^{13}C_{measured-predicted}$ and $\Delta^{18}O_{measured-predicted}$, are plotted in Figure 4. Large variations are observed for each of the variables except for the oxygen isotopic composition of soil water, which remains relatively constant. Distinct seasonal variations are apparent in soil temperature, $\Delta^{18}O_{measured-predicted}$, and the $\delta^{13}C$ values of soil $CO_2$ and soil respired $CO_2$. The variations in $\delta^{13}C_r$ are larger than any previously reported, as far as we are aware. Variations in $\Delta^{13}C_{measured-predicted}$, soil $CO_2$ concentration, and the $Ca^{2+}$ concentration at calcite saturation deviate from seasonal regularity, especially during dry periods. Most importantly, during May 2008 both $\Delta^{13}C_{measured-predicted}$ and $\Delta^{18}O_{measured-predicted}$ approached zero at each of these three sites, meaning that soil $CO_2$ and soil water approached isotopic equilibrium with pedogenic carbonate.

## DISCUSSION

Minimum calcite solubility during the interval of study coincided with dry episodes during the spring and summer (Fig. 4) because soil $pCO_2$ was low and soil temperature was relatively high. These factors decrease the calcium activity required to precipitate calcite. Simultaneously, the calcium activity in the soil solution likely increased as soil water was lost through evapotranspiration. Both carbon and oxygen isotope equilibrium was achieved at the same time minimum solubility was reached, suggesting pedogenic carbonate forms when the soil is warm and very dry. The higher solubility and lack of isotopic equilibrium during the wet spring of 2007 compared with the dry spring of 2008 further support the idea that pedogenic carbonate forms only when the soil is very dry and moisture stress strongly limits soil respiration rates.

The interpretation that pedogenic carbonate forms during seasonal decreases in soil $CO_2$ concentration resolves the apparent paradox of precipitating carbonate at depth where $CO_2$ concentrations are usually many times higher than at the surface, where carbonate initially dissolved. From this theoretical perspective, it seems that large variations in soil $CO_2$ concentrations may be the most important mechanism behind pedogenic carbonate formation and may
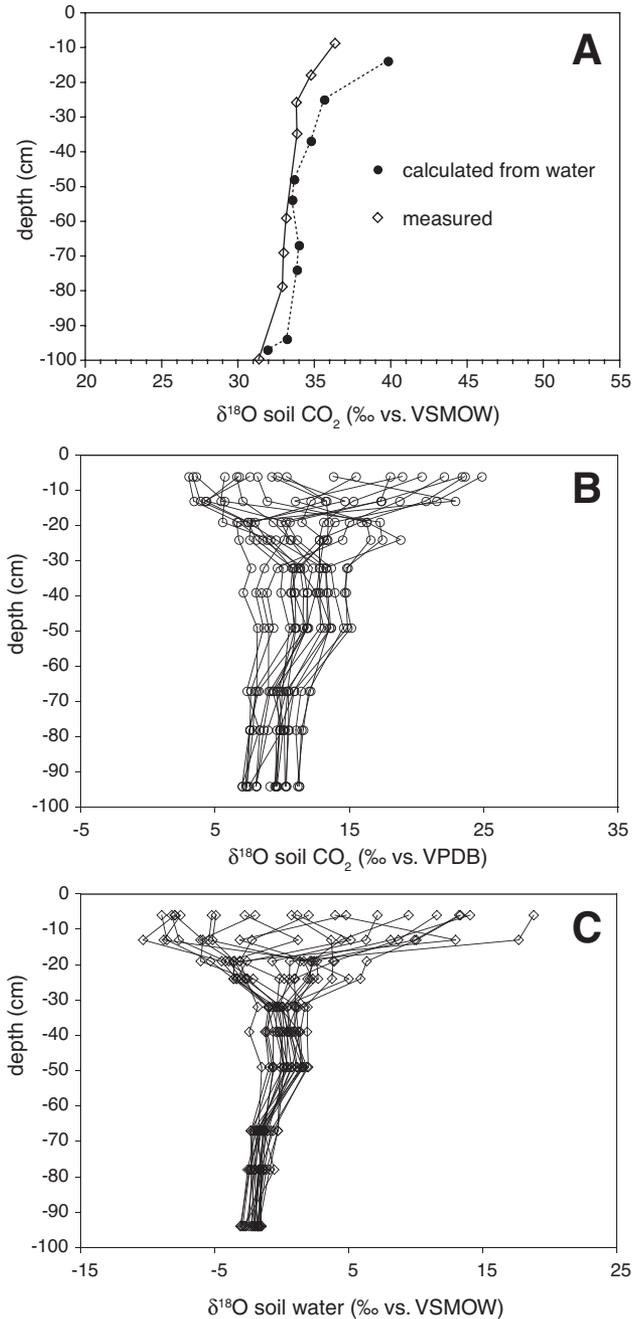


Figure 2. Relationship between the $\delta^{18}O$ values of soil $CO_2$ and soil water. (A) Comparison of the measured $\delta^{18}O$ values of soil $CO_2$ with calculated $\delta^{18}O$ values of soil $CO_2$ in equilibrium with measured $\delta^{18}O$ values of soil water. The close correspondence below ~30 cm indicates that $CO_2$ and water are near oxygen isotope equilibrium in this soil and that the $\delta^{18}O$ value of soil $CO_2$ can be used to calculate the oxygen isotopic composition of soil water. (B) $\delta^{18}O$ profiles of soil $CO_2$ (measured), and (C) soil water (calculated) from the Chihuahuan Desert Shrubland site. Each profile from the entire interval of study (September 2006–May 2008) is shown. $\delta^{18}O$ values of soil $CO_2$ were measured, whereas $\delta^{18}O$ values of soil water are calculated values in equilibrium with soil $CO_2$ at measured soil temperatures. The similarity among calculated soil water $\delta^{18}O$ values below 30 cm at all times of year suggests that the $\delta^{18}O$ value of water is nearly constant, that $CO_2$ and water are in isotopic equilibrium below ~30 cm in this soil, and that seasonal changes in the $\delta^{18}O$ value of soil $CO_2$ are driven by changes in soil temperature, which affect the equilibrium fractionation factor. VSMOW—Vienna Standard Mean Ocean Water; VPDB—Vienna Peedee Belemnite.
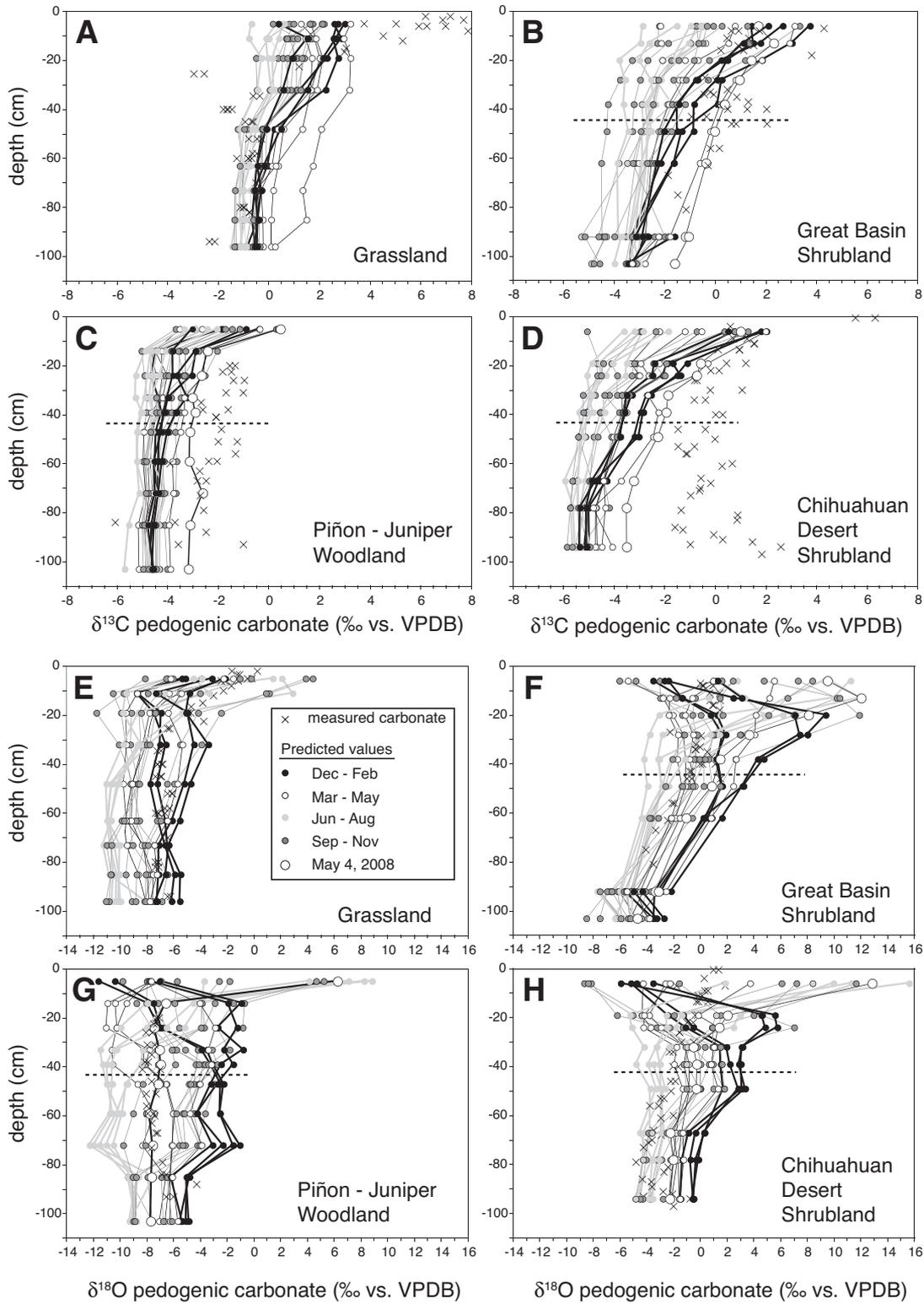
Figure 3. Profiles of the measured carbon and oxygen isotope values of pedogenic carbonate (same as in Fig. 1) and those predicted from measured soil-gas values. Predicted values are equilibrium values calculated from soil CO$_2$ at measured soil temperatures and include a correction for the anthropogenic change in the δ$^{13}$C value of atmospheric CO$_2$. Carbon isotope values are plotted in panels A–D, and oxygen isotope values are plotted in panels E–H. The key for all plots is shown in panel E. Results from both disturbed and undisturbed soil are shown at 92 cm for the Great Basin Shrubland. Dashed horizontal lines show the depth below which measured and predicted values are compared in Figure 4. Equilibrium conditions were most closely achieved on 4 May 2008, and the profiles for this date are highlighted by enlarged symbols. Soil gas was not collected at the grassland site on 4 May 2008. VPDB—Vienna Peedee Belemnite.
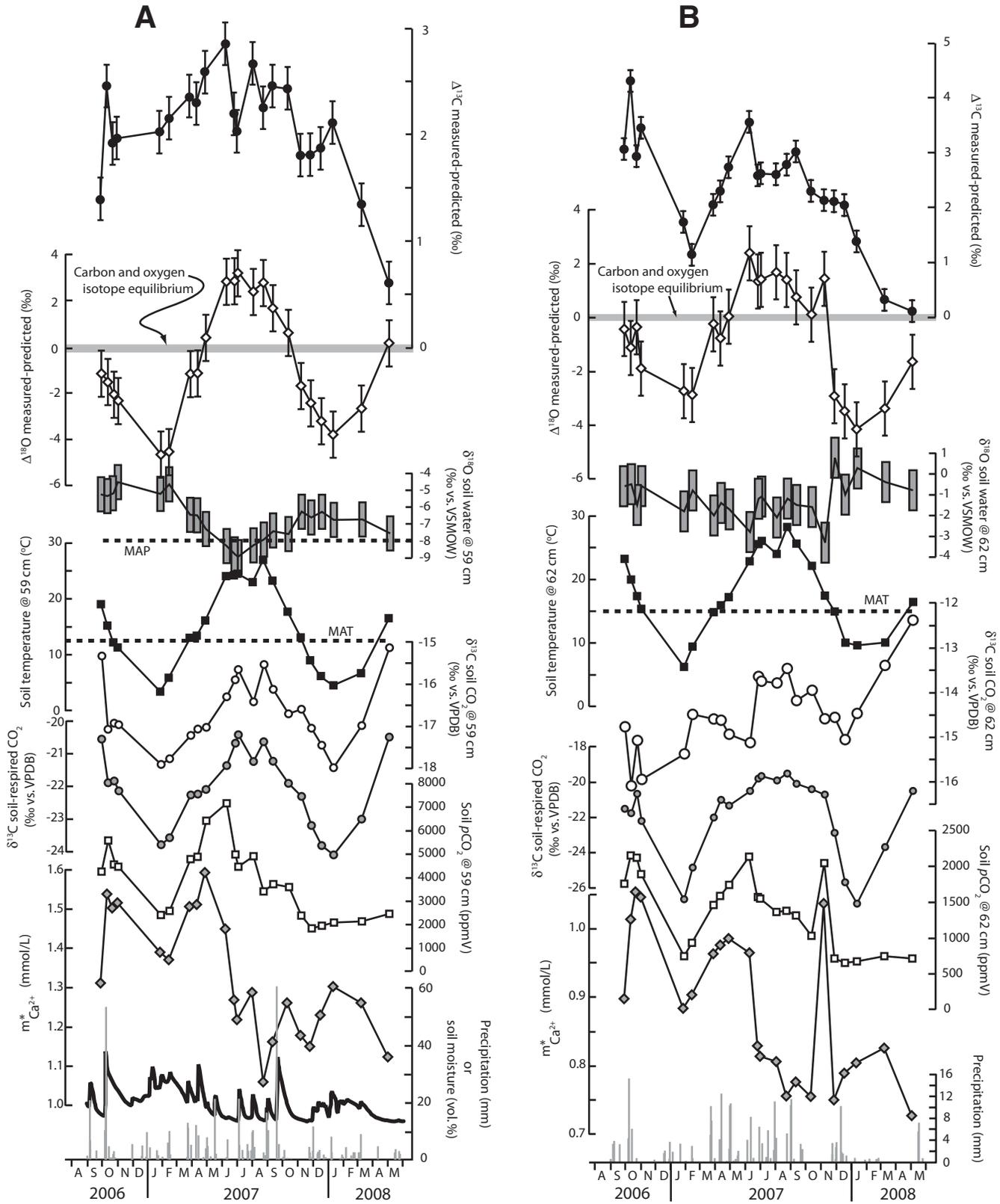
**Figure 4. Time series of soil variables. (A) Piñon-Juniper Woodland, (B) Great Basin Shrubland, and (C) Chihuahuan Desert Shrubland. In the subscripts measured-predicted,** *measured* **refers to measured values of pedogenic carbonate, and** *predicted* **refers to equilibrium carbonate values calculated from measurements of soil $CO_2$ using measured temperatures. $\delta^{13}C$ values of soil-respired $CO_2$ were calculated as described in Davidson (1995); $m^*_{Ca^{2+}}$ is the concentration of $Ca^{2+}$ in the soil solution at calcite saturation calculated from measured temperature and soil $pCO_2$ (Drever, 1982). (***Continued on following page***.)**
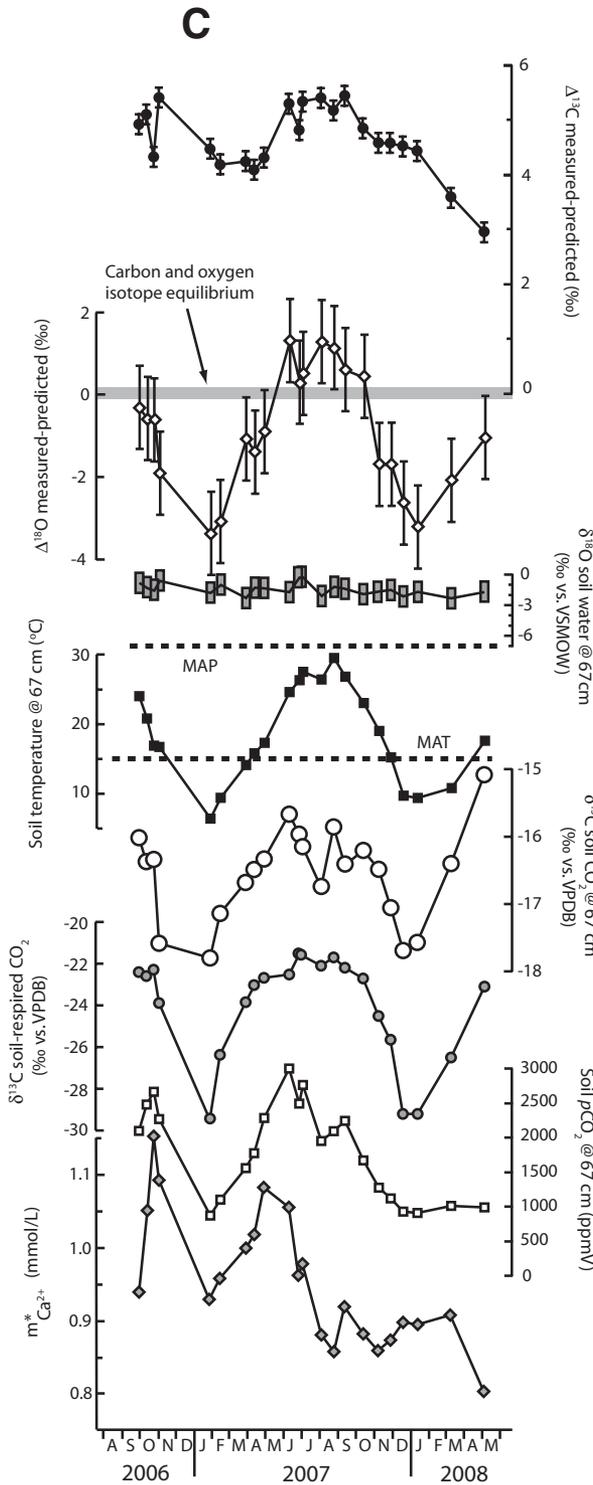
**Figure 4 (*continued*). Error bars on Δ¹⁸O<sub>measured-predicted</sub> reflect uncertainty of calculated soil water δ¹⁸O values. Symbol size reflects uncertainty for other values. Soil moisture (average of top 30 cm using time domain reflectometry) and precipitation were measured <100 m from the Piñon-Juniper and Great Basin Shrubland sites (these data can be accessed at http://sev.lternet.edu; Met Station 1 is near the Great Basin Shrubland site and Met Station 42 is near the Piñon-Juniper Woodland site). MAP—mean annual precipitation; MAT—mean annual temperature; VPDB—Vienna Peedee Belemnite; VSMOW—Vienna Standard Mean Ocean Water.**

be a universal characteristic of calcic soils. It is likely that high $CO_2$ concentrations during wet periods of the year are responsible for carbonate dissolution and the mobilization of Ca, whereas decreasing concentrations associated with warm, dry periods are responsible for carbonate precipitation. Wet-dry cycles therefore may be required for pedogenic carbonate formation.

Formation under seasonally dry conditions explains how pedogenic carbonate can form in monsoon climates where mean annual precipitation exceeds 1 m (Srivastava, 2001) but does not form in climates where the same amount of precipitation is more evenly distributed throughout the year. It is likely that a monsoon climate provides the wet-dry cycles required to move carbonate down through soils and deposit it at depth. In regions where precipitation patterns do not result in seasonal wet-dry cycles, pedogenic carbonate may form primarily during droughts and may accumulate only if droughts occur with sufficient frequency. Furthermore, seasonally biased pedogenic carbonate formation may explain a part of the scatter in the relationship between mean annual precipitation and the depth to pedogenic carbonate (Retallack, 2005). Carbonate may be leached deeper under diminished seasonality.

Low soil $pCO_2$ during pedogenic carbonate formation suggests that atmospheric $CO_2$ concentrations calculated using $CO_2$ paleobarometry (e.g., Ekart et al., 1999) have been overestimated. The $CO_2$ paleobarometer (Cerling, 1999) is particularly sensitive to $S(z)$, the biogenic component of soil $CO_2$, which is often assumed to be ~5000 ppmV in paleo-$pCO_2$ reconstructions. Recent studies have attempted to account for potential differences among paleosols by using $S[z]$ values that vary with paleolatitude (6000–4000 ppmV corresponding to 25–50°N, respectively; Nordt et al., 2003) or with soil morphology ($S(z)$ ranging from 2000 to 7500 ppmV; Montañez et al., 2007). However, lower $CO_2$ concentrations of <1000–2000 ppmV are more appropriate for the soils studied here. Soil $CO_2$ concentrations during pedogenic carbonate formation that are lower than previously assumed would reduce calculated paleoatmospheric $pCO_2$ values. Future studies should test the assumed 5000 ppmV value, which is based on measurements of mean growing season soil $pCO_2$, primarily in noncalcic soils (Brook et al., 1987; Solomon and Cerling, 1987).

In mixed $C_3$-$C_4$ communities and lower productivity soils, pedogenic carbonates have δ¹³C values that are biased toward a $C_4$ signal. The bias occurs for several reasons: (1) $C_4$ plants dominate over $C_3$ plants as temperature increases (e.g., Ehleringer et al., 1997), (2) the δ¹³C value of $CO_2$ respired by $C_3$ plants increases with

moisture stress (Ekblad and Högberg, 2001; Fessenden and Ehleringer, 2003; McDowell et al., 2004; Steinmann et al., 2004), and (3) decreasing soil respiration rates (in this case owing to moisture stress) result in a lower proportion of biogenic $CO_2$ in the soil. Pedogenic carbonate records the high $\delta^{13}C$ value of soil $CO_2$ resulting from these processes (Fig. 4; isotope equilibrium is associated with the highest $\delta^{13}C_r$ and $\delta^{13}C_s$ values). The $C_4$ bias has been documented in modern $C_3$-dominated ecosystems from eastern Washington State (Stevenson et al., 2005). As originally predicted by Cerling (1984), the $C_4$ bias is likely small in soils with high organic matter contents and high heterotrophic respiration rates in which decreases in respiration rate and changes in the $\delta^{13}C$ value of rhizosphere respiration have a relatively minor influence on the $\delta^{13}C$ value of soil $CO_2$. However, in the desert soils studied here, $\delta^{13}C_{pc}$ is 2–3‰ higher than mean growing season conditions would suggest (Fig. 4), indicating that the fraction $C_4$ biomass calculated by subtracting 15‰ from measured $\delta^{13}C_{pc}$ values could be overestimated by as much as 25%. While pedogenic carbonate may not always record average vegetation, it does record differences in vegetation between the Piñon-Juniper Woodland site and the Great Basin Shrubland site. In order to accurately reconstruct paleobiomes using pedogenic carbonate, more research needs to be undertaken to evaluate the specific effects of different vegetation on $\delta^{13}C_{pc}$ in modern soils.

Pedogenic carbonate in the soil at the Chihuahuan Desert Shrubland has $\delta^{13}C$ values several per mil higher than predicted from measured soil $CO_2$, even during the dry episodes when other soils attained equilibrium. The replacement of $C_4$ vegetation by *L. tridentata* would explain this observation. This interpretation is consistent with the northward expansion of the Chihuahuan Desert at the expense of Great Plains Short-Grass Steppe ($C_4$ dominated) in the study area over the past century (e.g., Gosz, 1993). At the grassland site the agreement between measured $\delta^{13}C_{pc}$ and the lowest predicted $\delta^{13}C_{pc}$, rather than the highest predicted $\delta^{13}C_{pc}$ values (Fig. 3), appears anomalous but is also likely the result of vegetation change. The $\delta^{13}C$ value of soil organic matter at this site is ~−19‰, ~5‰ lower than expected on the basis of the current $C_4$-dominated community. It is commonly observed in the southwestern United States that many of the first plants to colonize inset river terraces or other disturbed surfaces are $C_3$ shrubs, such as *Artemesia filifolia* (sand sage). Therefore, it is likely that $C_3$ vegetation previously occupied this terrace and that a portion of the pedogenic carbonate formed under the influence of these $C_3$ plants. The inferred recent vegetation change at the Chihuahuan Desert Shrubland and grassland sites suggests that the $\delta^{13}C$ value of pedogenic carbonate is not rapidly reset over a time interval of decades to centuries.

Pedogenic carbonate forms from soil water with a $\delta^{18}O$ value similar to mean annual precipitation at the Piñon-Juniper Woodland site (Fig. 4A) but appears to form from soil water influenced by evaporation at the Chihuahuan Desert Shrubland site (Fig. 4C). The calculated $\delta^{18}O$ value of soil water at 67 cm depth in the Chihuahuan Desert Shrubland soil is consistently 5–6‰ higher than the estimated $\delta^{18}O$ value of mean annual precipitation. Given that seasonal changes of this magnitude are not observed below ~25 cm in this soil (Fig. 2), it is likely that evaporation does not have a direct influence at depth but that the $\delta^{18}O$ value of percolating water is strongly influenced by mixing with evaporated water in the shallow subsurface. The formation of pedogenic carbonate from water influenced by evaporation explains the high $\delta^{18}O$ value of the carbonate in this soil, and probably also the high $\delta^{18}O_{pc}$ values observed in the soil at the Great Basin Shrubland site, when compared with carbonate at the Piñon Woodland site (Fig. 1). If it is assumed for paleoelevation calculations that pedogenic carbonate forms from water with a $\delta^{18}O$ value equivalent to mean annual precipitation, then formation from evaporated water would result in paleoelevation underestimates.

Models of calcic soil development agree with the conclusions of the present study, predicting that pedogenic carbonate forms during warm, dry periods (e.g., McFadden and Tinsley, 1985). Liu et al. (1996) concluded that pedogenic carbonate from southern Arizona, USA, forms from evaporated soil water at maximum summer temperatures, whereas Quade et al. (1989b) argued that pedogenic carbonate in the Spring and Grapevine Mountains of Nevada, USA, forms during the wettest time of year. It is important to consider that carbonate formation can occur whenever the soil solution becomes supersaturated, which may occur at different times of year in different climates. Solubility considerations suggest, however, that supersaturation is most likely to occur when the soil is warm and dry, making formation during wet conditions improbable.

## CONCLUSIONS

Isotopic equilibrium of pedogenic carbonate with soil $CO_2$ and soil water was attained in the studied soils in early May 2008 during a dry episode when calcite solubility was at a minimum. Therefore, arguments based on both stable isotope geochemistry and solution chemistry support the conclusion that pedogenic carbonate forms when the soil is warm and very dry, not during mean growing season conditions as typically assumed. The strong seasonal bias in pedogenic carbonate formation has the following implications for the development of calcic soils and for the use of pedogenic carbonate as a paleoenvironmental proxy.

(1) The seasonal variation in soil $CO_2$ concentrations driven by wet-dry cycles may be the most important factor in the mobilization and deposition of carbonate in soils. In stronger monsoon climates, seasonal wet-dry cycles may enable pedogenic carbonate formation despite high mean annual precipitation. In continental and other climates where precipitation is more evenly distributed throughout the year, pedogenic carbonate likely forms during droughts.

(2) In semiarid or arid regions, pedogenic carbonate provides an artificially $C_4$-biased vegetation record. Although the carbon isotopic composition of pedogenic carbonate does not record the average composition of vegetation growing in these regions, it does vary between biomes and may, with further calibration, be used to distinguish between different paleobiomes.

(3) Failure to consider the effects of evaporation, which evidently influences soil water even below 50 cm in soils formed in arid regions, on the $\delta^{18}O$ value of pedogenic carbonate could result in underestimates of paleoelevation because calculated $\delta^{18}O$ values of meteoric water could be too high. The use of mean annual temperature to calculate $\delta^{18}O$ values of meteoric water from paleosol carbonate probably results in $\delta^{18}O$ water values that are slightly too low and therefore, all else being equal, overestimates of paleoelevation. It is possible that these underestimates and overestimates cancel each other.

(4) Low soil $CO_2$ concentrations during pedogenic carbonate formation (<1000–2000 ppm in the soils studied here) indicate that atmospheric $CO_2$ may have been previously overestimated using $\delta^{13}C$ values of paleosol carbonates.

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