

Pedothem carbonates reveal anomalous North American atmospheric circulation 70,000–55,000 years ago

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Our understanding of climatic conditions, and therefore forcing factors, in North America during the past two glacial cycles is limited in part by the scarcity of long, well-dated, continuous paleoclimate records. Here, we present the first, to our knowledge, continuous, millennial-resolution paleoclimate proxy record derived from millimeter-thick pedogenic carbonate clast coatings (pedothems), which are widely distributed in semiarid to arid regions worldwide. Our new multiisotope pedothem record from the Wind River Basin in Wyoming confirms a previously hypothesized period of increased transport of Gulf of Mexico moisture northward into the continental interior from 70,000 to 55,000 years ago based on oxygen and carbon isotopes determined by ion microprobe and uranium isotopes and U-Th dating by laser ablation inductively coupled plasma mass spectrometry. This pronounced meridional moisture transport, which contrasts with the dominant zonal transport of Pacific moisture into the North American interior by westerly winds before and after 70,000–55,000 years ago, may have resulted from a persistent anticyclone developed above the North American ice sheet during Marine Isotope Stage 4. We conclude that pedothems, when analyzed using microanalytical techniques, can provide high-resolution paleoclimate records that may open new avenues into understanding past terrestrial climates in regions where paleoclimate records are not otherwise available. When pedothem paleoclimate records are combined with existing records they will add complimentary soil-based perspectives on paleoclimate conditions.

paleoclimate | carbon oxygen uranium isotopes | U-series dating | pedogenic carbonate | Marine Isotope Stage 4

During the last two glacial–interglacial cycles, North America experienced some of its most variable and dramatic changes in climate during recent Earth history. These climates were not only temporally dynamic but also, spatially nonuniform (1, 2) in ways that are not yet completely clear. In part, this lack of clarity is because the most informative records—those that are long, continuous, and dated with millennial or better resolution—have been derived primarily from speleothems and/or lake sediments that are absent or rare in large regions of the continent.

In contrast, soil carbonate is nearly ubiquitous in arid and semiarid climates, and pedothems (from Greek: *πέδον*, *pedon*, “soil”; and *θέμα*, *théma*, “deposit”), consisting of dense laminated pedogenic carbonate clast coatings, are common in these regions (*SI Appendix*, Fig. S1). After they are formed, pedothems are geochemically closed and retain intact U-Th systematics as evidenced by coherent monotonic age progressions spanning tens of thousands of years (*SI Appendix*, Figs. S2–S4). Stable isotopes of O and C, strongly bound in the carbonate group, also retain their original isotopic compositions and can provide continuous records of paleoclimate conditions for soils that have persisted through millennia of subaerial exposure (3, 4).

Here, we show that micrometer-scale variations in O, C, and U isotopic ratios in carbonate pedothems preserve a continuous, datable record of environmental conditions for the last 120 ka (thousand years) in soils of the Wind River Basin (WR) of northwestern Wyoming. This record was accessed by applying laser ablation U-series dating and ion microprobe C and O stable isotope analyses. Developing this approach and applying it to midcontinent North America allow us to examine a nearly continuous record of the hydroclimates of the most recent glacial cycles in central North America, a region where records of such duration are otherwise unavailable. These data are then compared with other continental records and atmospheric circulation simulations (2, 5–9) to provide deeper insight into the spatial and temporal variabilities in North American paleoclimate.

A midcontinent North American climate record is of particular interest, because previous work (3) has hinted that, during Marine Isotope Stage 4 (MIS 4; 71–57 ka) (10), atmospheric circulation over North America shifted from a state dominated by easterly flow of Pacific Ocean-sourced moisture to one dominated by northerly flow of Gulf of Mexico-sourced moisture into the continental interior. If correct, such a shift in atmospheric circulation should produce an identifiable signal in the O isotope composition of precipitation and

Significance

We show for the first time, to our knowledge, that pedogenic (soil) carbonate mineral accumulations can preserve continuous paleoclimate records that rival the temporal resolution of widely used archives, such as speleothems or lake sediments. Using microanalysis of oxygen, carbon, and uranium isotopes coupled with uranium series dating, we find evidence for a distinct shift in atmospheric circulation in North America’s interior from 70,000 to 55,000 years ago, a finding that highlights the influence of large continental ice sheets on atmospheric circulation. Perhaps most significantly, this work shows that pedothems, which are common in arid and semiarid regions around the world, are a rich archive of paleoclimate information for continental landscapes.

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the productivity of regional flora that are recorded in the O and C isotopic compositions of pedogenic carbonate as we show below.

Carbonate Pedothems

The WR contains a suite of Pleistocene fluvial terraces capped by soils that have persisted through multiple glacial–interglacial climates (3, 4, 11). These soils contain carbonate pedothems consisting of millimeter-thick sequences of conformable laminations attached to the bottoms of alluvial gravel clasts. The O isotopic composition of the carbonate ($\delta^{18}\text{O}_c$) should reflect the O isotope composition of precipitation ($\delta^{18}\text{O}_p$) (3) mediated by the soil temperature during carbonate precipitation if evaporative enrichment can be excluded as we discuss below. Although $\delta^{18}\text{O}_p$ is correlated with atmospheric temperature, storm moisture source and trajectory also play a strong role, especially in midlatitudes (12–14). The C isotope composition of pedogenic carbonate ($\delta^{13}\text{C}_c$) is controlled by the proportion of C3- to C4-type vegetation and the soil respiration rate, which are both affected by mean annual temperature and mean annual precipitation (MAP) amount (15, 16). When secondary carbonate forms in soils, U is incorporated at parts per million levels, whereas poorly soluble Th is not; thus, U-series dating techniques may be applied (4, 17). Furthermore, during decay of ^{238}U to its daughter nuclide ^{234}Th , an α -particle (^4He) is ejected from the ^{238}U nucleus. The resulting ^{234}Th recoils in the mineral matrix, making it and its daughter ^{234}U vulnerable to mobilization by soil water movement. This process enriches the ^{234}U : ^{238}U ratio of soil pore water, with greater enrichment during periods of low soil water flux. As a result, the initial ^{234}U : ^{238}U ratio of pedogenic carbonate (^{234}U : $^{238}\text{U}_i$), which may be calculated from the measured ^{234}U : ^{238}U ratio and the associated U-Th age, is inversely related to the rate of soil water infiltration and reflects changes in paleoprecipitation amount (9, 18). Thus, using these three isotope systems, pedogenic carbonate records past precipitation source, vegetation type and amount, and precipitation amount. In this study, we developed time series of O, C, and ^{234}U : ^{238}U isotope ratios from transects through laminated pedogenic carbonate clast coatings.

We collected clasts with attached pedothems (*SI Appendix, Fig. S1*) from soil trenches in fluvial terrace 4 of (11) in the WR (43.198°, –108.769°) (Fig. 1). The age of stabilization of the fluvial terrace surface and the onset of soil development is estimated to be 167 ka (± 6.4) based on ^{230}Th /U dating of the innermost carbonate of pedothem samples collected from various soil depths and analyzed in previous work (4). Two samples from different locations in the 20- to 73-cm-deep soil horizon (samples A-2-07A and A-2-05B) were cut, polished, and inspected to locate regions of dense, translucent primary carbonate. Ages along the transects were constrained by ^{230}Th /U dates determined by laser ablation inductively coupled plasma (ICP) -MS on adjacent 93- μm -diameter spots (*Methods, Fig. 2, and SI Appendix, Figs. S2–S4 and Table S1*), with age models constructed using the StalAge algorithm (19). Variations in $\delta^{18}\text{O}_c$ and $\delta^{13}\text{C}_c$ along the transects were measured by ion microprobe using 10- μm -diameter spots (*Methods, Fig. 2, and SI Appendix, Figs. S5–S8 and Tables S2 and S3*). These in situ microanalytical techniques provided time series with approximately millennial resolutions over most of their lengths, despite rates of carbonate formation that are typically $<100 \mu\text{m ka}^{-1}$ (Fig. 3*G*).

An essential aspect in determining whether $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values can be interpreted in terms of climatic influence is the extent to which equilibrium isotopic fractionation during calcite precipitation can be assumed. We performed paired C and O isotope analyses along carbonate laminations on three laminations from sample A-2-07A to examine the isotopic variability within carbonate of similar age (*SI Appendix, Table S4*). These three individual carbonate laminations show variability in $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ values only slightly outside of 2-SD uncertainty limits of individual analysis spots. We interpret these along-lamination transects to confirm that carbonate of similar ages is isotopically

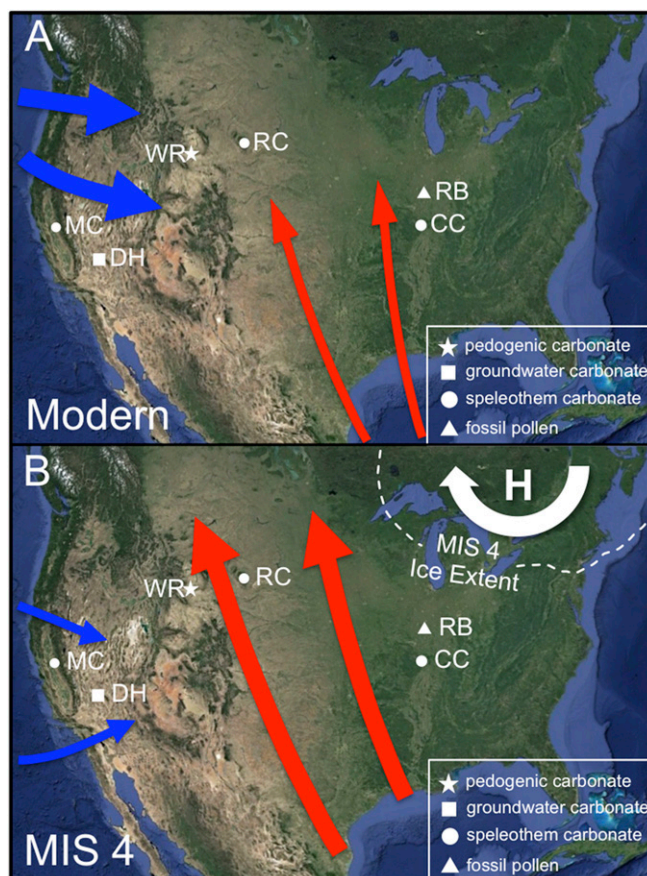


Fig. 1. Maps of (A) modern and (B) MIS 4 midlatitude North America atmospheric circulation scenarios. Blue arrows denote winter zonal atmospheric circulation; red arrows denote summer meridional circulation. The white arrow denotes persistent MIS 4 anticyclone. Locations are discussed in the text. CC, Crevice Cave, Missouri; DH, Devil's Hole, Nevada; MC, McLean's Cave, California; RB, Raymond Basin, Illinois; RC, Reed's Cave, South Dakota; WR, Wind River Basin, Wyoming.

homogeneous at the spatial scale of individual secondary ion mass spectrometry (SIMS) analysis spots ($\sim 10 \mu\text{m}$).

We measured similar isotope records in three time-transgressive transects on two different samples from different locations in the 20- to 73-cm-deep soil horizon, suggesting that the isotopes reflect conditions inherent to the soil rather than clast-scale processes. Accordingly, we merged results for these three transects into a composite dataset (designated WR A-2). To facilitate comparison with other data, we smoothed temporal trends in WR A-2 with a Gaussian kernel smoother at 0.5-ka bandwidth (Fig. 3 and *SI Appendix, Figs. S5–S8*) (20).

Modern Climate and $\delta^{18}\text{O}_c$ and $\delta^{13}\text{C}_c$ Values in the WR

The modern mean annual air temperature and MAP at our study site [43.198°, –108.769°; 1,679 m.a.s.l. (meters above sea level)] are $6.3 \text{ }^\circ\text{C}$ ($\pm 0.8 \text{ }^\circ\text{C}$) and 231 mm ($\pm 70 \text{ mm}$), respectively. Summer [June, July, August, September (JJAS)] mean air temperature and precipitation amounts are $17.2 \text{ }^\circ\text{C}$ ($\pm 3 \text{ }^\circ\text{C}$ intraseason) and 90 mm ($\pm 8 \text{ mm}$ intraseason), respectively (21). Nonsummer (months excluding JJAS) precipitation is dominated by zonal storm flow originating in the north Pacific, with average $\delta^{18}\text{O}_p$ values of -15.0‰ [Vienna Standard Mean Ocean Water (VSMOW)], and provides 61% of modern MAP. Summer (JJAS) meridional flow with average $\delta^{18}\text{O}_p$ values of -10.9‰ (VSMOW) is derived from the Gulf of Mexico and provides 39% of modern MAP (21–23).

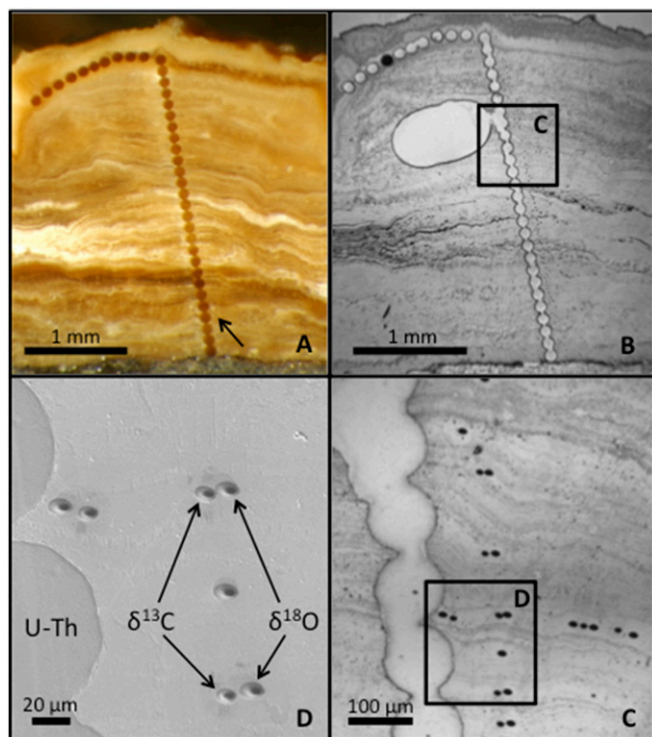


Fig. 2. Reflected light photomicrographs and SEM images of sample A-2-07A Traverse B. (A) Laser ablation ICP-MS analysis transects across (time-transgressive; arrow) and along (near-synchronous) pedogenic carbonate laminations. (B) $^{230}\text{Th}/\text{U}$ calibration sample (light gray; now filled with epoxy) drilled from the white oval with a 300- μm -diameter dental burr and analyzed using the spiked solution ICP-MS technique. (C) Magnified area of the box in B showing placement of paired SIMS spots for C and O analyses next to laser ablation ICP-MS spots (lighter gray; now filled with epoxy) produced during U-Th analyses for U-series dating and determination of initial U isotope ratios. Multiple SIMS spots along a single carbonate lamination (near center) show the reproducibility of C and O isotopic compositions at near-synchronous positions along the lamination. (D) Magnified area of the box in C showing detail of the spatial arrangement of C, O, and U-Th analysis spots.

The volume-weighted average annual $\delta^{18}\text{O}_p$ value is -13.4‰ (VSMOW).

Calculation of the expected $\delta^{18}\text{O}_c$ values of carbonate formed in equilibrium with $\delta^{18}\text{O}_p$ (or conversely, estimating past $\delta^{18}\text{O}_p$ from observed $\delta^{18}\text{O}_c$ values) requires consideration of the seasonality and temperature of soil carbonate formation. Soil carbonate formation occurs during periods of soil dewatering (24) and based on mean temperatures of pedogenic carbonate formation using Δ_{47} (“clumped” isotope) measurements, takes place at a range of temperatures from mean annual air temperature to warmer, depending on the seasonality of precipitation and soil dewatering and soil depth of carbonate formation (25–27). Measurements of pedogenic carbonate formation temperatures using Δ_{47} in southern Wyoming suggest that carbonate forms at temperatures that, in some cases, are 3 °C to 5 °C warmer than summer season air temperatures (i.e., ~ 20 °C to 22 °C) (28). Measured $\delta^{18}\text{O}_c$ values of Holocene pedogenic carbonates from southern Wyoming at elevations within ± 300 m of our study site have an average value of -11.9‰ [Vienna Pee Dee Belemnite (VPDB)] (28). This value is similar to the calculated $\delta^{18}\text{O}_c$ of carbonate formed in equilibrium with summer precipitation and summer air temperatures at our study site, which is -11.3‰ (VPDB). These predicted modern and measured Holocene $\delta^{18}\text{O}_c$ values are similar to the mid-Holocene $\delta^{18}\text{O}_c$ datum obtained from WR A-2 (-10.83‰ at 7.3 ka) (Fig. 3B

and *SI Appendix, Table S2*). Average $\delta^{13}\text{C}_c$ values of pedogenic carbonates in Holocene terraces in the WR are -3.6‰ ($\pm 0.6\text{‰}$; VPDB) (3), similar to the youngest $\delta^{13}\text{C}_c$ values in the WR A-2 record (Fig. 3F and *SI Appendix, Table S3*). Thus, the C and O isotopic compositions of the youngest laminations in the WR A-2 record are similar to those expected to form under modern conditions.

North American Paleoclimate Revealed by Pedothem Data

The WR multiisotope proxy record reported here begins at 120 ka (Fig. 3B and *SI Appendix, Tables S2 and S3*). The sampling frequency from 120 to 70 ka is low because of slow carbonate growth rates, and the $\delta^{18}\text{O}_c$ values vary $\sim 1\text{‰}$ around a mean of -11.2‰ from 120 to 70 ka. The trend of decreasing $\delta^{13}\text{C}_c$ values between 120 and 100 ka (Fig. 3F) is interpreted to reflect increases in soil and plant respiration rates. This trend was likely associated with warming temperatures in phase with increasing northern hemisphere summer solar insolation (Fig. 3A) after the end of the penultimate glaciation (29). From 100 to 80 ka, $\delta^{13}\text{C}_c$ values increase (Fig. 3F), suggesting a decrease in soil respiration rates likely caused by colder conditions that inhibit biological activity. A shift in vegetation C3:C4 ratios could explain changes in $\delta^{13}\text{C}_c$ values, but there is no evidence of this in the WR region (30).

A sharp increase in $\delta^{18}\text{O}_c$ values of $\sim 2\text{‰}$ occurs at ~ 70 ka, coincident with the onset of MIS 4 (Fig. 3B). Several effects could drive such an increase, such as change in the temperature during carbonate formation, increased evaporative enrichment of soil waters, change in the relative proportions of moisture derived from Pacific and Gulf of Mexico sources, or change in the seasonality of soil carbonate formation. It is important to consider the effects of temperature change during MIS 4 when global average temperatures were 2 °C to 5 °C lower than modern temperature (31). Temperature-dependent oxygen isotope fractionation between soil water and carbonate would be expected to yield higher $\delta^{18}\text{O}_c$ values at a rate of $0.2\text{‰ } ^\circ\text{C}^{-1}$ in response to colder temperatures. However, a temperature decrease of 10 °C is required to produce the $\sim 2\text{‰}$ increase observed in WR A-2 $\delta^{18}\text{O}_c$ values during MIS 4, which is not consistent with MIS 4 summer temperature estimates in Wyoming that are only 2 °C lower than modern temperatures (32). We also note that lower air temperatures should result in lower $\delta^{18}\text{O}_p$ values if moisture sources remained the same (12, 13), partially offsetting the effects of lower air and soil temperatures on carbonate–water fractionation.

Higher $\delta^{18}\text{O}_c$ values could result from increased evaporation of soil water; however, increased evaporative enrichment during MIS 4 is not consistent with decreased Northern Hemisphere summer insolation (Fig. 3A) and global cooling at this time (32, 33). Moreover, model-based simulations of paleoatmospheric circulation indicate that MIS 4 summers were 10–20% more cloudy than modern (32), indicating that the observed increase in $\delta^{18}\text{O}_c$ values is not because of ^{18}O enrichment by increased evaporation. Below, we consider change in the relative proportions of moisture sources and change in the seasonality of soil carbonate formation as other explanations for increased $\delta^{18}\text{O}_c$ values during MIS 4.

Anomalous Atmospheric Circulation 70,000–55,000 y Ago

Currently, $\sim 60\%$ of MAP in the WR is derived from the north Pacific and transported by zonal flow during the nonsummer months. The remaining $\sim 40\%$ of MAP is summer (JJAS) rain and primarily delivered by meridional flow from the Gulf of Mexico (21, 22, 34) (Fig. 1A). Holocene carbonate $\delta^{18}\text{O}_c$ values in Wyoming at elevations within ± 300 m of our study site reflect equilibration at summer soil temperatures, with soil waters having $\delta^{18}\text{O}$ values between MAP and summer precipitation (28). Thus, the $\delta^{18}\text{O}_c$ values that we observe in the WR A-2 record during MIS 4 most likely also reflect a mixed signal from soil waters derived from both winter and summer precipitation.

carbonate rinds along with small portions of the attached clasts of 4-mm thickness and 5-mm width were cut from the larger samples and cast into ~25-mm-diameter epoxy rounds (Buehler Epo-Thin) along with several grains of UW-C-3 calcite standard ($\delta^{18}\text{O}_c = -17.88\text{‰}$ VPDB; $\delta^{13}\text{C}_c = -0.91\text{‰}$ VPDB) (41). These mounts were polished by hand on rotary disk laps with 9- and then, 3- μm -diameter alumina–water slurry. Additional rotary polishing was done with 3- and 0.25- μm diamond paste in oil followed by a final hand polish with colloidal silica solution (0.05 μm), providing a flat polished surface. The polished samples were then cleaned and sputter-coated with Au to a thickness of ~60 nm. Samples were inspected with a Hitachi S3400N Scanning Electron Microscope at 1,000 \times magnification in secondary electron and backscattered electron modes to identify the most suitable SIMS sampling domains according to the criteria of (i) the most visible pure carbonate with no inclusions or discernable laminations with no other phases present and (ii) no cracks or voids in the sample surface. The large-radius, multi-collector CAMECA IMS 1280 at WiscSIMS focuses an $\sim 1.7\text{-nA } ^{133}\text{Cs}^+$ primary beam on the sample surface. The primary beam ablates 10- μm -diameter pits to a depth of $\sim 1\ \mu\text{m}$ by ablating $\sim 2\ \text{ng}$ carbonate. The spot to spot

reproducibility values for the data reported here are $\leq \pm 0.30\%$ 2 SDs for $\delta^{18}\text{O}$ and $\leq \pm 1.47\%$ 2 SDs (but typically $\sim \pm 0.70\%$) for $\delta^{13}\text{C}$. The reproducibility is determined by averaging the results of typically 8 UW-C-3 standard analyses that bracket each group of 10–15 sample analyses (42). After SIMS analysis, each analysis pit was imaged by SEM to confirm its location, the absence of cracks or inclusions, and symmetric pit shape.

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