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Quaternary International 67 (2000) 29–36

A paleoclimate reconstruction for southwestern Texas using oxalate residue from lichen as a paleoclimate proxy

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Received 15 January 2000; accepted 10 February 2000

Abstract

A calcium oxalate rock coating is ubiquitous on limestone surfaces inside dry rock shelters and under rock overhangs within the canyons of the southwestern Edwards Plateau in southwestern Texas. The oxalate was likely produced by epilithic lichens that flourished in these niches during dry climate regimes. During wet climate conditions the productivity of the lichen would be severely reduced due to physiological response to moisture regime. Thus, lichen productivity and the production of calcium oxalate may have changed through time in response to wet–dry climate fluctuations. Twenty-five AMS radiocarbon ages of rock crust samples collected from 14 sites demonstrate that oxalate was produced episodically during the middle and late Holocene. The occurrence of oxalate is correlated with periods of dry climate, whereas gaps in the record of oxalate deposition coincide with more mesic climate intervals. The results of this study demonstrate the potential for obtaining paleoclimate data from biogenic residues on rock surfaces. © 2000 Elsevier Science Ltd and INQUA. All rights reserved.

1. Introduction

Variations in global climate appear to have become more complex during the middle and late Holocene (O'Brien et al., 1995), which increases the difficulty of resolving the mechanisms of short-term (decadal/centennial scale) climate fluctuations and predicting near-future climate changes due to anthropogenic greenhouse gas emissions. To discriminate between potential mechanisms of short-term climate fluctuations (Rind and Overpeck, 1993) superimposed on modifications due to orbital variations will require high-resolution (decadal/centennial scale) paleoclimate data from various physiographic sections. Most continental paleoclimate records are based on fossil pollen, glacial advances and retreats, tree-line migrations, tree-rings, ice-core variations, and lake level changes which have provided a consistent centennial-scale Holocene climate record for northern latitudes (Williams and Wigley, 1983). However, these proxies are generally unavailable in arid and semi-arid regions, so data for paleoclimate modeling for areas such as the southwestern United States rely primarily on assemblages in pack rat middens, augmented with pollen data from archaeological sites and the occasional bog (e.g., Thompson et al., 1993). New sources of paleoclimate information are required to test and supplement existing data for many arid/semi-arid regions.

We present a new strategy for obtaining paleoclimate information using residues from past lichen activity on rock surfaces as a climate proxy. Many lichens occur only within specific environments; thus, evidence of past production of lichen with specific environmental requirements, coupled with radiocarbon dates of biogenic residues, could possibly provide high resolution paleoclimate information. Our study focuses on calcium oxalate produced by epilithic lichen that flourished episodically in southwestern Texas. We report here a paleoclimate reconstruction for the middle and late Holocene based on the temporal distribution of this biogenic residue, and compare these results with previous paleoclimate records from the region.

2. Study area

The southwestern Edwards Plateau near the confluences of the Pecos and Devils Rivers with the Rio Grande

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PII: S1040-6182(00)00006-9

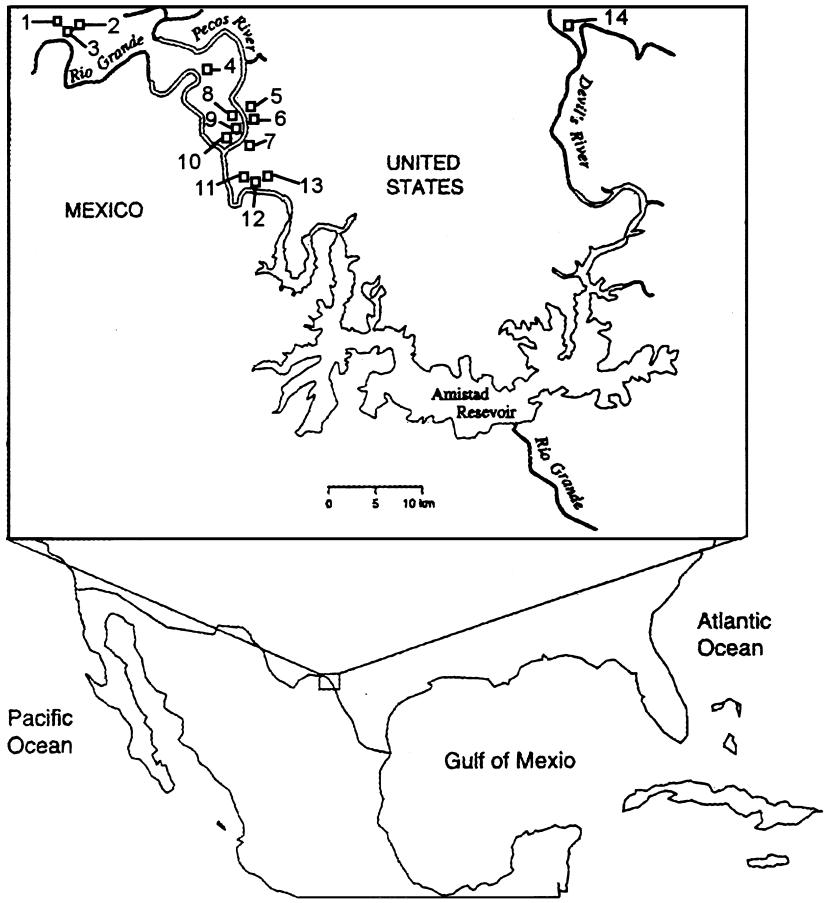

Fig. 1. Map showing the study area, which includes the region surrounding the confluences of the Pecos and Devils Rivers with the Rio Grande. Samples were collected from under rock overhangs and inside dry rock shelters between 29°39′ to 29°50′N and 100°51′ to 101°35′W. Closed circles mark approximate locations of sampled sites.

(Fig. 1) is an extensive Cretaceous limestone tableland with steep canyons incised by the rivers and tributaries. The canyon walls contain numerous dry rock shelters and rock overhangs that shield rock surfaces from rain and runoff. Limestone surfaces exposed to rain and runoff are generally coated with a dark stain (Fig. 2), while surfaces in sheltered areas are covered with a pale-brown (5 YR 7/4) to reddish brown (5 YR 4/4) calcium oxalate coating that was likely produced by past lichen activity (Russ et al., 1996). With the exception of small patches of lichen found at several sites, there is very little evidence of current lichen activity on surfaces within these shelters.

The present climate in the study area is semi-arid, with a mean annual rainfall of 498 mm. Mean annual temperature is 20.5°C, while annual mean maximum and minimum temperatures are 27.0°C and 13.9°C, respectively.

Records of Holocene climate change for the region have been established using palynological data from archaeological sites (Bryant and Holloway, 1985), the combination of palynological, plant macrofossil, and vertebrate fossil data (Toomey et al., 1993), and geomorphic interpretations (Blum et al., 1994). These reconstructions indicate a general decrease in effective moisture beginning at the end of the Pleistocene, with xerophytic plant species appearing $\sim$7000 rcyr BP.[1] There is general consensus that the driest interval occurred between 5000 and 2500 rcyrs BP, followed by a return to mesic conditions ca. 2500 rcyrs BP. However, Bryant and Holloway (1985) describe this mesic interval as brief, whereas Toomey et al. (1993) and Blum et al. (1994) suggest an extended period of relatively moist climate, possibly lasting until ca. 1000 rcyrs BP. The availability of paleoclimate proxies used for these reconstructions is limited

[1] We use rcyrs BP to refer to uncalibrated radiocarbon ages, and cal. yrs BP to refer to radiocarbon ages that have been calibrated using Calibeth Version 1.5 ETH Zurich (Swiss Federal Institute of Technology).

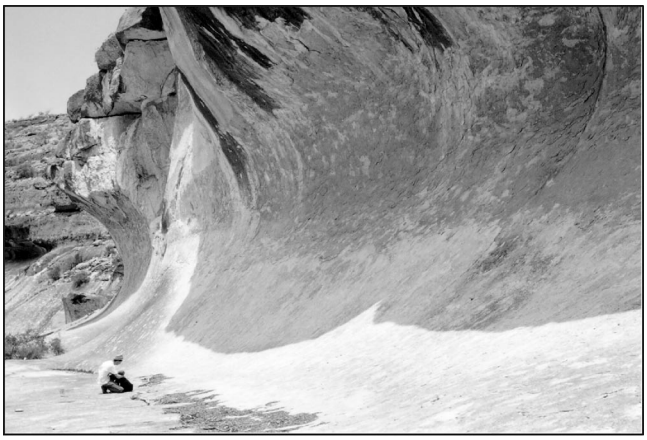

Fig. 2. Photograph showing a typical rock overhang. The rock surface protected from rain and runoff under the overhang is completely covered by the yellowish-brown calcium oxalate coating, while a dark stain (black) occurs on surfaces exposed to rain and runoff.

for the last 1000 years, but xeric conditions are generally inferred.

3. Calcium oxalate as a paleoclimate indicator

Calcium oxalate (whewellite, $CaC_2O_4 \cdot H_2O$) occurs as a thin coating (usually $\lesssim 0.5$ mm but up to 1.0 mm thick) on limestone surfaces that are sheltered from direct rain or runoff throughout the southwestern Edwards Plateau. The source of the calcium oxalate appears to be epilithic lichen based on morphological and biochemical similarities between the rock crust and recent lichen residues found in two sites (Russ et al., 1996). Gypsum ($CaSO_4 \cdot 2H_2O$) also occurs within the crust and in the basal limestone near the crust/substrate interface. The reported source of the gypsum is precipitation of calcium sulphate from water saturated with the ions percolating through the substrate and evaporating at the surface (Turpin, 1982). Silicates comprise a minor crust component, and are probably derived from eolian dust adhering to the surfaces when damp from dew or fog (Curtiss et al., 1985).

The ubiquity of oxalate on limestone surfaces that are not exposed to rain or runoff indicates that lichen flourished in these niches at some time in the past. We suggest the maximum productivity of the organism occurred during extremely dry climate conditions that reduced the moisture content of the Edwards limestone plateau. The desiccated rock surfaces would then provide the ideal substrate on which the lichen would thrive by allowing the organism to obtain requisite moisture via water vapor uptake, the most efficient mechanism for some xeric lichen species (Lange et al., 1988; Lange and Green, 1996). During relatively wetter periods the increased moisture content of the limestone plateau would reduce the productivity of the lichen due to a variety of possible physiological responses, which include blockage of CO_2 diffusion pathways in the thallus (Palmer and Friedmann, 1990; Lange and Green, 1996), a water imbalance that severely limits either the fungal or algal components of the lichen (Kappen, 1973, p. 325), or response to freezing water (Kappen, 1973, p. 328). Moreover, since substrate water would be saturated with calcium and sulfate ions due to dissolution of gypsum at the crust surface, the pH and/or ionic environment might also be deleterious to the lichen. Hence, we infer the lichen productivity and the production of calcium oxalate changed through time in response to fluctuations in the moisture regime.

To establish a record of climate change we measured the radiocarbon ages of calcium oxalate to establish periods of lichen productivity. We correlate clusters of ^{14}C data to dry climate regimes, whereas relatively wetter conditions correspond to gaps in the ^{14}C ages indicating periods of little or no oxalate production.

4. Experimental methods

Samples were collected at sites located between 29°39′ and 29°50′N and 100°51′ and 101°35′W by removing portions of limestone with attached crust from vertical or near vertical walls in rock shelters and under rock overhangs (Fig. 1). A specimen that contained a layer of prehistoric rock paint was also included in this study and was used to provide stratigraphic control. The expected age of the paint is between 2950 and 4200 rcyrs BP, based on previous radiocarbon studies of prehistoric paints from the region (Russ et al., 1990, 1992; Ilger et al., 1995).

Samples were analyzed using a JEOL 6400 scanning electron microscope (SEM) with an energy dispersive X-ray analyzer (EDS) and a binocular microscope to exclude those that showed evidence of recent biological activity or multiple periods of oxalate deposition. However, three samples that showed stratification of crust constituents (41VV167-1, 41VV129-1 and 41VV128-7) were selected for radiocarbon dating, with the upper and lower crust strata removed and analyzed independently. The prehistoric paint sample (41VV129-1) also showed stratification of crust constituents (Fig. 3), and each layer was removed and dated separately.

Samples were prepared for AMS ^{14}C dating by removing loose detritus from the surface by light scrubbing with deionized water. Between 10 and 30 cm^2 of the oxalate crust was removed from the substrate using a dental pick or mini-drill, ground with an agate mortar and pestle, then digested in 5% double distilled acetic acid or dilute phosphoric acid to remove carbonates. Samples were washed, filtered and dried, then combusted

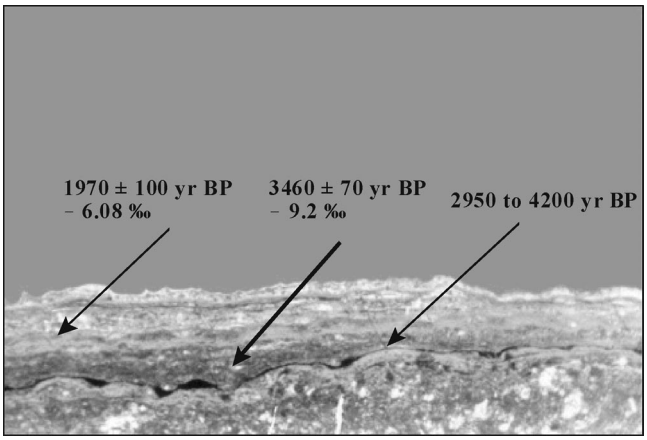

Fig. 3. Cross-sectional view of sample 41VV129-1 showing stratification of rock crust and layer of prehistoric rock paint. Two crust strata were removed and ^{14}C dated separately, yielding the ages 1970 ± 100 and 3460 ± 70 cal. yr BP for upper and lower layers, respectively. The crust covers a paint layer expected to have been produced between 2950 and 4200 yr BP, therefore the ages of the crust strata and paint layer are stratigraphically consistent. (Scale = 1 mm.)

at 950°C in the presence of CuO to produce CO_2. Graphite targets were prepared from the CO_2 using standard protocol for the AMS radiocarbon analysis (Vogel et al., 1987). The radiocarbon analysis was performed at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratories. When sufficient sample remained, a second aliquot was converted to CO_2 and the stable carbon isotope ratio ($\delta^{13}C_{PDB}$) measured by isotope ratio mass spectrometry (Boutton, 1991). These values were used for ^{14}C age corrections where available, otherwise the mean $\delta^{13}C_{PDB}$ value was used (Stuiver and Polach, 1977). Calibrated ^{14}C ages were calculated using Calibeth Version 1.5 ETH Zurich (Swiss Federal Institute of Technology).

Seventeen samples from 14 sites were included in this study, with the aim of establishing periods of oxalate production at various sites (Fig. 1). Also, multiple samples from three sites were analyzed to provide intra-site comparisons of oxalate ^{14}C ages. These include: (i) four samples from site 41VV89, two of which were collected ~ 1 m apart (41VV89-6A and 41VV89-5B),[2] a third from ~ 36 m away (41VV89-26), and a split of 41VV89-6A (41VV89-6A1 and 41VV89-6A2); (ii) two samples collected ~ 3 m apart from site Pressa4 were split, one into thirds (labeled Pressa4-1A, Pressa4-1B and Pressa4-1C) the other in half (labeled Pressa4-3A and Pressa4-3B), providing five ^{14}C ages from this site; and (iii) two samples collected ~ 16 m apart in site 41VV167, one of which (41VV167-1) showed a stratified crust so the upper and lower strata were removed and dated independently. The second sample from this site (41VV167-3) was used to test the acid treatment process described below.

Standards for radiocarbon and stable carbon isotope analyses were prepared from solutions of NBS ^{14}C standard oxalic acid (SRM 4990-C) and calcium chloride hydrate (99.99 + %) by mixing the solutions and filtering the calcium oxalate precipitant. Two samples (labeled CaOx 1-S and CaOx 2-S) were processed in the acetic acid solution, then washed and dried, while one sample (CaOx 3-S) remained untreated. The three samples were split, then processed for radiocarbon analysis.

Because we were concerned that clays in the samples could absorb acetate from the acetic acid during the removal of carbonates, we began using dilute phosphoric acid instead of acetic acid for the latter half of the samples radiocarbon dated. To test whether the acid type had an effect on the radiocarbon and stable carbon isotope measurements, we analyzed standard and crust (41VV167-3) sample splits, half of which were prepared using acetic acid while the other half using dilute phosphoric acid.

5. Results and discussion

5.1. Standards

AMS ^{14}C results from the standards demonstrate that the sample pretreatment protocol does not have a measurable affect on the radiocarbon ages and stable carbon isotopic values (Table 1). Furthermore, ^{14}C ages and $\delta^{13}C_{PDB}$ values obtained from the calcium oxalate standard and four crust sample aliquots digested in either acetic acid or phosphoric acid are statistically indistinguishable, indicating the type of acid used does not affect age or isotopic determinations (Table 2). Finally, radiocarbon ages from sample 41VV129-1 that contained two independent crust strata and a layer of prehistoric paint at the substrate/crust interface are in the correct stratigraphic order. The paint layer, expected to have been produced between 2950 and 4200 rcyrs BP, was below an oxalate stratum with an uncalibrated radiocarbon age of 3220 ± 60 rcyrs BP while the upper crust stratum produced an uncalibrated radiocarbon age of 2000 ± 80 rcyrs BP.

5.2. ^{14}C age distribution

The temporal distribution of radiocarbon ages indicates that the production of calcium oxalate occurred episodically during the middle to late Holocene, and nearly simultaneously at several sites at various times. For example, three overlapping ^{14}C ages (1970 ± 100, 2070 ± 90 and 2080 ± 120 cal. yr BP) indicate that

[2] Sample labels beginning with number 41 were collected from archaeological sites, where 41 indicates Texas, VV for Val Verde County, followed by the site number and then the sample number.

Table 1
AMS ^{14}C ages and $\delta^{13}C_{PDB}$ values of the calcium oxalate standard and 41VV167-3 sample aliquots used to test the experimental protocol and the affect of different acids on the analytical results[a]

Sample No.	CAMS No.	Fraction modern	^{14}C age (yr BP)	$\delta^{13}C_{PDB}$ (‰)[b]
Calcium oxalate standard				
CaOx 1-S	14412	1.3355 ± 0.0072	> Modern	
CaOx 1-S	14415	1.3436 ± 0.0088	> Modern	
CaOx 2-S	14413	1.3446 ± 0.0087	> Modern	
CaOx 2-S	14416	1.3516 ± 0.0076	> Modern	
CaOx 3-S	14414	1.3480 ± 0.0093	> Modern	
CaOx 3-S	14417	1.3374 ± 0.0132	> Modern	
Calcium oxalate standard treated with acetic (CH_3CO_2H) and phosphoric acids (H_3PO_4)				
S1-a (CH_3CO_2H)	29404	1.3307 ± 0.0067	> Modern	− 16.79
S1-b (CH_3CO_2H)	29405	1.3369 ± 0.0077	> Modern	− 16.60
S2-a (H_3PO_4)	29406	1.3434 ± 0.0068	> Modern	− 16.33
S2-b (H_3PO_4)	29407	1.3368 ± 0.0067	> Modern	− 16.21
Aliquots of sample 41VV167-3				
41VV167-3a (H_3PO_4)	29408	0.8443 ± 0.0054	1360 ± 60	− 9.92
41VV167-3b (H_3PO_4)	29409	0.8522 ± 0.0060	1280 ± 60	− 10.60
41VV167-3c (CH_3CO_2H)	29410	0.8467 ± 0.0048	1340 ± 50	− 10.24
41VV167-3d (CH_3CO_2H)	29411	0.8544 ± 0.0048	1260 ± 50	− 10.20

[a]Expected fraction modern of calcium oxalate control = 1.341.
[b]Measured $\delta^{13}C_{PDB}$ value of untreated calcium oxalate control = − 16.74‰.

oxalate production occurred at three different sites (41VV129, 41VV167 and 41VV83, respectively) at essentially the same time. We suggest that there were four primary periods of oxalate production based on clustering of the ^{14}C data (Table 2, Fig. 4). The average age difference within the defined clusters is less than 170 cal. yr BP, while the average age between the clusters is 810 cal. yr BP. Each cluster consists of data from multiple sites, which further supports concurrent lichen activity within various sites in the region.

5.3. Inter-site comparisons

The four ^{14}C ages from site 41VV89 range from 680 ± 80 to 1240 ± 30 cal. yr BP, all of which fall within the earliest cluster. The radiocarbon ages of the sample split (41VV89-6A and 41VV89-6A2) were 1240 ± 60 and 990 ± 60 cal. yr BP, respectively, whereas the ages of samples collected ~ 1 m (41VV89-5B) and ~ 36 m (41VV89-26) apart were 680 ± 80 and 820 ± 60 cal. yr BP, respectively. The scatter of data could indicate the rate at which the lichen spread in the site, different episodes of oxalate production, or inherent errors in the ^{14}C ages from the oxalate.

Five radiocarbon ages were obtained from two samples from site Pressa4. The first sample, Pressa4-1, was divided into approximately three equal splits, and the results showed disparate ^{14}C ages (Table 3). The second sample from this site, Pressa4-3, was split into halves, and yielded overlapping ages (6030 ± 80 and 6080 ± 80 cal. yr BP). Overall, the five ^{14}C ages from two Pressa4 samples ranged from 4140 ± 100 to 7320 ± 70 cal. yr BP. This strongly suggests multiple episodes of oxalate production within this site and on a small area of rock surface, and points to a potential problem for obtaining ^{14}C ages from single samples corresponding to one period of lichen productivity. We opted not to use the data from Pressa4-1 in our reconstruction because of the likelihood that the ages do not represent single episodes of oxalate production.

Multiple periods of lichen productivity within some sites is further evident by radiocarbon ages from stratified samples. The three samples where upper and lower oxalate strata were removed and analyzed separately yielded results which show that each strata within the individual sample was produced at a different time. From sample 41VV167-1 we obtained ^{14}C ages of 1360 ± 50 and 2070 ± 90 cal. yr BP for top and bottom layers, respectively, whereas for 41VV128-7 ages of 3010 ± 110 and 4670 ± 100 cal. yr BP were obtained for upper and lower layers. As previously noted, the sample with a paint layer (41VV129-1) also contained a stratified crust that yielded radiocarbon ages of 1970 ± 100 and 3460 ± 70 cal. yr BP for the upper and lower strata, respectively.

5.4. Paleoclimate reconstruction

We suggest that periods of high lichen productivity (as established by clusters of oxalate ^{14}C ages) reflect dry

Table 2
AMS ^{14}C ages and $\delta^{13}C_{PDB}$ values of oxalate crust

Location	Site and sample No.[a]	CAMS No.	^{14}C age (yr BP)[b]	$\delta^{13}C_{PDB}$ (‰)	Calibrated age (cal. yr BP)[c]	Calendar age (AD/BC)
9	41VV89-5B	15131	730 ± 80	− 12.93	680 ± 80	1270
9	41VV89-26	15130	890 ± 60	− 13.70	820 ± 60	1130
9	41VV89-6A2	15134	1060 ± 60	—	990 ± 60	960
3	41VV167-3[d]	[e]	1310 ± 30	− 10.24[d]	1240 ± 30	710
9	41VV89-6A1	15133	1330 ± 60	—	1240 ± 60	710
3	41VV167-1A (T)[f]	31153	1440 ± 60	—	1360 ± 50	590
11	41VV75-1	15132	1830 ± 70	—	1760 ± 80	190 AD
5	41VV129-1A (T)	15146	2000 ± 80	− 6.08	1970 ± 100	20 BC
12	41VV83-1[e]	[e]	2080 ± 90	—	2080 ± 120	130
3	41VV167-1B (B)	31154	2080 ± 60	− 9.7	2070 ± 90	120
7	41VV123-10	15135	2730 ± 50	− 8.3	2840 ± 50	890
6	41VV128-7B (T)	15143	2860 ± 80	− 7.59	3010 ± 110	1060
10	Pecos WB-2	31156	2860 ± 80	− 11.1	3010 ± 110	1060
4	41VV576-Ac	15145	3020 ± 70	− 9.85	3220 ± 100	1270
5	41VV129-1B (B)	15147	3220 ± 60	− 9.2	3460 ± 70	1510
2	Skiles-2	31155	3400 ± 60	− 11.6	3670 ± 90	1720
1	41VV165-1A	31162	3500 ± 60	− 11.7	3790 ± 80	1840
13	Pressa4-1A[g]	31157	3750 ± 60	− 11.6	4140 ± 100	2190
8	41VV90-1	11437	3990 ± 60	− 9.5	4500 ± 110	2550
6	41VV128-7D (B)	15144	4130 ± 60	—	4670 ± 100	2720
13	Pressa4-1C[g]	31159	4400 ± 60	− 11.6	5020 ± 120	3070
13	Pressa4-3A	31160	5230 ± 50	− 11.6	6030 ± 80	4080
13	Pressa4-3B	31161	5290 ± 60	− 11.4	6080 ± 80	4130
14	41VV888-1	11438	5570 ± 60	—	6380 ± 60	4430
13	Pressa4-1B[g]	31158	6420 ± 60	− 12.4	7320 ± 70	5370

[a]41VV- prefixes refer to archaeological sites; names (Skiles, Pressa, and Pecos) refer to non-archaeological sites. Parenthesized letters (T) and (B) refer to upper and lower crust strata, respectively, that were removed and analyzed separately.
[b]The measured $\delta^{13}C_{PDB}$ was used to calculate the ^{14}C age when available; otherwise, the average $\delta^{13}C_{PDB}$ value (− 10.5‰) was used for the calculation.
[c]Calculated using Calibeth Version 1.5 ETH Zurich (Swiss Federal Institute of Technology).
[d]Represents an average of four aliquots, two digested in 5% double-distilled acetic acid and two digested in dilute phosphoric acid.
[e]Datum is an average of 3 aliquots radiocarbon dated independently.
[f]The letters in parentheses in the first column refer to upper (T) and lower (B) strata from samples that showed two oxalate layers that were removed and analyzed separately.
[g]Data not used in paleoclimate reconstruction (see text).

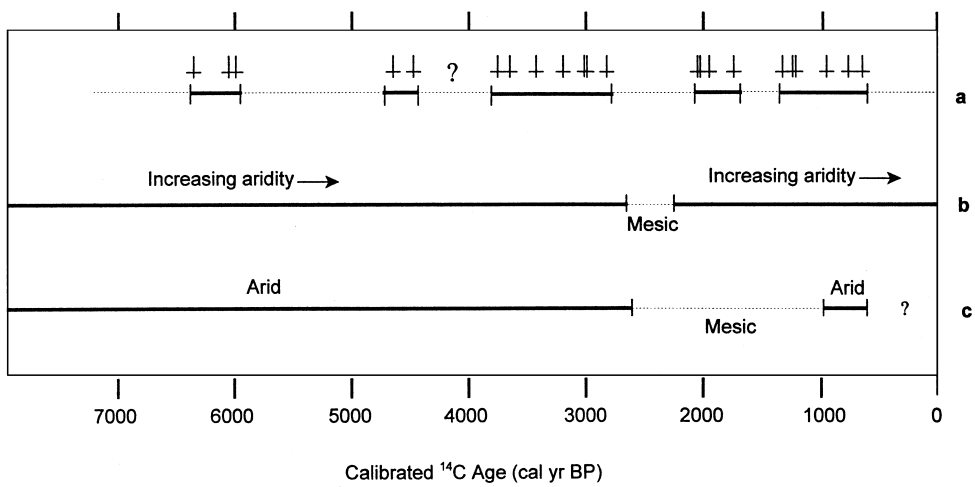

Fig. 4. (a) Temporal distribution of calibrated ^{14}C ages (cal. yr BP) of calcium oxalate residues from the southern Edwards Plateau. We propose that clusters of radiocarbon ages indicate dry climate periods, while gaps in the data correspond to periods of more wet conditions. We show four xeric episodes, punctuated by five mesic episodes. Also shown are paleoclimate reconstructions by (b) Bryant and Holloway (1985) based on palynological data and (c) Toomey et al. (1993) based on palynological, plant macrofossil, and vertebrate fossil data. Solid lines show arid periods, while dotted lines indicate mesic intervals. Arrows in B indicate periods of increasing aridity.

climate periods due to increased temperature and/or reduced precipitation (Fig. 3). Gaps in the oxalate ^{14}C record are interpreted as relatively wetter conditions when the lichen was absent or dormant. Accordingly, five xeric episodes are postulated for the middle and late Holocene: from 6380 to 6030 cal. yr BP, from 4670 to 4500 cal. yr BP, from 3790 to 2840 cal. yr BP, from 2080 to 1760 cal. yr BP, and from 1360 to 680 cal. yr BP. More moist conditions appear to have occurred during intervening periods (Fig. 3). The paucity of ^{14}C ages older than 6380 cal. yr BP limits our ability to evaluate earlier climate regimes.

This reconstruction is consistent with previous records from the southwestern Edwards Plateau (Bryant and Holloway, 1985; Toomey et al., 1993; Blum et al., 1994) in predicting the onset of dry climate at 7320 cal. yr BP (6420 rcyrs BP), and a dominant warm period from 5020 to 2840 cal. yr BP (4400–2730 rcyrs BP). We also agree with a return to wet–cool conditions $\sim$2500 rcyrs BP with a mesic period from 2840 to 2080 cal. yr BP (2730–2080 rcyrs BP); however, our data would suggest a brief xeric period between 2080 and 1760 cal. yr BP (2080–1830 rcyrs BP), followed by a return to more mesic conditions from 1760 to 1360 cal. yr BP (1830–1440 rcyrs BP). These ephemeral wet/dry climate episodes could account for the inconsistency between the previous reconstructions. It is possible that Bryant and Holloway (1985) recorded the rapid return to dry conditions after the brief mesic interlude at 2500 rcyrs BP, but failed to resolve the ensuing wet period that we indicate between 1830 and 1330 rcyrs BP. Toomey et al. (1993) and Blum et al. (1994) did not interpret a brief return to dry conditions after about 2070 rcyrs BP, resulting in the prediction of an extended wet period. Finally, our reconstruction does not match the dry conditions for the last 1000 years inferred by Bryant and Holloway (1985), Toomey et al. (1993) and Blum et al. (1994). Instead, we predict more moist conditions from about 730 rcyrs BP to the present.

5.5. Limitations and future directions

The results of this study indicate an episodic production of biogenic calcium oxalate in southwestern Texas, and thus presents a potential means for obtaining paleoclimate information based on radiocarbon ages from the residue. However, the reliability of oxalate radiocarbon ages representing wet–dry climate fluctuations is subject to three assumptions: (1) oxalate was produced only during dry climate conditions; (2) multiple episodes of oxalate production can be distinguished in samples selected for radiocarbon dating; and (3) bicarbonate from the substrate was not metabolized by the lichen. For assumption 1, similarities in the micromorphology and chemistry of the oxalate crust throughout the southern Edwards Plateau (Russ et al., 1996), as well as the characteristic microenvironment in which it occurs, suggests the biogenic substance was produced by either a single or similar lichen species. Further studies are needed to determine whether biomarker compounds occur in the crust, so specific organisms can be identified as the source of the oxalate. If the 2nd assumption is not true then measurements of oxalate ^{14}C ages would produce dates that are average ages of two or more periods of oxalate deposition, and would not correspond to climate regimes. We analyzed samples using optical microscopy and SEM in an attempt to exclude such samples in our data base. Moreover, we suggest new methods using lasers to combust independent oxalate strata in microstratified crusts (Watchman et al., 1993) could possibly be employed in future experiments to provide the selectivity in stratified samples. Finally, the 3rd assumption would cause anomalously old ^{14}C ages due to inclusion of "dead" carbon from the limestone. This does not occur to a substantial degree since the ^{14}C ages are relatively recent. Much older dates would be obtained if significant amounts of bicarbonate were incorporated within the oxalate. Furthermore, radiocarbon ages of discrete oxalate layers from stratified crust samples were in stratigraphic order, including the paint layer in sample 41VV129-1, further demonstrating that little if any limestone carbon was metabolized by the lichen.

The oxalate $\delta^{13}C_{PDB}$ values (mean $= -10.6‰$; range $= 7.6‰$) indicate an enrichment in ^{13}C compared to previous reports of $\delta^{13}C_{PDB}$ for lichen thalli, which range from -35 to $-14‰$ (Lange et al., 1988). As we argue above, the primary enrichment in ^{13}C cannot be due to an incorporation of limestone carbon. Instead, we suggest the ^{13}C enrichment reflects a specific metabolic shift such as that shown by Rivera and Smith (1979) for the production of solid oxalate by cacti. We cannot, however, rule out a minor bicarbonate component in the production of oxalate.

Finally, reconstructing wet–dry climate shifts based on lichen productivity requires sufficient clumping of the oxalate ^{14}C ages to differentiate between periods of oxalate production and episodes when no oxalate was produced. For our current data set (calibrated radiocarbon ages) we tested the uniformity of the temporal distribution of the ^{14}C ages across the interval of 0–ca. 7500 cal. yr BP using a Chi-square test of the deviation of the frequency of radiocarbon ages from a Uniform distribution (using BestFit software, Palisade Corp.). For this purpose, this interval was subdivided into a series of shorter time intervals and the frequency of ages within those intervals were tallied. Results therefore depend on the length of the intervals chosen. Five tests were run with 8–20 categories (intervals of ca. 350 to 900 yr). In no case did the Chi-square value approach significance (range of > 0.53 to > 0.85); thus, the statistical test does not indicate any deviation from a uniform distribution of

radiocarbon data. While more robust statistical treatments could be established to discriminate between data clusters in the present set, it is clear that additional radiocarbon data are required to obtain confidence in representing climate regimes based on clusters of ^{14}C ages.

6. Conclusions

Twenty-five AMS radiocarbon ages of calcium oxalate-rich rock crust samples from 14 sites in southwestern Texas suggests that oxalate was produced episodically during the middle and late Holocene. The occurrence of oxalate is correlated with periods of aridity, whereas gaps in the record of oxalate deposition are interpreted to coincide with more mesic intervals. The results of this study demonstrate the potential for obtaining paleoclimate data from biogenic residues on rock surfaces. Lithobiont communities are common in desert regions (Staley et al., 1982), and the distribution of these communities is dependent on environmental conditions (Danin, 1986, 1993). Knowledge of past activity of lichen or microbes with specific climate requirements, coupled with radiocarbon ages of metabolic byproducts, could provide a new source of paleoclimate information.

Acknowledgements

We thank J. Labadie, E. Brotherton, N. Chavez, D. Ing and J. Skiles for help with field work; R. Modarres, C. Christophi and G. Goodfriend for the statistical analysis; R. Palma and R. Cox for helpful discussions; and J. Southon for the AMS dating. Support for this research was provided by a Cottrell Science Award of Research Corporation, a grant from the National Center for Preservation Technology and Training, and an Arkansas State University Faculty Grant. We further acknowledge the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research.

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