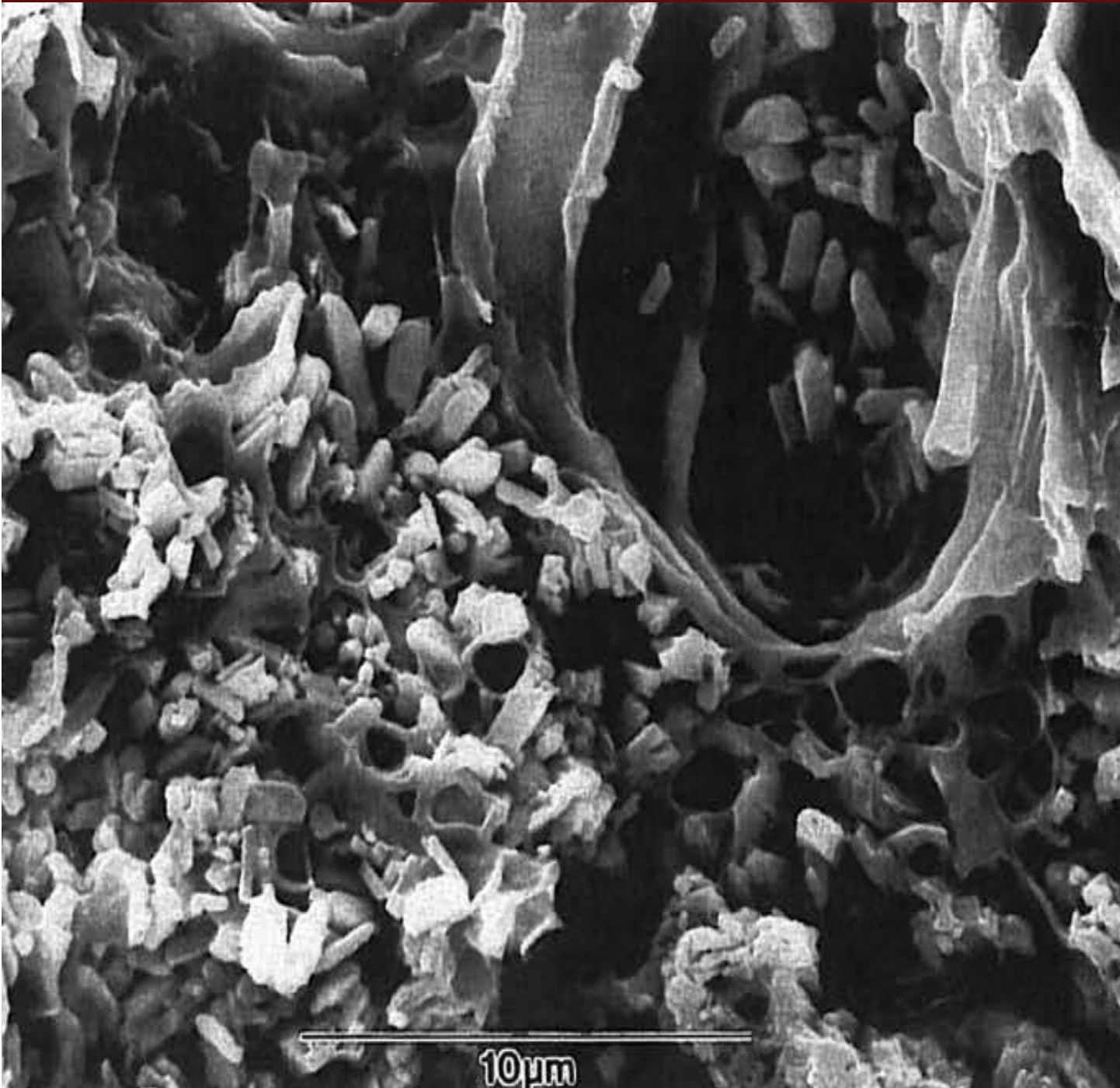




Origin of the Whewellite-Rich Rock Crust in the Lower Pecos Region of Southwest Texas and its Significance to Paleoclimate Reconstructions | 1996-03



National Park Service
U.S. Department of the Interior



National Center for Preservation Technology and Training

Origin of the Whewellite-Rich Rock Crust in the Lower Pecos Region of Southwest Texas and its Significance to Paleoclimate Reconstructions

JON RUSS

Department of Chemistry, Newberry College, Newberry, South Carolina 29108

RUSSELL L. PALMA

Department of Physics, Sam Houston State University, Huntsville, Texas 77341

DAVID H. LOYD

Department of Physics, Angelo State University, San Angelo, Texas 76909

THOMAS W. BOUTTON

Department of Rangeland Ecology and Management, Texas A&M University, College Station, Texas 77843

AND

MICHAEL A. COY

Electron Microscopy Center, Texas A&M University, College Station, Texas 77843

Received February 21, 1996

A calcium oxalate (whewellite)-rich crust occurs on exposed limestone surfaces in dry rock and open air shelters in the Lower Pecos region of southwest Texas. The crust, which also contains gypsum and clay, formed over silica-rich limestone during the Holocene. SEM and optical photomicrographs reveal similarities between whewellite microstructures and the lichen *Aspicilia calcarea*. This desert lichen is known to produce calcium oxalate, and has been found in several sites in the region. The ubiquity of the whewellite-rich crust in the Lower Pecos shelters suggests that the lichen flourished in the past. Since *A. calcarea* is a desert species, the virulence of the organism likely peaked during xeric climate episodes then waned during mesic periods. Thus, radiocarbon ages of whewellite would correspond to dry climate periods experienced in the region, while periods with few or no ^{14}C data would indicate wet climate episodes. A preliminary paleoclimate reconstruction based on fourteen AMS ^{14}C dates indicates the Lower Pecos experienced dry to wet climate fluctuations during the late Holocene. This reconstruction generally agrees with other models established for Texas.

INTRODUCTION

Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) is the primary constituent of a rock crust that occurs inside dry rock and open air shelters in the Lower Pecos region of southwestern Texas (Russ et al., 1994, 1995). Whewellite, and the polyhydrate weddellite, were generally considered rare in geological environments (Graustein et al., 1977; Žák and Skála, 1993), but are now known to be common components in natural rock accretions (Del Monte and Sabbioni, 1987; Del Monte et al., 1987; Watchman, 1990, 1991; Edwards et al., 1991; Scott and Hyder 1993; Chaffee et al., 1994; Watchman et al., 1995). Evidence indicates that some oxalate-rich crusts are produced by lichens (Del Monte and Sabbioni, 1987; Del Monte et al., 1987; Russ et al., 1995), although other biological and nonbiological mechanisms have also been proposed (Lazzarini and Salvadori, 1989; Watchman, 1990, 1991).

Characteristics of rock crusts are known to reflect the time frame and climate conditions present when they formed, and thus provide archaeological, geological, and paleoclimate information. For example, Dorn and his colleagues developed experimental methods for dating petroglyphs (e.g., Dorn and Whitley 1983) and geological events (Dorn et al., 1987; Dorn et al., 1987), and for establishing paleoenvironmental conditions (Dorn and DeNiro, 1985) based on properties of rock varnish. Watchman (1993) demonstrated the great antiquity of some Australian rock art by radiocarbon dating laminae of oxalate-rich crusts associated with a prehistoric rock painting. Also,

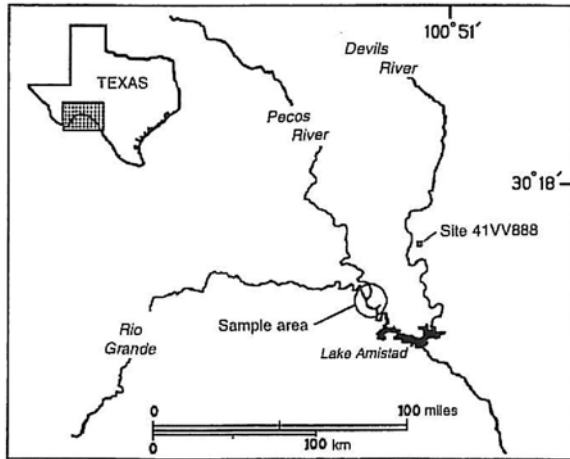


Figure 1. Map showing the geographical location of the study area.

Dragovich (1988) proposed paleoclimate changes using radiocarbon ages of calcium carbonate from carbonate-varnish stratification. We describe here the origin of a whewellite-rich rock accretion in the Lower Pecos region of Texas and propose its use as a paleoclimate indicator.

STUDY AREA

This study focuses on the rock crust that occurs in sheltered areas in the limestone cliffs along the lower Pecos River, the Rio Grande near the Pecos confluence, and canyon tributaries of the two rivers (Fig. 1). One sample (888-1) from a dry canyon near the Devils River was also included. The Lower Pecos region contains an extensive, nearly continuous archaeological record dating back more than 10,000 yr (Turpin, 1982; Hester, 1983, 1988) and is well known for extraordinary pictograph panels found at more than 250 sites. Rock art interpretation (Turpin, 1990) and ^{14}C dating (Russ *et al.*, 1990, 1992; Ilger *et al.*, 1995)

indicate that the oldest pictograph style, the Pecos River style, was produced between 4200 and 2950 yr B.P.

The Lower Pecos region is at the southwestern edge of the Edwards Plateau and is characterized by Cretaceous limestone, with deep canyons incised by the major rivers and their tributaries. Along the steep canyon walls are numerous dry rock shelters and rock overhangs. Exposed limestone in the canyons is covered with two distinct rock patinas: a dark-grey to black stain coats areas that receive direct rain and runoff, while a light-brown, whewellite-rich accretion covers surfaces inside sheltered areas. Because most pictographs occur in dry rock and open air shelters, the prehistoric paints are almost always associated with the whewellite-rich crust.

The present climate is semi-arid, with a mean annual rainfall of 498 mm/yr. Mean annual temperature is 20.5°C, while annual mean maximum and minimum temperatures are 27.0 and 13.9°C, respectively.¹

EXPERIMENTAL METHODS

Rock crust samples attached to the limestone substrate were collected from vertical or near vertical walls in rock shelters and under rock overhangs. Sampled areas were generally random within each site and away from painted areas, although paint samples from Pecos River style pictographs were included in this study. *Aspicilia calcarea* (identified by J. Marsh, personal communication, 1994), a lichen with a white surface deposit (pruina), was found in two shelters and collected for this study.

The mineralogy of the crust was established using powder X-ray diffractometry (XRD). Samples were prepared by removing the crust from the substrate with a minidrill, then grinding to a powder using an agate mortar and pestle. We removed the entire thickness of the crust and a small part of the substrate to ensure that all of the crust was analyzed. The mineral distribution and external features of the crust were established using an optical microscope and a Jeol 6400 scanning electron microscope equipped with an energy dispersive X-ray analyzer (SEM/EDS). Polished thin-sections and broken sections of the crust and lichen *A. calcarea* attached to 1-cm aluminum stubs were studied.

Twelve samples from nine sites were radiocarbon dated by accelerator mass spectrometry (AMS). Ten of the samples showed a single layer of crust which was completely removed for the radiocarbon analysis. Two samples (128-7 and 129-1) showed two whewellite laminae which were removed and dated separately. A paint layer also observed in the lower whewellite lamina of sample 129-1 was included in the dated material. The amount of organic carbon from the paint was expected to be much less than 1% of the datable carbon (Russ *et al.*, 1992; Ilger *et al.*, 1995).

Samples prepared for ^{14}C dating first had loose detritus removed by light scrubbing of the crust surface with deionized water and drying at 100°C. While observing with a binocular microscope, 10 to 20 cm² of the crust was removed from the substrate using a minidrill. The crust material was ground with an agate mortar and pestle and digested in 5% double distilled acetic acid for 2 days to remove carbonates and sulfates. The samples were thoroughly washed using double distilled water to remove acetic acid, then filtered and dried at 100°C. Each sample

¹ Data from the National Oceanic and Atmospheric Administration Amistad Dam station from 1965 to 1994.

was combusted at 950°C in the presence of CuO to produce CO₂, which was then reduced to graphite with H₂ at 550°C in the presence of a cobalt catalyst. The graphite was submitted for radiocarbon dating to the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratories. When sufficient sample remained, a second aliquot was combusted at 950°C in the presence of CuO and the stable carbon isotope ratio ($\delta^{13}\text{C}_{\text{PDB}}$) of the resulting CO₂ measured on a Micromass 903 isotope ratio mass spectrometer (Boutton, 1991). Precision on $\delta^{13}\text{C}_{\text{PDB}}$ values was 0.1‰.

Calcium oxalate control samples for radiocarbon analysis were prepared from solutions of NBS standard ¹⁴C oxalic acid and calcium chloride hydrate (99.99+%) by mixing the solutions and filtering out the calcium oxalate precipitant. The control was divided into three samples, two of which were processed in the acetic acid solution, washed, and dried, while the other remained untreated. The three calcium oxalate controls were then processed for radiocarbon analysis.

RESULTS

Description of the Crust

The whewellite-rich rock crust appears very pale brown (10 YR 7/4; Munsell Soil Color Charts, 1994) to reddish brown (5 YR 4/4), generally with an irregular surface that has botryoidal and spherical protuberances extending about 0.5 mm above the surface (Fig. 2A). The morphology of these surface features resembles the surface of *Aspicilia calcarea* (Fig. 2B). The crust is thin, usually less than 0.5 mm thick but up to 1.0 mm thick, with most samples showing a single layer of crust, although several had distinct stratification. Pictograph samples have a thin (~0.1 mm), continuous layer of paint encapsulated within the crust. The paint layers did not appear disrupted, even when occurring near the bottom of the crust.

Whewellite, gypsum, quartz, and calcite were the principal minerals identified using XRD (Table 1). Two-dimensional elemental dot maps of polished thin sections showed silicon (quartz) nonuniformly distributed within the limestone substrate, while sulfur (gypsum) occurred primarily in the crust as well as in pore and fissure spaces in the substrate. The crust is composed of microcrystalline whewellite, with tabular gypsum occurring as layers and intrusions into the whewellite phase. Whewellite microstructures resembling the thallus of *A. calcarea* were observed in cross-sectioned views using SEM (Fig. 3). The crust also contained traces of clay, as indicated by aluminum and silicon peaks in EDS spectra, but no clay particles were observed using SEM. Evidence of microorganisms in crust samples were rarely observed, although Kaluarachchi (1995, p. 67) noted what appeared to be cocci bacteria in one of five Lower Pecos paint samples studied using SEM.

Description of Aspicilia calcarea

The lichen *A. calcarea* was ~0.2 mm thick and covered throughout with small (~1 μm) calcium oxalate crystals. XRD analysis of the lichen pruina indicated that weddellite (CaC₂O₄ (2 + x)H₂O) was the primary component, with quartz, calcite, and a trace of gypsum also present (weddellite was not observed in any of the crust samples). The lichen surface and thallus structures are shown in Figures 2 and 3, respectively.

Radiocarbon Ages and $\delta^{13}\text{C}_{\text{PDB}}$ of Whewellite

Radiocarbon ages and stable carbon isotope data for the 14 rock crust samples are shown in Table 2. The ages range from 730 ± 80 to 5570 ± 60 yr B.P., with the oldest date from a geographically distinct site (41VV888) near the Devils River. The remainder of the ¹⁴C ages fall into four clusters when plotted in temporal profile (Fig. 4). In cases where samples had two strata, a comparison of ages obtained for the upper (128-7B and 129-1A) and corresponding lower (128-7D and 129-1B, respectively) strata indicate internal consistency with stratigraphic conformability. The ages of the oxalate layers associated with the prehistoric paints were also consistent with previously deduced pictograph ages. For example, sample 129-1B (3220 ± 60 yr B.P.) contained prehistoric paint expected to date between 2950 and 4200 yr B.P. based on the pictograph style. Also, sample 576-Ac (3020 ± 70 yr B.P.) was collected from the same site as two pictographs dated 3000 ± 70 and 3355 ± 65 yr B.P. (Russ et al., 1992). Furthermore, sample 75-1 (1840 ± 70 yr B.P.) was taken from a site where the oxalate rock crust consistently overlies paints that are expected to date >2950 yr B.P. (Russ et al., 1992).

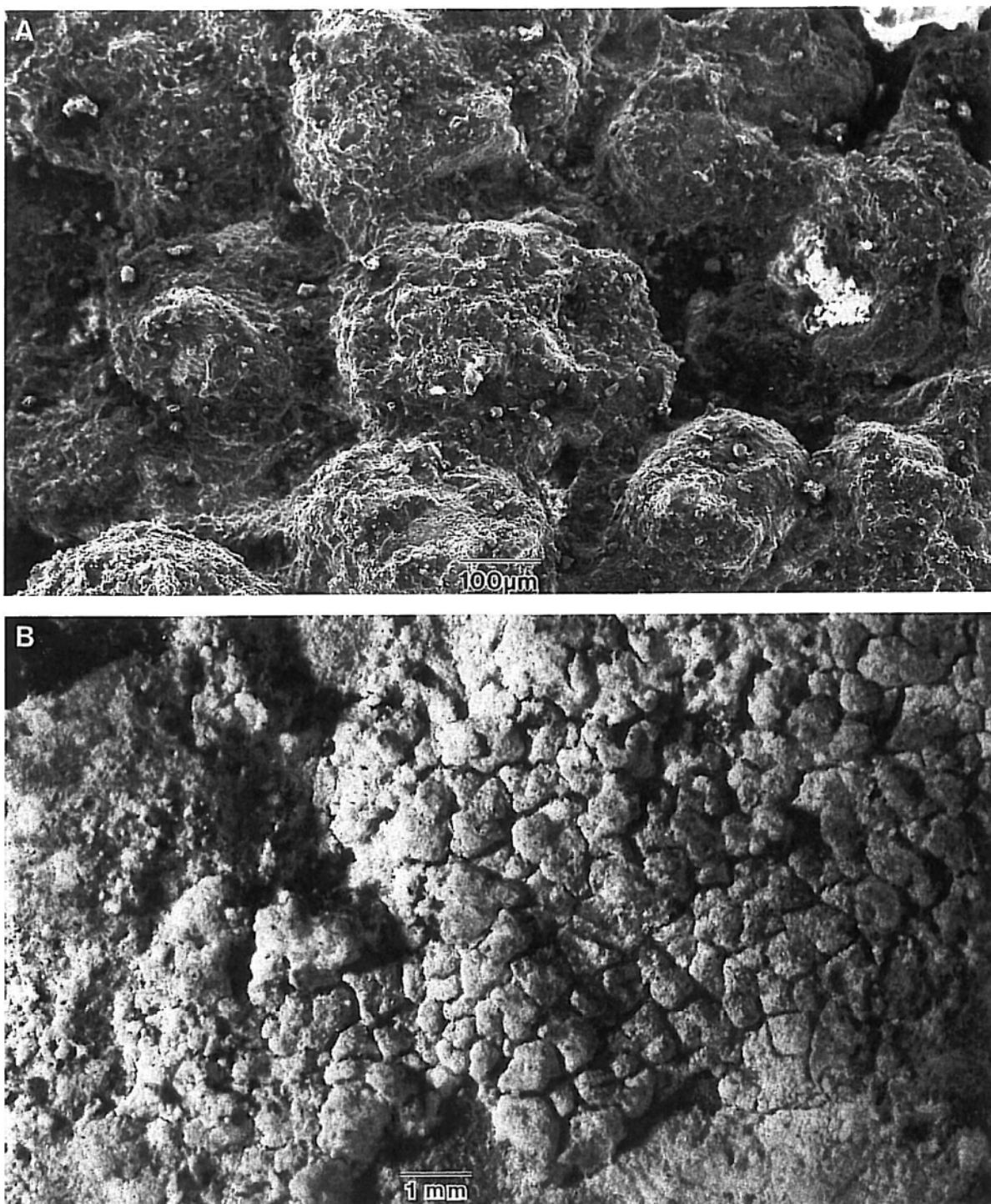


Figure 2. (A) SEM photomicrograph of whewellite-rich crust surface showing spherical protuberances. (B) Optical photomicrograph showing the surface of the lichen *Aspicilia calcarea*.

TABLE 1
Summary of X-Ray Diffraction Data for Rock Crusts and Lichen (*Aspicilia calcarea*) from the Lower Pecos Region

Site	Description	Mineral species ^a				
goatbone	Sample was from below a rock overhang; nonarchaeological site on east bank of Pecos River	wh		qtz	cal	
dinner plate	Sample was from below a rock overhang; nonarchaeological site on west bank of Pecos River	wh		qtz		
41VV18	Shallow rock shelter on east bank of Devils River	wh	gyp	qtz	cal	
41VV62	Rock shelter on west bank of Pecos River	wh		qtz	cal	
41VV65 (1)	Deep rock shelter on east bank of Pecos River	wh	gyp	qtz	cal	
41VV65 (2)	Deep rock shelter on the east bank of Pecos River	wh		qtz	cal	
41VV73	Large rock shelter in Seminole Canyon, a tributary of Rio Grande	wh		qtz	cal	
41VV76	Large rock shelter in Presa Canyon, a tributary of Rio Grande	wh	gyp	qtz	cal	
41VV78 (1)	Sample was from below a rock overhang on tributary of Rio Grande	wh		qtz	cal	
41VV78 (2)	Sample was from below a rock overhang on tributary of Rio Grande	wh	gyp	qtz	cal	
41VV83	Sample collected from under rock overhang adjacent to this rock shelter near west bank of Rio Grande	wh	gyp	qtz	cal	
41VV90	Deep rack shelter on Pecos River	wh	gyp	qtz	cal	
41VV210	Rock shelter on Pecos River	wh	gyp	qtz	cal	
41VV224	Rock shelter on west bank of Rio Grande	wh		qtz	cal	
41VV227	Rock shelter on wes1 bank of Rio Grande	wh	gyp	qtz	cal	
41VV888	Open shelter on tributary of Devils River	wh	gyp	qtz	cal	
41VV377	Lichen (<i>Aspicilia calcarea</i>) sample from shallow rock shelter in Pressa Canyon, a tributary of Rio Grande		gyp	qtz	cal	wed

^a Mineral identifications based on JCPDS nos. 20-321 for whewellite (wh), 33-311 for gypsum (gyp), 33-1161 for quartz (qtz), 24-27 for calcite (cal), and 17-541 for weddellite (wed).

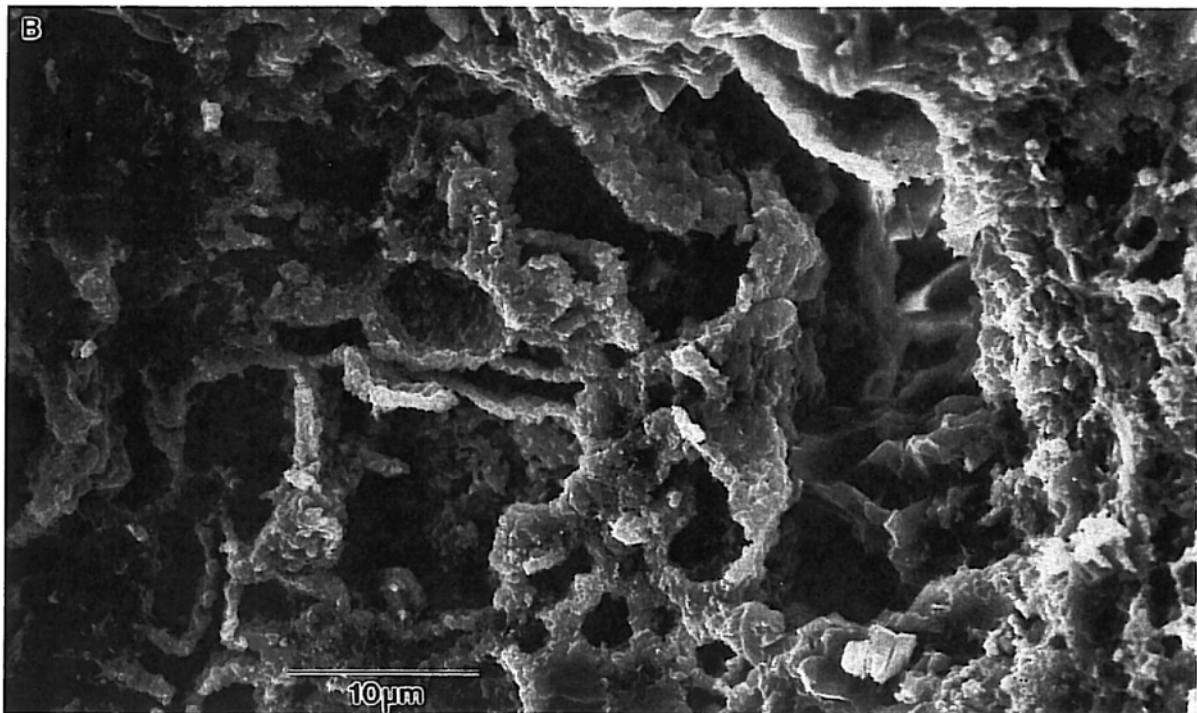
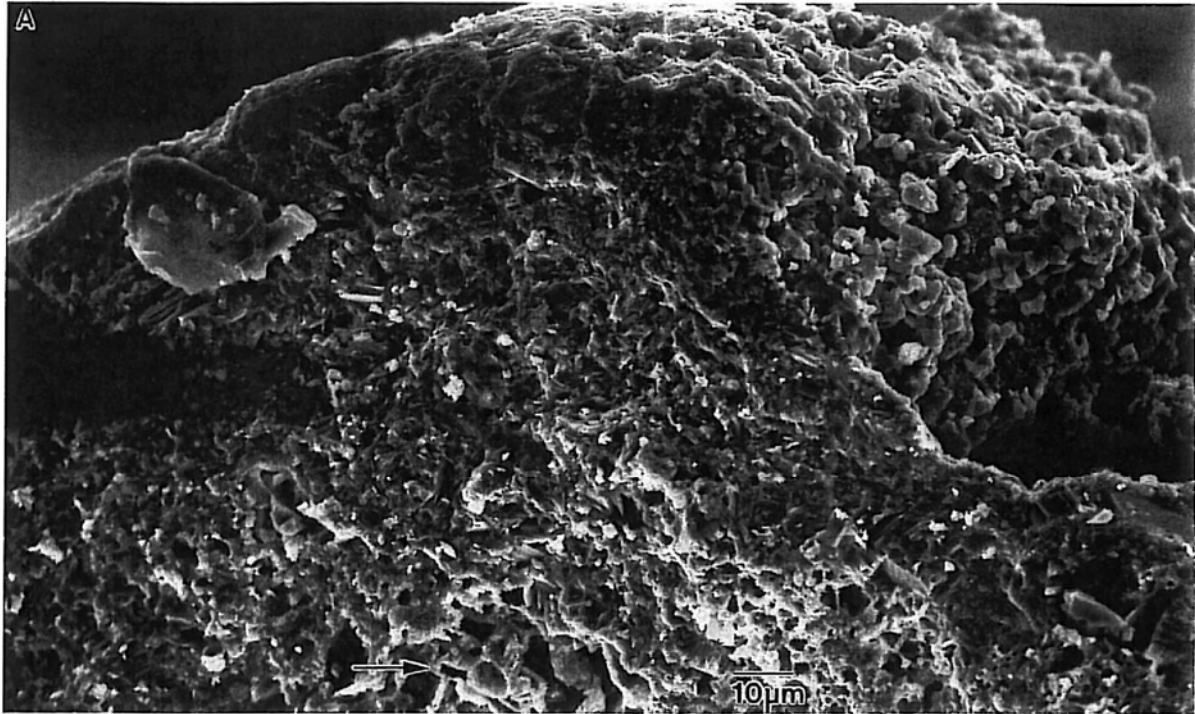
The results of the AMS calcium oxalate control samples, which were expected to have a fraction modern value of 1.341, ranged from 1.3355 ± 0.0072 to 1.3516 ± 0.0076 . These data show that the sample preparation did not have a measurable effect on the radiocarbon age of the crust samples.

The $\delta^{13}\text{C}_{\text{PDB}}$ values range from -6.08 to -13.70‰ (Table 2). No apparent correlation exists between the stable carbon isotope composition and the ^{14}C age, shelter type, distance from water, or thickness of crust.

DISCUSSION

Origin of the Whewellite-Rich Crust

The primary weathering occurring inside Lower Pecos rock shelters prior to the Holocene is thought to be limestone spalling induced by freeze–thaw cycles (Kochel, 1982, p. 268). Amelioration of the climate during the late Pleistocene/ early Holocene allowed the limestone walls inside the shelters to stabilize (D. G. Robinson, personal communication, 1995), and they have remained stable despite xeric-mesic fluctuations in the middle to late Holocene. The presence of intact Pecos River style rock art in more than 250 rock art sites indicates that many shelter walls have remained stable since at least 2950 to 4200 yr B.P.



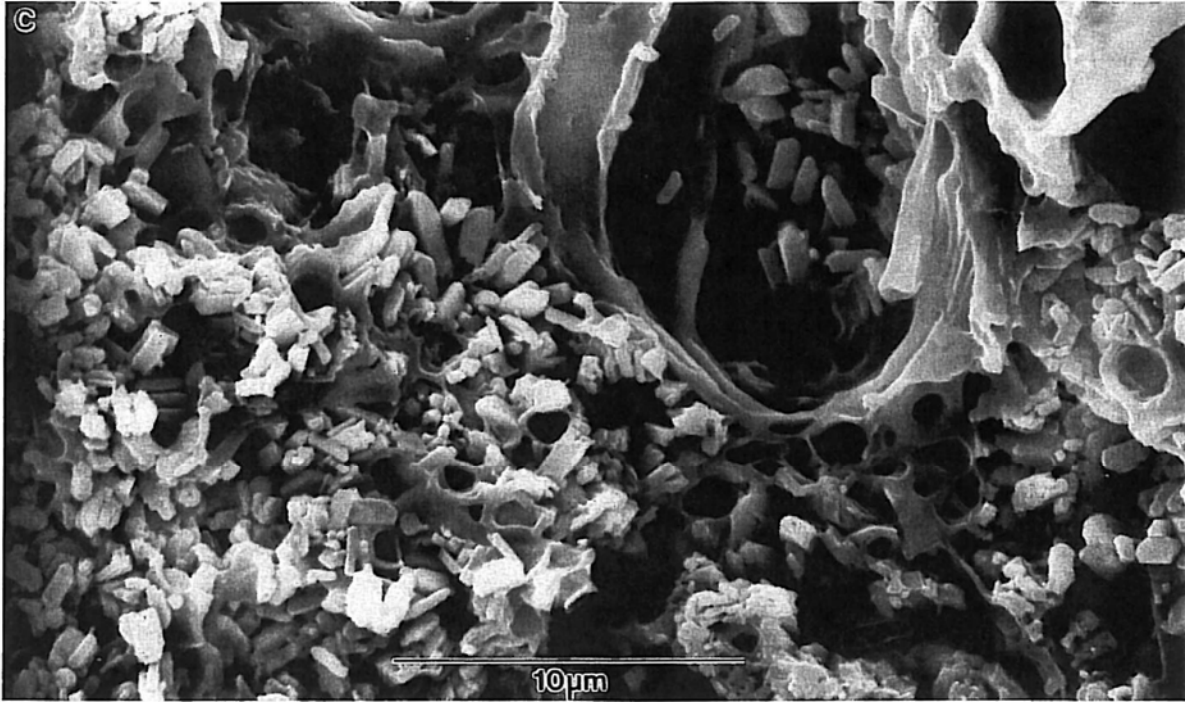


Figure 3. SEM photomicrographs of (A) whewellite microstructures in cross-sectional views of the crust; (B) magnified view of region indicated in 3A; and (C) cross-sectional view of the lichen *Aspiclia calcarea*.

The rock crust inside the shelters is composed of whewellite, gypsum, and clay, and covers limestone containing quartz. The gypsum results from efflorescence/subflorescence (Turpin, 1982, p. 197), processes that involve calcium and sulfate ions carried to the rock surface by water percolating through the substrate. Evaporation of the water at the rock surface causes gypsum to precipitate as layers and intrusions in the crust, and in the pores and fissures of the substrate (Winkler, 1975, pp. 117-119). The clay is likely derived from eolian matter adhering to the rock surfaces (e.g., Curtiss et al., 1985).

The evidence shows that the whewellite was likely produced by a lichen such as *A. calcarea* or a similar species (Russ et al., 1995). Whewellite microstructures in the crust are strikingly similar to features of *A. calcarea*, an epilithic lichen that occurs on limestone, produces calcium oxalate, inhabits cool or warm xeric environments, and does not contain rhizines (Poelt, 1973, p.619; Wadsten and Moberg, 1985). Because the paint layers below the crusts are not disrupted, it is inferred that the lichen that produced the whewellite was epilithic and without rhizines.

Lichens are well known to produce calcium oxalate (Syers et al., 1967; Wadsten and Moberg, 1985) that can form crusts on rock surfaces (DeI Monte et al., 1987). Moreover, they are known to colonize such special habitats with little or no precipitation, acquiring moisture from atmospheric water vapor (Lange, 1988). Although the pruina on the *A. calcarea* sample from the Lower Pecos is composed of weddellite, this mineral is metastable and decomposes to whewellite (Frey-Wyssling, 1981). Moreover, Ascaso et al. (1982) reported that lichens preferentially produce whewellite when on dry rock, and weddellite on rocks that are hydrated.

Fungi are also known to inhabit rocks in desert environments (Staley et al., 1982) and can produce calcium oxalate when associated with various soils (Graustein et al., 1977; Verrecchia, 1990; Verrecchia et al., 1990). However, the relative amount of calcium oxalate in the crust is far greater than that of the clay; thus, eolian transport could not supply the requisite organic matter necessary for fungi to produce the whewellite. Furthermore, studies of rock art dating (e.g., Ilger et al., 1995) have demonstrated that the limestone in the Lower Pecos region has a low content of organic matter.

The $\delta^{13}\text{C}_{\text{PDB}}$ values of the oxalate have a 7.62‰ range and are significantly higher than those reported for lichen thalli (Lange, 1988). This discrepancy could be due to the different metabolic pathways that produce thalli and exuded oxalate. For example, Rivera and Smith (1979) found that $\delta^{13}\text{C}_{\text{PDB}}$ of calcium oxalate (primarily whewellite) from cacti in western Texas was approximately 5‰ higher than that of woody fibers from the same plants. If calcium oxalate from lichens is also enriched by 5‰ relative to the remainder of the organism, then the intact lichens that produced the oxalate in Table 2 would have had $\delta^{13}\text{C}_{\text{PDB}}$ values ranging from -18.7 to -12.6‰. These

TABLE 2
Radiocarbon Ages and $\delta^{13}\text{C}_{\text{PDB}}$ Data of Oxalate Rock Crusts

Site no.	Sample no.	CAMS no.	^{14}C age ^a (yr B.P.)	Calibrated ^{14}C age ^b	$\delta^{13}\text{C}$ (‰ PDB)	Cluster
41VV89	89-5B	15131	730 ± 80	1265 ± 75 A.D.	-12.93	1
41VV89	89-26	15130	890 ± 60	1131 ± 63 A.D.	-13.7	1
41VV89	89-6A2	15134	1070 ± 60	952 ± 61 A.D.	*	1
41VV89	89-6A1	15133	1330 ± 60	707 ± 57 A.D.	*	1
41VV75	75-1	15132	1840 ± 70	175 ± 84 A.D.	-8.6	2
41VV129	129-1A ^c	15146	2000 ± 60	18 ± 71 B.C.	-6.08	2
41VV83	83-1	11146	2080 ± 50	114 ± 75 B.C.	*	2
41VV123	123-10	15135	2730 ± 60	898 ± 57 B.C.	-8.13	3
41VV128	128-7B ^c	15143	2860 ± 60	1055 ± 92 B.C.	-7.59	3
41VV576	576-Ac	15145	3020 ± 70	1266 ± 100 B.C.	-9.85	3
41VV129	129-1B ^d	15147	3220 ± 60	1513 ± 67 B.C.	-9.2	3
41VV90	90-1	11437	3990 ± 60	2547 ± 112 B.C.	-9.5	4
41VV128	128-7D ^d	15144	4130 ± 60	2723 ± 97 B.C.	*	4
41VV888	888-1	11438	5570 ± 60	4427 ± 112 B.C.	-10.5	

^a The measured $\delta^{13}\text{C}_{\text{PDB}}$ was used in calculating the ^{14}C age when available; otherwise, the average $\delta^{13}\text{C}_{\text{PDB}}$ (-9.4‰) was used for the calculation

^b Calibrated radiocarbon ages calculated using the computer program Calibeth Version 1.5 ETH Zurich (Swiss Federal Institute of Technology).

^c Top stratum of a two strata sample.

^d Lower stratum in a two strata sample.

* No data available.

values would be within the upper portion of the range reported for lichen thalli (-35 to -14‰; Lange and Ziegler, 1986). While the $\delta^{13}\text{C}_{\text{PDB}}$ results could indicate some bicarbonate effect, as Lapeyrie (1988) demonstrated for fungi, this is highly unlikely because this would produce anomalously old radiocarbon dates that would not be consistent with the age of the exposed rock surfaces and the associated paints.

Paleoenvironmental Implications

Many lichen species are known to occur within specific environmental regimes. Klappa (1979) recognized the far-reaching implications of understanding characteristic weathering features produced by past lichen activity for developing paleoclimate reconstructions. Danin et al. (1982; Danin, 1986, 1993) used lichen weathering features to develop a paleoclimate model for Israel, but the inability to date these features directly sometimes limits the accuracy of such reconstructions. From the evidence presented above, the whewellite in Lower Pecos rock crust is a biogenic residue produced by a specific lichen; thus, there is significant potential for obtaining accurate paleoclimate data.

Whewellite was found to be ubiquitous on surfaces in sheltered areas throughout the Lower Pecos (Russ et al., 1995) and covers vast areas of limestone. This indicates that the lichen community must have flourished in this particular habitat. Since *A. carcareae* is a xeric lichen, the whewellite was likely produced primarily during dry periods, specifically when the substrate was dry. Under these conditions, the organism would obtain its requisite moisture by means of dew, fog, and water vapor, mechanisms used by a variety of desert lichens (Kappen, 1973; Lange, 1988). The two major rivers converging in the Lower Pecos provide a

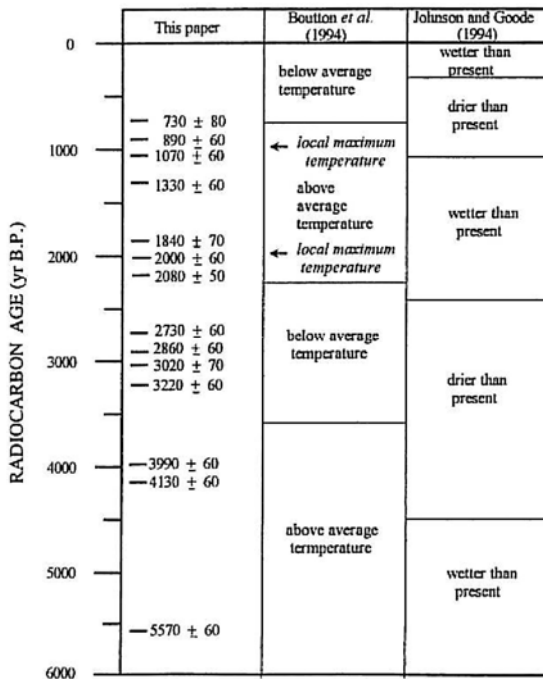


Figure 4. Temporal profile of the ^{14}C ages of oxalate crust along with paleoclimate reconstructions for central Texas.

source of water even during long periods of drought. Moreover, rock surfaces in shelters on which lichens grew can obtain and retain a great deal of condensation moisture, even under dry desert conditions (Winkler 1975, p. 102). The oxalate pruina would then benefit the lichens by retaining water and reducing the calcium concentration of the water on the rock surface (Wadsten and Moberg, 1985; Whitney and Arnot, 1987).

During wet periods, the vitality of the lichens would be severely reduced due to a variety of physiological reasons, including response to freezing water (Kappen, 1973, p. 328), an imbalance in water conditions that severely limits the virulence of either the fungi or algal components of the lichens (Kappen, 1973, p. 325), and inundation with water from the substrate that was saturated with calcium and sulfate. Thus, during mesic conditions the organism would be stressed, reducing growth and oxalate production, and gypsum would be deposited on the crust surface and in voids left by decaying lichen matter.

We suggest that ^{14}C ages of the whewellite correspond to xeric climate regimes, while gaps in the data indicate mesic periods. Nine of the fourteen ^{14}C ages correlate with dry climate episodes inferred by Johnson and Goode (1994) based on geomorphological, paleontological, and palynological data, mostly from the eastern Edwards Plateau of central Texas. Six of our data (clusters 3 and 4) fall within the Edwards Dry interval between about 4500 and 2500 yr B.P., while three of four data in cluster 1 fall within a brief dry interval between 1100 and 300 yr B.P. (Johnson and Goode, 1994, Fig. 2). However, Johnson and Goode (1994) indicate a mesic climate between about 2500 and 1100 yr B.P., whereas cluster 2 of our data occurs between 2080 and 1840 yr B.P. Nordt *et al.* (1994; Boutton *et al.* 1994), however, predict local maximum paleotemperatures at 2000 and 1000 yr B.P. based on stable carbon isotope ratios of organic matter from paleosols and alluvial deposits in central Texas. These peak temperatures are in excellent agreement with dry climates predicted from clusters 1 and 2, whose ages average 1005 and 1970 yr B.P., respectively. However, Nordt *et al.* (1994) and Humphrey and Ferring (1994) predict low temperatures (and inferred wet climatic conditions) from about 4000 to 2500 yr B.P. Our cluster 3, which ranges from 3220 to 2730 yr B.P., implies a dry episode for the Lower Pecos during this period.

Bryant and Holloway's (1985) paleoclimate model for southwest Texas, based on palynological data from archaeological sites in the Lower Pecos, indicates that the region experienced a continuous drying trend during the late Holocene that was interrupted about 2500 yr B.P. by a brief mesic interlude. This brief wet episode correlates with a gap in our data from 2730 to 2080 yr B.P. Two other gaps in our data, from 1840 to 1330 yr B.P. and from 3990 to 3220 yr B.P., correspond to periods when the human population in the Lower Pecos was at a maximum (Turpin, 1990).

CONCLUSIONS

Evidence indicates that dry limestone rock shelters in Lower Pecos canyons were an ideal niche for the desert lichen species *Aspicilia calcarea* during xeric climate episodes. We hypothesize that the virulence of the organism waxed and waned in response to shifts from dry to wet climate in the region. The lichen produced a calcium oxalate (whewellite) residue on the shelter walls during dry periods that can be radiocarbon dated to establish when the lichen flourished; thus, the oxalate serves as an indicator of past xeric climate regimes. Based on 14 radiocarbon ages of the whewellite, we infer wet–dry climate fluctuations during the late Holocene that are in good agreement with models established for other regions of Texas. Because our reconstruction is based on a completely independent mechanism—the vitality of a lichen—it should provide a useful check on paleoclimate models based on other evidence. Furthermore, the ubiquity of the whewellite rock crust in natural environments suggests that this technique may be a potentially valuable paleoclimate indicator of wide applicability.

The preliminary paleoclimate reconstruction proposed here suggests a ca. 1000-yr wet/dry climate cycle for the Lower Pecos. We emphasize, however, that this inference is dependent on two important assumptions: (1) that the lichens did not metabolize or incorporate carbon from the carbonate substrate during the production of the oxalate; this would cause anomalous ^{14}C ages that are not representative of the time the lichens were viable; and (2) that deposition of the whewellite during two different arid climate episodes can be distinguished based on sample stratigraphy; radiocarbon dates from samples in which multiple deposits of the oxalate are not discernable would not be representative of xeric episodes.

ACKNOWLEDGMENTS

The authors thank S. Turpin, R. Ralph, F. Garcia, J. Skiles, and E. Brotherton for assistance in sample collection; K. Dowell for help with the lichen analysis; M. He and I. Perry for assistance with stable carbon isotope measurements; and J. Southon for AMS dating. We gratefully acknowledge J. Labadie and A. Watchman for helpful discussions and criticisms. We also thank V. Bryant and P. Bierman for reviewing this paper and providing helpful comments and criticisms that improved the manuscript. This research was supported by a Cottrell College Science Award of Research Corporation and grants from The National Center

for Preservation Technology and Training and the Robert A. Welch Foundation.

REFERENCES

- Ascaso, C., Galvan, J., and Rodriguez-Pascual, C. (1982). The weathering of calcareous rocks by lichen. *Pedobiologia* 24, 219-229.
- Boutton, T. W., Archer, S. R., and Nordt, L. C. (1994). Climate, CO₂ and plant abundance. *Nature* 372, 625-626.
- Boutton, T. W. (1991). Stable carbon isotope ratios of natural materials: I. Sample preparation and mass spectrometric analysis. In "Carbon Isotope Techniques" (D. C. Coleman and B. Fry, Eds.), pp. 155-171 Academic Press, New York.
- Bryant, V. M., and Holloway, R. G. (1985). A late Quaternary paleoenvironmental record of Texas: An overview of the pollen evidence. In "Pollen Records of Late Quaternary North American Sediments" (V. M. Bryant and R. G. Holloway, Eds.), pp. 39-70. Dallas, Texas.
- Chaffee, S. D., Hyman, M., Rowe, M. W., Coulam, N. J., Schroedl, A., and Hogue, K. (1994). Radiocarbon dates on the All American Man pictograph. *American Antiquity* 59, 769-781.
- Curtiss, B., Adams, J. B., and Ghiorso, M. S. (1985) Origin, development and chemistry of the silica-alumina coatings from the semi-arid regions of the island of Hawaii. *Geochimica et Cosmochimica Acta* 49, 49-56.
- Dania, A. (1986). Patterns of biogenic weathering as indicators of paleoclimates in Israel. *Proceedings of the Royal Society of Edinburgh* 89B, 243-253.
- Danin, A., Gerson, R., Marton, K., and Garty, J. (1982). Patterns of limestone and dolomite weathering by lichens and blue-green algae and their paleoclimate significance. *Palaeogeography, Palaeoclimatology, Palaeoecology* 37, 221-233.
- Danin, A. (1993). Pitting of calcareous rocks by organisms under terrestrial conditions. *Israeli Journal of Earth Science* 41, 201-207.
- Del Monte, M., and Sabbioni, C. (1987). A study of the patina called 'Scialbatura' on imperial Roman marbles. *Studies in Conservation* 32, 114-121.
- Del Monte, M., Sabbioni, C., and Zappia, G. (1987). The origin of calcium oxalates on historical buildings, monuments and natural outcrops. *The Science of the Total Environment* 67, 17-39.
- Dom, R. I., and DeNiro, M. J. (1985) Stable carbon isotope ratios of rock varnish organic matter: A new paleoenvironmental indicator. *Science* 227, 1472-1474.
- Dorn, R. I., DeNiro, M. J., and Ajie, H. O. (1987) Isotopic evidence for climatic influence on the alluvial-fan development in Death Valley, California. *Geology* 15, 108-110.
- Dorn, R. I., Turrin, B. D., Jull, A. J. T., Linick, T. W., and Donahue, D. J. (1987). Radiocarbon and cation-ratio ages for rock varnish on Tioga and Tahoe morainal boulders of Pine Creek, Eastern Sierra Nevada, California, and their paleoclimate implications. *Quaternary Research* 28, 38-49.
- Dorn, R. I., and Whitley, D. S. (1983) Cation-ratio dating of petroglyphs from the Western Great Basin, North America. *Nature* 302, 816-818.
- Dragovich, D. (1988). Desert varnish and environmental change near Broken Hill, Western New South Wales. *Earth-Science Reviews* 25, 399-407.
- Edwards, H. G. M., Farwell, D. W., and Seaward, M. R. D. (1991). Raman spectra of oxalates in lichen encrustations on Renaissance frescoes. *Spectrochimica Acta* 47A, 1531-1539.
- Frey-Wyssling, A. (1981). Crystallography of the two hydrates of crystalline calcium oxalate in plants. *American Journal of Botany* 68, 130-141.
- Graustein, W. C., Cromack, K., and Sollins, P. (1977). Calcium oxalate: Occurrence in soils and effect on nutrient and geochemical cycles. *Science* 198, 1252-1254.
- Hester, T. R. (1983). Late Paleo-Indian occupations at Baker Cave, South-western Texas. *Bulletin of the Texas Archeological Society* 53, 101-119.
- Hester, T. R. (1988). A chronological framework for the Lower Pecos prehistory. *Bulletin of the Texas Archeological Society* 59, 53-64.
- Humphrey, J. D., and Ferring, C. R. (1994). Stable carbon evidence for latest Pleistocene and Holocene climatic change in north-central Texas. *Quaternary Research* 41, 200-213.
- Ilger, W., Hyman, M., Southon, J., and Rowe, M. (1995). Dating pictographs with radiocarbon. *Radiocarbon* 37, 299-310.
- Johnson, L., and Goode, G. T. (1994). A new try at dating and characterizing Holocene climates, as well as archeological periods, on the eastern Edwards Plateau. *Bulletin of the Texas Archeological Society* 65, 1-51.
- Kaluarchchi, W. D., (1995). "Scanning Electron Microscope Study of Prehistoric Rock Paints and Natural Rock

- Accretion." Unpublished Master of Science Thesis, Sam Houston State University.
- Klappa, C. F. (1979) Lichen stromatolites: criterion for subaerial exposure and a mechanism for the formation of laminar calcretes (caliche). *Journal of Sedimentary Petrology* 49, 387-400.
- Kappen, L. (1973). Response to extreme environments. In "The Lichens" (V. Ahmadjian and M. E. Hale, Eds.), pp. 599-632. New York.
- Kochel, R. C. (1982). Quaternary geomorphology of Seminole Canyon State Historical Park. In "Seminole Canyon: The Art and Archeology" (S. A. Turpin, Ed.), pp. 227-276. Austin, Texas.
- Lange, O. L., and Ziegler, H. (1986). Different limiting processes of photosynthesis in lichens. In "Biological Control of Photosynthesis" (R. Marcelle, H. Cljisters and M. Van Poucke, Eds.) pp. 147-161, Dordrecht, Netherlands.
- Lange, O. L. (1988). Ecophysiology of photosynthesis: performance of poikilohydric lichens and homoiohydric Mediterranean sclerophylls. *Journal of Ecology* 76, 915-937.
- Lapeyrie, F. (1988). Oxalate synthesis from soil bicarbonate by the mycorrhizal fungus *Paxillus involutes*. *Plant and Soil* 110, 3-8.
- Lazzarini, L., and Salvadori, O. (1989). A reassessment of the formation of the patina called Scialbatura. *Studies in Conservation* 34, 20-26.
- "Munsell Soil Color Charts." (1994). Macbeth Division of Lollmorgan Instruments Corporation.
- Nordt, L. C., Boutton, T. W., Hallmark, C. T., and Waters, M. R. (1994). Late Quaternary vegetation and climate changes in central Texas based on isotopic composition of organic carbon. *Quaternary Research* 41, 109-120.
- Poelt, J. (1973). Classification. In "The Lichens" (V. Ahmadjian and M. E. Hale Eds.), pp. 599-632. New York.
- Rivera, E. R., and Smith, B. N. (1979). Crystal morphology and ¹³carbon/ ¹²carbon composition of solid oxalate in cacti. *Plant Physiology* 64, 966-970.
- Russ, J., Hyman, M., Shafer, H. J., and Rowe, M. W. (1990). Radiocarbon dating of prehistoric rock paintings by selective oxidation of organic carbon. *Nature* 348, 710-711.
- Russ, J., Hyman, M., and Rowe, M. W. (1992). Direct radiocarbon dating of rock art. *Radiocarbon* 34, 867-872.
- Russ, J., Palma, R. L., and Booker, J. L. (1994). Whewellite rock crusts in the Lower Pecos region of Texas. *Texas Journal of Science* 46, 165-172.
- Russ, J., Palma, R. L., Loyd, D. H., Farwell, D. W., and Edwards H. G. M. (1995). Analysis of the rock accretions in the Lower Pecos region of southwest Texas. *Geoarchaeology* 10, 43-63.
- Scott, D. H., and Hyder, W. D. (1993). A study of the California Indian rock art pigments. *Studies in Conservation* 38, 155-173.
- Staley, J. T., Palmer, F., and Adams, J. B. (1982). Microcolonial fungi: Common inhabitants on desert rocks? *Science* 215, 1093-1094.
- Syers, J. K., Birnie, A. C., and Mitchel, B. D. (1967). The calcium oxalate content of some lichens growing on limestone. *The Lichenologist* 3, 409-414.
- Turpin, S. A. (1982). "Seminole Canyon: The Art and Archeology." Research Report 83. Texas Archeological Survey, The University of Texas at Austin.
- Turpin, S. A. (1990). Speculation on the age and origin of the Pecos River style, southwest Texas. In "American Indian Rock Art 16" (S. Turpin, Ed.), pp. 99-122. Austin, Texas.
- Verrecchia, E. P. (1990). Litho-diagenetic implications of the calcium oxalate-carbonate biogeochemical cycle in semiarid calcretes, Nazareth, Israel. *Geomicrobiology Journal* 8, 87-99.
- Verrecchia, E. P., Dumont, J.-L., and Rolko, K. E. (1990). Do fungi building limestones exist in semi-arid regions? *Naturwissenschaften* 77, 584-586.
- Wadsten, T., and Moberg, R. (1985). Calcium oxalate hydrates on the surface of lichens. *Lichenologist* 17, 239-245.
- Watchman, A. L. (1990). A summary of occurrences of oxalate-rich crusts in Australia. *Rock Art Research* 7, 44-50.
- Watchman, A. L. (1991). Age and composition of oxalate-rich crusts in the Northern Territory, Australia. *Studies in Conservation* 36, 24-32.
- Watchman, A. (1993). Evidence of a 25,000-year-old pictograph in northern Australia. *Geoarchaeology* 8, 465-473.
- Watchman, A., Sale, K., and Hogue, K. (1995). Conservation of the Rendezvous Creek and Nursey Swamp 2 aboriginal painting sites, Namadgi National Park, ACT. *Conservation and Management of Archaeological Sites* 1, 25-34.
- Whitney, K. D. and Arnott H. J. (1987). Calcium oxalate crystal morphology and development in *Agaricus bisporus*. *Mycologia* 79, 180-187. Winkler, E. M. (1975). "Stone: Properties, Durability in Man's Environment." Springer-Verlag, New York.
- Žák, K., and Skála, R. (1993). Carbon isotopic composition of whewellite (CaC₂O₄ • H₂O) from different geological environments and its significance. *Chemical Geology* 106, 123-131.