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USING PETROGRAPHY AND GEOCHEMISTRY TO DETERMINE THE ORIGIN AND FORMATION MECHANISM OF CALCITIC PLANT MOLDS; RHIZOLITH OR TUFA?

CYNTHIA M. LIUTKUS
Department of Geology, Appalachian State University, P.O. Box 32067, Boone, North Carolina 28608, U.S.A.
e-mail: liutkuscm@appstate.edu

ABSTRACT: **Rhizoliths, root casts, and rhizocretions are prolific in the geologic record, and their morphology and isotopic signatures can be important indicators of paleoenvironment and paleoclimate. In a semiarid playa in Nevada, the calcite plant encrustations preserved at the playa surface resemble rhizoliths (morphologically) and would seem to indicate pedogenesis and root activity. The features are preserved as short, thin, upright and/or overturned tubes that often exhibit an apron at the base. Branching is rare, and the tubes can be filled with sediment or calcite, or left open. However, detailed macroscopic, microscopic, and geochemical analyses of these features reveal that they are, instead, macrophyte (stem) encrustations that form in standing water. While these features form in a manner similar to paludal tufa, they do not resemble typical tufa deposits (e.g., barrages, mounds, cascades); instead, they mimic rhizoliths. This study describes the macroscopic and microscopic characteristics of these features and distinguishes them from rhizoliths so that they can be accurately identified in the geologic record. Furthermore, this study identifies a more appropriate method of interpreting the stable-isotope values of these tufa-like plant molds. These types of carbonates are faithful recorders of ambient aquatic conditions (e.g., geochemistry) as well as local hydrologic parameters (e.g., water depth) when the playa surface is flooded, but their geological application is restricted to a partial annual signal (e.g., plant growing season, presence of standing water on the playa). It is important to correctly identify these types of plant encrustations in the geologic record, since (1) their presence indicates a shallow standing body of water (rather than a paleosol) and (2) their isotopic composition records not only an ambient, aquatic signal but an extremely restricted climatic signal that should not be interpreted with models for pedogenic carbonates.**

INTRODUCTION

In lake margin regions, mineralized plant remains are often preserved and can be important ecological indicators. These organosedimentary structures can take on a wide variety of forms (including calcitic plant casts, molds, or petrifaction) and can precipitate under pedogenic (vadose zone) or aquatic conditions. Accurate identification and description of the plant trace is therefore critical in order to properly interpret the depositional environment (e.g., subaerial vs. subaqueous) and accurately reconstruct the paleoclimate.

An extensive body of literature exists that describes the formation and preservation of pedogenic plant cast/mold carbonates (Klappa 1980; Cohen 1982; Mount and Cohen 1984; Wright et al. 1995; Driese et al. 1997; Alonso-Zarza 2003; Kraus and Hasiotis 2006; Cramer and Hawkins 2009) and interprets the isotopic composition of the preserved calcite (found in a wide array of environments) with respect to climatic and vegetative conditions (Mount and Cohen 1984; Cerling 1984; Cerling and Hay 1986; Cerling et al. 1988; Cerling and Quade 1993; Kelley and Yonker 1993; Sikes et al. 1999; Wynn 2000; De Wet et al. 2002; Levin et al. 2004; Cramer and Hawkins 2009). Pedogenic carbonates can be found in lake margin and palustrine environments and form under the conditions described by Klappa (1980). The soil CO_2 diffusion-equilibrium model relates fluctuations in carbonate-derived carbon isotopes in the vadose zone as the result of shifts in C_3/C_4 vegetation. Evaporation and precipitation dictate the oxygen isotope values of pedogenic carbonate that forms in equilibrium (Cerling 1984).

Tufa deposits are equally abundant in lacustrine, lake-margin, and spring environments (Scholl and Taft 1964; Ford 1989; Pedley 1990; Ford and Pedley 1996) and may record the geochemical parameters of the ambient aquatic environment (Andrews et al. 2000; Kirby et al. 2001, 2002; Alonso-Zarza 2003; Rogerson et al. 2008). Formed by a combination of CO_2 degassing and microbial effects under nonthermal conditions, tufa carbonates can produce mounds, towers, lateral sheets, and barrages, many of which encrust macrophytes. Their stable-isotope values record local aquatic conditions, such as evaporation/precipitation ratios and hydrologic mixing of fresh and saline waters ($\delta^{18}O_{calcite}$) as well as organic activity ($\delta^{13}C_{calcite}$) (Andrews et al. 2000; Nelson et al. 2001; Alonso-Zarza 2003; Johnson et al. 2009).

That these types of pedogenic and/or tufa carbonates form in lake-margin environments is not disputed. However, the processes responsible for creating each type of carbonate are dramatically different, and therefore proper identification of ancient carbonate deposits is critical when interpreting their geochemistry or paleoenvironmental significance. The research presented here documents the presence of calcite plant stem molds from a modern playa environment that, morphologically, resemble rhizoliths (pedogenic) but yet form in a manner similar to tufa. This study describes the macroscopic and microscopic characteristics of these plant molds, differentiates them from similar carbonate forms (e.g., rhizoliths), compares them to similar tufa-like deposits, and discusses a more appropriate method for interpreting their stable-isotope values.

This research is significant to the fields of sedimentology, ichnology, and isotope paleoecology in that calcite plant molds, plant casts, and rhizoliths previously identified in lacustrine and palustrine sediments may not have formed pedogenically, but instead formed in an aquatic environment similar to the one discussed here. Specifically, these tufa-like carbonate encrustations form quickly and in equilibrium (with respect to oxygen) with the surrounding aquatic environment, therefore recording different environmental parameters than pedogenic precipitates. Furthermore, in a playa setting such as described here, the precipitation of plant molds is confined to the growing season of the plant host as well as the seasonal presence of standing water on the playa surface. Therefore, the carbonate geochemistry records only a small portion of the annual climate cycle. Interpreting the presence of these carbonate plant molds in the geologic record as pedogenic features (e.g., rhizoliths), as well as interpreting their isotopic signature using the soil CO_2 diffusion-equilibrium model, may lead to a misinterpretation of paleoenvironmental conditions. Therefore, it is critical to delineate the characteristic features of these nonpedogenic, tufa-like plant molds so that they are identified accurately in the rock record and interpreted properly.

BACKGROUND ON RHIZOLITHS AND PALUDAL TUFA

Pedogenic rhizoliths form in the vadose zone, beneath the sediment surface, and are calcite envelopes that precipitate around, and often preserve, roots. Various forms of rhizoliths exist depending on the mode of preservation (see Klappa 1980 for a discussion of rhizolith types). Their morphology resembles singular or branching calcite tubes that are circular in cross section. Rhizoliths are often confused with burrows, but they can be distinguished by their downward-branching behavior, irregular diameters, and the presence of plant material or texture impressions on the inner wall (Klappa 1980). Formation of a calcite envelope around the root structure of a plant can be triggered by numerous processes: (1) microbial and/or fungal respiration, (2) root decay producing CO_2, which then dissolves and reprecipitates as calcite around the root, and/or (3) suppressed CO_2 production, as roots become unproductive, and subsequent $CaCO_3$ precipitation (Klappa 1980; Wright and Tucker 1991). It is important to note that rhizoliths have been noted around both living and dead plant roots (Klappa 1980; Semeniuk and Meagher 1981).

In thin section, rhizoliths exhibit various features that indicate precipitation in the vadose zone. Mount and Cohen (1984) describe Plio-Pleistocene rhizoliths from Koobi Fora, Kenya, and discuss the presence of thin, isopachous rims of spar that cement sand grains together. It is these cemented sand grains that create a sheath around the plant and preserve the root trace. Additionally, they report the presence of microstalactitic textures and meniscuslike spar cements on sand grains within the rhizoliths, indicative of calcite that precipitates from pore water that clings to the undersides or edges of sand grains in the vadose zone. Klappa (1980) describes thin sections of rhizoliths as having an alveolar texture and a weak concentric layering of micrite. The roots themselves can create localized features that further indicate a vadose-zone origin, such as rhizobrecciation, elongate glaebules, and horizontal sheet cracks (Klappa 1980).

Pedley (1990) classified tufas (cool, freshwater carbonate deposits) into various categories based on morphology and formation mechanism. Precipitation of calcite is driven by a combination of physicochemical and biomediated processes. CO_2 degassing causes a decrease in the pCO_2 of ambient water and can stimulate calcite precipitation under certain geochemical conditions. Evaporation, temperature change, and/or the dilution of saline brines by freshwater inflow of springs can lead to this decrease in pCO_2. Biofilms may also form around inundated macrophytes due to the colonization of various bacteria, cyanobacteria, and algae (Pentecost and Riding 1986; Pedley 1992, 1994; Thompson and Ferris 1990; Thompson et al. 1997; Rogerson et al. 2008). Many of these organisms can precipitate calcite as a metabolic byproduct (e.g., *Synechococcus*), but in the absence of these microorganisms, the presence of the biofilm may be enough to trap detrital lime mud and create a calcite sheath around a macrophyte (Pentecost and Riding 1986; Pedley 1994). The "paludal model" of tufa formation describes carbonates that precipitate on poorly drained slopes and alluvial valley bottoms where spring water seeps through the local vegetation and precipitates a calcite crust called fringe cement (Pedley 1990). The resulting deposit is a lateral, thin sheet of calcite with abundant macrophyte encrustations (Pedley 1990) and "microdetrital tufa" that resembles lime mud (Ford and Pedley 1996). The tufa calcite produced by each formation mechanism (physicochemical vs. biomediated) is morphologically distinct in thin section: inorganic precipitates often exhibit isopachous fringe cements with possible dogtooth crystals whereas the biomediated calcite resembles micrite and/or peloids (Pedley 1992, 1994; Ford and Pedley 1996). In ancient tufa deposits, proper identification of these morphologies can provide crucial information about the formation mechanism (inorganic vs. biomediated) and aid in paleoenvironmental interpretation.

SITE LOCATION AND HYDROLOGY

Calcitic plant stem molds are found on the playa surface at Pilot Valley, located in the Pilot Range on the western edge of the Great Salt Lake Desert in eastern Nevada (Fig. 1). The Silver Island Mountains separate the valley from the Bonneville Salt Flats to the east. Low precipitation ($<$ 150 mm/year) and high summer potential evapotranspiration (2500 mm/yr) is typical, with rainfall peaking in the spring (Lines 1979). High summer temperatures and low winter temperatures create an annual mean temperature range of 17°C to 33°C (Fan et al. 1997).

The regional vegetation at Pilot Valley consists of C_3 shrubs (rabbitbrush [*Chrysothamnus* sp.], greasewood [*Sacrobatus* sp.], and sagebrush [*Artemisia* sp.]) as well as CAM plants (e.g., pickleweed [*Salicornia* sp.]) and a C_4 halophytic grass (saltgrass [*Distichlis* sp.]). Pickleweed and saltgrass are both saline-tolerant, and are predominantly found near the more saline springs. Evaporation in the region is consistently high, and by mid-summer many plants on the mudflat are encrusted with salt and carbonate (Malek et al. 1990; Menking et al. 2000).

Two types of water circulation drive the hydrologic mixing at Pilot Valley (free convection and forced convection; see Fan et al. 1997) and dictate the geochemistry of the waters that emerge in springs along the playa margin. Free convective flow forces dense, saline water to sink beneath the playa surface, where it mixes with fresher groundwater, recirculates, and then reemerges as saline springs on the western playa margin (Duffy and Al Hassan 1988; Fan et al. 1997). Alternatively, forced convection occurs as precipitation on the surrounding highlands drains into the alluvial fans on Pilot Peak. The freshwater migrates to the toe of the fan under a hydraulic gradient and emerges as springs along the hinge line (Fan et al. 1997). This complex hydrology dictates the presence of freshwater springs in the northwestern region of the playa and more saline springs along the southwestern edge, and directly influences the locations where the plant molds are found.

METHODS

In order to quantify the shape of the plant molds from Pilot Valley, the maximum length, diameter, and thickness of the calcite rim (when not infilled) of each mold were measured using digital calipers (Table 1). Whenever possible, the length and diameter of a single tube were

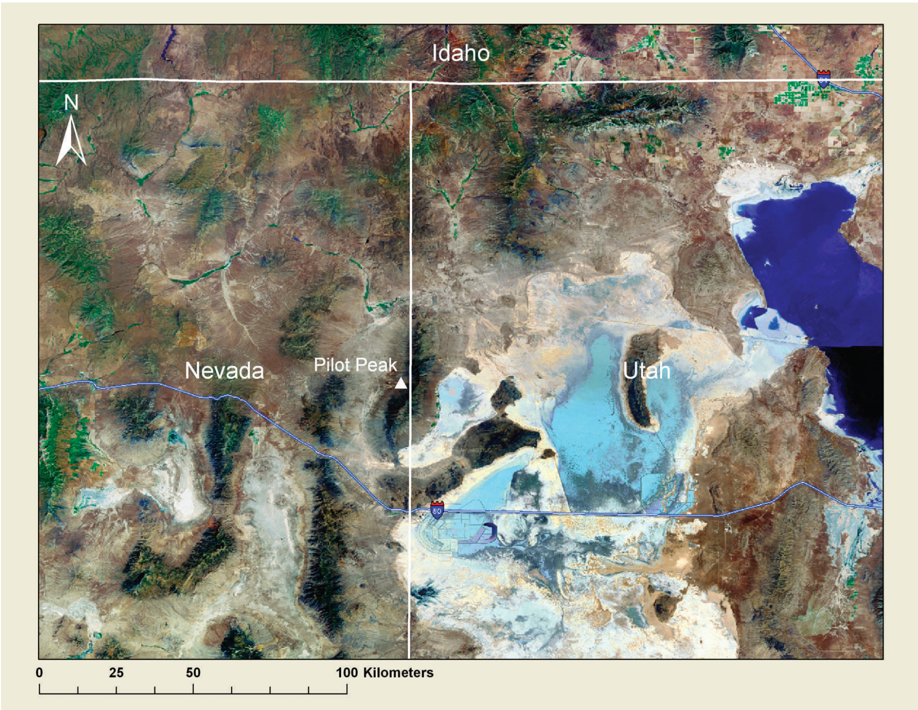

FIG. 1.—Illustration of Pilot Valley region, created using 1 km MODIS (Moderate Resolution Imaging Spectroradiometer) satellite imagery. The state boundary between Utah and Nevada runs through the Pilot Range (Pilot Peak is labeled), and the Pilot Valley playa (the arcuate white and light blue region) lies immediately to the east (< 10 km from the state line). In this image, the Pilot Valley playa has standing water on the surface. The Great Salt Lake is shown to the east, for reference.

measured; data from branching or composite samples (more than one tube) are not included.

Petrographic analysis of plant mold thin sections was completed using a Leica DM EP model petrographic microscope. Thin sections of the plant molds were cut perpendicular to the long axis of the sample in order to identify changes in calcite morphology from the center to the edge.

Uncoated thin sections were also analyzed using the FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM). Backscatter electron images were collected using a working distance of 11.4 mm (micritic sample) and 15.9 mm (sparry sample), voltage of 25.0 kV, and spot size of 6.0 to characterize bulk compositional differences within the samples. Energy-dispersive spectroscopy (EDS) was used to collect elemental composition on specific regions of each sample (e.g., edge, center).

Stable-isotope values were derived from 28 samples of plant molds (148 analyses) and 1 bulk carbonate sample (Halls Spring). Prior to analysis, all samples were washed and sonicated in distilled water at room temperature for 10 minutes to remove detritus and dissolve any remnant salt. A clean surface was uncovered by sawing off the rough end of the calcite tube perpendicular to the long axis. Using a high-speed drill fitted with a 0.5 mm drill bit, powdered samples of carbonate were taken at 0.5 mm intervals staggered across a transect of the clean surface (from edge to center to opposite edge). Stable-isotope analyses were run in the Stable Isotope Laboratory at Rutgers University in the Department of Geological Sciences. Samples were loaded into a multi-prep device and were reacted in 100% phosphoric acid at 90°C for 13 minutes before being analyzed on the Micromass (Optima) dual-inlet mass spectrometer. Both $\delta^{13}C$ and $\delta^{18}O$ values were obtained and the values reported versus the Vienna Pee Dee Belemnite (V-PDB) by analysis of a lab standard calibrated to the National Bureau of Standards (NBS) #19 with values of 1.95‰ and −2.20‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively (Coplen et al. 1983). Standard deviation (1 σ) of the standards was 0.08‰ and 0.05‰ for $\delta^{18}O$ and $\delta^{13}C$, respectively. Isotopic values with precision error greater than 0.01 were excluded from the dataset.

Water samples from 7 springs on the playa were collected for $\delta^{18}O_{water}$ analysis. Sample preparation involved pipetting 2 ml of the water sample into a 5 ml vial, bubbling CO_2 through the water for 10 seconds in a glove bag, and then capping the vial. The CO_2 in the headspace above the water sample was allowed to equilibrate isotopically at 40°C for 8 hours before analysis on a Micromass (Optima) dual-inlet mass spectrometer with an attached Multi-Prep device. The data are reported as V-SMOW (Standard Mean Ocean Water) (Table 2). Duplicate samples were run and the values averaged. The 1 σ standard deviation of the $\delta^{18}O_{water}$ standards analyzed along with the samples was 0.07‰.

RESULTS AND OBSERVATIONS

Macroscopic Description and Distribution

None of the springs at Pilot Valley currently produces tufa mounds, sheet carbonates, bioherms, and/or travertine deposits, which are often typical features of springs and lake-margin environments (Pedley 1990; Ford and Pedley 1996; Evans 1999; Alonso-Zarza 2003; Pedley et al. 2003). Instead, the carbonate deposits found on the western edge of Pilot Valley are restricted to calcite tubes found upright and overturned on the playa surface and calcite encrustations of plant stems. These tubes and plant encrustations are found only in the southern portion of the valley near the margins of saline springs. The features discussed here are not found *in* the springs proper, but are instead located on the adjacent playa surface and can be 30 m or more away from the spring source.

Singular, isolated, vertical and/or overturned calcite tubes are found at the sediment surface. Each tube can be filled with unconsolidated (or weakly cemented) sediment (Fig. 2A), completely filled with calcite (Fig. 2B), or left open (Fig. 2C). Few samples exhibit branching (e.g., tubes bifurcating off the main opening; Fig. 2D), and single tubes are more common. The tubes are robust and do not taper in any direction. In rare instances, plant material is still evident along the inner edge of the tube, which suggests that these features are (1) plant derived, and (2) external molds.

TABLE 1.—*Measured length, diameter, and thickness of calcite plant molds.*

Sample ID	Year Collected	Length (mm)	Diameter (mm)	Rim Thickness (mm)
PV03(7)	2003	18.8	4.5	0.8
50 m W of Agony Spring W6	2004	22.0	5.5	1.5
50 m W of Agony Spring W2	2004	20.5	7.4	1.8
Little Salt Spring 4	2004	13.6	7.1	2.8
Little Salt Spring 3	2004	24.6	7.2	1.2
PV03(1)	2003	11.2	6.5	0.6
50 m W of Agony Spring W5	2004	14.3	7.3	1.4
Agony 2003 (1)	2003	12.8	6.6	0.7
PV03(9)	2003	8.5	11.5	2.2
PV03(4)	2003	6.4	6.3	1.1
PV03(2)	2003	4.9	4.6	0.3
NW of Agony NW2	2004	16.4	6.7	1.4
NW of Agony NW3	2004	15.9	7.8	3.5
PV03(6)	2003	8.7	4.3	1.6
Little Salt Spring 2	2004	9.6	3.9	1.2
PV03(10)	2003	24.2	4.7	infilled
PV03(8)	2003	5.9	4.9	0.8
Agony W1	2004	18.1	8.5	2.2
PV03(12)	2004	14.1	4.4	0.6
Little Salt Spring 5	2004	19.6	4.1	1.0
Agony W3	2004	13.0	5.9	1.5
Little Salt Spring 1	2004	14.0	4.2	1.4
Agony W2	2004	broken	6.3	1.7
Agony NW1	2004	28.2	7.5	2.7
Slope Spring	2004	17.0	5.7	1.9
not labeled	2004	18.7	5.4	1.0
not labeled	2004	8.1	6.2	0.8
not labeled	2004	21.1	6.6	0.6
not labeled	2004	16.0	8.5	4.0
not labeled	2004	12.6	6.0	0.9
not labeled	2004	19.0	5.3	2.7
not labeled	2004	27.9	9.8	2.2
not labeled	2004	17.9	5.0	infilled
not labeled	2004	21.3	5.3	1.1
not labeled	2004	14.8	6.3	1.3
not labeled	2004	18.9	6.6	infilled
not labeled	2004	13.4	6.3	infilled
not labeled	2004	15.8	5.6	infilled
not labeled	2004	10.8	5.2	2.8
not labeled	2004	18.3	8.6	1.5
not labeled	2004	37.0	5.5	1.7
not labeled	2004	22.3	5.1	2.0
not labeled	2004	15.7	5.4	infilled
not labeled	2004	13.9	6.6	1.6
not labeled	2004	15.0	6.3	1.4
not labeled	2004	16.4	7.2	infilled
not labeled	2004	16.6	8.3	infilled

Most of the plant molds are ~ 4.9–37.0 mm long (average = 16.4 mm, n = 46), but one sample was 8.0 cm long (Table 1). The longer samples intersect the sediment surface at an oblique angle and do not extend far beneath the sediment surface. In fact, none of the molds extends more than ~ 10 mm below the sediment surface, and therefore most of the calcite tube remains above the sediment.

The diameters of the molds range from 3.9 mm to 11.5 mm, with an average diameter of approximately 6.3 mm (n = 47), and the average thickness of the calcite wall is 1.6 mm (Table 1). The inner wall of the calcite tube is most often smooth, while the outer wall is irregular. Rarely, the impression of exterior plant texture can be found on the inner surface of the tube, producing elongate striations in the calcite (Fig. 2E). Occasionally, living plants can be found to have stem molds forming presently (Fig. 2F). Often these are in regions near an evaporating pool of water on the playa, and the grassy plants that colonize these regions are coated with calcite and halite.

Calcite extends laterally at the base the mold (outward) like an apron. This apron can be at the extreme base of the tube (Fig. 3A), medial (Fig. 3B), or at both ends (Fig. 3C) but, in all cases, does not extend more than ~ 2 mm away from the main calcite tube. Not all molds exhibit this feature, but when a single apron is present it can be used as an effective indication of the sediment surface (as well as the mold's original orientation). Only one sample had aprons at both ends (Fig. 3C). In this case, the thicker, more bulbous end is interpreted as the sediment interface since the thinner end of the mold was left open and the more robust end was filled with sediment.

All of the plant molds found at Pilot Valley are concentrated at the sediment surface. Several test pits were dug into the playa sediments near locations of current plant mold abundance, and no "preserved" or fossil plant molds were located. Additionally, plant molds were prolific during July and August field visits; no calcite encrustations were found during spring and late fall, and vegetative cover near the spring fringes is significantly reduced at these times.

Microscopic Description

In thin section, the plant molds exhibit two calcite morphologies: micrite (microcrystalline lime mud) and spar. Each mold exhibits only one type of calcite. Most of the molds exhibit concentric layers of fenestral micrite that contains siliciclastic detritus (Fig. 4A). These micritic plant molds also contain abundant whole or fragmented ostracod shells (Fig. 4B) and diatoms, and relict plant material often remains cemented to the stem hole (Fig. 4C). Polygonal cracks within the micrite are apparent, and in several samples, iron staining is noted. The micritic molds can exhibit a thin indurated outer edge, but many do not. Several samples also contain a geopetal infill (Fig. 4D).

Other samples consist of a thin ring of isopachous, bladed (Folk 1965) sparry calcite crystals that exhibit undulose extinction and convergent curved twin planes similar to radiaxial fibrous calcite (Fig. 4E; Tucker and Wright 1990; Scholle and Ulmer-Scholle 2003). No biological material is found within the calcite of the sparry molds (e.g., ostracods, diatoms, original plant material), but concentric rings of fine-grained, clastic detritus (inclusions) can be found parallel to the nucleation surface and perpendicular to the bladed calcite crystals (Fig. 4F).

Backscatter electron images indicate compositional variations within the micritic samples, with darker bands concentrated near the central stem hole and brighter bands near the edge of the mold (Fig. 5A). EDS results of the darker material indicate a high abundance of silicon, calcium, carbon, and aluminum (in decreasing order) with minor traces of magnesium and potassium. The brighter edges of the micritic molds have a higher proportion of calcium and only minor inputs of carbon, silicon, and aluminum. The higher proportion of silicon, aluminum, and magnesium in the central, darker material indicates a silty, micritic composition that contains siliciclastic detritus as well as organic material (carbon) left behind by the plant host. The brighter rim regions, with a higher proportion of calcium and only minor amounts of silicon (siliciclastic detritus) and no carbon (organic material), represent "cleaner" calcite. The backscatter electron image of a sparry calcite plant mold indicates no noticeable compositional difference (Fig. 5B). While halite encrustation is noted on some plants in the field, the presence of halite was not noted in either the micritic or sparry molds.

Stable-Isotope Results

Liutkus and Wright (2008) previously reported the measured $\delta^{18}O_{water}$, $\delta^{13}C_{calcite}$, and $\delta^{18}O_{calcite}$ values from the Pilot Valley samples, and those data are reproduced here in order to clearly illustrate the critical

TABLE 2.—$\delta^{18}O_{water}$ values of springs sampled at Pilot Valley. All values reported as V-SMOW.

Sample ID	$\delta^{18}O$ ‰	Average (‰)
AGONY SPRING 2003	−15.2	
AGONY SPRING 2003	−15.0	−15.1
AGONY SPRING 7/17/04	−14.8	
AGONY SPRING 7/17/04	−14.8	−14.8
AGONY SPR DRAIN 7/17/04	−7.7	
AGONY SPR DRAIN 7/17/04	−7.6	−7.7
AGONY SPRING SW 7/17/04	−13.0	
AGONY SPRING SW 7/17/04	−13.0	−13.0
HALLS SPRING SOURCE 7/16/04	−15.8	−15.8
HALLS SPRING 02 2002	−11.8	
HALLS SPRING 02 2002	−11.6	−11.7
HALLS SPRING 03 2002	−12.6	
HALLS SPRING 03 2002	−12.5	−12.6
HALLS SPRING SOURCE 01 2003	−16.0	
HALLS SPRING SOURCE 01 2003	−16.1	−16.0
HALLS SPRING SOURCE 04 2002	−14.1	
HALLS SPRING SOURCE 04 2002	−14.2	−14.1
LITTLE SALT SP 7/17/04	−0.2	
LITTLE SALT SP 7/17/04	−0.1	−0.2
NEW SPRING 2003	−15.4	
NEW SPRING 2003	−15.6	−15.5
NEW SPRING 7/16/04	−14.2	
NEW SPRING 7/16/04	−14.2	−14.2
SINKHOLE SPRING 7/17/04	−15.0	
SINKHOLE SPRING 7/17/04	−15.0	−15.0
TESSA SPRING 2003	−15.9	
TESSA SPRING 2003	−16.0	−15.9
TESSA SPRING 7/16/04	−15.8	
TESSA SPRING 7/16/04	−15.8	−15.8
SLOPE SPRING 2003	−10.5	
SLOPE SPRING 2003	−10.4	−10.4
SLOPE SPRING 7/17/04	−8.4	
SLOPE SPRING 7/17/04	−8.3	−8.3

environmental information that is recorded by this specific type of carbonate. The $\delta^{18}O_{water}$ values of the springs (near which the plant molds were found) are reported in Table 2. The $\delta^{13}C_{calcite}$ values of the plant mold samples range from 0.4‰ to 4.7‰ (average = 2.8‰, 1 σ = 0.99), and $\delta^{18}O_{calcite}$ values vary from −14.7‰ to −6.7‰ (average = 12.0‰, 1 σ = 1.96) (Fig. 6).

DISCUSSION

While the Pilot Valley plant molds may resemble root casts, rhizoliths, and/or rhizocretions (Klappa 1980; Cohen 1982; Mount and Cohen 1984; Cerling and Hay 1986; Wynn 2000; Levin et al. 2004; Cramer and Hawkins 2009), various lines of evidence indicate that they are not pedogenic features, do not preserve any root material, and instead form in standing-water conditions (rather than in the vadose zone) above the sediment surface. This suggests a formation mechanism similar to paludal tufa, despite a morphological resemblance to rhizoliths and dissimilarity to typical tufa deposits such as barrages, mounds, and/or cascades (Pedley 1990).

Due to the different formation mechanisms that precipitate rhizoliths and tufa-like plant encrustations, the macroscopic as well as microscopic morphology of each organosedimentary structure should be distinct. Therefore, in order to accurately identify these tufa-like plant molds in the geologic record, their morphological characteristics must be identified correctly. Several features differentiate these tufa-like plant encrustations from rhizoliths: (1) the presence of the calcite apron at the end of the tube, (2) the isopachous rim of bladed, sparry calcite, (3) the presence of aquatic microfossils, and (4) the consistent tube width.

The presence of the apron around the bases of the calcite tubes indicates that the stem of the plant is encrusted down to the sediment surface. In order for most of the calcite tube to be formed above the sediment surface, calcite must precipitate in shallow standing water on the playa above the water–sediment interface and below the air–water interface. (Formation of calcite around the plant stem in air is improbable since the aquatic medium is the source of dissolved ions.) In addition, the apron also negates the possibility that the tubes were originally buried within the sediment and subsequently uncovered, since the apron's presence often denotes the sediment–water interface.

Radial sparry calcite crystals indicate the uninhibited growth of calcite outwards from a central nucleation point, such as would occur as calcite precipitates from an aqueous solution (Scholle and Ulmer-Scholle 2003). Thus, the presence of radial, bladed calcite crystals in the sparry sample supports a subaqueous precipitation. While pedogenic rhizoliths can also exhibit radial, bladed calcite (e.g., Mount and Cohen 1984), it often occurs as a primary cement that is found as a thin (< 0.1 mm), isopachous rim on sand grains that are cemented together to create a mold of the plant root. The plant molds from Pilot Valley differ, however, because the sparry calcite does not cement sand grains and, instead, creates a thick (up to 1 mm or more) rim around the plant stem. The difference in the thickness of the sparry calcite between pedogenic rhizoliths and the plant molds from Pilot Valley may simply reflect the amount of water available to precipitate calcite in pedogenic (thin films of pore water around sand grains) versus aquatic (shallow standing water) environments, respectively.

Remains of microfossils (such as ostracods and diatoms) are abundant in the micritic plant molds, and further support the interpretation of a subaqueous precipitation of calcite above the sediment surface. These microorganisms are not infaunal, and therefore must be colonizing a plant stem (rather than a root) that is submerged within standing water.

Finally, the plant molds from Pilot Valley have a consistent width and do not taper in any direction. This is yet another key difference between these forms and rhizoliths, the latter of which may exhibit a tapered end as the calcite envelope reaches the root terminus (Klappa 1980).

Since the calcite tubes form as a direct precipitate from standing water, they do not form in the manner of pedogenic carbonates, which form in the vadose (unsaturated) zone in equilibrium with soil moisture beneath the sediment surface. Submerged (and/or subaqueous) soils can form in environments that have seasonal or permanent standing water (e.g., Brady and Weil 2008); however, the plant molds at Pilot Valley still should not be considered pedogenic since (a) they form outside the soil realm (above the sediment–water interface) and (b) their formation need not coincide with pedogenesis (e.g., calcite precipitation can occur shortly after plant submergence in one season).

Since the molds form in standing water, the height of the calcite tubes may be a proxy for water depth on the playa surface at the time of their formation (Table 1) (Riding 1979). In support of this, one sample did exhibit a small apron at both the base and the top of the mold, suggesting that it had reached the maximum extent of the water level (Fig. 3C). The average and range of lengths recorded by the plant molds (Table 1) emphasizes that these calcite tubes form in very shallow water (most often < 2 cm deep).

The Plant Host

Despite a moderate diversity of flora, the morphology and distribution of most of the plants excludes them from being the host of the plant molds (e.g., stem diameter is too large, stem has frequent bifurcation, surface texture is not consistent with inner wall impressions, non-saline tolerant). Liutkus and Wright (2008) discussed, however, that a distinctive growth behavior does point to saltgrass (*Distichlis* sp.) as the

FIG. 2.—Morphology of Pilot Valley plant stem molds. All scale bars show 0.5 cm. **A)** View looking down the long axis of the plant mold. Notice that the mold has an indurated rim and is filled with weakly cemented sediment. The apron at the base of the mold is visible under the scale at bottom. **B)** This mold has been completely filled with calcite cement, with only a slight remnant depression where the plant stem used to emerge. **C)** Tube is left open, with no calcite or sediment infill. **D)** Branching type of mold, with a long main tube oriented vertically, and two small bifurcations to the right (arrows). **E)** View of the inner wall of the mold. Elongate striations are noticeable on the wall of the void where the stem made an impression in the surrounding calcite. **F)** Field photograph of saltgrass plants on the Pilot Valley playa encrusted in salt and calcite. Note that many of the plants are still alive and upright, while a few are recumbent. Sample tube for scale is approximately 11.5 cm long.

likely plant host since calcite tubes are often found within calcified linear cracks on the playa surface (Fig. 7A). Saltgrass rhizomes grow in a linear fashion and, at discrete intervals, produce successive shoots (Fig. 7B). The saltgrass sprouts can emerge through even clay-rich sediments, and since saltgrass is a halophytic grass, it is able to withstand the harsh saline, alkaline conditions on the playa. Furthermore, the surface texture (striated, nonsegmented) and stem diameter of saltgrass (< 10–20 mm) is consistent with the morphology of the plant stem molds. In support of

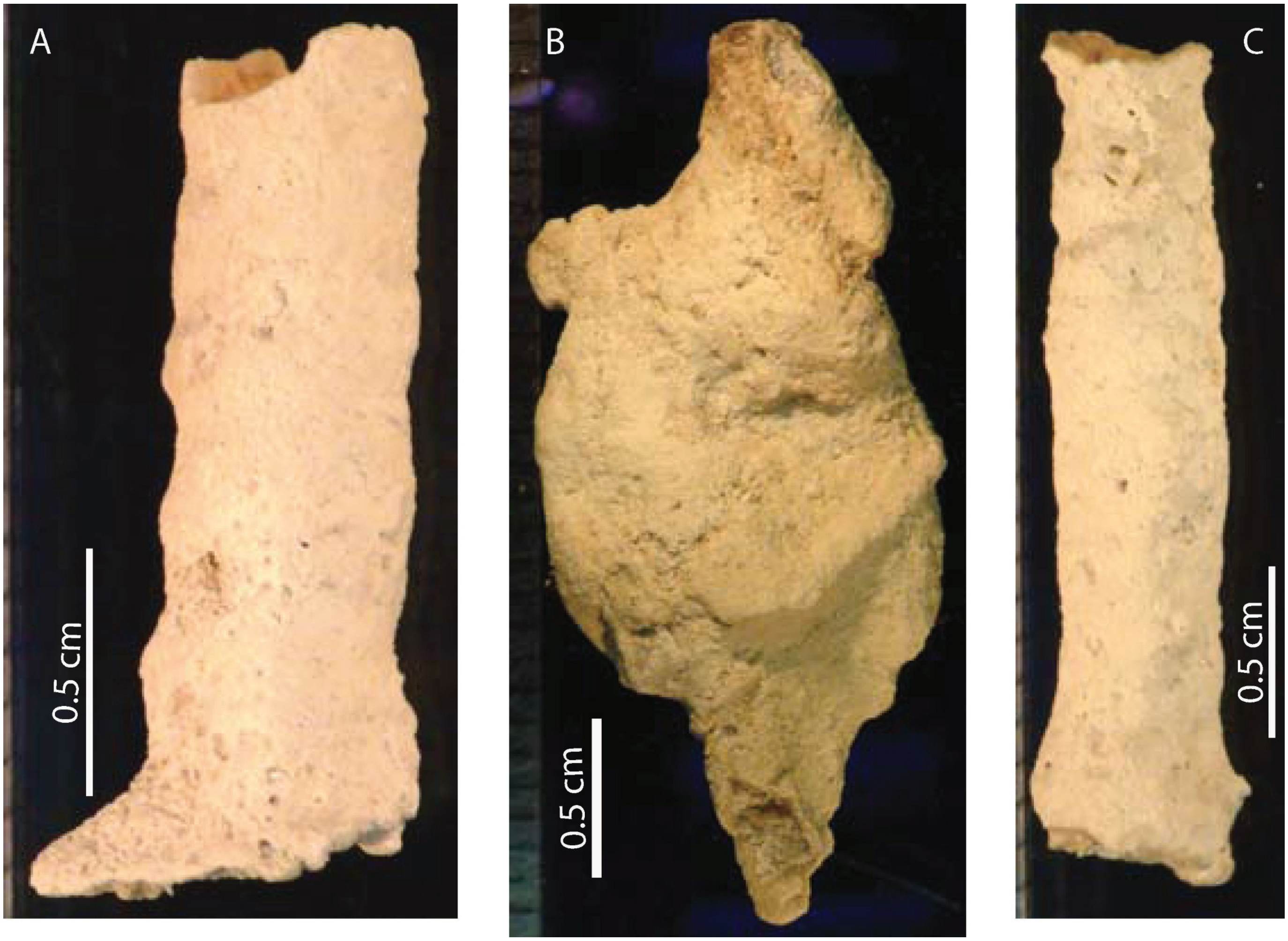

FIG. 3.—Contrasting view of the apron structure seen in many samples. The apron can appear **A)** at the base of the mold, **B)** in the middle of the mold (at a slight angle, tilted towards the left), or **C)** at both ends.

this interpretation, stem molds are found only around the saline springs (electrical conductivity > 10 mS/cm) to the south of the playa (where saltgrass is one of the few plants able to survive) and are not found in regions where saltgrass is absent (e.g., near the fresher springs to the north). Thus, the plant encrustations likely form around saltgrass plants due to the fact that the halophytic grass is hardy and can withstand inundation. Therefore, it is the most prevalent plant around the fringes of the spring pools and, by default, is the most encrusted macrophyte.

Geochemical results also suggest that the molds formed around saltgrass. Measured $\delta^{13}C_{calcite}$ values from individual plant molds range from 0.4‰ to 4.7‰ and (allowing for fractionation between soil-respired CO_2, DIC, and calcite) are consistent with precipitation in an ecosystem dominated by C_4 plants (Liutkus and Wright 2008). At Pilot Valley, only one C_4 plant (saltgrass) is dominant on the playa surface where the plant molds are found and therefore must be the plant host for the calcite molds.

Coupling the morphological characteristics with the $\delta^{13}C_{calcite}$ signature of these types of carbonates may, therefore, be extremely useful in reconstructing the local paleoenvironment. The plant host may be identified by growth behavior and morphology and then confirmed by the $\delta^{13}C_{calcite}$ value to provide an accurate assessment of the local vegetation.

The Stimulus for Calcite Precipitation

Liutkus and Wright (2008) suggested that, during periods of episodic flooding (perhaps after spring snowmelt), the springs on the western edge of Pilot Valley overflow onto the playa. This interpretation is favorable due to the fact that the $\delta^{13}C_{calcite}$ and $\delta^{18}O_{calcite}$ values of the carbonates cluster tightly based on their geographic location on the playa (e.g., by the spring to which they are closest). Furthermore, concentric "berms" of sediment and plant debris were noted around several of the springs, and could be evidence of this spring "flooding" event. During this time, plants on the spring margins are inundated with spring water and submerged until the intense evaporation in the region completely dries the playa surface (as it does seasonally).

Saltgrass is not an aquatic plant, but it can survive being submerged for approximately 24 days (Ungar 1966). At this time, it is unclear as to whether metabolic activity (e.g., respiration, photosynthesis, decomposition) by the saltgrass plant can sufficiently affect the aquatic microenvironment around the plant stem and trigger calcite precipitation. While the plant stem is still green and the plant continues to photosynthesize, gas exchange through the stem could create conditions that thermodynamically favor calcite precipitation by decreasing pCO_2 in the water and increasing pH, locally (Morel and Hering 1993; Langmuir 1997). However, at this time there is no evidence to suggest that the

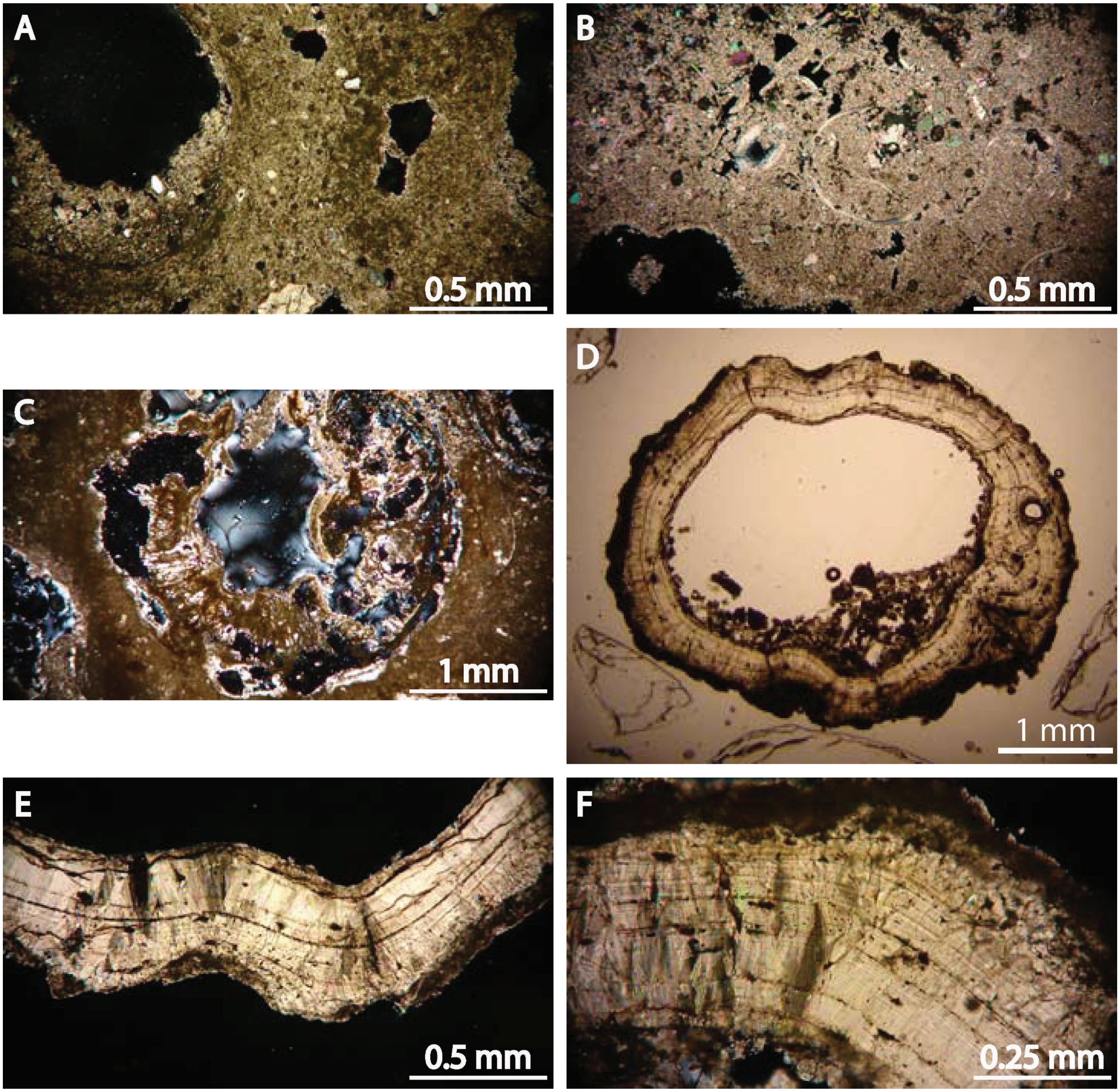

FIG. 4.—Petrographic images of micritic (A–C) and sparry (D–F) plant molds. **A)** Micritic plant mold with stem hole to the top left. Note the included clastic silt grains and the fenestral nature of the calcite. A geopetal infill is also present in the stem hole. Crossed-polarized light (XPL). **B)** Micritic plant mold with stem hole to the bottom left. Thin section reveals several cross sections of ostracod valves (e.g., center). XPL. **C)** Micritic plant mold with stem hole oriented in center. Note the presence of organic material still included in the central hole (evidenced by the brown, cellular material to the bottom left of the hole). XPL. **D)** Sparry stem mold, showing geopetal infill. Plane-polarized light (PL). **E)** Sparry stem mold, with stem hole oriented to the top of the image. Radial, bladed sparry calcite crystals emanate from the central rim of isopachous, blocky calcite. XPL. **F)** Sparry stem mold, with stem hole to bottom left. Note the concentric lines of clastic inclusions that are parallel to the nucleation surface, and crosscut the radial, bladed calcite crystals. XPL.

saltgrass plants are able to extract CO_2 from the surrounding water. Furthermore, once the calcite begins to form around the plant stem, this process would cease, as the plant stem becomes isolated from the surrounding aquatic medium. Thick calcite rims (e.g., on the sparry plant molds) suggest that calcite precipitation continues even after the initial rind forms around the plant, and therefore a mechanism independent of the plant host seems more likely.

Evaporation is the major control on the $\delta^{18}O_{water}$ values found on the playa surface that dictate the $\delta^{18}O_{calcite}$ values seen in the plant mold calcite (Liutkus and Wright 2008). Models of $\delta^{18}O_{water}$ that assume Rayleigh distillation indicate that, in some cases, $>$ 70% of the source water has to evaporate in order to yield the $\delta^{18}O_{water}$ values needed to precipitate calcite with the measured $\delta^{18}O_{calcite}$ values (Liutkus and Wright 2008; Table 2). This indicates that evaporation is a first-order

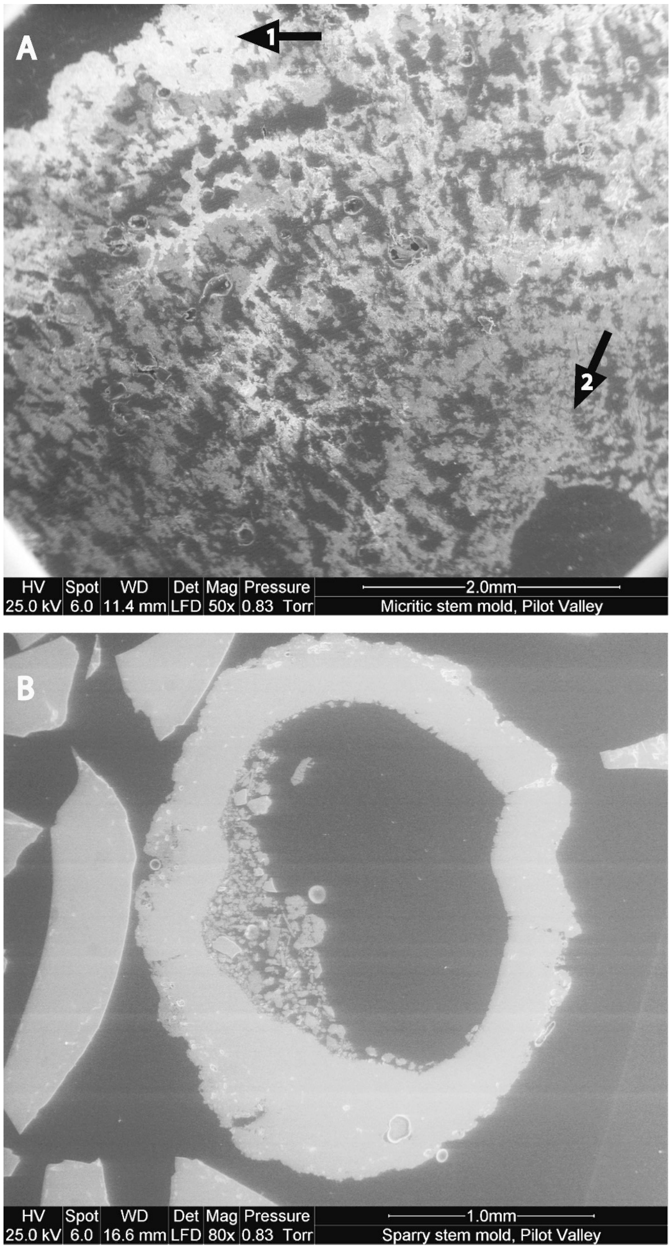

FIG. 5.— Backscatter electron images of **A)** micritic plant mold and **B)** sparry plant mold. EDS results indicate that the bright regions (Arrow 1) in Part A correspond with a calcitic composition, whereas the darker regions (Arrow 2) indicate the presence of more silt and carbon. Note that the composition of the sparry calcite plant mold (**B**) is uniform.

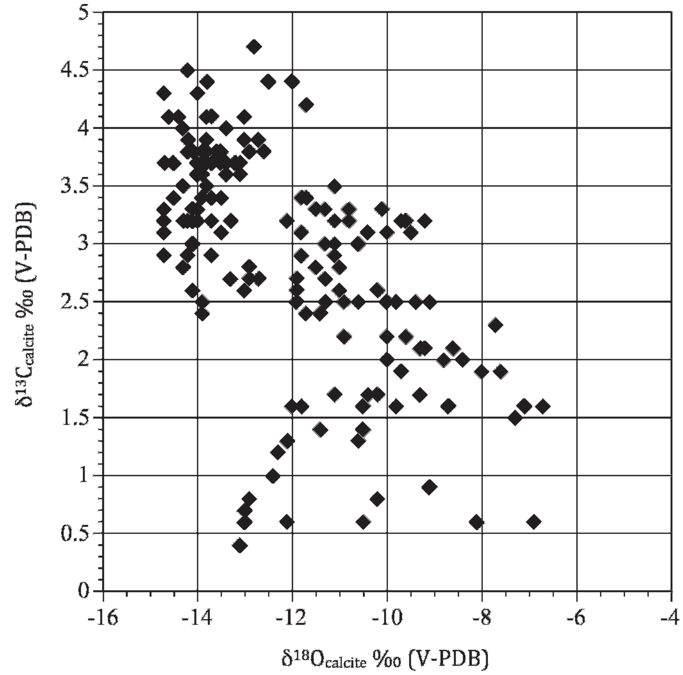

FIG. 6.—Plot of $\delta^{13}C_{calcite}$ versus $\delta^{18}O_{calcite}$ values from Pilot Valley carbonate samples. Data are replotted from Liutkus and Wright (2008).

control on calcite precipitation. In support of this, there are other features on the playa surface (e.g., pebbles, bone) that become encrusted with calcite, and it is therefore more likely that, as evaporation begins to modify the standing water on the playa (by decreasing pCO_2), this process triggers the precipitation of a calcite rind around the plant stems (and causes a subsequent increase in $\delta^{18}O_{water}$ values). A concurrent effect is the high temperature of the water, which can also decrease pCO_2, decrease bicarbonate ion solubility, and stimulate calcite production (Wright and Tucker 1991). This interpretation of the stimulus for calcite precipitation is consistent with the data, since the measured $\delta^{18}O_{calcite}$ and $\delta^{18}O_{water}$ values indicate high evaporation (Liutkus and Wright 2008) and the length of the plant molds (this study) suggests shallow water, which favors high temperatures. This physicochemical precipitation of calcite around plants resembles the paludal tufa model of Pedley (1990) and is supported by the presence of isopachous, fringe cement on the sparry plant molds.

The morphology of the micritic plant molds provides additional evidence that the calcite forms in conditions of shallow, standing water, but also indicates that precipitation can be biomediated and formed in two ways. Some micritic molds exhibit a thin, indurated rind that is completely infilled with micrite and fine-grained siliciclastic detritus. This suggests that the initial stage of precipitation creates a calcite rind around the living or dying plant stem, which is then subsequently infilled with micrite after the plant decays away. This rind is likely a biofilm that traps detrital micrite (similar to a stromatolite) and forms a carbonate envelope around the living plant (Pedley 1992). The presence of ostracods and diatoms within the samples supports the interpretation that the calcite tube is then flushed with water and sediment once the plant host dies and decays away. Geopetal structures seen in several micritic molds further suggest that an initial tube is formed by precipitation of an indurated rind and is then infilled as the tube subsequently overturns on the sediment surface.

Not all samples show this indurated rind, however. Other samples are simply composed of concentric layers of micrite and have an open stem hole at the center. Plant material is restricted to the edge of the inner stem opening and suggests that a micritic concretion forms outward (concentrically) around the plant stem. These micritic samples still exhibit aquatic microfossils and appear to have concentric layers of calcite that radiate away from the central plant stem hole (Fig. 5A). The microfossils and concentric layering of these forms still suggest a biomediated form of calcite precipitation, but the mechanism differs slightly from those samples with the indurated rim in that the oldest calcite is nearest to the central hole and is then coated by successively younger layers of calcite outward. In the samples with the rim, the oldest material is found at the indurated edge, which is then infilled with younger material.

One sparry mold did exhibit concentric rings of fine-grained, clastic inclusions perpendicular to the radial, bladed calcite crystals (Fig. 4F). The concentric rings of clastic inclusions and radiaxial calcite crystals

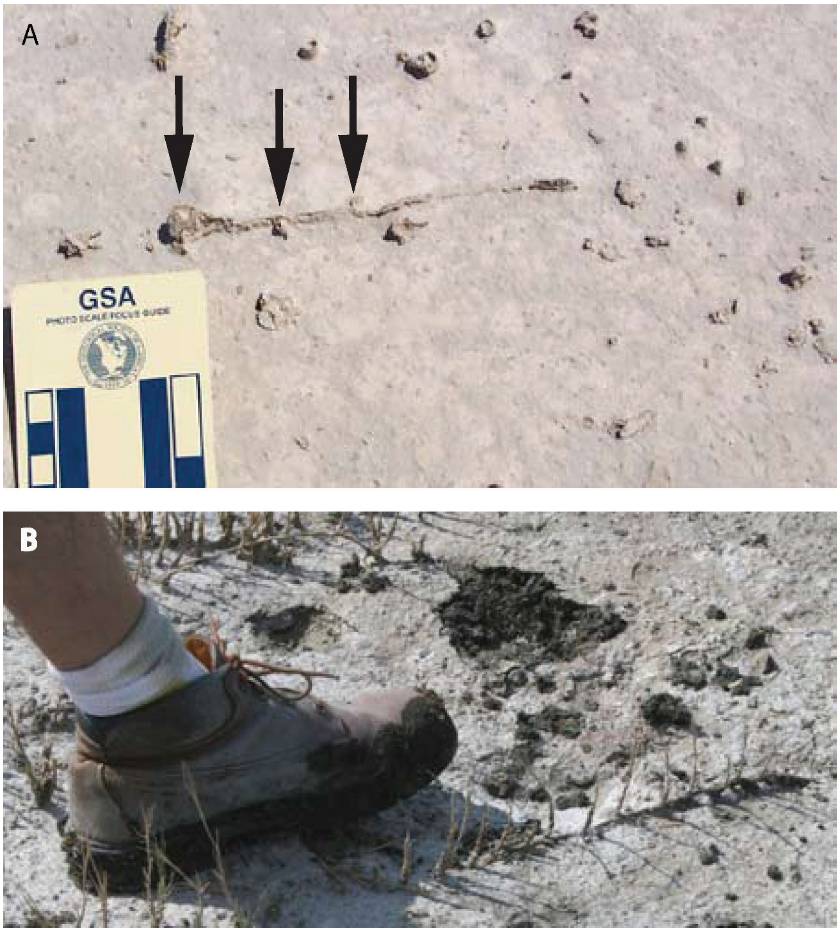

FIG. 7.—**A)** Photograph of elongate crack seen on the playa surface. The crack has been calcified, and several circular tubes can be seen within the calcified crack (arrows). The photo scale shows centimeters (left) and inches (right). **B)** Due to rhizome propagation beneath the sediment, saltgrass plants grown in discrete lineaments along the playa and spring margins. In this photo, the plant at the center of the photo has a portion of the rhizome exposed above the surface (to the right).

emanate outward, away from the stem hole. Therefore, this sample records an initial stage of calcite precipitation (closest to the plant stem hole) and subsequent outward concentric growth rings (represented by the inclusions) that may represent extremely short periods of time (e.g., days, flooding events). The ''age'' of the calcite in these sparry-type molds is opposite of the micritic calcite molds that have an indurated rim; the oldest material is closest to the center in the sparry molds, whereas the oldest material is the farthest from the center in the micritic molds. These different formation types of the micritic and sparry plant molds have significant implications for microsampling studies of calcite tubes such as these, and the interpretation of short-term climate change from their isotopic record.

Implications for the Rock Record

The presence of rhizoliths in the fossil record is often an indication of a paleosol. While the plant molds discussed here may mimic the morphology of rhizoliths, specific characteristics (e.g., apron, presence of ostracods) and geochemical values (e.g., $\delta^{18}O_{calcite}$) are distinctive enough to distinguish them from pedogenic root carbonates. Furthermore, the presence of these nonpedogenic plant molds in the fossil record can indicate standing-water conditions, rather than unsaturated (vadose zone) conditions inferred from pedogenic carbonates; therefore, the proper identification of these structures in the geologic record is critical.

The $\delta^{18}O_{calcite}$ values of these features do not record vadose-zone soil-moisture values (as pedogenic carbonates do) and instead record ambient surface water conditions that are sensitive to (1) evaporation and precipitation ratios, especially in a closed-basin setting such as a playa, as well as (2) the geochemistry (e.g., temperature, $\delta^{18}O_{water}$) of the neighboring springs on the playa surface. Furthermore, interpretation of the $\delta^{13}C_{calcite}$ values of the plant-mold calcite is complicated by the production of biofilms and fractionation by microorganisms, as well as physicochemical effects. Admittedly, plant-respired CO_2 is likely the dominant control on the original dissolved inorganic carbon (DIC) values (especially in a system such as Pilot Valley where DIC concentrations are extremely low; see Oliver 1992). However, as residence time on the playa increases and equilibration with atmospheric CO_2 ($\sim -8‰$) continues, DIC values may begin to approach equilibrium conditions with atmospheric CO_2 to produce $\delta^{13}C_{calcite}$ values near 1–2‰ (Emrich et al. 1970). Additionally, organic activity may fractionate DIC and cause enrichment of the $\delta^{13}C_{calcite}$ values.

While the presence of these plant molds can be an ecological indicator (e.g., a proxy for minimum water depth), it is important to note that the geochemical information contained in these carbonates does not record a complete or annual signal. The formation of these features is dictated by the presence of standing water on the playa surface and is limited to the growing season of the plant host (saltgrass is abundant in $\sim$ July through September). Therefore, use of their isotopic values as a proxy for climate conditions (e.g., water temperature, evaporation/precipitation ratios) is limited. However, since the calcite that forms these stem molds precipitates so quickly (average 1.6 mm of calcite precipitated within one growing season), it can record a ''snapshot in time'' with respect to the geochemical information contained therein and can provide useful information as to the *seasonal* surface conditions on the playa.

As isotopic studies of plant carbonates becomes more precise (with the use of micromilling and laser sampling), understanding the relative age of the calcite in these types of aquatic plant molds has significant implications for interpreting short-term climate change. Identifying the formation mechanism of each plant mold (e.g., an initial rim that then infills vs. a concentric, outward layering of inorganically precipitated sparry calcite) is critical in order to accurately interpret variations in isotopic value and/or calcite composition that may track seasonally fluctuating environmental parameters.

A Suggestion for Clarification

While these plant stem molds appear to resemble rhizoliths, their formation mechanism and ecological indications are quite different. Indeed, they are, instead, macrophyte encrustations (or paludal tufa, to use the terminology of Pedley 1990). However, in the rock record, these calcite plant molds may often be confused with the pedogenic form. Thin-section microscopy, coupled with a detailed analysis of the macroscopic features and surrounding sediments, may help to illuminate the difference. Perhaps a new term should be proposed for those plant stem molds that are found to be part of a paludal tufa system yet lack the other features typical of a tufa deposit?

The term "phytocretion" is proposed as an accurate and appropriate term for mineral precipitates that (a) form around a plant stem (or part other than a root), (b) form above the sediment surface, (c) form in standing water, and (d) may not be associated with typical, widespread tufa and/or travertine deposits such as mounds, oncoids, sheets of intraclast tufa, and/or basal humus or gyttja layers. Since the prefix "*phyto-*" (Greek) simply implies that a plant part is being preserved, the term "phytocretion" implies that a mineral precipitate (in this case, calcite) forms an external mold of a plant. This is consistent with the classification rubric of Klappa (1980) and uses the term "concretion" to imply that a tubular concretion of calcite forms around the plant stem. Given the abundant terminology that exists to describe root preservation (e.g., rhizolith, rhizocretion, root cast), the term "phytocretion" is instead a more generalized term that should indicate that a part of the plant *other than the root* provides the nucleation site for a mineral precipitate.

CONCLUSIONS

While the phytocretions discussed here may resemble rhizoliths found in pedogenic environments, their stable-isotope values as well as specific morphologic characteristics clearly indicate that they form in a unique environment that is above the sediment surface and in standing water. Therefore, they indicate saturated conditions and, due to their formation process, can be a proxy for water depth during the time of formation. Each of these can be a powerful tool for paleolandscape reconstruction when these types of structures are found (and correctly identified) in the geologic record.

However, since their formation is limited by the growing season of the plant host (in this case, *Distichlis* sp.) as well as the presence of standing water on the playa, these plant molds can record only a partial annual signal within their calcite (e.g., $\delta^{18}O_{water}$, temperature). Therefore, use of their $\delta^{18}O_{calcite}$ values as a record of average annual temperature or precipitation conditions is inadequate. Furthermore, the initial stable-isotope conditions that influence these carbonates differ somewhat from their pedogenic counterparts, and thus cannot be interpreted using the same method. Therefore, proper identification of these plant molds in the fossil record is crucial to the appropriate interpretation of the depositional environment as well as the local geochemical parameters during the time of formation.

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