THE NATURE OF A WHEWELLITE-RICH ROCK CRUST ASSOCIATED WITH PICTOGRAPHS IN SOUTHWESTERN TEXAS

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Summary—*A whewellite-rich rock crust covers vast areas of limestone inside dry rock shelters and under rock overhangs throughout the Lower Pecos Region in southwestern Texas (USA). The natural rock crust, composed primarily of whewellite and gypsum with lesser amounts of quartz and silicates, encapsulates the paints of the extraordinary pictographs at more than 250 rock art sites in the region. The authors propose a model that describes the origin of each crust constituent and the evolution of these surfaces. Furthermore, they describe the relationship between the ancient paints and crust matrices, information that is necessary for the development of sound conservation strategies.*

Introduction

The calcium oxalate minerals whewellite ($CaC_2O_4{\bullet}H_2O$) and weddellite ($CaC_2O_4{\bullet}(2{+}x)H_2O$) are now realized to be common on rock surfaces. The substrates on which they are known to occur include granite, marble, limestone and sandstone, as well as glass, plaster and wood. Geographically, oxalate coatings have been reported in the northern Mediterranean (Greece, Italy and Spain) [1-4], Australia [5, 6], and the southwestern United States (California [7], Utah [8] and Texas [9]). In Europe the oxalates are generally associated with stoneworks [3] but also exist on natural rock outcrops [10], including those with ancient rock paintings [11]. In Australia and the United States, the minerals have been identified on rock surfaces associated with prehistoric pictographs.

The origin of whewellite and weddellite on exposed surfaces is not fully understood. Proposed sources include natural processes such as biological activity of organisms living on or within the stone [1, 2, 10, 12], reactions of organic compounds in rain or aerosols at the atmosphere/rock boundary [5, 6], reactions and/or deposition of dissolved organic matter in runoff [11], and animal urine [13]. Artificial sources such as purposeful applications of oxalic acid, casein or other substances to preserve or enhance stonework have also been proposed in some cases [2, 13]. There is general agreement, though, that oxalate coatings associated with prehistoric rock art were produced naturally [6, 11, 12]. However, the disparity in crust characteristics suggests they were formed via different mechanisms.

In cases where the oxalate-rich crusts are associated with pictographs, the ancient paints are generally encapsulated within the crust matrices [6, 7, 9, 14] causing the artifacts to appear faded or be obscured completely, yet the patina may also protect the paintings from weathering and fix the paints to the substrate. Therefore, the development of conservation strategies aimed at enhancing and/or preserving rock art requires that the association of the paint and crust constituents be known.

Finally, there is substantial potential that oxalate coatings can provide important information such as the age of pictographs [14, 15] and palaeoclimate data [12]. These methods involve radiocarbon analyses, therefore there needs to be a consistent model that describes the source and evolution of the carbon in the dated substances.

The aim of this paper is to describe the origin and evolution of the whewellite-rich crust associated with prehistoric rock paintings in the Lower Pecos Region of southwest Texas. The natural rock crust, which also consists of gypsum ($CaSO_4{\bullet}2H_2O$), quartz (SiO_2) and silicates, encapsulates the ancient paints, and we describe the relationship between the paint components and crust matrices.

The Lower Pecos Region

The Lower Pecos Region is generally described as the area surrounding the confluences of the Pecos and Devils Rivers with the Rio Grande (Figure 1). The area is at the southwestern edge of the Edwards Plateau, a massive Cretaceous limestone platform with steep canyons incised by rivers and tributaries. Along the canyon walls are numerous rock overhangs and dry rock shelters. The limestone surfaces in the shelters and under the overhangs, i.e., surfaces that do not receive rain or runoff, are coated with a whewellite-rich crust, while a dark stain occurs on the surfaces exposed to liquid water (Figure 2).

The current climate is semi-arid, with a mean annual rainfall of $498 mm.yr^{-1}$ and mean annual temperature of 20.5°C. Palaeoclimate reconstructions indicate the region experienced a rapid climate change at the end of the Pleistocene, followed by a general warming-drying trend with several reversals to wetter and/or cooler climates during the Holocene [16-19].

The Lower Pecos has an extensive, nearly continuous archaeological record that spans the Holocene [20, 21]. More than a thousand archaeological sites have been identified, about 250 of which contain rock art. The dominant rock art form is pictographs, although petroglyphs have also been identified in at least eight sites [22]. The pictographs

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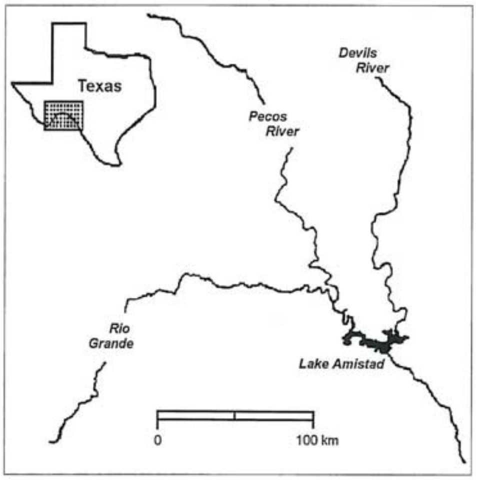

Figure 1. *Map showing the approximate extent of the Lower Pecos Region of Texas.*

occur mostly along the back walls and ceilings of dry rock shelters and under rock overhangs, and so are associated with the whewellite-rich crust.

Five distinct pictograph styles have been defined for the Lower Pecos, each attributed to separate cultural occupations [23]. The oldest and predominant rock art style, the Pecos River Style, is characterized by large, polychromatic anthropomorphic and abstract figures (Figure 3). Turpin [23] argued this style was produced between 3000-4000 years ago when the human population in the region was at a maximum. Radiocarbon dating experiments utilizing a low-temperature, oxygen plasma to isolate organic carbon in Pecos River Style paints yielded ^{14}C AMS dates that range between 2950-4200 years BP [24-26], ages that agree with the archaeological interpretation.

The dominant colours of Pecos River Style pictographs are red and black, with lesser use of yellow, orange and white. The paint pigments are inorganic, primarily iron oxides and manganese oxides for the red and black, respectively [27, 28]. Recent studies also suggest that an organic substance was added to the original paint mixture to suspend the mineral pigments in a liquid medium and/or to act as a binder [9, 29].

Analytical methods

Crust samples were collected from surfaces inside dry rock shelters and under rock overhangs, including archaeological and non-archaeological sites. The surfaces sampled were generally inaccessible to animal contact. Small flakes containing red or black paint were also collected from pictographs at two rock art sites (41VV576 and 41VV129).[1] The paint samples were from Pecos River Style pictographs, hence the paints are expected to be between 3000 and 4000 years old. Also included in this study were samples of rock surfaces from two shallow rock shelters that contained recent lichen activity. The lichen was tentatively identified as *Aspicilia calcarea* [12].

The crust mineralogy was obtained using a Rigaku computer automated D/MX IIIV BX X-ray powder diffractometer (XRD). Samples were prepared for analysis by removing the crust from the substrate with a dental pick or Dremel tool, then grinding into a powder with an agate mortar and pestle.

The distribution and morphology of the crust and paint constituents were established using a JEOL 6400 scanning electron microscope (SEM) equipped with a Noran I-2 Integrated Imaging X-ray Microanalysis System (EDS). We used two-dimensional EDS maps of polished thin-sections to ascertain the relative distribution of principal minerals present, with the exception of whewellite. We mapped elements diagnostic to the minerals, which include sulphur for gypsum, silicon and aluminium in combination for silicates, and silicon alone for quartz. Iron and manganese were mapped to show the location of paint layers. The distribution of phosphorus was also ascertained because it is commonly observed in whewellite-rich rock crusts [2, 5, 30]. Whewellite could not be mapped directly because calcium,

Figure 2. *Photograph of a typical rock overhang along Pressa Canyon in Seminole Canyon State Historical Park. The light-brown whewellite-rich crust covers the surface under the overhang while a dark stain coats rock exposed to rain and runoff.*

Figure 3. *Photograph of a Pecos River Style anthropomorphic pictograph in Fate Bell Shelter (41VV74) located in Seminole Canyon State Historical Park.*

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[1] The number 41 represents the State of Texas, VV represents Val Verde County, and the last number is the archaeological site number.

oxygen and carbon are ubiquitous in the samples; however, the distribution could be inferred in many cases based on the absence of the other minerals.

Crust and paint micromorphologies were studied using SEM/EDS by analyzing broken sections mounted on 1cm aluminium stubs and Au/Pd coated. Samples were analyzed systematically by producing a continuous series of photomicrographs (2000X) in cross-sectional view, extending from the crust surface into the substrate. The elemental composition of each constituent observed in the photomicrographs was ascertained using EDS spot analysis which was then marked directly on the photomicrograph, creating a continuous, high magnification compositional/morphological map of the crust in cross-section. Samples were also studied using a Bruker IFS66 Fourier-transform Raman spectrometer with a FRA106 Raman module and Raman microscope attachment. The FT-Raman analysis provided additional data on the distribution of whewellite and the nature of the paint materials. Magnified (400 X) surface and cross-sectional views were analyzed, with good quality Raman spectra obtained from a spot diameter of about 201μm. The utility of this technique for analyzing oxalate encrustations and pigments has been demonstrated [31]; furthermore, this method allowed *in situ* analysis of organic matter in paint layers [9].

Radiocarbon ages of the whewellite were measured using accelerator mass spectrometry (AMS) ^{14}C dating. The experimental protocol for the analyses has been described previously [12].

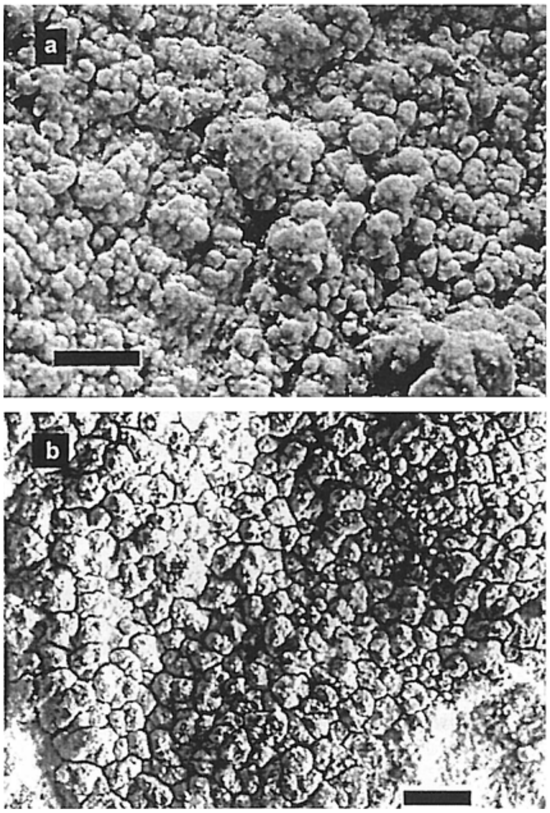

Figure 4. *Optical photomicrographs showing (a) spherical protuberances on the surface of the whewellite-rich crust, (b) the surface of a lichen (tentatively identified as Aspicilia calcarea) found inside tao shallow rock shelters in the Lower Pecos Region. The pruina on this lichen has been identified as weddellite by XRD. Scale bar = 1mm.*

Results and discussion

General description of the whewellite-rich, crust

The whewellite-rich crust was found to occur on the vast majority of rock surfaces not exposed to rain or runoff. The crust was thin, usually less than 0·5mm but up to 1.0mm thick, with a colour that ranged from very pale brown (10 YR 7/4) to reddish brown (5 YR 4/4). The surfaces were generally covered with small spherical protuberances extending about 0.5mm above the surface, giving a botryoidal appearance (Figure 4a), although in some shelters the surfaces appeared smooth and/or coated with dust. Most samples studied had only a single crust layer, though several showed stratification.

Whewellite was the primary component of the crust. Weddellite was not present in any of the crust samples analyzed using XRD, although weddellite was reported at one site (41VV83) in the region based on XRD analysis [28]. Gypsum was the second most abundant crust component, and quartz and silicates were minor constituents. The pruina on the lichen samples proved to be weddellite.

Whewellite was found only in the crust layer—there was no evidence of whewellite in the substrate. The micromorphology of the whewellite was generally equant microcrystalline; however, distinct whewellite microstructures were observed in samples from three sites, features strikingly similar to the thallus of the lichen *A. calcarea* (Figures 5 and 6). Whewellite also formed an outer shell of the spherical protuberances on the crust surface, while the interiors were generally filled with gypsum. In one case, though, features similar in form to lichen hyphae were observed within the spherical protuberance (Figure 7).

Gypsum occurred at the surface of essentially all crust samples studied here. The mineral also occurred within the crust as conglomerates with whewellite, as micro-veins and independent strata in the crust, and within cracks and voids in the substrate (Figures 8 and 9). Gypsum appeared platy in SEM images and was easily distinguished from the other crust components.

While quartz was mainly native to the limestone substrate, several samples contained silica skins at the substrate/crust interface (Figure 10). Silica skins are common on rock surfaces [32]; however, this is the first evidence of this type of crust in the Lower Pecos. Silicates occurred mostly within the whewellite phase of the crust and at the crust surface, but were also present within the substrate. The morphology of silicate constituents was indistinguishable from surrounding materials.

The majority of samples contained elevated concentrations of phosphorus within the crust, as observed in EDS

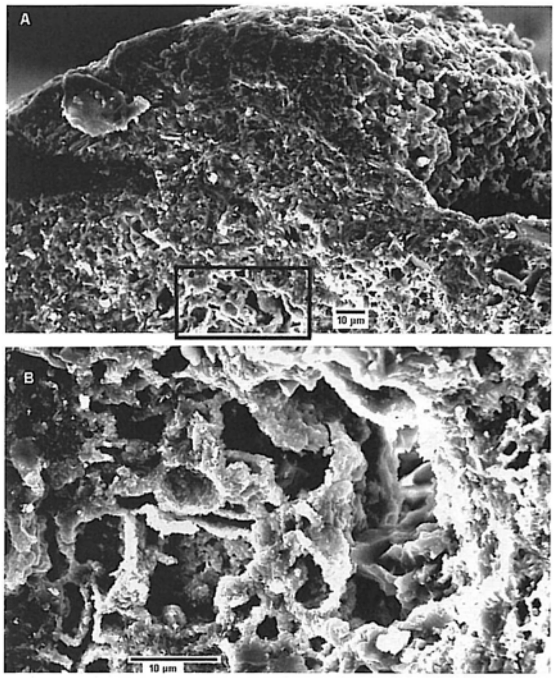

Figure 5. *SEM photomicrographs showing whewellite microstructures observed in a sample from site 41VV576.*

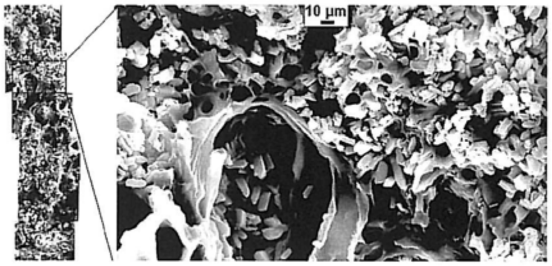

Figure 6. *SEM photomicrographs of A. calcarea collected from a shallow rock shelter. The high magnification view shows thallus structures that are strikingly similar to features observed within the crust (see Figure 5).*

spot analyses and EDS maps (Figures 8 and 9) of both crust and paint samples. However, no phosphorus-containing mineral was indicated in XRD diagrams, nor were there distinguishing features in the crust in the areas that contained the element.

Origin of the Lower Pecos rock crust

Each principal crust constituent was likely the result of an independent process. We propose the following crust-forming mechanisms.

Origin of whewellite

The pervasiveness of whewellite in the Lower Pecos, covering vast areas of limestone, indicates a natural origin for the organic mineral. The most probable source of the oxalate was an epilithic lichen, either *A. calcarea* or a similar species, that proliferated in the sheltered microhabitats. We base this hypothesis on the following evidence:

ii(i) Lichen are well known to produce oxalate coatings (pruina) and to colonize special habitats such as rock shelters with little or no precipitation [33]. Although the pruina on the *A. calcarea* studied here consisted of weddellite, this mineral phase is metastable and spontaneously dehydrates to whewellite [34].

i(ii) The surface of the crust, specifically the spherical protuberances, resembles the surface of the lichen (Figure 4b). These features were probably isidia, ascocarps or lobules which are common on lichen surfaces [35].

(iii) Whewellite microstructures in the crust, which we suggest are fossils of the original source of the oxalate, resemble the thallus of *A. calcarea.* Although such observations were not common, water moves through the substrate and crust episodically which would partially dissolve and reprecipitate the oxalate causing a reorientation of the original structures.

(iv) Hyphae-like features within spherical protuberances (Figure 7) are consistent with the presence of fungi. Since there is insufficient organic matter in the substrate for an unlichenized fungus to thrive, these structures were likely formed by a lichen mycobiont.

(v) The presence of phosphorus in rock crusts could be an indicator of biological activity; moreover, *A. calcarea* is known to concentrate phosphorus [36].

(vi) Radiocarbon analyses indicate a biological source of the oxalate carbon, ruling out an inorganic source for the carbon. Furthermore, the ^{14}C data (Figure 11) demonstrate that the oxalate was produced episodically during the mid and late Holocene, specifically during periods of dry climate [12]. This is consistent with a biological source such as a lichen that is sensitive to fluctuations in environmental conditions.

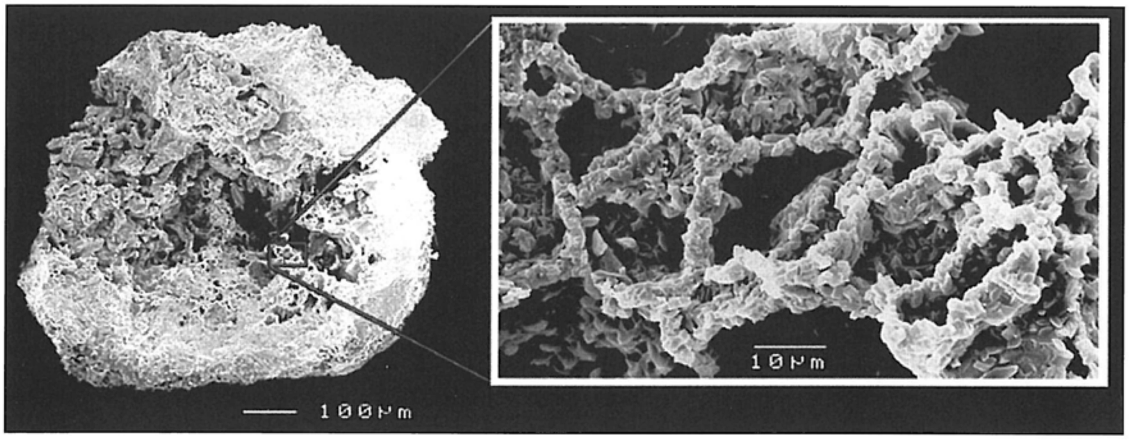

Figure 4. *SEM photomicrograph showing the interior of a spherical protuberance. Most of these features were filled with gypsum, but in this case hyphae-like features were observed.*

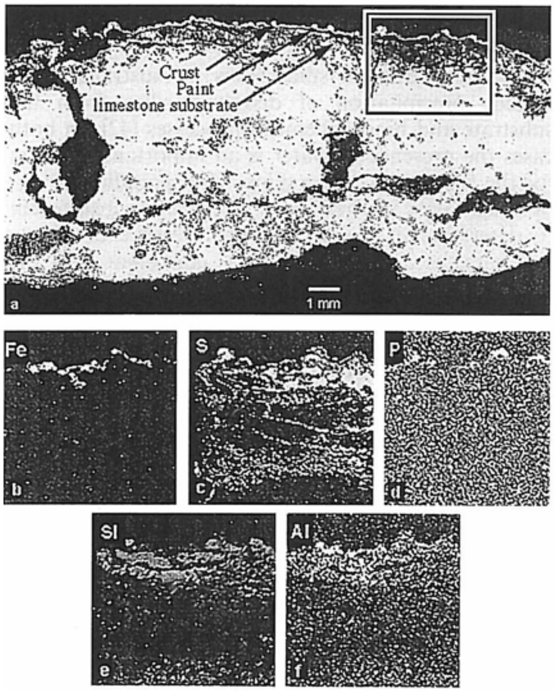

Figure 4. *(a) Optical photomicrograph of a polished thin section of a sample from site 41VV576. Box indicates the region where elemental maps were established. Elemental maps of (b) iron, which indicates the paint layer; (c) sulphur, which shows the distribution of gypsum; (d) phosphorus; (e) silicon; (f) aluminium. The distribution of silicates was inferred by the presence of both aluminium and silicon, while the distribution of quartz was established where silicon occurs alone.*

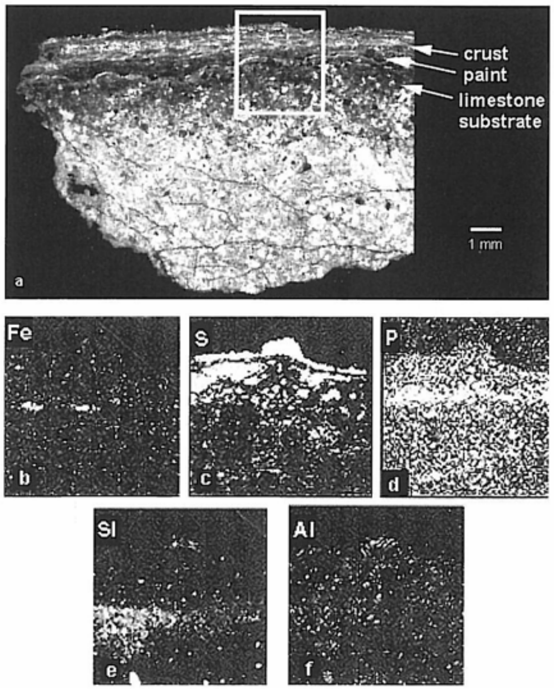

Figure 4. *(a) Optical photomicrograph of a polished thin section of a sample from site 41VV129. Box indicates the region where elemental maps were established. Elemental maps of (b) iron, which indicates the paint layer; (c) sulphur, which shows the distribution of gypsum; (d) phosphorus; (e) silicon; (f) aluminium. The distribution of silicates was inferred by the presence of both aluminium and silicon, while the distribution of quartz was established where silicon occurs alone.*

Origin of gypsum

Turpin [37] first noted the detrimental effects of gypsum subflorescence on Lower Pecos pictographs. Our evidence, which showed gypsum integrated within whewellite and in fissures and voids in the substrate, is consistent with an efflorescence/sub-florescence mechanism [38]. Furthermore, the occurrence of gypsum within surface protuberances and as conglomerates with whewellite suggests the mineral precipitated within voids in the lichen structure and cavities left after the organism decayed.

Efflorescence would occur primarily during wet climate conditions when pore water percolating through the limestone carries sulphate ions to the rock surface, which would result in gypsum precipitating at or near the stone surface as the surface water evaporates. Samples that showed gypsum stratification (Figure 9) further suggest that this process occurred episodically.

It is unlikely that the gypsum in the Lower Pecos crust was the result of reactions of atmospheric SO, [39, 40], since the distribution and morphology of the mineral showed that sulphate migrated from the substrate toward the stone surface. Future studies of the stable sulphur isotopes could provide definitive results as to the source of the sulphate [41].

Origin of silica skins

Proposed sources of silica skins in Australian sites include precipitation of dissolved silica from the substrate and biogeochemical processes [42]. In both cases the presence of water is an important criterion for the formation of the skins. The sporadic findings of silica skins in the Lower Pecos were insufficient to determine its origin, but the presence of quartz and silicates in the limestone is consistent with the substrate being the source of the silica.

The silica skins were observed in two samples (sites 41VV576 and 41VV129) both of which showed silica at the crust/substrate interface and well below the paint. This stratigraphy demonstrates the skin formed prior to the oxalate and the application of the paints. Radiocarbon ages of whewellite from sites 41VV576 and 41VV129 were 3020 ± 70 and 3220 ± 60 BP, respectively, hence the silica skins formed prior to these dates.

Silica skins are considered important to rock art conservation since the coatings protect rock art from graffiti and bind paints to the basal rock [42]. In Lower Pecos sites, silica skins may play an important role in keeping the crust (and paints) attached to the substrate; thus further investigations on the nature and occurrence of the skins are warranted.

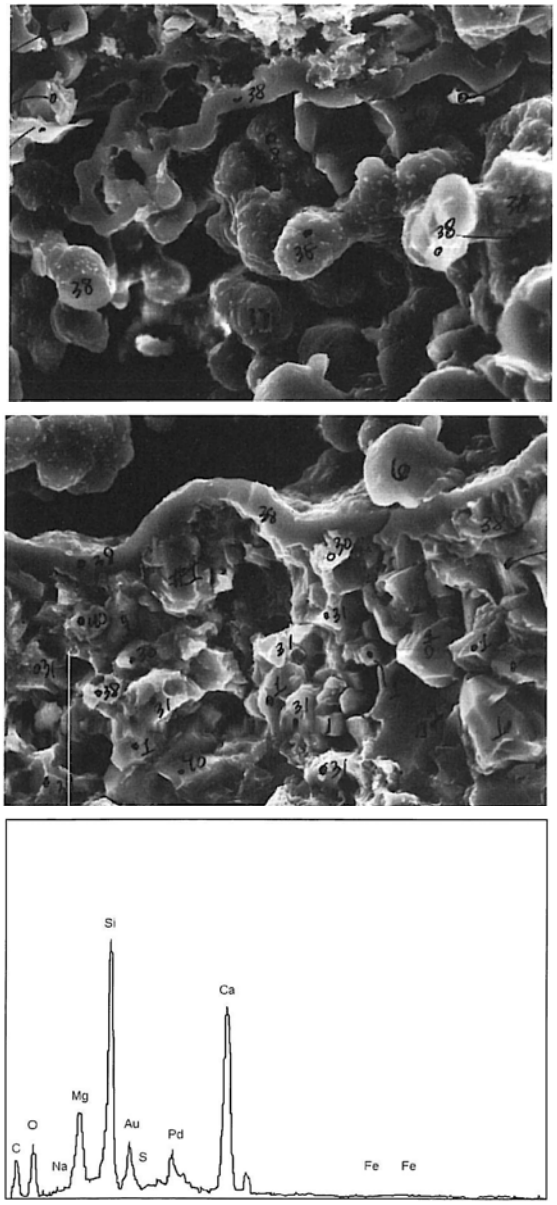

Figure 5. *SEW photomicrograph of silica skin observed in a sample from 41VV576. The accompanying EDS spectrum shows the preponderance of silicon in this feature.*

Origin of silicates

Silicates, predominantly kaolinite, were common in the crust, occurring mostly within the whewellite phase and at the crust surface. The most likely source of this component was aeolian material adhering to surfaces while damp with dew or fog, then becoming fixed, a mechanism proposed by Curtiss *et al.* for silica-alumina crusts in semi-arid regions [43]. Many dry rock shelters that contain rock art also have dirt floors that can contribute substantial quantities of silicates to the rock surface and obscure the rock art. At two extensively visited sites, 41VV73 (Fate Bell Shelter) and 41VV187 (Parida Cave), site managers have placed rubber mats on trails inside the shelters to reduce airborne matter during visits; however, the vast majority of sites do not have such preventive measures.

Origin of phosphorus

Phosphorus was a common component in the majority of samples studied, as established by EDS spot analyses and EDS mapping (Figures 8 and 9), although the phosphorus-containing compound was not determined. Phosphorus has been identified in many oxalate coatings [2, 5, 13 (and references within), 28, 30], but neither the mineralogy nor the source of the component has been determined. We suggest phosphorus in Lower Pecos crusts was the result of *A. calcarea,* since this lichen and others are known to accumulate the element, although the original source is not known

[36]. We can definitely rule out proposed sources of phosphorus outlined by Salvadori and Realini [13] such as milk, bone, casein, urine, guano, pigeon droppings, or any materials purposely applied, based on the nature of the Lower Pecos crust.

Phosphorus was also present in each of the paint samples analyzed, although not necessarily in the paint layer (Figure 9). Recently, it was speculated that phosphorus in paint samples from Panther Cave (41VV83) was the result of bone fragments introduced into the paint during preparation of the paint mixtures [28]. However, since phosphorus was common in samples that do not contain paint and not always associated with the paint layer, it is far more likely that it is a natural constituent of the crust. Since lichen and microbes can concentrate phosphorus, further studies of the source of the element could provide key evidence of specific biological activity.

Evolution of the Lower Pecos rock crust

Each accretion process likely occurred during specific time periods and climate conditions. Indeed, the periods of oxalate production established by radiocarbon dates of whewellite correlate with periods of warm/dry climate predicted by various palaeoclimate reconstructions for the Lower Pecos [16-19], while gaps in the data correlate with cool/wet conditions. Hence, we propose the following model based on the distribution of the crust components, ^{14}C data and palaeoclimate models for the evolution of the Lower Pecos rock crust (Figure 11).

Prior to the Holocene, the primary weathering process on the surfaces inside rock shelters was exfoliation due to freeze-thaw cycles that caused substantial surface spalling [44. 45]. With the amelioration of the climate at the onset of the Holocene, the limestone surfaces inside the shelters began to stabilize. The initial crust to form on these stabilized surfaces was likely a silica skin, which we suggest formed during the early Holocene (l0 000 to 6000 years BP) when the climate was considerably wetter than any time since. The formation of silica skins overlapped episodes of freeze-thaw exfoliation, producing the discontinuous, sporadic coating currently observed. During this same period gypsum efflorescence would have occurred also, contributing to the instability of the rock surfaces during this period.

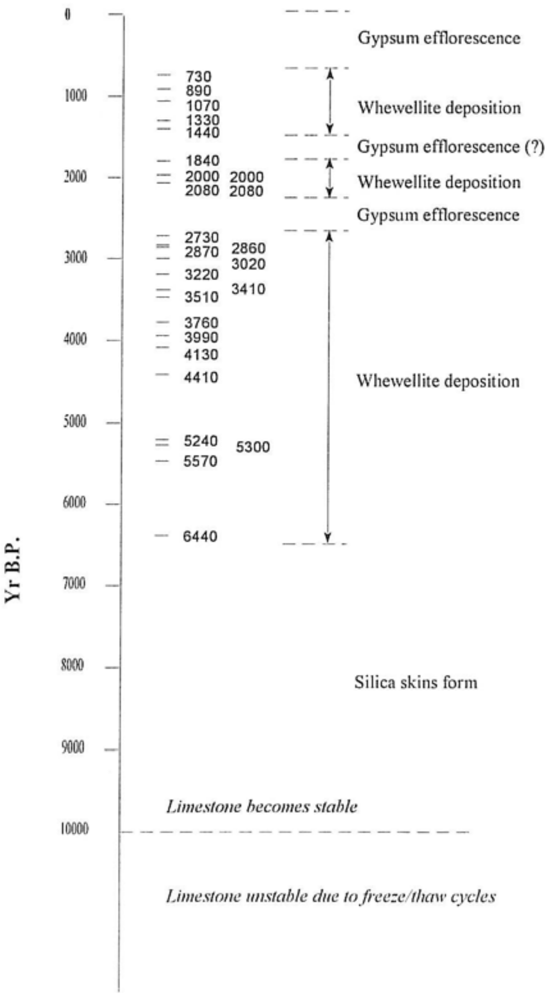

Figure 6. *Schematic showing the evolution of the Lower Pecos rock crust. Included here are the radiocarbon data.*

The production of whewellite began about 6000 years ago (the oldest oxalate ^{14}C age is 6440 ± 50 BP), which also coincides with the onset of the Holocene Climate Optimum when summer temperatures were 2 to 4°C higher than at present throughout continental North America [46]. Since *A. calcarea* is a xeric, epilithic species, the organism would thrive in dry climates, specifically when the substrate was dry, obtaining requisite moisture by the uptake of water vapor [33]. Thus, Lower Pecos shelters were ideal niches for the lichen during xeric climate episodes, and the organism flourished throughout the dry middle Holocene.

The late Holocene was characterized by at least two, possibly three, reversals to cooler/wetter climate. Wet conditions would severely limit the vitality of *A. calcarea* due to a variety of physicological reasons including response to freezing water [47] or a water imbalance that limits the mycobiont or photobiont components of the lichen [33, 48]. Furthermore, the lichen would be inundated with water from the substrate saturated with calcium and sulphate ions which would be detrimental to the organism. Hence, during wet climate regimes the lichen would become dormant or die, and gypsum efflorescence would become the dominant accretion process.

The first major reversal to cooler/wetter climates occurred around 2500 years BP [16], which corresponds to a gap in the oxalate ^{14}C data between 2730 and 2080 years BP. We also predict a second short mesic interlude based on a gap in the oxalate ^{14}C ages between 1840 and 1440 years BP, although there are conflicting palaeoclimate data on whether there was a shift in the climate during this period. The final gap in the data begins at 730 years BP, which corresponds to the onset of the Little Ice Age, a period when global temperatures were markedly lower than at present [46]. There is no evidence of later oxalate production, as shown by the lack of ^{14}C data, so the last crust constituent formed was gypsum, which is observed on the sample surfaces studied.

Silicates would attach to surfaces when the surface was damp from dew or fog. The primary association of silicates with whewellite could be due to the larger surface areas of the lichen, longer exposure times, and/or more aeolian matter during dry climate conditions.

The majority of the rock paintings were produced between 3000 and 4000 years BP, thus there was a significant chance that the paints were applied to surfaces with whewellite and/or the mineral was subsequently produced on the paint surface. Furthermore, the paints experienced two, possibly three, episodes of gypsum efflorescence.

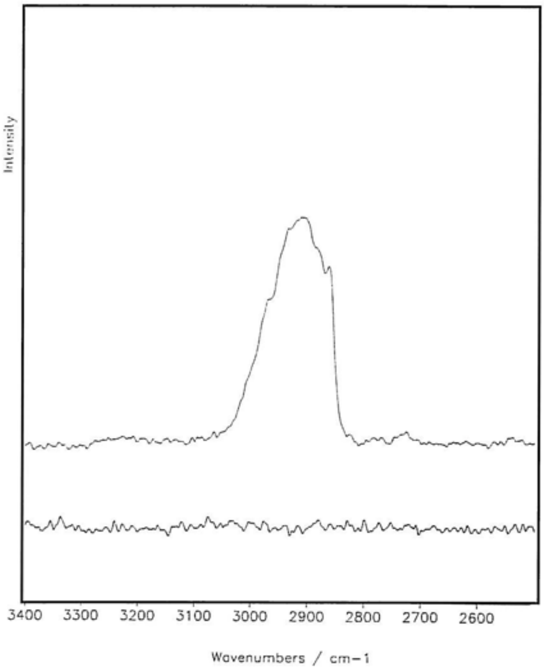

Figure 7. *FT-Raman spectrum of black paint from site 41VV576 (top) showing the wavenumber region from 2500 to 3400cm^{-1}. The broad feature centered at 2936cm^{-1} and with prominent shoulders at 2852 and 2964cm^{-1} is indicative of the presence of CH_2 groups, while the weaker band at 2720cm^{-1} is assignable to a terminal $C(CH_3)_2$ group. Note that these spectral features were absent in the Raman spectrum of the red painted regions (bottom).*

Relationship between prehistoric paints and rock crust

Paint samples were analyzed to ascertain the relationship between the paint constituents and crust matrices. This information is vital to the development of conservation strategies and to evaluate potential changes in the chemistry of the original paints. Results indicate there are similarities between samples from the two sites, as well as characteristics unique to each site and each sample. Similarities include:

(a) All the paint layers were encapsulated within the crust; however, the constituents adjacent to the paints were not consistently the same.

(b) The external surface of the crust was either a combination of gypsum and silicates, or a conglomerate of whewellite, gypsum and silicates.

(c) The paint layers were thin, typically ≤ 100µm, and appeared to be continuous under the optical microscope with no evidence of disruption, even where oxalate was deposited over the paint.

(d) Silicates were omnipresent within both red and black paints, suggesting clays were either added as an extender in the original paint recipe or a natural component of the pigment source. Analysis of extenders in palaeopaints from European sites has proved useful in establishing relationships between rock art panels and individual motifs [49] and could thus prove fruitful in the case of Pecos River pictographs.

(e) The FT-Raman analysis showed that organic matter was present in the black paints from the two sites, although not present in red paints (Figure 12). Organic matter is often assumed to be a necessary component in ancient rock paints for suspending mineral pigments in a liquid medium and/or to fix paints to the stone. The FT-Raman results show clearly that organic matter was present, as evidenced by prominent peaks in the spectra between 2500 and 3400cm-1 due to aliphatic $\nu(CH_3)$ and $\nu(CH_2)$ vibrations, and a weaker band at 2720cm^{-1} assignable to the $\nu(C(CH_3)_2)$ group.

The study of the paints from the two sites also showed characteristics unique to each site, which we describe below.

Site 41VV576

Samples from this site, which is under a rock overhang in a dry canyon tributary of the Pecos River, had a single crust layer 250-550µm thick covered with numerous spherical protuberances. Most of the crust was a whewellite/gypsum/silicate conglomerate, although several areas showed micro-veins of gypsum within whewellite. Silica skins were also observed in samples from this site.

The paints were generally ~100µm thick, and located 100µm below the crust surface. The paint layers occurred above either a whewellite/silicate mixture or whewellite/silicate/gypsum conglomerate. The interpretation is that the paint was originally applied to a whewellite/silicate surface, then gypsum migrated into this existing material, including the paint layer in some cases.

EDS maps of a sample from this site showed gypsum present at the crust surface, within the crust matrix, and in the substrate (Figure 8). The maps also indicated elevated concentrations of phosphorus in the crust, and high concentrations of silicates and quartz under the crust and in the substrate.

Site 41VV129

The crust in this large, U-shaped, dry rock shelter adjacent to the Pecos River ranged up to 1.0mm thick, and was the thickest and most complex patina studied. The crust surface appeared smooth and dusty. In cross-section, the crust showed distinct stratification, with the strata composed of conglomerates, including two layers primarily of whewellite and two of gypsum. The relatively thin paint layer (50-80µm thick) was located ~1mm below the crust surface and incorporated within the lower whewellite stratum. We radiocarbon-dated the two layers of whewellite separately, obtaining ages of 2000 ± 60 and 3220 ± 60 years BP for the upper and lower strata, respectively. Thus, the age of the lower whewellite layer was consistent with the expected age of the rock paint. This further demonstrates the utility of radiocarbon-dating oxalate laminae to obtain estimates of rock art ages [15].

The EDS map of iron showed a discontinuous paint layer (Figure 9), although under the optical microscope the paint appeared continuous. The map of sulphur showed clearly that the crust surface was predominately gypsum, with significant quantities of the mineral throughout the crust. Phosphorus was also indicated in EDS maps, but in the crust, not in the paint. Quartz was present in only a small area in the substrate under the crust in the samples analyzed.

Conclusions

The aim of this paper was to describe the nature of the whewellite-rich crust associated with prehistoric pictographs in the Lower Pecos Region. We present evidence for a lichen source of the whewellite, mainly fossil microstructures observed in the crust and a logical correlation between dry climate conditions and oxalate production. While we can rule out many previously proposed sources of oxalate such as purposeful application of substances to preserve the rock art, animal urine or contact, and organic matter in runoff, there is insufficient evidence to negate reactions of organic matter in atmospheric aerosols at the rock surface or activity of other microbes.

Whewellite- and weddellite-rich crusts have often been implicated as having detrimental effects on stone surfaces, destabilizing the substrate and causing surface exfoliation. The oxalate-rich crust in the Lower Pecos has persisted in many sites for thousands of years, and even longer periods in Australian rock art sites [25]; thus, the presence of calcium oxalates should not be categorically deemed deleterious to surfaces on which they occur.

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References

1 Del Monte, M., and Sabbioni, C., 'A study of the patina called *scialbatura* on imperial Roman marbles', *Studies in Conservation* 32 (1987) 114-121.

2 Lazzarini, L., and Salvadorio, O., 'A reassessment of the formation of the patina called scialbatura', *Studies in Conservation* 34 (1989) 20-26.

3 Realini, M., and Toniolo. L., editors, *Proceedings of the II International Symposium: The Oxalate Films in the Conservation of Art,* Centro C.N.R., Milan (1996).

4 Garcia-Vallés, M., Blázquez, F., Molera, J., and Vendrell-Saz, M., 'Studies of patinas and decay mechanisms leading to the restoration of Santa Maria de Montblanc (Catalonia, Spain)', *Studies in Conservation* 41 (1996) 1-8.

5 Watchman, A., 'A summary of occurrences of oxalate-rich crusts in Australia', *Rock Art Research* 7 (1990) 44-50.

6 Watchman, A.L., 'Age and composition of oxalate-rich crusts in the Northern Territory, Australia', *Studies in Conservation* 36 (1991) 24-32.

7 Scott, D.H., and Hyder, W.D., 'A study of the California Indian rock art pigments', *Studies in Conservation* 38 (1993) 155-173.

8 Chaffee, S.D., Hyman, H., Rowe, M.W., Coulam, N.J., Schroedl, A., and Hogue, K., 'Radiocarbon dates on the All American Man Pictographs', *American Antiquity* 59 (1994) 769-781.

9 Russ, J., Palma, R.L., Loyd, D.H., Farwell, D.W., and Edwards, H.G.M., 'Analysis of the rock accretions in the Lower Pecos Region of southwest Texas', *Geoarchaeology 10* (1995) 43-63.

10 Del Monte, M., Sabbioni, C., and Zappia, G., 'The origin of calcium oxalates on historical buildings, monuments and natural outcrops', *The Science of the Total Environment* 67 (1987) 17-39.

11 Chiari, G., 'Calcium oxalate: sporadic findings of some interest' in *Proceedings of the II International Symposium: The Oxalate Films in the Conservation of Art,* ed. M. Realini and L. Toniolo, Centro C.N.R., Milan (1996) 49-58.

12 Russ, J., Palma, R.L., Loyd, D.H., Boutton, T.W., and Coy, M.A., 'Origin of the whewellite-rich rock crust in the Lower Pecos Region of southwest Texas and its significance to paleoclimate reconstructions', *Quarternary Research* 46 (1996) 27-36.

13 Salvadorio, O., and Realini, M., 'Characterization of biogenic oxalate films' in *Proceedings of the II International Symposium: The Oxalate Films in the Conservation of Art,* ed. M. Realini and L. Toniolo, Centro C.N.R., Milan (1996) 337-351.

14 Watchman, A., and Hatte, E., 'A nano approach to the study of rock art: "The Walkunders", Chillagoe, North Queensland, Australia', *Rock Art Research* 13 (1996) 85-92.

15 Watchman, A., 'Evidence of a 25,000-year-old pictograph in Northern Australia', *Geoarchaeology* 8 (1993) 465-473.

16 Bryant, V.M., and Holloway, R.G., 'A late Quaternary paleoenvironmental record on Texas: an overview of the pollen evidence' in *Pollen Records of Late Quaternary North American Sediments,* ed. by V.M. Bryant and R.G. Holloway, American Association of Stratigraphy and Palynology, Dallas (1985) 39-70.

17 Humphrey, J.D., and Ferring, C.R., 'Stable carbon evidence for latest Pleistocene and Holocene climate change in north-central Texas', *Quaternary Research* 41 (1994) 200-213.

18 Nordt, L.C., Boutton, T.W., Hallmark, C.T., and Waters, M.R., 'Late Quaternary vegetation and climate changes in central Texas based on isotopic compositions of organic carbon', *Quaternary Research* 41 (1994) 109-120.

19 Johnson, L., and Goode, G.T., '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 (1994) 1-51.

20 Hester, T.R., 'A chronological framework for the Lower Pecos prehistory', *Bulletin of the Texas Archeological Society* 59 (1988) 53-64.

21 Turpin, S.A., 'Time out of mind: the radiocarbon chronology of the Lower Pecos River Region' in *Papers on Lower Pecos Prehistory,* Studies in Archeology 8, Austin (1991) 1-49.

22 Labadie, J.H., 'Petroglyphs in the Lower Pecos Region of southwest Texas' in *Rock Art Papers 9,* San Diego (1992) 111-120.

23 Turpin, S.A., 'Speculation on the age and origin of the Pecos River style, Southwest Texas' in *American Indian Rock Art 16,* Austin (1990) 99-122.

24 Russ, J., Hyman, M., Shafer, H.J., and Rowe, M.W., 'Radiocarbon dating of prehistoric rock paintings by selective oxidation of organic carbon', *Nature* 348 (1990) 710-711.

25 Russ, J., Hyman, M., Shafer, H.J., and Rowe, M.W., 'Direct radiocarbon dating of rock art', *Radiocarbon* 34 (1992) 867-872.

26 Ilger, W., Hyman, M., Southon, J., and Rowe, M.W., 'Dating pictographs with radiocarbon', *Radiocarbon* 37 (1995) 299-310.

27 Zolensky, M., 'Analysis of pigments from prehistoric pictographs, Seminole Canyon State Historical Park' in *Seminole Canyon: The Art and Archeology, Research Report* 83, Austin (1982) 277-284.

28 Hyman, M., Turpin, S.A., and Zolensky, E., 'Pigment analyses from Panther Cave, Texas', *Rock Art Research* 13 (1996) 93-103.

29 Reese, R., Hyman, M., Rowe, M., Derr, J., and Davis, S., 'Ancient DNA from Texas pictographs', *Journal of Archeological Science* 23 (1996) 269-277.

30 Ford, B., MacLeod, I., and Haydock, P., 'Rock art pigments from Kimberley Region of Western Australia: identification of the minerals and conversion mechanisms', *Studies in Conservation* 39 (1994) 57-69.

31 Edwards, H.G.M., Farwell, D.W., Jenkins, R., and Seaward, M.R.D., 'Vibrational Raman spectroscopic studies of calcium oxalate monohydrate and dihydrate in lichen encrustations on Renaissance frescos', *Journal of Raman Spectroscopy* 23 (1992) 185-189.

32 Watchman, A., 'What are silica skins and how are they important in rock art conservation?', *Australian Aboriginal Studies* 1 (1990) 21-29.

33 Lange, O.L., and Green, A.T.G., 'High thallus water content severely limits photosynthetic carbon gain of central European epilithic lichens under natural conditions', *Oecologia/* 108 (1996) 13-20.

34 Frey-Wyssling, A., 'Crystallography of the two hydrates of crystalline calcium oxalate in plants', *American Journal of Botany* 68 (1981) 130-141.

35 Jahns, H.M., 'Anatomy, morphology, and development' in *The Lichens,* Academic Press, New York (1973) 3-57.

36 Syers, J.K., and Iskandar, I.K., 'Pedogenetic significance of lichens' in *The Lichens,* Academic Press, New York (1973) 225-248.

37 Turpin, S.A., *Seminole Canyon: The Art and Archeology, Research Report* 83, Austin (1982).

38 Winkler, E.M., *Stone: Properties, Durability in Man's Environment,* Springer-Verlag, New York (1975) 230.

39 Gauri, K.L., Chowdhury, A.N., Kulshreshtha, N.P., and Punuru, A.R., 'The sulfation of marble and the treatment of gypsum crusts', *Studies in Conservation* 34 (1989) 201-206.

40 Skoulikidis, TH., and Charalambous, D., 'Mechanism of sulphation by atmospheric SO, of the limestones and marbles of the ancient monuments and statues', *British Corrosion Journal* 16 (1981) 70-77.

41 Rösch, H., and Schwarz, H.J., 'Damage to frescoes caused by sulphate-bearing salts: where does the sulphur come from?', *Studies in Conservation* 38 (1993) 224-230.

42 Watchman, A., 'Composition, formation and age of some Australian silica skins', *Australian Aboriginal Studies* 1 (1992) 61-66.

43 Curtiss, B., Adams, J.B., and Ghiorso, M.S., 'Origin, development and chemistry of the silica-alumina coatings from the semi-arid regions of Hawaii', *Geochimica et Cosmochimica Acta* 49 (1985) 49-56.

44 Bryant V.M., and Shafer, H.J., 'The Later Quaternary paleoenvironment of Texas: a model for the archeologist', *Bulletin of the Texas Archeological Society* 48 (1977) 1-25.

45 Robinson, D.G., 'Stratigraphie analysis of Bonfire Shelter, Southwest Texas: pilot studies of depositional processes and paleo-climate', *Plains Anthropologist* 42 (1997) 33-40.

46 COHMAP members, 'Climatic changes of the last 18,000 years: observations and model simulations', *Science* 241 (1988) 1043-1050.

47 Kappen, L., 'Response to extreme environments' in *The Lichens,* Academic Press, New York (1973) 599-632.

48 Poelt, J., 'Classifications' in *The Lichens,* Academic Press, New York (1973) 599-632.

49 Menu, M., and Watler, P., Prehistoric cave paintings PIXE analysis for the identification of paint "pots"', *Nuclear Instruments and Methods in Physics Research* B64 (1992) 547-552.

50 Wadsten, T., and Moberg, R., 'Calcium oxalate hydrates on the surface of lichens', *Lichenologist* 17 (1985) 239-245.

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Résumé—*Une croûte de roche riche en whewellite recouvre de vastes zones de calcaire dans les abris et cavités répartis tout autour de la région de Lower Pecos dans le Sud-Ouest du Texas (USA). La croûte de roche naturelle, composée avant tout de whewellite et de gypse avec des quantités moindres de quartz et de silicates, englobe les peintures d'extraordinaires pictogrammes sur plus de 250 sites d'art rupestre de la région. Les auteurs proposent un modèle décrivant l'origine de chaque croûte et l'évolution de ces surfaces. Ils décrivent en outre la relation entre les peintures et les croûtes matricielles, information nécessaire au développement des méthodes de conservation acoustiques.*

Zusammenfassung—*Im gesamten Gebiet der Lower Pecos in Südwesttexas (USA) finden sich whewellitreiche Felsenkrusten, die weite Teile von Kalkstein in trockenen Felsenhöhlungen und unter Felsenüberhängen bedecken. Diese natürlichen Felsverkrustungen, die sich hauptsächlich aus Whewellit und Kalk mit geringen Anteilen von Quartz und Silikaten zusammensetzen, bedecken die Farben von außergewöhnlichen Piktogrammen an mehr als 250 Standorten mit Höhlenmalerei in dieser Region. Die Verfasser entwickeln ein Modell zur. Beschreibung des Ursprungs jeder dieser Schichtbestandteile und zur Entstehung dieser Oberflächen. Darüberhinaus erklären sie den Zusammenhang zwischen den alten Farben und der Krustenstruktur, Informationen, die für die Entwicklung fehlerfreier Konservierungsstrategien benötigt werden.*

Resumen—*Extensas areas de culiza en el interior de abrigos rupestres y bajo salientes de rocas, a lo largo de la región del bajo Pecos, en el suroeste de Texas (USA), se encuentran recubiertos de incrustaciones en forma de costras de roca ricas en whewelita. Los componentes primordiales de estas incrustaciones, la whewelita y el yeso con cantidades menores de cuarzo y silicatos, recubren las pinturas en forma de extraordinarios pictogramas de más de 250 enclaves de arte rupestre en la región. Los autores proponen un modelo que describe el origen del constituyente de cada incrustación y la evolución de estas superficies. Se describen además las relaciones entre las pinturas antiguas y las matrices de las incrustaciones, información necesario para el desarrollo de estrategias de conservación bien fundadas.*