Two Independent Methods for Dating Rock Art: Age Determination of Paint and Oxalate Layers at Eagle Cave, TX

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ABSTRACT

This study demonstrates a novel approach to overcoming challenges associated with obtaining reliable radiocarbon dates for rock paintings. Using two independent methods, we obtained ages for Pecos River style paintings at Eagle Cave in Langtry, Texas. The first method employed plasma oxidation to isolate organic carbon directly from the paint layer for accelerator mass spectrometry C-14 measurement. The second method treated mineral accretion layers with phosphoric acid to isolate calcium oxalate for plasma oxidation cleaning, combustion, and C-14 measurement to obtain minimum and maximum ages for the paintings. Radiocarbon dates for the paintings are statistically indistinguishable, with a weighted average of 3280±70 ^{14}C years BP calibrated to 1740-1420 cal BC (3690-3370 cal BP) at 2 sigma (95.4%) probability. Radiocarbon assays obtained for the overlying accretion layers are younger and underlying accretion layers are older. The chronological stratigraphy of the accretion and paint layers supports the validity of both dating methods. With accurate and reliable dating methods, rock paintings in the region can be studied alongside excavated cultural deposits to provide a more complete understanding of this hunter-gather society. These methods for dating rock paintings can be applied to many rock art provinces around the world.

1. Introduction

The primary objective of this study was to establish the age of rock paintings at Eagle Cave in the Lower Pecos Canyonlands of southwest Texas using two independent methods. The first method employed low-temperature plasma oxidation to obtain direct radiocarbon dates on organic paint components. The second method isolated oxalate mineral accretions for radiocarbon dating to constrain the age of paint layers with minimum and maximum ages. Paint and oxalate age results, including replicate measurements on the same pictograph, demonstrate that the rock art panel at Eagle Cave was created 3500 years ago. To our knowledge, this is the first rock art dating study that provides independent verification of results with minimum, direct, and maximum ages

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for a single pictograph. The approach we present here addresses issues that researchers encounter when dating rock paintings.

Paint is comprised of three primary components: (1) pigment, which is the material that provides color; (2) binder, the component that holds the pigment together; and (3) vehicle or emulsifier to carry or disperse the pigment particles. Painted onto a rock surface, the original paint recipe is absorbed into the rock support. Consequently, paint samples consist of paint, rock substrate, and associated accretionary minerals (Fig. 1). If the pigment is charcoal, then there is often sufficient organic material present in a paint sample for radiocarbon dating. However, most rock art assemblages around the world were created with mineral pigments: reds, oranges, browns, and yellows are usually iron oxide/hydroxide minerals of various oxidations states and degrees of hydration, and black is often a manganese oxide/hydroxide instead of charcoal (Rowe, 2001). Inorganic pigments cannot be radiocarbon dated because they do not contain carbon. Nonetheless, pictographs with inorganic pigments potentially can be radiocarbon dated if the prehistoric artists used organic materials as a binder or vehicle and enough of these have survived for accurate and reliable measurements.

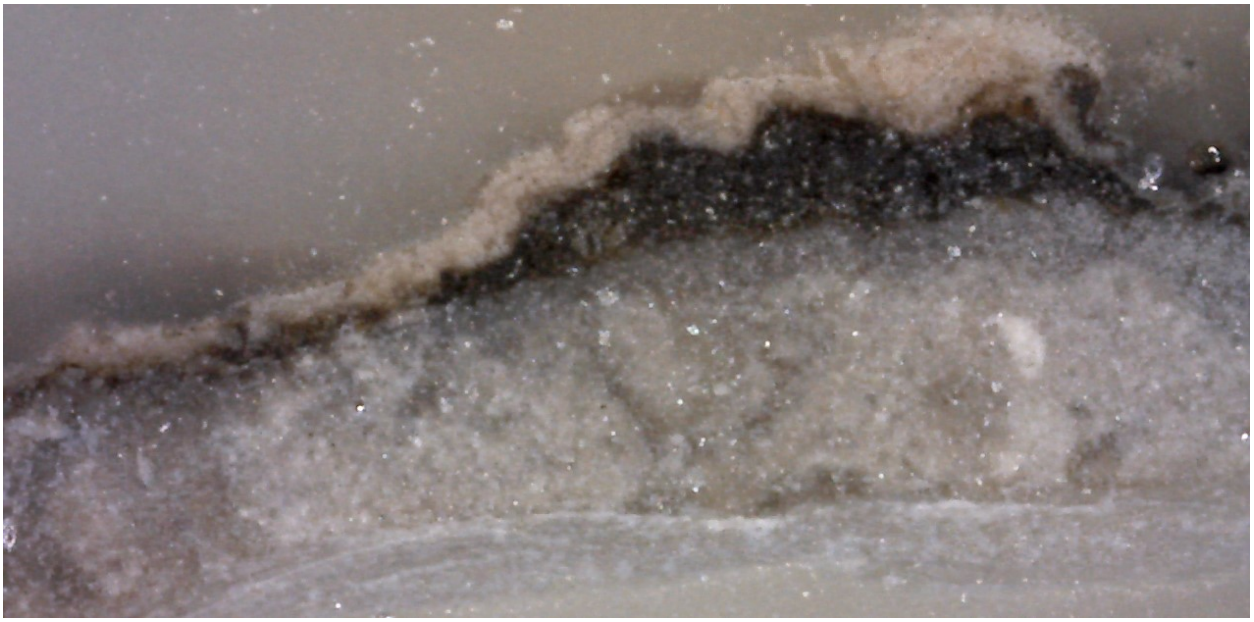

Fig. 1. Cross-section of a black paint sample (1 and 1') from Eagle Cave. For scale, the width of the section shown is ~0.5 cm. The black paint layer varies from 50 to 250 μm and consists of manganese mineral pigment, calcite, whewellite, and gypsum. Overlying the paint is a cream-colored whewellite, calcite, and gypsum mineral accretion. Underlying the paint is a grey layer of calcite and whewellite. The rock substrate is a dolomitic limestone.

Obtaining reliable radiocarbon dates for rock paintings presents a challenge. The most significant concern is extracting sufficient carbon related to the painting event for accelerator mass spectrometry (AMS) radiocarbon dating. The amount of carbon present in both organic and inorganic pigmented paint samples is small, much less than what is available for other types of archaeological artifacts. While the analysis of ≥100 µg carbon is routine, AMS can measure samples as small as 15 µg carbon. McDonald et al. (2014) had a 50% success rate on dating paint samples from the Western Desert in Australia. Samples ranged in size from 2 to 200 mg of paint and associated minerals. Fifty percent of these samples contained 20-240 µg organic carbon for dating, whereas many of the smaller samples (those less than <10 mg in size) had <10 µg carbon that were too small for AMS measurement.

Another significant issue involves physical and chemical contamination inherent in rock shelter or cave environments. Organic contamination in the form of microbes, lichen, plant fibers, spider webs, and other matter can occur on the surface of and within the rock substrate. Also, previous documentation efforts sometimes involved treating rock paintings with kerosene or gasoline to improve photography (Gebhard, 1960:16; Chaffee et al., 1994). Even the mineral surface to which the artist applied the paint often contains carbon-based minerals (limestone and/or whewellite) and presents a source of contamination that must be isolated or removed prior to analysis. It is crucial that control samples of unpainted rock substrate (backgrounds) are collected directly adjacent to paint samples and analyzed in a parallel fashion to ascertain if there is contamination in the rock substrate that affects the ability to obtain a reliable date for a painting.

1.1 Methods for Dating Rock Paintings

Several laboratories have radiocarbon dated rock paintings using acid-base-acid (ABA) pretreatment, combustion, and AMS measurement (Rowe 2012). A unique application of ABA pretreatment was employed to directly date beeswax rock art, occurring in northern Australia (Nelson et al., 1995; Taçon et al., 2004). However, radiocarbon dates determined using ABA pretreatment primarily have been obtained for charcoal pigment (e.g., Van der Merwe et al., 1987; Valladas et al., 1992, 2001; Valladas, 2003; Sand et al., 2006; Morwood et al., 2010; Bonneau et al., 2011; Simek et al., 2013; Samson et al., 2017). As in all archaeological applications where charcoal is dated, caution is advised in interpreting these dates due to *old wood* and *old charcoal* effects (Schiffer, 1986; Bednarik, 1994). Radiocarbon dates on charcoal pictographs should be considered maximum ages for painted images unless these effects can be ruled out.

Other techniques have been used by researchers to determine minimum and/or maximum ages for the production of rock art. Optically-stimulated luminescence (OSL) of

quartz grains (Roberts et al., 1997, 2000; Yoshida et al., 2003) and radiocarbon dating of charcoal inclusions (Finch et al., 2019, 2020) have been used to date mud wasp nests that are over or under art layers in Australia. Uranium-series dating has provided minimum ages for calcite formations that cover paintings in dark zone caves (e.g., Aubert et al., 2007; Pike et al, 2012; Aubert et al., 2014; Hoffmann et al., 2016; Hoffmann et al., 2018; Pons-Branchu et al., 2020).

1.1.1 Plasma Oxidation

Developed by Marvin Rowe's laboratory at Texas A&M University, plasma oxidation has been used to radiocarbon date the organic constituents in over 300 pictographs worldwide (e.g., Rowe, 2012; Baker and Armitage, 2013; McDonald et al., 2014; Rowe et al., 2016; Russ et al., 2017; Steelman et al., 2019). The plasma oxidation technique has been verified by successfully dating known-age materials from radiocarbon laboratory intercomparisons (Steelman et al., 2004; Steelman et al., 2017) and pictographs with archaeologically constrained ages (Hyman and Rowe, 1997; Armitage et al., 2001). For quality control, it is important to test samples of known age to ensure that laboratory methods and measurements produce accurate results. Standard materials should mimic the samples being analyzed, but there is no known-age standard for rock art. However, a known-age test of the plasma oxidation technique was performed on charcoal pigment from three Mayan hieroglyphic calendar dates inscribed on the cave walls at Naj Tunich, with statistical agreement between the measured radiocarbon ages and the individual calendar dates for each of the three panels (Armitage et al., 2001).

Plasma oxidation is an alternative to combustion and utilizes an electrical discharge instead of heat (Fig. 2). Radiocarbon dating normally involves three steps: chemical pretreatment to remove contaminants; isolation of carbon; and AMS radiocarbon measurement. Typically, after chemical pretreatment (most often ABA washes), combustion is used to oxidize organic samples to water and carbon dioxide, which is then converted to graphite for AMS measurement. Plasma oxidation is used instead of combustion for the second step. A low-temperature plasma is an electrically excited gas composed of neutral atoms, both negative and positive molecular and atomic ions, and electrons. Electrons gain kinetic energy from an oscillating electric field, while the temperatures of the gas components are increased by elastic collisions between the electrons and the gas. However, electrons are thermally isolated from the gas components by their very large mass differences. Temperatures of the plasma gas, thus, can remain near ambient temperatures at the same time the electrons are sufficiently energetic to break molecular bonds. The active species in the plasma phase allow oxidation reactions that normally occur only at high temperatures to proceed at low temperatures.

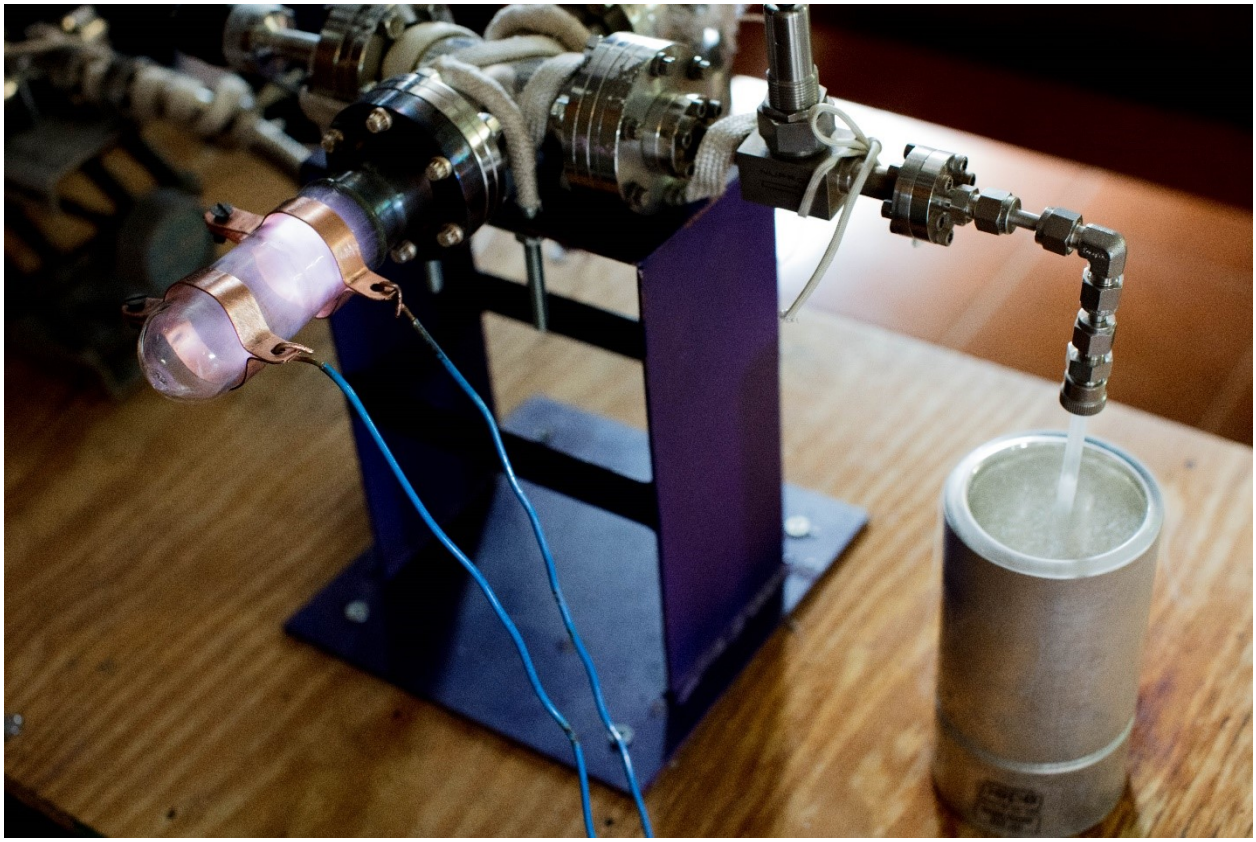

Fig 2. Plasma oxidation instrument with an electrical glow discharge used to oxidize organic material in paint samples for AMS radiocarbon dating. A glass tube immersed in liquid nitrogen collects product carbon dioxide and water.

The plasma oxidation technique is particularly amenable for dating rock paintings. At operating temperatures below the decomposition temperature of any carbon-containing minerals (such as limestone/carbonate or whewellite/oxalate), oxygen plasma discharges convert organic matter in a paint sample to water and carbon dioxide. The carbon dioxide gas is collected for AMS radiocarbon dating. Only organic carbon is extracted, leaving the inorganic mineral portion of the paint sample intact as a solid in the reaction chamber. This is perhaps the most important advantage of plasma oxidation: extensive acid pretreatments used to remove carbonate and oxalate minerals prior to combustion are not necessary when plasma oxidation is used. For example, Bonneau et al. (2011, 2017) calculated that approximately 50-60% of charcoal paint samples from South Africa were dissolved during ABA pretreatment. Much of this loss is likely due to the dissolution of calcite, but significant amounts of charcoal are also dissolved during ABA protocols. Potentially half of a charcoal sample could be lost during ABA pretreatments. When

plasma oxidation is used, these harsh acid washes are not necessary and this loss is avoided, allowing much smaller paint samples of charcoal, as well as the limited amount of organic material (binders/vehicles/emulsifiers) present in an inorganic-pigmented paint sample to be radiocarbon dated. The plasma oxidation technique provides a direct method for dating pictographs with either charcoal or inorganic pigments.

1.1.2 Oxalate Dating

Radiocarbon dating oxalate mineral accretions to constrain the ages of rock paintings was pioneered by Alan Watchman in Australia (e.g., Watchman, 1991; Watchman, 1993, Watchman and Campbell, 1996; Watchman et al., 2000, 2005, 2010). Soon after, in the Lower Pecos Canyonlands, Jon Russ explored oxalate dating to construct paleoclimate models (Russ et al., 1994, 1995, 1996, 1999, 2000). Numerous studies have utilized the technique to provide minimum or maximum ages for pictographs around the world (e.g., Hedges et al., 1998; Steelman et al., 2002; Mazel and Watchman, 2003; Scott et al., 2005; Ruiz et al., 2012; Jones et al., 2017; Pecchioni et al., 2019).

There are several hypotheses addressing the formation of calcium oxalate rock coatings, including biological sources such as bacteria (Di Bonaventura et al., 1999, Hess et al., 2008), fungi (Gadd et al., 2014; Ortega-Morales et al., 2016), lichen (Del Monte et al. 1987; Hernanz et al., 2007), and mixed microbial communities (Gorbushina, 2007), as well as chemical reactions of dissolved organic acids in rain aerosols at the rock/atmosphere boundary (Watchman, 1991). Russ et al. (1995, 1996, 1999) concluded that the oxalate crust surfaces in the Lower Pecos are strikingly similar to microcolonial fungi and lichens, based on their botryoidal morphology. More recently, Hess et al. (2008) identified 20 species of oxalate-producing microbes from surface accretions collected from the Lower Pecos. These data provide strong evidence that there are and were multiple sources contributing to the production of the oxalate-rich coating that encapsulates the ancient paints in the Lower Pecos Canyonlands. No matter which method of production is responsible, the source of the carbon is atmospheric, meaning that the carbon is contemporaneous with oxalate crust formation. Stable isotope and radiocarbon measurements on modern lichen and oxalate demonstrate that carbon in oxalate biofilms originates from atmospheric carbon dioxide and that, once formed, there is no significant carbon exchange with the substrate (Beazley et al., 2002). As such, radiocarbon ages of oxalate coatings correlate with periods when the microbial communities flourished on the rock surfaces in the past (Russ et al., 2000; Beazley et al., 2002) and thus date the formation of the rock coating. Therefore, by radiocarbon dating calcium oxalate strata overlying and underlying a pigment layer, it is possible to determine minimum and maximum ages for a pictograph.

1.2 Lower Pecos Canyonlands

The Lower Pecos Canyonlands are situated at the edge of the Edwards Plateau and the Chihuahuan Desert. The northern half of the region lies in southwest Texas, USA and the southern half in Coahuila, Mexico. Near the region's center, the Pecos and Devils Rivers converge with the Rio Grande. Over millennia, these rivers and their tributaries have sliced through masses of gray and white limestone rock to create a dramatic landscape incised by deep, narrow gorges.

Rockshelters here contain some of the best-preserved and longest records of hunting and gathering lifeways in North America, from 13,000 years ago to European contact (McCuistion, 2019). Preserved within these dry rockshelters are deeply stratified deposits containing a wide assemblage of artifacts, such as tools made from wood, stone, and bone, matting, basketry, snares, fire-starting kits (Shafer, 2013), and medicinal and sacramental plants (Boyd and Dering, 1996; Terry et al., 2006). Preserved on the walls of these rockshelters are rock paintings, or pictographs, spanning greater than four thousand years of production (Kirkland and Newcomb, 1967; Shafer, 1986; Turpin, 1990; Turpin, 1995; Boyd, 2003; Boyd, 2013; Boyd and Cox, 2016; Harrison Macrae, 2018). Pecos River style, is by far the most abundant and visually impressive rock art in the region. Easily recognized by its multicolored designs and striking anthropomorphic and zoomorphic figures, Pecos River style murals are often ambitious in their scale and technical in their execution (Fig. 3). They are the defining archaeological phenomenon of the Lower Pecos Canyonlands and the subject of this study.

To identify the mineral pigments in Pecos River style paintings, researchers have conducted chemical analyses using techniques such as powder X-ray diffraction (XRD), scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS), and inductively coupled plasma mass spectrometry (ICP-MS) (Zolensky, 1982; Hyman et al., 1996; Russ et al., 2012; Bu et al., 2013). They determined that red and yellow pictographs contain an array of iron oxide/hydroxide minerals, and that black pictographs contain manganese minerals. Subsequent elemental analyses using portable X-ray fluorescence spectroscopy (pXRF) of paintings at ten sites in the region, including Eagle Cave, confirmed these results (Koenig et al., 2014).

To identify organic constituents within the paint, additional research using both chemical analyses and experimental archaeology have been conducted. Early attempts to extract ancient DNA from the pictographs indicated the binder was from deer or bison (Reese et al., 1996), though these results have not been replicated (Mawk et al., 2002). Fatty acid analysis using gas chromatography has also produced inconclusive results

(Spades and Russ, 2005). However, ethnographic texts (del Hoyo, 1960:492) and experimental archaeology (Boyd and Dering, 2013:180-81) suggest that deer tallow or marrow likely served as a binder and that saponins from yucca, also known as “soap root” (*Yucca spp*) mixed with water served as an emulsifier or thinner. Because microgram-levels of organic matter have survived in the prehistoric paint, researchers have been able to extract and convert the organic constituents into carbon via plasma oxidation for AMS radiocarbon dating.

Fig. 3. Portion of a Pecos River style mural at Rattlesnake Canyon (41VV180). The central anthropomorph (1.2 m tall) is portrayed with a small, black rabbit-ear headdress and red wrist and elbow adornments.

1.2.1 Dating Lower Pecos Pictographs

Pecos River style pictographs were the first paintings dated using low-temperature plasma oxidation (Russ et al., 1990; Rowe, 2009). Using this technique, researchers obtained thirty experimental radiocarbon assays for seventeen figures distributed across nine sites. Assays range from 4200 to 1450 years BP, with a calibrated age range of

approximately 3000 B.C. to A.D. 700 (Hyman and Rowe, 1997; Rowe, 2004, 2005; Bates et al., 2015).

Dating an oxalate accretion covering a Pecos River style painting at 41VV129, Russ et al. (1996, 2000) obtained a minimum age of 3220±60 years BP (CAMS-15147). In the Lower Pecos Canyonlands, chemical analyses using SEM-EDS, XRD, Fourier transform infrared (FTIR), and Raman spectroscopies have shown that oxalate mineral accretions are ubiquitous on the limestone surfaces and encapsulate rock paintings (Russ et al., 1995; Edwards et al., 1998). Although these natural crusts give the paintings a faded appearance, they preserve the art by reducing weathering and cement paint to the basal rock. A primary component of the accretions is whewellite (calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$). Weddellite (calcium oxalate dihydrate, $CaC_2O_4 \cdot 2H_2O$), calcite, gypsum, and quartz are also present (Russ et al., 1996). Average crust thickness ranges from 170 to 850 µm. Previous direct dates for Pecos River style rock art and a single oxalate date place production of the murals within the Middle to Late Archaic (6000 – 1000 years BP).

While the rock paintings of the Lower Pecos Canyonlands have been the subject of numerous dating projects, the majority of these were conducted in the 1990s as part of an experimental dating program. The samples were collected to determine if it was possible to chemically date rock paintings containing inorganic pigments and an organic binder/vehicle/emulsifier. Sampling was opportunistic on badly deteriorated paintings. Reported assays for Lower Pecos rock art during this experimental phase of radiocarbon dating rarely included data considered essential today. Often results were published only with site names and stylistic classifications and did not include sampling locations or photographs of the sampled figures. Control experiments on unpainted rock substrate (backgrounds) to identify potential contaminants were not initially conducted. In contrast, this current study was undertaken as part of a rigorous documentation effort at Eagle Cave.

1.2.1 Eagle Cave

Eagle Cave (41VV167) is a large dry rockshelter located in a short box-canyon tributary to the Rio Grande along the US/Mexico border in Langtry, Texas. The deeply stratified deposits contained within Eagle Cave preserve the remains of hunter-gatherer lifeways spanning at least 13,000 years (McCuistion, 2019:113). Excavations began in the 1930s (Davenport 1938) and were expanded upon in the 1960s (Ross 1965). The most recent period of excavation was conducted by the Ancient Southwest Texas Project at Texas State University, San Marcos (https://aswtproject.wordpress.com/category/eagle-cave/) from 2014 to 2017 (Willis et al., 2016; Koenig et al., 2017; Nielsen, 2017; McCuistion, 2019).

Prior to the Ancient Southwest Texas Project, Shumla documented and analyzed the poorly preserved Pecos River style rock art mural located along the downstream end of the shelter (Fig 4). This included production of a high-resolution panorama using GigaPan photography, production of a 3D color model of the rock art panel using structure from motion (SfM) photogrammetry (Koenig et al., 2019), elemental analysis of the paintings using pXRF (Koenig et al., 2014), and analysis of mural stratigraphy using digital microscopy (records on file at Shumla). These methods, especially theWe identified, photographed, and illustrated figures in the panel and assigned each figure a permanent reference code.

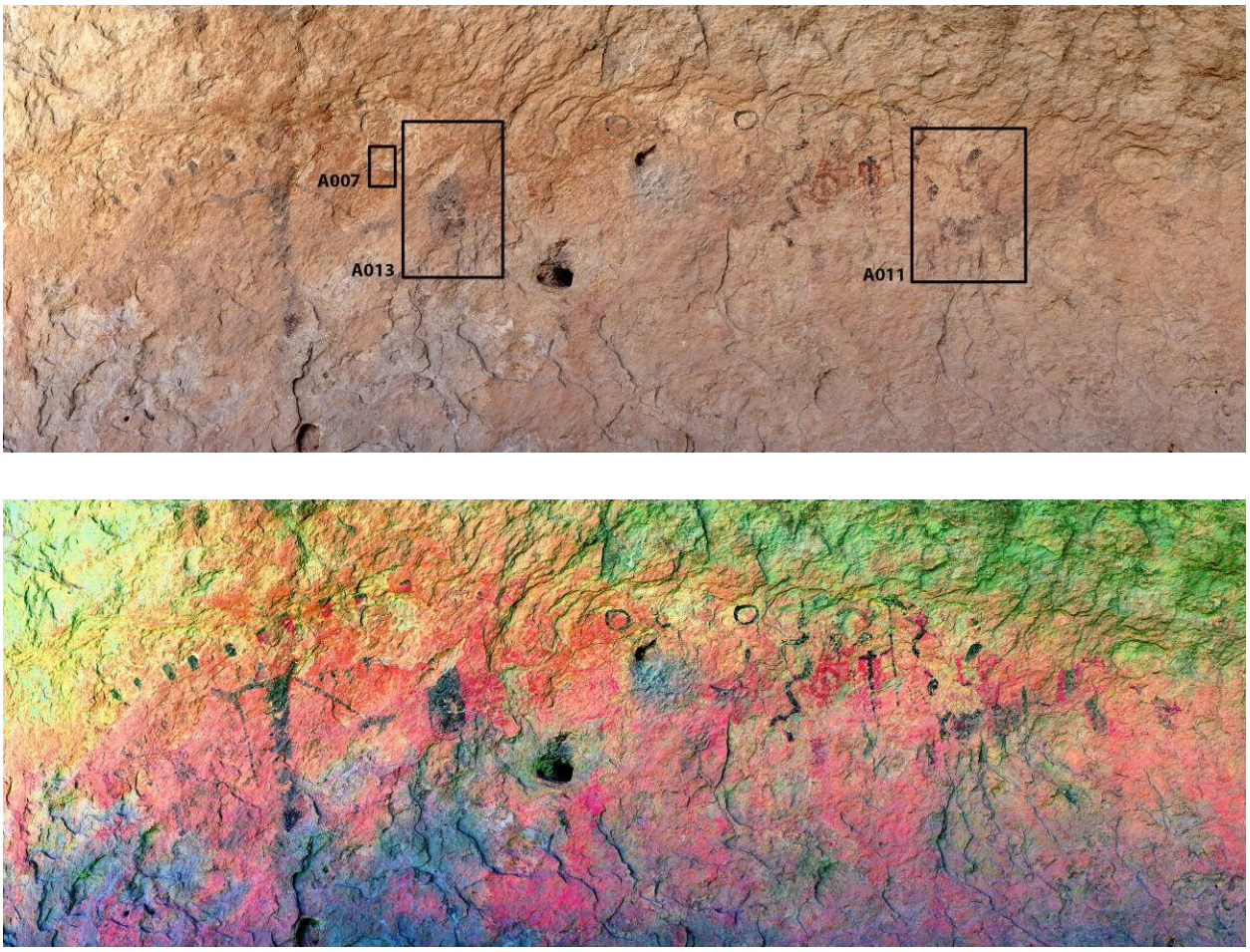

Fig 4. The rock art panel at Eagle Cave spans 30 meters in width. The top panorama shows the sampling locations for A007, A011, and A013 (see Figs. 5, 6, and 7). The bottom photograph is enhanced using the ydt channel of DStretch (Harman, 2005).

2. Experimental Methods

2.1 Sample Collection

We collected samples for radiocarbon analysis from three Pecos River style anthropomorphic figures (reference codes A007, A011, and A013) (Figs. 5, 6, and 7). Samples were taken from fragile areas on the panel where the painted rock surface was already spalling away from the shelter wall. For this reason, these Eagle Cave samples were larger (2-6 cm^2) than we normally collect (2-3 cm^2) when sampling rock paintings. We wore latex gloves and used individual sterile scalpel blades to remove one sample from each of the paintings. Samples were placed in pre-baked (500°C) aluminum foil squares, which were then stored in labeled plastic bags. We also collected background samples from adjacent unpainted rock as controls to investigate levels of organic contamination in the rock substrate. The paint and background samples were collected from locations high on the wall, inaccessible to sheep and goats that might rub against the paintings. We took photographs before and after collection and mapped each sampling location with a total data station.

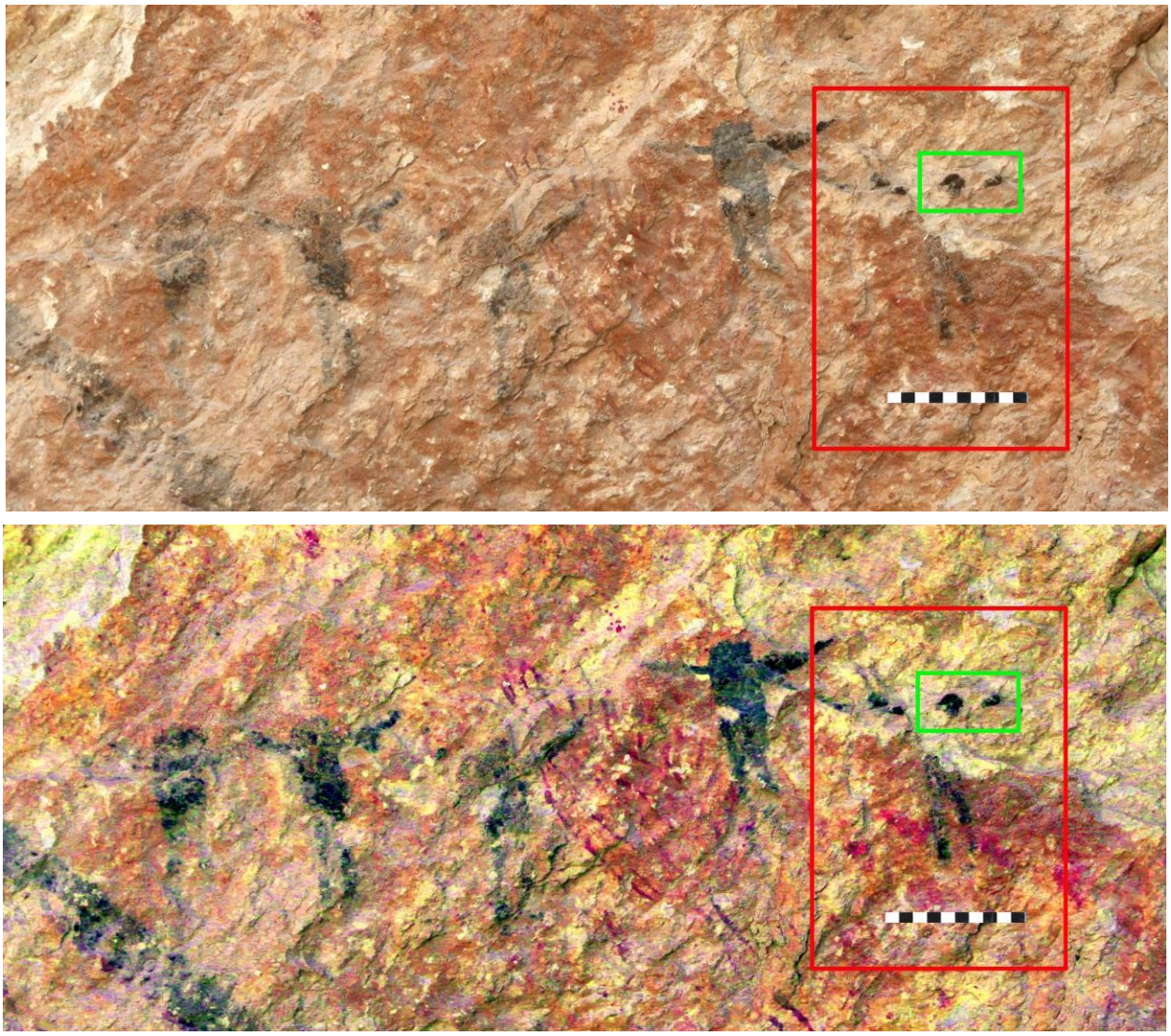

Fig. 5. Sample 1 and 1’ were collected from A007, one in a series of five small black anthropomorphs. The image is heavily obscured by accretions. Its upper torso is badly spalled, and the remaining imagery is fragile. Immediately upon contact of the scalpel blade with the art, a paint flake with a surface area of 6 cm^2 detached from the wall. We divided this large sample into two subsamples for duplicate analyses. The bottom photograph has been enhanced using the ydt channel of DStretch (Harman, 2005).

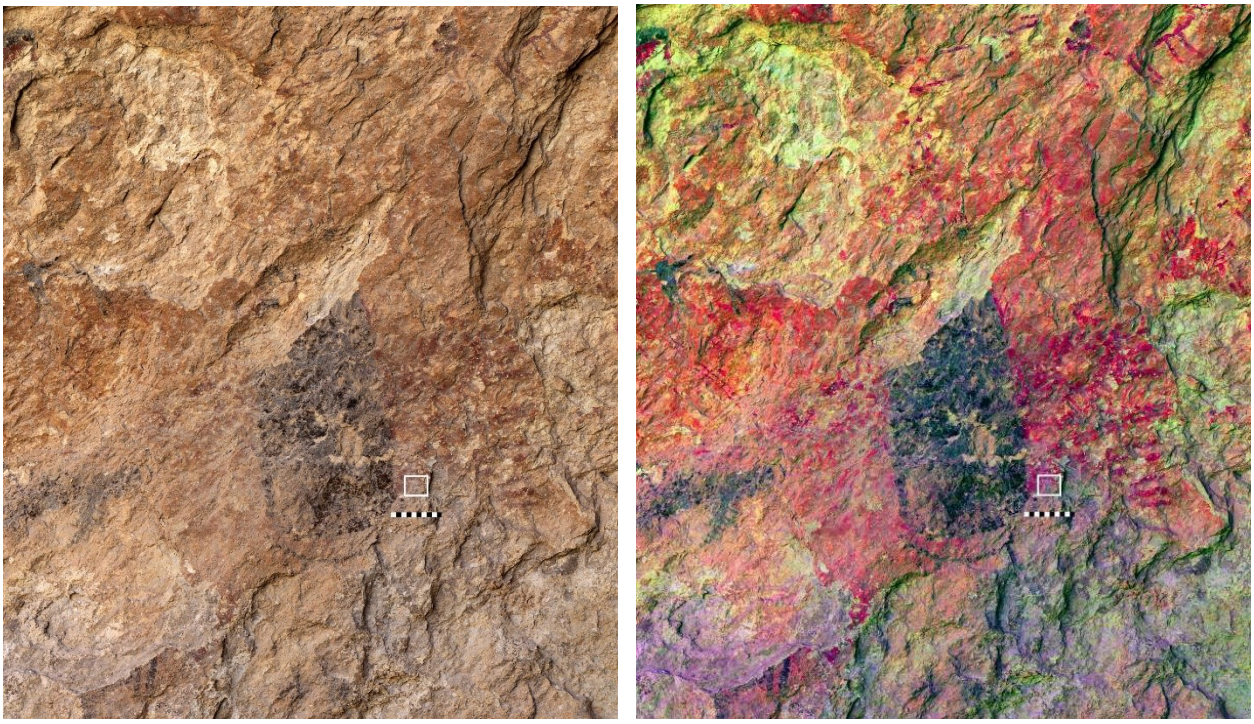

Fig. 6. Sample 2 was collected from A013, a poorly preserved black anthropomorph with large red wings. We collected a thin sample with a surface area of 2 cm^2 from within the red wing of the figure. The right photograph has been enhanced using the ydt channel of DStretch (Harman, 2005).

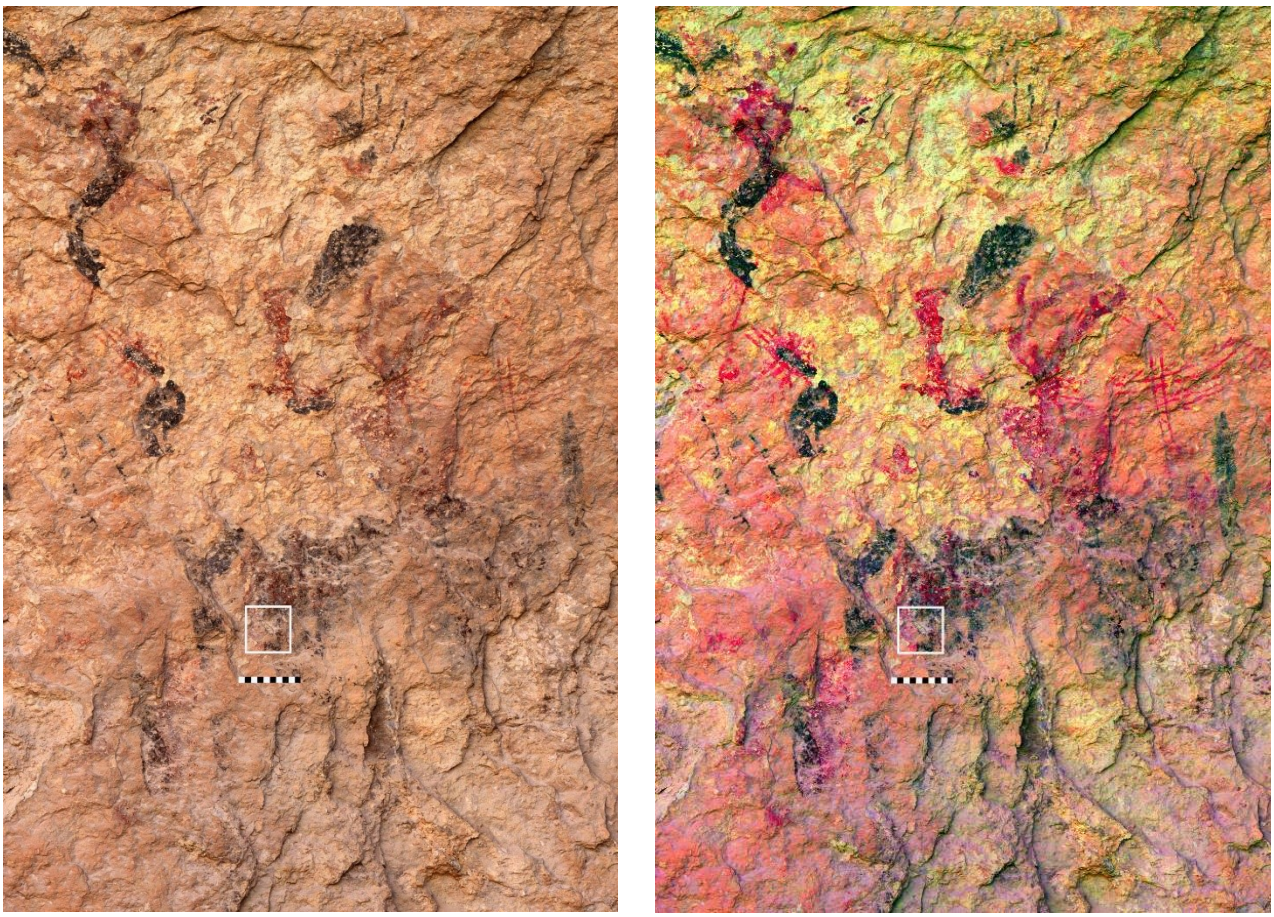

Fig. 7. Sample 3 was collected from A011, a black anthropomorph with a red head and a black headdress resembling a rabbit's ear. We collected the radiocarbon sample from within the figure's torso just below a large spall. The sample had a surface area of 3 cm^2. The right photograph has been enhanced using the ydt channel of DStretch (Harman, 2005).

2.2 Chemical Pretreatment

For samples 1, 1', and 3, we used individual sterile scalpel blades to remove three layers: (1) outer accretion layer; (2) paint layer; and (3) underneath accretion layer. Sample 2 was too thin to section, so only a single layer was removed that included the paint and associated minerals, but no separate accretion layers. We performed these dissections under a stereomicroscope at X10 to X40 magnification taking care not to include any paint in the outer or underneath layers. For the background or control samples of unpainted rock, the entire surface of each rock flake was removed as a powder. Though we wore latex gloves, we only manipulated samples with pre-baked aluminum foil or sterile scalpel blades to avoid the addition of laboratory contamination. Under magnification, we did not observe any physical contaminants (plant fibers, rootlets, spider webs) in these samples. Chemical contamination (such as kerosene/gasoline) is often invisible, and the parallel analysis of backgrounds/controls of unpainted rock are necessary to ascertain its presence.

For paint and background samples, we conducted two sequential base washes (3 mL of 1 Molar sodium hydroxide) in an ultrasonic water bath at 50°C for one hour each to remove any potential humic acid contamination. Humic acids, naturally present in soil samples and derived from the decay of organic matter, appear brownish-orange in a basic solution. With no color change observed, we rinsed samples with Milli-Q water and filtered them onto quartz-fiber filters that had been previously sterilized at 500°C in a muffle furnace. The solid samples were then dried in a 110°C oven prior to plasma oxidation.

For the outer and underneath oxalate layers, we conducted four sequential acid washes (3 mL of 1 Molar phosphoric acid) in an ultrasonic water bath at 50°C for one hour each to remove calcite in the accretions and limestone rock. Upon addition of the first acid solution, the samples bubbled noticeably releasing carbon dioxide from the reaction of the acid with carbonate minerals. Samples were rinsed with Milli-Q water, filtered onto sterilized quartz-fiber filters, and dried in a 110°C oven prior to plasma oxidation cleaning. Before and after acid treatment, we employed XRD and FTIR spectroscopy to confirm the complete removal of carbonate minerals and the continuing presence of oxalate minerals (Figures 8 & 9) (Steelman et al., 2002; Russ et al., 2017). XRD patterns were collected using a Bruker D8 Advanced Bragg-Brentano XRD diffractometer, with a 2.2 kW Cu X-ray tube maintained at an operating current of 40 kV and 25 mA. FTIR spectra were acquired with a Nicolet iS50FT instrument with a diamond attenuated total reflectance (ATR) attachment, using 32 scans over a range of 600 to 4000 cm^{-1} and a spectral resolution of 4 cm^{-1}.

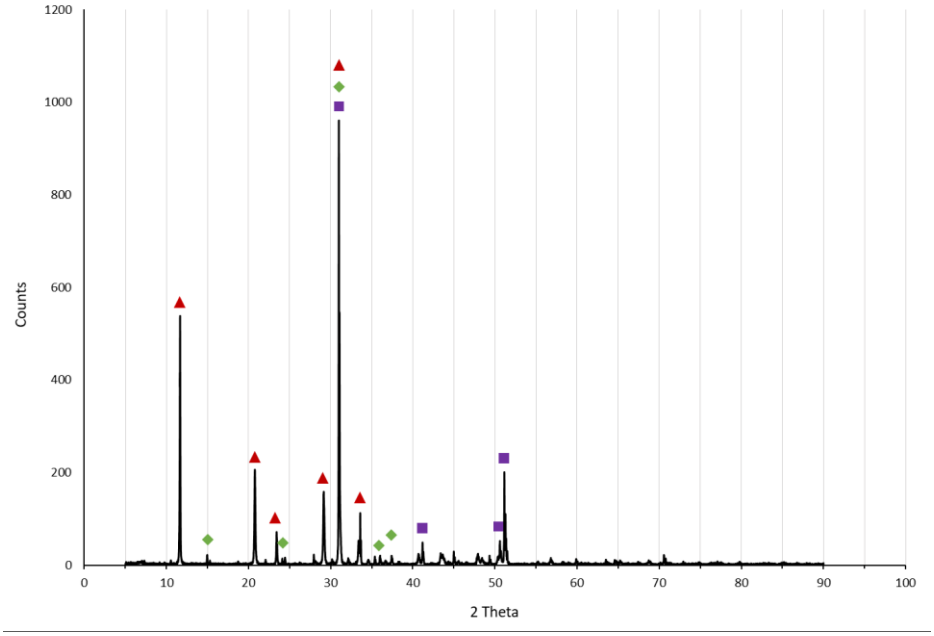

Fig. 8. Powder XRD diffraction pattern of an accretion sample prior to acid treatment, confirming the presence of gypsum (red triangles), calcite (purple squares), and whewellite (green diamonds).

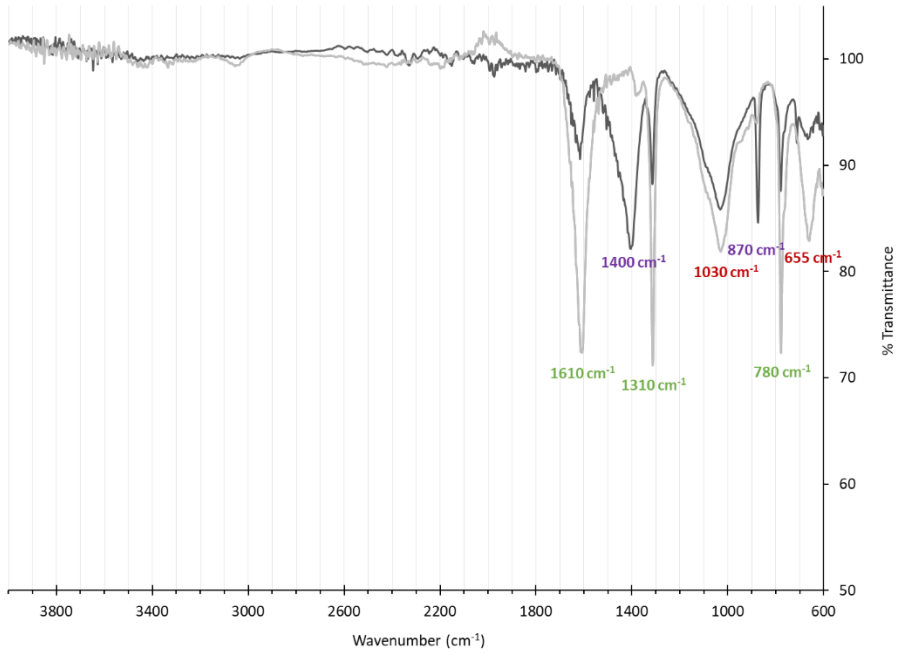

Fig. 9. FTIR spectra of an accretion sample before (black) and after (grey) dilute phosphoric acid treatment, indicating the removal of carbonate minerals (purple). The solid residue combusted for AMS radiocarbon dating contained oxalate (green) and sulfate (red) ions associated with whewellite and gypsum, respectively.

2.3 Plasma Oxidation

We used a custom-built plasma oxidation apparatus to convert organic material in samples into carbon dioxide for AMS radiocarbon dating. Glow discharges were produced by radio frequency (RF) capacitive coupling with two external copper electrodes on either end of a glass sample chamber (Fig. 2). For detailed plasma oxidation experimental methods, see McDonald et al. (2014). Collected carbon dioxide from paint samples was sent to the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory for graphitization and radiocarbon measurement. We processed background samples in a parallel fashion and noted negligible amounts of organic carbon, indicating that there was no significant physical or chemical contamination in the rock substrate.

For the outer and underneath oxalate layers, we used the low-temperature plasma oxidation technique to completely remove organic contamination that might have been included in mineral samples due to either environmental or laboratory handling (Russ et al., 2017). After successive 1-hour oxidations at 100 W and 1 torr of oxygen gas, each mineral sample was removed once ≤0.3 µg carbon was extracted indicating that organic contamination had been eliminated. With both carbonate and organic carbon removed, the purified oxalate sample was sent to CAMS for combustion, graphitization, and radiocarbon measurement. Silver was added during the CAMS combustion procedures to scavenge sulfur as in McFarlane et al (2013).

3. Results & Discussion

3.1 Rock Art Dates

Age results for paint samples processed using plasma oxidation are shown in Table 1 and Fig. 10. Stable carbon isotope values for paint samples were assumed to be -25‰, as carbon dioxide samples were too small to take a split for isotope ratio mass spectrometry (IRMS). Three of the paint samples (1, 1', 2) contained sufficient organic carbon for dating, whereas sample 3 did not contain enough (<10 µg) carbon for reliable AMS measurement. Error ranges are large, as carbon samples are small. For example, sample 2 is only 20 µg carbon and has a ±270 years BP error. Radiocarbon dates for duplicate samples 1 and 1', as well as sample 2 are statistically indistinguishable. All three dates pass a chi-squared test indicating that they are coeval, with a weighted average of 3280±70 years BP calibrated to 1740-1420 cal BC (3690-3370 cal BP) at 2 sigma (95.4% probability) using the R_Combine function of the OxCal computer program version 4.4.2 (Bronk Ramsey, 2009, 2017) with IntCal20 curve data from Reimer et al. (2020) (Fig. 11).

Table 1. Plasma oxidation results

Sample	Layer	Mass[a] (mg)	Carbon[b] (µg)	µg/mg ratio	CAMS ID	^{14}C Date (BP)	Calibrated Range (2σ, 95.4%)
1	black paint	172	40	0.2	170031	3210±110	1900 - 1200 cal BC
1b	background	160	0.3	0.002			
1’	black paint	114	40	0.4	170819	3310±90	1880 - 1410 cal BC
1’b	background	154	0.6	0.004			
2	red paint	23	20	0.9	170820	3400±270	2500 - 1000 cal BC
2b	background	89	0.3	0.003			
3	black paint	40	<10	<0.2			
3b	background	195	0.6	0.003			

[a] Mass of solid paint sample.

[b] Mass of organic carbon extracted from paint sample that was used for AMS graphite target.

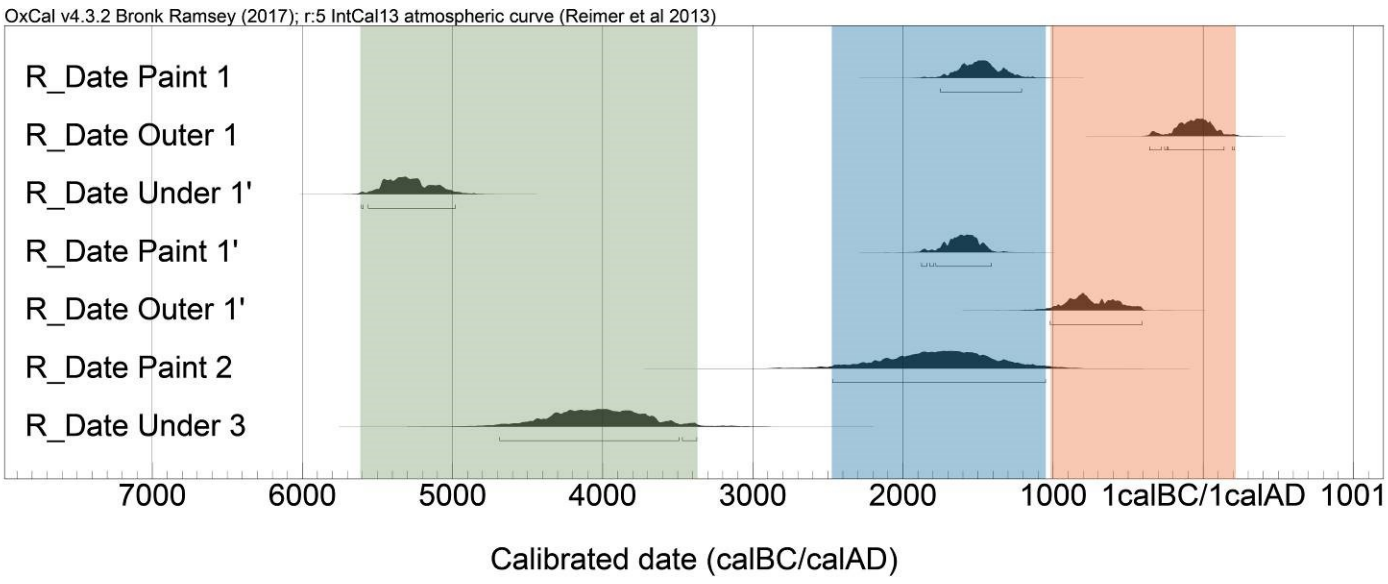

Fig 10. Calibrated paint (blue) and oxalate age ranges (green and orange) for Eagle Cave.

Organic carbon levels in unpainted rock backgrounds were negligible (≤1%) suggesting that extracted organic carbon is from the paint alone (binder, vehicle, and/or emulsifier) with insignificant contamination from the rock substrate (see normalized µg/mg ratios in Table 1). If we had found significant levels of contamination in the background samples, we would not have been able to radiocarbon date the paintings as there would be no way to distinguish or separate the organic carbon that was associated with the painting event and the contamination. As discussed above, it is imperative to test control samples (backgrounds) of unpainted rock to rule out the possibility of organic contamination in the rock substrate.

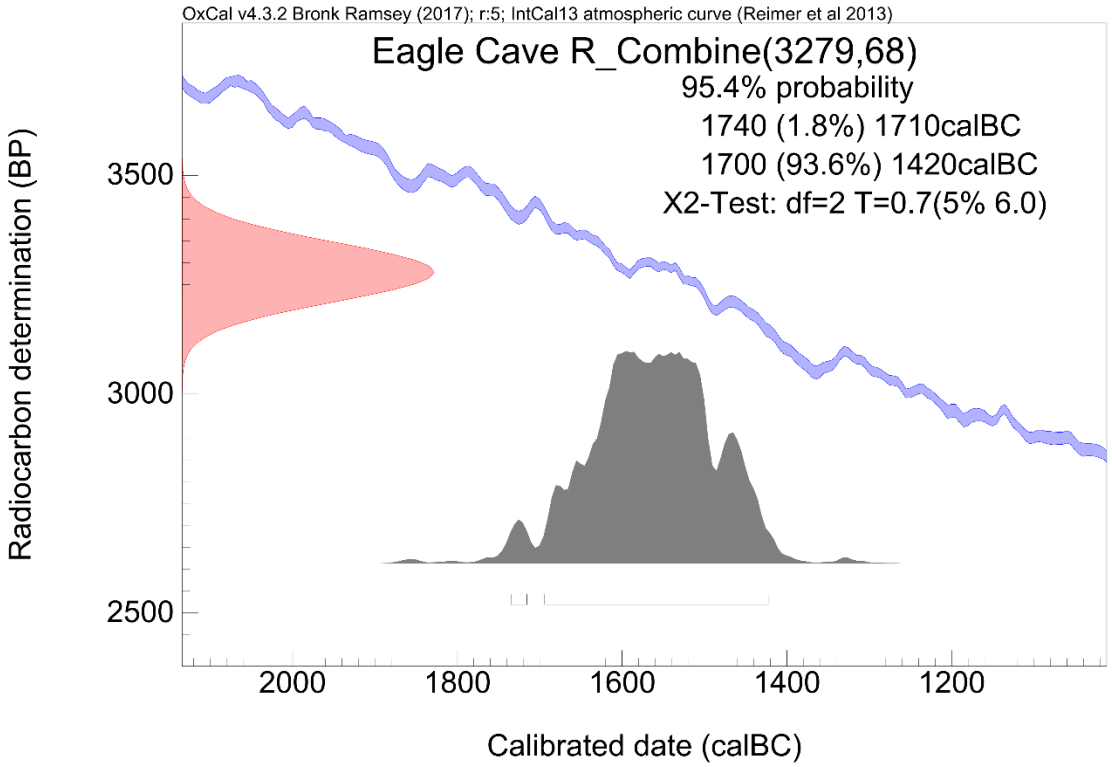

Fig. 11. Weighted average of the three paint dates (samples 1, 1', and 2). While each individual measurement has a large standard error due to the small size of the AMS graphite targets, the weighted average of the three results has a ±70 ^{14}C years BP error range that narrows the age of production for the art at Eagle Cave.

3.2 Oxalate Dates

Age results for oxalate layers are shown in Table 2 and Fig. 10. We obtained ages for both the outer and underneath layers for sample 1', but only the outer layer for sample 1 and the underneath layer for sample 3. Sample 2 was too thin to attempt oxalate dating.

Oxalate radiocarbon ages were calculated using a stable carbon isotope value of -11‰, the average value measured by IRMS for Lower Pecos calcium oxalate samples (Russ et al., 2000). In comparison to the paintings, overlying accretion layers are younger and underlying accretion layers are older. This correctly ordered, chronological stratigraphy of the accretion and paint layers supports the validity of both dating methods.

Table 2. Oxalate results

Sample	Layer	Mass[a] (mg)	Carbon[b] (µg)	CAMS ID	^{14}C Date (BP)	Calibrated Range (2σ, 95.4%)
1	outer	14	40	170032	2030±90	360 cal BC - 210 cal AD
1	underneath	34	<10			
1’	outer	7	30	170034	2620±120	1100 - 400 cal BC
1’	underneath	34	30	170033	6340±140	5700 - 4900 cal BC
3	outer	12	<10			
3	underneath	97	20	170821	5200±290	4700 - 3300 cal BC

[a] Mass of solid accretion sample before phosphoric acid pretreatment.

[b] Mass of oxalate carbon combusted for AMS graphite target.

We noted some disparity in the outer oxalate ages (1: 2030 BP and 1’: 2620 BP) and underneath oxalate ages (1’: 6340 BP and 3: 5200 BP), which is not unusual even within a single site. For example, oxalate ages measured by Ruiz et al. (2012) at the Spanish site Cueva del Tio Modesto ranged from 2800 to 5210 ^{14}C years BP, and at Abrigo de los Oculados ranged from 2610 to 4675 ^{14}C years BP. And, in the Lower Pecos, Russ et al. (2000) observed ranges of 730 to 1330 years ^{14}C BP for samples taken one meter apart on the shelter wall at 41VV89. A radiocarbon determination for an oxalate accretion is a weighted average of the deposited layers’ ages. If layers are thicker in one place than in another area, disparate ages would result. Even so, overlying oxalate accretions will provide minimum ages for rock paintings as any mixture of the outer layers is still younger than any underlying paint or accretion layers. Likewise, underlying oxalate layers will provide maximum ages for rock paintings as the mixture of the underneath layers is still older than any overlying paint or accretions layers. Reported oxalate layers may not reflect a single event of formation, but instead represent the weighted average age of the oxalate crust material. Interestingly, the oldest oxalate age of 6340 ^{14}C years BP that we

obtained in this study demonstrates that the shelter wall at Eagle Cave has been stable for at least this long.

3.3 Employing Multiple Methods to Date Rock Paintings

To verify the accuracy and reliability of rock art dating techniques, test samples should be analyzed using different methods. Perhaps the most studied pictograph for testing rock art dating methods is a painting at Toca do Serrote da Bastiana in Brazil. Steelman et al. (2002) used plasma oxidation to determine a direct age of 3730±90 ^{14}C years BP for a red anthropomorph, and a minimum age of 2490±30 ^{14}C years BP for an oxalate accretion overlying the painting. Using a third method, Fontugne et al. (2013) confirmed these results at Toca do Serrote da Bastiana by radiocarbon dating the calcite in the accretion, as well as cross-dating using both Th-230/U-234 and C-14 at another nearby site of Toca da Gamerleirinha. Unfortunately, thermoluminescence (TL) and electron paramagnetic resonance (EPR) ages of 35,000 years old by Watanabe et al. (2003) contradicts these other results. Rowe and Steelman (2003) suggested that the use of TL and EPR for dating calcite deposited in open-air shelters may suffer from inadequate correction for the incorporation of undissolved carbonate dust into the calcite layer as it formed. In fact, Fontugne et al. (2013) obtained a calculated age range of 1028 to 4906 years BP (median of 2957 years BP) for the accretion based on the percentage of dead carbon from the carbonate host rock.

In the previous example, minimum ages and a direct date were obtained for a painting at Toca do Serrote da Bastiana. Russ et al. (2017) also obtained a minimum oxalate age and a direct date on pyrolyzed carbon in an Olmec painting at Oxtotitlán Cave in Mexico. Other researchers have used cross-dating of calcite covering prehistoric paintings to obtain minimum ages using uranium-series and radiocarbon dating (e.g., Plagnes et al., 2003; Valladas et al., 2017); in essence, using two different techniques to date the same material. At Eagle Cave in the Lower Pecos Canyonlands, we isolated oxalate mineral accretions for radiocarbon dating to constrain the age of paint layers with *both* a minimum and maximum age and used low-temperature plasma oxidation to obtain direct radiocarbon dates for the paintings. We utilized two different methodologies to radiocarbon date two discrete materials associated with prehistoric paintings.

4. Conclusions

This rock art dating study at Eagle Cave is significant in that it is the first to combine an oxalate minimum age, direct age on organic constituents in the paint layer, and an oxalate maximum age for a single pictograph. We used plasma oxidation to obtain direct radiocarbon dates for two Pecos River style paintings. We also analyzed a duplicate

sample from one of these paintings. These three AMS measurements are coeval with a weighted average of 3280±70 years BP calibrated to 1740-1420 cal BC (3690-3370 cal BP) at 95.4% probability. Radiocarbon assays on oxalate mineral accretions for overlying layers are younger and underlying accretion layers are older, bracketing the direct dates with minimum and maximum ages. The chronological stratigraphy of the accretion and paint layers supports the validity of both dating methods. This radiocarbon study firmly places the production of the dated figures at the end of the Middle Archaic in the Lower Pecos at 3500 years ago.

Methodologically, our procedures for dating paint samples and oxalate accretions are advantageous as sample material is not lost during harsh acid and base washes (Bonneau et al., 2011; Jones et al., 2017). The primary benefit of low-temperature plasma oxidation is that operating conditions are below the decomposition temperature of carbonate and oxalate minerals inherent in pictograph samples. Only organic carbon is extracted, leaving the inorganic mineral portion of samples intact as a solid in the reaction chamber. For paint samples, only dilute base washes are necessary prior to plasma oxidation and AMS measurement. For oxalate samples, only a dilute phosphoric acid treatment to remove carbonates with confirmation by FTIR (Steelman et al., 2002), followed by plasma oxidation cleaning, was necessary to purify the oxalates for radiocarbon assay. This is only the second use of plasma oxidation to clean organic contamination from oxalate accretion samples (Russ et al., 2017).

A significant issue associated with dating rock paintings involves physical and chemical contamination inherent in rock shelter or cave environments. Physical contamination, such as plant fibers and rootlets, can sometimes be removed from samples under magnification. However, chemical contamination, such as kerosene or humic acids, are invisible. While humic acids can be removed using a dilute base wash, other unknown contaminants could still be present. The parallel analysis of background/control samples of unpainted rock are necessary to ascertain the presence of organic contamination in the rock substrate. For these Eagle Cave samples, microgram-levels of organic matter had survived in the prehistoric paint and there was negligible organic contamination in the associated rock substrate. Thus, we were able to use plasma oxidation and AMS to radiocarbon date the paint samples.

We have used two independent methodologies to date two discrete materials – organic binders/vehicles in paint layers and oxalate mineral accretions. For rock art around the world, plasma oxidation holds great promise in dating the organic constituents of charcoal and inorganic-pigmented rock paintings, as well as a pretreatment cleaning method for oxalate accretion samples prior to combustion and AMS dating. Steelman's laboratory at Shumla has recently constructed a new multi-chamber plasma oxidation instrument that

will be able to conduct batch processing of multiple samples at one time, allowing this technique to become more widely available for research collaborations. Multi-laboratory efforts to date the same pictographs via different analytical techniques should be embraced and encouraged by the archaeological and scientific communities.

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