Implications for Rock Art Dating from the Lower Pecos Canyonlands, TX: A Review

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Abstract

The Lower Pecos Canyonlands was the first study area where the method of plasma oxidation was employed to extract organic material from prehistoric rock paintings for accelerator mass spectrometry radiocarbon dating. During the developmental phase of this method, Rowe's laboratory at Texas A&M University obtained 32 radiocarbon measurements for Lower Pecos rock art: 29 dates for 16 paintings of the Pecos River style, and 3 additional dates for paintings of other styles found within the region. We evaluate these legacy dates based on contextual, compositional, and measurement elements, concluding that these experimental results are problematic and should not be used to draw archaeological conclusions. Building on knowledge gained during the development of the technique, Rowe established field and laboratory methods to address issues impacting the reliability and precision of radiocarbon results. Steelman's laboratory at Shumla Archaeological Research & Education Center has implemented these and additional protocols, including: (1) proper documentation of sampling locations so that the provenience of the sample is known (contextual); (2) analysis of unpainted control background samples to identify the presence or lack of contaminants in the rock substrate (compositional); (3) chemical pretreatment with base to remove any potential humic acid contamination (compositional); and (4) improved laboratory procedures to ensure that laboratory contamination is avoided (measurement). Using this methodology, Steelman's laboratory has obtained eleven radiocarbon results for four rock art sites in the region: 6 dates for Pecos River style paintings; 1 date for a red zigzag painting of another style; and 4 oxalate minimum/maximum ages. Three of these AMS measurements are from a single composition and pass a χ^2-test consistent with being coeval. To our knowledge, this data also presents the first minimum, direct, and maximum age for a single pictograph. This review suggests that future dating research in the region will produce a refined chronology for age comparisons between different rock art sites, painting styles, and even sub-styles – adding to our knowledge of the hunter-gatherers who lived in this painted landscape.

keywords: plasma oxidation; AMS radiocarbon dating; pictographs; rock art; Lower Pecos Canyonlands, Texas; Pecos River style

"Studies of prehistoric art are presently marginal to archaeology because, with few exceptions, we can't date it and so we cannot firmly correlate it with our increasingly detailed archaeological records. If we are to incorporate this most valuable artefactual material into mainstream archaeological reconstruction, we must learn how to date it reliably." (Chaloupka et al., 2000:10).

1. Introduction

Pictographs are images painted on boulders or cave and rock shelter walls that have the potential to provide remarkable insight into prehistoric cultures worldwide. However, as noted by Chaloupka in the quote above, the wealth of information afforded through this "valuable artefactual material" rarely has been incorporated into mainstream archaeology due to our inability to obtain reliable dates. In the early 1990s, Marvin Rowe and his laboratory at Texas A&M University pioneered rock art dating by using plasma oxidation[1] to extract organic constituents contained in rock paintings (e.g., charcoal, binders, vehicles, additives) for accelerator mass spectrometry (AMS) radiocarbon dating. Pictographs from the Lower Pecos Canyonlands of southwest Texas and Coahuila, Mexico were the first samples analyzed by Rowe and his team using the plasma oxidation method. Here, we review 32 published and previously unpublished radiocarbon dates obtained by Rowe's laboratory for Lower Pecos pictographs. Information about these legacy dates was compiled from journal articles, book chapters, dissertations, laboratory notebooks, and personal communications (Russ, 1991; Chaffee, 1993; Reese, 1994; Ilger, 1995; Pace, 1996; Armitage, 1998; Mawk, 1999; and references therein). We explain the experimental details gleaned from these sources and assess the validity of the Lower Pecos pictograph legacy dates. It is important to note, that while Rowe was optimistic about the potential of plasma oxidation and AMS to radiocarbon date pictographs, he considered these Lower Pecos experimental dates provisional and urged caution in their interpretation and application due to many of the same elements we discuss below (Rowe, 2004). We do not intend this article to be a comprehensive review of the plasma oxidation method, but rather an examination and review of rock art dates from the Lower Pecos Canyonlands.

[1] Previously referred to as *plasma-chemical extraction (PCE)*, *plasma-chemical oxidation (PCO), low-temperature plasma oxidation,* and *low-energy plasma radiocarbon sampling (LEPRS)*, we will refer to the methodological technique as simply *plasma oxidation*.

Over the past five years, Steelman's laboratory has obtained seven direct radiocarbon dates on pictographs and four indirect oxalate minimum/maximum ages for rock paintings. These results employ fully developed experimental procedures informed by more than 20 years of experience and experimentation with the plasma oxidation method. The current state of research suggests that future dating projects in the region will produce a refined chronology for age comparisons between different rock art sites, painting styles, and even sub-styles – adding to our knowledge of the hunter-gatherers who lived in this painted landscape.

2. Dating Rock Paintings

Placing rock art in a chronological context allows images to be studied together with excavated cultural remains from a given archaeological period. The incorporation of rock art studies alongside other archaeological specialties, such as lithics, ceramics, and weaving techniques, is crucial for studying past cultures. However, pictographs represent a challenge for radiocarbon dating: (1) images are painted on rock substrates, which often include carbon-containing minerals such as carbonates and oxalates; (2) the amount of carbon to date is small, orders of magnitude less than would be available from a typical organic artifact; (3) little is known about the organic binders and/or vehicles used in making ancient paints; (4) physical contamination must be removed; and (5) organic material unassociated with painting activity can occur in unpainted rock. We describe methods used to address these challenges, focusing on the plasma oxidation technique used to obtain AMS dates for both charcoal and inorganic-pigmented rock paintings.

Several techniques have been used by researchers to determine minimum and/or maximum ages for the production of rock art. Radiocarbon dating of oxalate mineral crusts (whewellite and weddellite) has been used to provide indirect ages for numerous pictographs around the world (e.g., Watchman, 1991, 1993; Hedges et al., 1998; Watchman et al., 2000; Steelman et al., 2002; Mazel and Watchman, 2003; Rowe and Steelman, 2003; Steelman and Rowe, 2005; Watchman et al., 2005, 2010; Ruiz et al., 2012; Russ et al., 2017; Jones et al., 2017; Pecchioni et al., 2019). 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) has been used to date mud wasp nests that are over or under art layers in Australia, supporting a hypothesis that

Gwion paintings were produced approximately 12,000 years ago. Uranium-series dating has provided minimum and maximum ages for calcite formations that cover paintings in dark zone caves, primarily in Europe and Asia (e.g., Aubert et al., 2007; Pike et al., 2012; Aubert et al., 2014; Shao et al., 2017; Aubert et al., 2018; Hoffman et al., 2018; Slimak et al., 2018; Pons-Branchu et al., 2020). Of particular promise is the use of cross-dating of $^{230}Th/^{234}U$ and ^{14}C dating of calcite covering prehistoric paintings (Plagnes et al., 2003; Valladas et al., 2017a).

Additional research has focused on directly dating the organic constituents of rock paintings. Paint consists of two primary components: (1) pigment, which is the material that provides color and (2) vehicle, which is composed of a binder, and when necessary, a solvent. Some paint recipes also include additives, such as extenders and emulsifiers. Many paint recipes also included organic and inorganic materials to increase the efficacy of paint on a supernatural level (Bucklow, 2009; Magaloni Kerpel, 2014). When applied onto a porous rock surface, paint is absorbed into the rock support. Consequently, samples collected for analysis consist not only of paint, but also the rock substrate and associated accretionary minerals (Fig. 1).

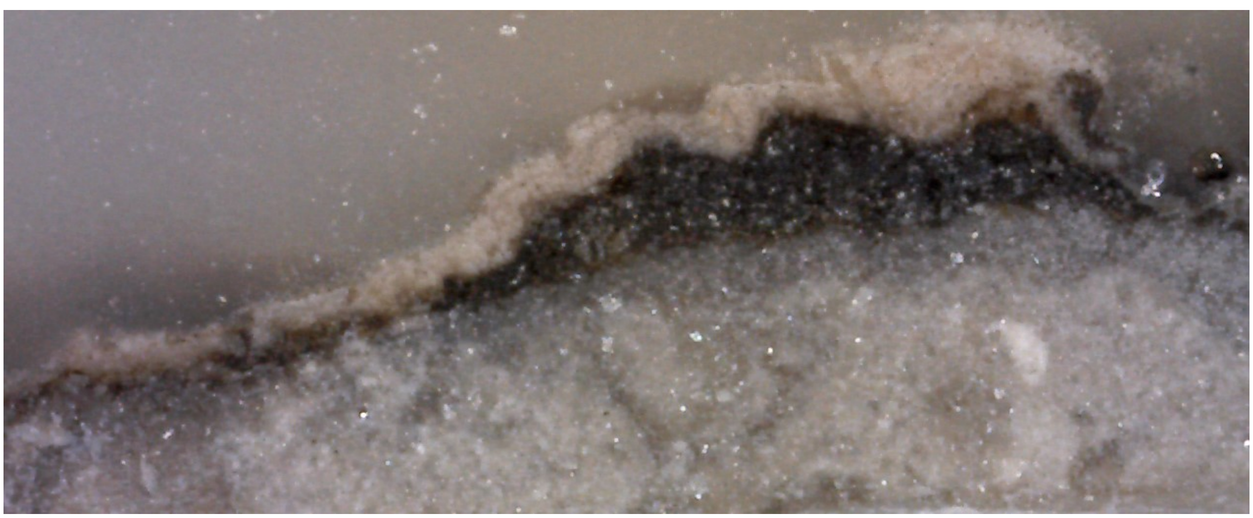

Fig. 1. Cross-section of a black paint sample (1 and 1') from Eagle Cave. For scale, the width of the section shown is ~0.5 cm. The black paint layer varies from 50 to 250 μm and consists of manganese mineral pigment, calcite, whewellite, and gypsum. Overlying the paint is a cream-colored whewellite, calcite, and gypsum mineral accretion. Underlying the paint is a grey layer of calcite and whewellite. The rock substrate is a dolomitic limestone. Mineral identifications were determined using X-ray diffraction (Steelman et al., 2021).

If the pigment is an organic material, such as charcoal, there is often sufficient carbon present in a paint sample for radiocarbon dating. Worldwide, the first direct dates for rock art were obtained by Van der Merwe et al. (1987) on charcoal pigment from a South African rock painting. Since then, several laboratories have radiocarbon dated carbon-based pigmented rock paintings using acid-base-acid (ABA) pretreatment, combustion, and AMS measurement (see Aubert, 2012; Langley and Taçon, 2010; Steelman and Rowe, 2012; Rowe, 2012 for review articles). 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 obtained using ABA pretreatment and AMS measurement primarily have been obtained for charcoal or carbon black pigment (e.g., Clottes, 1999; Sand et al., 2006; Morwood et al., 2010; Bonneau et al., 2011; Clottes and Geneste, 2012; Simek et al., 2013; Samson et al., 2017; Valladas et al., 1992, 2001, 2017b; Valladas, 2003). 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.

Most rock art assemblages around the world were created with inorganic mineral pigments. Reds, oranges, browns, and yellows are usually iron oxide/hydroxide minerals of various oxidation states and degrees of hydration, and black is often a manganese oxide/hydroxide instead of charcoal. Inorganic pigments cannot be radiocarbon dated because they do not contain carbon. However, if the prehistoric artists used organic vehicles or additives in the paint recipe, and enough of these have survived in a conserved state, plasma oxidation can be used to extract organic carbon for AMS radiocarbon dating.

2.1 Plasma Oxidation

With the introduction of AMS in the late 1970s (Bennet et al., 1977; Nelson et al., 1977), the possibility of radiocarbon dating the small amount of organic carbon present in a rock art sample became possible. 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. In the 1990s, Rowe hypothesized that an oxygen glow discharge could be used to successfully oxidize and isolate organic carbon from paint samples for AMS radiocarbon dating (Russ et al., 1990, 1991). Plasma oxidation is an alternative to combustion for the second step and utilizes an electrical discharge instead of heat.[2] This idea was inspired by the use of hydrogen plasmas to restore metallic artifacts by chemically reducing them (Daniels, 1979, Vepřek et al., 1988; Rowe, *personal communication*).

A custom-built plasma oxidation apparatus converts organic material in paint samples to carbon dioxide for AMS radiocarbon dating. Glow discharges are produced by radio frequency (RF) capacitive coupling with two external copper electrodes on either end of a glass sample chamber (Fig. 2). 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 can remain near ambient temperatures (<150°C) 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.

The plasma oxidation technique is particularly amenable for dating rock paintings. At operating temperatures (<150°C) that are below the decomposition temperature of minerals such as whewellite/oxalate (>400°C) and limestone/carbonate (>750°C) (Johnston, 1910), 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 (inorganic pigments, rock substrate, and associated mineral accretions) intact as a solid in the reaction chamber (Russ et al., 1992b; Chaffee et al., 1993b). Carbonate minerals are commonly associated with rock paintings, as either a limestone

[2] The method of plasma oxidation should not be confused with Bird et al. (2010) use of a continuous-flow commercial plasma asher as a pretreatment technique prior to combustion of the remaining solid residue, as an alternative to acid-base-oxidation-stepped combustion (ABOx-SC) for dating older samples.

rock substrate or an accretion (even on sandstone rock substrates). These carbonate minerals often consist of dead carbon that no longer contains ^{14}C due to extreme age and their inclusion would result in an older measured age than the true age of a sample. For example, using plasma oxidation, Armitage et al. (2001) obtained four AMS dates with an average radiocarbon date of 1440±50 ^{14}C years BP on a Mayan charcoal paint sample, whereas a portion of the sample treated only with the usual ABA treatment and combustion gave an age of 11,770±100 ^{14}C years BP. For rock art studies, another consideration is that acid washes conducted during ABA pretreatment may not completely remove carbon-containing oxalate minerals, which are commonly associated with rock surfaces (Hedges et al., 1998; Armitage et al., 2001). If not removed, remaining oxalate would be incorporated into the dated material if combustion is used. Therefore, the resultant radiocarbon assay would be a weighted average of the organic material in the painting and the carbon in the calcium oxalate accretion, which might be older or younger than the painting event.

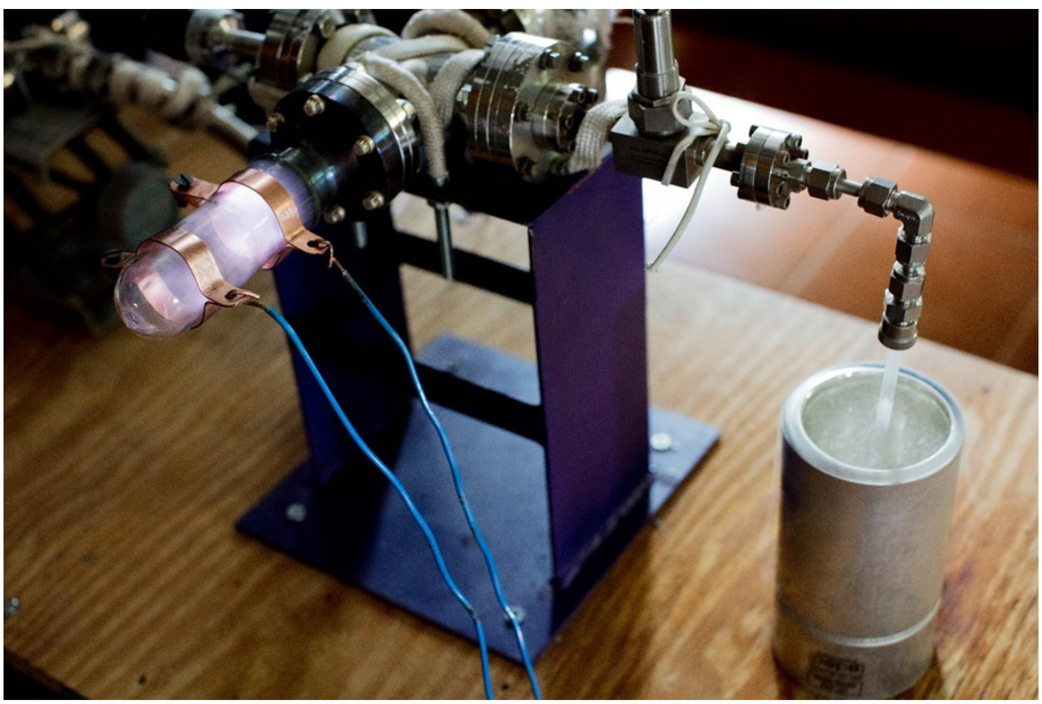

Fig 2. Plasma oxidation instrument used to oxidize organic material in paint samples for AMS radiocarbon dating. A glass tube immersed in liquid nitrogen collects product carbon dioxide and water.

The most important advantage of plasma oxidation is that extensive acid pretreatments used to remove carbonate and oxalate minerals prior to combustion are not necessary. Organic carbon that would be lost during harsh acid pretreatments is retained using the plasma method and is available for oxidation and radiocarbon measurement. Bird et al. (2010) states that ABA often results in significant dissolution of samples, when only a small proportion of the material that is lost in pretreatment is likely to be exogenous contamination. This is a serious issue as it means that important archaeological samples, on occasion, are not dateable due to excessive removal of material during pretreatment. For example, Bonneau et al. (2011) 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 (Bonneau et al., 2017). 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.

3. Lower Pecos Canyonlands

With over 350 documented rock art sites, the Lower Pecos Canyonlands of southwest Texas was the original study area for developing the plasma oxidation technique to radiocarbon date rock paintings (Rowe, 2013). Published in *Nature*, Russ et al. (1990) obtained the first radiocarbon date for organic vehicles/binders in an inorganic-pigmented rock painting. The Lower Pecos region is centered at the confluence of the Pecos and Devils Rivers with the Rio Grande (Turpin, 1995, 2004). This region extends approximately 150 kilometers north and south of the United States–Mexico border, and approximately 80 kilometers east and west of where the Pecos flows into the Rio Grande (Fig. 3). The arid landscape is incised by deep, narrow canyons containing thousands of rock shelters. Hunter-gatherer groups occupied these shelters throughout the Holocene, leaving behind one of the best-preserved and longest records of Native American lifeways in North America (Turpin, 1991; Shafer, 2013). Excavation of dry rock shelter deposits has yielded a wide assemblage of artifacts, such as tools made from stone, bone, and wood, and items made from plant fibers such as baskets, sandals, and cordage (Shafer, 1986; Boyd and Dering, 1996; Terry et al., 2006). Mobiliary art in the form of small painted pebbles, engraved stone plaquettes, and freshwater mussel shells are not uncommon in the dry shelters (Parsons, 1986; Castañeda et al., 2019a). However, it is the parietal art for which the region is most noted. The rock art of the Lower Pecos includes five main categories: Pecos River (Kirkland and Newcomb, 1967; Turpin, 1982, 1990a; Boyd, 2003, 2013, 2016; Harrison Macrae, 2018), Red Linear (Turpin, 1984, 1990b, 2005; Boyd et al., 2013), Red Monochrome (Turpin, 1986a), Bold Line Geometric (Turpin, 1986b), and Historic (Turpin, 1989).

Fig. 3. Map of the Lower Pecos archaeological region, with approximate locations of sites discussed in this review.

3.1 Inorganic Pigment Analyses

The majority of rock paintings in the Lower Pecos region were produced with mineral-based pigments. Using X-ray diffraction (XRD) (Hyman et al., 1996; Zolensky, 1982), Solveig Turpin and colleagues determined that various shades of red, orange, and yellow Pecos River style pictographs were produced with iron minerals: primarily hematite [α-Fe_2O_3] and maghemite [γ-Fe_2O_3], with goethite [α-FeO(OH)], lepidocrocite [γ-FeO(OH)], magnetite [Fe_3O_4], and ferrihydrate [Fe_5O_7OH] also present. Black pigments were made with manganite [MnO(OH)] or pyrolusite (β-MnO_2), again with various iron minerals present. Preliminary analyses to source red and yellow pigments using laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) suggest that limonite from siltstones found in the canyons was the most likely source of some pigments (Russ et al., 2012, Bu et al., 2013). Based on these compositions, ancient artists most likely prepared and manipulated mineral pigment samples through mixing, grinding, density separation, and heating to produce specific shades of red and yellow (*e.g.*, Pomiès et al., 1999; Salomon et al., 2015). Additional inorganic pigment analyses in the region has focused on using non-destructive portable X-ray fluorescence (pXRF) for different categories of rock art across the landscape, including Pecos River, Red Monochrome, Red Linear, and Historic Period styles (Koenig et al., 2014; Castañeda et al., 2019b; Steelman et al., 2020a, 2020b). These pXRF results confirmed that reds and yellows are painted with iron minerals and blacks are most often painted with manganese pigments.

3.2 Organic Analyses of Pictographs

In the Lower Pecos, chemical analyses to identify the organic materials used in ancient paint recipes have been conducted with limited success and inconclusive results (Rowe, 2001b). Early attempts to extract ancient DNA from the pictographs indicated the binder was from an ungulate (deer or bison) (Reese, 1994; Reese et al., 1996a,b), though these results have not been replicated (Mawk, 1999; Mawk et al., 2002). Fatty acid analysis using gas chromatography has also produced inconclusive results, with similar trace levels of fatty acids in paint samples and control samples of unpainted rock (Spades and Russ, 2005). Using Raman spectroscopy, Russ et al. (1995) and Edwards et al. (1998) detected CH-stretching bands of organic compounds in a sample of black paint from Jackrabbit Shelter (41VV576) that was radiocarbon dated to 3355±65 ^{14}C years BP (Russ et al., 1992b,c). Another sample of red paint from Jackrabbit Shelter showed NH, CHN, -C=C-C=C- conjugation, and an aromatic quinonoid functional group (Edwards et al., 2000). The organic material from these two samples has not been identified and are the only two samples (of ten analyzed) to show this feature from Raman spectroscopy research done in the late-1990s (Edwards et al., 1998, 2000). However, these findings are significant as it demonstrates that organic material is detectable. In addition, 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. Stable carbon isotope values for organic material extracted from Lower Pecos pictographs range from -20 to -26‰ (Ilger et al., 1995); though far from definitive, these values are consistent with a mixture of deer bone marrow and yucca materials. Because microgram-levels of organic matter have survived in prehistoric paint, the method of plasma oxidation is able to extract and convert the organic constituents into carbon dioxide for AMS radiocarbon dating. For Lower Pecos pictographs, sufficient amounts of carbon for AMS radiocarbon measurement are collected from paint samples and negligible amounts of carbon are found in adjacent unpainted rock samples (backgrounds/controls). Thus, we know that the organic material being dated is associated with the paintings; however, we have not chemically identified what that material might be.

4. A Review of the Legacy Dates

We conducted a systematic examination of the radiocarbon assays obtained by Rowe's laboratory based on three of the four factors discussed in Taylor and Bar-Yosef (2014:131) that can affect the accuracy and precision of radiocarbon dates: (1) contextual; (2) compositional; (3) systemic; and (4) measurement elements. Accuracy is defined as how close results are to the true value. Precision is defined as how close results are to each other and can be described by the standard deviation of replicate samples. Systemic elements can cause anomalies in radiocarbon age determinations when there is a failure to appropriately calibrate, correct, or normalize results (Taylor and Bar-Yosef 2014:131,149-157). These factors are related to the radiocarbon calibration curve and reservoir effects. As these effects are limited for Lower Pecos radiocarbon dates, they will not be discussed further. We evaluate the contextual, compositional, and measurement elements for legacy Lower Pecos pictograph dates below. Pictograph dates that are possibly anomalous due to these factors are marked with an “X” in Table 1. Refer to *Supplemental Materials S1* for detailed experimental methods for these legacy radiocarbon dates.

4.1 Contextual Elements

Contextual elements can cause anomalies in radiocarbon age determinations when there is a failure to accurately determine and document the physical relationship between the collected sample and the targeted event or cultural expression for which one is seeking a temporal designation (Taylor and Bar-Yosef, 2014:131-136). The material being dated must be related to the event of interest. A lack of provenience is a common problem with legacy dates.

Proper documentation of sampling locations is imperative for the archaeological information associated with an age result. As rock fragments must be removed from the wall for destructive analysis, researchers must properly record the rock art prior to radiocarbon dating projects. This often includes comprehensive photography with a color checker and scale, measurements, listing of attributes associated with the image, and illustration. Only then should sampling be conducted. Researchers must precisely establish and document the sampling location, both within the sampled rock art image and the location of the image within the broader context of the rock art panel. Unfortunately, for the legacy dates in Table 1, there are few instances of known sample provenience: one drawing at 41VV75 (Fig. 4); one painting at Cueva Quebrada (41VV162a) (Fig. 5); one painting at the Lewis Canyon Tinaja site (41VV233) (Fig. 6); and two paintings at Jackrabbit Shelter (41VV576) (Fig. 7 and 8). All other results were published only with site names and stylistic classifications and did not include sampling locations or photographs of the sampled figures. Thus, contextual information is missing for the majority of the legacy dates impacting the archaeological value of the age determinations (Table 1).

Table 1. Legacy Radiocarbon Dates for Lower Pecos Pictographs

Site/Sample [a]	Style [b]	Mass [c] (mg)	Carbon [c] (µg)	AMS ID	Radiocarbon Date [d] (^{14}C years BP)	Corrected [e] (^{14}C years BP)	Reference	Evaluation Elements		
								Contextual	Compositional	Measurement
41VV50										
3	PRS	unk	unk	AA-8699	2950±60		Chaffee et al., 1993b	X	X	
41VV75										
1	PRS	unk	4200	ETH-5909	3865±100	3920±100	Russ et al., 1990	X	X	X
29A	PRS	500	unk	CAMS-17316	2750±50		Hyman and Rowe, 1997a	X	X	
29B	PRS	500	unk	CAMS-17897	3190±60		Hyman and Rowe, 1997b	X	X	
37A	PRS	137	715	CAMS-14087	2950±60		Ilger et al., 1996	X	X	
37B	PRS	301	870	CAMS-14088	3580±60		Ilger et al., 1996	X	X	
37C	PRS	193	730	CAMS-14089	3240±60		Ilger et al., 1996	X	X	
37D	PRS	165	960	CAMS-14090	3210±60		Ilger et al., 1996	X	X	
37E	PRS	unk	unk	CAMS-17990	3550±90		Hyman and Rowe, 1997a	X	X	
37F	PRS	unk	unk	CAMS-18206	3680±60		Hyman and Rowe, 1997b	X	X	
47A	PRS	659	170	CAMS-23927	3690±80		Pace et al., 2020	X	X	
47B	PRS	409	180	CAMS-25384	3790±60		Pace et al., 2020	X	X	
47C	PRS	510	250	CAMS-26762	3440±50		Pace et al., 2020	X	X	
47D	PRS	590	150	CAMS-25368	2340±80	rejected	Pace et al., 2020	X	X	X
47E	PRS	624	280	CAMS-25885	3310±50		Pace et al., 2020	X	X	
47F	PRS	587	250	CAMS-25884	3900±60		Pace et al., 2020	X	X	
50	UNC	unk	unk	CAMS-29315	1280±80		Hyman and Rowe, 1997b		X	
41VV124										
1	PRS	unk	175	CAMS-34204	1970±80		Rowe, 2004	X	X	
2	PRS	unk	75	CAMS-48212	1460±80		Rowe, 2004	X	X	
3	PRS	unk	130	CAMS-60896	1960±60		Rowe, 2004	X	X	
4	PRS	unk	80	CAMS-60935	2420±80		Rowe, 2004	X	X	
41VV162a										
1	UNC	54	900	AA-10549	1280±45	1280±150	Ilger et al., 1994		X	
41VV233										
1	UNC	2450	1790	AA-9270	1315±50	1125±85	Ilger et al., 1995		X	
41VV576										
1a	PRS	3200	900	ETH-6962	3355±65	4130±65	Russ et al., 1992a,b,c		X	X
1b	PRS	3200	400	AA-7063	4200±90		Chafee et al, 1993a,b		X	
3A	PRS	650	2000	ETH-7047	3000±70	3400±70	Russ et al., 1992a,b, 1993		X	X
3B	PRS	650	2000	AA-8426	1450±75	rejected	Chaffee et al., 1994a		X	X
41VV696										
1	PRS	unk	60	CAMS-62184	3010±100		Rowe, 2005	X	X	
41VV612										
1	PRS	unk	50	CAMS-25882	3920±120		Rowe, 2000	X	X	
San Vicente										
2	PRS	unk	220	CAMS-43673	1930±70	1930±300	Rowe, 2004	X	X	
3	PRS	unk	230	CAMS-45378	2570±60	2570±300	Rowe, 2004	X	X	
Abrigo Diego										
2	PRS	unk	210	CAMS-45379	2500±60	rejected	Rowe, 2000	X	X	

[a] Replicates are defined as different samples collected from the same painting or paint fragments divided into multiple sub-samples (designated with capital letters, e.g. 3A or 3B). Aliquots are defined as separate carbon samples for AMS measurement extracted from the same paint sample (designated with lowercase letters, e.g. 1a or 1b).
[b] For rock art styles, PRS is Pecos River style and UNC is unclassified, images that have no clear characteristics associated with any of the defined rock art styles in the Lower Pecos Canyonlands.
[c] We were unable to locate this information for some of these legacy dates; "unk" is "unknown"
[d] For paint samples, the $\delta^{13}C$ value was assumed to be -25‰ as no split of the carbon dioxide was sampled for IRMS measurement.
[e] Early experiments in the laboratory introduced modern contamination or were influenced by contamination in the rock substrate. Ages were corrected using a mass balance calculation based on the age of dated contamination. See original references.

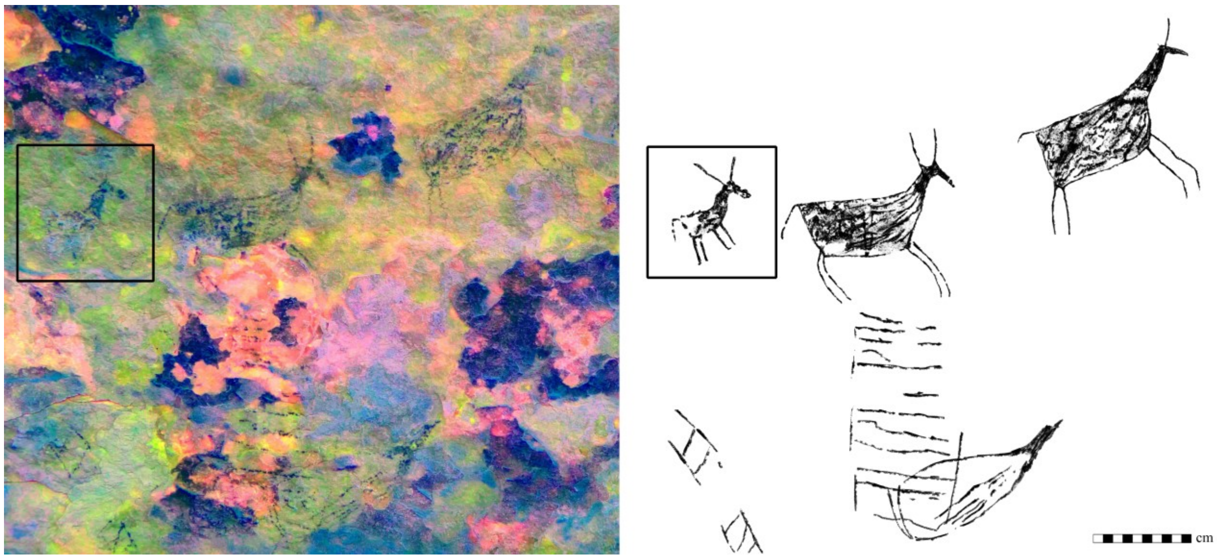

Fig 4. Section of the panel at 41VV75 containing charcoal dry-applied drawings of deer and geometric figures (Rowe, 2003; Boyd et al., 2014). The dated pictograph is the small quadruped with short legs located in the upper left corner of the photograph and illustration. The photograph is enhanced using DStretch color channel ybk (Harman, 2005).

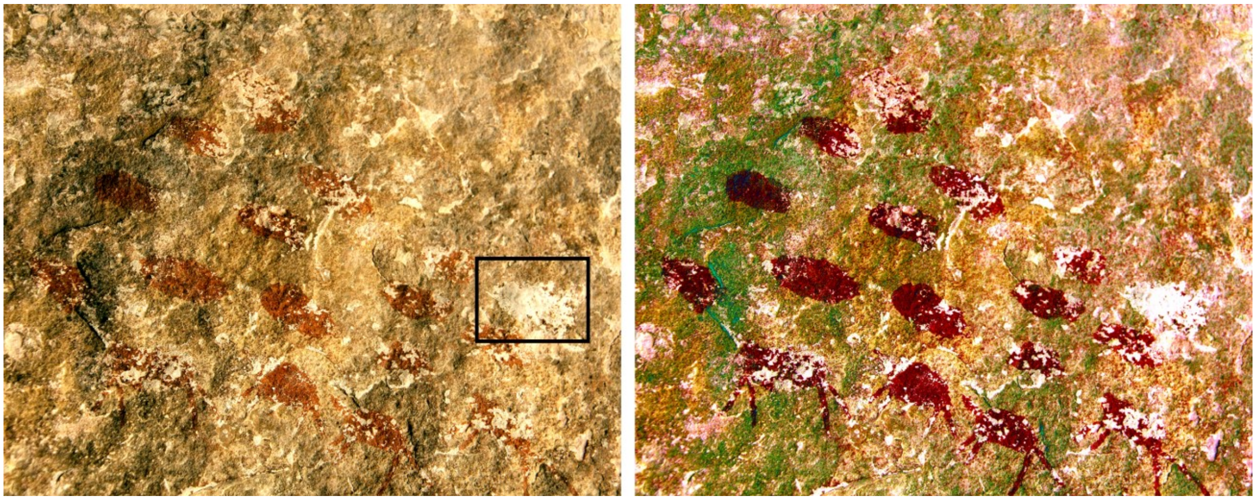

Fig. 5 Paint sample 41VV162a-1 was collected from a red oval at Cueva Quebrada as indicated by the box. The photograph on the right has been enhanced using DStretch color channel rgb0 (Harman, 2005). For scale, each oval is approximately 3 cm in width.

Fig. 6 Paint sample 41VV233-1 was collected from a red anthropomorph at the Lewis Canyon Tinaja site. The height of the figure is 85 centimeters. The right photograph is enhanced using DStretch color channel crgb (Harman, 2005).

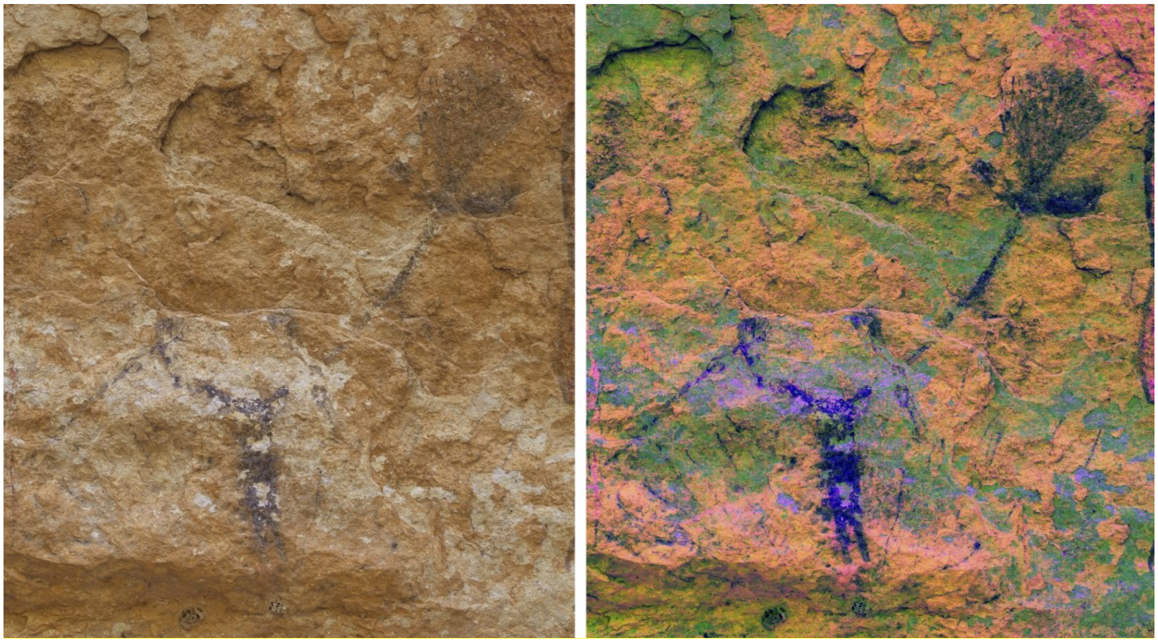

Fig. 7 At Jackrabbit Shelter, the sampling location and image provenience for paint sample 41VV576-1 is known. The paint sample was collected from the upper body of this black anthropomorph. The height of the body is ~1 meter. The right photograph is enhanced using DStretch color channel rgb (Harman, 2005).

Fig. 8 At Jackrabbit Shelter, the sampling location and image provenience for 41VV576-3 is known. A red paint sample was collected from the body of this anthropomorph. The height of the figure is ~1.5 meters. The right photograph is enhanced using DStretch color channel ydt (Harman, 2005).

4.2 Compositional Elements

Compositional elements can cause anomalies in radiocarbon age determinations when there is a failure to isolate indigenous organics and/or effectively exclude exogenous organics through physical and chemical pretreatment (Taylor and Bar-Yosef 2014:131,136-144). These compositional elements are related to the identity of the organic material being dated. Appropriate chemical pretreatment procedures remove contamination and isolate organics related to the event of interest. Depending on the age of any contamination, these effects can be minimal or can be significant. In addition, stable carbon isotope measurements correct for fractionation effects from natural variations in the $^{13}C/^{12}C$ ratios ($\delta^{13}C$) due to, for example, differences in photosynthetic pathways, place within the food chain, or marine environments. As stable carbon isotope values for organic material extracted from Lower Pecos pictographs range from -20 to -26‰ (Ilger et al., 1995), fractionation effects are considered minimal.

Paint samples from the Lower Pecos Canyonlands were collected by Rowe's laboratory over the course of several years. The first radiocarbon date for a Pecos River style painting from 41VV75 was accomplished on an exfoliated rock spall found on the shelter floor. Further sampling involved the use of metal blades to remove spalls or flaking paint from highly degraded paintings. In the laboratory, samples were rinsed in distilled, deionized water to clean the rock flakes prior to scraping the paint layer off as a powder with a metal blade. This powder, consisting of accretion, paint, and some underlying rock substrate, was examined under a microscope to remove visible contaminants such as spider webs, rootlets, etc. (Miller et al., 2002).

Control experiments on unpainted rock substrate (backgrounds) to identify potential contaminants were not initially conducted. Possible contamination could be present in the rock substrate and mineral accretions which could skew results (Hyman and Rowe, 1997b; Livingston et al., 2009). While none of the measurements suggest contamination by hydrocarbons, photographers in the 1950s and 60s were known to have treated Texas pictographs with kerosene to bring out their colors (Gebhard, 1960:16). Thus, possible kerosene contamination is something that radiocarbon researchers need to be aware of when working in the area (Chaffee et al., 1994c).

This highlights the importance of analyzing an unpainted control sample located adjacent to painted areas sampled for dating.

In addition, chemical pretreatment with base washes to remove potential humic acid contamination was only accomplished on a limited number of Lower Pecos rock art samples. While humic acids are common contaminants for many archaeological artifacts buried in soils, there has been little investigation as to whether humic acids are present in inorganic-pigmented pictograph samples. However, base treatment may help dissolve rootlets and other contaminants that are too small to be observed or physically removed from samples. Interestingly, in two studies, radiocarbon results for non-treated versus base-treated pictograph samples are statistically indistinguishable (Armitage, 1998; Pace et al., 2000). However, Steelman et al. (2017) has observed color changes associated with humic acid contamination in charcoal pigments from other regions and recommend continuing base treatment when using plasma oxidation. In addition to humic acids, significant portions of charcoal components are also dissolved by base treatment. For European cave paintings, Valladas et al. (2003) has dated these base fractions for Paleolithic charcoal pigment samples to determine the amount of humic contamination present.

Unfortunately, for these Lower Pecos legacy dates, every single measurement is problematic due to either a lack of chemical pretreatment or a control measurement on unpainted background rock (Table 1 and S1). In some cases (41VV162a-1, 41VV233-1, San Vicente-2, San Vicente-3, Abrigo Diego-2) where control samples were tested, contamination levels in analyzed backgrounds were significant. Mass balance calculations using the age of the contamination corrected these results, but questions remain about the validity of these dates.

4.3 Measurement Elements

Measurement elements can cause anomalies in radiocarbon age determinations when there is a failure to identify laboratory-based errors, such as undetected sample contamination, instrument malfunction, and mathematical calculations (Taylor and Bar-Yosef 2014:131,144-149). These statistical and experimental factors involve an understanding that conventional radiocarbon ages are reported as 1σ error. It is important to remember that radiocarbon results do not indicate a specific point in time, but express a time interval within which there is a given probability that the age lies.

The initial Lower Pecos dates (41VV75-1, 41VV75-47D, 41VV576-1a, 41VV576-3A, 41VV576-3B) suffered from modern contamination introduced during experimental laboratory procedures (Table 1), though calculations were able to estimate corrected ages (Russ, 1991; Chaffee, 1993). Modifications were made to the plasma oxidation apparatus to improve vacuum conditions, along with several procedural improvements to minimize this effect. For example, argon plasmas were effectively employed to remove adsorbed atmospheric carbon dioxide from the surfaces of the glass sample chamber and the powdered rock art samples prior to oxidation (Chaffee, 1993; Chaffee et al., 1993b, 1994b; Ilger, 1995).[3]

Replicate samples were analyzed to test the precision of results. Replicates are defined as different samples collected from the same painting or paint fragments divided into multiple sub-samples (designated in Table 1 with capital letters, e.g., 3A and 3B). Aliquots are defined as separate carbon samples for AMS measurement extracted from the same paint sample (designated with lowercase letters, e.g., 1a or 1b). When combining radiocarbon ages, a $\chi 2$-test is typically performed before calculating a weighted average and pooled standard deviation. An average is typically a better representation than any one measurement. Unfortunately, for the Lower Pecos rock paintings initially analyzed by Rowe's laboratory, the variance for replicate dates is large and results fail a $\chi 2$-test. With a larger associated error than the counting statistics reported with AMS radiocarbon results, Rowe (2001a, 2004) calculated the standard deviation of replicate analyses on the same painting and reported an uncertainty of ±250-300 ^{14}C years BP (±1*s*).

4.4 Critical Evaluation

Marvin Rowe's contributions to rock art dating and archaeology cannot be overstated. His pioneering work has produced hundreds of publications, numerous graduate students, and

[3] Argon plasmas were not conducted on sample 41VV75-1 and samples from 41VV576, but this modification was utilized on all other Lower Pecos paint samples. Livingston et al. (2009) report that Rowe has eliminated the use of the argon plasma to remove surface-adsorbed carbon dioxide since 2005 after noticing a limited effect on results. However, the Steelman laboratory has continued the use of argon plasmas.

revolutionized the field of rock art research. While we critique the legacy dates obtained for the Lower Pecos during the experimental phase of the plasma oxidation technique, we do so with tremendous respect and gratitude for Rowe's groundbreaking achievements.

Our examination of the legacy rock art dates from the Lower Pecos has led to the following conclusions:

(1) *Lack of provenience, pretreatment, background controls.* Due to a lack of contextual (sampling location information), compositional (chemical pretreatment and background analysis), and measurement (laboratory contamination) elements, the 32 dates obtained by Rowe's laboratory are problematic. We have chosen not to calibrate the legacy dates and conclude that these experimental results should not be used to draw archaeological conclusions. There is a difference between having radiocarbon measurements versus reliable age determinations.

(2) *No statistical agreement.* Unfortunately, for the Lower Pecos rock paintings initially analyzed by Rowe's laboratory, the variance for replicate dates is large and results fail a χ^2-test. With a larger associated error than the counting statistics reported with AMS radiocarbon results, Rowe (2001a, 2004) calculated the standard deviation of replicate analyses on the same sample and reports an uncertainty of ±250-300 ^{14}C years BP (±1*s*). Nonetheless, the experimental radiocarbon results obtained by Rowe's laboratory placed Lower Pecos rock paintings into the broad chronological time span of the Archaic Period.

(3) *One date is no date.* A single date for a painting should not be used to define a chronology or timeline for an entire rock art style. Two of the dated images are labeled as unclassified in Table 1, but have previously been categorized as Red Linear and Red Monochrome styles (Ilger et al., 1994, 1995). At Cueva Quebrada (41VV162a), the one experimental date is for a red oval painting and not a diagnostic figure of the Red Linear style (Fig. 5). At the Lewis Canyon Tinaja site (41VV233), the dated figure does not exhibit the typical characteristics of the Red Monochrome style except for splayed digits and bent elbows (Fig. 6). In rock art dating studies, often only one or two samples are radiocarbon dated and the temptation is to place the resulting age upon an entire style or category of painting. However, as the radiocarbon adage goes – one date is no date.

5. A Review of Current Research

Building on more than 20 years of experience using plasma oxidation in the dating of pictographs, Steelman and her colleagues have refined methods and established protocols to avoid anomalies in radiocarbon age determinations for rock paintings. We now employ fully developed field and laboratory procedures: (1) proper documentation of sampling locations so that the provenience of the sample is known (contextual); (2) analysis of unpainted control background samples to identify the presence or lack of contaminants in the rock substrate (compositional); (3) chemical pretreatment with base to remove any potential humic acid contamination (compositional); and (4) improved laboratory methods to ensure that laboratory contamination is avoided (measurement). After the developmental phase of the plasma oxidation technique, this methodology has been successfully applied to rock art sites around the world by Rowe and his former graduate students (see list of references in Rowe, 2012, as well as Baker & Armitage, 2013; McDonald et al., 2014; Duncan et al., 2015; Loendorf et al., 2016; Rowe et al., 2016; Viñas et al., 2016; Russ et al., 2017; Loendorf et al., 2017; Steelman et al., 2017, 2019; Quigg et al., 2020). See *Supplementary Materials S2* for detailed field and laboratory methods conducted by Steelman's laboratory for paint and oxalate accretion samples.

In the Lower Pecos, Steelman has utilized this improved plasma oxidation methodology to obtain 11 radiocarbon assays – six dates for paintings of the Pecos River style, one date for a red zigzag painting in another rock art style, and four dates for associated oxalate accretions to obtain minimum/maximum ages for paintings and provide independent verification of results (Bates et al, 2015; Steelman et al., 2021) (Table 2). Oxalate dating in the region was originally conducted by Russ et al. (1994, 1995, 1996, 1999, 2000) to support a paleoclimate reconstruction for southwest Texas. Whewellite (calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$) is ubiquitous on the limestone canyon and rockshelter walls of the Lower Pecos Canyonlands (Edwards et al. 1998, 2000). During the formation of oxalate coatings, biological sources (bacteria, fungi, lichen, microbes, etc.) incorporate carbon from the atmosphere into oxalic acid which is then precipitated onto the rock surface as calcium oxalate (Hess et al., 2008). Oxalate carbon is, thus, contemporary with when the calcium oxalate rock coating formed (Beazley et al., 2002). So, by radiocarbon dating calcium oxalate, we can determine when a coating formed. At 41VV129, an oxalate accretion covering a paint layer was previously dated to 3220±60 ^{14}C years BP (CAMS-15147), providing the only oxalate minimum age for a Pecos River style painting (Russ et al. 1996, 2000) prior to the Eagle Cave study discussed below (Steelman et al., 2021).

5.1 Results

For all sites studied below, organic carbon levels in unpainted rock backgrounds were negligible (≤1%), indicating that there was no significant physical or chemical contamination in the rock substrate. Normalized ratios are used to compare the amount of carbon in a paint sample to the amount of contamination in a background sample (Table 2). These normalized ratios are calculated by dividing the micrograms of carbon extracted by the mass (mg) of the solid samples. 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. It is imperative to test control samples (backgrounds) of unpainted rock to rule out the possibility of organic contamination in the rock substrate. In addition, chemical pretreatment with base solution suggested that humic acid contamination was negligible.

Radiocarbon results were calibrated using the OxCal computer program version 4.4.2 (Bronk Ramsey, 2009, 2020) with IntCal20 curve data from Reimer et al. (2020). 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).

5.1.1 Black Cave Annex (41VV76a)

41VV76a-1. Black Cave Annex, 41VV76a, is located within Seminole Canyon State Park & Historic Site. One panel at the annex contains a composition portraying a Pecos River style anthropomorph surrounded by five deer measuring 35 to 50 centimeters in length. Each deer is impaled with a red spear, and has hooves and dewclaws. The artist used controlled strokes to create lines of paint inside the body to in-fill the deer figures. Bates et al. (2015) reported a radiocarbon result of 1465±40 ^{14}C years BP (545-655 cal AD) (Table 2) for one of the black Pecos River style deer (Fig. 9). Oxalate accretion dating was not attempted on this sample.

Table 2. Review of Current Research

Site/Sample	Style [a]	Mass [b] (mg)	Carbon [c] (µg)	µg/mg ratio [d]	CAMS ID	Radiocarbon Date [e] (^{14}C years BP)	Calibrated Range (2σ, 95.4%)	Cal BP (2σ, 95.4%)	Reference
41VV76a									
1 black paint	PRS	55	110	2	152885	1465 ± 40	545 - 655 cal AD	1405 - 1295	Bates et al., 2015
1 background		100	0.9	0.009					
41VV167									
1 outer oxalate		14	40		170032	2030 ± 90	360 cal BC - 220 cal AD	2300 - 1730	Steelman et al., 2021
1 black paint	PRS	172	40	0.2	170031	3210 ± 110	1900 - 1200 cal BC	3900 - 3100	Steelman et al., 2021
1 underneath oxalate		34	<10						
1 background		160	0.3	0.002					
1’ outer oxalate		7	30		170034	2620 ± 120	1100 - 400 cal BC	3000 - 2300	Steelman et al., 2021
1’ black paint	PRS	114	40	0.4	170819	3310 ± 90	1880 - 1410 cal BC	3830 - 3360	Steelman et al., 2021
1’ underneath oxalate		34	30		170033	6340 ± 140	5700 - 4900 cal BC	7600 - 6900	Steelman et al., 2021
1’ background		154	0.6	0.004					
2 red paint	PRS	23	20	0.9	170820	3400 ± 270	2500 - 1000 cal BC	4500 - 2900	Steelman et al., 2021
2 background		89	0.3	0.003					
3 outer oxalate		12	<10						
3 black paint	PRS	40	10	0.2					
3 underneath oxalate		97	20		170821	5200 ± 290	4700 - 3300 cal BC	6700 - 5300	Steelman et al., 2021
3 background		195	0.6	0.003					
41VV1573									
1 red paint	UNC	120	190	1	181636	2275 ± 30	400 - 205 cal BC	2350 - 2155	unpublished
1 background		151	0.9	0.006					
2 red paint	PRS	80	105	1	181637	3420 ± 40	1880 - 1615 cal BC	3830 - 3565	unpublished
2 background		73	0.6	0.008					
41VV2326									
1	PRS	100	180	2	183925	2160 ± 35	360 - 50 cal BC	2310 - 2000	unpublished
1b background		120	0.6	0.005					

[a] For rock art styles, PRS is Pecos River style and UNC is unclassified, images that have no clear characteristics associated with any of the defined rock art styles in the Lower Pecos Canyonlands.
[b] Mass of solid paint or oxalate sample prior to any chemical pretreatment.
[c] Mass of carbon used for AMS graphite target.
[d] Normalized ratios are used to compare the amount of carbon in a paint sample to the amount of contamination in a background sample. These normalized ratios are calculated by dividing the micrograms of carbon extracted by the mass (mg) of the solid samples (see Steelman et al., 2019:120 for a more detailed explanation). For 41VV76a, as an example, 0.009/2 X 100 = 0.4% contamination.
[e] For paint samples, the $\delta^{13}C$ value was assumed to be -25‰ as no split of the carbon dioxide was sampled for IRMS measurement. For oxalate samples, 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).

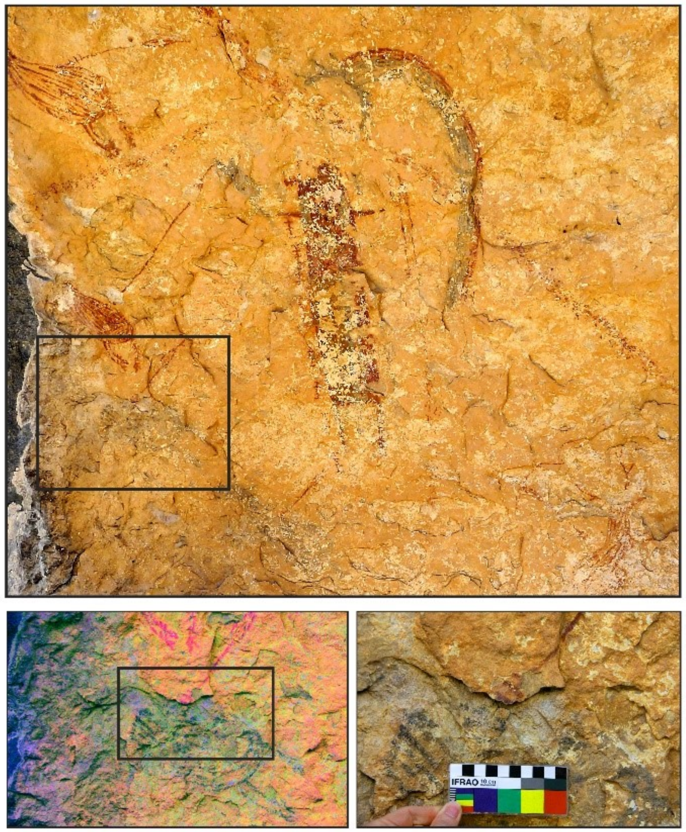

Fig. 9 Paint sample 41VV76a-1 was collected from the deer indicated within the box (Dstretch ac). The sampling location is shown in the bottom left enhanced photograph (DStretch _yxx_1.23_0.30_1.74; Harman, 2005) and the bottom right photograph.

If this had been the only younger result for the style, we would have most likely dismissed it as an outlier. Instead, it instigated our examination of Rowe's previous results and resulted in the compilation of this review. This radiocarbon date on a black deer at Black Cave Annex has a known provenience, a background control with negligible contamination, and was chemically pretreated with sodium hydroxide to remove any potential humic acid contamination prior to oxidation. From a laboratory perspective, there is no reason to suspect this result. However, it is only one measurement. More work should be done to corroborate this result.

5.1.2 Frost Felines Site (41VV2326)

41VV2326-1. Frost Felines, 41VV2326, is a Pecos River style rock art site located along the Rio Grande. Although preservation of the panel is poor, the surviving composition portrays two red anthropomorphic figures with feline attributes facing each other in profile (Fig 10). The anthropomorph on the left is predominantly infilled and lacks paraphernalia and body adornments. Both anthropomorphs have open mouths, and the one on the left has teeth. Speech-breath, in the form of large, well-defined red dots, float between the two figures. Boyd and Busby (2021) propose that the red dots passing between the two figures at Frost Felines represent measured words of ritualized speech, soul-breath loaded with potency and with sound. Here we report a radiocarbon age of 2160 ± 35 ^{14}C years BP (360-50 cal BC) (Table 2) for the red infilled anthropomorph (Steelman, unpublished result). We attempted oxalate accretion dating for this sample, but there was insufficient carbon for AMS measurement in both the overlying and underlying accretion.

5.1.3 Continental Groove Site (41VV1573)

The Continental Groove Site, 41VV1573, is a south facing rockshelter located on the bank of the Pecos River. The shelter walls contain prehistoric paintings, as well as thousands of incisions and groove marks. A sample from a red zigzag line characteristic of Bold Line Geometric style (41VV1573-1) and second sample from a red Pecos River style anthropomorph (41VV1573-2) were collected for radiocarbon dating. We were able to extract sufficient carbon from the organic constituents of the paints samples for AMS measurement. We also attempted oxalate accretion dating for both of these paintings, but there was insufficient carbon for AMS measurement.

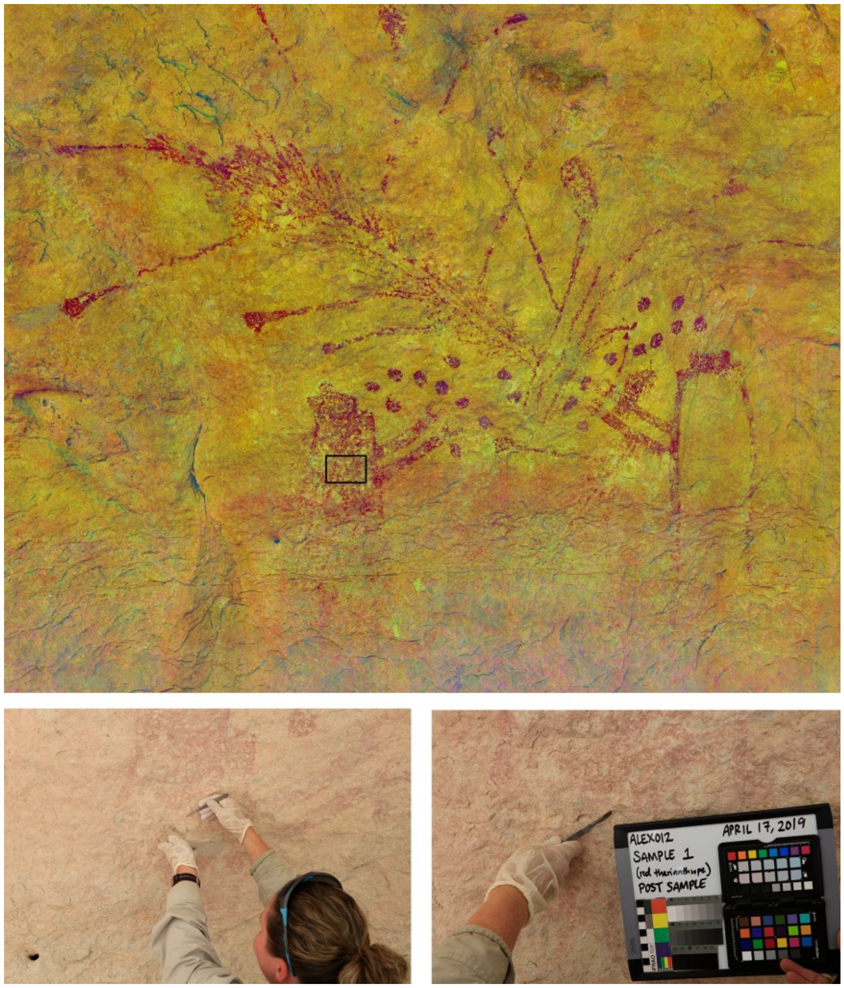

Fig. 10 Paint sample 41VV2326-1 was collected from the red infilled anthropomorphic figure at Frost Felines. The sampling location is indicated by a box in the top photograph. Below Steelman collects the paint sample and photographically documents the sampling location before and after collection. For scale, the anthropomorphic figures with feline characteristics are ~1 meter tall. The top photograph is enhanced using DStretch crgb (Harman, 2005).

41VV1573-1. We report an age of 2275±30 ^{14}C years BP (400-205 cal BC) (Table 2) for a red zigzag painting (Fig. 11) (Steelman, unpublished result). Zigzag paintings in the region are often assigned to the Bold Line Geometric style. If this classification is correct, then this is the first assay obtained for this poorly defined rock art style. Turpin (1986) suspected Bold Line Geometric to be a more recent rock art style, dating to after AD 200. However, this result at the Continental Groove Site places this red zigzag into an earlier phase of the Late Archaic Period (1500 BC – 1000 AD). However, as stressed above, a single date for a painting should not be used to define the chronology for an entire rock art style.

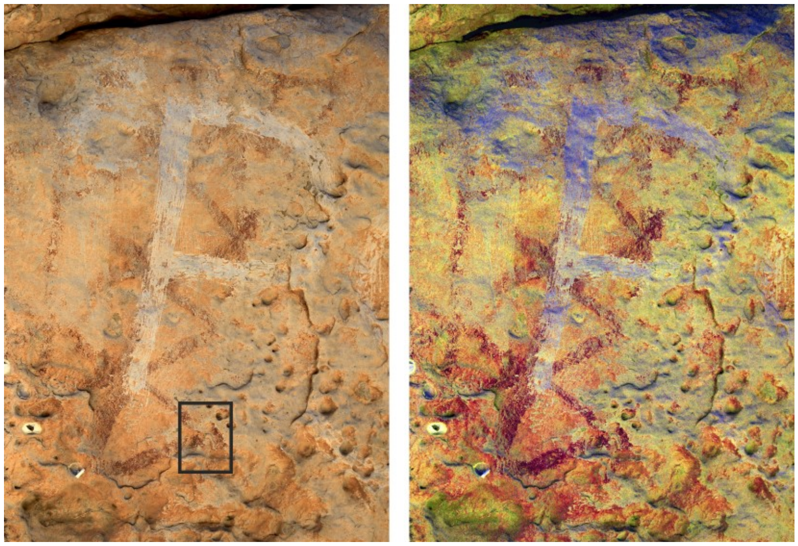

Fig. 11 Paint sample 41VV1573-1 was collected from a red zigzag painting at the Continental Groove Site. The sampling location is outlined with a box in the left photograph. Note the modern graffiti, letter P, incised over the prehistoric pictograph. The red vertical lines and zigzag lines are ~55 cm tall. The right photograph is enhanced with DStretch color channel lds (Harman, 2005) .

The red zigzag line superimposes a finely executed figurative petroglyph (Fig. 12). As portions of red paint filled in the incised designs, this radiocarbon date not only provides a direct date for the painted element, but also a minimum date of production for the petroglyph. The radiocarbon result for the painted zigzag provides our first relative date for production of a finely incised petroglyph in the region, suggesting the designs at the Continental Groove Site were created before 205 BC.

Fig. 12 Detail photograph of the incised lines that have been infilled with paint by the later addition of the red zigzag at the Continental Groove Site. For scale, the width of this photograph is ~10 cm.

41VV1573-2. We report a radiocarbon age of 3420±40 ^{14}C years BP (1880-1615 cal BC) (Table 2) for a paint sample collected from a red Pecos River style anthropomorph (Fig. 13) (Steelman, unpublished result). This figure has a U-shaped head and is wielding an object referred to as a power-bundle, which is diagnostic of Pecos River style paintings (Boyd and Dering, 1996).

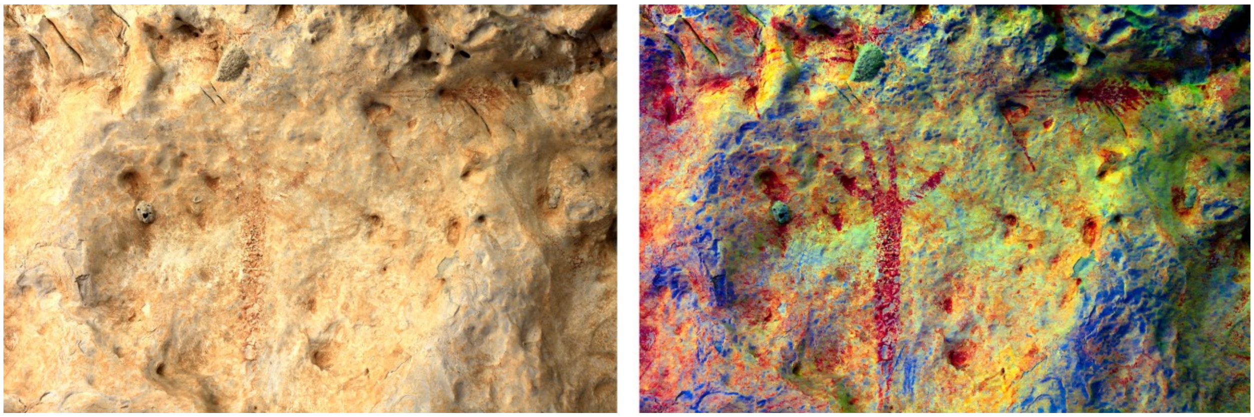

Fig. 13 Paint sample 41VV1573-2 was collected from the upper body of this red anthropomorph. The right photograph is enhanced with DStretch color channel lds (Harman, 2005). For scale, the anthropomorph is ~ 40 cm tall.

5.1.4 Eagle Cave (41VV167)

41VV167-1, 41VV167-1', 41VV167-2, 41VV167-3. 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 (Fig. 14). The deeply stratified deposits contained within Eagle Cave preserve the remains of hunter-gatherer lifeways spanning at least 13,000 years (McCuistion, 2019:113). The method employed in the analysis of these paintings was novel in that it was the first to determine an oxalate minimum age, direct date on organic constituents in the paint layer, and an oxalate maximum age for a single pictograph (Table 2). Steelman et al. (2021) used plasma oxidation to obtain direct radiocarbon dates for two Pecos River style paintings (41VV167-1 and 41VV167-2). A duplicate sample from 41VV167-1 was also dated (41VV167-1'). Sample 41VV167-3 had insufficient carbon for AMS measurement. Field microscopy and construction of Harris Matrices established the painting sequence of the mural and determined that it represents a composition produced through a single painting episode. Therefore, the ages of the paintings are coeval. The three radiocarbon dates on paintings from Eagle Cave pass a χ^2-test, with a weighted average of 3280±70 ^{14}C years BP, calibrated to 1740-1420 cal BC. 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 (Table 2). 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 (cal BP).

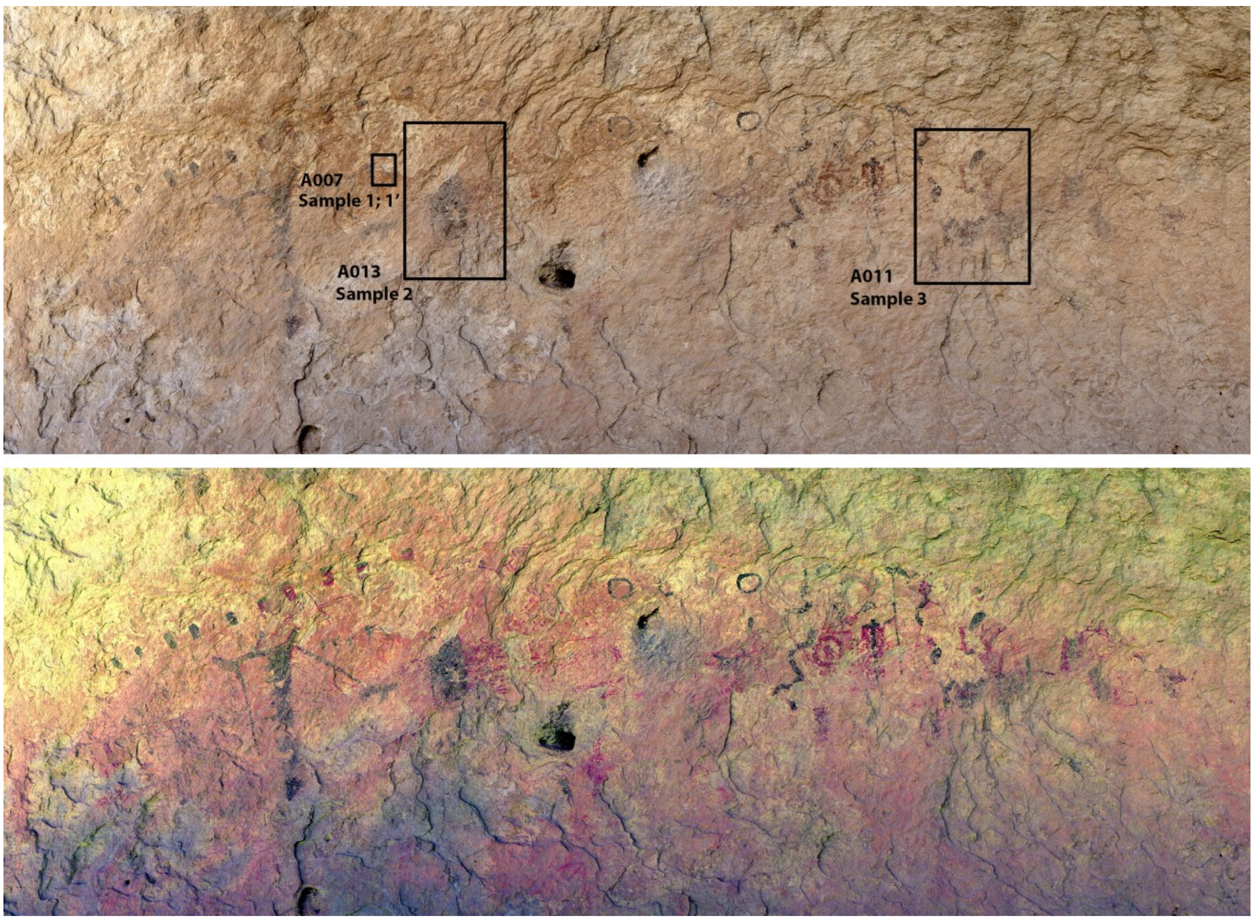

Fig. 14 The rock art panel at Eagle Cave spans 30 meters in width. The top panorama shows the sampling location for paint samples 41VV167-1 and 41VV167-1' (A007), 41VV167-2 (A011), and 41VV167-3 (A013). The bottom photograph is enhanced using DStretch color channel yxx_2.50_0.36_1.14 (Harman, 2005).

6. Conclusions

It has been 30 years since the first radiocarbon date for rock art in the Lower Pecos was published. The initial samples collected in the 1990s by the Rowe laboratory were analyzed to determine if it was even possible to date inorganic-pigmented rock paintings. The answer is yes, but we have strong reservations about the accuracy and precision of the legacy dates obtained during the initial experimental/development phase of the plasma oxidation technique. Over the past three decades, methodological improvements in the technique have facilitated reliable dating of pictographs. Plasma oxidation has been used to radiocarbon date over 300 pictographs worldwide – including charcoal pigments and the organic constituents of inorganic-pigmented paintings (see list of references in Rowe, 2012). The plasma oxidation technique has been verified by successfully dating known-age materials from radiocarbon laboratory intercomparisons (Steelman, 2004; Steelman et al., 2004; Steelman et al., 2017) and pictographs with archaeologically constrained ages (Hyman and Rowe, 1997b; Rowe, 2009). In addition, 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).

With the preliminary data from Steelman's laboratory, we have begun to date motifs with identifiable attributes to answer archaeological questions. Using improved methodology, we now have eleven radiocarbon assays for four rock art sites within the Lower Pecos Canyonlands (Table 2). Of particular note, Steelman et al. (2021) obtained three AMS measurements on a single composition at Eagle Cave that pass a χ^2-test consistent with being coeval: 3280±70 ^{14}C years BP, calibrated to 1740-1420 cal BC. Dating studies should focus on replicate analyses to test the accuracy and precision of results. These preliminary results suggest that future rock art dating projects in the region will produce a refined chronology that can be used for age comparisons between different rock art sites, painting styles, and even sub-styles.

In conjunction with detailed rock art documentation, Steelman's laboratory at Shumla is embarking upon a new radiocarbon dating campaign to learn more about the people who lived among these canyons and created these spectacular paintings. With over 350 rock art sites in the region, many more dates are needed to understand the geographical and chronological distribution of pictograph production in the Lower Pecos. The preliminary data presented in this review is just a meager beginning. Future research will provide a refined chronology for different styles of rock art in the region, and open up the possibility of identifying chronological sub-styles within the Pecos River rock art tradition that persisted for thousands of years. With more precise chronologies, comparisons between different motifs, sub-styles, and styles can be made. With reliable and accurate radiocarbon dates for pictographs, it is vital that researchers begin to incorporate this important iconography into mainstream archaeological reconstruction, as Chaloupka hoped in the opening quote of this paper (Chaloupka et al., 2000:10). 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 has recently constructed a new multi-chamber plasma oxidation instrument at Shumla that will be able to conduct batch processing of multiple samples at one time, allowing this technique to become more widely available for chronometric research both in the Lower Pecos as well as for other rock art provinces around the world.

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