Strategies for ^{14}C Dating the Oxtotitlán Cave Paintings, Guerrero, Mexico

Jon Russ, Mary D. Pohl, Christopher L. von Nagy, Karen L. Steelman, Heather Hurst, Leonard Ashby, Paul Schmidt, Eliseo F. Padilla Gutiérrez, and Marvin W. Rowe

We present a study of rock art at the Oxtotitlán Cave in Guerrero, Mexico (Figure 1), that suggests that the robust mural tradition in Mesoamerica began with cave paintings. Styles range from Archaic-type abstract shapes, perhaps dating before 2000 B.C., to human figures and animals arranged in narrative scenes of the Formative period dating after 2000 B.C. At Oxtotitlán, the spectacular, oversized, polychrome portrait of a bird-costumed character attributed stylistically to the Formative period (1500–400 B.C.) Olmec culture high on the rock face has, in particular, left prehistorians puzzled about social intentions and connections across Mexico (Figure 2). Here we report the strategy used to select, analyze, and prepare rock paint samples for radiocarbon analysis. We used a variety of analytical methods that have previously been employed in rock art studies, but in combination to minimize the impact on the paintings and yield reliable radiocarbon dates.

OXTOTITLÁN ROCK ART

When the Oxtotitlán Cave paintings in Mexico first became known to archaeologists in the late 1960s (Gay 1967; Grove 1970, 2007), the imposing image of a human figure on a throne (Panel

ABSTRACT

Oxtotitlán Cave paintings have been considered among the earliest in Mesoamerica on stylistic grounds, but confirmation of this hypothesis through absolute dating has not been attempted until now. We describe the application of advanced radiocarbon strategies developed for situations such as caves with high carbon backgrounds. Using a low-temperature plasma oxidation system, we dated both the ancient paint and the biogenic rock coatings that cover the paint layers at Oxtotitlán. Our research has significantly expanded the time frame for the production of polychrome rock paintings encompassing the Early Formative and Late Formative/Early Classic periods, statistically spanning a long era from before ca. 1500 cal B.C. to cal A.D. 600.

Los murales de la Cueva de Oxtotitlán, de acuerdo con criterios estilísticos, han sido considerados entre los más tempranos de Mesoamérica. Sin embargo, hasta la fecha esta hipótesis no había sido corroborada mediante fechamiento absoluto. En este trabajo se describe la aplicación de técnicas de radiocarbono avanzadas, las cuales han sido desarrolladas para lugares como cuevas con un elevado fondo de carbón. Fechamos tanto la pintura antigua como los recubrimientos biogénicos que cubren las capas de pintura utilizando un sistema de oxidación de plasma a temperatura baja. Nuestras investigaciones han ampliado de manera significativa el intervalo temporal de la pintura mural policroma en Mesoamérica, abarcando los periodos del Formativo Temprano al Formativo Tardío/Clásico Temprano, desde antes de aproximadamente 1500 cal a.C. hasta 600 cal d.C.

Advances in Archaeological Practice 5(2), 2017, pp. 170–183

DOI:10.1017/aap.2016.10

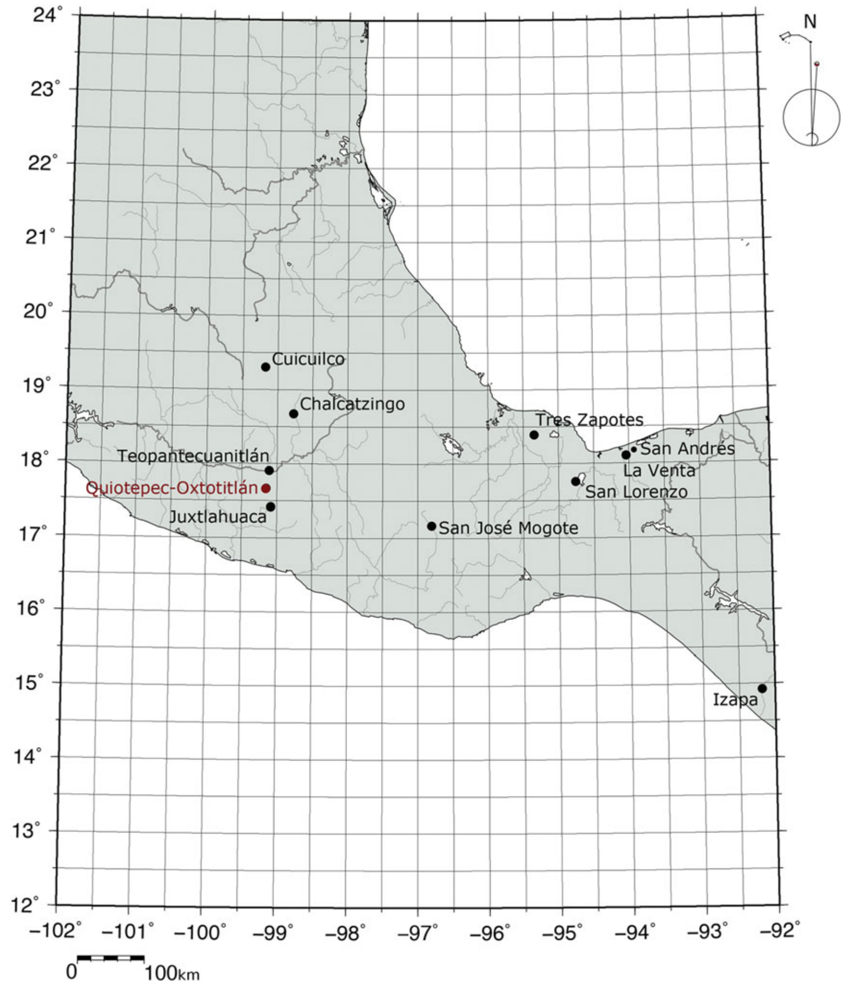

FIGURE 1. Map of the location of the Oxtotitlán cave paintings, Guerrero, Mexico, and other significant Formative period archaeological sites. Oxtotitlán is part of the larger site complex of Quiotepec-Oxtotitlán.

C-1, Figure 2) captured everyone's attention. With a dramatic placement high on the cliff face above the south arm of the cave, the painting has stylistic and iconographic similarities with monuments from major urban Olmec centers on the Gulf Coast of Mexico. The Gulf Coast Mexico Olmec built some of Mesoamerica's earliest cities, the dynastic seats of Mesoamerica's first kings (Clark and Pye 2006; Coe 1995; Coe and Diehl 1980; Cyphers 1997, 2004a, 2004b; Drucker 1952; Drucker et al. 1959; González Lauck 1996, 1997, 2010). Gulf Olmec cities are renowned for their synthesis of monumental sculpture and urban design. The Oxtotitlán painting presented a new dimension both in media and in geographical provenience, inviting questions about the artists of Oxtotitlán and their relationship with the Gulf Coast.

One of the largest but most enigmatic polychrome paintings covers a rock face (Panel C-2, Figure 3) at ground level in front of the south rockshelter entrance, directly below the enthroned figure (C-1). Although a considerable amount of paint loss from natural exfoliation of the rock surface has made it difficult to ascertain what the painting represents, areas of red, green, black, and yellow paint are still visible. Grove's (1970) earlier research reported black jaguar spots on the lower part of the rock face, possibly referencing deep-rooted jaguar-focused rain ceremonialism. Though difficult to discern with the naked eye, these spots are visible in computationally enhanced images of the painting.

Other polychrome panels painted across the front of the cave have been neglected in comparison because they are less ambitious and less visually accessible. Nevertheless, the Mexican government project (Instituto Nacional de Antropología e Historia, INAH) to clean the paintings of dirt and graffiti under the direction of Sandra Cruz Flores (Cruz Flores 2003, 2004, 2005) has revealed new visual details in these panels. In addition, recent developments in imaging have further assisted our efforts in new documentation. Specifically, Hurst and Ashby identified the outline of a human head behind a large shield (Panel 4–05, Figure 4) in front of the north shelter. The shield image, previously designated as Painting 8 by Grove (1970), is not a stand-alone symbol but is part of a larger scene similar in scale to the C-1 painting.

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

FIGURE 2. Photograph of an enthroned figure painted in Olmec style sitting on a throne (Panel C-1) and its context above the south rockshelter grotto. The base of the figure is 9 m above the rockshelter floor. Sample location indicated by arrow.

EXPERIMENTAL STRATEGIES

The collage of paintings at Oxtotitlán is complex, but with no visual means to establish temporal information such as superimposed paint layers or temporally sensitive elements. Radiocarbon dating the paints was the key to unraveling the relationships among paintings inscribed in the cave. Our study focused on Panels C-1, C-2, and 4–05 because of intriguing questions about the subject matter and the availability of green, red, and black paints that could potentially contain organic carbon for radiocarbon dating. A principal objective of the study was to establish chronologies of individual rock paintings at the site either by direct radiocarbon dating paint components or by constraining ages by ^{14}C dating the natural, biogenic coatings that encrust the paint layers.

Thin (~ 1 mm) coatings on limestone surfaces within the Oxtotitlán site were visually observed on painted and unpainted panels. One of the most common constituents of natural rock coatings on limestone and sandstone inside dry rockshelters and open-air sites is calcium oxalate. Oxalate-rich coatings occur globally and have been identified at a multitude of rock art sites, usually via chemical studies of rock paints. There is considerable evidence that oxalates in rock coatings are biogenic, the byproduct of bacteria (Bonaventura et al. 1999; Hess et al. 2008; Rusakov et al. 2015), fungi (Gadd et al. 2014; Monte 2003; Ortega-Morales et al. 2016), lichens (Del Monte and Sabbioni 1987; Russ et al. 1996), and mixed microbial communities (Gorbushina 2007). Evidence suggests that all carbon in oxalate biofilms originates from atmospheric carbon dioxide (Beazley et al. 2002) and that, once formed, there is no carbon exchange with the substrate (Watchman 1993). As such, radiocarbon ages of oxalates would correlate with periods when the microbial communities flourished on the rock surfaces in the past (Caneva 1993; Russ et al. 2000) and thus date the formation of the rock coating.

At sites where oxalates cover or encapsulate ancient rock paints, and the stratigraphy of the coating relative to the paint layers can be discerned, ^{14}C analysis of the oxalate can be used to determine minimum or maximum ages for paintings. This approach has been used at sites worldwide since Watchman (1991) first radiocarbon dated oxalate coatings in Australia. Since then,

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

FIGURE 3. Image of Panel C-2 with enhanced zones of black paint featuring the jaguar spots initially identified by Grove (1970). Sample location indicated by blue circle.

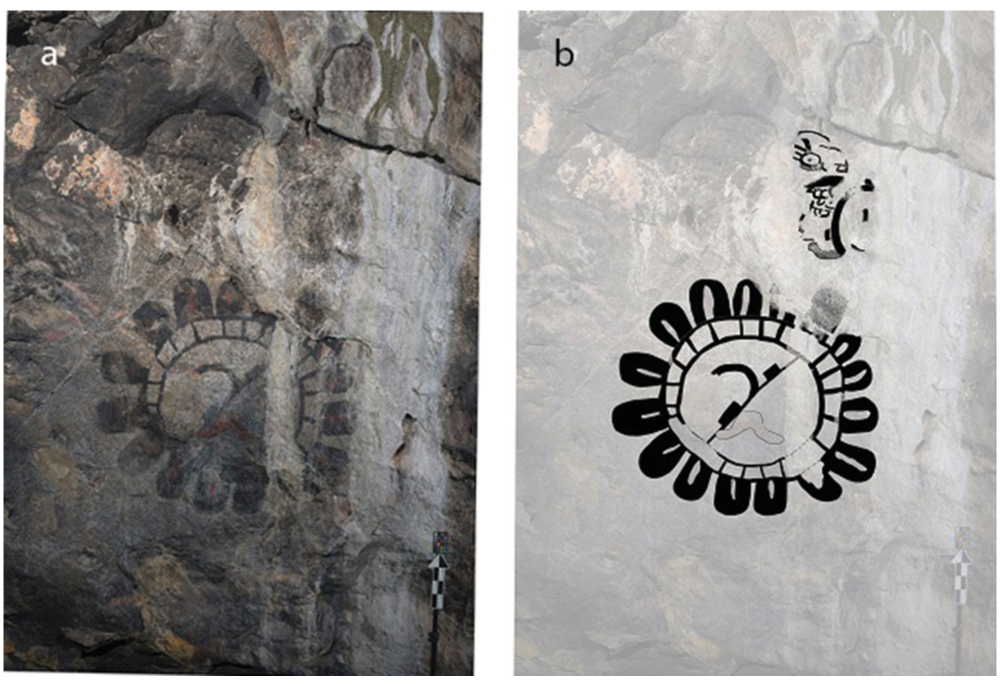

FIGURE 4. (a) Photograph of a figure holding a shield (Panel 4-05). A human head in profile is visible behind the shield. Photo by Joseph Gamble, 2012. (b) Illustration of Panel 40-5 by Heather Hurst and Leonard Ashby, 2016. The face in upper right holding the shield was previously undocumented. This composition may extend both down and to the west (right).

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

^{14}C ages of oxalate rock coatings have been used to constrain the age of ancient paintings at numerous sites in Australia (David et al. 2013; Watchman et al. 2000; Watchman et al. 2005), as well as sites in Africa (Mazel and Watchman 2003), the Iberian Peninsula (Ruiz et al. 2012), North America (Whitley 2013), and South America (Steelman et al. 2002).

Our sampling strategy at Oxtotitlán focused mainly on black paints because of the possibility that the pigments were prepared using pyrolyzed carbon (PyC), the byproduct of incomplete combustion of plants or animal fats and referred to as charcoal, soot, carbon black, or lampblack. Many black paints used to create parietal rock art in antiquity were constructed from manganese and iron oxide minerals (Chalmin et al. 2003; Chalmin et al. 2006; Hyman et al. 1996; Koenig et al. 2014; Littmann 1975; Magaloni, Newman, et al. 1995; Vázquez et al. 2008; Zoppi et al. 2002); however, PyC was also commonly used, thus providing a source of carbon for direct radiocarbon analysis (Baker and Armitage 2013; Bonneau et al. 2011; López-Montalvo et al. 2014; Magaloni 2001; Morwood et al. 2010; Valladas et al. 1992; Valladas et al. 2001).

For red and green paints, the pigments are invariably mineral-based; however, in order to produce a paint, it is necessary to suspend the mineral particles in a liquid medium (vehicle) that also serves to bind pigments to the substrate (binder). It is generally hypothesized that carbonaceous substances such as seed oils, plant resins, vegetable gums, animal fats, or beeswax were added to create a liquid paint mixture, thereby providing a source of organic carbon for radiocarbon dating (Ilger et al. 1995; Magaloni 1998; Magaloni, Pancella, et al. 1995; Morwood et al. 2010; Russ et al. 1990; Wright 2008, 2010). Here we employed a low-temperature oxygen plasma system to isolate carbonaceous carbon used in the original paint mixtures from carbon-rich minerals in the substrate and natural rock coatings, allowing for direct radiocarbon dating of the artifacts (Rowe 2009). Excited oxygen in the plasma system reacts with organic carbon yielding carbon dioxide (CO_2). The reactions occur below the decomposition temperatures of carbon-rich minerals such as calcite ($CaCO_3$), the primary component of limestone and present in sandstone. Both of these rock types are common substrates used for ancient rock paintings. Oxalate minerals whewellite ($CaC_2O_4 \cdot H_2O$) and weddellite ($CaC_2O_4 \cdot 2H_2O$) are prevalent in natural rock coatings and are also stable in the plasma and so do not interfere with the radiocarbon analysis (Armitage et al. 2001; Ilger et al. 1995).

METHODS

Preliminary Analyses and Sample Selection

To distinguish between inorganic, mineral-based pigments and PyC pigments, we analyzed the paintings in situ using a handheld portable X-ray fluorescence (HHpXRF) spectrometer. This technique has proven effective in the study of rock art primarily because it is noninvasive and provides qualitative/semi-quantitative data on chemical elements in the paints (Koenig et al. 2014; Newman and Loendorf 2005; Roldán et al. 2010; Rowe et al. 2011). The method is especially useful for discriminating between mineral-based and carbon-based pigments, and thus for identifying specific paintings that could potentially be ^{14}C dated (Beck et al. 2013; Koenig et al. 2014; Rowe et al. 2011). While there has been controversy surrounding the use of HHpXRF for *quantitative* analyses of archaeological materials (Shackley 2010), our goal was simply to establish whether manganese or iron concentrations in paints were above the natural background levels of the bedrock.

A handheld Innov-X Alpha Series pXRF with a silver anode X-ray tube source and a Si-PIN diode detector was operated in "soil mode" using 40 kV excitation energy with 30-second analysis times. A Hewlett Packard iPAQ personal digital assistant was interfaced to the instrument to control the analyses and to store data. We analyzed multiple locations on each painting at the site and then analyzed non-painted surfaces adjacent to the paintings to establish the background composition of the limestone substrate and natural rock patinas.

Results of these analyses showed elevated iron for red paints and elevated copper for green paints, compared to the background. Nevertheless, manganese and iron concentrations in all black paintings at the site measured below the detection limit of the instrument or were statistically the same as the background compositions, i.e., $\leq .014 \pm .004$ % (McPeak et al. 2013). This fact is in contrast to analyses of black paints in the Lower Pecos Canyonlands, Texas, where measured concentrations of manganese in black paintings were consistently and significantly greater than ambient concentrations (Koenig et al. 2014). At the Oxtotitlán site, it was clear that red and green pigments are mineral-based but that the black paints are most likely carbon-based, results that are consistent with Mesoamerican colorant manufacture used in later periods (Magaloni 2001).

We focused on three areas at the site to collect samples for further laboratory study to explore the feasibility of obtaining ^{14}C ages of the paintings. We collected paint samples from Panel C-1 (enthroned figure, Figure 2), Panel C-2 (jaguar figure, Figure 3), and Panel 4–05 (shield figure, Figure 4). We selected areas on the paintings where small chips were in the process of natural exfoliation to minimize damage to the imagery, and that we judged free of possible contamination from graffiti, cleaning, or restoration. Samples were removed by slight prying using a pre-cleaned knife blade and allowed to drop onto a sheet of aluminum foil that was then wrapped, labeled, and placed in a plastic sample bag. Samples were collected such that the paint layers remained intact on a small section of the substrate. We also collected non-painted samples directly adjacent to sampling areas to provide chemical and stratigraphic information on the background that included the natural rock coating and the basal limestone.

Laboratory Analyses

To characterize the paints and natural rock coatings, we used Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) Spectroscopy, Environmental Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (ESEM-EDS), and optical microscopy of polished thin-sectioned samples.

ATR-FTIR. We used a Perkin-Elmer Spectrum 100 with a diamond-zinc selenide composite ATR that allowed

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

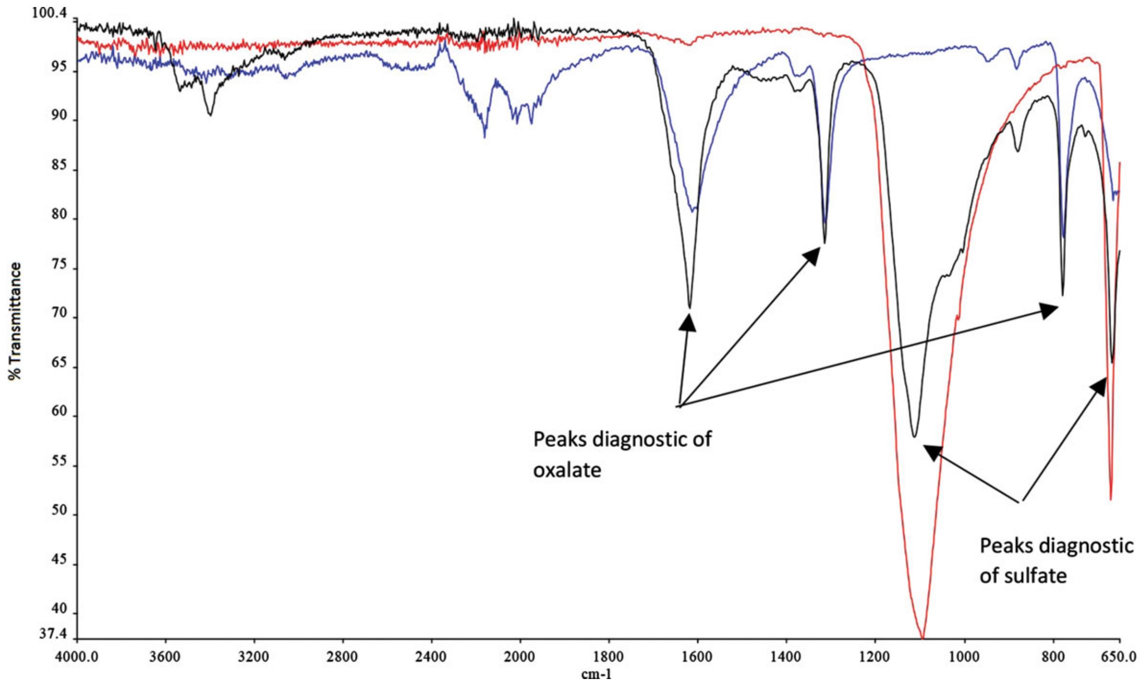

FIGURE 5. An example of an Attenuated Total Reflectance–Fourier transform Infrared (ATR-FTIR) Spectroscopy spectrum from the analysis of a sample collected near Panel C-1 (black spectrum). Also shown are overly spectra from the analysis of a calcium oxalate standard (blue) and a calcium sulfate standard (red) demonstrating that the coating is primarily oxalate and sulfate.

microgram-sized samples to be analyzed. The ATR-FTIR analysis of the natural rock coating consistently showed the presence of oxalates and sulfates, the former based on the broad carbonyl peak at 1,610 cm^{-1} and sharp diagnostic peaks at 1,300 cm^{-1} and 790 cm^{-1}, and the later based on the broad peak at 1,110 cm^{-1} and a sharp peak at 655 cm^{-1} (Figure 5). A peak at 1,400 cm^{-1} indicative of carbonate was also detected in several samples, likely from inclusion of calcite from the limestone substrate.

ESEM-EDS. The micromorphology, microstratigraphy, and elemental compositions of paints and coatings were established using a Philips XL 30 ESEM operated at 30 keV in the "wet mode." We analyzed sample surfaces and cross-sectional views of bifurcated samples, as well as powdered aliquots scraped from samples using a needle.

ESEM images revealed that the pigment used in the black colorant from the C-1 painting was distinctly different from the pigment used for Panel 4–05. In the former, the paint layer appeared amorphous under high magnification; moreover, the paint was not incorporated within the coating or substrate, but instead formed a distinct stratum between the coating and basal limestone. EDS analysis of the pigment material showed that it was predominately carbon (Figure 6). These results are consistent with a petroleum-based pigment, either asphalt or processed bitumen (Argáez et al. 2011), a result that precludes using the black paint sample from Panel C-1 for ^{14}C analysis. Mesoamerican peoples used bitumen for many purposes, such as decoration, as a sealant, and as an adhesive, especially in Mexico's southern Gulf Coast lowlands where the material occurs naturally (Wendt and Cyphers 2008). A rare example of bitumen (*chapopote*) wall paint is noted at the Mayan site of Bonampak in Chiapas, Mexico (Magaloni 2001:181–184).

The pigment in the shield figure (Panel 4–05) consisted of small, black particles with dimensions $\sim 5\ \mu m \times \sim 20\ \mu m$ that were dispersed within the coating (Figure 7). These particles were also carbon-based, as demonstrated in the EDS analysis of the particles (Figure 7), with estimated carbon/oxygen (C/O) ratios between .2–.3. This C/O ratio, together with particles sizes $> .2\ \mu m^2$, suggests that the particles are PyC with size and compositional properties between charcoal and soot (Hedges et al. 2000; Preston and Schmidt 2006).

ESEM images of cross-sectioned samples further demonstrated that the natural coating is heterogeneous with a mixture of microcrystals and platy crystals. The morphologies and elemental concentrations are consistent with whewellite and/or weddellite for the microcrystals, while the platy crystals, along with the presence of sulfur, indicates gypsum ($CaSO_4 \cdot 2H_2O$) (McPeak et al. 2013; Russ et al. 1999). Optical microscopy of polished thin-sections revealed that the thickness of the oxalate/sulfate rock coating was $\sim$ .5 mm and completely covers the paint layers.

AMS ^{14}C Dating Strategies

Based on the analyses described above, we concluded that there were three possible options for establishing direct or relative ^{14}C ages of several of the paintings: (1) direct dating of PyC pigment from the shield figure, (2) direct dating of a carbonaceous vehicle/binder used to construct red and red/green paints from the C-1 and C-2 paintings, and (3) radiocarbon analysis of the oxalate coatings superimposing paints to obtain minimum ages.

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

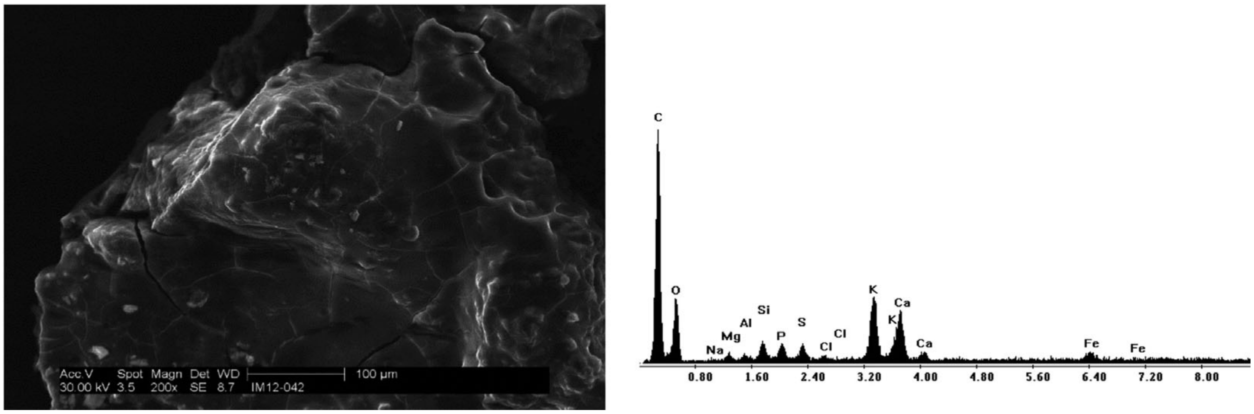

FIGURE 6. Environmental Scanning Electron Microscopy image (1,200x magnification) of the amorphous black paint (left) and an Energy Dispersive X-ray Spectroscopy spot analysis spectrum of the amorphous paint region (right).

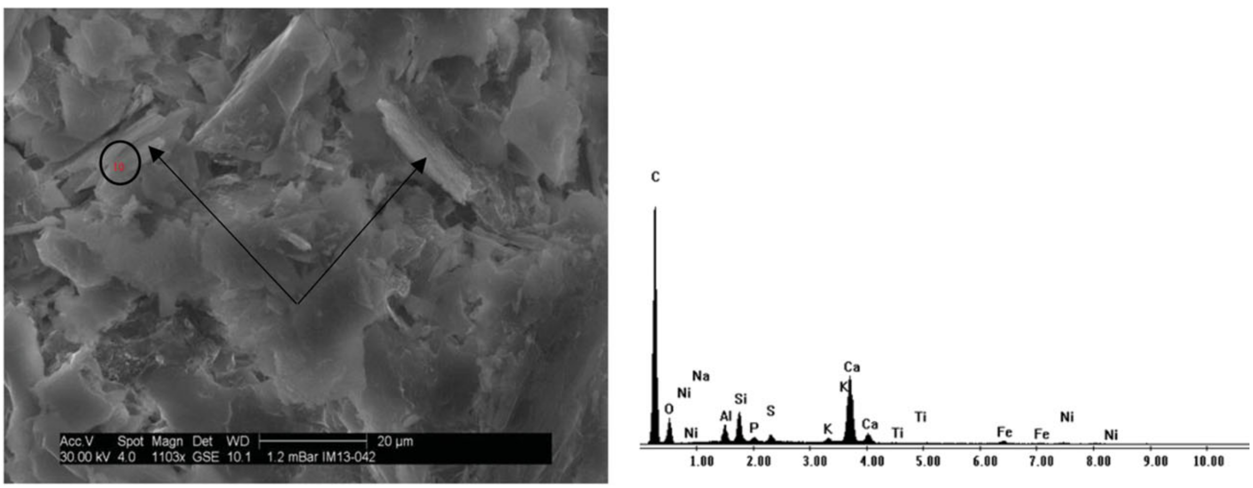

FIGURE 7. Environmental Scanning Electron Microscopy image of black particles in a black paint sample from the Panel 4-05 (Shield figure). The arrows indicate pigment particles. The Energy Dispersive X-ray Spectroscopy spectrum at right was collected at the circle in this image.

For these experiments, we employed a low-temperature oxygen plasma methodology for three primary purposes: (1) to oxidize and extract carbon from the PyC pigment in the shield figure for direct AMS ^{14}C analysis; (2) to evaluate whether an organic binder/vehicle was used to produce the red and red/green composite paints, and, if present, extract the organic carbon for radiocarbon analysis; and (3) to pretreat the oxalate samples by removing organic contaminants from the mineral coatings prior to the ^{14}C analysis (Rowe 2009; Steelman and Rowe 2012).

The low-temperature plasma oxidation system creates electronically excited oxygen molecules within an enclosed glass chamber that react with organic matter at a low temperature (∼100°C), yielding carbon dioxide and water. The excited oxygen does not react with oxidized forms of carbon such as carbonates and oxalates, and the low-temperature prevents thermal decomposition of these compounds (Armitage et al. 2001; Ilger et al. 1995). Thus, the excited oxygen reacts solely with reduced organic carbon yielding CO_2 that can be cryogenically isolated on a liquid nitrogen cold finger that is flame-sealed for ^{14}C analysis. This technique was originally developed for extracting organic carbon in prehistoric rock paints for ^{14}C analysis, especially those on carbonate surfaces (Russ et al. 1990) and has proved to be effective for radiocarbon dating these artifacts (Rowe 2009; Steelman and Rowe 2012).

We prepared the paint and oxalate samples for the plasma treatment by removing loose detritus from the surfaces with light scrubbing using ultrapure water (18.2 MΩ) and drying them in a 60°C oven overnight. Sample surfaces, including paints and oxalate coatings, were separated from the limestone substrate using a razor knife. The resulting powders were analyzed via ATR-FTIR to confirm the presence of oxalate and evaluate the amount of carbonate included in the sample. The samples were then exposed to an oxygen plasma discharge following the procedures described by McDonald et al. (2014).

(1) Direct ^{14}C analysis PyC from the Shield Figure (Panel 4–05). The sample from the shield figure had a 3 cm × 3 cm surface area with approximately two-thirds of the sample covered with

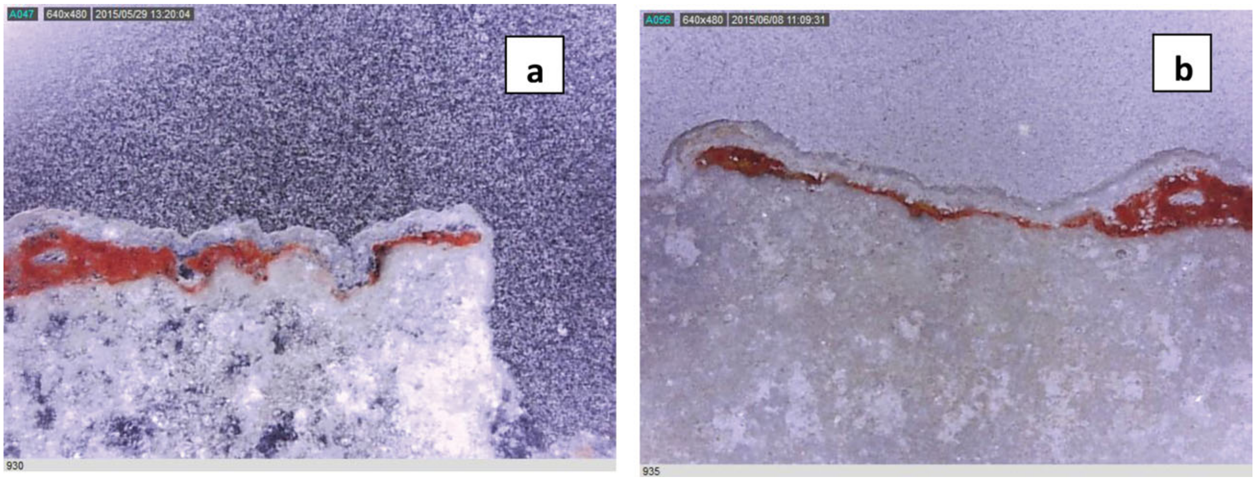

FIGURE 8. Optical microscope images of polished thin-sections showing the stratigraphy of the oxalate layer, paint layer, and substrate from samples collected at Panel C-2. The image on the right (a) shows a sample with red and green pigments, with green paint on top of red. The image on the right (b) shows only red paint.

pigment while the remaining one-third was void of paint and contained only the natural rock coating. The paint and the unpainted surfaces were removed separately, providing one sample that was a mixture of paint and natural coating and a second consisting of only the coating, both from the same specimen. The samples were scraped from the substrate while we observed them under a dissection microscope to ensure that the two areas were not cross-contaminated.

The two samples were treated separately using a low-temperature oxygen plasma system. The 1.5 hr plasma oxidation of the paint sample yielded 40 μg of datable carbon (in the form of carbon dioxide) that was sealed in a glass ampoule and sent to the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory (CAMS-LLNL) for ^{14}C analysis. Afterward, we continued plasma exposure of the paint sample until no more carbon was extracted, thereby removing residual organic matter from the remaining oxalate. The "cleaned" oxalate sample was processed for AMS ^{14}C analysis as described below.

Plasma oxidation of the unpainted portion of the sample yielded $\leq$10 μg carbon, insufficient for an accurate ^{14}C measurement. Thus, we assume that the carbon extracted from the paint was predominately from the PyC pigment, with minimal background contamination. Nevertheless, plasma treatment of background samples from other areas at the site contained significant amounts of carbon.

(2) Direct ^{14}C Dating of a Binder/Vehicle in Paints from Panels C-1 and C-2. A second strategy for determining the chronologies of the rock paintings was via plasma extraction of organic matter that might have been added to the inorganic pigments in the original paint mixture. It is generally surmised that mineral pigments such as copper and iron in green and red paints, respectively, needed to be suspended in an oily (organic) medium (vehicle) to produce a paint and to bind the pigments to the rock surface (binder). If such a vehicle/binder was an organic substance, and if the carbon could be extracted using low-temperature plasma oxidation, then we could ^{14}C date the paint (Rowe 2009; Steelman and Rowe 2012).

We selected paint and background samples from two areas at the Oxtotitlán site for these experiments, a red-green composite paint from Panel C-1 (enthroned figure) and a red paint from Panel C-2 (jaguar figure). Unfortunately, plasma treatment of the non-painted, background samples collected near the paintings yielded considerable amounts of carbon, equivalent to that produced by the treatment of paint samples. Organic substances can occur on rock surfaces with oxalates due to microbial activity that results in the formation of oxalates (Spades and Russ 2005). We concluded that there was excessive organic matter in the natural rock coating (i.e., the background) that precludes obtaining reliable ^{14}C dates from a binder or vehicle (Livingston et al. 2009).

As with the paint sample from the Panel 4–05 shield figure, we continued to oxidize the C-1 and C-2 paint samples until no measurable carbon dioxide was produced during the plasma reaction. This effectively removed the organic matter in the paint and coating, leaving only the oxalate component of the biofilm that covered the painting to be further processed for ^{14}C analysis.

(3) ^{14}C Dating of Oxalate Rock Coatings. We ^{14}C dated five calcium oxalate coating samples, three of which occurred on top of paint layers and two from unpainted surfaces adjacent to rock paintings including the Panel C-1 enthroned figure and Panel 4–05 shield figure. The oxalate coating superimposes paint layers (Figure 8), indicating that the production of the rock art would have occurred *prior* to the oxalate deposition; therefore, the oxalate ^{14}C ages represent *minimum* ages of the paintings.

We prepared the samples for ^{14}C measurement by first removing loose detritus from sample surfaces with light scrubbing using ultrapure water and drying them overnight in a 60°C oven. Coatings and paints were scraped from the substrate using a razor knife under magnification with a dissection microscope. The powdered samples were then reacted in the low-temperature oxygen plasma, first to measure the quantity of organic matter so as to

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

TABLE 1. AMS ^{14}C Ages of a Black Paint Pigment and Oxalate Rock Coatings.

Area within Site	Sample Description	CAMS #	^{14}C age (yr B.P.)[a]	Calibrated Age (2σ)[b]
Panel 4-05	Black paint (PyC)	163262	1980 ± 190[c]	500 cal B.C.–cal A.D. 600 (94.5%)
Panel 4-05	Oxalate coating covering the paint	163266	1370 ± 30	cal A.D. 605–690 (95.4%)
Panel 4-05	Oxalate coating from non-painted surface adjacent to Shield Figure	163267	590 ± 90	cal A.D. 1250–1470 (95.4%)
C-1	Oxalate coating background for C-1 Mural	173339	3705 ± 30	2200–1980 cal B.C. (95.4%)
C-2	Oxalate coating superimposed on red and green pigment	173340	1410 ± 35	cal A.D. 575–670 (95.4%)
C-2	Oxalate coating superimposed on red pigment	173341	3195 ± 30	1520–1410 cal B.C. (95.4%)

[a]Sample sizes were too small to measure the stable carbon isotope ratios. Radiocarbon ages were calculated using a stable carbon isotope value of −11 per mil, as the average value for calcium oxalate samples in the Lower Pecos Canyonlands of Texas (Russ et al. 2000).

[b]Calibration was performed using the OxCal computer program version 4.2.3 (Bronk Ramsey 2009, 2013) with IntCal13 curve data from Reimer et al. (2013).

[c]The large uncertainty is due to a small sample size (40 μg of C).

evaluate the feasibility of directly dating organic matter in the paint, and second to eliminate the reduced carbon in the samples that might interfere with ^{14}C dates of the oxalate coating.

Once cleaned via the oxygen plasma treatment, aliquots of the samples were analyzed using ATR-FTIR to test for the presence of carbonates. Samples were then placed in pre-cleaned glass centrifuge tubes with ~3 mL of 1.0 M phosphoric acid (HPLC grade) and ultra-sonicated for 45 minutes to remove carbonates. The tubes were centrifuged, the supernatant was removed, and then the tubes were rinsed twice using ultrapure water. Samples were dried overnight in a 90°C oven, and aliquots were reanalyzed using an ATR-FTIR to confirm that all carbonates had been removed. The powdered samples were then sent to CAMS-LLNL for combustion of the oxalates to carbon dioxide, followed by reduction to graphite for an AMS ^{14}C target.

RESULTS

All the black paintings in the Oxtotitlán site were constructed from pigments other than manganese or iron, based on the absence of these elements in the HHpXRF analyses on site. This finding suggests that the black pigments were produced from carbon-based materials. We also ascertained in the laboratory that the rock coatings that cover the paintings are composed mainly of calcium oxalate and calcium sulfate, the former having a biogenic origin. We measured the radiocarbon age of one prehistoric paint sample, three oxalate coatings that superimpose paint layers, and two oxalates samples collected adjacent to the rock art (Table 1). An overarching goal of the study was to establish the age of the iconographic Panel C-1, but unfortunately this was not accomplished. We discovered that the black pigment used to construct the artifact was carbon-based but composed of asphalt or processed bitumen and thus could not be radiocarbon dated. This is, to our knowledge, the first identification of a petroleum-based pigment used in prehistoric rock art. Although the age of the oxalate coating next to the painting dated to 3705 ± 30 yr B.P., the oxalate in Panel C-1 occurs both above and below the paint layer and thus cannot constrain the age of the paint (Figure 9).

The experiment to radiocarbon date the Panel 4–05 shield figure appears reliable. The pigment was identified as PyC with particle size and composition between charcoal and soot. This organic carbon in the paint was directly radiocarbon dated as 1980 ± 190 yr B.P. The oxalate layer covering the paint was radiocarbon dated as 1370 ± 30 yr B.P., which is stratigraphically consistent since the coating occurs on top of the paint layer and so should be younger. The results of the two oxalate ages from Panel C-2 (3195 ± 30 yr B.P. and 1410 ± 35 yr B.P.), both of which were superimposing paint layers, indicate that these artifacts were produced prior to 3,195 years ago as a *minimum* age.

The radiocarbon ages from all oxalates at the site range from 590 to 3705 yr B.P. This disparity in ages is not unusual 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 yr B.P., and the range of two samples at Abrigo de los Oculados was 2610 to 4675 yr B.P. As oxalate layers form over time, a weighted average of the dated material is obtained. If layers are thicker in one place than in another area, disparate ages would result.

CONCLUSIONS

This study provided an opportunity to apply two rock art dating strategies on a single sample, thereby providing a test of these dating techniques. We identified a paint sample from Panel 4–05 that contained both a pigment made from pyrolyzed carbon and a biogenic rock coating that superimposed the paint layer. We used a low-temperature oxygen plasma to isolate the carbon in the paint from the carbon-rich limestone substrate and oxalate coating to obtain a direct measurement of the radiocarbon age of the pigment. Furthermore, the oxygen plasma treatment "cleaned" the residual sample of organic carbon without loss of biogenic oxalate, a loss that would have occurred using traditional wet chemistry acid-base treatments. Only a direct acid treatment to remove carbonates was necessary to prepare the oxalates for the radiocarbon assay. The resulting radiocarbon ages of the two separate materials from Panel 4–05 were stratigraphically consistent, with the age of paint (1980 ± 190 yr B.P.) being older than the biogenic rock coating that covers the

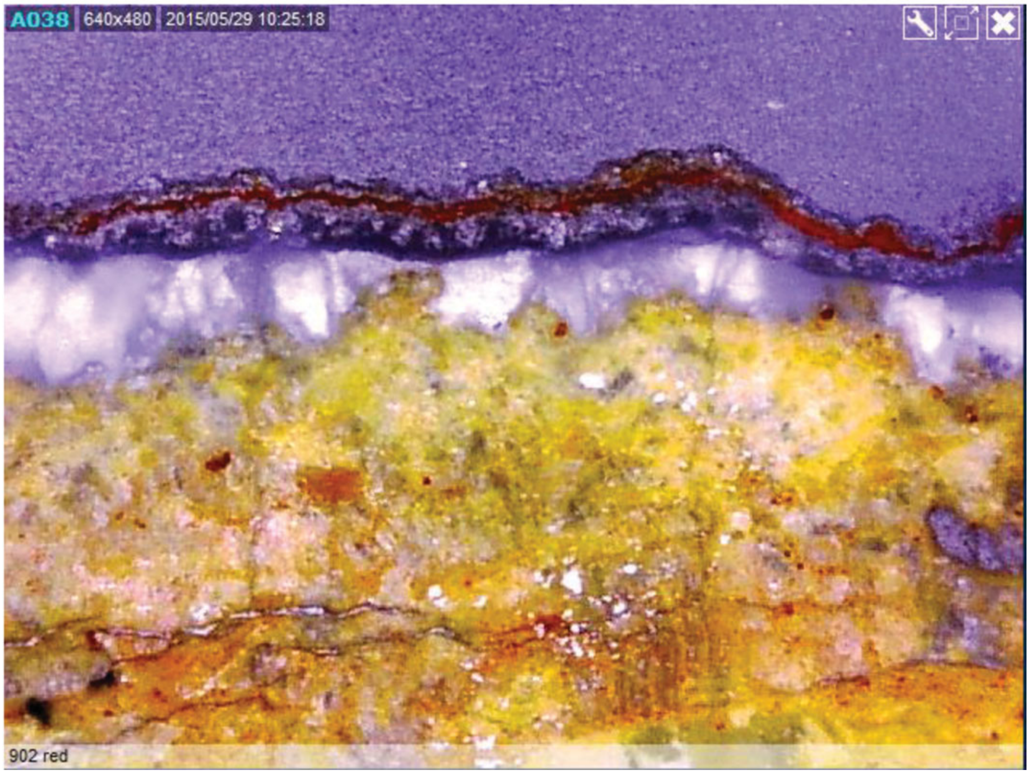

FIGURE 9. Optical micrograph of a polished thin-section of a sample from Panel C-1. The paint layer in this sample occurs within the oxalate coating and so we cannot deduce a relative age of the paint layer.

paint (1370 ± 30 yr B.P.). We conducted a direct test with a positive result from two methods most often used to determine or constrain rock art chronologies.

The consistency of the measured radiocarbon ages of the PyC in the paint and the biogenic coating provides confidence in the data and the methodology. Previously, Armitage et al. (2001) directly tested the plasma oxidation applied to PyC by radiocarbon dating charcoal in rock paint from Mayan hieroglyphs that contained calendar dates. The measured radiocarbon ages of the charcoal proved to be older than the calendar dates by between 110 and 140 years. While this is not a significant discrepancy in terms of rock art, these results do reinforce caution when evaluating radiocarbon ages from PyC in rock art paints. The most pressing problems are from the use of "old wood" to produce the pyrolyzed carbon (Schiffer 1986), "old charcoal" in constructing the paints, and the necessity of analyzing very small samples (Armitage 2001).

Another unique strategy used here was the oxygen plasma treatment of oxalate samples to remove organic contaminants in lieu of using acid-base methods. This protocol was also applied to oxalate coatings covering rock paints from Panel C-2, where paints underlie the rock coating. The radiocarbon age for one sample was the oldest measured at the site, suggesting that the paints were applied prior to 3195 ± 30 yr B.P. A second sample from the same panel yielded an age of 1410 ± 35 yr B.P. This significantly younger age does not necessarily compromise the older date. Oxalate biofilms form over long periods of time, and the radiocarbon age of a particular coating sample reflects the average of the periods of production of the organisms that produce the oxalates.

DISCUSSION

Our research significantly expands the periods of cave use at Oxtotitlán, and the sequence of dates shows that episodes recurred over time adding to our appreciation of Mesoamerican sacred landscapes and ritual practice. The radiocarbon date from the oxalate covering a paint layer demonstrates that the polychrome painting tradition extends back much earlier than the Formative period (1500–400 B.C.) date assigned on stylistic grounds to the bird-costumed, enthroned figure's portrait (Panel C-1). Radiocarbon results on oxalate of 1520–1410 cal B.C., a *terminus ante quem* marker, point to polychrome painting (Panel C-2), in the early part of the Early Formative period, the earliest evidence for this medium in Mesoamerica.

The large polychrome painting designated Panel C-2 testifies to ancient ceremonialism. Grove (1970) identified what he thought were jaguar spots arrayed across the panel when he viewed it in the late 1960s, possibly aligning the cave with the jaguar character. Our enhanced photographs support Grove's identification of the darker markings visible in images as jaguar spots (Figure 3). If the identification is correct, the panel may refer to rain rituals focusing on the jaguar of the kind practiced historically in this area, including at Oxtotitlán's nearest settlement Acatlán (Díaz

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

Vázquez 2003; Gutiérrez and Pye 2010). Thus, we propose that Oxtotitlán was a significant regional ritual center from the beginning of the Formative period and perhaps even earlier.

The Early Formative, or earlier, oxalate date for Oxtotitlán's Panel C-2 suggests that an elaboration of rituals at regional nature shrines, with a sacred template of mountain-cave-water source, preceded the human-built Formative ceremonial centers that often incorporated or imitated these features. Early offerings at El Manatí's natural hill-spring complex, across Mexico in Veracruz, date to about the same time or earlier. Note that those first offerings to the spring water included concretions probably formed by water in a cave and transported to El Manatí (Ortiz and Rodríguez 1999).

In contrast, the shield figure painting (Panel 4–05) is uncommon among Formative period imagery. The date for the shield figure places it at the end of the Late Formative period (400 B.C. to A.D. 150) or within the Classic period (A.D. 150 to 650), an era when mural painting becomes ubiquitous across Mesoamerica. Contemporaneous examples at Teotihuacán, Monte Albán, and Las Higueras in Mexico and Maya examples at Holmul, Uaxactún, and Río Azul in Guatemala demonstrate the variety of styles, contexts, and content associated with wall painting that proliferates at sites both large and small at this time. The Oxtotitlán shield figure, painted on the outer edge of the north shelter, looks toward the east, into the rockshelter and also in the direction of the rising sun. This scene predates later Postclassic imagery that elite actors commissioned with analogous themes. One example is Late Postclassic portraits that Aztec rulers had carved of themselves on the rock outcrop of the sacred retreat Chapultepec Hill in their capital Tenochtitlán just prior to Spanish contact. The Chapultepec Hill sanctuary features springs and an oracular cave in addition to the hill or mountain, like Oxtotitlán. The image of the last ruler Mocteuczoma II faces east, toward the rising sun, probably holding a shield in his left hand (Hajovsky 2012, 2015; Nicholson 1959). Among earlier paintings from the first to sixth centuries A.D., shield-bearing figures include tomb paintings at Palenque where nine painted individuals accompany what is believed to be a dynastic founder to the Underworld, a sacred place related to caves (Robertson 2000).

Cave painting is present across Mesoamerica, and beyond, from the Archaic period; yet at the caves in Guerrero, pictographs transformed into a new art form that was the foundation for muralism in Mesoamerica. During the Formative period in Guerrero, sites such as Oxtotitlán were using polychrome paint technology and complex figurative scenes in pictographs prior to the innovation and widespread adoption of plaster technology. We suggest that mural painting on plaster, now recognized as a major Mesoamerican medium, might have begun with cave painting and that polychrome art was one of the significant innovations in cave painting in the Formative period from the start. To date, the earliest murals known are Maya wall paintings from San Bartolo, Guatemala, ca. 300–100 B.C., which use Olmec maize god imagery (Saturno et al. 2005; Saturno et al. 2006; Taube et al. 2010), perhaps indicating that both ideological and technological innovations spread from Formative period sites like Oxtotitlán. Later painted works, including the well-known murals from Bonampak (ca. 790 A.D.) (Miller and Brittenham 2013) and Cacaxtla (ca. 650 to 950 A.D.) (Brittenham 2015), as well as Late Classic cave painting at Naj Tunich (Stone 1995), elaborate on scenes of ceremonialism, palace, rulership, war activities, and ritual associated with rain and fertility; these examples demonstrate continuing use of painted cave walls and human-built spaces as a medium for engaging occult religious and political content.

In sum, the dated samples from the Oxtotitlán paintings provide evidence for a tradition of polychrome rock art preceding intensive human-built ceremonial complexes in Guerrero or the Gulf Coast regions. At Oxtotitlán Cave, we trace a lineage extending from the earliest dated polychrome painting related to jaguar imagery (Panel C-2) to the more elaborate Olmec Formative-style enthroned bird-costumed human image (Panel C-1). Paint and oxalate dates suggest that a newly identified image (Panel 4–05) of a human brandishing a shield likely post-dates the Olmec-style enthroned bird-costumed human portrait (Panel C-1). They document the significance of the cave as a site of continued painting and associated ritual through periods of dramatic social change at the end of the Late Formative period and into the Early Classic period. The radiocarbon dates of this study will enable a more contextualized analysis of the Oxtotitlán iconography and the longevity of ritual practice at landscape shrines outside of habitation areas.

Acknowledgments

We thank the Consejo de Arqueología of the Instituto Nacional de Antropología e Historia (INAH) of Mexico and Blanca Padilla of INAH-Guerrero for permission to study Oxtotitlán. We were aided in Mexico City by INAH conservationist Sandra Cruz Flores and in Guerrero by residents of Acatlán, particularly Gabriel Lima Astudillo, INAH's citizen cave guardian. This research was funded by the Waitt Foundation of the National Geographic Society, the National Endowment for the Humanities (Grant No. RZ-51497-12), and the National Science Foundation SUN Network Advance Grant (No. 0820080). We also thank four anonymous reviewers for suggestions that improved this manuscript.

Data Availability Statement

All project data, including digital images, will be available through the academic archiving system at Florida State University, Tallahassee. All paint and coating samples, including those processed for the radiocarbon analysis and thin-sections, will be stored at the Rhodes College Chemistry Department, Memphis, Tennessee. The original drawings of the rock art images will be archived at Skidmore College, Saratoga Springs, New York, and will be made available upon request.

REFERENCES CITED

Argáez, Carlos, Erasmo Batta, Josefina Mansilla, Carmen Pijoan, and Pedro Bosch
2011 The Origin of Black Pigmentation in a Sample of Mexican Prehispanic Human Bones. *Journal of Archaeological Science* 38:2979–2988.

Armitage, Ruth A., James E. Brady, Allan Cobb, John R. Southon, and Marvin W. Rowe
2001 Mass Spectrometric Radiocarbon Dates from Three Rock Paintings of Known Age. *American Antiquity* 66:471–480.

Baker, Suzanne M., and Ruth Ann Armitage
2013 Cueva La Conga: First Karst Cave in Nicaragua. *Latin American Antiquity* 24:309–329.

Beazley, Melanie J, Richard D. Rickman, Debra K. Ingram, Thomas W. Boutton, and Jon Russ
2002 Natural Abundances of Carbon Isotopes (^{14}C, ^{13}C) in Lichens and Calcium Oxalate Pruina: Implications for Archaeological and Paleoenvironmental Studies. *Radiocarbon* 44:675–683.

Beck, Lucile, Dominique Genty, Sophia Lahlil, Matthieu Lebon, Florian Tereygeol, Colette Vignaud, Ian Reiche, Elsa Lambert, Hélène Valladas, Evelyne Kaltnecker, Frédéric Plassard, Michel Menu, and Patrick Paillet
2013 Non-Destructive Portable Analytical Techniques for Carbon *In Situ* Screening before Sampling for Dating Prehistoric Rock Paintings. *Radiocarbon* 55(2–3):436–444.

Bonaventura, Maria Pia Di, Maddalena Del Gallo, Paola Cacchio, Claudia Ercole, and Aldo Lepidi
1999 Microbial Formation of Oxalate Films on Monument Surfaces: Bioprotection or Biodeterioration? *Geomicrobiology Journal* 16(1): 55–64.

Bonneau, Adelphine, Fiona Brock, Tom Higham, David G. Pearce, and A. Mark Pollard
2011 An Improved Protocol for Radiocarbon Dating Black Pigments in San Rock Art. *Radiocarbon* 53(3):419–428.

Brittenham, Claudia
2015 *The Murals of Cacaxtla: Power of Painting in Ancient Central Mexico*. University of Texas Press, Austin.

Bronk Ramsey, Christopher
2009 Bayesian Analysis of Radiocarbon Dates. *Radiocarbon* 51:337–360.
2013 On-line *OxCal version 4.2.3*. https://c14.arch.ox.ac.uk/oxcal/OxCal.html, accessed August 26, 2016.

Caneva, Giulia
1993 Ecological Approach to the Genesis of Calcium Oxalate Patinas on Stone Monuments. *Aerobiologia* 9(2–3):149–156.

Chalmin, Emilie, Michel Menu, and Colette Vignaud
2003 Analysis of Rock Art Painting and Technology of Paleolithic Painters. *Measurement Science and Technology* 14:1590–1597.

Chalmin, Emilie, Colette Vignaud, Hélène Salomon, F. Farges, J. Susini, and M. Menu
2006 Minerals Discovered in Paleolithic Black Pigments by Transmission Electron Microscopy and Micro-X-Ray Absorption Near-Edge Structure. *Applied Physics A* 83:213–218.

Clark, John E., and Mary E. Pye (editors)
2006 *Olmec Art and Archaeology in Mesoamerica*. National Gallery of Art, Washington, D.C.

Coe, Michael D.
1995 *The Olmec World: Ritual and Rulership*. Princeton University Art Museum in association with Harry N. Abrams, New York.

Coe, Michael D., and Richard A. Diehl
1980 *In the Land of the Olmec*. University of Texas Press, Austin.

Cruz Flores, Sandra
2003 Informe de los Trabajos de Conservación y Restauración de las Pinturas Rupestres del Sitio Arqueológico de Oxtotitlán, Municipio de Chilapa, Guerrero. Primera Temporada de Trabajo. Technical report. Coordinación Nacional de Conservación del Patrimonio Nacional. Subdirección de Conservación. Instituto Nacional de Antropología e Historia.
2004 Informe de los Trabajos de Conservación y Restauración de las Pinturas Rupestres del Sitio Arqueológico de Oxtotitlán, Municipio de Chilapa, Guerrero. Segunda Temporada de Trabajo. Technical report. Coordinación Nacional de Conservación del Patrimonio Nacional. Subdirección de Conservación. Instituto Nacional de Antropología e Historia.
2005 Informe de los Trabajos de Conservación y Restauración de las Pinturas Rupestres del Sitio Arqueológico de Oxtotitlán, Municipio de Chilapa, Guerrero. Tercera Temporada de Trabajo. Technical report. Coordinación Nacional de Conservación del Patrimonio Nacional. Subdirección de Conservación. Instituto Nacional de Antropología e Historia.

Cyphers, Ann
1997 Los Felinos de San Lorenzo. In *Población, Subsistencia y Medio Ambiente en San Lorenzo Tenochtitlán*, edited by Ann Cyphers, pp. 227–242. Universidad Nacional Autónoma de México, Mexico City.
2004a Escultura Monumental Olmeca: Temas y Contextos. In *Acercarse y Mirar: Homenaje a Beatriz de la Fuente*, edited by Maria Teresa Uriarte and Leticia Staines Cicero, pp. 51–73. Universidad Nacional Autónoma de México, Mexico City.
2004b *Escultura Olmeca de San Lorenzo Tenochtitlán*. Instituto de Investigaciones Antropológicas, Universidad Nacional Autónoma de México, Mexico City.

David, Bruno, Jean-Michel Geneste, Fioni Petchey, Jean-Jacques Delannoy, Bryce Barker, and Mark Eccleston
2013 How Old Are Australia's Pictographs? A Review of Rock Art Dating. *Journal of Archaeological Science* 40:3–10.

Del Monte, Marco, and Cristina Sabbioni
1987 A Study of the Patina Called Scialbatura on Imperial Roman Marbles. *Studies in Conservation* 32:114–127.

Díaz Vázquez, Rosalba D.
2003 *El Ritual de Lluvía en la Tierra de los Hombres Tigre: Cambio Sociocultural en una Comunidad Náhuatl (Acatlán, Guerrero, 1998–1999).* Consejo Nacional para la Cultura y las Artes, Mexico City.

Drucker, Philip
1952 *La Venta, Tabasco. A Study of Olmec Ceramics and Art*. Bulletin 153. Smithsonian Institution, Bureau of American Ethnology, Washington, D.C.

Drucker, Philip, Robert Heizer, and Robert Squier
1959 *Excavations at La Venta, Tabasco, 1955*. Bulletin 170. Smithsonian Institution, Bureau of American Ethnology, Washington, D.C.

Gadd, Geoffrey M., Jaleh Bahri-Esfahani, Qianwei Li, Young J. Rhee, Zhan Wei, Marina Fomina, and Xinjin Liang
2014 Oxalate Production by Fungi: Significance in Geomycology, Biodeterioration and Bioremediation. *Fungal Biology Reviews* 28:36–55.

Gay, Carlo T. E.
1967 Oldest Paintings in the New World. *Natural History* 4:28–35.

González Lauck, Rebecca
1996 La Venta: An Olmec Capital. In *Olmec Art of Ancient Mexico*, edited by Elizabeth P. Benson and Beatriz de la Fuente, pp. 73–81. National Gallery of Art, Washington, D.C.
1997 Acerca de Pirámides de Tierra y Seres Sobrenaturales: Observaciones Preliminares en Torno al Edificio C-1, La Venta, Tabasco. *Arqueología* 17:79–97.
2010 The Architectural Setting of Olmec Sculpture Clusters at La Venta, Tabasco. In *The Place of Stone Monuments*, edited by Julia Guernsey, John E. Clark, and Barbara Arroyo, pp. 129–148, Dumbarton Oaks, Washington, D.C.

Gorbushina, Anna A.
2007 Life of the Rocks. *Environmental Microbiology* 9(7):1613–1631.

Grove, David C.
1970 The Olmec Paintings of Oxtotitlan Cave, Guerrero, Mexico. *Studies in Precolumbian Art and Archaeology* No. 6. Dumbarton Oaks Trustees for Harvard University, Washington, D.C.
2007 The Middle Preclassic Paintings at Oxtotitlan, Guerrero. Foundation for the Advancement of Mesoamerican Studies. Electronic document, http://www.famsi.org/research/grove, accessed April 3, 2016.

Gutiérrez, Gerardo, and Mary E. Pye
2010 Iconography of the *Nahual*. Human-Animal Transformations in Preclassic Guerrero and Morelos. In *The Place of Stone Monuments: Context, Use, and Meaning in Mesoamerica's Preclassic Transition*, edited by Julia Guernsey, John E. Clark, and Barbara Arroyo, pp. 27–54. Dumbarton Oaks, Washington, D.C.

Hajovsky, Patrick T.
2012 Without a Face. Voicing Moctezuma II's Image at Chapultepec Park, Mexico City. In *Seeing Across Cultures in the Early Modern World*, edited by Jeanette F. Peterson and Dana Leibsohn, pp. 171–192. Routledge, London.
2015 *On the Lips of Others: Moteuczoma's Fame in Aztec Monuments and Rituals*. University of Texas Press, Austin.

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

Hedges, John I., Geoffrey Eglinton, Patrick G. Hatcher, David L. Kirchman, Carol Arnosti, Sylvie Derenne, Richard P. Evershed, Ingrid Kögel-Knabner, Jan W. de Leeuw, Ralf Littke, Walter Michaelis, and J. Rulkötterin
2000 The Molecularly-Uncharacterized Component of Nonliving Organic Matter in Natural Environments. *Journal of Organic Geochemistry* 31:945–958.

Hess, Darren, Dana J. Coker, Jeanette. M. Loutsch, and Jon Russ
2008 Production of Oxalates In Vitro by Microbes Isolated from Rock Surfaces with Prehistoric Paints in the Lower Pecos Region, Texas. *Geoarchaeology* 23(1):3–11.

Hyman, Marian, Solveig A. Turpin, and Michael E. Zolensky
1996 Pigment Analyses from Panther Cave, Texas. *Rock Art Research* 13(2):93–103.

Ilger, Wayne, Marian Hyman, John Southen, and Marvin W. Rowe
1995 Dating Pictographs with Radiocarbon. *Radiocarbon* 37(2):299–310.

Koenig, Charles W., Amanda M. Castañeda, Carolyn E. Boyd, Marvin W. Rowe, and Karen L. Steelman
2014 Portable X-Ray Fluorescence Spectroscopy of Pictographs: A Case Study from the Lower Pecos Canyonlands, Texas. *Archaeometry* 56(S1):168–186.

Littmann, Edwin R.
1975 Short Methods for the Identification of Pigments. *American Antiquity* 40:349–353.

Livingston, Andrew, Eugenia Robinson, and Ruth Ann Armitage
2009 Characterizing the Binders in Rock Paintings by THM-GC-MS: La Casa de Las Golondrinas, Guatemala, a Cautionary Tale for Radiocarbon Dating. *International Journal of Mass Spectrometry* 284:142–151.

López-Montalvo, Esther, Valentín Villaverde, Clodoaldo Roldán, Sonia Murcia, and Ernestina Badal
2014 An Approximation to the Study of Black Pigments in Cova Remigia (Castellón, Spain). Technical and Cultural Assessments of the Use of Carbon-Based Black Pigments in Spanish Levantine Rock Art. *Journal of Archaeological Science* 52:535–545.

Magaloni, Diana
1998 El Arte en el Hacer: Técnica Pictórica y Color en las Pinturas de Bonampak. In *La Pintura Mural Prehispánica en México: Área Maya, Bonampak, Vol II*, edited by Beatriz de la Fuente, pp. 49–80. Universidad Nacional Autónoma de México, Instituto de Investigaciones Estéticas, Mexico City, México.
2001 Materiales y Técnicas de la Pintura Mural Maya. In *La Pintura Mural Prehispánica en México: Área Maya*, edited by B. de la Fuente and L. Staines Cicero, pp. 155–198. Universidad Nacional Autónoma de México, Instituto de Investigaciones Estéticas, Mexico City.

Magaloni, Diana, R. Newman, L. Balos, V. Castaño, R. Pancella, and Y. Fruh
1995 An Analysis of Mayan Painting Techniques at Bonampak, Chiapas, Mexico. *Material Research Society Symposium Proceedings* 352:381–388.

Magaloni, Diana, R. Pancella, Y. Fruh, Jaqueline Cañetas, and V. Castaño
1995 Studies on the Mayan Mortars Technique. *Material Research Society Symposium Proceedings* 352:483–489.

McDonald, Jo, Karen L. Steelman, Peter Veth, Jeremy Mackey, Josh Loewen, Casey R. Thurber, and T. P. Guilderson
2014 Results from the First Intensive Dating Program for Pigment Art in the Australian Arid Zone: Insights into Recent Social Complexity. *Journal of Archaeological Science* 46:195–204.

McPeak, Joseph, Mary Pohl, Christopher von Nagy, Heather Hurst, Marvin W. Rowe, and Jon Russ
2013 Physicochemical Study of Black Pigments in Prehistoric Paints from Oxtotitlán Cave, Guerrero, Mexico. In *Archaeological Chemistry VIII*, edited by Ruth A. Armitage and James H. Burton, pp. 123–143. American Chemical Society Press. Washington, D.C.

Mazel, Aron D., and Alan L. Watchman
2003 Dating Rock Paintings in the uKhahlam-Drakensberg and the Biggarsberg, KwaZulu-Natal South Africa. *Southern African Humanities* 15:59–73.

Miller, Mary, and Claudia Brittenham
2013 *The Spectacle of the Late Maya Court: Reflections on the Murals of Bonampak.* University of Texas Press, Austin.

Monte, Michela
2003 Oxalate Film Formation on Marble Specimens Caused by Fungus. *Journal of Cultural Heritage* 4:255–258.

Morwood, Michael J., Grahame L. Walsh, and Alan L. Watchman
2010 AMS Radiocarbon Ages for Beeswax and Charcoal Pigments in North Kimberley Rock Art. *Rock Art Research* 27(1):3–8.

Newman, Bonita, and Lawrence. L. Loendorf
2005 Portable X-Ray Fluorescence Analysis of Rock Art Pigments. *Plains Anthropologist* 50:277–283.

Nicholson, Henry B.
1959 The Chapultepec Cliff Sculpture of Motecuhzoma Xocoyotzin. *El México Antiguo, Revista Internacional de Arqueología*, vol. IX:424–442.

Ortega-Morales, Benjamin O., José Narváez-Zapata, Manuela Reyes-Estebanez, Patricia Quintana, Susana del C. De la Rosa-García, Heather Bullen, Sergio Gómez-Cornelio, and Manuel J. Chan-Bacab
2016 Bioweathering Potential of Cultivable Fungi Associated with Semi-Arid Surface Microhabitats of Mayan Buildings. *Frontiers in Microbiology* 7:1–12.

Ortiz, Ponciano, and María del Carmen Rodríguez
1999 Olmec Ritual Behavior at El Manatí: A Sacred Space. In *Social Patterns in Pre-Classic Mesoamerica*, edited by David C. Grove and Rosemary Joyce, pp. 225–254. Dumbarton Oaks, Washington, D.C.

Preston, Caroline M., and Michael W. Schmidt
2006 Black (Pyrogenic) Carbon: A Synthesis of Current Knowledge and Uncertainties with Special Consideration of Boreal Regions. *Biogeosciences* 3:397–420.

Reimer, P. J., E. Bard, A. Bayliss, J. W. Beck, P. G. Blackwell, C. B. Ramsey, C. E. Buck, H. Cheng, L. R. Edwards, P. M. Grootes, T. P. Guilderson, H. Haflidason, I. Hajdas, C. Hatte, T. J. Heaton, D. L. Hoffmann, A. G. Hogg, K. A. Hughen, K. F. Kaiser, B. Kromer, S. W. Manning, M. Niu, R. W. W. Reimer, D. A. Richards, E. M. Scott, J. R. Southon, R. A. Staff, C. S. M. Turney, and J. van der Plicht
2013 IntCal13 and Marine13 Radiocarbon Age Calibration Curves 0–50,000 Years cal BP. *Radiocarbon* 55(4):1869–1887.

Robertson, Merle G.
2000 Murals Found in Subterranean Tomb of Temple XX. *Pre-Columbian Art Research Institute (PARI) Journal* 31:1–4.

Roldán, Clodoaldo, Sonia Murcia-Mascarós, José Ferrero, Valentín Vilaverde, Esther López, Inés Domingo, Rafael Matínez, and Pere M. Guillem
2010 Application to Field Portable EDXRF Spectrometry to Analysis of Pigments of Levantine Rock Art. *X-Ray Spectrometry* 39:243–250.

Rowe, Marvin W.
2009 Radiocarbon Dating of Ancient Rock Paintings. *Analytical Chemistry* 81:1728–1735.

Rowe, Marvin W., Robert Mark, Evelyn Billo, Margaret Berrier, Karen L. Steelman, and Eric Dillingham
2011 Chemistry as a Criterion for Selecting Pictographs for Radiocarbon Dating: Lost Again Shelter in the Guadalupe Mountains of Southeastern New Mexico. *American Indian Rock Art* 37:37–47.

Ruiz, Juan F., Antonio Hernazb, Ruth Ann Armitage, Marvin W. Rowe, Ramon Viñas, José Gavira-Vallejo, and Albert Rubio
2012 Calcium Oxalate AMS ^{14}C Dating and Chronology of Post-Palaeolithic Rock Paintings in the Iberian Peninsula. Two Dates From Abrigo de los Oculados (Henarejos, Cuenca, Spain*). Journal of Archaeological Science* 39(8):2655–2667.

Rusakov, Aleksei V., Aleksei D. Vlasov, Marina S. Zelenskaya, Olga V. Frank-Kamentetskaya, and Dmitry Y. Vlasov
2015 The Crystallization of Calcium Oxalate Hydrates Formed by Interactions Between Microbes and Minerals. In *Lecture Notes in Earth System Sciences*, edited by Olga V. Frank-Kamentetskaya, Elena G. Panova, and Dmitry Y. Vlasov, pp. 357–377. Springer International Publishers, Basel.

Russ, Jon, Marian Hyman, Harry J. Shafer, and Marvin W. Rowe
1990 Radiocarbon Dating of Prehistoric Rock Paintings by Selective Oxidation of Organic Carbon. *Nature* 348:710–711.

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press

Russ, Jon, Russell L. Palma, Thomas W. Boutton, and Michael A. Coy
1996 Origin of the Whewellite-Rich Rock Coating in the Lower Pecos Region of Southwest Texas and Its Significance to Paleoclimate Reconstructions. *Quaternary Research* 46:27–36.
Russ, Jon, Warna D. Kaluarachchi, Louise Drummond, and Howell G. M. Edwards
1999 The Nature of a Whewellite-Rich Rock Crust Associated with Pictographs in Southwestern Texas. *Studies in Conservation* 44:91–103.
Russ, Jon, David Loyd, and Thomas. W. Boutton
2000 A Paleoclimate Reconstruction for Southwest Texas Using Oxalate Residue from Lichens as a Paleoclimate Proxy. *Quaternary International* 67:29–36.
Saturno, William A., Karl A. Taube, David Stuart, and Heather Hurst
2005 *The Murals of San Bartolo, El Petén, Guatemala Part 1: The North Wall.* Mesoamerican Series Vol. 7. Center for American Studies, Bamardsville, North Carolina.
Saturno, William, David Stuart, and Boris Beltrán
2006 Early Maya Writing at San Bartolo, Guatemala. *Science* 311:1281–1283.
Schiffer, Michael B.
1986 Radiocarbon Dating and the "Old Wood" Problem: The Case of the Hohokam Chronology. *Journal of Archaeological Science* 13(1): 13–30.
Shackley, M. Steven
2010 Is There Reliability and Validity in Portable X-Ray Fluorescence Spectrometry (PXRF)? *SAA Archaeological Record* 10(5):17–20, 44.
Spades, Sarah, and Jon Russ
2005 GC-MS Analysis of Lipids in Prehistoric Rock Paints and Associate Oxalate Coatings from the Lower Pecos Region, Texas. *Archaeometry* 47(1):115–126.
Steelman, Karen L., Richard Rickman, Marvin W. Rowe, Thomas W. Boutton, Jon Russ, and Niede Guidon
2002 Accelerator Mass Spectrometry Radiocarbon Ages of an Oxalate Accretion and Rock Paintings at Toca do Serrote da Bastiana, Brazil. In *Archaeological Chemistry* 831, edited by Kathryn A. Jakes, pp. 22–35. American Chemical Society Press, Washington, D.C.
Steelman, Karen L., and Marvin W. Rowe
2012 Radiocarbon Dating of Rock Paintings: Incorporating Pictographs into the Archaeological Record. In *A Companion to Rock Art*, edited by Jo McDonald and Peter Veth, Chapter 32, pp. 565–582. Blackwell Publishing, Oxford.
Stone, Andrea J.
1995 *Images from the Underworld Naj Tunich and the Tradition of Maya Cave Painting.* University of Texas Press, Austin.
Taube, Karl, David Stuart, William Saturno, and Heather Hurst
2010 *The Murals of San Bartolo, El Petén, Guatemala Part 2: The West Wall.* Center for Ancient American Studies, Bamardsville, North Carolina.
Valladas, Hélène, Hélène Cachier, P. Maurice, F. Bernaldo de Quirós, Jean Clottes, Victoria Cabrera Valdés, Paloma Uzquiano Ollero, Maurice Arnold
1992 Direct Radiocarbon Dates for Prehistoric Paintings in the Altamira, El Castillo and Niaux Caves. *Nature* 357:68–70.
Valladas, Hélène, N. Tisnérat-Laborde, H. Cachier, M. Arnold, F. Bernaldo de Quirós, V. Cabrera-Valdés, J. Clottes, J. Courtin, J. J. Fortea-Pérez, C. Gonzáles-Sainz, and A. Moure-Romanillo
2001 Radiocarbon AMS Dates for Paleolithic Cave Paintings. *Radiocarbon* 43:977–986.
Vázquez, Cristina, Marta S. Maier, Sara D. Parera, Hugo Yaacobaccio, and Patricia Solá
2008 Combining TXRF, FT-IR and GC–MS Information for Identification of Inorganic and Organic Components in Black Pigments of Rock Art from Alero Hornillos 2 (Jujuy, Argentina). *Analytical and Bioanalytical Chemistry* 391(4):1381–1387.
Watchman, Alan L.
1991 Age and Composition of Oxalate-Rich Crusts in the Northern Territory, Australia. *Studies in Conservation* 36(1):24–32.
1993 Evidence of a 25,000-Year-Old Pictograph in Northern Australia. *Geoarchaeology* 8:465–473.
Watchman, Alan, L. Bruno David, I. J. McNiven, and Josephine M. Flood
2000 Micro-archaeology of Engraved and Painted Rock Surface Crusts at Yiwarlarlay (the Lightning Brothers site), Northern Territory, Australia. *Journal of Archaeological Science* 27(4):315–325.
Watchman, Alan L., Susan O'Conner, and Rhys Jones
2005 Dating Oxalate Minerals 2 - 40ka. *Journal of Archaeological Science* 32:369–374.
Wendt, Carl J., and Ann Cyphers
2008 How the Olmec used Bitumen in Ancient Mesoamerica. *Journal of Anthropological Archaeology* 27:175–91.
Whitley, David S.
2013 Rock Art Dating and the Peopling of the Americas. *Journal of Archaeology* DOI: 10.1155/2013/713159, accessed March 13, 2017.
Wright, Véronique
2008 Étude de la Polychromie des Reliefs Sur Terre Crue de la Huaca de la Luna Trujillo, Pérou. British Archaeological Reports (BAR S1808), *Paris Monographs in American Archaeology* 21. Archaeopress, Oxford.
2010 Pigmentos y Tecnología Artística Mochicas: Una Nueva Aproximación en la Comprension de la Organización Social. *Bulletin de l'Institut Français d'Etudes Andines* 39(2):299–330.
Zoppi, Angela, Gigio F. Signorini, Franco Lucarelli, and Luca Bachechi
2002 Characterisation of Painting Materials from Eritrea Rock Art Sites with Non-Destructive Spectroscopic Techniques. *Journal of Cultural Heritage* 3:299–308.

AUTHORS INFORMATION

Jon Russ ■ Department of Chemistry, Rhodes College, Memphis, TN 38104, USA (russj@rhodes.edu)

Mary D. Pohl ■ Department of Anthropology, Florida State University, Tallahassee, FL 32306, USA

Christopher L. von Nagy ■ Department of Anthropology, University of Nevada, Reno, NV 89547, and Department of Anthropology, Florida State University, Tallahassee, FL 32306, USA

Karen L. Steelman ■ Shumla Archaeological Research & Education Center, Comstock, TX 78837 ksteelman@shumla.org

Heather Hurst ■ Department of Anthropology, Skidmore College, Saratoga Springs, NY 12866, USA (hhurst@skidmore.edu)

Leonard Ashby ■ Artist, Ballston Spa, NY 12866, USA

Paul Schmidt ■ Instituto de Investigaciones Antropológicas, Universidad Nacional Autónoma de México, Ciudad de México 04510, México (paul@unam.mx)

Eliseo F. Padilla Gutiérrez ■ Museo Nacional de Antropología, INAH, Av. Paseo de la Reforma y Gandhi s/n, Col. Polanco, Delegación Miguel Hidalgo, Ciudad de México 11560, México (eliseopadilla@gmail.com)

Marvin W. Rowe ■ Office of Archaeological Studies, Center for New Mexico Archaeology, PO Box 2087, Santa Fe, NM 87504, USA

https://doi.org/10.1017/aap.2016.10 Published online by Cambridge University Press