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Portable X-ray fluorescence of Lower Pecos painted pebbles: New insights regarding pigment choice and chronology

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ABSTRACT

Painted pebbles are the primary mobiliary art found in the Lower Pecos Canyonlands of southwest Texas and northern Mexico. Previous studies of these artifacts have focused on stylistic variation of the imagery and interpretation of the role these artifacts played within Lower Pecos societies. The focus of this study is the use of portable X-ray fluorescence on Lower Pecos painted pebbles to conduct elemental analyses to identify the pigment used by ancient artists in the paint recipe for painted pebble production. Using a sample of recently excavated painted pebbles, as well as a sample from a private collection, a total of 254 pXRF measurements were collected on 70 pebbles. We determined that charcoal was used as a pigment for black paintings and that iron-based mineral pigments were used for red paintings. The newly excavated pebbles range in age from 6500 to 700 RCYBP, and the stratigraphic and chronologic context of these pebbles provides a dataset for analyzing not only pigment selection, but allows us to also address changes in painted pebble production through time. This paper summarizes the results from the pXRF analysis, and discusses the larger archaeological implications for Lower Pecos painted pebbles.

1. Introduction

Painted pebbles are commonly found artifacts in the Lower Pecos Canyonlands of southwest Texas and northern Mexico (e.g., Davenport and Chelf, 1941; Jelks, 1962; Mock, 1987; Parsons, 1965; Turpin and Middleton, 1998; Turpin et al., 1996), and share characteristics with other mobiliary painted plaquettes and pebbles found in archaeological contexts around the world (Arthur and Murray, 2014; Heizer, 1953; Lang, 1904; Rifkin et al., 2015; Ritchie, 1971; Roldán et al., 2013; Roldán García et al., 2016; Tolksdorf et al., 2018). While portable X-ray fluorescence (pXRF) has been utilized to study parietal rock paintings by numerous researchers (Beck et al., 2014; Dostal and Smith, 2015; Huntley (née Ford), 2012; Huntley et al., 2015; Koenig et al., 2014; Lins and Price, 2011; Miller et al., 2011; Newman and Loendorf, 2005; Olivares et al., 2013; Robinson et al., 2015; Roldán et al., 2010; Rowe et al., 2011; Sepúlveda et al., 2015; Wesley et al., 2014); the use of X-ray spectroscopy for the analysis of pigments associated with prehistoric mobiliary art has been more limited (e.g., Rifkin et al., 2016; Roldán et al., 2013; Roldán García et al., 2016). Previous pigment analyses in the Lower Pecos were focused on parietal rock paintings, and were conducted using destructive, laboratory-based instrumentation including X-ray diffraction (XRD) (Hyman et al., 1996; Zolensky, 1982) and inductively coupled plasma mass spectrometry (ICP-MS) (Bu et al., 2013; Russ et al., 2012), as well as non-destructive, portable X-ray fluorescence (pXRF) (Koenig et al., 2014). The focus of this study is the use of pXRF on painted pebbles to provide insight into pigment selection and chronology of Lower Pecos painted pebble production.

In the Lower Pecos, painted pebbles are typically stream-rolled, thin, ovate pebbles with painted designs (e.g., Mock, 2012; Prewitt, 2014). These artifacts have been the subject of numerous studies, focused mainly on stylistic variation of the imagery and interpretation of the role these artifacts played within Lower Pecos societies (Mock, 2011, 2012, 2013; Parsons, 1986; Roberts, 2014). We utilized pXRF spectroscopy to conduct elemental analyses of paint on Lower Pecos painted pebbles recently excavated at Eagle Cave (41VV167) and Sayles Adobe (41VV2239) in Eagle Nest Canyon near historic Langtry, Texas. These excavations yielded a total of 55 painted pebbles ranging in age from ~6500–700 RCYBP, and these artifacts represent the best-provenienced painted pebbles in the region. The stratigraphic and chronologic context of the Eagle Cave and Sayles Adobe pebbles provides a dataset for analyzing not only pigment selection for painted pebble

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production using pXRF, but also allows us to address the potential for changes in painted pebble production through time. This study is the first to utilize a chemical analysis technique in order to identify the pigments used in the production of Lower Pecos mobiliary art.

We collected pXRF measurements on 28 painted pebbles from Eagle Cave and Sayles Adobe to determine the elements used in pigment production. To expand our sample of painted pebbles, we assayed an additional 42 specimens from a private collection. In total, 254 pXRF measurements on 70 painted pebbles determined that iron-based mineral pigment was used for red paintings, and an organic material such as charcoal was used as a pigment for black paintings. We did not analyze any yellow or white paint, as these colors are found only rarely on Lower Pecos mobiliary art and were not present on the pebbles in our sample. Our analytical protocol did not entail the sampling of pigments and we used only non-invasive pXRF instrumentation. The advantage of pXRF is that it is a non-destructive technique that is easily accessible to archaeologists, and pigment can be analyzed in situ without having to remove a sample from the artifact. Further, pXRF is a fast and efficient way to produce large datasets on multiple artifacts with rapid data acquisition times.

While the original objective of this study was to determine the elemental composition of painted pebble pigments, our non-destructive pXRF results on numerous artifacts from different time periods have allowed for a larger discussion in regards to the archaeological implications of painted pebble production in relation to chronology, iconography, and comparison to other forms of Lower Pecos art. Previous X-ray pigment analyses found that the most common parietal art in the region, which was produced concurrently with painted pebbles, consistently has manganese-based black pigments (Hyman et al., 1996; Koenig et al., 2014; Zolensky, 1982). Thus, we can begin to address ideological function of pigment choice between parietal and mobiliary art. Further, Lower Pecos painted pebbles were produced at various times during the Holocene, with a potential hiatus in production during the mid-Holocene, yet the pigment choice remained the same. For future work, the discovery of charcoal pigments holds great potential for directly dating the painted pebbles themselves. Although our research focuses on the Lower Pecos region, this case study methodology can be applied to other archaeological regions, as it exemplifies the utility of non-destructive pXRF pigment studies for comparing the technological practices between mobiliary and parietal art.

1.1. Lower Pecos Canyonlands

The rocky, semi-arid desert environment of the Lower Pecos Canyonlands is situated at the southwestern edge of Texas' Edwards Plateau, and extends south into the Burro Mountains of Coahuila, Mexico (Fig. 1). The landscape is incised by deep canyons containing hundreds of rockshelters that provided refuge for hunter-gatherer groups throughout the Holocene (Turpin, 2004). This arid region is known for the excellent preservation afforded by dry rockshelters, which have produced a wide assemblage of perishable artifacts and host an array of pictographic images ranging in age from 4200 RCYBP to historic times (Alexander, 1974; Bates et al., 2015; Boyd, 2003, 2016; Jackson, 1938; Kirkland and Newcomb, 1967; Martin, 1933; Parsons, 1965; Pearce and Jackson, 1933; Rowe, 2009; Shafer, 2013; Turpin, 2004). The rock art of the region is categorized into five main styles: Pecos River; Red Linear; Red Monochrome; Bold Line Geometric; and Historic (Boyd, 2003, 2016; Boyd et al., 2013; Gebhard, 1960; Jackson, 1938; Turpin, 1984, 1986a, 1986b, 1990, 2004). Further descriptions of the material culture and pictographs are available in a variety of previous publications, and will not be discussed here (e.g., Black and Dering, 2001; Boyd, 2003, 2016; Shafer, 1986, 2013; Turpin, 2004). Of importance for this study are the well preserved painted pebbles from many of the region's rockshelters.

Located in the western portion of the Lower Pecos is Eagle Nest Canyon (ENC), a short box-canyon tributary to the Rio Grande (Fig. 1). This small canyon has been the scene of intermittent archaeological investigations since the 1930s (e.g., Basham, 2015; Bement, 1986; Castañeda, 2015, 2017; Davenport and Chelf, 1941; Dibble and Lorrain, 1968; Rodriguez, 2015; Ross, 1965; Sayles, 1935). Recent archaeological excavations have recovered well-provenienced painted pebbles from Eagle Cave and Sayles Adobe.

Sayles Adobe (41VV2239) is an open-air terrace site located near the confluence of Eagle Nest Canyon and the Rio Grande. Excavations at this deeply stratified terrace site yielded intermittent occupation spanning at least 5000 years. Five painted pebbles were recovered from stratigraphic context (Pagano, 2019).

Eagle Cave (41VV167) is the largest dry rockshelter in ENC, and has received the most substantial excavations of all ENC sites. The deposits contained within Eagle Cave preserve the remains of hunter-gatherer lifeways spanning at least 10,000 years (Koenig and Black, 2017). Excavations began in the 1930s (Davenport, 1938), were expanded upon in the 1960s (Ross, 1965), with the most recent period of excavation from 2014 to 2017 (e.g., Koenig et al., 2017; Nielsen, 2017). The recent excavations recovered 50 painted pebbles, 37 of which are from secure stratigraphic context. The three major excavation episodes at Eagle Cave contribute to one of the largest single-site collections of painted pebbles in the region.

1.1.1. Lower Pecos Canyonlands Mobiliary art

Painted pebbles found in the Lower Pecos are generally water-polished, thin, ovate stones. Although most common in the Lower Pecos Canyonlands, painted pebbles have also been recovered in the Texas Trans-Pecos and Central Texas regions (Roberts, 2014). Liquid black paints are the most common, although there are instances of liquid red paint and dry-applied black and red designs (Mock, 2012; Prewitt, 2014). Sometimes red pigment is used as a wash either behind or on top of the black pigment, and in rare instances yellow or white pigment was applied to the pebbles (Davenport and Chelf, 1941; Mock, 2011, 2012). Most early researchers suggested the origin of the black pigments was derived from either charcoal, soot, manganese oxide, or asphalt (Alexander, 1974:129; Davenport and Chelf, 1941; Parsons, 1967). However, no chemical analyses had been conducted on painted pebble pigments prior to the present study.

Although predominantly found in rockshelters, painted pebbles also occur in open-air sites (e.g., Johnson Jr, 1964:70–71; Pagano, 2019), and it is likely that preservation and excavation bias contribute to the abundance of painted pebbles from sheltered sites versus open-air locations. Further, there is not a correlation between the co-occurrence of painted pebbles and parietal art within shelters (Roberts, 2014:74). Unlike the parietal imagery on rockshelter walls, which are commonly large compositions involving numerous images (Boyd, 2016), painted pebbles are not often found with other painted pebbles. The only known instances of multiple painted pebbles found in situ together are at Bonfire Shelter (41VV218) and Sayles Adobe, both located within Eagle Nest Canyon. At Bonfire Shelter, three pebbles were found carefully placed adjacent with one another in a fiber layer (Dibble and Lorrain, 1968:61). Each of the pebbles had a different design, which has been hypothesized to represent a storytelling event (Mock, 2011:117). In more recent work, at least three painted pebbles were found in a cache at Sayles Adobe (Pagano, 2019).

Typically painted pebbles have been found in midden deposits consisting of fiber, burned rock, and other detritus (Mock, 2013). For example, nearly all of the painted pebbles recovered during recent excavations at Eagle Cave were found within burned rock layers associated with baking desert plants in earth ovens (see Dering, 1999; Black and Thoms, 2014 for discussion and descriptions of earth ovens). Additionally, many painted pebbles were subsequently used as handstones, presumably for knapping activities (Mock, 2012). There is one instance of polished pebbles recovered in a funerary context reported from Fate Bell Shelter (41VV74); however, these pebbles had no obvious painted designs (Pearce and Jackson, 1933:68). Even though

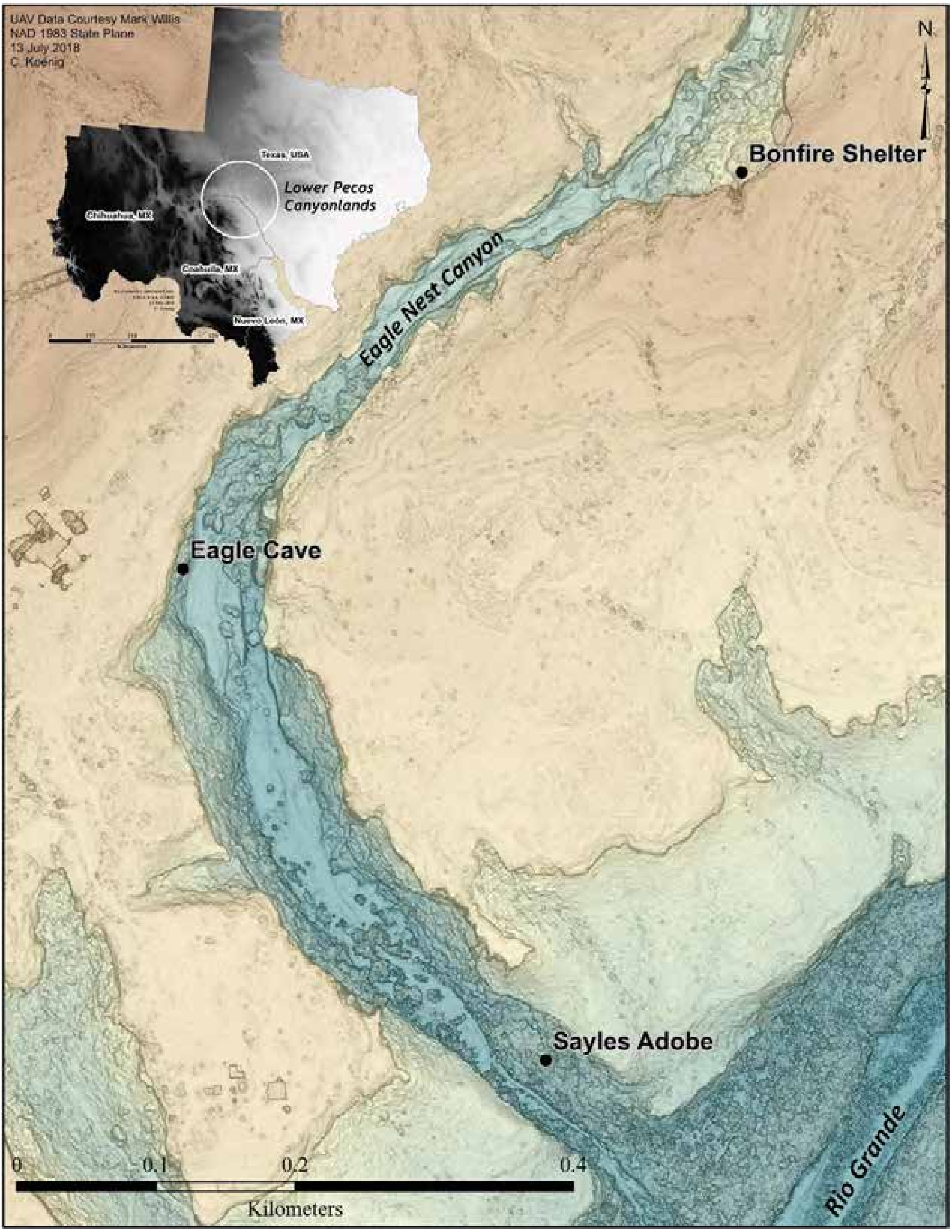

Fig. 1. Location of the Lower Pecos Canyonlands (inset) with a map of Eagle Nest Canyon and major sites discussed in the text.

there are no known painted pebbles in a funerary context from the Lower Pecos, there are two examples from Central Texas rockshelters (Field, 1956:167, 176).

Numerous interpretations have been put forth regarding how painted pebbles functioned in Lower Pecos society, most of which propose female associations. Shafer (1986:167) suggests leaf and fiber wrappings found around some painted pebbles indicate an association with menstrual taboo. Mock (2011) further posits the designs and the medium on which they are painted (river-rolled stones) cements their function as metaphors for women and female-associated myths and legends. Some motifs have been interpreted as portraying human-like attributes such as faces (Davenport and Chelf, 1941; Parsons, 1986:185)

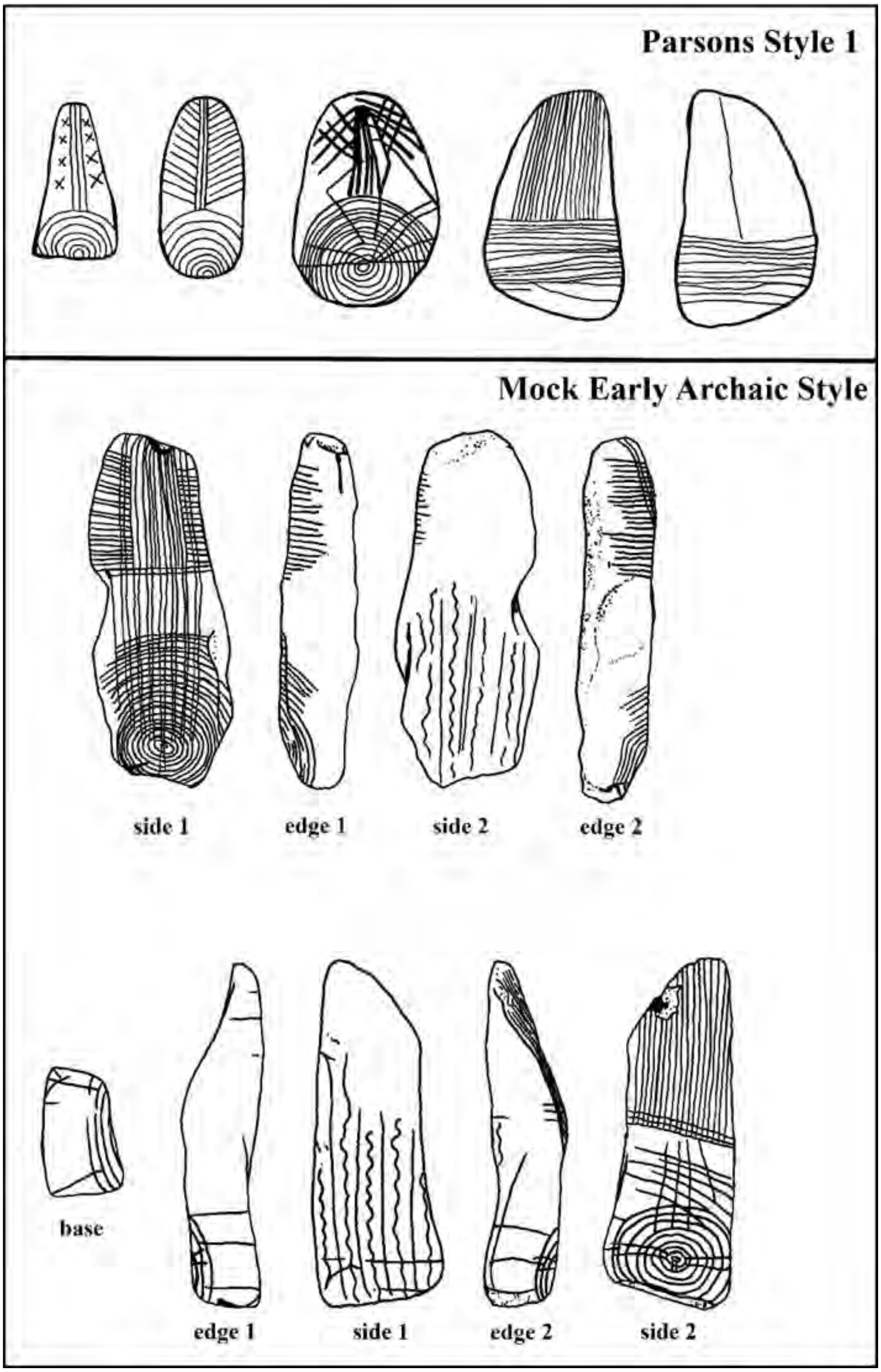

Fig. 2. Examples of fine-line, geometric pebbles, redrawn from Parsons (1986) and Mock (2013). Parsons referred to these as Style 1, and Mock assigned this group to the Early Archaic.

and/or genitalia—most commonly female (Mock, 1987, 2011:121). Mock (1987:112) also asserts these items could have been personal charms or amulets that might have been substituted for the corporeal human body during curing rituals or other ceremonies.

The most common studies regarding painted pebbles have been those of iconography and stylistic classification. The first major classification system was put forth by Parsons (1965, 1986), who split the pebbles into six styles based on artistic elements. More recently, Mock (2011, 2013) also produced a stylistic classification that combined some of Parsons' previous styles, resulting in four painted pebble types. Within both the Mock and Parsons stylistic categories, they present Style 1 as a fine-line, Early Archaic style of painted pebble (8000–6000 RCYBP). This style often includes geometric imagery such as concentric circles, paired sets of parallel lines, or intersecting straight lines (Fig. 2). Mock and Parsons' remaining styles are executed with bolder, thicker lines and show a variety of geometric and figurative elements (Fig. 3). However, these stylistic classifications are not well established chronologically, and "Until they are put into their proper chronological sequence…styles can tell us little about the evolution of art…" (Parsons, 1967:33). The reader is directed to Parsons (1986) and Mock (2013) for a more detailed descriptions of each painted pebble style.

Previous researchers have hypothesized painted pebbles were

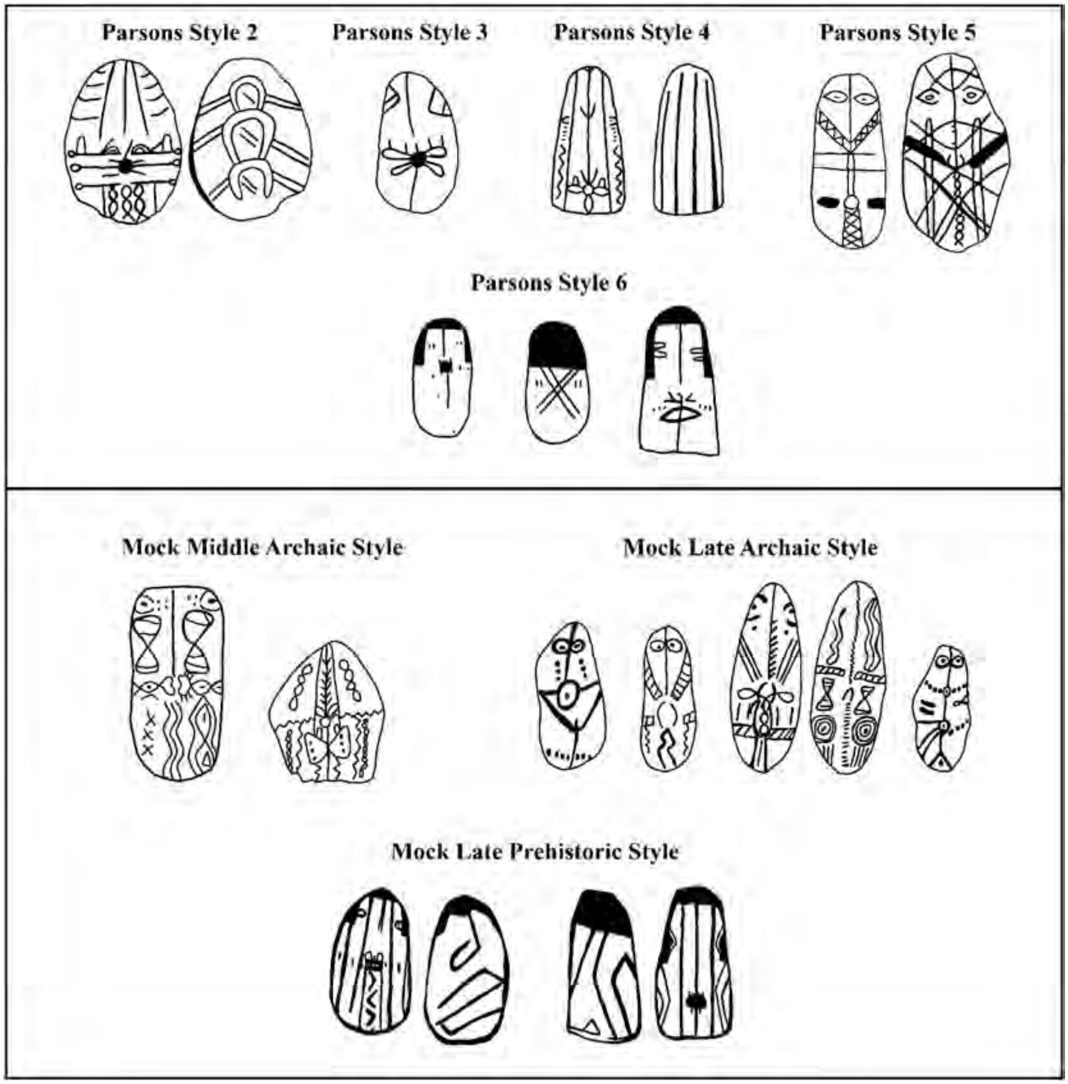

Fig. 3. Examples of bold-line, figurative pebbles, redrawn from Parsons (1986) and Mock (2013). These pebbles were split into different styles by Parsons and Mock based on iconography. Mock assigned each style to a different time period.

produced throughout the Early Archaic (9000–6000 RCYBP), Middle Archaic (6000–3000 RCYBP), Late Archaic (3000–1000 RCYBP), and Late Prehistoric (1000–350 RCYBP) periods (Mock, 2011, 2012, 2013; Shafer, 1986:130; Turpin, 2004; Turpin and Middleton, 1998). However, developing a chronology for painted pebbles is difficult because nearly all the excavations that recovered painted pebbles took place between 1930 and 1970. Most of these excavations yielded few radiocarbon dates, and the stratigraphic provenience is usually attributed to broad stratigraphic units (e.g., Alexander, 1970, 1974; Collins, 1969; Davenport, 1938; Dibble, 1967; Dibble and Lorrain, 1968; Martin, 1933; Maslowski, 1978; Ross, 1965; Parsons, 1963, 1965). As Parsons (1967:33) notes, "A few excellent carbon-14 dates have been obtained on strata that produced painted pebbles, but these have served to place only two styles: Style 1…with associated dates ranging from 4110-6810 BC…and Style 5 dated…between 500 B.C.- A.D. 500." Unfortunately, not much progress has been made in securely dating painted pebbles; however, this paper makes a first effort in using refined stratigraphic context to place painted pebble styles in time.

2. Materials and methods

We used a hand-held Innov-X Systems Alpha Series pXRF device with a silver (Ag) anode X-ray tube source and a SiPIN diode detector, powered by a Li-ion rechargeable battery. The instrument was operated in Soil mode, which uses a 40 kV excitation energy, to analyze for elements from Ti to Bi. We used Alloy 316 provided by the manufacturer for standardizing the pXRF upon each instrument start-up. Compton Normalization calibration calculations converted measured characteristic line intensities for each element into weight percent concentrations. A Hewlett Packard iPAQ personal digital assistant was used in the field to control the instrument and store data, which were exported into a spreadsheet for data analysis. During data collection, elemental concentrations are displayed on the palmtop computer screen attached to the instrument.

2.1. Control measurements of unpainted rock

For each painted pebble artifact, we assayed at least one background control area of unpainted stone to make certain that observed elemental levels were from pigment minerals and not the rock substrate. For most handheld pXRF instruments that measure elements > Ti in atomic mass, the sampling depth is greater than 200 µm in a cone-shaped volume penetrating the pigment layer and underlying rock (Huntley (née Ford), 2012; Roldán et al., 2013). Thus, when analyzing thin paint layers, the information obtained will be both from the paint layer as well as the rock substrate.

2.2. Replicate measurements

Replicate measurements for both painted areas and unpainted stone were also conducted. We tested for precision of our pXRF measurements by collecting replicate readings, both in the same spot and at different spots on the mobiliary artifacts. We calculated the mean, standard deviation, and coefficient of variation for replicate measurements for each individual pebble to describe the variation and precision of replicate measurements.

2.3. Analyses

Using 60-second analysis times, we obtained 254 pXRF measurements on 70 painted pebble artifacts. The painted pebbles examined for this study come from three different sources: a private collection ($n = 42$) and the recently excavated painted pebbles from Eagle Cave ($n = 25$) and Sayles Adobe ($n = 3$) (Pagano, 2019). Of the pXRF measurements, 130 tested black paint, 7 examined red paint, and 2 analyzed locations with both black and red paint. In addition, we analyzed 115 background control areas to compare the observed elemental levels between the pigment and the rock substrate, and conducted 64 replicate analyses for both painted and unpainted areas.

2.4. Sample provenience and description

2.4.1. Sayles Adobe

At Sayles Adobe, five painted pebbles were recovered in Late Prehistoric deposits dating to between 1000 and 700 RCYBP (Pagano, 2019). As previously discussed, three of these pebbles were likely part of a cache. All five of the painted pebbles were painted with a liquid black paint and have figurative imagery (Fig. 4). Because Sayles Adobe is an open-air terrace, the preservation of the painted pebbles is variable, and only three of the five pebbles were analyzed (Supplemental Table 1, Supplemental Fig. 1).

2.4.2. Eagle Cave

Locations and stratigraphic contexts of the recently excavated painted pebbles from Eagle Cave are presented in Fig. 5. Of the 50 painted pebbles recovered from Eagle Cave, 27 were point-provenienced with a total data station (TDS), 10 have provenience to excavation unit-layers (following methodology from Koenig et al., 2017), and 13 are from disturbed contexts. The painted pebbles from Eagle Cave can be clustered into two time periods: the earlier pebbles date from 6500 to 5700 RCYBP ($n = 24$), and the later pebbles date from 2800 to 2050 RCYBP ($n = 13$) (Koenig and Black, 2017; Supplemental Fig. 2). For this analysis, only 25 pebbles with well-preserved pigment were assayed with pXRF. Of these 25 pebbles, 19 are well-provenienced and 6 are from disturbed context (Fig. 5; Supplemental Table 2, Supplemental Figs. 3, 4, and 5). All of the analyzed pebbles were painted with a liquid black paint.

The early painted pebbles found at Eagle Cave conform to Parsons' (1986) and Mock's (2013) Style 1, with geometric imagery executed in ultra-fine-line brush strokes (See Figs. 2 and 6). All the late period painted pebbles have a myriad of figurative imagery painted in bolder lines (Figs. 3 and 7). However, we did not encounter enough stratigraphic separation to confidently divide these late painted pebbles into chrono-stylistic types following Mock (2013) or Parsons (1986).

2.4.3. Private collection

An additional 42 painted pebbles were analyzed from a private collection that were collected from various Lower Pecos rockshelters between the 1930s–1960s (Fig. 8). These pebbles came from multiple sites, and have unknown proveniences. A majority of the analyzed pebbles have liquid black paint, seven have dry-applied black designs, and four pebbles were executed with red paint. Further, most of the pebbles in this collection have a variety of figurative designs that fall within Parsons' Styles 2–6 and Mock's Styles 2–4. There are no fine-line geometric examples in the private collection (Supplemental Table 3, Supplemental Figs. 6, 7, and 8).

3. Results & discussion

We focused our data analysis on manganese (Mn) and iron (Fe), as pXRF has proven effective at identifying these elements in Lower Pecos parietal art pigments (Koenig et al., 2014). The only other elements detected were titanium, zinc, arsenic, strontium, zirconium, and

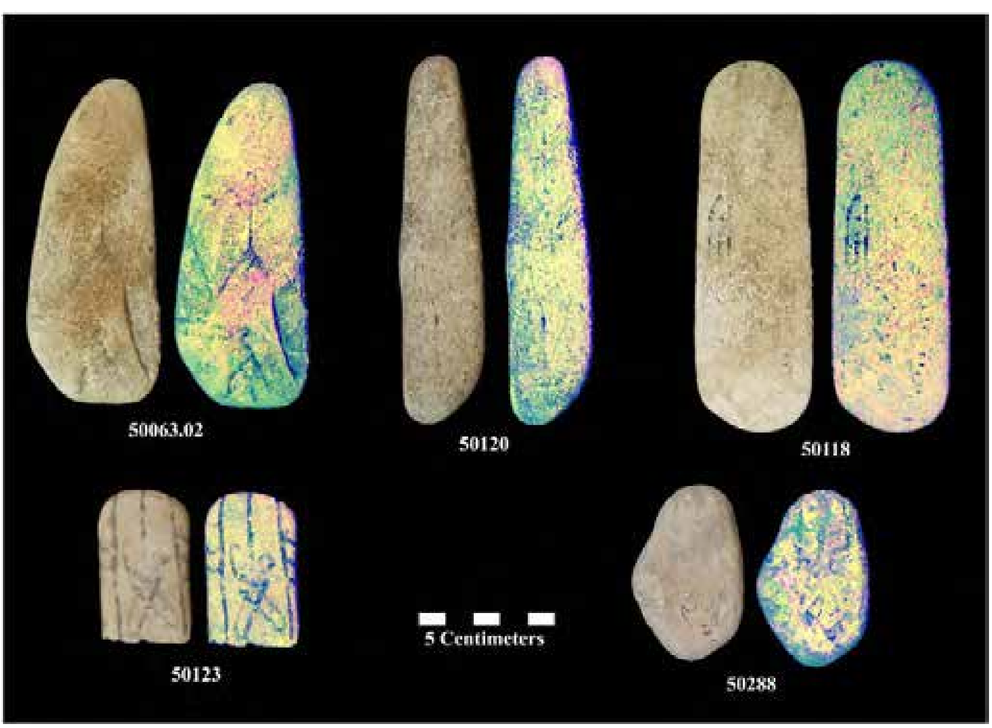

Fig. 4. The five excavated painted pebbles from Sayles Adobe in real color and DStretch YBK enhancement (Harman, 2005). Pebbles 50063.02, 50120, and 50118 were recovered in close proximity with each other. Pebble 50123 was recovered 30 cm below the other three pebbles and is believed to have been vertically displaced due to post-depositional processes. It is likely all four of these pebbles were originally cached together (Pagano, 2019).

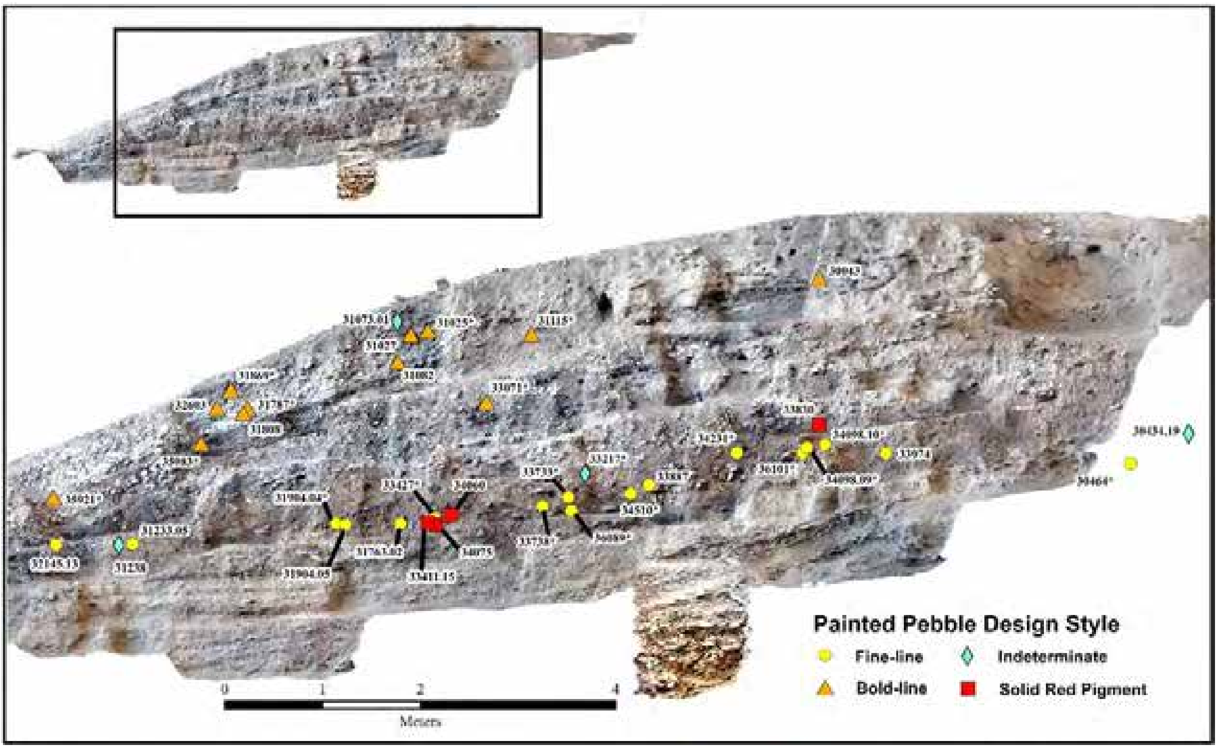

Fig. 5. Backplot of 37 provenienced painted pebbles recovered during recent excavations at Eagle Cave. Pebble ID numbers with an asterisk (*) were assayed for this study. Based on general characteristics of the painted designs, the pebbles are divided into four categories: Fine-line, Bold-line, Indeterminate, and Solid Red Pigment. There is over 1 m of vertical separation between the upper (bold-line) and lower (fine-line) clusters.

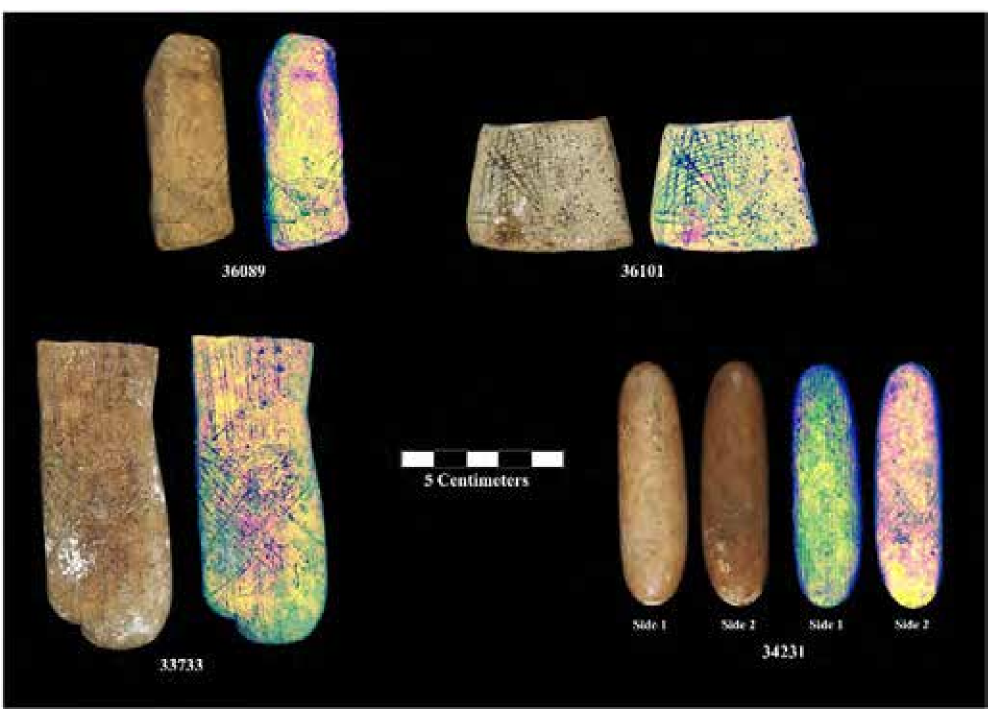

Fig. 6. Examples of fine-line, geometric painted pebbles from Eagle Cave in real color and DStretch YBK enhancement.

barium. The levels for these elements in the paint and the unpainted rock substrate overlap at 2*s*, indicating that the detection of these trace elements is due to their presence in the underlying rock substrate and that they are *not* part of the paint constituents. All other elements were reported as < LOD, where the instrumental limit of detection is defined as the lowest amount of substance present in a sample that can be distinguished from the absence of that substance in a sample. LOD is estimated from replicate analyses (typically $n = 20$) of a blank sample (not containing the analyte of interest) and is defined as three times the standard deviation of a blank. During factory calibration, pXRF manufacturers analyze interference-free standards to determine LODs that are programmed into the analyzer software. Of interest to our study,

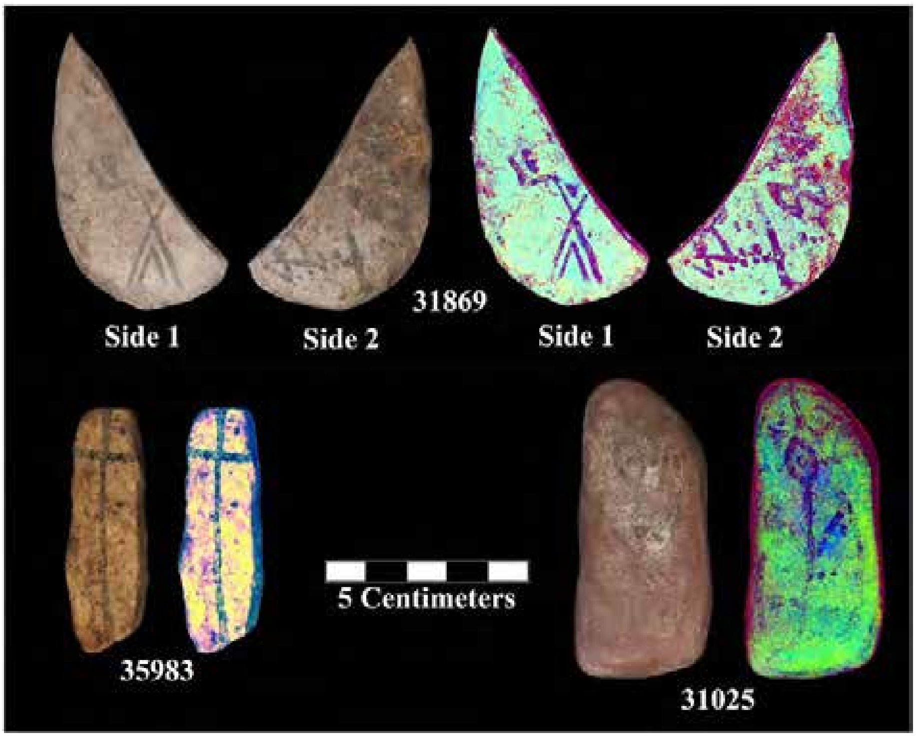

Fig. 7. Examples of bold-line, figurative painted pebbles from Eagle Cave in real color and DStretch YBK Hue Shift (31869), YBK (35983), and LAB (31025) enhancements.

instrument LODs for Fe and Mn are ~100 ppm.

Results are shown in Figs. 9, 10, 11, 12, 13, and 14. Readings < LOD are plotted as 100 ppm, as this is the approximate limit of detection. When only one measurement was collected for a painted or unpainted background location, the error bars on the graphs represent the ± 1*s* instrumental error of the pXRF for that particular measurement based on source/detector fluctuations and counting statistics. When replicate measurements were obtained, whether on the same

Fig. 8. Examples of bold-line, figurative painted pebbles from the private collection. No fine-line, geometric pebbles were present in this collection.

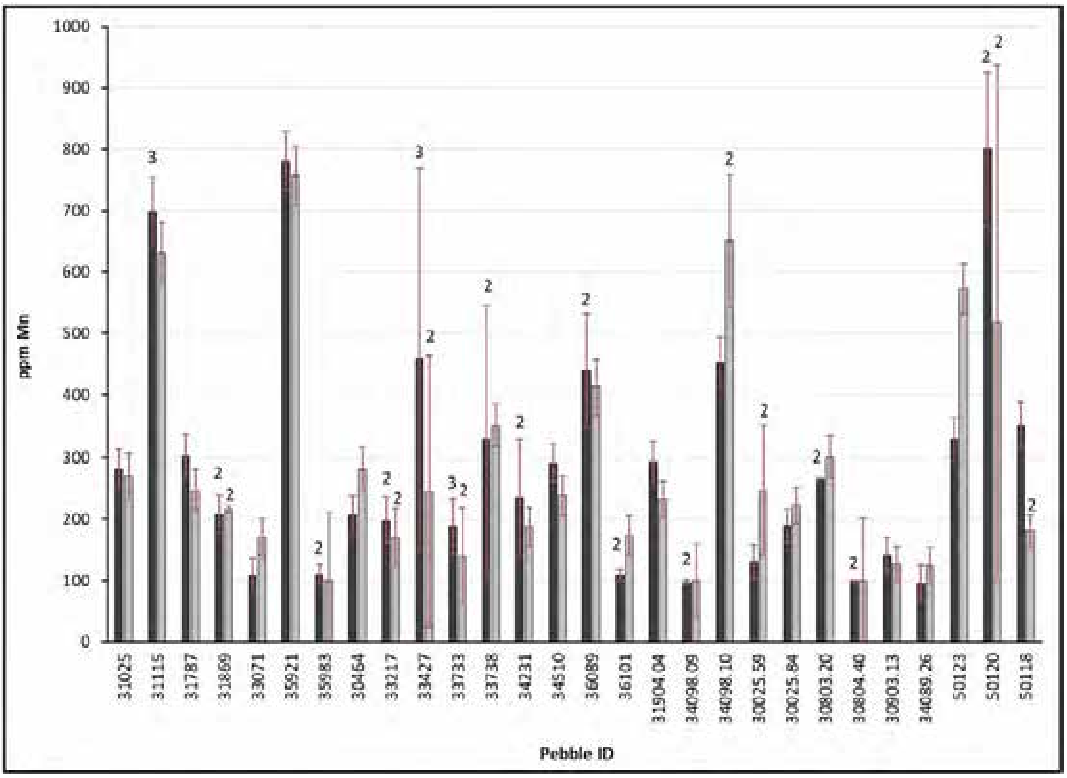

Fig. 9. Manganese levels for black paint (shown as black bars) and associated control measurements (shown as grey bars) on pebbles excavated from Eagle Cave and Sayles Adobe. Error bars represent ± 1s.

location or at different locations on the same pebble, these values were averaged and their standard deviation was calculated and shown as ± 1*s* error bars. This averaging of replicate measurements takes into account matrix effects and other sources of sample variation. The number of measurements (*n*) is located above the error bars; if there is no number, those results are for a single measurement. See

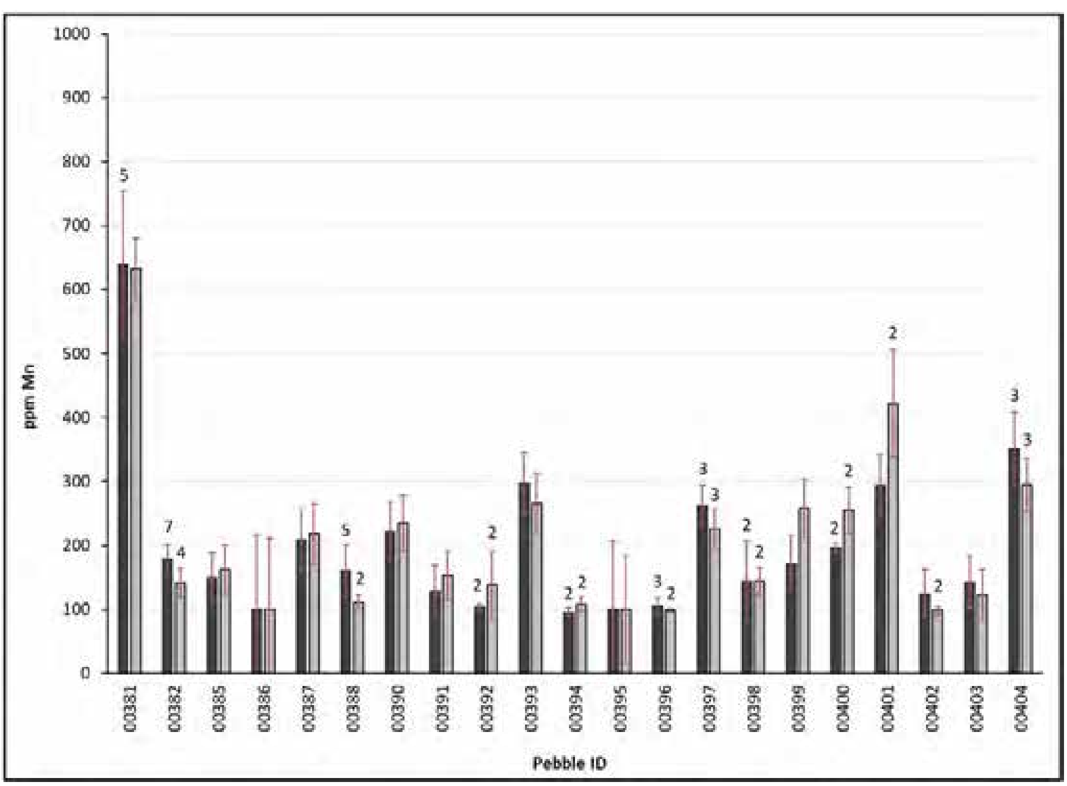

Fig. 10. Manganese levels for black paint (black) and associated control measurements (grey) on pebbles 00381–00404 from a private collection. Error bars represent ± 1s.

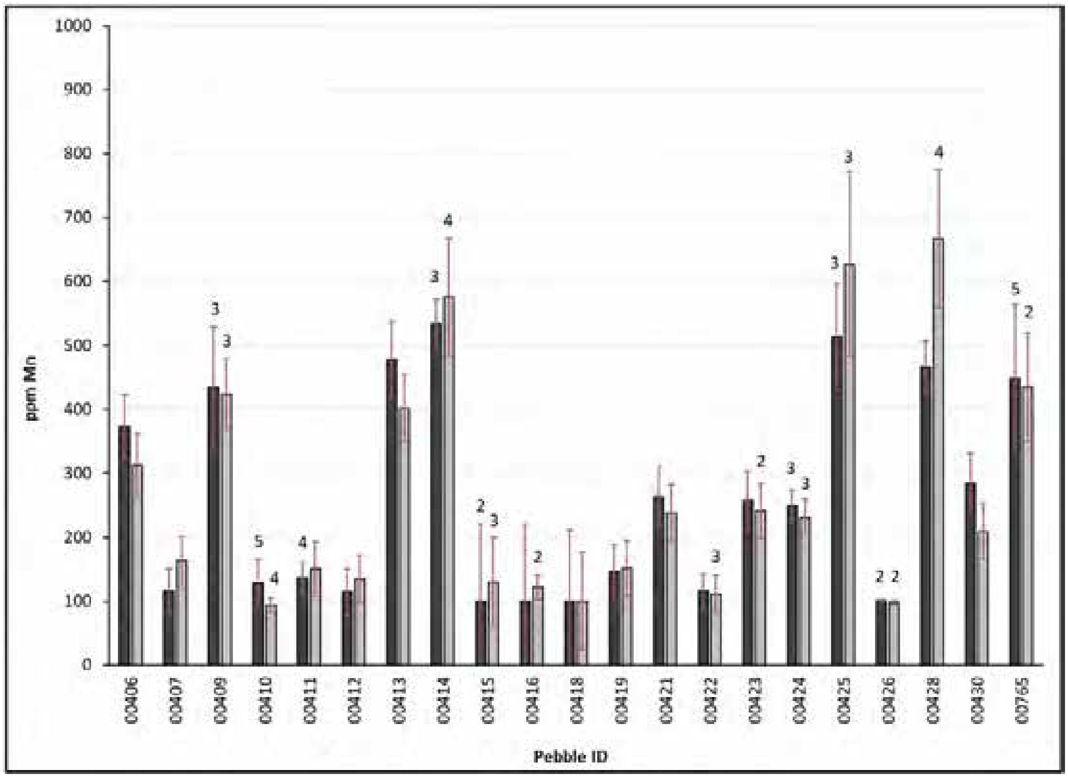

Fig. 11. Manganese levels for black paint (black) and associated control measurements (grey) on pebbles 00406-00765 from a private collection. Error bars represent ± 1s.

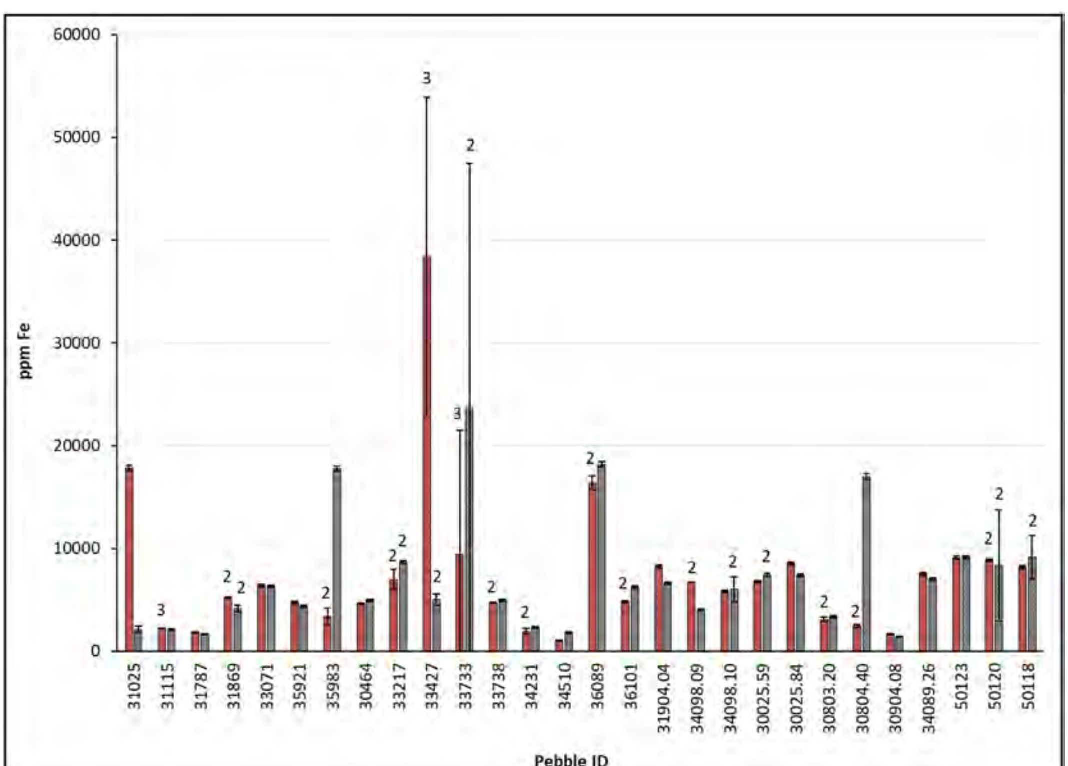

Fig. 12. Iron levels for black paint (shown as red bars) and associated control measurements (shown as grey bars) on pebbles excavated from Eagle Cave and Sayles Adobe. Error bars represent ± 1s.

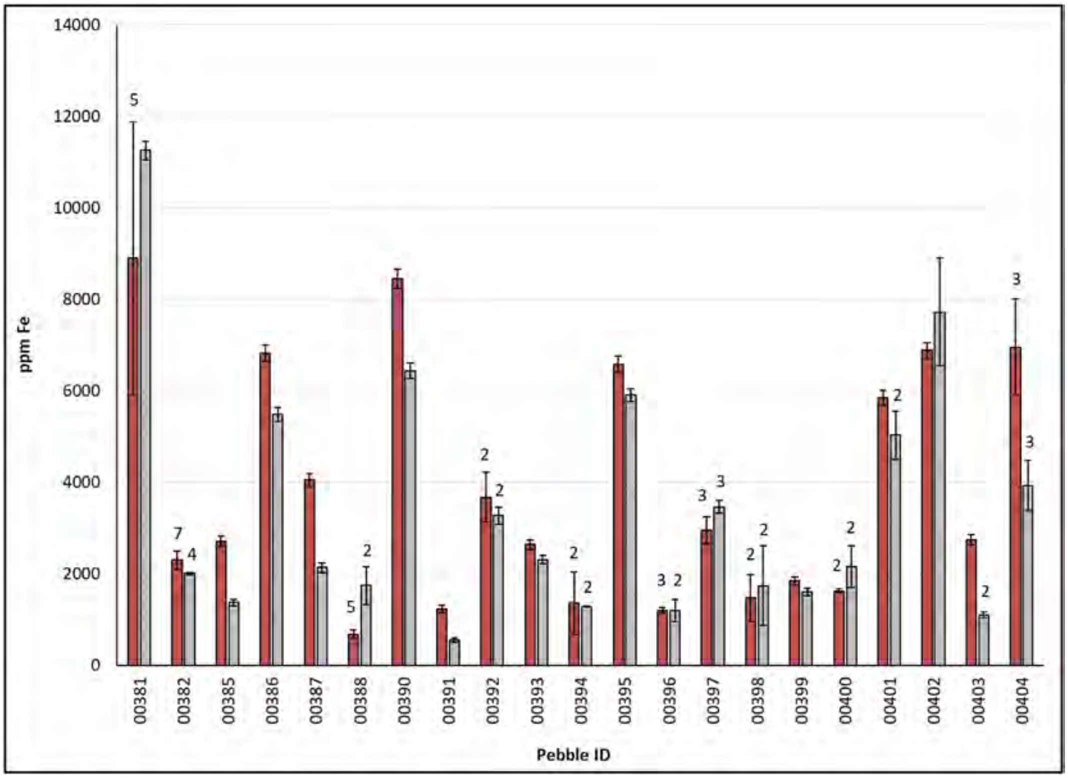

Fig. 13. Iron levels for black paint (red) and associated control measurements (grey) on pebbles 00381–00404 from a private collection. Error bars represent ± 1s.

Supplemental Figs. 1, 3, 4, 5, 6, 7, and 8, and Supplemental Tables 1, 2, and 3 for assay locations and corresponding measurements.

3.1. Controls measurements of unpainted rock

Manganese levels for the unpainted areas ranged from < LOD to 757 ppm Mn, with a median value of 217 ppm Mn ($n = 116$). Iron levels for the unpainted areas ranged from 550 to 24,938 ppm Fe, with a

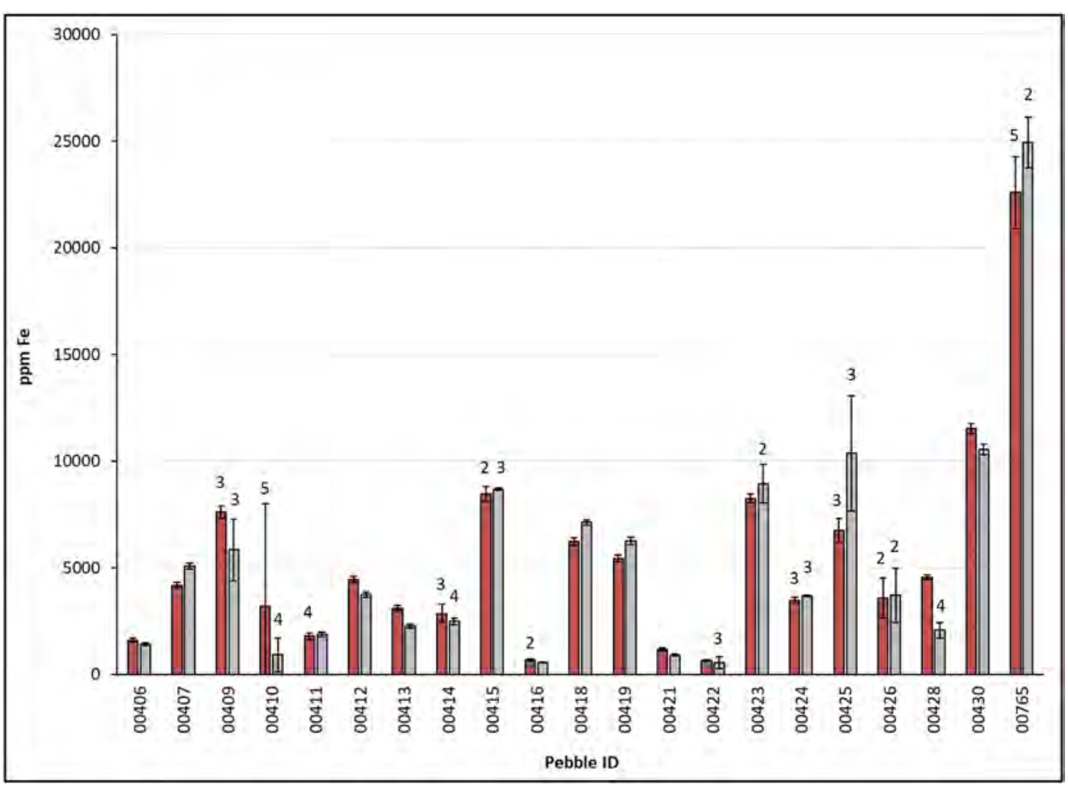

Fig. 14. Iron levels for black paint (red) and associated control measurements (grey) on pebbles 00406–00765 from a private collection. Error bars represent ± 1s.

median value of 4104 ppm Fe (n = 116). These results demonstrate that there are measureable levels of manganese and iron in the unpainted areas of the pebbles. These control readings are important to compare to the elemental levels of paint measurements so that we may determine if the levels in the painted areas are statistically greater than those for the unpainted rock.

3.2. Replicate measurements

Replicate measurements are advised for any pXRF study, as the variation that we observed was often larger than expected from instrumental error alone. For example, when holding the pXRF instrument in place during 2–3 replicate measurements on the same spot, the coefficient of variation for replicate measurements range from 0.5% to 66% with an average of 15% for Mn levels for black paintings (n = 20). Elemental concentrations at different spots on the same pebble varied slightly more, with the coefficients of variation ranging from 2% to 68% with an average of 18% for Mn levels for black paintings (n = 24). In a previous study on parietal art in the region, this difference was significantly larger (Koenig et al., 2014). Due to limitations of analyzing thin paint layers with pXRF these elemental results are not quantitative for various reasons as discussed in Huntley (née Ford) (2012) and Koenig et al. (2014): sample inhomogeneity; paint thickness and X-ray penetration depth; pigment area; irregular-shaped surfaces; limits of detection; background levels in rock substrate; and no standardization or calibration. The variability of replicate pXRF measurements (see raw data in Supplementary tables) on "infinitely thin" paint layers demonstrates that the technique is qualitative or semi-quantitative at best for the analysis of paint layers on stone (Rowe et al., 2011). Thus, we caution against the use of quantitative statistical tests for pXRF data when analyzing thin paint layers.

3.3. Black mobiliary pigment

3.3.1. Manganese results

Manganese levels for areas of black paint and unpainted stone for 70 painted pebbles are shown in Figs. 9, 10, and 11. Manganese levels for black paint range from < LOD to 889 ppm Mn, with a median value of 210 ppm Mn (n = 133). As reported above, manganese levels in unpainted areas range from < LOD to 757 ppm Mn, with a median value of 217 ppm Mn (n = 116). Overall, Mn levels for locations with, and without, black paint overlap at 2s, indicating there is no statistical difference in manganese levels between the paint and unpainted rock. This suggests that an organic pigment such as charcoal was used to produce the black paints. However, as each mobiliary painting is on a different rock substrate, a direct comparison between the manganese levels of painted and unpainted stone from each painted pebble is warranted. As shown in Figs. 9, 10, and 11, several pebbles have pigment with slightly elevated measurements of manganese compared to their associated unpainted background. However, when taking into account error bars, the painted and unpainted assays overlap at 2s for all instances, except Sayles 50123 and Sayles 50118 (Fig. 9; Supplemental Fig. 1). Sayles 50123 has substantially more manganese in the background measurement than in the painted area. In contrast, Sayles 50118 has a higher manganese reading in the painted area than in the background. Further analysis on Sayles 50118 may be warranted to confirm its composition, as only one pXRF measurement was conducted on the painted area.

3.3.2. Iron results

Iron levels for areas of black paint and unpainted stone for 70 painted pebbles are shown in Figs. 12, 13, and 14. Iron levels for black paint range from 662 to 38,375 ppm Fe, with a median value of 4592 ppm Fe (n = 132). As reported above, iron levels for the unpainted areas ranged from 550 to 24,938 ppm Fe, with a median value of 4104 ppm Fe (n = 116). The differences in iron measurements between painted and unpainted areas of each pebble were compared to determine if an iron-based mineral was used to produce the black paint. Over 20% of the pebbles analyzed (n = 19) resulted in elevated levels of iron in the painted areas in comparison to the unpainted rock, with error bars not overlapping at 2s. Of these 19 pebbles, it is important to note that three pebbles from the private collection (00381, 00410, and 00428) had overlapping black and red paint at the assay locations which likely contributed to high iron readings for the black paint. In fact, for pebble 00381, there was no true background measurement as red paint covers the entirety of the surface (see Supplemental Fig. 4). However, this does not explain the elevated iron levels for the other 16 pebbles. These results may indicate the use of a black or dark grey iron mineral, such as magnetite [Fe_3O_4] and maghemite [γ-Fe_2O_3], or it could represent high variation of iron levels within the rock substrate.

Although our previous pXRF analysis of Lower Pecos parietal art demonstrated the use of manganese minerals and charcoal pigments to produce black paint (e.g., Koenig et al., 2014), a previous XRD study indicates iron rich minerals may have also been used to produce black pigments. Zolensky (1982) and Hyman et al. (1996) conducted XRD analysis of pigments at sites in Seminole Canyon State Park & Historic Site and detected iron rich minerals in black paint samples. In both studies, Hyman et al. (1996:Table 1) and Zolensky (1982:Table II-1) almost always observed more than one mineral present in a single paint sample. A manganese mineral (manganite [MnO(OH)] or pyrolusite [β-MnO_2]) was present in every black paint sample even in instances when black iron minerals such as magnetite [Fe_3O_4] and maghemite [γ-Fe_2O_3] were also identified. Within the paint samples analyzed by Hyman et al. (1996) and Zolensky (1982), no black paint was identified containing only iron minerals.

This is an important distinction because we did not observe high measurements of manganese in the painted areas on the pebbles using pXRF. We suspect that the elevated iron levels for pebbles with only black paint (n = 16) may be due to the high variation of iron found in the unpainted rock and suggests the absence of manganese indicates an organic black pigment such as charcoal. The pXRF signals for manganese and iron are sensitive and easy to determine, with no interfering lines from other elements. However, there is no pXRF signal for carbon that would be present in an organic material such as charcoal. The discovery of charcoal paintings is demonstrated by the absence of manganese, as has been done with other studies (Roldán et al., 2013; Rifkin et al., 2016). The majority of painted pebbles analyzed in our study (77%) were not painted with either a manganese or iron black mineral, suggesting an organic material such as charcoal was used to produce the black color.

The pXRF data reported here for Lower Pecos mobiliary art is only an elemental analysis technique, but molecular analysis with XRD to identify minerals and/or Raman or infrared spectroscopy to identify functional groups might elucidate the composition of the black pigment used on these painted pebbles. However, with non-destructive portable Raman spectroscopy, most spectra on stone artifacts exhibit strong fluorescence making functional group assignments difficult. For example, when Rifkin et al. (2016) utilized pXRF, portable reflectance FTIR, and portable Raman on plaques from Apollo 11 Cave in Namibia, they did not obtain reflectance FTIR spectra for the black pigments as they tend to absorb infrared radiation and only three of the plaques showed Raman peaks at 1300 cm^{-1} and 1600 cm^{-1} for amorphous carbon. In a different study Roldán et al. (2013) were not able to observe clear bands for either manganese oxides or charcoal with a laboratory bench-top FTIR. For the Lower Pecos painted pebbles analyzed in this study, destructive sampling of pigment from the pebbles for laboratory-based XRD analysis was not possible. The use of pXRF allowed us to non-destructively test a large dataset for the presence or absence of manganese black minerals to identify the pigments used by ancient artists to create Lower Pecos painted pebbles. The availability of pXRF to most archaeologists makes this technique feasible for these types of studies on mobiliary art.

3.4. Red mobiliary pigment

The only red paints that we analyzed were on four painted pebbles from the private collection. Elevated levels of iron were detected for 7 locations of red paint and 2 locations of red and black paint on 4 different painted pebbles. These iron levels range from 2285 to 11,760 ppm Fe, with a median value of 6445 ppm Fe ($n = 9$). For the unpainted areas of these pebbles, iron levels ranged from 410 to 2670 ppm Fe, with a median value of 2101 ppm Fe ($n = 12$). The Fe values for painted rock is statistically greater than the unpainted rock, and the values to do not overlap at 2*s*. These elevated iron results for the painted areas suggest that a red iron mineral was used as pigment. Based on the XRD parietal art studies, varying shades of red, orange, and yellow 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 (Hyman et al., 1996; Zolensky, 1982). Pigment compositional analysis is complicated, as ochre and ore samples used for grinding to make pigments are not homogeneous, and almost certainly contain multiple minerals. Further, ancient artists may have prepared and manipulated ocher samples through grinding, density separation, and heating to produce specific shades of color (Lorblanchet et al., 1990:10). While red pigment is rare on painted pebbles, it is noteworthy that a mineral pigment was used in at least some instances.

4. Archaeological implications

4.1. Painted pebble chronology and iconography

Previous analyses on Lower Pecos painted pebbles have focused nearly exclusively on stylistic variation, and archaeologists have assigned painted pebbles to time periods based on differences in iconography. With one exception—the fine-line geometric style—the remainder of the styles lack securely dated contexts to aid in seriation. Radiocarbon dates from Eagle Cave and Sayles Adobe securely place painted pebbles into three regional time periods: Early Archaic (6500–5700 RCYBP), Late Archaic (2900–2050 RCYBP), and Late Prehistoric (1000–800 RCYBP). Within Eagle Nest Canyon, we did not find any painted pebbles in Middle Archaic deposits (see Fig. 5). We found the Early Archaic fine-line, geometric style from both Parsons' (1986) and Mock's (2013) typologies was the only variety to hold clear stratigraphic merit (see Figs. 2, 5, and 6). The remainder of the bold-line, figurative styles from Parsons' and Mock's typologies were stratigraphically undifferentiated in both Late Archaic (see Figs. 3 and 5) and Late Prehistoric deposits (see Fig. 4). However, the stratigraphic and chronologic data from Eagle Cave and Sayles Adobe painted pebbles should not be blindly applied to the entire region.

There is not enough available data to argue that painted pebbles were *never* produced in the Middle Archaic; but, their absence in the Eagle Cave deposits during this time period is noteworthy. Eagle Cave has contributed one of the largest samples of painted pebbles in the region, and previous excavations in Eagle Cave (Davenport, 1938; Ross, 1965) report a similar lack of painted pebbles in Middle Archaic deposits. Other studies have reported painted pebbles dating to the Middle Archaic, but unfortunately the excavations were in shallow rockshelters (e.g., Mock, 2012) or do not provide stratigraphic description of where the pebbles were recovered (e.g., Turpin and Eling Jr., 2017:106; Turpin and Middleton, 1998). Accepting the reported Middle Archaic context of Lower Pecos painted pebbles is made more difficult by the simple fact that rockshelters are incredibly challenging sites for establishing chronologic sequences. Humans, in addition to natural formation processes, have contributed to make rockshelters some of the most stratigraphically complex of all archaeological sites (Farrand, 2001; Goldberg and Macphail, 2006). Eagle Cave is no different; however, recent excavations had a distinct advantage over previous work because excavation methodology focused on sampling from a large profile exposure (see Fig. 5). This allowed the excavators to maintain better stratigraphic control, and directly associate defined stratigraphy with radiocarbon dates and recovered artifacts (see Koenig et al., 2017).

Much better locations for establishing secure stratigraphic context of artifacts are alluvial terraces, like Sayles Adobe. All of the painted pebbles recovered from Sayles Adobe occurred in Late Prehistoric deposits; but, the iconographic styles present on the pebbles (Fig. 4) match with Parsons' (1986) and Mock's (2013) proposed Archaic painted pebble styles (see Figs. 3 and 4) rather than Late Prehistoric style of pebbles. Although the painted pebble assemblage from Sayles Adobe is small, terrace sites are optimal locations to aid in establishing painted pebble chronology due to the depositional environment. Of great importance for painted pebble chronology is Arenosa Shelter (41VV99), a stratified rockshelter-terrace site located near the confluence of the Pecos River and Rio Grande. Along with Eagle Cave, Arenosa has contributed one of the largest collections of painted pebbles, with pebbles found in Late Archaic and Late Prehistoric deposits dating to the last 2000 years (Dibble, 1967). Because of the well-stratified deposits at Arenosa, and the new stratigraphic understanding of Eagle Cave, these two sites offer the largest sample of provenienced specimens. These sites should be the focus of future painted pebble research for understanding when painted pebbles were produced and utilized by Lower Pecos hunter-gatherers, as well as creating a refined chronology of the bold-line, figurative styles.

4.2. Implications of charcoal pigments in painted pebble production

One of the most surprising aspects of the pXRF analysis was the perpetual use of charcoal as the black pigment for painted pebbles regardless of age and iconography. Given the potential Middle Archaic hiatus, and the distinct differences in iconography and execution between Early and Late Archaic pebbles, we were expecting variation in the selection of black pigment materials. The persistent use of charcoal pigments for painted pebble production sharply contrasts with the use of manganese black pigments in Pecos River Style parietal art produced during the Middle and Late Archaic periods (4200–1450 RCYBP) (Bates et al., 2015). A previous study conducted by Koenig et al. (2014) utilized pXRF to determine the elemental composition for black and red Lower Pecos parietal art. A total of 248 pXRF measurements at 10 rock art sites identified manganese and iron minerals as the main constituents of Pecos River Style black and red paints, respectively. It is intriguing that although both the parietal and mobiliary art were contemporaneous during the Late Archaic, charcoal and manganese pigments appear to be purposefully selected for different applications.

Koenig et al. (2014) also assayed an unidentified style of black miniature paintings which did not contain manganese, suggesting the use of a charcoal pigment. In addition to a dry-applied charcoal deer that was directly radiocarbon dated (Boyd et al., 2014; Rowe, 2003), the Koenig et al. (2014) study was the first widespread documentation of charcoal parietal paintings in the area. The identification of both charcoal and mineral-based pigments within Lower Pecos parietal art is important because it demonstrates that the organic and mineral constituents of paints are preserved within Lower Pecos rockshelters even though the paintings are fully exposed to natural weathering processes. Similarly, the preservation afforded by the region's dry rockshelters (including Eagle Cave) preserves a wide array of buried perishable artifacts spanning at least 10,000 years (Shafer, 2013; Turpin, 2004), including the paint on painted pebbles. Therefore, we can reasonably assume that the paints produced and applied in parietal and mobiliary contexts have remained well-preserved and relatively unchanged from the original paint mixture.

We posit that the differences in pigment choice between mobiliary and parietal art, rather than being a result of post-depositional degradation of paints, is instead related to cultural values associated with the pigment and subject matter. For instance, in a study analyzing pigments in the Florentine Codex, Kerpel (2014:35) found there was a pattern between the use of organic pigments for depicting earthly images, versus mineral pigments for depicting otherworldly images; "Thus it is apparent that their use in images was related not directly to their tone but rather to their materiality and provenance, implying that colors had a specific significance based on their raw material and their natural state." Previous Lower Pecos work has hypothesized different functions for the parietal art and painted pebbles, with parietal art being otherworldly in nature (e.g., Boyd, 2016) and painted pebbles operating as women's totems (Mock, 2013; Roberts, 2014:81). Although more research is needed to further hypotheses surrounding the function of painted pebbles in Lower Pecos society, the results of this pXRF analysis demonstrate that there are specific pigment sources used for different aspects of the visual culture.

5. Conclusions and future research

In this study we analyzed 70 painted pebbles from the Lower Pecos using pXRF, and determined the use of charcoal pigments for the production of black paints. The tested painted pebbles span over 6000 years, and the use of charcoal pigments is persistent through time and iconographic variation. The consistent use of charcoal pigments, and the stratigraphic contexts reported for the newly excavated painted pebbles from Eagle Cave and Sayles Adobe, challenges the stylistic typologies that have been put forth for the region. Based on the stratigraphic sequence at Eagle Cave, there is a possible hiatus of painted pebble production in the Middle Archaic, and additional work at well-stratified sites may elucidate the chronology of these artifacts. However, these types of excavations are uncommon, and a more feasible research avenue may be to utilize existing collections to further refine the stylistic chronology.

One research avenue that must be pursued is the direct dating of painted pebbles. Radiocarbon dating via plasma oxidation has been used effectively for parietal art (e.g., Bates et al., 2015; Steelman and Rowe, 2002) but it has never been attempted for mobiliary art. Although it would be experimental for painted pebbles, it should be feasible to extract enough carbon from the paint via plasma oxidation to date the production of a painted pebble rather than dating its depositional context. This is especially true for the many painted pebbles that were excavated without rigorous stratigraphic documentation and/or limited radiocarbon dating during early excavations in the region (e.g., Alexander, 1970, 1974; Collins, 1969; Davenport, 1938; Dibble, 1967; Dibble and Lorrain, 1968; Martin, 1933; Maslowski, 1978; Ross, 1965; Parsons, 1963, 1965). In addition, if enough carbon can be extracted from the paint, there is the potential for conducting isotopic analysis on the charcoal within the paint. If the isotopic signature from the charcoal can be precisely measured, researchers may be able to source the charcoal to C3, C4, or CAM plants the same way other analyses have sourced mineral pigments to locations on the landscape via ICP-MS or other destructive analyses (e.g., Bu et al., 2013; Russ et al., 2012). If we can identify the plant types used to produce the black charcoal pigments, we will build a stronger dataset to understand painted pebble pigment selection. Direct dating will be essential to refine the painted pebble chronology for the region, and warrants a dedicated future study.

Within the Lower Pecos, painted pebbles were produced at the same time as several different types of parietal art, but it appears that distinct black pigments were selected for different applications (mineral pigments for parietal vs. charcoal for mobiliary). These differences in pigment choice suggest cultural values played a strong role in pigment selection. This is a research avenue that must be further pursued, and not just for the Lower Pecos. Archaeological regions across the world have parietal and mobiliary art that were produced at the same time and even perhaps by the same people. We recommend the use of pXRF as a quick, non-destructive method to begin the process of comparing differing art forms from a single region and gain insight into the subtleties of pigment selection, and potential cultural implications.

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Appendix A. Supplementary data

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