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# PORTABLE X-RAY FLUORESCENCE SPECTROSCOPY OF PICTOGRAPHS: A CASE STUDY FROM THE LOWER PECOS CANYONLANDS, TEXAS*

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*We evaluate the effectiveness of non-destructive portable X-ray fluorescence spectroscopy (pXRF) for elemental analysis of pictographs at 10 sites in the Lower Pecos Canyonlands of Texas. Considerations and limitations of pXRF analysis are discussed to inform future research. We found that manganese and iron minerals were the main constituents of black and red paints, respectively. However, 40 pXRF measurements from 31 images tested at 41VV75 and 41VV76 did not contain manganese, suggesting charcoal pigment—the first widespread documentation of charcoal figures in the area. The identification of charcoal-based pigments is important for rock-art and radiocarbon studies in the region.*

*KEYWORDS:* pXRF, ROCK ART, PAINTINGS, PECOS RIVER STYLE, RED LINEAR STYLE, CHARCOAL PIGMENT, MANGANESE PIGMENT

## INTRODUCTION

The use of portable X-ray florescence spectroscopy (pXRF) is becoming more common in the field of rock-art research for conducting elemental analysis of prehistoric pictographs. The first reported use of a pXRF spectrometer to study rock art was by Newman and Loendorf (2005), and subsequently this non-destructive technique has been used worldwide to address different rock-art research questions (e.g., Rowe *et al*. 2011; Huntley 2012; Roldan *et al*. 2010; Olivares *et al*. 2013). Elemental studies of paintings may be useful in determining pigment types; and, in addition, differences in elemental composition may distinguish between distinct painting episodes on a single panel or even across the landscape. For example, if black paintings of a particular style were made using manganese minerals, while black paintings of another style were made using charcoal pigment, then technological information about paint production would be ascertained. However, researchers must be wary: pXRF is not a magic gun that can provide answers to any and all research questions related to elemental composition. Therefore, in order to explore the potential—and pitfalls—of conducting pXRF analysis, the present study was undertaken.

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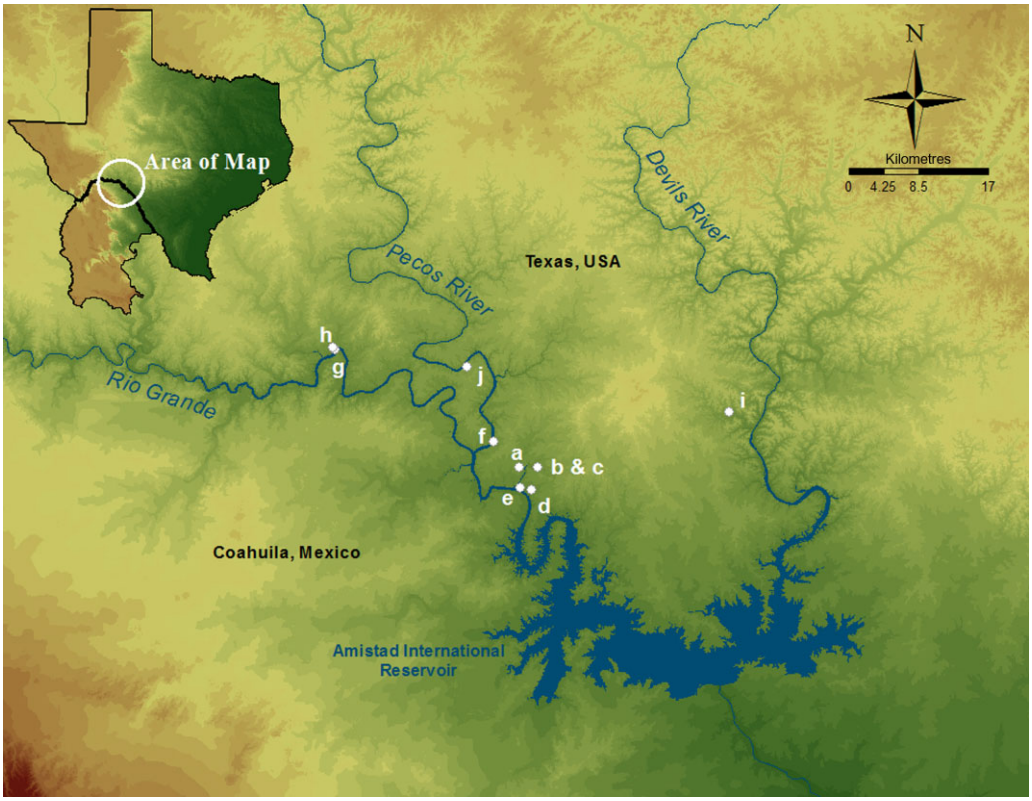


Figure 1 *The Lower Pecos Canyonlands of Texas. pXRF analyses were conducted at 10 sites: a, 41VV75; b,c, 41VV76 and 41VV76a; d, 41VV78; e, 41VV83; f, 41VV124; g, 41VV165; h, 41VV167; i, 41VV1230; j, 41VV2010.*

The Lower Pecos Canyonlands of Texas is ideal for a case study because previous pigment analyses have been conducted in the area (e.g., Zolensky 1982; Hyman *et al*. 1996; Bu *et al*. 2013) and a long-term rock-art recording project is currently under way (e.g., Johnson *et al*. 2011; Boyd *et al*. 2013). The objectives of this present study are twofold: (1) to first describe the methodological and analytical considerations researchers must acknowledge prior to conducting any pXRF study; and (2) to evaluate the effectiveness of pXRF for conducting a preliminary elemental analysis of prehistoric pictographs in the Lower Pecos. Data were collected from 10 different sites[1] within the Lower Pecos Canyonlands (Fig. 1), all containing varieties of pictographic rock-art styles. Early in our survey, we discovered three panels of black paintings at 41VV75 and 41VV76 that did not contain manganese as the primary mineral constituent. Black paints lacking manganese as the mineral pigment are typically carbon (charcoal) based (e.g., Armitage *et al*. 2000; Diaz-Granádos *et al*. 2001; Steelman *et al*. 2004). Previous pigment studies within the Lower Pecos had found that manganese and iron minerals were the main constituents of black and red paints, respectively. By taking into account the different considerations discussed below regarding pXRF studies, we decided that the identification of manganese- versus

[1]With the help of a local rancher, Jack Skiles, we also visited 41VV1924 and 41VV1956, two exposed manganese outcrops. We conducted pXRF spectroscopy on numerous ore rocks and the manganese content was very high, registering ≥10% in every case. Surprisingly, many of the manganese rocks were friable and easy to powder, even with our hands.

charcoal-based black pigments was an appropriate study for pXRF. Thus, subsequent pictograph analysis focused on sampling as many black figures as possible to determine whether additional charcoal-painted figures could be identified.

### *The Lower Pecos Canyonlands*

The rocky, semi-arid region known as the Lower Pecos Canyonlands of south-west Texas and northern Mexico is located at the south-western edge of the Edwards Plateau, within sight of the Burro Mountains in Coahuila (Fig. 1). This landscape is incised by deep, narrow canyons that slice through massive greyish-white limestone bedrock, remnants of a huge shallow sea that covered the region during the Cretaceous period. Wind and water erosion produced hundreds of rockshelters in the canyon walls that provided refuge for prehistoric inhabitants. Groups of hunters and gatherers periodically occupied the rockshelters throughout the Holocene, leaving behind a well-preserved archaeological record.

The walls of over 200 shelters host an array of pictographic images ranging in age from 4200 years ago to after the time of European contact (Jackson 1938; Kirkland and Newcomb 1967; Boyd 2003; Turpin 2004). The Pecos River style rock art is the most prominently represented. Twenty-five radiocarbon dates have been obtained and range from 4200 to 2750 years BP (Rowe 2009). Steelman *et al*. (2014) examine these results in a recent review, including a new radiocarbon result of $1465 \pm 40$ years BP (CAMS-152885) determined by Bates *et al*. (2014). Pictographic elements of the Pecos River style murals include anthropomorphs, zoomorphs, a wide range of geometric imagery, and enigmatic figures that are not identifiable as human or animal.

Red Linear style portrays humans engaged in group activities and animals such as deer and canids (Gebhard 1960; Turpin 1984). Unlike Pecos River style, Red Linear anthropomorphs frequently include gender markers and average approximately 10 cm in height (Boyd *et al*. 2013). There is one radiocarbon assay of $1280 \pm 150$ years BP (AA-10549) for a Red Linear pictograph of a red/orange oval at Cueva Quebrada (41VV162A) (Ilger *et al*. 1994a).

Turpin (1986a) described and tentatively dated the Bold Line Geometric style to the Late Prehistoric Period. As its name conveys, the style is characterized by bold, geometric designs, including zigzag, lattice and herringbone patterns. Small human- and insect-like forms painted in deep red are the only figures that are not geometric.

The youngest of the four styles is referred to as Red Monochrome style. It portrays static, frontally posed human figures grasping bows and arrows, and realistically depicted animals in profile or dorsal view (Kirkland 1938; Gebhard 1960; Turpin 1986b). There is one radiocarbon date of $1125 \pm 85$ years BP (CAMS-11891) for a Red Monochrome pictograph (Ilger *et al*. 1995). Although younger in age than the Pecos River and Red Linear styles, there are relatively few known Red Monochrome sites.

### *Previous pigment analysis of Lower Pecos pictographs*

A formative study initiated by pioneering rock-art researcher, archaeologist Solveig Turpin, and conducted by Mike Zolensky analysed 32 Pecos River style pigment samples from Panther Cave (41VV83), finding that the red pictographs were made using iron minerals and the black pictographs were made using manganese minerals (Zolensky 1982; Hyman *et al*. 1996). Hyman *et al*. (1996) utilized a technique called X-ray diffraction (XRD), which can yield the specific mineral (molecular) content of the pigments. For instance, among the many iron ores that may be present in a pigment, XRD can distinguish between:

- hematite, $Fe_2O_3$, with colours varying from red to brown to dark purple pigments;
- limonite, $FeO(OH)\cdot nH_2O$, often used for yellow pigment, but which may be dark brown;
- goethite, FeO(OH), which can produce pigments of yellowish grey to grey–brown;
- magnetite, $Fe_3O_4$, which is black; and
- any other iron-containing mineral.

Hyman *et al*. (1996) always observed more than one iron mineral present in a single paint sample. 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. Alternatively, to produce specific colours, the ancient artists may have mixed ochre or mineral samples or heated ochre samples to change colour and in the process changed the mineral content of the original ochre (e.g., Lorblanchet *et al*. 1990).

We used a different technique, pXRF, which is more limited—it only detects the elements present in the pigments and yields no molecular information. For any of the iron minerals, pXRF will only ascertain that iron (Fe) is present. In spite of this, pXRF analysis has the advantage that it is non-destructive, can be carried to sites and the pictographs can be analysed *in situ*. If the colour is known, then the presence of a specific element may allow us to infer the mineral used, especially if previous XRD studies have been conducted in the area. For the black paintings studied here, pXRF is able to reveal whether manganese (Mn) is present in the paint. If so, then, we can infer that a manganese mineral such as manganite (MnO(OH)) or pyrolusite ($\beta$-$MnO_2$) was used. High levels of iron may also suggest the black mineral, magnetite ($Fe_3O_4$).

The pXRF technique selected is ideal for this particular study because the signals for manganese and iron are sensitive and easy to determine, with no interfering lines from other elements. Even so, there is no pXRF signal for carbon that would be present in an organic material such as charcoal. The discovery of charcoal paintings would be demonstrated by the absence of manganese and iron. However, there are significant considerations that need to be addressed when using pXRF. An understanding of the phenomenon of X-ray fluorescence is important to interpreting analytical results and determining the types of research questions that pXRF may be able to answer (Huntley 2012). And, although pXRF allows for rapid data acquisition, a good research design and an appreciation of methodological limitations are necessary for any pXRF study.

### *Considerations for elemental analysis of pictographs using pXRF*

A pXRF instrument consists of an X-ray tube source and a solid-state diode detector at angles visible in the sampling window. Primary (incident) X-rays emitted from the source strike atoms in the analyte with sufficient energy to eject low-energy inner shell electrons, creating an unstable ion. When this occurs, an electron from a higher-energy, outer orbital fills the vacancy—releasing energy in the form of secondary (fluorescent) X-rays. The energy of any given secondary X-ray is characteristic of a specific element, allowing qualitative identification of elements present in a sample. In addition, the detector also counts the number of secondary X-rays from the sample, allowing quantitative elemental concentrations to be determined.

In the past decade, there has been a dramatic increase in the application of pXRF to archaeological materials, mainly due to a decrease in instrumentation cost (Shackley 2010). However, pXRF units have higher detection limits and measure a smaller range of elements compared to laboratory-based instruments, due to less powerful battery packs and miniaturized X-ray tubes (Guilherme *et al*. 2008; Huntley 2012). Even though portable EDXRF instruments and newer handheld pXRF instruments have improved the sensitivity of minor and trace elements—in addition to the analysis of lower atomic mass elements—elemental fingerprinting to determine

pigment sources in rock art is most probably not possible with handheld pXRF (Rowe *et al*. 2011). Many laboratory-based methods are able to answer more far-reaching research questions such as sourcing and elemental fingerprinting (cf., Bu *et al*. 2013). Below is a list of considerations when conducting handheld pXRF analysis of pictographs.

*Sample inhomogeneity* Inherent in rock-art paint samples is the variability of elemental concentrations introduced during paint production, paint application and weathering. Levels will vary with the amount of mineral pigment added to the paint recipe. And even if the same mineral ore is used as pigment, elemental concentrations can vary because of different amounts of extenders, binders and/or vehicles added during paint manufacture. During application of the paint on to the wall, there will be inhomogeneity from one full paintbrush to the next full brush. Over time, differential degradation of paint from location to location on the rock surface will also affect sample homogeneity. Elements not associated with pigment, but with rock substrate and mineral accretions, can be absorbed into the paint layer. For elemental analyses that attempt pigment sourcing, correlation between major (>1%) elements such as iron in red pigments with minor (0.1–1%) and trace (<0.1%) elements differentiates which elements are associated with the pigment. Normalization of correlated minor and trace elements with the major pigment element (e.g., Fe for red) corrects for differences in the amount of pigment present (Resano *et al*. 2007). For less sensitive handheld pXRF, variability of elemental concentrations even affects the ability to determine minor and major elements in the original mineral pigment.

*Paint thickness and X-ray penetration depth* With each application, the paint thickness differs. Huntley (2012, 79) observed variations from 7 to 275 μm for paintings in Australia; Resano *et al*. (2007, 8951) observed variations from 2 to 5 μm for paintings in Spain. In the Lower Pecos Canyonlands, Russ (1991, 192, 195, 200) observed ~100 μm pigment layers in cross-section micrographs.

Pigment layers are 'infinitely thin' in relation to pXRF, as incident X-rays will pass through the pigment layer into the rock substrate (Huntley 2012). Therefore, the analysis is not just of the pigment layer, but any associated minerals—which may have a very different elemental composition than the pigment. Sampling depths range from hundreds to tens of thousands of micrometres, depending upon the energy of the secondary fluorescent X-rays. 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 minerals.

*Pigment area* Commonly encountered in pXRF rock-art studies, the primary incident X-ray target area is problematically larger than the surface area of many paintings. The spot size for most pXRF instruments is ~1 cm in diameter, corresponding to an analysis area of ~0.8 $cm^2$. When analysing infilled motifs, the entire sampling area is typically covered in paint, resulting in information related to the pigment as desired, whereas fine-line drawings <1 cm wide incorporate the analysis of more rock substrate than paint. For our study of Lower Pecos paintings, we took photographs of each pXRF measurement location so that we could account for differences in measured concentrations between infilled and fine-line motifs.

*Mineral accretions* Both painted and unpainted limestone surfaces are often covered by mineral accretions (Rowe 2001; Steelman and Rowe 2012). It is impossible to physically separate pigment layers from accretion and substrate, as applied paint has been dispersed into porous underlying accretion and rock substrate. Weathering also causes the infiltration of substrate and

accretionary minerals into the pigment layer and often the formation of an accretion layer over the paint layer, making the images appear faded. Demonstrating this, Bu *et al*. (2013) found uniform calcium levels throughout accretion, pigment and rock substrate layers in Lower Pecos rock paintings using LA–ICP–MS. Resano *et al*. (2007) observed the same occurrence for Spanish rock paintings. In the Lower Pecos, Russ *et al*. (1996) and Hyman *et al*. (1996) have shown that the ≤100 μm accretion contains calcite ($CaCO_3$), calcium oxalate ($CaC_2O_4$) and sometimes gypsum ($CaSO_4$). The presence of calcium oxalate is interesting, as it is formed from atmospheric carbon and can be used as an independent method to obtain both minimum and maximum radiocarbon dates for rock art (Russ *et al*. 2000; Steelman *et al*. 2002; Ruiz *et al*. 2012). For elemental analysis, this incorporation of mineral substrate and accretion creates difficulties in obtaining analytical information on only the original pigment. Both incident and fluorescent X-rays penetrate not only the minerals of the pigment layer, but any surface accretion, underlying accretion and some undefined volume of the rock substrate.

*Irregular-shaped surfaces* In most cases, the analysed rock surface is not flat. Uneven surfaces can cause air gaps between the instrument window (with the source and detector) and the rock surface, introducing error in fluorescence intensities. Air attenuates low-energy secondary X-rays from light atomic mass elements (<Ti), but has only a negligible effect for higher atomic mass elements measured with most handheld pXRF instruments (Potts *et al*. 2005; Huntley 2012).

*Mineral structure* Mineral structure, including grain size and density, may affect attenuation of secondary fluorescent X-rays and pXRF sensitivity. For example, Huntley (2012, 81–2) determined grain size for Australian rock-art pigments of the order of 5–500 μm. Elemental analysis would only be detected for the outer portions of some mineral grains, especially for lighter atomic mass elements (<Ti). This is less of an issue for handheld pXRF instruments that measure only higher atomic mass elements (>Ti).

*Limits of detection and background levels in rock substrate* For elements that are present in very low levels, the pXRF instrument may report that they are below the limit of detection (<LOD). LOD 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 analyse interference-free standards to determine LODs that are programmed into the analyser software. Of interest to our study, instrument LODs for Fe and Mn are ~100 ppm.

The elemental levels in paint measurements must be compared to elemental levels in unpainted rock. Even though the pXRF instrument reports a number for elemental concentration, this does not mean that the element is present in significant amounts in the paint layer. In unpainted rock, background levels for measured elemental concentrations are often higher than LOD. Thus, it is important to note the minimum and maximum levels for unpainted rock background measurements. We used median and maximum values for unpainted rock as thresholds.

*No standardization or calibration* We used Alloy 316 provided by the manufacturer for standardizing the pXRF upon each instrument start-up. However, we did not analyse international or readily available standards, such as materials analysed by another method (e.g., Phillips and Speakman 2009; Shackley 2010). In any analytical technique, the periodic publication of standard analyses, along with instrument settings and parameters, confirm validity and reliability.

If only semi-quantitative comparisons are being made, correction with an internal standard is not necessary. However, for pigment sourcing on a limestone substrate, an internal standard such as calcium could be used to correct for differences in sample matrix, short and long-term instrument drift, and sample volume inaccuracies. As calcium is not detected with all handheld pXRF instruments and calcium levels are most probably >10% for limestone substrates, strontium levels may be a good surrogate for calcium, as strontium substitutes for calcium in the crystal lattice of limestone.

*Semi-quantitative pXRF analysis* In short, the variability of pXRF measurements on rock art is due to a number of reasons, which combine to make pXRF semi-quantitative at best. It must be emphasized that the concentration units (ppm) displayed by the instrument are not meaningful and are for rough, relative comparisons only (Rowe *et al*. 2011). The determination of iron and manganese concentrations—or the lack thereof—within paints represents a suitable study within the limitations of handheld pXRF.

## EXPERIMENTAL METHODS

We used a handheld 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 analyse for elements from Ti to Bi. Compton normalization calibration calculations converted measured characteristic line intensities for each element into weight per cent concentrations. A Hewlett Packard iPAQ personal digital assistant is used in the field to control the instrument and store data, which is exported into a spreadsheet for data analysis.

We used 30 s analysis times. In addition, we analysed areas of unpainted rock adjacent to paintings (backgrounds/controls) to make certain that observed elemental levels were from pigment minerals and not the rock substrate. Elemental concentrations are displayed on the palmtop computer screen attached to the instrument. This type of feedback in the field is satisfying, as results can be discussed immediately with collaborators.

## RESULTS AND DISCUSSION

We collected a total of 225 pXRF measurements on black, red, yellow and white paintings[2] (Table 1), as well as 23 pXRF measurements on unpainted limestone. The majority of measurements were on black paintings, as this was our focus. We concentrated our data analysis on iron and manganese. The only other element consistently found in measureable levels was strontium, a minor component of the limestone rock substrate. We attempted to normalize the iron and manganese levels with strontium levels; however, there was no change in trends of the data. Therefore, raw iron and manganese concentrations were used for comparison.

To test for precision, we collected replicate measurements for 22 paintings, both in the same spot and at different spots on the same motif. When holding the pXRF instrument in place during four replicate measurements on the same spot, the standard deviation of measurements averaged 600 ppm Fe for red paintings and 200 ppm Mn for black paintings. Elemental concentrations at

[2]Only four measurements were made for white pigment, with results inconclusive as to mineral.

Table 1 *A summary of pXRF measurements taken to determine pigments used in the production of pictographs at 10 sites in the Lower Pecos Canyonlands*

| *Site name* | *Site number* | *Total** | *Number of measurements* | | |
|---|---|---|---|---|---|
| | | | *Red pigment* | *Yellow pigment* | *Black pigment* |
| 41VV75 | 41VV0075 | 30 | 1 | | 29 |
| Black Cave | 41VV0076 | 21 | | | 21 |
| Black Cave Annex | 41VV0076a | 12 | | | 12 |
| Eagle Cave | 41VV0167 | 18 | 7 | | 11 |
| Halo Shelter | 41VV1230 | 39 | 5 | 1 | 33 |
| Mountain Laurel | 41VV2010 | 4 | | | 4 |
| Painted Shelter | 41VV0078 | 15 | 5 | 1 | 9 |
| Panther Cave | 41VV0083 | 28 | | | 28 |
| Skiles Shelter | 41VV0165 | 21 | 4 | 3 | 14 |
| White Shaman | 41VV0124 | 33 | 3 | | 30 |
| Total | | 221 | 25 | 5 | 191 |

*Without 23 background measurements and four white paintings.

different spots on the same motif varied significantly more, with an average standard deviation ~1200 ppm for both Fe and Mn. These variations are probably due to considerations discussed above.

### *Unpainted rock backgrounds*

In order to determine background thresholds, we collected 23 pXRF measurements on unpainted limestone at five of the studied sites. We observed no apparent trends in levels related to site. Manganese levels in the unpainted limestone ranged from <LOD to 650 ppm Mn, with a median value of <LOD that is ~100 ppm Mn. Iron levels in the unpainted limestone ranged from 1200 to 5500 ppm Fe, with a median value of 2000 ppm Fe. We used median values to minimize the possible influence of outliers, but also considered maximum background levels.

### *Red and yellow pigment*

At six sites, we assayed 26 yellow and red pictographs of various shades with 30 pXRF measurements (Fig. 2). The majority of red Pecos River style pictographs consistently have elevated iron levels, confirming that they are composed of mineral-based pigments. Variability of the iron measurements is expected and is most probably a reflection of the pigment colour and the paint thickness, as well as the paint surface area, in the pXRF sampling window. For example, the highest iron level observed was 43 530 ppm for a dark red, infilled unidentified figure from 41VV78 (Fig. 3) and the three lowest levels are for red paint remnants. Three figures that have replicate measurements at 41VV165 and 41VV167 are easily identifiable by the tight cluster of results visible in Figure 2. Six measurements fall below the maximum iron levels in the unpainted rock, but five are above the background median value (2000 ppm Fe) and all are most probably composed of iron-based pigment. Of these six measurements, three are paint remnants, two are unidentified and one is a Red Linear painting.

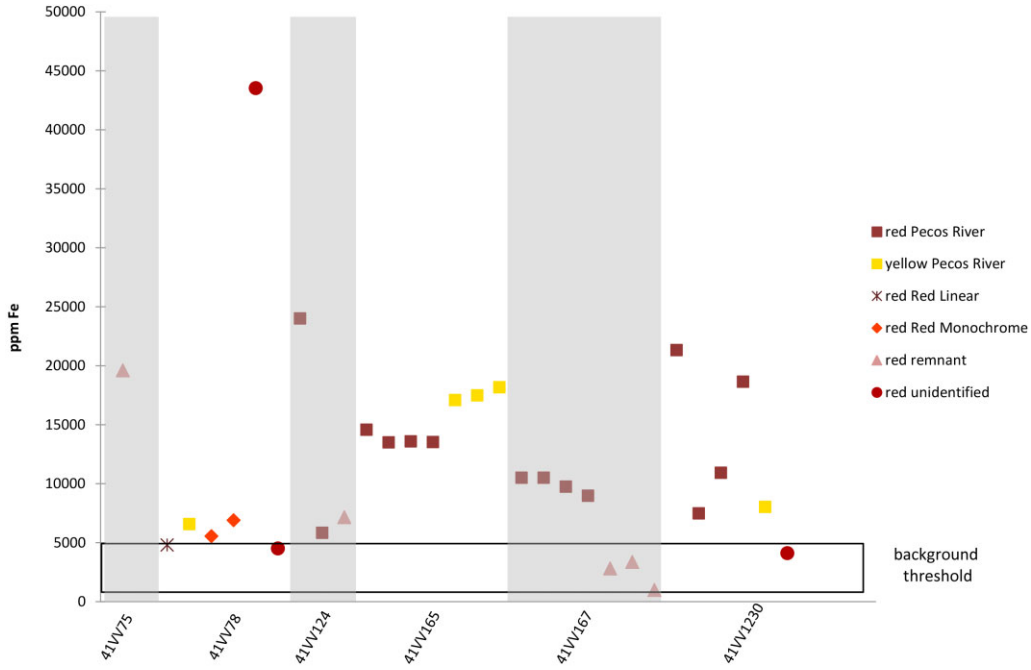


Figure 2 *Semi-quantitative pXRF results for red and yellow pigment. The background threshold shows the minimum and maximum iron levels in unpainted rock.*

Interestingly, three samples of dark purple/red pigments sampled from 41VV75 and 41VV167 contained >3500 ppm Mn, whereas the rest of the red pigments had <LOD for Mn. In two dark red pigments analysed by Hyman *et al*. (1996), both iron and manganese minerals were detected with XRD. This suggests that ancient artists either mixed iron and manganese minerals or used a naturally heterogeneous ore to produce the unique dark purple/red coloured pigment.

These results agree with the work of Hyman *et al*. (1996), who studied 32 Pecos River pictographs in Panther Cave with XRD and found that all shades of yellow and red paints (from browns to oranges to reds to dark purples) were produced using a myriad of iron oxide/hydroxide minerals, including hematite ($\alpha$-$Fe_2O_3$), maghemite ($\gamma$-$Fe_2O_3$), goethite ($\alpha$-FeOOH), lepidocrocite ($\gamma$-FeOOH), magnetite ($Fe_3O_4$) and ferrihydrate ($Fe_5O_7OH$). Rowe *et al*. (2011) also observed iron enrichment in red pictographs analysed in the Guadalupe Mountains, New Mexico. Furthermore, using LA–ICP–MS, Bu *et al*. (2013) found that red pictographs in the Lower Pecos contained elevated iron levels.

### *Black pigment*

We assayed 162 black pictographs via 191 pXRF measurements at 10 sites (Figs 4 and 5). The majority of measurements ($n = 144$) contain significant levels of manganese above the maximum background level. Interestingly, 40 readings had manganese levels <LOD. Seven measurements fall below the maximum Mn level in the unpainted rock, but above the background median (<LOD). Although we cannot be certain, these images are most probably composed of manganese pigment. Even a thin, dry-applied line (<1 cm in width) of unidentified style at Panther Cave


Figure 3 *An unidentified anthropomorph from 41VV78 with the highest observed iron level.*

(41VV83) returned a reading of 426 ppm Mn.[3] Also at Panther Cave, a black Red Linear style anthropomorph (<1 cm in width) recently discussed by Boyd *et al*. (2013) has an elevated manganese level of 424 ppm Mn.

At all 10 sites, black Pecos River style paintings have significant manganese levels, suggesting that they are composed of mineral-based pigment. This corroborates the findings of Hyman *et al*. (1996) at Panther Cave. Other researchers have determined that manganese

[3]We were expecting thin, dry-applied black lines to be made with charcoal, which would have a <LOD Mn level. The presence of dry-applied manganese lines could be the result of a deer bone manganese stylus like the one recovered by Martin (1933, 23) from the Shumla Caves.

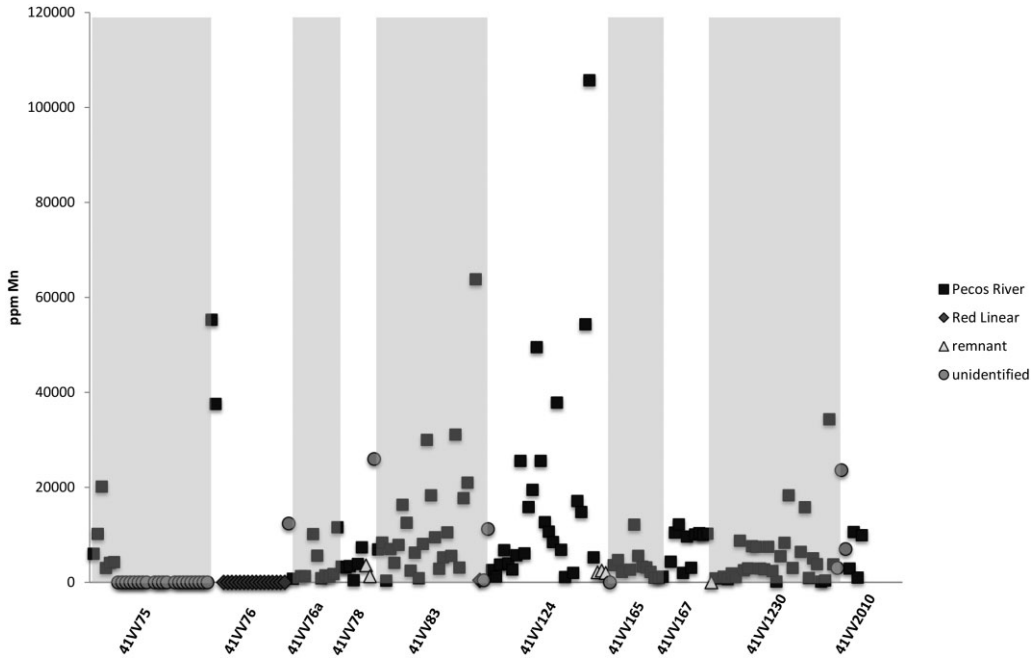


Figure 4 *Semi-quantitative pXRF results for all black pigments analysed. Measurements resulting in >LOD are graphed as zero, even though the limit of detection is 100 ppm Mn.*

pigments were used for black paintings worldwide (Chalmin *et al*. 2003, 2007; Sepúlveda *et al*. 2012).

Surprisingly, 40 measurements from 31 black Red Linear and unidentified pictographs had manganese levels <LOD, suggesting that they were made using charcoal instead of mineral pigment. Hyman *et al*. (1996) reported no incidence of charcoal paints at Panther Cave. In this study, we found three panels with charcoal pictographs:

(1) a panel of deer at 41VV75, shown in Figure 6;
(2) a panel at 41VV76, shown in Figure 7; and
(3) another panel at 41VV75, shown in Figure 8.

*Charcoal deer panel at 41VV75* Located near the middle of shelter 41VV75, we identified 13 black, dry-applied charcoal pictographs of an unidentified style. The panel includes nine deer, two geometric forms resembling nets and two figures so badly deteriorated that identification was not possible. When analysed by pXRF, nine drawings in the panel had <LOD Mn. This corroborates the findings of Hyman and Rowe (1997) when they radiocarbon dated a small paint sample from one of the miniature (~8 cm long) black deer (Fig. 6), reporting an age of 1280 ± 80 years BP (CAMS-29315). During plasma oxidation prior to radiocarbon dating, the black colour of the paint sample turned to white ash, suggesting that the sample was charcoal. If the pigment had been manganese, the black colour would have persisted. Rowe (2003) discussed the same deer, erroneously describing the deer as Red Linear when it is of an unknown style. A recent correction can be found in Boyd and Rowe (2014).

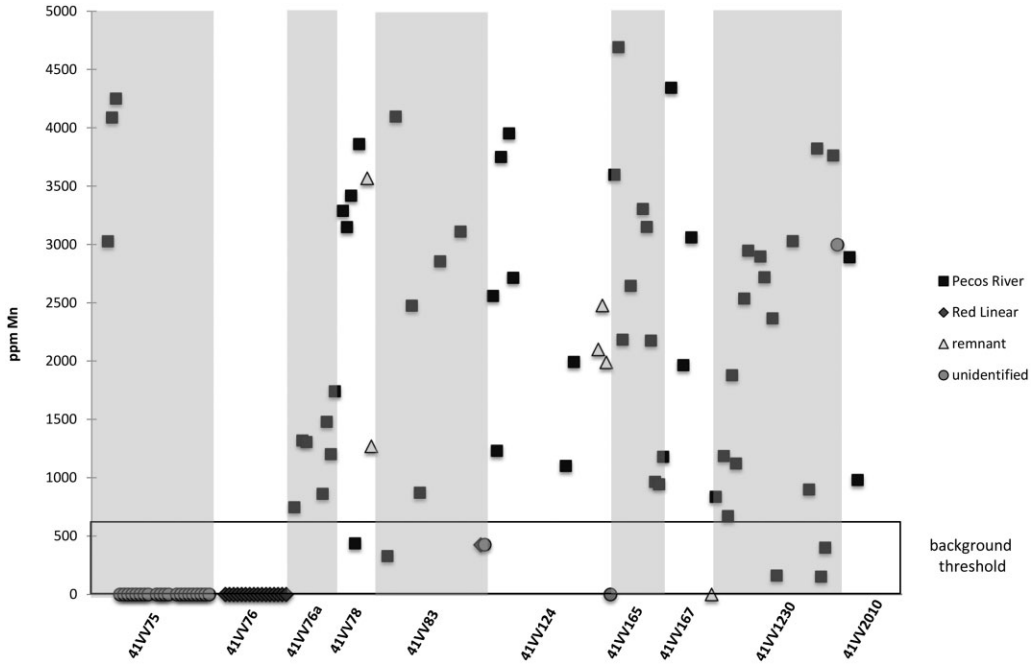


Figure 5 *Semi-quantitative pXRF results for black pigment showing values below 5000 ppm Mn. The background threshold shows the minimum and maximum iron levels in unpainted rock. Measurements resulting in >LOD are graphed as zero, even though the limit of detection is 100 ppm Mn.*

*Charcoal panel at 41VV76* Black Cave (41VV76) is located approximately 3 km from 41VV75. High on the wall, interspersed throughout cemented gravels, there are black and red anthropomorphic and zoomorphic figures (Fig. 7). Due to their size, head adornments and close association with Red Linear zoomorphs, Boyd *et al*. (2013) classified these black and red figures as Red Linear. Interestingly, none of these anthropomorphs are portrayed with gender markers or wielding paraphernalia typically associated with the Red Linear style. We obtained 17 <LOD Mn pXRF measurements on 15 of these black Red Linear paintings. On the basis of this analysis, we are confident these figures were painted using charcoal-based pigment.

*Charcoal panel at 41VV75* The third charcoal panel, located low on the shelter wall at 41VV75, consists of small black and red anthropomorphic, zoomorphic and enigmatic figures (Fig. 8). The preservation of this panel is extremely poor, and because this site has not been recorded using SHUMLA rock-art recording methods (cf., Johnson *et al*. 2011; Boyd *et al*. 2013), we did not place these figures into any of the accepted stylistic categories for Lower Pecos rock art—hence the classification as unidentified. These figures share a resemblance with some of the black Red Linear figures at 41VV76. We collected 14 measurements on seven figures with <LOD Mn. Once again, we are confident that these figures were painted using charcoal-based pigment.

### *Radiocarbon dating charcoal figures*

These findings are of critical interest because these panels contain the only known charcoal pictographs in the Lower Pecos. Charcoal images can be more reliably radiocarbon dated because

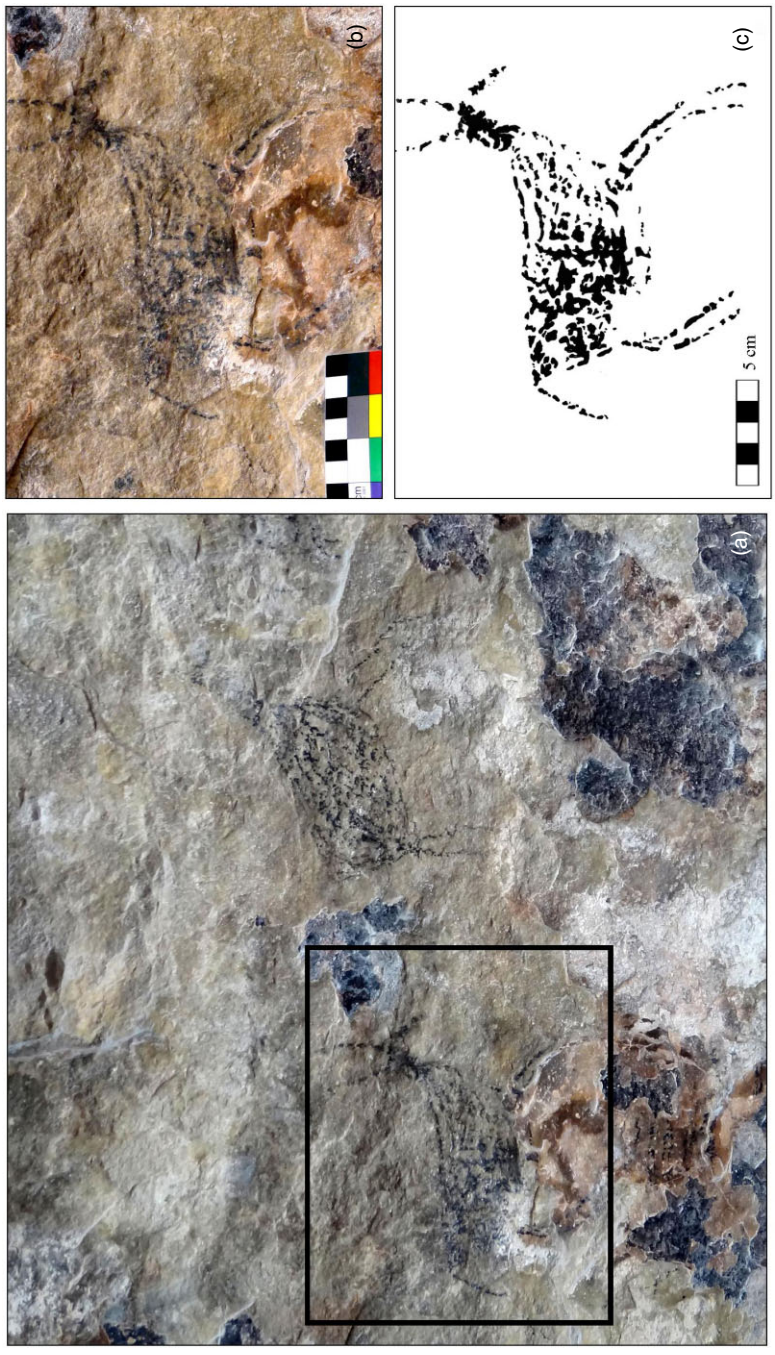


Figure 6 *A panel of previously dated charcoal deer at 41VV75: (a) two deer of an unidentified style; (b) a close-up photograph; (c) an illustration.*

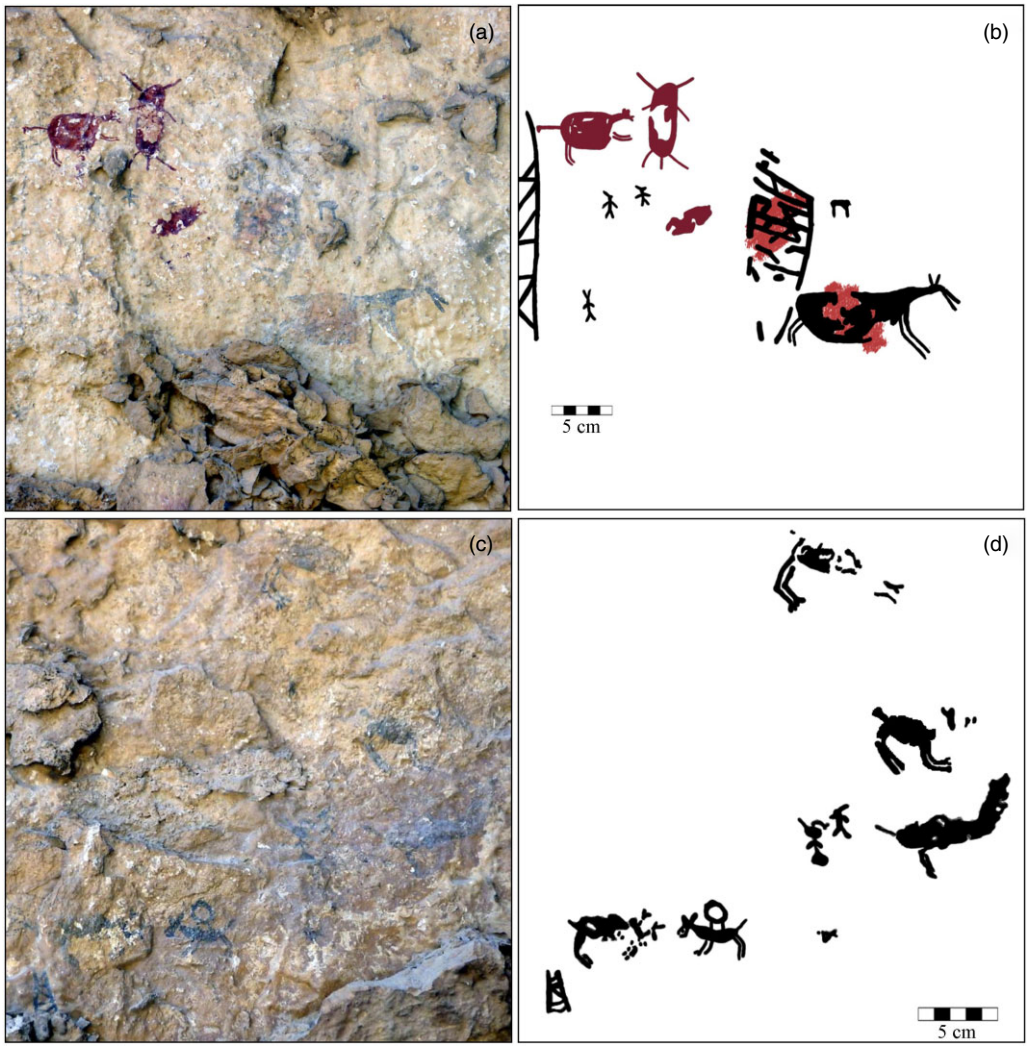


Figure 7 *Two panels of Red Linear charcoal figures at 41VV76.The top two images (a,b) depict a series of red and black anthropomorphic, zoomorphic and geometric imagery. In photograph (a), the red pigment appears darker than the black. In illustration (b), the red pigment is shown in grey. The bottom two images (c,d) portray a series of black anthropomorphic, zoomorphic and enigmatic imagery.*

the organic material is known. But dating charcoal pigment does not indicate the age of a rock painting; it dates the death of a tree. There are two caveats that apply when dating charcoal of any archaeological source—that of *old wood* (Schiffer 1986) and *old charcoal* (Bednarik 1994). In desert regions, charcoal may have been made from *old wood*, a tree that had been dead for many years, perhaps centuries. Alternatively, *old charcoal*, previously burned wood, could be found on the ground and used as a pigment. The bottom line is that radiocarbon dating of charcoal pigments can only produce a *maximum* age for the creation of the image.

How can we be certain that non-mineral-based black paints contain charcoal? We cannot. However, with over two decades of experience in rock-art dating, the Texas A&M University

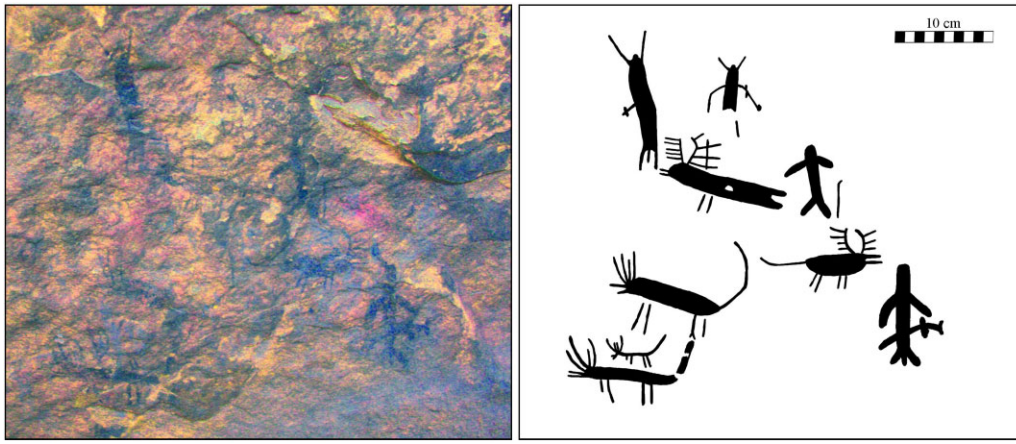


Figure 8 *An illustration of charcoal anthropomorphic and zoomorphic imagery of an unidentified style in a poorly preserved panel at 41VV75.*

archaeological chemistry group has invariably found that charcoal was used as a pigment for black pictographs that did not contain manganese. For example, charcoal pigments were used in pictographs from Arizona (Armitage *et al*. 2000; Steelman *et al*. 2004), California (Armitage *et al*. 1997), Missouri (Diaz-Granádos *et al*. 2001), Montana (Keyser *et al*. 2011), South Dakota (Rowe *et al*. unpublished data, 1996), Texas (Hyman *et al*. 1999), Utah (Chaffee *et al*. 1994) and Wisconsin (Steelman *et al*. 2001). The archaeological chemistry group has also had the same experience internationally: from Angola (Hyman and Rowe 1997), Australia (Armitage *et al*.1998; David *et al*. 1999, 2000, 2001), Belize (Rowe *et al*. 2001), Brazil (Steelman *et al*. 2002; Rowe and Steelman 2003), France (Ilger *et al*. 1994b), Guatemala (Armitage *et al*. 2001; Rowe and Steelman 2004), Russia (Steelman *et al*. 2002) and Spain (Steelman *et al*. 2005). We confirmed the presence of charcoal pigment by visual observation of wood grains when looking at paint samples under high magnification or with scanning electron microscopy. In addition, when oxidizing samples for radiocarbon dating, black charcoal paints turn to white ash, whereas black mineral paints retain their black colour. Other black paintings, such as in the European Palaeolithic caves, are generally composed of charcoal pigments (Valladas 2003). An examination of a bibliography on rock-art dating (Rowe 2012) leads to the same conclusion, although this may be skewed, as black charcoal paintings would be selected for dating because charcoal contains significantly more carbon than inorganic-pigmented paintings. Thus, it appears highly likely that if manganese or iron is not the pigment in black pictographs, charcoal almost certainly is. In fact, in only a few known instances are manganese pigments used for black paintings (Hyman *et al*. 1996; Chalmin *et al*. 2003, 2007; Sepúlveda *et al*. 2012).

## CONCLUSIONS

On the basis of our analysis, we have demonstrated that black pictographs in the Lower Pecos were primarily produced using manganese pigments, and red and yellow paintings were produced using iron pigments. These findings support the seminal work of Zolensky (1982) and Hyman *et al*. (1996) at Panther Cave. Interestingly, 40 pXRF measurements from black pictographs showed no indication of manganese. This establishes the presence of an organic material

such as charcoal, in black pigment. Further, Hyman and Rowe (1997) described a black charcoal deer at 41VV75. That observation was confirmed here and extended to the deer, nets and indeterminate imagery found in close proximity. We also discovered charcoal paintings low on the shelter wall at 41VV75, resembling black Red Linear figures at 41VV76, which were also determined to be made using charcoal pigment. An additional black Red Linear figure at Panther Cave is most probably made using manganese pigment.

We acknowledge that this study is only a preliminary survey of Lower Pecos pictographs using pXRF, but the results for black Red Linear figures are intriguing and raise several questions. Were most black Red Linear figures produced using charcoal pigments? Or are the black figures at 41VV75 and 41VV76 composed of different pigments because they represent a distinct stylistic subset of Red Linear? If Red Linear and Pecos River pictographs were painted using distinct pigments, are the variations in paint recipes the result of cultural or functional differences? These questions are difficult to answer at this time due to the limited number of black Red Linear figures that were sampled as part of this study. In fact, few black Red Linear figures are known, and to conduct a study focused on black Red Linear would require more than the known sample size (cf., Boyd *et al*. 2013). More thorough analyses of pigments using pXRF and other laboratory-based analytical techniques, as well as statistical analyses of stylistic variations, need to be undertaken to address these more sophisticated archaeological questions.

While handheld pXRF may not be able to answer detailed questions regarding pigment sourcing and mineral composition, it has been proven that the technique can be used effectively and non-destructively to determine the elemental composition of pictographs. pXRF is only one tool in the suite of analytical techniques available not only for the Lower Pecos, but for researchers worldwide. With the aid of pXRF, future pigment studies for rock art might include: (1) both preliminary and detailed analysis of black pictographs across a larger sample; (2) the regional distribution of paintings produced using manganese- or charcoal-based pigments; (3) analysis of different painting styles; and/or (4) the selection of charcoal pigment for radiocarbon dating. Regardless of the research questions posed, future studies must first take into consideration the limitations of pXRF in order to create a valid research design.

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