Analyzing Red Pictographs With Portable X–ray Fluorescence

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Portable X–ray Fluorescence (pXRF) is one of the few analytical techniques that allows in situ and non–destructive assessment of pigments used in pictographs. Previous research with this technique has successfully identified minerals in rock paintings of different colors including red (iron) and green (chromium). In our recent pXRF analysis of paintings at Picture Cave, Texas, we were also able to establish that at least two different batches of paint were used at the site. This compositional variation allows previously unavailable insight into the associations among different figures at the site.

This paper summarizes the results of an Energy Dispersive X–ray Fluorescence (EDXRF) analysis undertaken with a portable X–ray Fluorescence (pXRF) spectrometer at Picture Cave on Fort Bliss, Texas. The Picture Cave paintings are exclusively red designs that include masks, cloud terraces, horned serpents, birds, and goggle–eye figures. The paintings occur in a series of chambers that penetrate the cliff face to different depths across an area of approximately 45 meters long and 75 meters above the floor of a short unnamed canyon in the Hueco Mountains east of El Paso, Texas (Figure 1). Designs at the site are part of the Jornada Mogollon tradition and are considered to have been made circa A. D. 1300–1450.

EDXRF is a non–destructive analytical technique that is one of the few methods that allows collection of compositional data from *in situ* rock art elements. Geochemical characterization of rock art pigments included both major elements and trace elements in the paint. Control data were also collected from the surrounding natural rock surfaces. This analytical approach is commonly used in rock art pigment studies because comparison of the painted and unpainted natural surfaces is necessary to assess pigment composition (Iriarte et al. 2009; Newman and Loendorf 2005).

Picture Cave and other nearby rock shelters were initially recognized as significant sites in the early 1900s by El Paso area residents who were interested in protecting antiquities. They sent letters regarding the caves to the Smithsonian Institution, which led Frank H.H. Roberts (1929:1) to visit the region. Subsequently, Hattie Cosgrove made illustrations of the pictographs at Picture Cave as part of a campaign by Harvard's Peabody Museum to find and excavate major archaeological sites in the southwestern United States

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Figure 1. *Picture Cave rock alcoves where seventeen pictograph panels were recorded (panoramic view by Robert Mark).*

(Cosgrove 1947:33, 156–157). In 1974, Kay Sutherland and members of the El Paso Archaeological Society completed a more modern recording of paintings at the site (Sutherland 1976).

The paint used at Picture Cave is all macroscopically similar, and the EDXRF research provides insight into the nature of the figures that was not available to these previous researchers. Analyses of compositional data from the paintings indicates they were made from iron rich pigments, which suggests that ochre–based paint was used to produce all of the pictographs. These data also suggest that paint of different compositions was employed to produce the figures, and two or more paint batches appear to have been used. These data suggest figures at the site are not precisely contemporaneous, and/or they were painted by different people.

Methodology

The following discussion summarizes the methodology employed in the rock art pigment analysis undertaken at Picture Cave. All data were collected using a Bruker Tracer III–V, which is a fully portable EDXRF that allows the collection of high quality compositional data. This approach is non–destructive and the analyses were completed without adversely affecting the rock art figures.

Compositional Analysis of Pigments

Prehistoric pictographs throughout the United States were created using a variety of naturally occurring pigments including ochre (to produce purple, brown, red, or yellow), charcoal or manganese (for black), malachite or celadonite or fuschite (to make green designs), and kaolinite (to produce white) (Loendorf 1994, Newman and Loendorf 2005). All of the prehistoric pictographs analyzed as part of this project consisted of red designs, and based on their appearance they were assumed to have been produced using ochre (iron oxide). As will be discussed further below, the results of the EDXRF analysis support the conclusion that the painted designs were made using iron based pigments.

Ochres are among the earliest pigments used by humankind, and they are derived from naturally tinted sediments that contain iron–bearing minerals. Yellow ochre acquires its color from the presence of hydrated iron oxide (Fe_2O_3), while red ochre is the anhydrate form of Fe_2O_3. Brown ochre is a partially hydrated form of iron oxide. Purple ochre has a different hue caused by variation in the average particle size, but it is chemically identical to red ochre. Yellow and brown ochre can be turned red if heated sufficiently to drive off the water.

Mineralogically, ochres are generally intermixed with other materials such as quartz, clay, gypsum, and/or mica. These impurities may vary among iron oxide sources, which allow the identification of pigments produced using different raw materials (Popelka–Filcoff 2006). Furthermore, prehistoric artisans may have intentionally added materials to ochres to act as binding or extending agents that served to facilitate and prolong the fastening of paint to stone surfaces, and/or as agents to reduce to amount of the pigment that was required (Jercher et al. 1998). Therefore, the chemical composition of pigments may be unique in both space and time, making it theoretically possible to distinguish between different ochre sources and/or different paint recipes used to produce elements at different sites or in separate painting episodes within a site.

Figure 2. *EDXRF data collection from Element BB at Picture Cave, Fort Bliss.*

Data Collection Procedures

During rock art data collection at Picture Cave, the Tracer III–V was mounted on an adjustable tripod and the nosepiece aperture was placed directly in contact the rock surface (Figure 2). By positioning the instrument with as much direct contact to the rock as possible, geometry effects are reduced. All analyses were conducted for a 150–second real time count. The raw X–ray count data were processed on a laptop computer using S1PXRF software developed by Bruker. Using this method it was possible to view the EDXRF data as they were collected, which allowed comparison among readings as well as immediate identification of the atoms present in the assayed materials. This information was employed to refine both the data collection procedures and the numbers and types of locations selected for analysis.

The S1PXRF program stores spectral data as a multichannel memory, with each channel (40eV/CHAN) having its own counts gathered over the 150 second analysis time (i.e., the number of X–ray pulses accumulated by the detector in that specific energy window during the time of the analysis). Each reading was assigned a unique number, and a XRF data collection form was completed for each analysis. This form includes information regarding sample location, color, surface contamination, as well as any comments.

The Bruker Tracer III–V is equipped with a rhodium X–ray tube and a Peltier–cooled silicon PIN diode detector. The detector has a resolution of approximately 170 eV full width at half maximum (FWHM) for 5.9 KeV X–rays (at 1000 counts per second) in an area of 7.0 mm² (Phillips and Speakman 2009:1258). The X–ray tube generates a 4.0 mm diameter beam, which can be configured to operate at different energies, and has a user replaceable beam filter. Two different instrument configurations that are effective for identifying elements that are common in prehistoric paints were employed in the analysis (Bruce Kaiser, personal communication 2010). Thus, when possible, two separate measurements were taken for each assayed location, including painted areas and natural rock surfaces.

In the first configuration, the instrument was set to operate at 40 KeV and 12 µA. A beam filter (commonly called the "rock filter") composed of 304 µm of aluminum (Al), 152 µm of copper (Cu), and 25 µm of titanium (Ti), was placed between the X–ray tube and the sample. The rock filter stops X–rays below 17 keV from reaching the sample thus eliminating any X–rays of that energy from being elastically or inelastically scattered by the sample into the detector. It also allows for more efficient detection of the rare earth elements (i.e., rubidium, strontium, yttrium, zirconium, and niobium) that commonly vary among geologic deposits and are therefore frequently employed in archaeological raw material sourcing studies.

Using this configuration, elements present in the underlying rock surface to a depth of up to roughly 4 mm are also detected. Therefore, control readings from the surrounding natural rock surface were also taken. When possible a control data point in close proximity to the pigment reading was collected for each location that was sampled within the painted areas. However, as a result of time constraints it was necessary to decrease the rock surface readings, and the subsequent analyses employ grouped control readings.

In the second instrument setting the analyzer was set to operate at 15 KeV and 12 µA. A titanium beam filter was inserted, and a vacuum was employed to remove air from the device. This configuration facilitates the detection of low atomic weight elements that are the primary constituents of lithic materials (e.g., silicon, calcium). Although it is not possible to detect elements lighter than magnesium, this setting increases the sensitivity to elements between magnesium and iron on the periodic table. In this configuration, it is only possible to detect elements on or near the surface of the rock, which limits contamination of the pigment data by elements present in the natural underlying rock face. Depending on the thickness of the pigment, however, it is still possible that the atoms in the natural rock face will also be detected by the instrument. Therefore, control data points were also collected from the unmodified rock face following the procedures described above for the 40 KeV readings.

In order to analyze variation in the composition of the pigment within a given pictograph, where possible a minimum of three readings for each of the two instrument settings were collected from each analyzed element. As a result, for most elements more than 6 readings were collected per pictograph. Including the control data points, a total of up to 12 readings were collected for each analyzed pictograph. Each analysis was conducted for 150 seconds, resulting in roughly 30 minutes of EDXRF data collection per analyzed pictographic element.

Data Analysis

The raw spectral data collected using the two analysis settings were normalized using the inelastic (or Compton) peak of the rhodium backscatter at 19.4–22.3 KeV. These X–rays are produced by the sample scattering a small portion of the incident X-ray beam back into the detector, and are therefore theoretically constant if the specimen is "infinitely" thick (i.e., thicker than the depth that rhodium X–rays can penetrate through the natural rock matrix) and the X–ray tube produces the same number of X–rays per unit time. This procedure controls for error introduced by uneven surfaces where space exists between the rock art panel surface and the EDXRF aperture, as well as the slight variances in the X–ray beam intensity.

Data analysis included both visual examination of the raw spectral data, and statistical examination of the normalized elemental X-ray count data. Because of heterogeneity in natural rock surfaces at Picture Cave, the X–ray count were not converted into concentrations in parts per million (ppm values) for the elements present. Instead, the X-ray counts data were normalized and variations within the data were-analyzed. "This semi quantitative method is equally useful, and in some cases is more reliable than the quantitative method which is conventionally applied" (Miksic et al. 1994:32).

EDXRF Analyses Results

Because the instrument settings affect the X–ray count results, the titanium filter (15 KeV) data and the rock filter (40 KeV) data are considered separately in the following analyses. The natural rock at Picture Cave consists of limestone, the compositional of which is heterogeneous. Consequently, the control readings taken from areas that appeared to be unpainted are highly variable. Furthermore, elements present in the pigments also occur in the natural rock substrate. Although these factors complicate analyses of the EDXRF data, it is still possible to identity significant variation in the compositional data.

Picture Cave Rock Filter Data

T–tests for Equality of Variances indicate that arsenic (Figure 3, p=0.016, equal variances not assumed), iron (Figure 4, p=0.000, equal variances not assumed), copper (Figure 5, p=0.013, equal variances not assumed), and zinc (Figure 6, p=0.003, equal variances not assumed) are significantly different in the pigment and the control sample 40KeV readings. This suggests that the pigment used to produce the pictographs contained arsenic, iron, copper, and zinc. However, as will be discussed further below, it also appears that the composition of the pictograph pigments varies within the site. Furthermore, it is highly probable that additional elements are present in the pigments as well, because the heterogeneity of the underlying rock surface complicates the detection of some elements that could be present in both the natural rock and the pigment itself. These data suggest that the pigments contained a substantial amount of iron, which is consistent with the use of ochre–based paint for the production of the pictographs at site.

Previous research has also identified copper, zinc, and arsenic in ochre samples from Arizona and Missouri. Popelka–Filcoff found that a consistent set of elements are associated with iron–oxides. She argues that "elements found to be associated with Fe, as well as important for distinguishing sources, generally were members of the first row transition metals and rare earth elements, with the addition of As and Sb" (Popelka–Filcoff 2006:170). She argues that these elements are likely to substitute for iron in the octa-

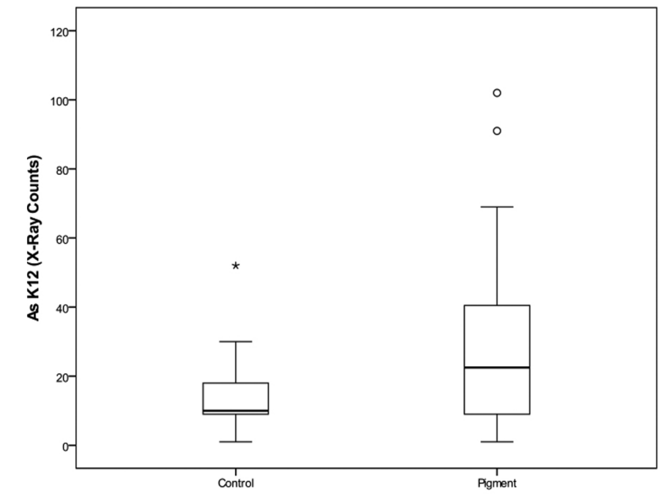

Figure 3. *Boxplots of arsenic X-ray pulses per analysis time (150 seconds) for control and painted locations at Picture Cave, 40KeV with rock filter.*

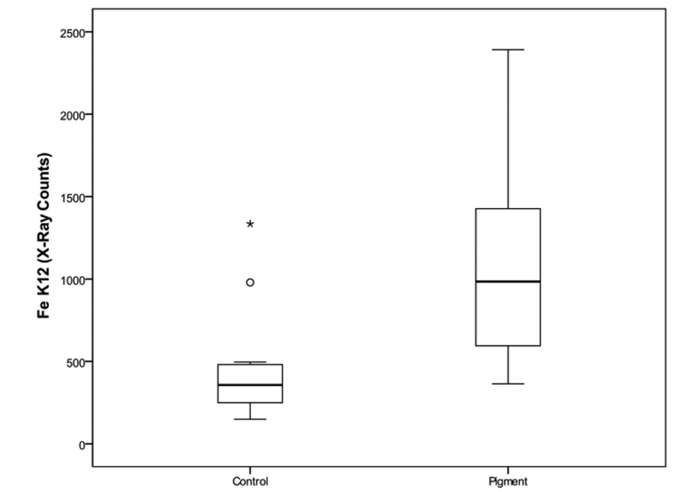

Figure 4. *Boxplots of iron X-ray pulses per analysis time (150 seconds) for control and painted locations at Picture Cave, 40KeV with rock filter.*

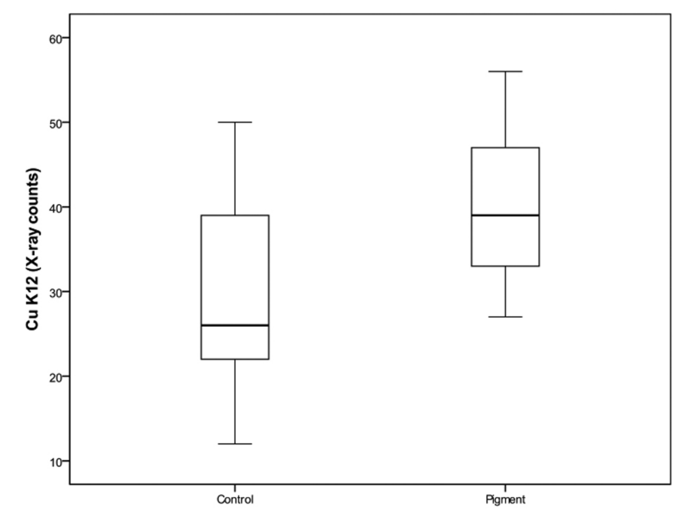

Figure 5. *Boxplots of copper X-ray pulses per analysis time (150 seconds) for control and painted locations at Picture Cave, 40KeV with rock filter.*

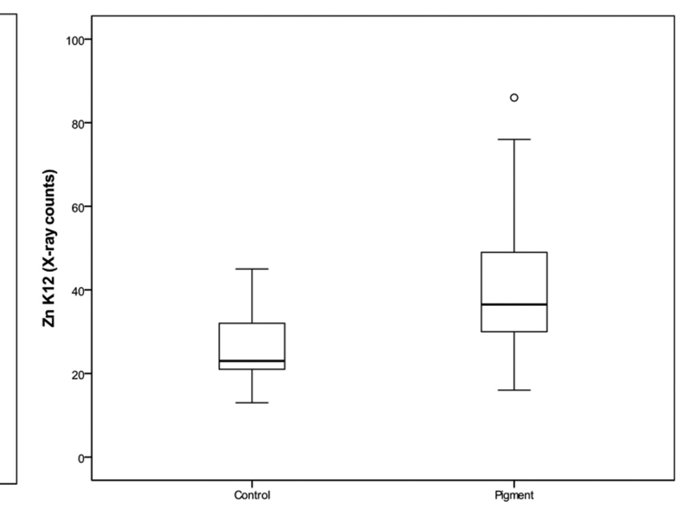

Figure 6. *Boxplots of zinc X-ray pulses per analysis time (150 seconds) for control and painted locations at Picture Cave, 40KeV with rock filter.*

hedral structure of ochre. Further, she maintains that the substitution of transition metals may produce color variation among ochres, which may have affected the selection of pigments from different sources. She also suggests that the acidity of the iron may effect the substitution of elements, and "[a]t higher pH, iron may act as more of a soft acid, with larger atomic radii and lower charges, with the substitution of As, Sb and other soft acids more likely" (Popelka–Filcoff 2006:171).

Variation among the pigment readings suggests the possibility that separate figures in the rock shelter were produced using different pigment mixtures (Figure 7). Figure 8 presents boxplots for arsenic X-ray count data by rock art figure. Rock art figures on Panel 9 and Panel 1 including AA, BB, HH all have lower readings on average for arsenic suggesting these figures were made from pigments that contained less of this material. Figures CC, K, V, and Y on Panel 1 and the elements on Panel 8 all have higher X-ray count readings suggesting they may have been made from a different pigment mixture that contained more arsenic. Interestingly, elements AA, BB, and HH are all located on the right side of Panel 1, while figures K, V, and Y are all

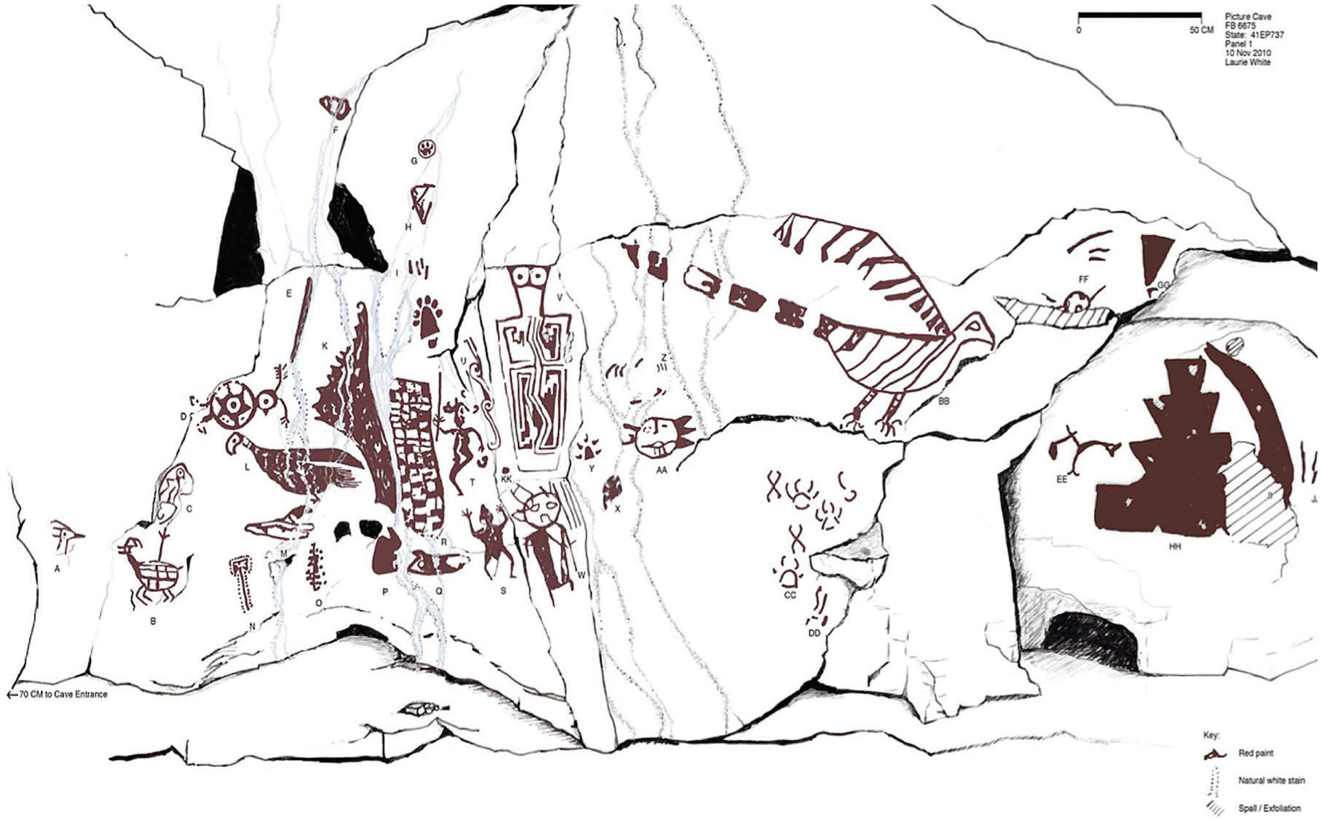

Figure 7. *Panel 1 at Picture Cave (illustration by Laurie White).*

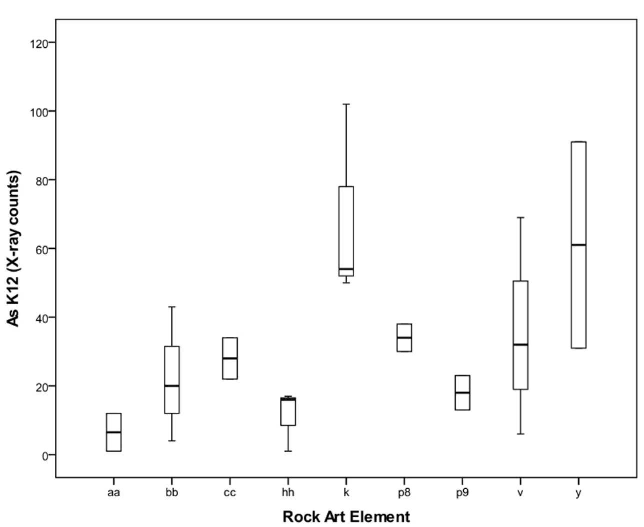

Figure 8. *Boxplots of arsenic X-ray pulses per analysis time (150 seconds) by prehistoric rock art element at Picture Cave (letters are for elements on Panel 1), 40KeV with rock filter.*

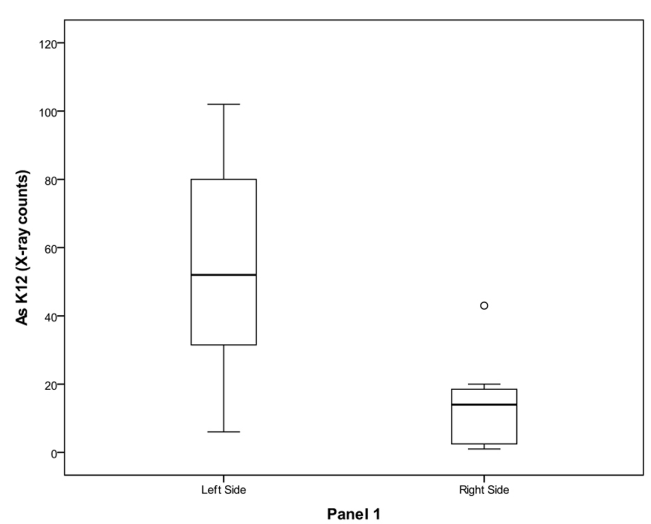

Figure 9. *Boxplots of arsenic X-ray pulses per analysis time (150 seconds) by the side of Panel 1 at Picture Cave (excludes element CC), 40KeV with rock filter.*

on the left side of the same panel. Figure CC is the only element from the right side of Panel 1 that has a higher arsenic value.

In order to increase the sample size of readings it is necessary to combine elements from the two sides of Panel 1 (Figure 9). Values for the left and right sides of the panel are statistically significantly different, and the T–test for Equality of Variances probability is 0.009, equal variances not assumed. With the exception of iron (p=0.005, equal variances not assumed)

Figure 10. *Panel 8 at Picture Cave.*

Figure 11. *Panel 9 at Picture Cave.*

the readings for all of the other atoms are not significantly different for the two sides of the panel. Furthermore, the values for arsenic are not significantly different for the natural rock control readings taken on the two sides of the panel (T–test p=0.585, equal variances not assumed). This suggests the differences in the pigment readings are not exclusively the result of variation in the natural rock surface.

It is possible that the differences between the left and right sides of Panel 1 are the result of differential weathering. The elements on the left side are closer to the opening of the rock shelter, and there is evidence for differential exposure to water on the two sides of the panel. However, element CC is located on the right side and it has arsenic readings that are more similar to the left side elements, and the readings for other pigment constituents including copper and zinc are

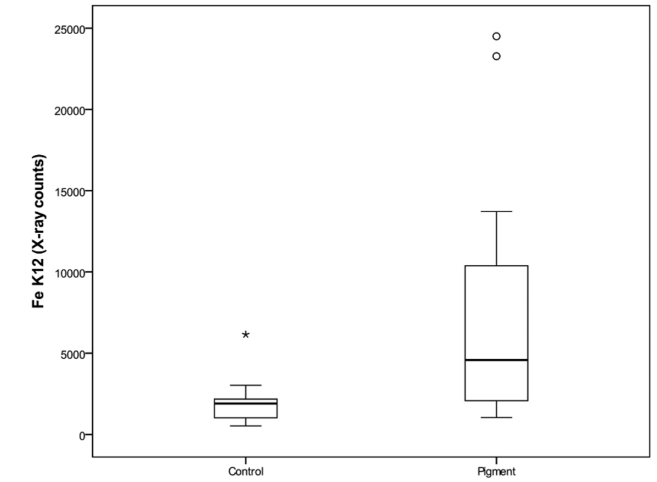

Figure 12. *Boxplots of iron X-ray pulses per analysis time (150 seconds) for control and pigmented locations at Picture Cave, 15KeV with Ti filter.*

not statistically different for the two sides of the panel. Although the sample sizes are small (two readings for each panel), it also appears that the arsenic values for Panel 9 are more similar to right side of Panel 1, while the readings for Panel 8 are more similar to the left side of Panel 1. Panels 8 and 9 (Figures 10 and 11) are both located along the back wall of the shelter away from the mouth, suggesting that location within the shelter alone does not determine variation in the pigment composition.

In aggregate, these data suggest that different ochre–based pigments may have been used to paint the pictographs at Picture Cave. Elements AA, BB, and HH on Panel 1 and Panel 9 may have been produced from similar pigments, while CC, K, V, and Y on Panel 1 and Panel 8 may have been produced from a different paint. It is possible that these figures were executed by different artists at a given time or at different points in time. With the available data it is not possible to rule out that differential weathering or some other factor may account for the apparent differences in arsenic values at the shelter, and additional research is necessary to further test the possible variation in the paint composition within the site.

Picture Cave Ti Filter Data

Of the elements detected using the Ti filter and 15 KeV X–rays at Picture Cave, only iron has statistically significant values for the pigment and control readings. The T–test for Equality of Variances for iron has a probability of 0.006 with equal variances not assumed (Figure 12). As previously observed, these data are consistent with the use of an ochre–based paint at the shelter. It also appears that stochastic variation in the background rock data masked the presence of other elements, and/or the paints used at the site did not include substantial amounts of the atoms between magnesium and manganese on the periodic table.

Conclusions

This study focused on the compositional analysis of rock art pigments employed at Picture Cave. These investigations confirmed that as previously assumed, pigments used at the site consisted of ochre. It also appears that the paint used at the site did not include substantial amounts of the atoms between magnesium and manganese on the periodic table, and/or stochastic variation in the background rock masked the presence of these elements.

Analysis of the EDXRF data also identified possible variation in the chemical composition of paints that may be related to temporal and/or synchronic variation among the pictographs at the site. The results of the 40KeV analysis proved to be more analytically useful, and iron is the only light element that varied significantly between the control and pigments readings taken using 15KeV, the Ti filter, and the vacuum attached.

Spectral data collected from Picture Cave suggest the possibility that figures on the right side of Panel 1 and Panel 9 may have been created using one type of paint that contained comparatively little arsenic. Figures on the left side of Panel 1 and Panel 8 may possibly have been produced from a different paint mixture that included more arsenic. This patterning suggests the possibility that figures at the site were executed by different artists at a given time, and/or over the course of time. Additional data, including further characterization of the natural rock surfaces and pigmented areas are necessary to evaluate this possible variation.

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