

CHARACTERIZING LATE PRE-CONTACT MISSISSIPPIAN PAINT RECIPES
IN THE SOUTHEASTERN UNITED STATES

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Degree

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To a house full of boys who drive me crazy and keep me sane.

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ABSTRACT

In the southeastern United States, paint was ever-present during the Mississippian period (A.D. 1000-1600). People used it to decorate and/or sanctify a variety of media including mounds, structures, pottery, textiles, statuary, rock and cave art, and even the body. While many scholars have focused on deciphering paintings and motifs, little attention has been directed towards understanding the composition of the paint. This in large part is due to the destructive nature of traditional analytical analysis techniques that required a sample to be taken from the artifact. Recent technical advancements, however, have led to analytical instrumentation capable of providing compositional data rapidly, *in-situ*, and completely non-destructively.

In this dissertation, I use two such instruments, portable X-ray fluorescence spectrometry (PXRF) and fiber-optic reflectance spectrometry (FORS) to examine the constituents of Mississippian period paints from three groups of archaeological media: rock art, stone statuary, and pottery. The goal of this research is to reveal the constituents or ingredients artists selected for the manufacture of paints and to determine if paint recipes differ with respect to archaeological context. A second objective is to establish a solid methodology for analyzing archaeological materials using PXRF and FORS techniques.

Results indicate that late prehistoric paint recipes vary in a few select cases across the archaeological media analyzed. The basic recipe consists of a chromophore that was mixed with water before being applied to the media. Red and yellow paints were created using hematite, goethite, or limonite as chromophores, while organic (vegetal) carbon was used to create black paints. In some cases of red paint, evidence for the addition of manganese and gypsum minerals was also identified. All of the ingredients found to make paints were readily available in the landscape. Variations in paint recipes found can be attributed to the technical functions they may

have served for the performance of the paint or they could be indicative of culturally symbolic additions. In addition to unraveling paint compositions, this dissertation highlights the efficacy of using non-destructive techniques like PXRF and FORS to garner the physical material characteristics of precious cultural heritage materials.

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CHAPTER I: INTRODUCTION, BACKGROUND, AND RESEARCH QUESTIONS

Paint has been used as a medium to convey meaning for as long as people have been making marks (Siddall 2018). Since their discovery in Europe the famous early cave paintings such as Lascaux, Chauvet, and Altamira have fascinated archaeologists and the public. Images depict animals with striking realism in vibrant colors and were selectively placed by the painter in locations to create a complete artistic composition, or story, as the visitor maneuvers through the cave passages. These artistic compositions, however, are not the earliest representations of pigment manufacture and use in the archaeological record. The use of color, or pigment, dates as far back as the Middle Stone Age in Africa, ca. 100,000 years ago to Blombos Cave in South Africa. This site has the earliest example of modified pigment in the form of mineral hematite, along with evidence of paint preparation (Henshilwood et al. 2011). Artifacts found at the site include a small carved slab of ochre along with a pigment processing kit (containing ochre pieces, bone, charcoal, grindstones, and hammerstones), and evidence for a liquefied ochre-rich mixture that was stored in abalone shells (Moyo et al. 2016). It is from these beginnings that we see pigments used in a variety of archaeological contexts throughout the world.

The rich history of pigments and paints is not limited to the Old World. Those traditions were carried with peoples as they dispersed into the New World ca. 14,000 years ago. The earliest evidence for the use of paint in North America comes from the Cooper Bison Site in Oklahoma. The Cooper Bison site is a stratified large-scale bison (*Bison antiquus*) kill site dating to the Folsom culture ca. 12,800-12,100 cal yr. BP. In addition to the stone tools and well-preserved bone beds, one skull is adorned with a red zigzag painted design (Bement 1999:51; Carter and Bement 2003). In addition to paint, early contexts of ochre use are also dated as far

back as the Paleoindian. The Gordon Creek site in northern Colorado and the Anzick site in Montana both represent mortuary contexts where burials were covered with powdered red ochre (Anderson 1966, 1967; Lahren and Bonnicksen 1974). Occurrences of red ochre have also been reported in a variety of other contexts during this period including habitation floors, in caches, on the surfaces of grinding stones, on the bones of big game animals, and on tools that were used to kill and process animals from a variety of Paleoindian sites in the Plains region of North America (Roper 1991:293-297). In the southeastern region of North America, the earliest evidence for prehistoric pigment is from the 48th Unnamed Cave site in Tennessee that contains a black charcoal pictograph dating to nearly 6,000 years old (Simek and Cressler 2009). In fact, many areas in the Southeast contain deeply rooted and complex pre-Contact art traditions (Charles 2010; Coy et al. 1997; Diaz-Granados and Duncan 2000; Faulkner et al. 1986, 2004; Henson and Martz 1979; Sabo and Sabo 2005; Simek et al. 2013).

While rock art traditions in the Southeast date back as far as the Archaic period, much of the corpus of painted rock art was made during the Mississippian period (ca. A.D. 1000-1600). This period was characterized by large earthen platform mounds with associated structures on top and villages arranged around a centralized plaza, increased populations with organized chiefdom level societies, a dependence on corn agriculture, changes in pottery styles (Chapman 1977, 1985; Faulkner 1988, 2002; Griffin 1967; Lewis and Kneberg 1946; Lewis et al. 1995; Pauketat 2012), and increased territoriality and warfare (Dye 2009; Smith 2007). Additionally, during this time art, iconography, ritual, and exchange became more prominent in the archaeological record. Manifestations of religious practices included a variety of distinct iconographic motifs (Reilly and Garber 2007), animal forms, ceremonial objects, costume embellishments, and human forms. These were entrenched in how Mississippian cultures viewed

their cosmos: a layered universe, with a middle world occupied by people, plants and animals; an upper world of sky spirits associated with light and life; and an underworld of powerful spirits associated with darkness, death, and renewal (Lankford 2004, 2007; Reilly 2004).

It is in this cultural context of the Mississippian period that paint, or more appropriately color, becomes more prominent in the archaeological record, and it can be found in each ‘layer’ of the Mississippian universe. Color is also tied to this cosmology; color symbolism for instance plays an important part in the shamanistic system of the Cherokees (Mooney 1891:342). While there is diversity in the color systems used among different groups of the Cherokee, black was generally taken as a symbol of death, while red was associated with life (Hudson 1976; Mooney 1970). Hudson (1976) describes directionality as being tied to colors. The east is Sun, red, sacred fire, blood, life, and success; the West is Moon, the souls of the dead, black, and death; North was cold, blue and purple, trouble, and defeat; South was warmth, white, peace, and happiness; North or the “upward” direction was brown. Yellow is attributed with trouble, although the direction is unclear (Hudson 1976:132). The Creek used reds for medicines (“Red Medicines”), such as the “red root” derived from the inner bark of the root of a species of willow, and red cedar (Hudson 1976:340-341).

This color symbolism can also be viewed in the archaeological record. Pre-Contact earthen mounds, constructed to access the upper world, were not covered in grass as was long believed but rather created and capped with colored earth (Anderson 2012; Pursell 2004; Sherwood and Kidder 2011). Reds and whites especially were used to symbolize with color their important role in human interaction with the spirit world (Pursell 2013). Work by Simek et al. (2013) has demonstrated that the caves (natural access to the underworld) and rockshelters (natural mounds on a gigantic scale) that occur across the Cumberland Plateau

region of Tennessee were sometimes painted to reflect this tiered Mississippian cosmology. Red images predominate high along the mountain rockshelters while black images are found primarily within the dark recesses of caves, reflecting a cosmogram on a very large scale (Simek et al. 2013:443). Color or paint permeated everyday life, weaving together the sacred and profane. Evidence suggests that structures built atop mound summits were painted, sometimes with elaborate designs (Barzilai 2017; Polhemus 1987:224). Paint was also used to decorate pottery vessels with colors ranging from red, yellow, white, and black (Cherry and Mainfort 2009; Hilgeman 2000; Steponaitis 2009[1983]). Paints were even used to decorate the body (La Flesche 1995[1932]; Radin 1923; Swanton 1922).

Paint was very common during the Mississippian period. The preceding examples represent only a small fraction of the totality of cases where pigments and paints were used by Mississippian cultures (Hall 1997; Knight et al. 2010; O'Brien and Wood 1998; Power 2004; Smith 2007; Smith and Miller 2009). Paint was used to decorate and/or sanctify a variety of media. While many scholars have focused on deciphering painted designs or motifs, very little attention has been directed towards understanding the technology of paint production itself and how that technology may enhance our overall understanding of how Mississippians used the paint. Colors, motifs, and the manner and timing of paint applications are all a part of a culturally defined communication code (Brain 1979; Ebin 1979). In this regard, paint itself reflects social, religious, and political systems.

In this dissertation, I examine the constituents of Mississippian paint through two relatively new non-destructive analytical techniques, portable X-ray fluorescence spectrometry (PXRF) and fiber-optic reflectance spectroscopy (FORS). The goal of this research is twofold—to reveal paint constituents, or ingredients, used on a variety of archaeological media and to

establish a scientific methodology for analyzing paints using PXRF and FORS. Each chapter in this dissertation represents a case study for different painted archaeological media. Although each chapter provides enough background information to establish the necessary context, the remainder of the introductory sections are devoted to an overview of the physics of PXRF and FORS, their advantages and limitations, and a literature review of the relevant materials analyses that have been conducted on prehistoric paints. Finally, I conclude the chapter by defining specific research hypotheses and goals for this dissertation.

Portable X-Ray Fluorescence Spectrometry (PXRF)

X-ray fluorescence spectrometry is a well-established analytical technique for the qualitative and quantitative elemental analysis of a wide range of materials in both industrial and research realms. I discuss specific instrumental parameters briefly in each research chapter of this dissertation, a full overview of the physics behind PXRF, specific instrumental parameters, and a summary of the advantages and limitations of PXRF in archaeological studies is intended to lay a foundation for the following chapters.

All portable, handheld XRF instruments work under the same basic principles of X-ray physics regardless of the instrument manufacturer. The analysis of major, minor, and trace elements is based on the behavior of atoms when they interact with radiation. Residing in the region between gamma rays and ultraviolet radiation, X-rays are a short wavelength (high energy-high frequency) form of electromagnetic radiation (Jenkins 1999; Jenkins and Vries 1973) (Figure 1).

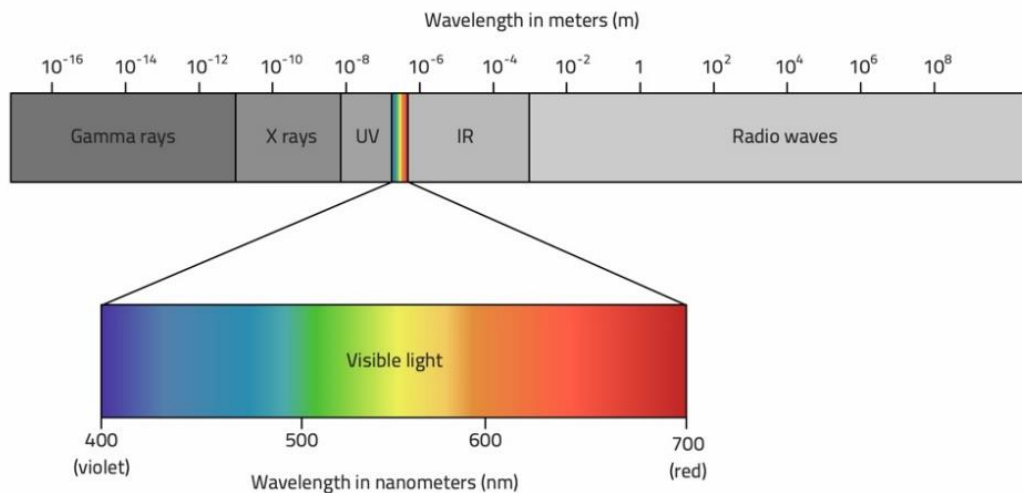


Figure 1: Diagram of the electromagnetic spectrum.

PXRF uses a beam of X-rays to irradiate the surface of a specimen. If the energy of the incoming radiation is sufficient, it will dislodge a tightly held inner electron in the atom of an element. Once an electron is dislodged from its orbit, the atom becomes unstable and an outer shell electron will move to fill the vacancy. This transference of an electron from an outer shell to an inner shell releases energy commonly referred to as *fluorescence* in the vernacular (Jenkins 1999; Jenkins and Vries 1973). Figure 2 depicts this transference. For example, when a K shell electron moves out of the atom entirely it is replaced by an electron from the L line electron shell. X-rays of the highest intensity during these transitions are called alpha transitions. The movement of an L shell electron to a vacancy in the K shell emits $K\alpha_1/K\alpha_2$ radiation and is the most frequent transition, resulting in the most intense and easily measured peak (Shackley 2011:17). Based on these principles, it is possible to determine the composition and proportional concentrations of elements in a sample by bombarding it with radiation that exceeds the binding

energy of the electrons in the atoms and detecting the energy and characteristic X-rays emitted from each element.

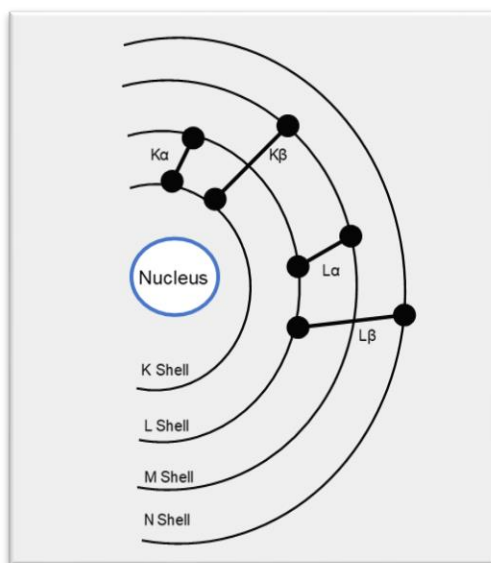


Figure 2: Schematic view of orbital transitions due to X-ray fluorescence.

There are several types of X-ray fluorescence spectrometers. Recent advancements, however, have led to the rapid development of high precision handheld, or portable X-ray instruments. For this dissertation, I used a Bruker Tracer III-V and Tracer III-SD models. The Tracer III-V is based on SiPIN detector, while the III-SD has a proprietary X-Flash Silicon Drift Detector (SDD) providing enhanced speed and sensitivity. Both models have a rhodium X-ray source, enabling the identification of most elements heavier than magnesium with a spectrum from 1-40keV. The X-ray tube is used to excite the specimen with X-ray photons, which are in turn used to excite secondary X-ray photons characteristic of the atoms present in the specimen. The resulting spectrum is recorded with the instrument detector and software converting the incoming pulses to a spectral waveform.

Due to the attenuation of low-energy fluorescence X-rays, elements lighter than silicon on the periodic table cannot effectively be detected. Attenuation in the air also occurs for elements whose atomic weight is lighter than calcium on the periodic table. To mitigate this problem, I used a small portable vacuum pump during all analyses in this dissertation. The vacuum pump functions to displace the air path within the instrument, reducing the effects of attenuation that occur between the surface of the specimen and analyzer window (Potts and West 2008:8). I made Every effort to reduce the space between the specimen and the analyzer window to reduce the magnitude of any additional air attenuation. Those elements with the highest sensitivity are from the K-line series with absorption edges just below the energy of the characteristic emission lines from the excitation source.

A flat specimen surface is ideal as it is more properly aligned with the analytical plane of the instrument. In this regard, archaeological samples can present a unique challenge for analysis. In this dissertation, I made every effort to approximate this ideal condition. For the irregular and curved surfaces of rock art and statuary, the nose of the instrument was maneuvered in such a way that the analysis plane, or window, aligned perpendicular to the location being analyzed. A flat plane on pottery sherds was easier to obtain. In instances of curved pottery sherd surfaces, a flat plane could be achieved over the window by placing a small weight on top of the sherd to hold it down and keep it flush with the analysis window.

Once a sample is analyzed, the resulting analytic spectra can be qualitatively evaluated for the presence or absence of elements and relative quantities of elements in relation to one another. Spectral data can also be converted into numbers suitable for quantitative and semi-quantitative analyses. Qualitative analysis comprises basic element identification and relative comparisons of similar samples. Quantitative analyses are somewhat more difficult because they

require a set of calibration standards. Several assumptions must also be met for these calibrations to work. Firstly, the data must be homogenous, or sufficiently well mixed to be practically homogenous. Secondly, the reference set used to create the calibration must consist of the same material. Lastly, every element present in the sample must also be present in the reference set, and that reference set must encapsulate the minimum and maximum of every element. In addition to the above parameters, data must be taken with the same instrumental parameters (i.e. the same energy, current, filter, and atmosphere). If these requirements are met the PXRF data can be translated to quantitative chemical units, which can, in turn, be used to source materials. Paint is a cultural material and inherently variable in composition. While a few internationally accepted calibrations exist for heterogeneous matrix materials like sediments and rocks (Rowe et al. 2012), they are still inadequate for the application of a range of archaeological cultural materials. In addition, this dissertation does not seek to *source* prehistoric paints or their materials. Instead, the goal is to characterize the ingredients used in the creation of prehistoric paints and examine the variability of paint recipes from different cultural contexts. Toward achieving this goal, a semi-quantitative analysis is appropriate. While empirical calibrations can be used to provide highly accurate results, using a calibration does not add any new information that was not already present in the raw spectral data. A calibration simply translates the variation present in the spectra into chemical weight percentiles (quantitative data). In this research I observed the presence and absence of elements to provide qualitative data interpretations. Additionally, I conducted a semi-quantitative spectral evaluation using ARTAX 7. This software converts spectra using Bayesian Deconvolution to determine net peak areas (NPAs) of the elements present in the analyzed specimen. The software deconvolutes each spectrum through stripping routines that calculate the intensity of each element of interest and “strip” them from

overlapping elements to eliminate matrix effects (i.e. mass absorption and overlap effects) that can occur during analysis (Lachance and Claisse 1994; Shackley 2011:21). The resulting NPAs represent the net photon count for each element.

The advantages of using PXRF combine both practical and economic factors. First and foremost, this elemental technique is completely non-invasive and non-destructive, perhaps the most important factor in analyzing sensitive cultural materials. Other analytical techniques like Instrumental Neutron Activation Analysis (INAA) and traditional benchtop XRF systems require samples of the target materials to be removed and ground, homogenized into powder before analysis. While samples can be ground for PXRF analysis, if proper parameters and methods are used, the reliable and accurate elemental composition can be obtained without any prior destructive preparation to the artifact. Shugar and Mass (2012) provide an excellent overview of various methodologies, protocols, and limitations of PXRF in dealing with the complexities of individual archaeological materials. As the name suggests, PXRF is highly portable (handheld), allowing for *in-situ* analysis of artifacts that may or may not be removed from their location in museums or those that are physically immovable like rock art. PXRF analyses are also rapid. Raw chemical composition data can be obtained in a matter of minutes depending on the mass of the specimen and elements under analysis. This combination of portability and rapid analysis enables operators to make real-time judgments about what materials to analyze next, an interactive sampling and analysis capability that can have immediate results on shaping interpretations of artifacts in the field. All of these advantages culminate in the ability to provide a high precision analysis for multiple elements within a single sample. The advantages of PXRF are not limitless. Since PXRF instruments broke onto the archaeological scene in the early 2000s, several articles and books have cautioned the use of PXRF as point-and-shoot, all-knowing black

box of information (Shackley 2010). PXRF analysis of cultural materials is complex and does require careful consideration of physical matrix effects (i.e. related to particle size, surface irregularity, sample mineralogy, and moisture), chemical matrix effects (including absorption and enhancement), and spectral interferences, especially when conducting quantitative analyses for tying source locations to artifacts. Speakman and Shackley warn that “it is the user who is ultimately responsible for accuracy and reproducibility” (2013:1439).

PXRF provides surface analytical measurements and while a variety of factors can influence the penetration depth of X-rays, the instrument identifies the composition of the surface layer with greater sensitivity than the bulk. This makes PXRF an ideal analytical technique for analyzing elemental constituents of prehistoric paint. However, there are factors to consider during the analysis of prehistoric paints. Natural weathering and post-depositional processes can affect the paint layer thickness on a surface. If the paint is not sufficiently thick, there is potential for X-rays to penetrate through the paint layer and into the underlying material. While thick and prominent paint layers were selected for the analyses in this dissertation, additional PXRF readings were acquired from all of the unpainted, substrate material. These readings serve as an elemental controls and aid in determining true paint constituents. Additionally, as will be seen, these readings can provide other, unanticipated information.

Fiber Optic Reflectance Spectroscopy (FORS)

Reflectance spectroscopy involves the differential reflection and scattering of light as a function of wavelength (Hapke 2012:27). Reflectance spectroscopy is used by a range of scientists such as geologists, meteorologists, geographers, and agronomists. It is also commonly employed by planetary scientists to learn about the surfaces and bodies within our solar system.

FORS has also been used in art examination and art conservation for at least the last two decades for the identification of pigments (Cavaleri and Nervo 2013; Cheilakou et al. 2014; Galeotti and Mazzeo 2009; Picollo et al. 2000) and dyestuffs (Gulmini et al. 2013). Reflectance spectroscopy can be used to identify materials through different sections along the electromagnetic spectrum including the visible, near-infrared, and thermal-infrared regions (see Figure 1), and while the information obtained from these regions corresponds to different molecular information, the physics behind the spectroscopy is similar.

Reflectance spectroscopy can generally be defined as the ratio of the irradiance (amount of light) coming off an object to that which is incident (light that illuminates a surface). Measurements are done in reference to a white standard, providing data for the apparent reflectance of the object being analyzed. Technically, FORS uses fiber optic cables to project the incident beam into the sample where it is reflected, scattered, and transmitted through the sample material. The light is reflected back towards the source, collected by the fiber optic cable and directed to the detector optics. Spectral software depicts this data as a waveform shape comprised of reflectance maxima (peaks) and absorptions (valleys) that can be broad or narrow features.

Matter is composed of atoms that are held together by covalent and electrovalent bonds to form molecules. The nature of these bonds is what enables them to vibrate with a characteristic frequency. Without any external excitation, bonds will be in their normal mode of vibration or their ground state. However, when these bonds are excited by an external source, the potential exists for an energy change to occur if the bond is capable of accepting the energy based on quantum mechanics (Buaman 1962). These changes can be manifested by four different types of energy states: translational, rotational, vibrational, and electronic. Different amounts of energy

are required for each of these types of transitions, resulting in their manifestation in different parts of the electromagnetic spectrum. Pertinent to FORS analysis are vibrational and electronic transitions. Vibrational energy occurs when two atoms move relative to each other (Farmer 1974; Gupta 2003:36). The frequency of vibration depends on the strength of the bond in a molecule and their masses. The electronic energy state is related to the configuration of electrons surrounding the nucleus. Emission of a photon occurs as a result of a change in an energy state to a lower one (Burns 1993; Clark 1999). Vibrational energy level changes occur in the thermal-infrared and short-wave infrared regions, while electronic energy level changes occur in the visible, near infrared, ultra-violet, and X-ray regions. Other phenomena related to FORS include fundamental absorption, overtones, and combination bands. Fundamental absorption is a normal mode of vibrations. Each vibration can also occur at roughly multiples of the original fundamental frequency (Clark 1999). These are referred to as overtone when they involve multiples of a single fundamental mode, and combinations when they involve different modes of vibrations. Overtone bands are harmonics that specifically occur at frequencies that are integer multiples of the fundamental frequency of an absorption. Combination bands are formed at frequencies that are the sum of the two fundamental frequencies.

The visible and near-infrared region (VNIR) occurs at 400 nm—1000 nm and spectral features here are dominated by electronic processes in transitional metals. Iron is the most important constituent having properties in this region. Due to the charge-transfer effect—where energy is absorbed, raising the energy level of electrons so they migrate between adjacent ions but do not become completely mobile—iron spectra result in a steep fall-off in reflectance towards visible blue and a rise towards infrared (Sherman and Waite 1985). The short-wave infrared region (SWIR) region encompasses 1000nm—3000 nm on the electromagnetic

spectrum. Many rock-forming mineral groups (silicates, oxides, carbonates, phosphates, sulfates, nitrates) have molecular vibrational processes in the SWIR (and Thermal Infrared, TIR) parts of the electromagnetic spectrum and are the result of bending and stretching molecular motions distinguished as fundamentals, overtones, and combinations. This region contains spectral features of hydroxyls and carbonates. Hydroxyl ion, a widespread constituent occurring in rock forming minerals like in clays and micas, has a vibrational fundamental absorption band at around 2740-2770 nm and an overtone at 1440 nm. These features interfere with similar features observed in water molecules (at 1400 nm and 1900 nm). If hydroxyl ions occur in combination with aluminum and magnesium (as they do in some clays for example), several sharp absorption features can be seen in the 2100- 2400 nm region (Gupta 2003:39-42). If clays are present, there will also be a sharp decreasing spectral reflectance beyond 1600 nm (Abrams et al. 1977). Carbonates also have features produced by combinations and overtones in the SWIR region at roughly 1900 nm, 2300 nm, and 2550 nm. Features at 1900 nm and 2300 nm can interfere with water and clay spectral features. To confirm carbonates, a combination of features at 1900 nm and 2350 nm and an extra feature at 2500 nm can be diagnostic.

The instrument I used in this research is an ASD FieldSpec 4 Standard-Res Spectroradiometer, manufactured by Malvern Panalytical. It is fully portable and is used in a wide range of remote sensing applications for a range of industries. It is capable of collecting spectral data in the visible, near-infrared, and short-wave infrared ranges—350-2500 nm in 2151, 1-nm spaced spectral bands. The spectral resolution at 700 nm is 3 nm, while at the 1400/2100 nm it is 10 nm. Scanning time occurs in 100 milliseconds, enabling rapid data collection in the field. There are three detectors in this instrument, one visible-near infrared (VNIR) and two short-wave infrared (SWIR). A 1.5 m fiber optic cable is attached with a default sensor field of

view of 25°. In addition to the base instrument, an ASD Muglight is fitted to the end of the fiber optic cable to gather reliable reflectance and absorbance measurements, while mitigating measurement errors associated with stray light and specular reflected components. To this, a neoprene sleeve was added to the Muglight to provide a soft buffer between the Muglight and the artifact being analyzed. The Muglight enables accurate measurements regardless of outside or inside lighting conditions. It is equipped with a tungsten quartz halogen bulb to provide the artificial light source.

Materials analyzed by reflectance spectrometry can range from simple to highly complex. Bruni et al. (2005) compared fiber optic visible-NIR reflectance spectroscopy to Raman spectroscopy on a 16th-century Italian fresco and found that visible-NIR spectra are easy to acquire and characteristic for different pigments. In particular, they were able to confirm red as ochre and yellow pigments as yellow ochre. They cautioned, however, that fiber optic visible-NIR spectroscopy can identify pure pigments but is less useful when mixtures of pigments are encountered. Minerals consist of combinations of cations and anions which may occur as major, minor, or trace constituents in the reflectance data. Similarly, rocks—aggregates of minerals—are highly complex and variable. It is possible, however, to broadly describe spectral characters of both. As with the PXRF instrument, I took readings with the ASD FieldSpec 4 on both paint and on bare, unpainted surfaces as controls to aid in mineral characterization. Unlike the numerous archaeological analyses using PXRF in recent years, FORS is relatively new to the discipline of archaeology.

Pre-Contact Paint Compositional Analyses

This section is intended to provide a review of the relevant literature to highlight the variety of analytical methods that have been used in prehistoric pigment compositional studies, and to underscore the kinds of information that can be garnered from such studies. The primary objective of compositional analyses is to identify groups or, for the purposes of this dissertation, related raw materials, that provide insight into archaeological questions. Although different methods and techniques are described, all of them use the analytical techniques to generate chemical “fingerprints” that enable the identification of materials. This information, in turn, can be used to examine material components, variability, and source materials. In some instances, they are also applied to artifact authentication and certainly to the conservation and preservation of cultural materials.

The history of compositional studies of archaeological materials was pioneered by scientists in the sixteenth through eighteenth centuries (Caley 1951; Harbottle 1982; Hudson 1992; Pollard and Heron 2008). Many of these early analyses were on metallic alloys, glass, and ceramics using gravimetric methods. Gravimetry involved “the determination of elemental composition through the weighing of an insoluble product of a definite chemical reaction involving that element” (Pollard and Heron 2008:3), which limited these early studies to the identification of one element at a time. It was not until the 1920s and 1930s that new instrumental methods like optical emission spectroscopy (OES) were developed, enabling scientists to determine multiple trace elements with greater sensitivities (Glascock 2016). From the 1950s until the present, the number of scientific techniques has grown significantly. Many spectroscopic methods are based on the interaction of energy with matter, involving the electrons surrounding the nucleus, followed by the emission, absorption, transfer, or reflection of energy

as light. Other techniques involve the excitation of the atomic nucleus. Techniques based on optical wavelengths in the visible (or near visible) region include optical emission spectroscopy (OES), atomic absorption spectrometry (AAS), inductively coupled plasma emission spectrometry (ICP-AES, sometimes referred to as ICP-OES, meaning optical emission spectrometer; and sometimes coupled with Mass Spectrometry, ICP-MS). Techniques using X-rays include X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), proton-induced X-ray emission (PIXE), and scanning electron microscopy (SEM). Other methods employed in compositional analyses include neutron activation analysis (NAA), chromatographic techniques, such as gas chromatography (GC), and a range of infrared and Raman spectroscopy (IR), the most common of which is Fourier transform infrared spectrometry, FTIR. For techniques that use spectrometry, mass spectrometers (MS) can be used as a more sensitive detector for an established technique, such as ICP-MS. While this list is not exhaustive, it does highlight the range of analytical techniques that can be employed with each providing unique compositional data to answer questions concerning of archaeological materials.

Specific to paint studies, a range of these techniques have been employed by researchers to analyze rock and cave art, painted pottery, and a variety of other painted media. These in turn are described below with consideration given to a range of analytical methods including destructive, minimally destructive, and non-destructive techniques.

Rock and Cave Art

In the American Southeast, Carstens and Knudson (1959) conducted the first paint analysis on rock art was conducted by Carstens and Knudson in 1959. They used a 1.5 m A.R.L. Emission Spectrometer with a high precision source using a D.C. arc to analyze six pigment

samples, from three different archaeological sites in Alabama and Tennessee. Nearly identical results were reported for each of the samples showing strong spectral evidence for iron and faint traces of other metals. Although they could not determine whether the trace metals were present in the pigments or from the rock substrate, they concluded that the red paints analyzed were nearly pure hematite, and the yellow paints were identified as an ochre or limonite (Carstens and Knudson 1959:52-53).

One of the sites included in the Carstens and Knudson (1959) report, Paint Rock, was separately analyzed by Loubser (2007) using SEM coupled with energy-dispersive spectroscopy (SEM-EDS). The Paint Rock site sits at the Tennessee-North Carolina border and contains two separate art panels. The first panel lies in Tennessee and was sampled by Carstens and Knudson described above. The other panel is a single, bi-chrome rectilinear image situated some seven meters high on the bluff face in North Carolina. Loubser (2007) collected three small samples (two from the red and one from the yellow paint) and conducted a SEM-EDS analysis. Results revealed high quantities of iron in both the red and yellow paints and high quantities of sulfur and calcium in the yellow paint only. Bow and Simek (2014) later conducted a PXRF analysis of the same pictograph and found similar results. The red paint was primarily composed of iron, while the yellow paint contained high quantities of iron, sulfur, and calcium. The presence of sulfur and calcium in the yellow paint likely indicates the acquisition of the yellow pigment from the natural hot springs nearby; testing of the hot springs itself, however, has not been conducted (Loubser 2007).

Black pigments from Dunbar Cave, a Mississippian period site in Tennessee, were analyzed using SEM-EDS. Simek et al. (2012) found that the pictograph pigment differed from the limestone substrate only in the elevated presence of carbon. They found no other differences

or binder ingredients, which suggested that the images were created using raw charcoal pencils or charcoal mixed with water as a paint (Simek et al. 2012:23-24). A similar, simple paint recipe was also identified at the Painted Bluff site in Alabama using PXRF. Here, reds and yellows were created from an iron-rich ochre mixed with water to create a liquid paint (Simek et al. 2012, 2020). Historic paints were also identified at Painted Bluff based on historical descriptions, visual characteristics, and the presence of large quantities of lead in the elemental data.

In the Mid-South, work by Blankenship (2015) on black and red pigments sampled from Picture Cave, Missouri (Diaz-Granados and Duncan 2015) suggests clays may have been added to paint recipes; different application methods were also identified. SEM-EDS and electron microprobe (EMP) analyses were conducted to explore the microstructure and elemental composition of a sample of the paints and controls from the unmodified cave stone. Results indicated that black paints were created with burned wood, or charcoal, that were mixed with clay prior to its application to the cave wall. Red paints were manufactured with an iron-oxide mineral, likely hematite, and an iron-rich ochre. For the red paint, it was unclear whether clay was intentionally mixed with ground hematite or if clay was present as a naturally occurring component of the ochre itself. Different applications were also noted based on visual characteristics of the paint: one image was produced using a dry charcoal pencil, while other images were created with liquid paint. The overall conclusion drawn from the compositional analysis was that the pigments and paint recipes used in Picture Cave varied and represented distinctive mixtures by multiple people, temporal differences, or symbolic variations due to the images being portrayed (Blankenship 2015).

In Montana and Wyoming PXRF has been used to identify green paints by Newman and Loendorf (1999), who concluded that the chromium present in pictographs was sourced from the

mineral fuchsite. Furthermore, they identified lead in a series of pictographs from a site in south-central Montana, suggesting the images were retouched or repainted with modern paints to enhance their visibility. Black paints have also been characterized in Montana and Wyoming as being created with charcoal chromophores (Keyser et al. 2011; Steelman et al. 2001).

In California, rock art compositional analyses indicate variable paint recipes. In Baja California, paints do not contain any binders except for water, and the chromophores used to create red and orange pigments were mineral in origin (i.e. hematite), and the black was vegetal charcoal (Viramontes et al. 2008). Guitierrez and Hyland (2002), however, found black recipes at other sites in the region containing manganese chromophores and vegetal binders. In the Great Basin region of California, Whitley and Dorn (1999) conducted XRF and SEM analyses of red and white pigments. They concluded that red pigment was sourced from a nearby hot spring, while the white was from another unidentified source. Ethnographic data suggest hot springs were supernaturally potent places (like the rock art sites) and may therefore have provided important pigment sources (Whitley 2000; Whitley et al. 2005). Organic binders have also been identified in Chumash rock art in central California. Scott et al. (1996) used FTIR and GC-MS and identified a mixture of antelope and human blood added to black in a pigment cake.

A considerable amount of research has been conducted on the pictographs within the Lower Pecos region of Texas (Boyd 2003; Macrae 2018; Shafer 2003). Some early studies using XRD concluded that red pictographs were made using iron minerals and the black pictographs were made using manganese minerals (Hyman et al. 1996; Zolensky 1982). In recent years, PXRF studies on red, yellow, and black paints have shown varying recipes including the use of ochre and manganese minerals (Bu et al. 2013; Castañeda 2019a, 2019b; Koenig et al. 2014). Artists created reds and yellows using a myriad of iron oxide minerals, sometimes mixed with

manganese to create dark colored images. Blacks were created using primarily manganese, but some images were also created with charcoal-based pigments (Edwards et al. 1999; Koenig et al. 2014). Further PXRF testing on painted pebbles from the Lower Pecos Canyonlands indicate charcoal and iron-based mineral pigments were used by artists to create black and red painted pebbles respectively (Castañeda 2019b). Elsewhere in Texas, PXRF was used to recognize that prehistoric artists may have created red paintings using different ochre sources based on the amount of naturally occurring arsenic within the paint (Loendorf and Loendorf 2013). In Texas, ungulate blood has also been identified as a binder in paint recipes through polymerase chain reaction (PCR) amplification and phylogenetic analysis (Reese et al. 1996a, 1996b).

Studies in rock and cave art outside the United States contribute to a large part of the published materials research on paint. Paleolithic cave art in Europe has been investigated by a wide range of analytical techniques including XRF, NAA, SEM-EDS, and RS (Beck et al. 2014; Dayet et al. 2014; de Sanoit et al. 2005; Gay et al. 2016; Guineau et al. 2002; Lahlil et al. 2012; Nuevo et al. 2012; Olivares et al. 2013). Paleolithic cave art consists primarily of three colors—red, yellow, and black—that artists prepared in different ways like grinding, mixing with an extender and/or binder, or by heating to enhance the properties of the paints (Aujoulat 2004; Chamlin 2003; Pomies et al. 1999; Resano et al. 2007; Vandiver 1968). Reds and yellows were produced by artists with iron ochres, hematite, goethite, or limonite (Garcia et al. 2016; Gray et al. 2016; Resano et al. 2007). Sometimes artists made blacks using manganese compounds mixed with carbon to create dark, rich images (Chamblin 2003; Guineau et al. 2002). Non-destructive Raman microscopy (RM) methods have indicated similar results for Paleolithic paintings from three different caves in France, and Smith et al. (1999) argued that RM was a sufficient technique to provide mineralogical compositional information concerning paints in the region.

Pottery

Considerable work has been conducted on the compositional analysis of ceramic paints in the American Southwest (Cordell and Habicht-Mauche 2012; Duane and Neff 2007; Huntley et al. 2006; Speakman 2005; Speakman and Neff 2002, 2005, Van Keuren et al. 2013) through laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS). Ferguson et al. 2015 used PXRF to expand a previous LA-ICP-MS study of paint recipes used on a sample of late pre-Hispanic village pottery from eastern Arizona. These researchers effectively demonstrated that PXRF can be used to acquire complementary compositional data from painted pottery. The authors analyzed whole vessels and found that multiple paint mixtures were used on single vessels to achieve variable hues. Due to the limitations of LA-ICP-MS, Van Keuren and colleagues' (2013) analysis from the same sample only indicated a single recipe. Similar results of paint mixtures in the Southwest have also been noted by van der Weerd et al. (2004). Using non-destructive RM, they analyzed black pigments of Puebloan black-on-white pottery. Results indicated that black pigments were made by Puebloan peoples using mixtures of mineral manganese and carbon-based chromophores with little, to no, evidence of other organic materials. On some sherds maghaemite and magnetite were also found alternatively or mixed with a carbonaceous pigment.

In the American Mid-South, Baumann et al. (2013) analyzed black paints from negative painted pottery from the Angel Mounds site in Indiana. The authors used a variety of analytical methods including X-ray diffraction, X-ray fluorescence, field emission scanning electron microscope (FESEM), synchrotron-based m-X-ray fluorescence mapping (m-XRF), and μ -X-ray adsorption near-edge structure (μ -XANES) to clarify the methods of manufacture for negative painted pots based on the element compositions of the paint, ceramic paste, and

associated inclusions. With respect to paint specifically, they concluded that artists created a mixture of ground hematite and goethite that was mixed with water then applied as a wash to the vessel; then, the negative design patterns were laid out with a resist—a layer applied to expose or define a design in negative space—and an organic black pigment was finally applied by the artists via smudging.

Other Archaeological Media

A limited amount of other painted prehistoric archaeological media is also worth mentioning. The use of red and yellow, hematite-rich, ochres as pigments was global, and many researchers have carried out hematite provenance studies using a range of analytical techniques (Clark 1976; David et al. 1993; Erlandson et al. 1999; Mrzlack 2003; Popelka-Filcoff 2006; Popelka-Filcoff et al. 2008; Wallis et al. 2016; Young 2000). These studies use a range of instrumentation to analyze archaeological fragments and compare them to known source locations, or to assess variability in ochre types present at a site or group of sites. For my purposes in this dissertation (and paint sourcing more generally), comparing provenance data on ochre fragments to paint is problematic. What these studies provide, however, is information about the natural elemental variability that can be present in ochre and ochre-bearing deposits. This, in turn, can be used to inform iron-based paint analyses on archaeological media.

As noted above, much research on paint composition was undertaken by a variety of museums and art conservationists on historical paintings (Bacci et al. 1992), which necessitate the use of non-destructive and non-invasive methodology. Virtually all of the FORS analyses that have been conducted on paints or pigments have occurred in fine art conservation (Bacci et al. 2007), rather than archaeology. Archaeological media that have been analyzed using FORS

include wood (Sandak et al. 2010), chert (Parish 2016), soil and sediments (Linderholm et al. 2019), and rock art (Linderholm et al. 2015). Linderholm et al. (2015) specifically discuss NIR spectroscopy at Swedish and Norwegian Stone Age rock paintings. This primary goal was to classify and separate rock paintings and pigments from the geological background based on NIR spectroscopy. While they were not able to determine pigment composition for the red paints (likely because iron-rich minerals are characterized in the visible-near infrared), their study highlights issues that can arise during measurement on thin paints. Thinly painted pictographs displayed nearly identical spectral profiles to the background rock, complicating identification.

Pronti et al. (2018) caution against using reflectance spectroscopy for identifying pigments in historic painted artworks. These often contain paint mixtures or paint overlays, leading to different components contributing to the final reflectance spectrum. A number of reference databases have been developed for artist's materials (Picollo and Radicati 2011; Pisani et al. 2017), although Pronti et al. (2018) argue that the full spectrum of paints and paint mixtures used by artists over several centuries cannot be fully compiled into a holistic reference database. While the pre-Contact pigments I analyzed in this dissertation are not likely to be as complex as historic paint mixtures, my research highlights, again, the need to obtain analytical measurements on the underlying material upon which prehistoric paints were applied. While FORS is a (mostly) surficial method, Pronti et al. (2018) and Cavaleri et al. (2013) prove that spectra on historic artworks can be amalgamations of multiple layers. In contrast, Longoni et al. (2020) combine FORS with visible-excited spectrofluorimetry to successfully characterize a range of historic synthetic pigments.

Horn (2018) offers a different perspective on VIS and SWIR reflectance spectroscopy, concentrating on the detection capabilities for ochre paints, binders, binder deterioration and

binder qualities. In this publication, a set of experiments was conducted on manufactured paints using ochre and a variety of binders (i.e. egg yolk and white, linseed oil, gum acacia, kangaroo blood, chicken fat, emu oil, sandalwood oil, and plain water). These experimental samples were then subjected to accelerated UV deterioration in an effort to simulate rock art paint weathering/preservation conditions. A range of spectral features were recognized in the VIS-NIR results for raw ochres and each of the binding materials prior to the accelerated ageing process. For binders, the simulated ageing process altered the profiles from their original states. Specifically, vegetable fats could not be detected in the aged samples, while animal fats showed little change. These experiments further highlighted issues with adding potential binders to paints—emu oil and chicken fat acted as non-binders for paint, leading to a poor adherence of the paint to the rock. Water, on the other hand, acted as a powerful binding agent for the paint.

One of the few publications that use PXRF and FORS instrumentation in tandem on archaeological materials is Fischer and Hsieh (2017). Here, these techniques were used to distinguish Chinese blue-on-white porcelain from different production sites. They examined both the porcelain body in addition to the glaze by PXRF and used both instruments to assess blue pigments on the ceramics. Results indicated that the ceramics analyzed could be linked with production sites, and the blue pigment composition was identified as cobalt-based. What this publication highlights is how elemental data (PXRF) can be used in conjunction with mineralogical data (FORS) to make meaningful interpretations of archaeological materials.

This literature review is not exhaustive of all the various compositional analyses conducted on archaeological paints, but the value of such methods for archaeological investigations is clear. While many compositional studies aim to source materials, several simply examine variability to address larger archaeological questions. My dissertation research is among

the latter, keeping in mind Harbottle's reminder to practitioners of chemical characterizations methods:

“... with a very few exceptions, you *cannot unequivocally* source anything. What you *can* do is characterize the object, or better, groups of similar objects found in a site or archaeological zone by mineralogical, thermoluminescent, density, hardness, chemical, and other tests, and *also characterize the equivalent source materials, if they are available, and look for similarities to generate attributions*. A careful job of chemical characterization, plus a little numerical taxonomy and some auxiliary archaeological and/or stylistic information, will often do something almost as useful: it will produce groupings of artefacts that make archaeological sense. *This, rather than absolute proof of origin, will often necessarily be the goal*” [Harbottle 1982:15; emphasis added].

What is further evident from this brief review is that nearly all compositional studies in the archaeological literature were carried out by destructive analytical instrumentation (even if in some cases minutely destructive). New spectrometers, however, have enabled non-destructive, *in-situ* measurements (Beck et al. 2014; Koenig et al. 2014; Lahlil et al. 2012; Linderholm et al. 2015; Linderholm et al. 2015; Newman and Loendorf 2005; Shugar and Mass 2012) capable of determining pigment compositions. Results from these analyses demonstrate that significant information regarding the production and use of prehistoric paints can be obtained without affecting cultural heritage materials whatsoever. With these new improved methods, sample sizes can be increased, enabling a more complete picture of pigment use in the archaeological record. It is important to note that many publications used a combination of analytical

instruments to gain both elemental and mineralogical profiles, which provided the most holistic approach towards compositional analyses.

Research Questions

I investigate two major research questions through the course of the ensuing chapters. These research directives broadly concern the topics introduced at the beginning of the chapter:

1. *What are the primary constituents, or ingredients, of Mississippian period paint recipes in the Southeastern United States?*

To answer this question, three different case studies of Mississippian paints are analyzed to assess what materials or ingredients were selected by pre-Contact artists in the southeastern region. This work does not seek to source ingredients and tie them to the surrounding landscape (at least, not yet) but to examine the technology employed by pre-Contact Mississippian period peoples. What ingredients did they use to produce paints and did those ingredients differ following the context in which they used them? I hypothesize that differences in paint colors will reveal different material properties, especially since the primary colors displayed can only be achieved by certain chromophores (as described above). A second problem addressed in this research is to determine if the composition of paints differs depending on the material or media of their context. The case studies presented represent three different contexts in which paint was used—rock art (Chapter II), statuary (Chapter III), and pottery (Chapter IV). These contexts range from the sacred to profane and the potential for differences in paint recipes can be explored based on social as well as functional characteristics.

2. *Do non-destructive analytical techniques such as PXRF and FORS provide interpretative value for archaeological investigations?*

A major goal of this dissertation is to add to a growing body of archaeological research involved in identifying the material properties of artifacts. Identifying material properties can give insight into the technological practices and networks of human interaction that can lead to a holistic understanding and interpretation of pre-Contact cultures. The cost of such analyses until recently was often prohibitive and usually involved detriment to the artifact. New and innovative techniques require solid methodologies and refinement before they can be applied to a larger sample. Here, I seek to build a database of information for pre-Contact Mississippian period paints that can be used for future analyses.

These questions are addressed in the three subsequent chapters. The general format of this dissertation is a multi-part or manuscript style as defined by the Department of Anthropology at the University of Tennessee, Knoxville. Chapters II, III and IV are manuscripts presenting the original research and analysis components of this dissertation in three separate but related essays. In essence, each of these chapters serves as a case study in the material composition of Mississippian period paints in the Southeast. In Chapter II, I examine pre-Contact paint recipes from Mississippian culture rock art contexts in southern Illinois through PXRF analysis. In this chapter, I examine rock art from several locations on the landscape to address the research questions outlined above. In Chapter III I focus on a different context in which paint was applied, Mississippian period stone statuary. Lastly, in Chapter IV I examine a third large corpus of painted artifacts—pottery. In that chapter, I examine one of the larger collections of

painted pottery in the Tennessee region, from the Hiwassee Island archaeological site. Through each of these chapters, I use analytical instruments to address the research questions outlined above. The final chapter in this dissertation, Chapter V is an overall concluding chapter that encapsulates the larger implications and interpretations of how Mississippian period artists/artisans used paints.

Transition from Chapter I to Chapter II

In Chapter I, the main research objectives and hypotheses were outlined, a comprehensive technical overview of PXRF and FORS were provided, and a brief literature review on the analysis of pre-Contact paints was summarized. This chapter laid the groundwork for subsequent chapters of this dissertation.

Next, we move into this dissertation's first case study. Chapter II examines pre-Contact, Proto-Historic, and Historic period rock art paintings from southern Illinois by PXRF. This work represents one of the largest data sets of analyzed rock art *via* PXRF in the Mississippian region with seven archaeological sites and nearly forty individual pictographs evaluated. While the mechanics of PXRF were described in Chapter I, the following chapter discusses the specific methodology and instrumental parameters that were used for the analysis of the southern Illinois pictographs. Since analysis took place over several locations, an overview of each site is included, and the pictographs contained within each are detailed. This information is used alongside the compositional data to interpret pre-Contact and historic paint use in the larger context of the southeastern Illinois region.

CHAPTER II: PORTABLE X-RAY FLUORESCENCE (PXRF) ANALYSIS OF ROCK ART PAINTINGS IN SOUTHERN ILLINOIS

This chapter is prepared for publication by Sierra M. Bow, Mark J. Wagner, and Jan F. Simek, as:

Bow, Sierra M., Mark J. Wagner, and Jan F. Simek (2020) Portable X-Ray Fluorescence (PXRF) Analysis of Rock Art Paintings in Southern Illinois. *In preparation*.

This chapter is a research chapter. The text of this chapter regularly uses the pronouns “we” and “our” to reference the contributions of my co-authors, Drs. Mark J. Wagner and Jan F. Simek. It should be noted, however, that in addition to conducting the research and performing the analysis, I am the senior author. This work will be submitted to the *Midcontinental Journal of Archaeology*. This journal is the premier peer-reviewed, academic archaeology journal of the Midwest Archaeological Conference, which serves to promote and stimulate interest in the archaeology of the midwestern United States. The *Midcontinental Journal of Archaeology* specifically seeks original articles on Eastern Woodlands archaeology. Contributions can range in chronology and context but manuscripts that apply modern theories or methods to existing problems and data sets are especially relevant. In this dissertation, the main structure of the paper and the word count are compiled based on the journal guidelines. A typical paper for this journal is 7,500 to 10,000 words—inclusive of tables, references, and figure captions. Complete guidelines for preparing and submitting the manuscript to the journal can be found here: <https://www.tandfonline.com/toc/ymca20/current> Apart from the content and word requirements, all remaining formatting in this chapter follows guidelines set forth by the University of Tennessee Graduate School.

Abstract

Illinois contains a rich tradition of Native American rock art dating to the Mississippian and Historic periods (A.D. 1000-1835). There has been a long-standing interest in determining the composition of painted art in the region to aid rock art analysis. Ethical concerns about the removal of pigment samples, however, have limited these investigations. Here, we use portable X-ray fluorescence (PXRF) technology to non-invasively examine the elemental composition of Illinois pictographs in the field, without damaging or removing samples for laboratory analysis. We analyzed thirty-eight individual pictographs from seven sites across southern Illinois: 1) to determine the paint constituents or ingredients, and 2) to assess variability in the paint recipes

used. The elemental compositional data reveal that paint recipes predominantly involve a single chromophore (colorant) with few other additives. This suggests that the motif designs and colors were more important in the creation of the rock art, than were material components of paint recipes.

Introduction

Illinois contains nearly 100 Native American rock art sites that span the Archaic to Historic periods (Wagner 1996, 2009; Wagner et al. 2004, 2009, 2018). Certain sites dating to the Mississippian Period (A.D. 1000-1500) contain an array of red and black painted images depicting falcons, horned serpents, ogees, and bi-lobed arrows, among other subjects. Historic period rock art includes images of bison, an animal that first entered southern Illinois in the late seventeenth century (Wagner 1996:47-79). The earliest recording of rock art in Illinois was an account from Father Marquette in 1673 of the “Piasa Bird” (Armstrong 1887:9), painted high on the bluffs along the Mississippi River. The pictograph was a well-known landmark for river travelers from 1673 until 1856, when it was destroyed to furnish stone for a rock quarry (Jacobson 1985, 1986, 1991). Through the early to mid-nineteenth centuries other descriptions of Illinois art were reported (Ashe 1808:256-257; Pidgeon 1858; Priest 1838). It was not until the end of the nineteenth century, however, that detailed archaeological descriptions of Illinois rock art began to appear (Henderson 1884; Mallery 1893; McAdams 1887). In the early twentieth century by a variety of researchers produced more publications detailing Illinois rock (Bushnell 1913; Dearing 1956; Merwin 1937; Moyers 1931; Peithmann 1952), and after the 1970s systematic efforts at recording, photographing, and mapping Illinois rock art sites began in

earnest (Booth 1985; Jones 1989, 1993; Pulcher n.d.; Wagner 2002; Wagner et al. 1990, 1992; Wellmann 1979).

There has been a long-standing interest in documenting Illinois rock art, particularly in the southern portions of the state. Descriptions of motif design and technique have been at the forefront of this research, and in recent years, we have added efforts to determine the composition of the paints used to create these images. Techniques used in the past to identify material composition required the removal of pigment samples for laboratory analysis, and researchers rightly have been reluctant to conduct large scale analysis of pigments out of ethical concerns for the damage that this would cause the rock art. The development of non-destructive portable X-ray fluorescence (PXRF) technology, however, has made it possible to gain information concerning the pigment composition of rock art paintings by taking analytical measurements *in-situ* rather than requiring a sample for later analysis in a laboratory. X-ray fluorescence technology itself is not new; it has been used across various disciplines to determine the elemental composition of materials and is increasingly being used in archaeology to answer a wide range of research questions concerning the materials and technology used in the past.

In 2010 researchers at the Center for Archaeological Investigations (CAI) at Southern Illinois University Carbondale (SIUC) and the Department of Anthropology at the University of Tennessee, Knoxville (UTK) began a multi-year PXRF analysis of Native American rock art paintings in the southern Illinois region. The goal of this collaboration was to understand the constituents of pre-Contact, Proto-Historic and Historic aged pictograph paints in the region, something that had not yet been undertaken. Here, we present the culmination of work produced from that partnership with nearly forty individual pictographs analyzed from seven rock art sites distributed across southern Illinois. These sites span different chronological periods, contain

varying art motif designs, and include both red and black paints. Our primary goal for the compositional analysis is to reveal the constituents used in the manufacture of paints. Specifically, we are not *sourcing* paint recipes but instead providing an ingredient list and examining if variability in recipes exists within the sample of analyzed paint. Given our sample, we assume that paint recipes will be diverse. If paints are manufactured differently in relation to site or motif design, then the paint recipes and specific ingredients used could themselves represent culturally significant technological and/or artistic variation. To test this premise, we couple detailed descriptions of the art at each site with compositional data provided by PXRF.

Cultural Context

Illinois contains several physical divisions that have extensive rock exposures prime for the creation of rock art. In extreme southern Illinois, these include the Shawnee Hills and Ozark Divisions. The Shawnee Hills Division stretches roughly from the Mississippi River in the west to the Ohio River in the east and contains sandstones, limestones, and karst features as well as more resistant Pennsylvanian sandstones that create high bluffs, waterfalls, steep canyons, and overhangs. The Ozarks Division is characterized by bluffs and dissected uplands that border the east side of the Mississippi River Valley. This area also contains limestone exposures with karst features, sandstones that form steep-sided ravines and stream canyons, and cherty limestone areas (Schroeder et al. 1987:274). Many rock art sites identified in Illinois are in this region, due in part to the century-long interest of Southern Illinois University archaeologists (Merwin 1931; Pulcher 1970; Wagner 1996; Wagner and Swedlund 2009; Wagner et al. 2018). Rock art sites have been reported in the west and north-central parts of Illinois. No sites have been recorded in northwestern Illinois even though the physiography is suitable for the creation of rock art

(Wagner et al. 2018). Work by Lowe (1996) in Wisconsin just north of the Illinois-Wisconsin line (but in the same physiographic division) has recorded 150 sites. This suggests that, rather than a true absence of rock art in the area of northwestern Illinois, there is simply a lack of surveys designed to locate them.

The most complete information concerning rock art in the state comes from southern Illinois. Both pictographs and petroglyphs have been recorded along the walls of fallen roof sections, under small overhangs, on bluff faces, on isolated boulders, and in caves. Wagner et al. (2018) suggest that many rock art sites in Illinois date to the Mississippian (A.D. 1000-1500) and proto-historic to historic periods (A.D. 1500-1800). There is evidence for possible Archaic (7000-1000 B.C.) sites (Wagner et al. 1990:160-171) and Woodland period rock art (1000 B.C.-A.D. 1000) is also likely (Booth 1988:105-107; Wagner et al. 2018:107-109). Rock art sites with definite Mississippian-era designs are restricted to the Shawnee Hills and Ozarks divisions and have long been likened by researchers to the style of art found in the Cumberland and Tennessee River valleys and southeastern Missouri (McAdams 1887; Merwin 1937; Peithmann 1955; Wellmann 1979). These rock art sites include well established Mississippian motifs such as the cross-in-circle, sun circles, bi-lobed arrows, ogees, birds, ceremonial maces, axes or war clubs, and a variety of anthropomorphs, avimorphs, and quadrupeds (Wagner 1996:67-70). Most rock art in southern Illinois consists of petroglyphs (engraved designs).

Rock art sites in Illinois include both mundane and socio-religious activity sites (Wagner et al. 1990:249-251; Wagner et al. 2018). Originally identified by Henson (1986:85-108) in pre-Columbian rock art sites in Tennessee, Alabama, and Georgia, utilitarian and ritual sites differ with respect to the elaborateness of the images depicted and the location of sites on the landscape. Utilitarian sites are typically in sheltered areas on former trails or game routes. These

types of sites could have been used as resting stops or hunting camps and would have been publicly viewed by ordinary peoples. An example of such site would be the Buffalo Rock site that contains motifs such as a buffalo, moon, and star. The site is also situated along a well-known historic trading route. Ritual sites are usually more difficult to access. They typically display uniqueness or elaborateness in the images depicted and visitation to the sites would have been limited due to their difficult accessibility and/or remoteness on the landscape. The Whetstone Shelter exemplifies a rock art site that functioned as such a place (Wagner et al. 2018). Access to the rockshelter is reached by climbing 200 feet up a nearly vertical bluff face, and the rock art depicted conforms to Southeastern Ceremonial Complex iconographic symbols. If sites were differentially used in prehistory, then perhaps the paints contained within them may also be variable.

Methods

To examine the paint constituents, we used a Tracer III-V+ PXRF device manufactured by the Bruker Company. This is a handheld energy-dispersive instrument with silicon detectors allowing for the determination of multiple elements simultaneously within a sample. X-ray fluorescence is a process in which electrons within the specimen are displaced by incoming X-rays from the instrument. Once electrons are displaced, outer shell electrons fill those vacancies, and release a burst of energy that is characteristic of a specific element (Jenkins 1999; Jenkins and Vries 1973; Shackley 2011; Shugar and Mass 2012). This energy is detected by the instrument, which then categorizes the energies by element. By selecting the appropriate combination of instrumental parameters, specific elements can be identified, isolated, and yield important information about the overall character of the sample being analyzed.

For our purposes, two primary instrumental settings were used. The first was at 15kV, 35 μ A in conjunction with a vacuum pump attachment and a titanium filter to acquire low-Z elements on the periodic table. These settings allow X-rays from 3 to 12keV to reach the sample in order to analyze elements from Al to Fe on the periodic table. The second instrument setting was used to acquire higher elements on the periodic table. The instrument was set at 40kV and 30 μ A with a copper/titanium/aluminum filter. No vacuum pump attachment was used for this setting. This setting excites elements from Fe to Mo on the periodic table. We obtained multiple PXRF assays at each rock art site. To acquire accurate readings the instrument was attached to a tripod rig with an extending arm, which provided stabilization during data collection (Figure 3).

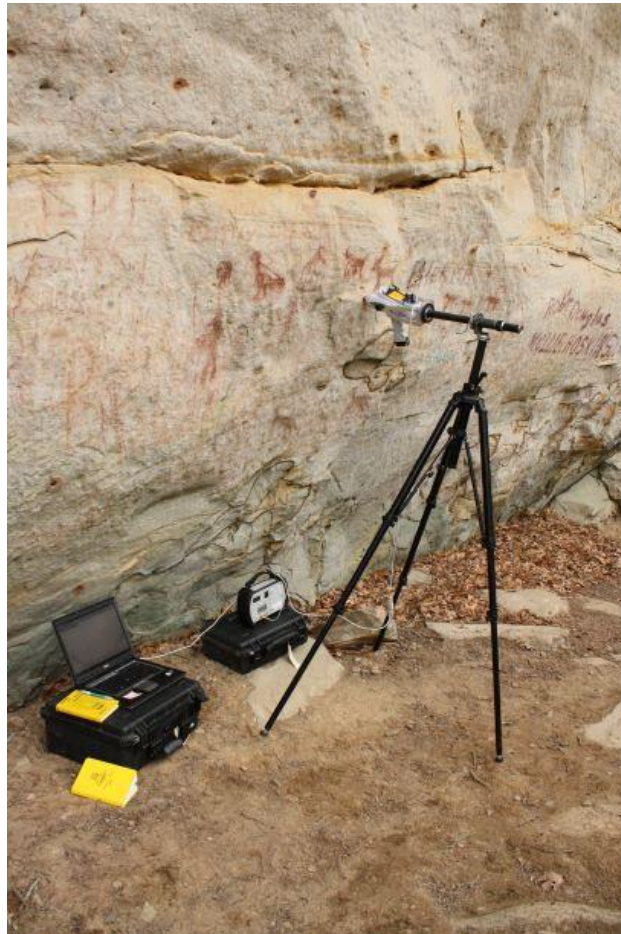
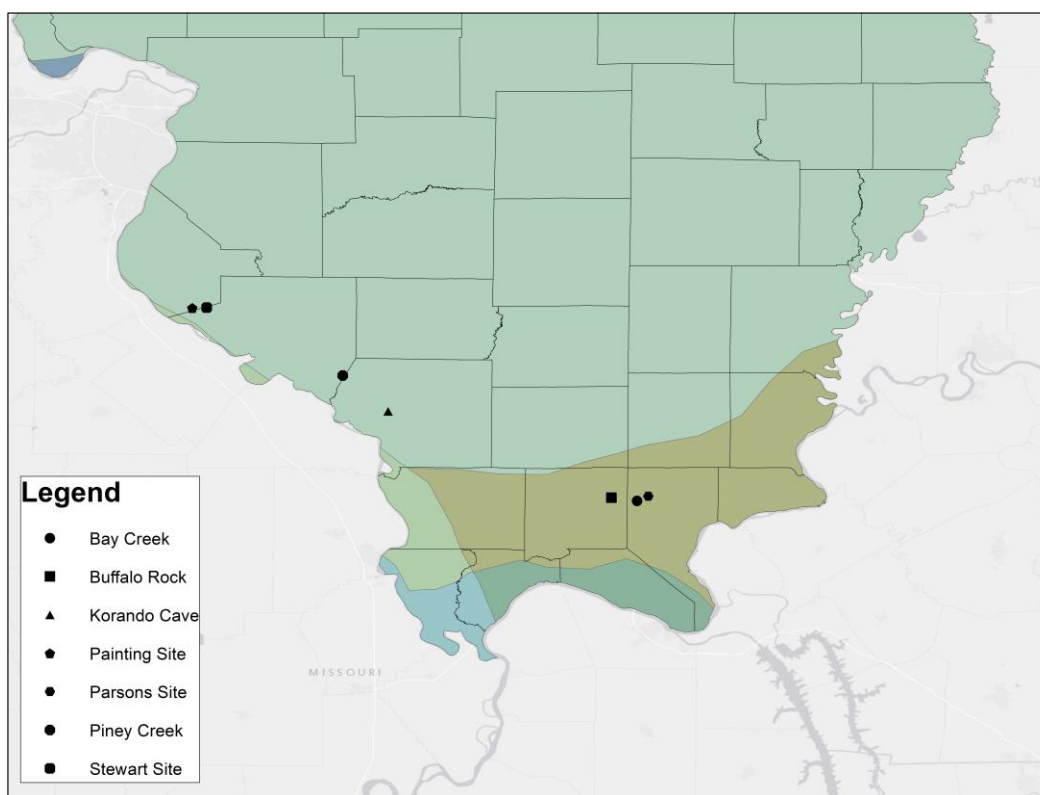


Figure 3: PXRF field set-up with extending tripod rig, laptop, and vacuum pump at the Piney Creek Site.

All PXRF readings were analyzed for 180 seconds. We took readings on the best possible location on the pictograph. Pictographs we selected for analysis were richly colored and could be easily accessed with out instrument rig. No pretreatment was applied to the area before the assay, making our analysis completely non-invasive. In addition to analyzing the pictographs, we also took several control readings of the bare unpainted rock surface at each archaeological site. Although the instrument identifies the composition of the surface layer (paint) with greater sensitivity than the bulk (rock substrate), a variety of factors can influence the penetration depth of X-rays. Natural weathering and post-depositional processes can affect the paint layer thickness on a surface. If the paint is not sufficiently thick, the potential for X-rays to penetrate through the paint layer and into the underlying material is very likely. While thick and prominent paint layers were selected for the analyses, additional PXRF readings were acquired from all of the unpainted, substrate rock at each site. This substrate reading is necessary to tease out the true paint recipe.

Study Sites

A total of seven rock art sites were analyzed across southern Illinois in the Shawnee Hills and Ozarks physiographic divisions (Figure 4). Five of the sites date to the Mississippian period (A.D. 1000-1600), one could be late Proto-Historic or early historic (ca. A.D. 1500-1700), and one is believed to date to the historic period (A.D. 1673-1835). Some of the sites are located along creeks or intermittent streams that flow into the Ohio River, while the others are located along or adjacent to the Mississippi River floodplain. Each of these sites is described below in turn from the west (Mississippi River drainage) to east (Ohio River drainage).



SITE NAME	IAS SITE NUMBER	AGE/CULTURAL AFFILIATION OF PICTOGRAPHS *	
PAINTING SITE	11Mo89	Mississippian	A.D. 1000-1600
STEWART SITE	11R6	Mississippian	A.D. 1000-1600
PINEY CREEK	11R26	Mississippian	A.D. 1000-1600
KORANDO CAVE	11J334	Mississippian	A.D. 1000-1600
BAY CREEK	11Pp52	Mississippian	A.D. 1000-1600
BUFFALO ROCK	11Js49	Historic	A.D. 1673-1835
PARSONS SITE	11Pp8	Proto-historic/Historic	A.D. 1500-1700

* Assumed age based on style, none of the images have been directly dated

Figure 4: Location and cultural affiliation of rock art sites analyzed.

Stewart Site

The Stewart Site is a sandstone shelter, roughly forming a half-dome measuring ca. 24 meters long by 11 meters deep. This site contains both petroglyphs and pictographs dating to the Mississippian Period. Other characteristics of the shelter include a partial roof collapse, which created a large oval opening in the ceiling in the eastern portion of the shelter (*Figure 5*). Water

runs through this opening during periods of heavy rain creating a temporary waterfall.

Petroglyphs at the site adorn the rear shelter wall. These include a horned serpent, a concentric circle, an avimorph, an antlered deer, and other images. The largest petroglyph in this area of the shelter is a creature with a serpentine body, a distinct head with short horns or antlers projecting from the top of the head, and a rectangular muzzle with upper and lower teeth or fangs. It also has a patterned body and sectioned tail, suggesting the image is of a rattlesnake.



Figure 5: The Stewart Site rockshelter. Image courtesy Mark J. Wagner.

These petroglyphs remained the only known images at the site from the 1950s until 2000, when a series of black and red pictographs were discovered on the ceiling and walls of the western end of the shelter away from the petroglyphs (Figure 6). The area of the shelter where these images were discovered is poorly illuminated. Additionally, damaged areas exist on the shelter walls as a result of cattle rubbing themselves against the lower portions over the years. A single red pictograph is located in this part of the shelter, consisting of an enigmatic series of eight vertical dashes located below a horizontally curved line measuring 17 cm long by 8 cm wide. The other pictographs comprise filled black images, some of which extend into now-exfoliated areas of the shelter wall. It is likely that additional drawings once existed at the site. Six identified black pictographs include a motif of a coiled rattlesnake within a bisected circle and five anthropomorphs holding bows, shields, or blankets. Several other indeterminate images are also present but are not clearly delineated. The most striking pictographs at the Stewart Site are the five anthropomorphs in various active poses and holding various accoutrements. There are three who hold shields or blankets in their outstretched arms. All are portrayed in frontal view and have either rectangular or triangular shields or mats attached to the ends of their outspread left arms. Each also holds vertical linear objects in their opposite hands, which could represent weapons or ceremonial maces.

In 1999, avocational archaeologists conducted limited excavations (6.8 m²) to a depth of 10-20 cm below the surface along the western portion of the shelter. SIUC archaeologists later identified two features within this excavation: a baked clay hearth and a possible basin that originated at ca. 20 cm below the surface. A recurved rim pottery sherd, indicative of a Late Woodland jar, was recovered at 20 cm below the surface in the excavation. The evidence at the Stewart Site suggests a Late Woodland or Mississippian cultural affiliation.

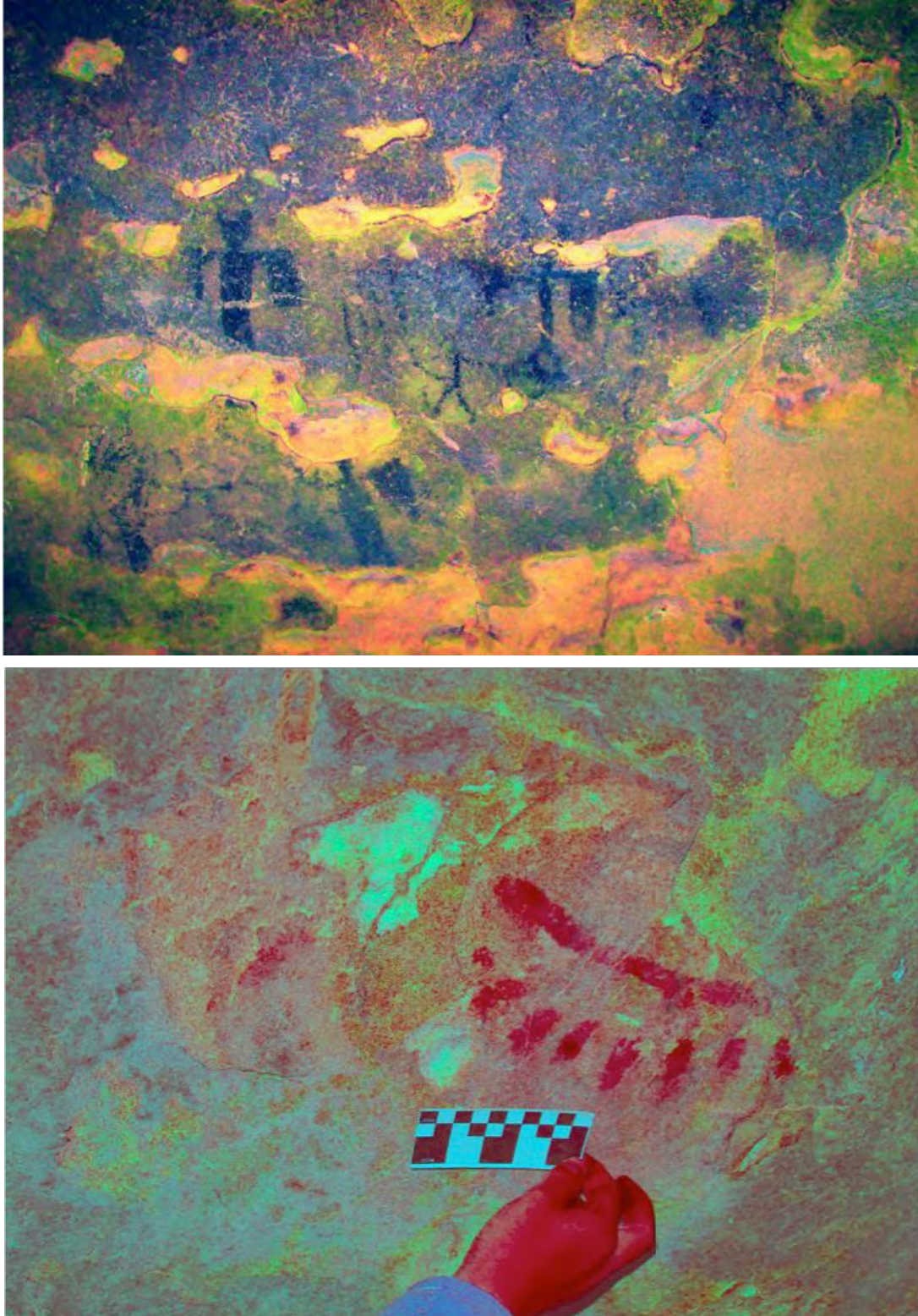


Figure 6: Enhanced black pictographs (above) and red pictograph (below) at the Stewart Site. Images enhanced with DStretch (see Appendix A). Images courtesy Mark J. Wagner.

The Painting Site

The Painting Site is the only known surviving bluff-face pictograph site of a series of such sites that once existed in southwestern Illinois (McAdams 1887: 21-36). The site directly overlooks the Mississippi River floodplain and consists of a narrow linear ledge with several red pictographs along a vertical face above the bluff ledge (Figure 7). The rock-floored ledge of the site slopes away from the paintings and lacks any archaeological deposits. Due to exposure and resulting natural weathering, the limestone cliff wall is today spalling away along the bluff, exfoliating pictographs along with the rock surface (Figure 8).

A series of red pictographs span an approximately 21m-long section of the vertical bluff face and are distributed into two groups, one at the northern end and another at the southern portion of the decorated area. The paintings in both groups are distributed around a series of four natural niches or cavities (one north and three south). Two of the niches have partially painted ceilings and all have either stone or recently formed silt floors that lack any archaeological deposits. These natural alcoves are large enough for ritual offerings or perhaps bundle burials, however, no physical trace of such material is present today. There are, however, earthen burial mounds located on the bluff top immediately above the site. We do not know if they were linked in some fashion to the rock art site.

Motifs at the Painting Site include geometrics, ogees, circles, anthropomorphs, avimorphs, and a ceremonial mace—the only known painted representation of a mace in southern Illinois (Figure 9). Paintings at the site consist of large (50 cm tall) and small (10 cm tall) images. Some figures appear to have been intended to be seen by viewers standing on the floodplain below, while the smaller pictographs had to be viewed standing at or near the ledge. Pictographs at the site are associated with the Mississippian Period based on the presence of the

ceremonial mace and ogee motifs, whose date range is known from their occurrence on other artifacts such as portable shell, copper, and stone (Phillips and Brown 1979). These items have been recovered in Mississippian-era contexts throughout the Southeast and suggest that the images at the Painting Site were likely created between A.D. 1000-1500 (Muller 1986:62; Waring and Holder 1945).



Figure 7: The Painting Site.



Figure 8: Red pictographs above niches in limestone bluff face at the Painting Site. Arrow highlights natural exfoliation of the bluff surface. Paint chips analyzed were obtained from exfoliated chips found on the ground under this panel.



Figure 9: Red pictographs at the Painting Site, including a Mississippian-era ceremonial mace (right). Images enhanced with DStretch (see Appendix A). Images courtesy Mark J. Wagner.

Piney Creek Site

The Piney Creek Site is a large rock shelter along a narrow interior creek valley that contains over 200 pictographs and petroglyphs, the largest number of art images of any site in Illinois (Wagner 2002). Additionally, there are four rock art sites nearby that contain painted and carved images identical in subject matter to those at Piney Creek (Wagner 2002). Based on motif stylistic elements, the images at the site may have been created as early as the Middle Woodland period (300 B.C.- A.D. 350); however, the bulk of images date to the Mississippian period (A.D. 1000-1500; Wagner 2002:104-108).

The Piney Creek Site contains four spatially distinct groups of pre-Contact rock art; our analysis focused on the eastern group (Figure 10). The most prominent art type at Piney Creek is petroglyphs, some of which are very elaborate. At least 30 pictographs are also present including



Figure 10: The Piney Creek Site, eastern panel of rock art.

quadrupeds, anthropomorphs, avimorphs, lines, swastikas, canoes, and other images (Figure 11). This site has seen repeated historic and modern graffiti, some of which have heavily damaged pre-Contact images. Some of these paintings are known to have been redrawn by Irvin Peithmann, an avocational archaeologist, in the 1950s in a misguided effort to “save” the pictographs. He used naturally occurring hematite to refresh the images (Wagner 2002).



Figure 11: Red pictographs at the Piney Creek Site. Images of a canoe (top left); quadrupeds (top right); anthropomorphs in opposition--one with a shield and another with a bow (bottom left); and a horned figure with upraised arms and quadrupeds (bottom right).

Two of the painted images are stylistically similar to the “Dancing Warrior” figure at the Rattlesnake Bluff site in Missouri, an image of an anthropomorph holding a mace in its

outstretched hand (Diaz-Granados and Duncan 2000:115). The first of these is a fine-line painting of a right-facing anthropomorph measuring 26 cm high by 30 cm wide (Figure 12). Unfortunately, a 1904 visitor to the site painted his name directly over this figure, obscuring details of the pre-Contact image. The shared stylistic details between this figure and the “Dancing Warrior” include semi-flexed legs, the body depicted in profile, and a rectangular shield held high in front of the body with the right arm raised in a striking position behind the head. The second image at the Piney Creek Site that shares stylistic similarities to the “Dancing Warrior” is smaller (15 cm tall) but also has a shield held in front of its body with its other arm raised behind its head in a striking position. This image is part of a small composition of three anthropomorphs. The second figure holds a shield and an undetermined linear weapon, possibly a rudimentary mace or war club, and stands in opposition to the third figure who holds a bow and arrow (Wagner 2002:76).

In the 1930s, a central section of the shelter floor was excavated by a former landowner in search of “Indian gold”. His efforts resulted in a trench over 2 m deep (Wagner 2002:34). In 1997, SIUC archaeologists excavated a single 2 m x 0.5 m unit west of this trench to determine whether the site contained intact archaeological deposits. The excavation identified what appeared to be the wall trench of a Mississippian period house, which cut through an earlier archaeological midden. This wall trench feature occurred ca. 87 cm below the surface. Artifacts recovered from within this feature include fired daub and shell-tempered pottery sherds. The base of the unit was cored down to 87 cm below the surface and revealed that the archaeological deposits extend downward for an additional 75 cm. Archaeological deposits present at the site may likely contain Archaic period deposits in addition to the Woodland and Mississippian ones encountered during the excavation. Other materials found in the excavated unit include ground

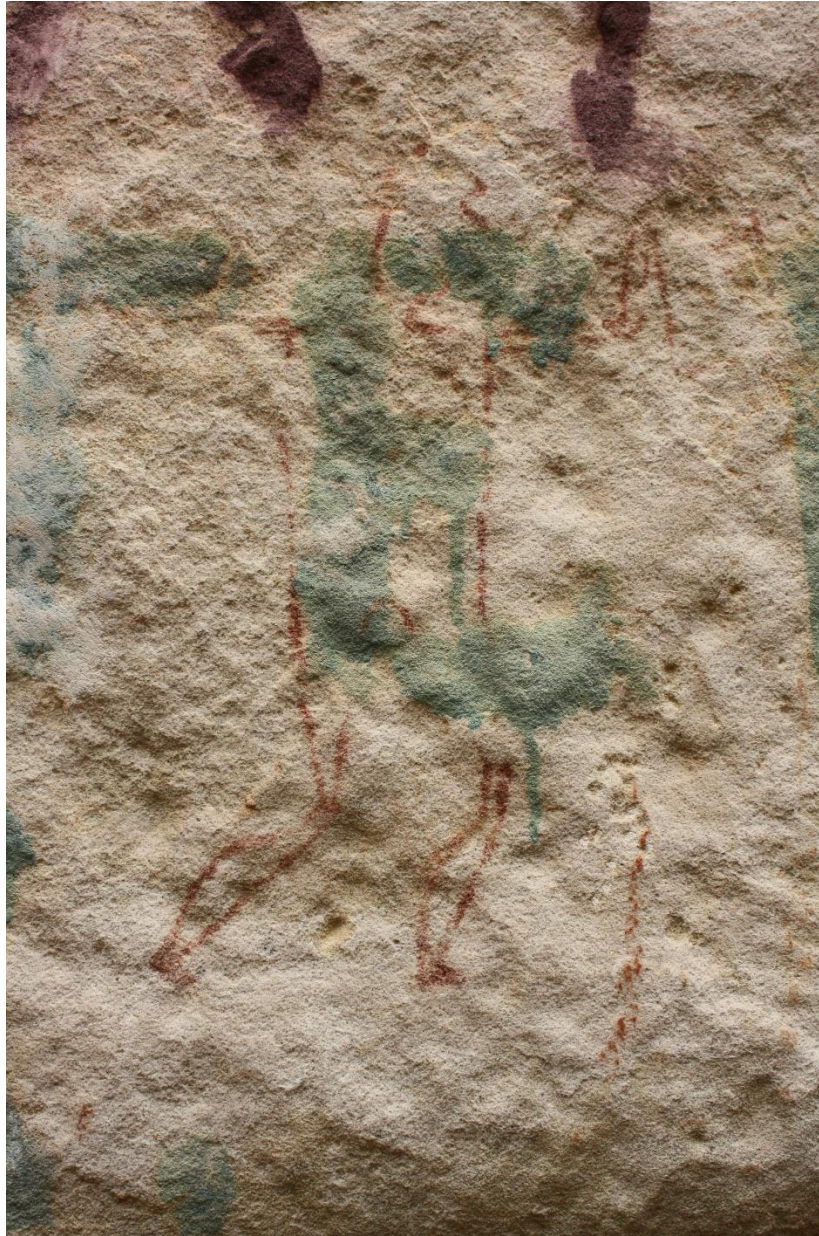


Figure 12: Red painted anthropomorph with a shield underneath the letter "E" located in the eastern portion of the shelter. The bottom right foot was analyzed by PXRf (Anthropomorph #1 in Table 4).

pieces of limonite, which could have been used in the creation of the pictographs at the site (Wagner 2002:34-37). Other culturally diagnostic artifacts recovered from the excavation unit and shelter floor include a Late Archaic/Early Woodland (1000 B.C.-A.D. 500) Motley type projectile point; Early and Middle Woodland (500 B.C.- A.D. 350) Crab Orchard pottery sherds;

Late Woodland Raymond phase pottery jar rims (A.D. 450-600); and Mississippian period ceramics (A.D. 1000-1500). At an adjacent site in the same creek valley, a terminal Late Woodland Dillinger phase (A.D. 900-1000) pottery jar rim was recovered (Wagner 2002:26, 37-42).

Korando Cave Site

Korando Cave is another half-dome-shaped sandstone shelter and cave located at the base of a narrow ravine. The shelter itself is rather large with a floor space of approximately 200 m² and a maximum roof height of approximately 10 m (Figure 13). Additionally, an intermittent creek drains the hillside above the shelter, creating a waterfall that flows over the shelter roof and falls onto the northern floor of the shelter.

The site contains a series of Mississippian period petroglyphs that depict upright birds with their tails spread wide and their wings extended downward. Other Mississippian period petroglyphs include a series of anthropomorphs that blend avian and human characteristics (Wagner et al. 1999). These images are located on both breakdown boulders on the shelter floor and arranged in rows on the walls of the front room of the shelter. Also depicted on the rock fall on the shelter floor is a scene in which a human-like archer is flanked by avimorphs—two behind and one in front. This scene is repeated twice, creating a larger composition with a varying degree of detail; one set appears more crudely executed than the other (Figure 14).



Figure 13: Korando Cave.

A small cave passage is present at the rear of the rock shelter. This passage extends 17 m into the hillside and contains two large rooms with black and red pictographs. The first room is an arch-shaped passageway, measuring 3 m long by 1.5 m wide (Figure 15). Avimorph petroglyphs identical to those carved onto the rock slab at the main shelter area are present in this room, and there are black pictographs (Figure 16). Both the pictographs and petroglyphs were created along the vertical walls. The second cave chamber is totally within the “dark zone”, meaning no natural sunlight penetrates this area. On the ceiling here is a single red geometric pictograph of a trapezoid crossed by a series of lines (Figure 15).

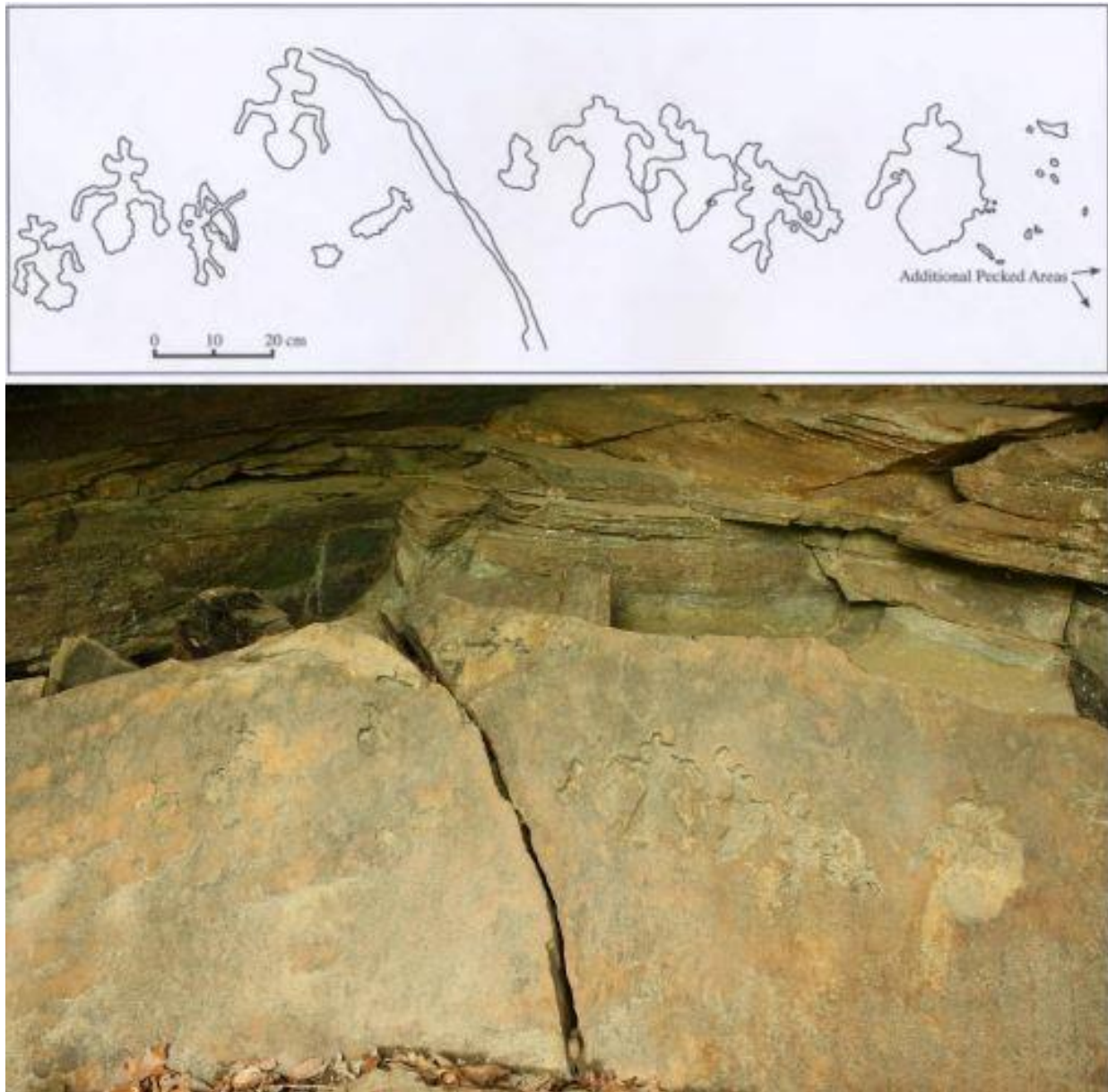


Figure 14: Petroglyphs on slab at front of the Korando site. Finely (left) and crudely (right) executed scene of a human-like archer surrounded by avimorphs. Images courtesy Mark J. Wagner.



Figure 15: Front room of the cave at Korando (left) and trapezoidal red pictograph in the rear room of the cave (right). Images courtesy Mark J. Wagner.

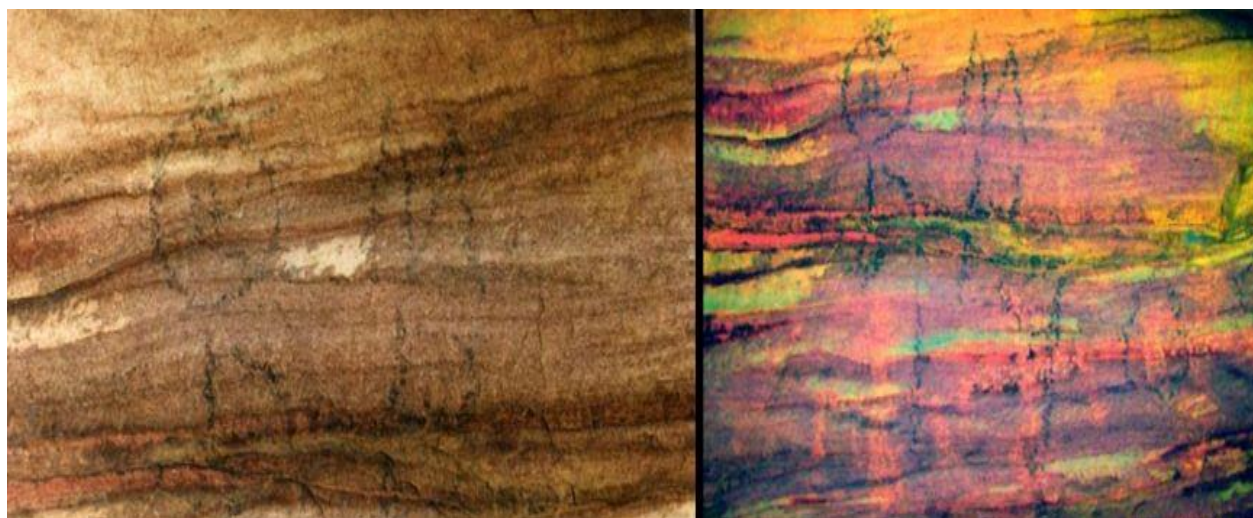


Figure 16: Black images in the front room of the cave at Korando depicting an anthropomorph with spears. Image on right is enhanced with DStretch (see Appendix A). Images courtesy Mark J. Wagner.

The subject matter of the art at Korando Cave suggests that the art dates to the Late Woodland/Mississippian period. The arrival of the bow and arrow in southern Illinois is generally accepted as A.D. 600-800 (Blitz 1988; Fowler and Hall 1979:560-561; Kelley et al. 1984:122); therefore, the portrayal of two human-like archers at the site provide a *terminus a quo* for this time. The head elements of the zoomorphic petroglyphs are also interpreted to be stylized representations of the Mississippian-era bi-lobed arrow motif. The zoomorphic figures carved into the cave chamber are simpler, with the head elements depicted as crosses, but at least one of the figures on the shelter floor boulders has a head element consisting of two bulbous lobes surmounted by a short central projection. This head element is virtually identical to the bi-lobed arrow headdresses often seen as part of the headdress of a supernatural figure—the birdman—that appears on shell and copper objects associated with the Southeastern Ceremonial Complex (Brown 2007; Phillips and Brown 1978; Reilly 2007). If this interpretation is correct, then these images should date to A.D. 1250-1400 (King 2007).

In the late 1950s and early 1960s, a group of amateurs dug at the Korando Shelter. In 2014, their large collection of artifacts was donated to Southern Illinois University. Items in this collection include Archaic period projectile points (5000-1000 B.C.) as well as Late Woodland (A.D. 600-900) and Mississippian period (A.D. 1000-1500) pottery sherds. Additionally, a temporally diagnostic pottery sherd dating to the Dillinger Phase (A.D. 900-1000) was recovered from the shelter floor by SIUC archaeologists in 1997 (Wagner et al. 1999:149-186).

Bay Creek Site

The Bay Creek Site is a large, low-roofed rockshelter that contains six panels of red pictographs (Figure 17). The site sits two miles upstream from the Millstone Bluff Site, an

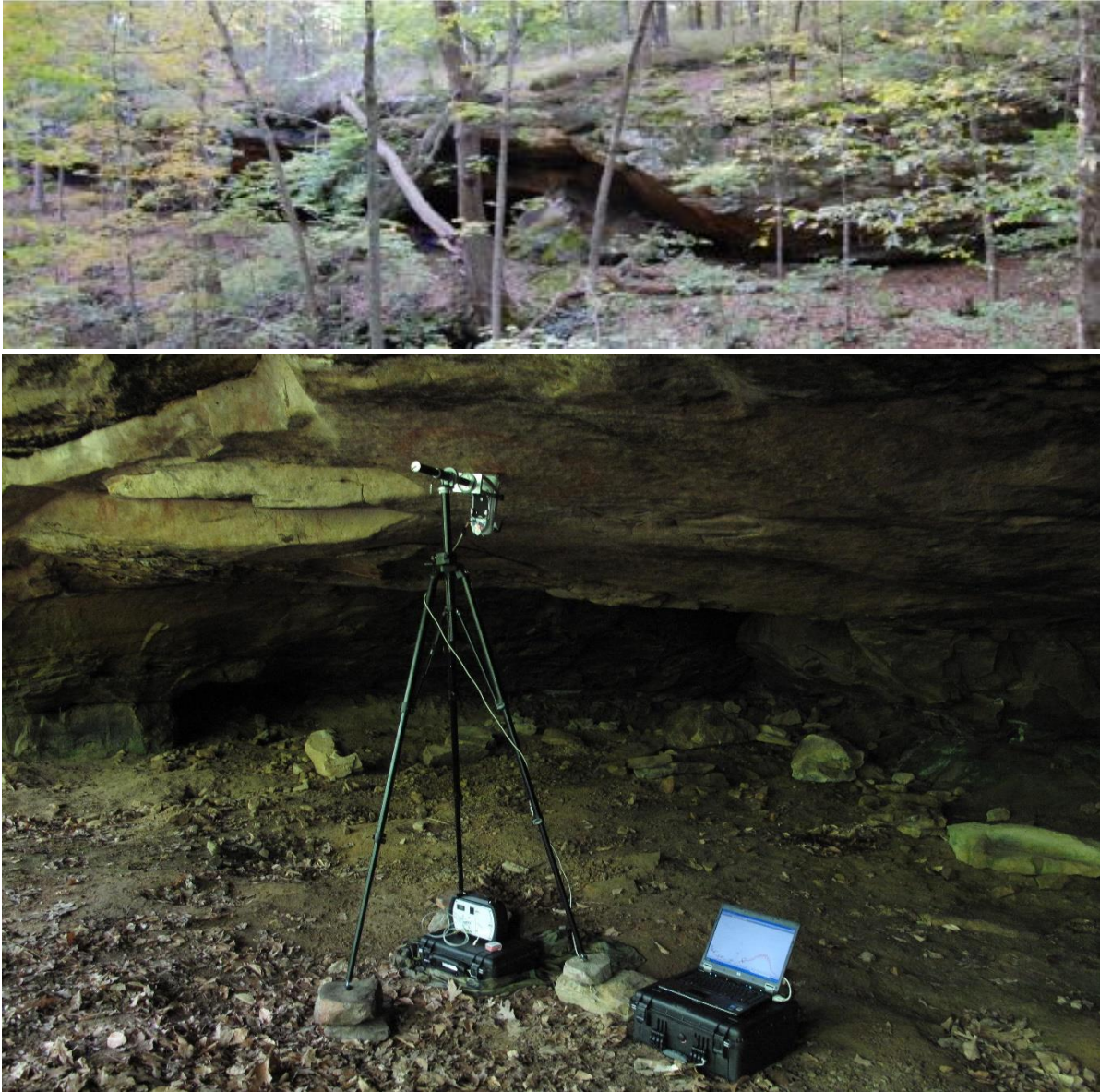


Figure 17: The Bay Creek Site. Images courtesy Mark J. Wagner and Jan F. Simek.

unplowed Late Mississippian (A.D. 1275-1500) village that sits atop a mesa-like hill and contains one of the most extensive collections of Mississippian-era petroglyphs in the region (Wagner et al. 2004:40-64). The Bay Creek Site falls within the boundaries of the proposed Millstone Bluff polity and may have been utilized by Late Mississippian peoples who identified with that community (Wagner et al. 2018). The Bay Creek Site rock art (Figure 18) includes a

disk in circle motif with an abstract line crossing through the outer ring, which may represent a serpent. Several ogees with circles at their center are also present, one of which sits next to a small dog figure with upright ears and an upwardly curving tail. Lastly, a curvilinear figure with a pointed triangular head is depicted.

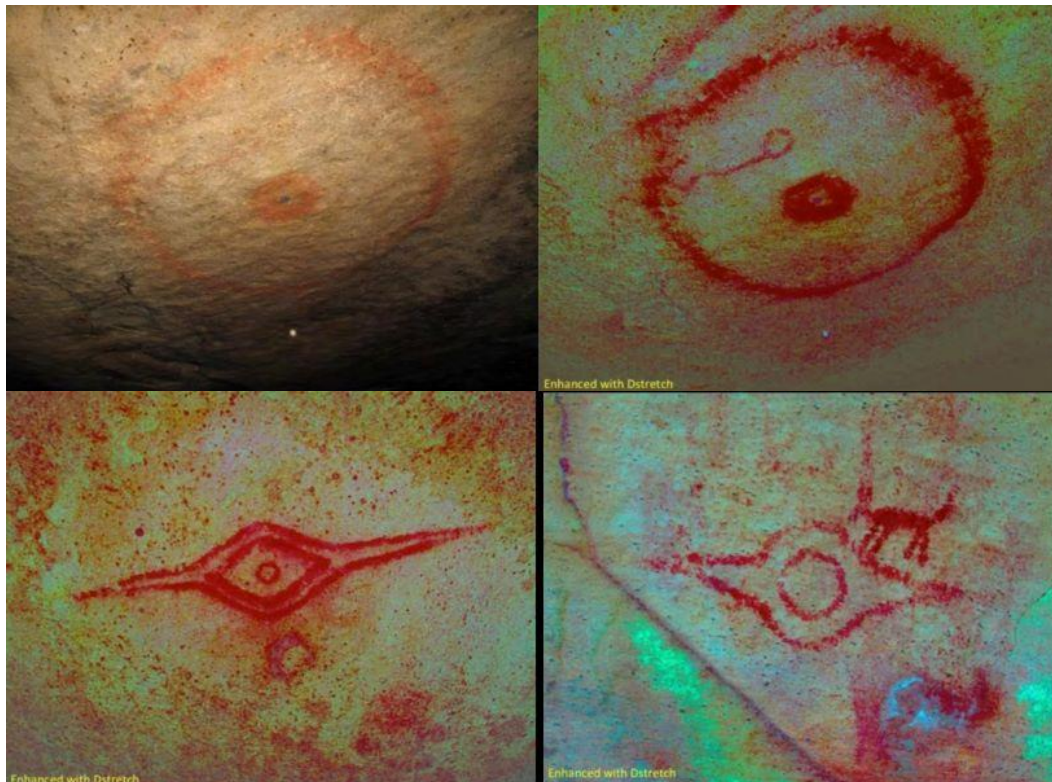


Figure 18: Red pictographs at Bay Creek. Circle motifs, original (upper left) and enhanced (upper right); ogee pictographs, both images enhanced with DStretch (see Appendix A). Photos courtesy Mark J. Wagner.

Archaeologists from the Shawnee National Forest conducted limited archaeological investigations at the site in 2012. Prior looting of the site was evidenced by the presence of shallow depressions along the rear shelter wall. Archaeologists excavated two 1 m x 1 m test units to 15 cm near the shelter drip line. Artifacts recovered from these excavations consist of an Archaic period projectile point base, a grit-tempered pottery sherd, and two Mississippian period

triangular arrow points. Seven fragments, ca. 14.5 grams, of hematite were also recovered, which could have potentially been used in the production of the rock art images at the site.

Buffalo Rock

Buffalo Rock is a west-facing rock shelter located in a narrow interior creek valley (Figure 19). The shelter itself is a high roofed, L-shaped sandstone overhand with a heavily eroded dirt floor that slopes westward towards a permanent spring-fed creek. Rock art images present at the site include a large faded reddish-orange painting of a bison on a vertical wall at the north end of the shelter (Figure 20), and a series of small paintings at the rear (east) of the shelter consisting of a small crescent moon, a star/planet, a cross, and miscellaneous areas of faded red ochre. The bison pictograph has been repainted historically numerous times, since at least the 1930s, by people using yellow or red ochre or other materials in an effort to enhance its appearance (Bonnell 1933:32; Moyers 1931:74).

No archaeological excavations have been conducted, nor have any culturally diagnostic artifacts been found to indirectly date the pictographs at Buffalo Rock. Therefore, the precise age of these images is unknown. The arrival of bison to Illinois has been identified through archaeological evidence from the Lonza-Caterpillar site in north-central Illinois to approximately 400 B.C. (Harn and Martin 2006: 9-13). Based on a variety of geological and biogeographical evidence, McMillian (2006:108) has argued for even greater antiquity for bison, beginning ca. 4200 B.C. with the establishment of full-blown prairie in central Illinois. Zooarchaeological evidence from sites in southern Illinois suggests a relatively late date for the arrival of bison in the region (McCorvie and Morrow 1993). Bison are noticeably absent from sites such as Millstone Bluff, located less than 10 miles west of Buffalo Rock site, while other relatively

uncommon species such as elk and mountain lion were represented in the faunal assemblage from Millstone Bluff (Butler and Cobb 2004). In southern Illinois, bison are not represented in large numbers until A.D. 1700.

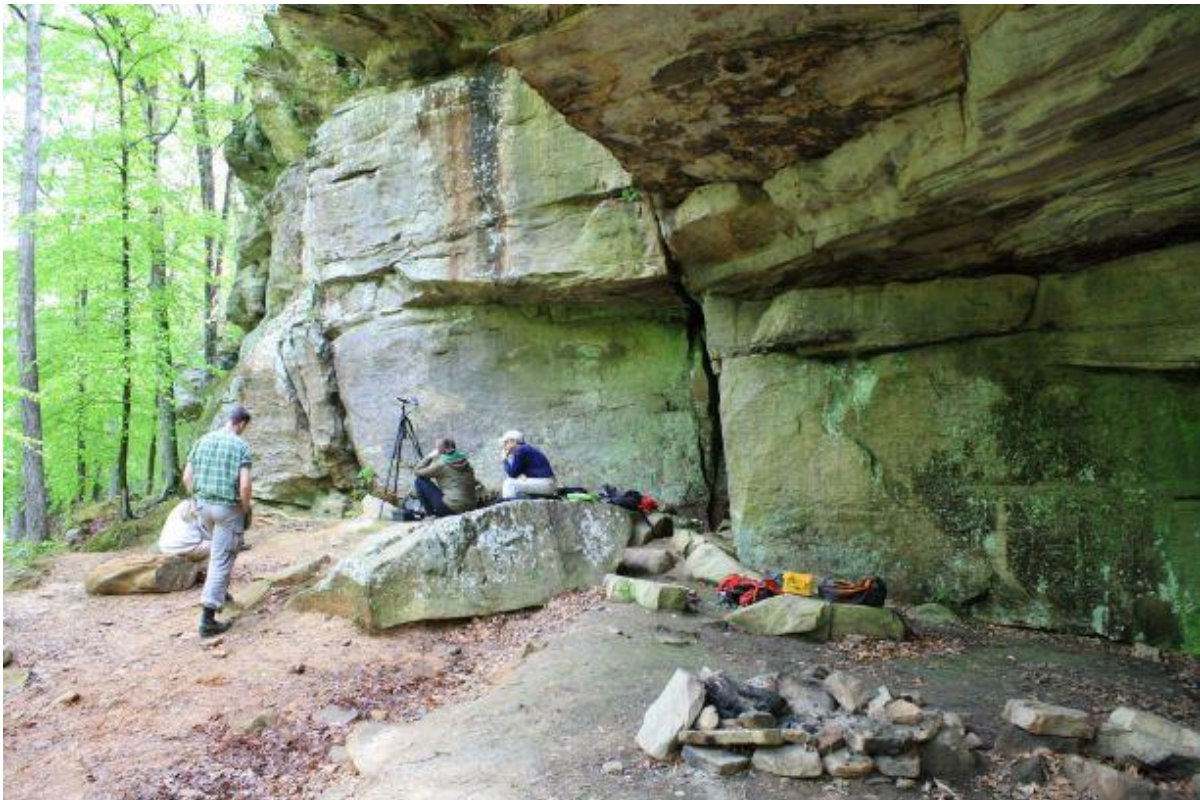


Figure 19: Buffalo Rock.

The bison painting at the Buffalo Rock site could have been created at any time between ca. 400 B.C. and A.D. 1835. Historical evidence, however, suggests that it most likely dates to ca. A.D. 1700-1800 (Wagner et al. 2010). The Golconda-Kaskaskia Trace, an important early travel and trade route during the eighteenth and nineteenth centuries that extended across southern Illinois, passes directly by the Buffalo Rock site. This trail intersected with the “Hunter’s Trace” or “Le Grande Trace” that originally linked the French posts of Ft. Massac on

the Ohio River and the town of Kaskaskia on the Mississippi River immediately south of the Buffalo Rock (McCorvie and Morrow 1993).

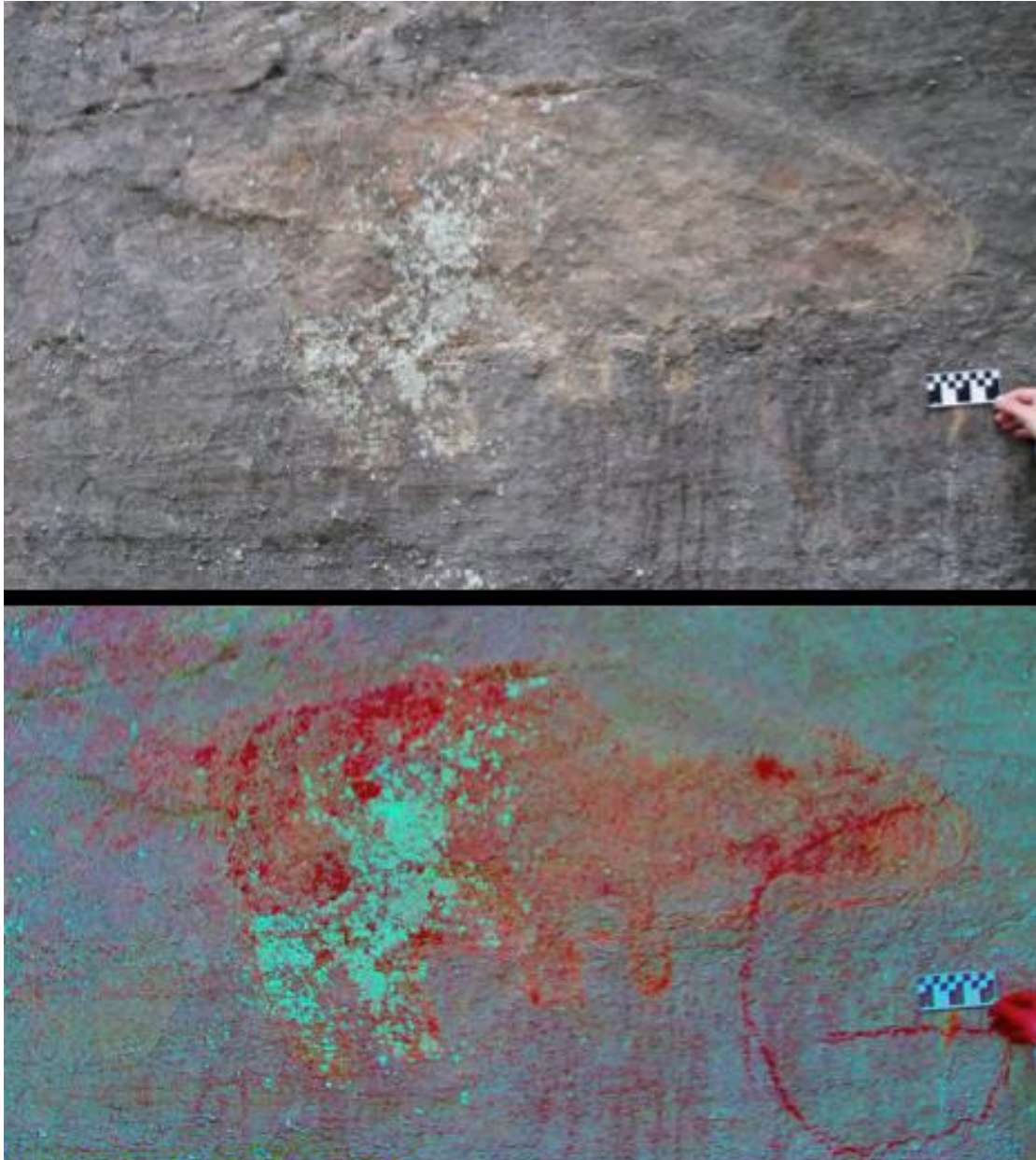


Figure 20: Original and enhanced images of the bison pictograph at Buffalo Rock. Image enhance with DStretch (see Appendix A). Photos courtesy Mark J. Wagner.

Several Great Lakes Algonquin Native American groups (Potawatomi, Kickapoo, Shawnee, and Mascouten) traveled through or lived in southern Illinois starting in the early eighteenth century. It was at this time that the number of bison in the lower Ohio River valley increased to the point where commercial hunting was productive. Many of the tanneries that were established had Native American hunters. In 1702 Charles Juchereau de St. Denys, former royal judge of Montreal, established a bison hide tannery along the lower Ohio River. He enticed Kickapoo-related Mascouten to migrate over 500 miles southward from their homes near the Great Lakes to establish a large village adjacent to his tannery (Fortier and Chaput 1969:385-406). British traders similarly employed Native American hunters in the region from 1765-1772. Based on the bison image, we believe the paintings at Buffalo Rock may have been created by Native American peoples associated with either of these Contact period bison hunting operations in the region.

Parsons Site

The Parsons Site is a massive south-facing shelter in the Shawnee Hills of southern Illinois that contains a series of red paintings distributed across ca. 4.5 m of the shelter ceiling (Figure 21). The painted images at the Parsons Site are notably different in subject matter than any discussed here or more generally at Mississippian period rock art sites in southern Illinois. Motifs include large circular to rectangular enclosures containing staked animal hides and enigmatic creatures (Figure 22); a large anthropomorph with a bison-like tail (Figure 23); a skinned and partially butchered animal carcass; nested serpentine meanders, birds (Figure 24); a quadruped (Figure 25); rayed circles inside of fringed squares; and other enigmatic designs.

One of the enclosure motifs consists of a large circle that has four smaller, rayed circles located along its perimeter (Figure 22). The upper part of the circle contains two flayed animal hides, both with T-shaped stakes driven through their legs. A third staked hide is located midway along an arrow shaft that extends out of the top of the circle. Directly beneath the two staked animal hides are two unidentified creatures. The smaller has a legless fringed lower body combined with an upper body that has human-like arms and fingers and a round head. The arms of this figure are raised. The second figure has a long linear body, fringed and forked tail, and barely visible horns on the top of its head. A badly faded rectangular enclosure is located adjacent to the circle enclosure described above. This motif also has four rayed circles along its perimeter with an arrow crossed by a staked animal hide extending to one side. This motif contains only a single large square fringed hide within its borders.



Figure 21: The Parsons Shelter (left) and PEXRF analysis of red pictographs on the ceiling (right).



Figure 22: Original (left) and enhanced (right) images of circles containing staked animal hides at the Parsons Site. Image enhanced with DStretch (see Appendix A). Image courtesy Mark J. Wagner.



Figure 23: Anthropomorph with bison attributes at the Parsons site. Image enhanced with DStretch (see Appendix A). Image courtesy Mark J. Wagner.

One of the most striking images in the shelter is a composite being that exhibits both animal and human-like attributes (Figure 23). It possesses a long bovine-like tufted tail and short forelegs. The forelegs, however, end in splayed fingers rather than hooves. An arrow extends through its head, and a second animal is depicted within its body. This creature is unlike any native to southern Illinois. It has a short bun-like tail and long neck and is very different in appearance from the bovine-like creature that contains it. This is a complex image, perhaps depicting a composite being of some kind.

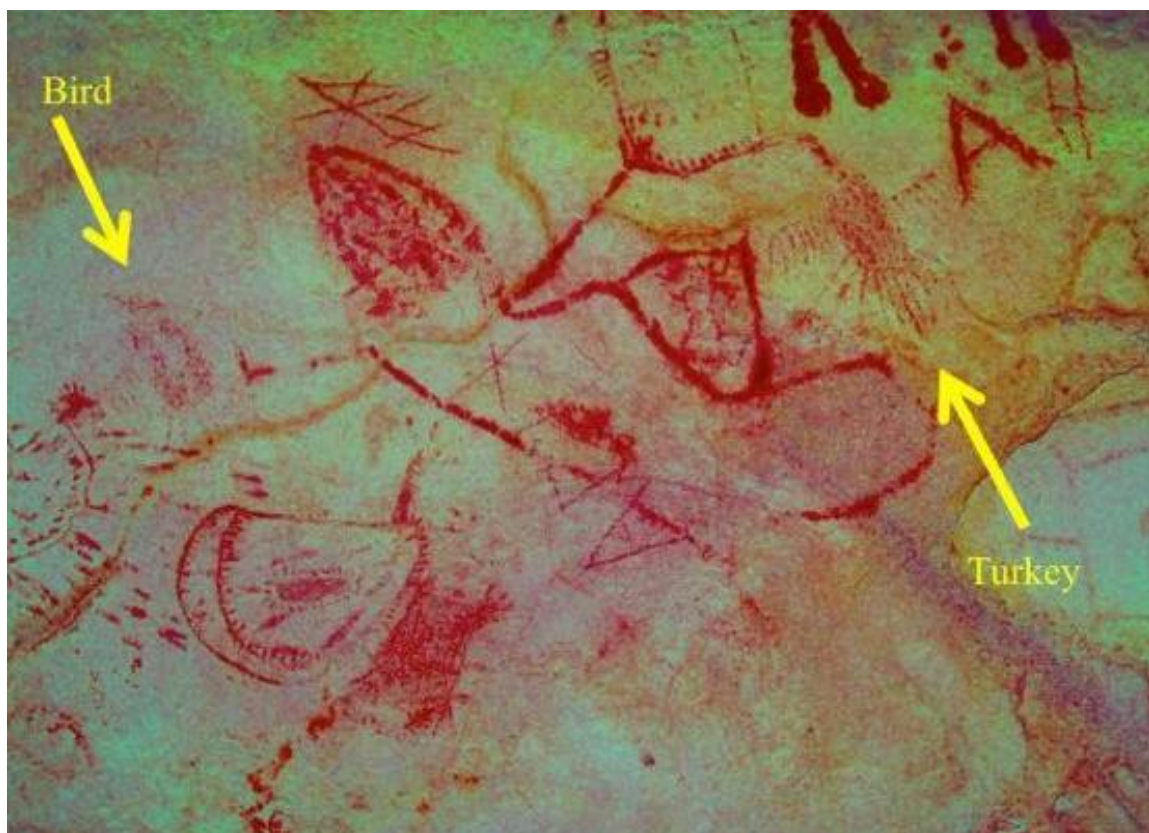


Figure 24: Birds and other red pictographs at the Parsons Site. Image enhanced with DStretch (see Appendix A). Image courtesy Mark J. Wagner.



Figure 25: Right facing quadruped at the Parsons Site. Imaged enhanced with D-Stretch. Image courtesy Mark J. Wagner.

Archaeological excavations have not been conducted at the Parsons Site. It has, however, been dug by looters. The former landowner informed us that, in the 1940s, a man used to board with him specifically to dig in the shelter. Based on the floor on the west end of the shelter, many looting episodes have occurred. In the spoil piles, we have observed lithic debitage, faunal remains, and—in one instance—a human cranial fragment. Pottery sherds are absent, suggesting that artifact diggers removed those along with finished lithic tools.

The painted images at the Parsons Site do not stylistically fit into the southeastern ceremonial symbols used during the Mississippian period in the region. This suggests the art at the Parsons Site likely dates to the proto-historic (ca. 1600-1672) or historic period (ca. 1673-1800). We note that the images are broadly like those that occur at rock art sites in the Great Lakes region (Dewdney and Kidd 1962; Perich and Furtman 2000), on the birchbark scrolls of

the Midewiwin society and the Algonquin motifs recorded by Henry Schoolcraft in the early 1800s (Schoolcraft 1851). The Mascouten believed in a powerful bison manitou (spirit) who lived beneath the earth (Thwaites 1899: 237-239) and given that many Mascouten were in the area at this time hunting bison, explains the presence of bison, hides, and bison-like rock art in the region.

Results

The seven rock art sites described above contain a wide range of motif designs. While most are executed in red paint, a few are in black. Now, we turn to the PXRF compositional results conducted on a sample of these motifs. The X-ray intensity represented by the spectrum peaks in our PXRF analysis is directly proportional to the concentration of each element in the specimen. To determine the composition of the pictographs, we used a two-pronged approach. First, all spectra were qualitatively examined and elements that were present or absent were identified. Second, a semi-quantitative spectral evaluation was conducted by converting spectra using Bayesian Deconvolution to determine Net Peak Areas (NPA) estimates of the elements present in the analyzed specimen. Each spectrum is deconvoluted through stripping routines that calculate the intensity of each element of interest and “strip” them from overlapping elements to eliminate matrix effects (i.e. mass absorption and overlap effects) that can occur during analysis (Lachance and Claisse 1994; Shackley 2011:21). The resulting NPA values represent the net photon count for each element. These values can be used to compare elemental concentrations between specimens without conversion to more quantitative format (Forster et al. 2011; Grave et al. 2012:1683). Once the NPAs were derived, they were normalized to rhodium. The PXRF instrument used contains a rhodium tube and provides a useful constant to measure and correct

intensity variations. The NPAs were then used to assess variability among the elements present in motifs from each site.

Stewart Site

We analyzed a total of three pictographs and one area of the bare, unpainted rock at the Stewart Site. The only red pictograph and two of the black anthropomorphic figures were included in the analysis (Table 1). Elements present in the pictographs and bare rock are Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Y, Nb, Zr, and minor amounts of Ba. The only noticeable difference in the spectra is in the amount of Fe. The red pictograph contains more Fe, while the black pictographs contain less. Black pigments can be produced by three chromophores: manganese, bone black, or charcoal. While manganese is present in the black pictographs it does not significantly vary from the control reading, suggesting that the manganese detected is from the sandstone and not the paint (Figure 26). If bone black [$\text{Ca}_3(\text{PO}_4)_2 + \text{CaCO}_3 + \text{C}$] was used to impart a black color, we would expect to see elevated levels of Ca and P. Only Ca is present in the spectra and is not elevated; instead the NPAs are similar in quantity to that of the control measurement. Phosphorus was not detected in either the pictographs or the control. Although PXRF cannot detect carbon, through the process of elimination, charcoal must have been the chromophore used to create these images. The red pictograph was made using an iron ochre chromophore. There are no other elements present in the spectra of the black or red pictographs to suggest a modern origin of the paint or any other additional ingredients to the paint recipes other than the primary chromophore.

Table 1: NPA Results from the Stewart Site.

PICTOGRAPH DESIGNATION	ELEMENT														
	Al	Si	S	K	Ca	Ti	Mn	Fe	Cu	Zn	Rb	Sr	Y	Zr	Nb
ANTHROPOMORPH #1	296	1488	82	155	1480	1613	40	7430	40	39	65	510	52	3419	30
ANTHROPOMORPH #2	309	2066	101	203	2038	1458	34	7852	41	61	57	529	59	3902	28
WING MOTIF	376	1965	79	369	1548	2288	82	18724	67	94	75	1052	18	3033	32
WING MOTIF	339	1675	17	236	813	1773	22	6465	23	72	47	529	51	1389	63
CONTROL	400	1900	52	454	1090	2533	62	12400	48	70	43	728	91	2085	34

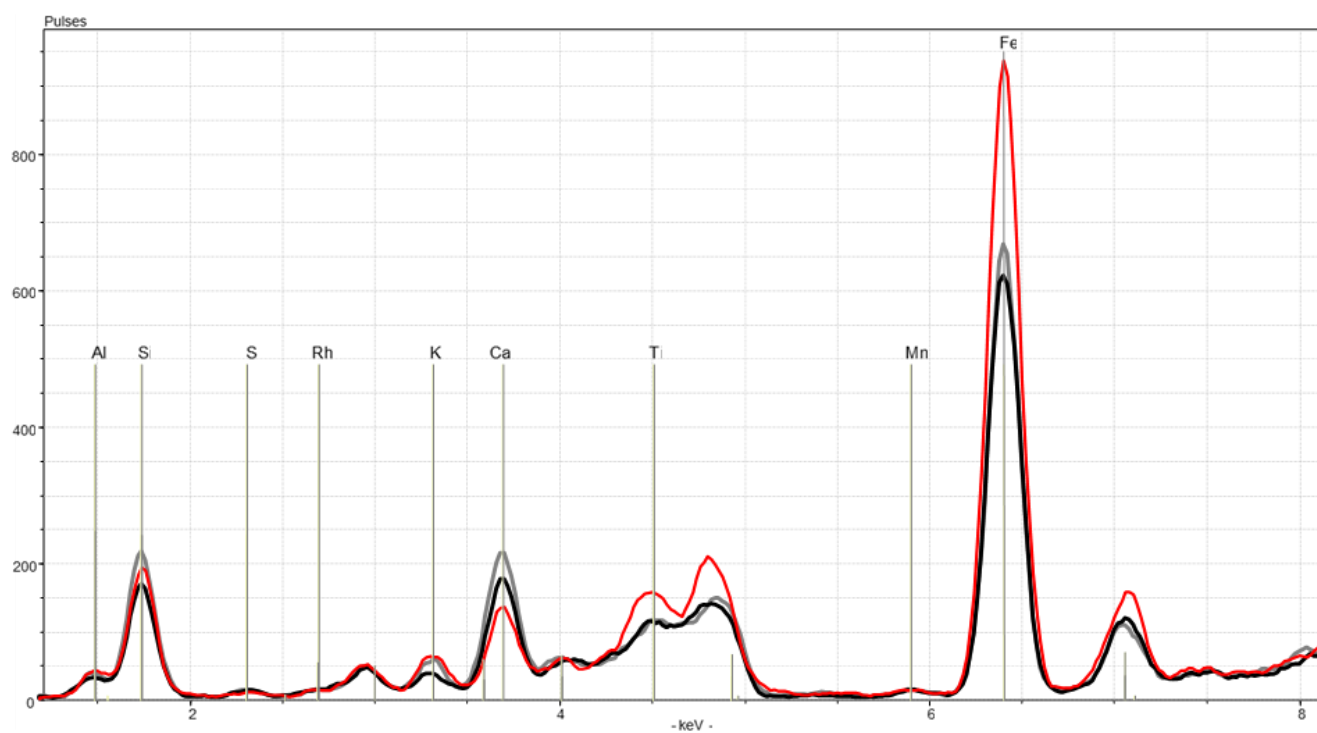


Figure 26: Spectral overlay of black pictographs and control readings at the Stewart Site. Anthropomorph #1 is black, Anthropomorph #2 is grey, and the control reading is depicted as the red line.

Painting Site

Due to the narrowness of the sloping ledge containing the pictographs, it was impossible to use the PXRF instrument in the field to directly analyze the images. Instead naturally detached exfoliated fragments with red paint were collected on the ledge directly beneath the paintings. These were analyzed in a laboratory setting using the same instrumental parameters. Where possible, the unpainted side of detached pieces was analyzed to serve as a bare rock control. Four detached painted pieces were analyzed, and we were able to take three control measurements (Table 2). Elements present include Al, Si, S, Ca, Ti, Fe, Cu, Zn, Rb, Sr, Y, and Zr. Primary differences between the control and paint reading are in the quantity of Fe. The paint chips contain more Fe than the bare limestone suggesting that paints used at the Painting Site consisted of an iron ochre chromophore.

Table 2: NPA Results from the Painting Site

SAMPLE	ELEMENT												
	Al Kα	Si Kα	S Kα	K Kα	Ca Kα	Ti Kα	Fe Kα	Cu Kα	Zn Kα	Rb Kα	Sr Kα	Y Kα	Zr Kα
PC #1	339	1709	1491	1332	52861	1244	14735	47	127	128	1297	89	794
PC #2	288	860	2623	1955	59971	1278	26498	37	128	254	1135	169	2389
PC #3	288	1078	1174	2047	54227	1272	14028	61	98	189	1276	141	2114
PC #4	292	1333	516	1493	53293	1128	15307	50	105	199	1012	123	1662
PC #5	326	1941	2712	1618	58739	1462	18078	60	118	192	1457	95	946
CTRL #1	312	2281	676	2049	53818	1276	15164	55	101	228	1155	158	2306
CTRL #2	259	933	4575	1374	66494	948	6720	47	94	185	1632	139	2043
CTRL #3	387	1814	1111	1720	105017	2047	17304	81	137	315	1854	165	2997

Piney Creek Site

At the Piney Creek Site, we analyzed a variety of pre-Contact and historic paintings. Eleven pre-Contact pictographs—including a canoe, five deer, three avimorphs, and three

anthropomorphs—were examined. One historic image and one modern graffiti image were also tested, and three bare rock control measurements were taken. Compositional data are shown in Table 3 and reveal interesting patterns. The bare sandstone shelter wall contains high quantities of silicon and relatively low concentrations of iron. There is a clear distinction between the richly painted motifs compared to the bare sandstone. Many of the more faded pictographs at the site are compositionally similar to the bare sandstone readings. For example, the canoe motif, a deer (Deer #2), bird, and shaman (Anthropomorph #3) are all chemically like the bare rock underlayer. While visually we can see that fading of these glyphs has occurred over time, the PXRF instrumentation is not sensitive enough to distinguish poorly preserved red pre-Contact pictographs unless other distinguishing elements are present to set it apart from the control readings.

Glyphs like deer #1 and #3-5, the turkey, the shaman with a shield (Anthropomorph #1), and the bowman (Anthropomorph #2) all contain much higher Fe levels and lower quantities of the Si, Sr, and Zr that makes up the sandstone. Interestingly, in this group there are some other elemental variations. The “Bowman” pictograph (Anthropomorph #2), Deer #3, and Deer #5 all contain manganese, which represents the only pre-Contact pictographs in the entire sample of southern Illinois pictographs with this addition. Manganese is not present in the bare sandstone control readings and therefore was added to the recipe before painting the images on the wall. Manganese is a naturally occurring mineral that can be used to create black pigments. At Piney Creek, it was used to create dark red images (Figure 27). The other pictograph with a distinctive chemical composition is Deer #4. This image contains high measures of both S and Ca, indicating that gypsum was likely added to the paint.

Table 3: NPA Results from Piney Creek.

PICTOGRAPH DESIGNATION	ELEMENT													
	Al Kα	Si Kα	S Kα	K Kα	Ca Kα	Ti Kα	Mn Kα	Fe Kα	Cu Kα	Zn Kα	Sr Kα	Zr Kα	Ba Kα	Pb Kα
ANTHROPOMORPH #1	281	3643		359	31	1613		6127	36	31	261	2952		
ANTHROPOMORPH #2	327	3653		727	28	1892	272	76719	39	97	331	4378		
ANTHROPOMORPH #3	339	3412		572	145	1769		2915	69	52	301	2301		
BIRD #1	314	4105		227	4	2008		4116	39	101	266	3653		
CANOE	313	3339		413	89	2022		3145	29	59	336	4318		
DEER #1 (ORIGINAL PAINT)	331	3064		542	15	1984		17338	18	62	397	4228		
DEER #1 (REPAINT)	309	3253		318	63	1434		14658	30	47	224	3387		
DEER #2	417	5014		428	23	2104		5419	88	116	295	6865		
DEER #3	250	2143		543	61	1341	348	42388	51	20	228	2326		
DEER #4	249	3141	379	310	3182	1375		10107	52	61	322	2682		
DEER #5	332	3798		487	84	1633	310	16234	19	69	314	4872		
HISTORIC PAINT #1	268	2048	1321	208	24	10646	981	3737	24	16	2594	3200	1865	10478
HISTORIC PAINT #2	348	4195		377	36	2229		4414	73	78	252	5240		
TURKEY #1	249	2850		299	203	1265		23760	61	49	223	1815		
TURKEY #2	299	3605		481	288	1769		11048	60	65	298	4000		
CONTROL #1	211	3412		211	48	1375		1391	21	23	211	4587		
CONTROL #2	358	4921		678	36	1632		2656	42	72	286	5446		
CONTROL #3	278	3442		420	44	1308		2073	39	42	334	3878		

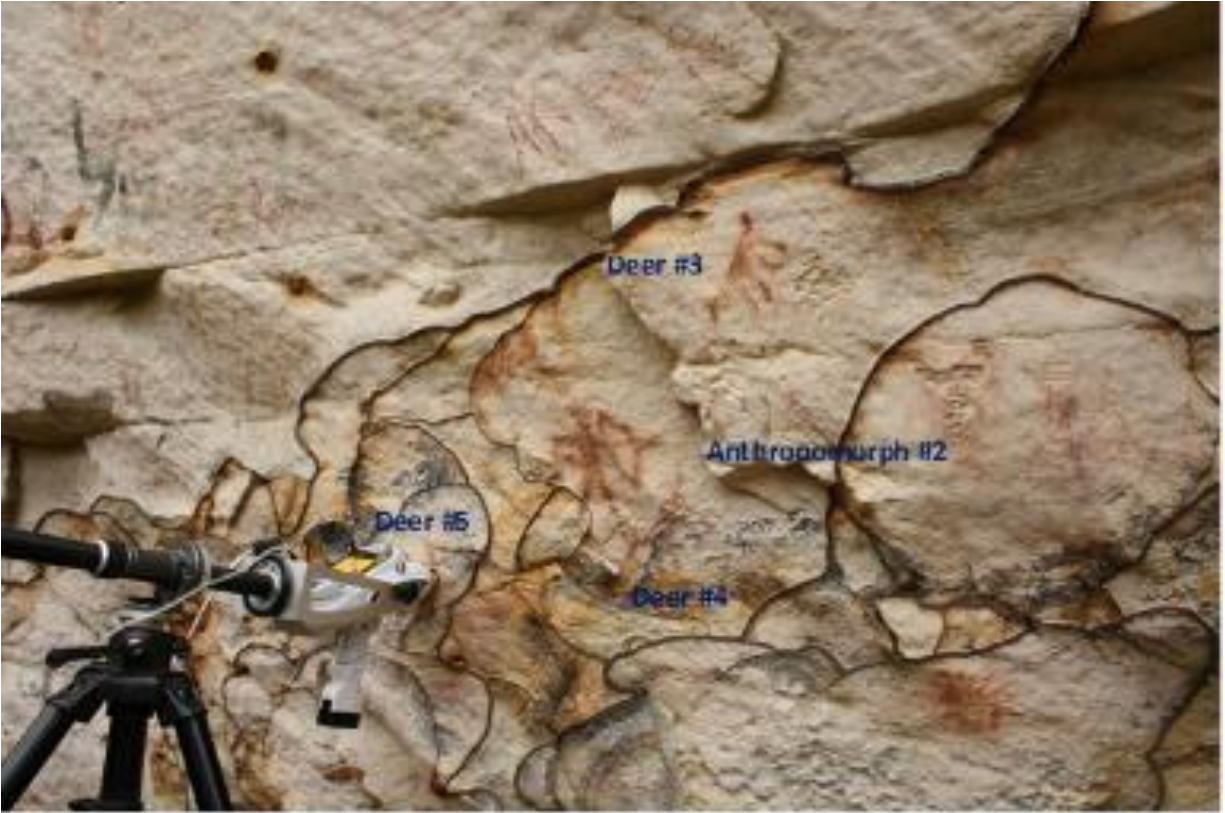


Figure 27: PEXRF analysis at the Piney Creek Site depicting the relative locations of Deer #3, 4, 5, and Anthropomorph #2.

For the pictographs that were historically refreshed at the Piney Creek Site, the paint used to recolor these glyphs does not differ elementally from the pre-Contact paints. Hematite, or iron ochre, is readily available in the Piney Creek ravine and was used by Peithmann when he repainted images. Even the historic “Mollie Hoskins” graffiti (Historic Paint #2) is chemically indistinguishable from some of the iron ochre pre-Contact paintings. If modern paint was used, we would expect to see elements like lead. Historic Paint #1 is a bluish-green paint on modern graffiti letters right below Historic Paint #2 (Figure 28). The elemental composition of this paint contains high quantities of S, Ca, Ba, and Pb.

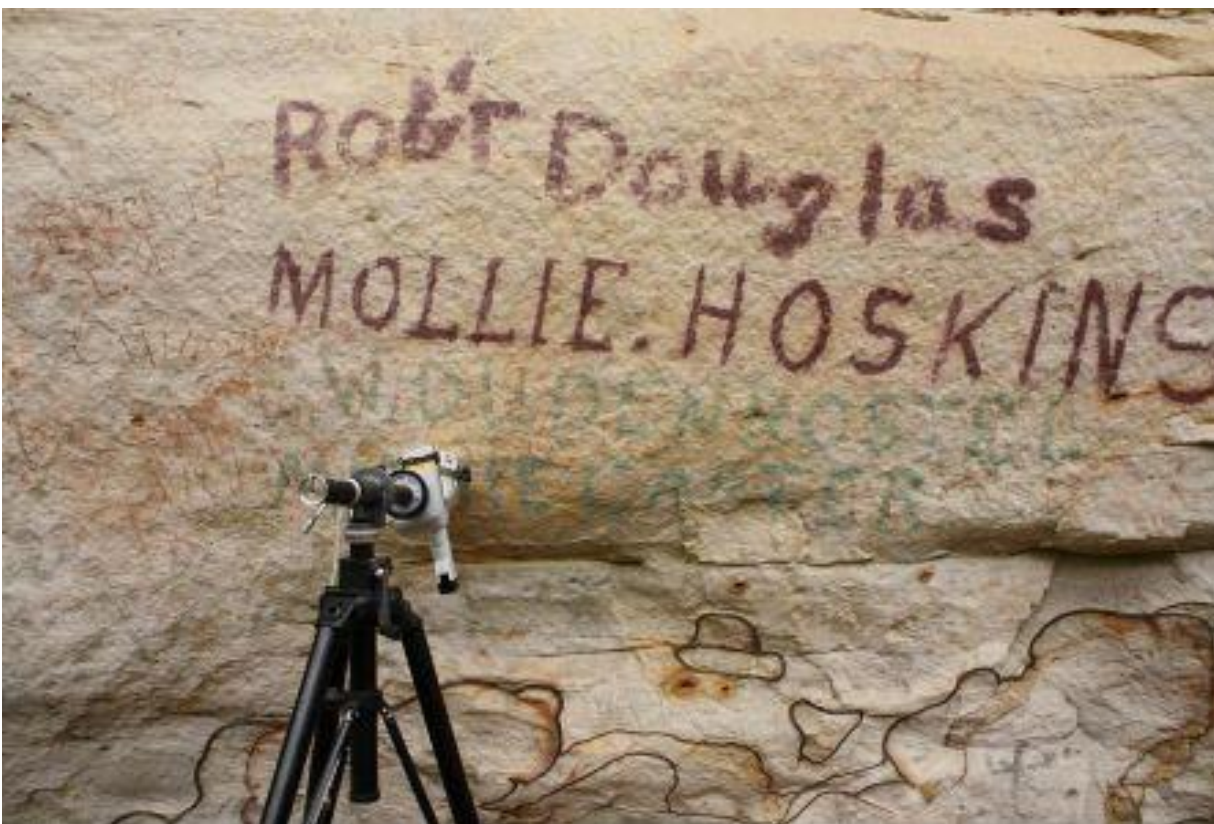


Figure 28: PXRF analysis of green graffiti modern paint at Piney Creek.

Korando Cave Site

At Korando Cave, we analyzed black charcoal line drawings in the outermost chamber of the cave. Due to the confines of the cave walls, we collected all assays by hand-holding the PXRF rather than using the tripod rig (Figure 29). We analyzed two black pictographs and one area of the bare, unpainted rock. Due to hand-holding the PXRF, we also shortened our analysis time down to 120 seconds. The PXRF results of these paintings were inconclusive due to a combination of hand-holding and the pictographs lines being too narrow for an adequate reading. Instrument stabilization ensures an accurate compositional measurement during the assay. Handholding produced too much instrument movement, resulting in spectra with significant spectral noise that made the identification of trace elements impossible. Producing a valid assay

via handholding on a vertical wall surface was nearly impossible, especially for the duration of 120 seconds. Due to the inability to acquire reliable compositional data, we chose not to analyze the red geometric pictograph further into the cave, which would have also necessitated handholding.

Some of the black images in the cave may be modern rather than prehistoric images (Simek et al. 2014). What were previously interpreted as human faces near the entrance to the cave (Wagner et al. 1999), appear to form the date “1918” when photographs are enhanced with DStretch, an image enhancing software (see Appendix A; Harmon, <https://www.dstretch.com/>). Given that these images were produced from a dry crayon application rather than a liquid paint, wood charcoal was likely the source material used to create the images regardless of their antiquity.

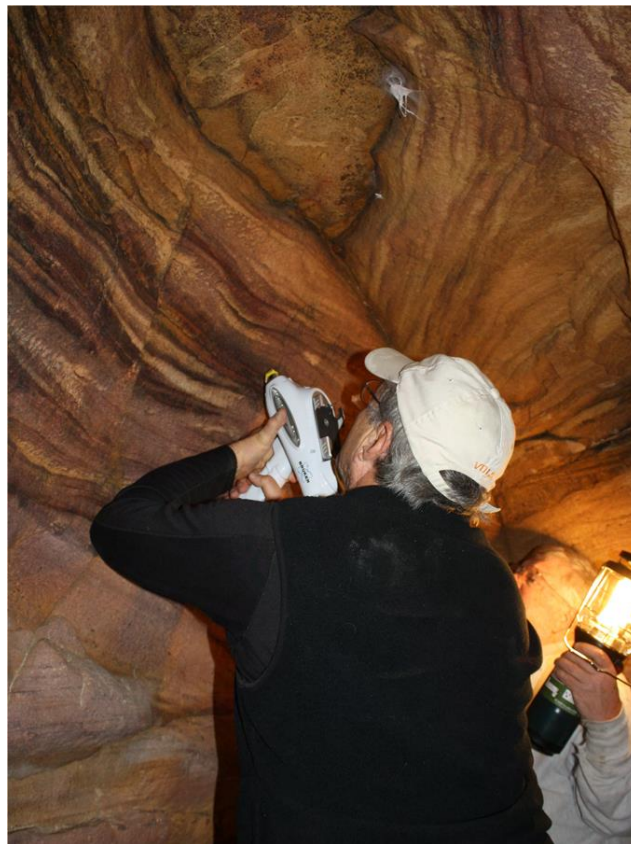


Figure 29: PXRF analysis by handholding of a black pre-Contact pictograph depicted in Figure 16.

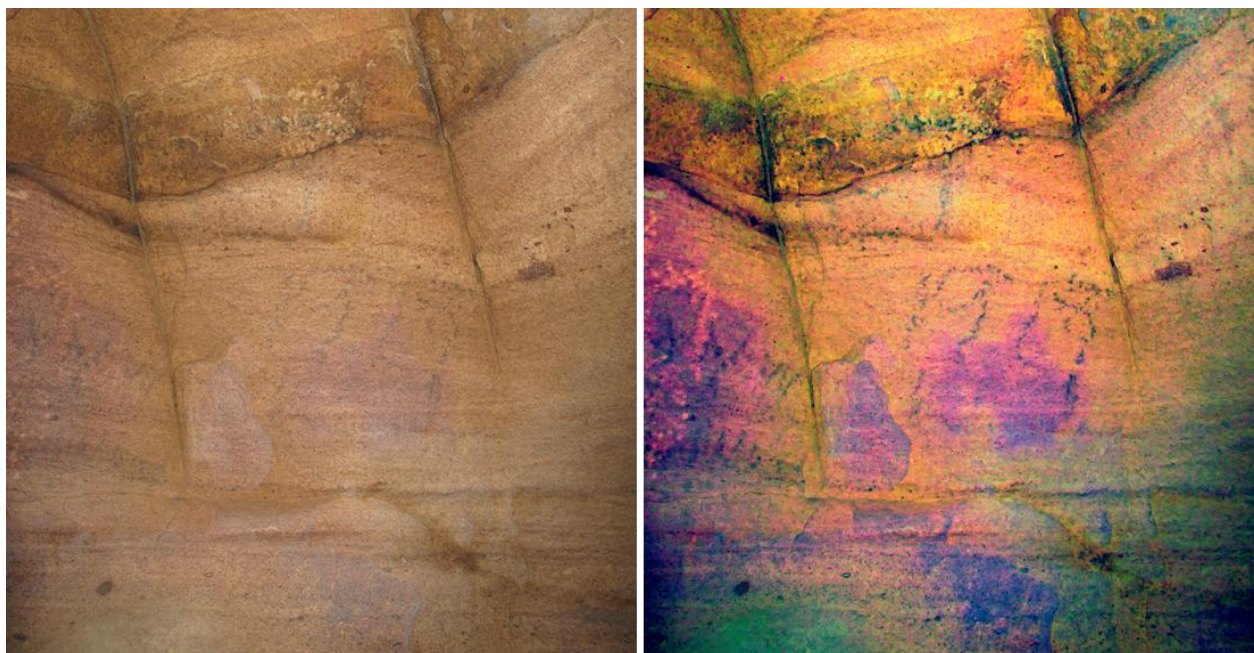


Figure 30: Historic black images in the front cave of Korando. Once the image was enhanced with DStretch (right; see Appendix A), the date "1918" could be identified. Images courtesy Jan F. Simek.

Bay Creek Site

At the Bay Creek Site, we analyzed seven paintings: two circle motifs, two ogees, a quadruped, and two sandstone rock controls. We also analyzed two fragments of raw hematite (mineral ochre) found on the shelter floor. All these motifs were either placed on the ceiling of the shelter or on high areas of the vertical wall. Due to these circumstances, we handheld the PXRF instrument to analyze two paintings (Ogee #2 and Quadruped #1). After reviewing the spectra, however, it was decided to not use the data because handhelding for 180 seconds again produced nonreplicable results. It is worth noting that the quadruped motif contains the highest relative concentration of Fe; this may reflect its better preservation. It is visibly the most prominent painting at the site.

The three remaining pictographs contained Al, Si, K, Ca, Ti, Fe, Cu, Zn, Sr, and Zr (Table 4). Ogee #1 contains the highest concentration of Fe and the lowest amount of Sr and Zr

when compared to the readings taken from the two circle motifs. The ogee motif is more color saturated, and that is reflected in the analytical data. The PXRF detects more underlying rock substrate when the paintings are lighter or more faded, as is the case with the circle motifs. Elements such as Si, Ca, Sr, and Zr are more prevalent than the Fe and are spectrally more like the bare rock controls than the darker pre-Contact paintings at the Bay Creek Site.

The red paintings at this site were created using a simple iron ochre chromophore with no apparent additives. The hematite analysis revealed that in addition to high quantities of Fe, several minor elements were also present including Al, Si, K, Ca, Ti, Zn, Rb, Sr, and Zr (Figure 31). Trace amounts of Mn and Cu were also recognized. Given that mineral ochre forms as a sedimentary deposit, clay minerals can be incorporated into its matrix, the result of which can be seen in the PXRF data. Therefore, the presence of these elements in the paint data is indicative of the chromophore and not of additional paint ingredients being incorporated at the site.

Table 4: NPA Results from Bay Creek.

PICTOGRAPH DESIGNATION	ELEMENT									
	Al Kα	Si Kα	K Kα	Ca Kα	Ti Kα	Fe Kα	Cu Kα	Zn Kα	Sr Kα	Zr Kα
CIRCLE GLYPH #1	233	46	8	272	990	608	31	82	226	1945
CIRCLE GLYPH #2	268	95	26	341	1251	781	36	53	147	1758
OGEE #1	302	808	1	352	1369	2278	48	71	108	1405
*OGEE #2	296	883	27	329	1325	2734	57	38	450	3459
*QUADRUPED #1	267	1336	54	433	1399	5404	50	39	253	3029
CONTROL #1	261	668	12	361	1646	1220	43	72	283	2705
CONTROL #2	244	1063	43	367	1171	2034	30	45	151	2038
* denotes glyphs that were not used in the final analysis										

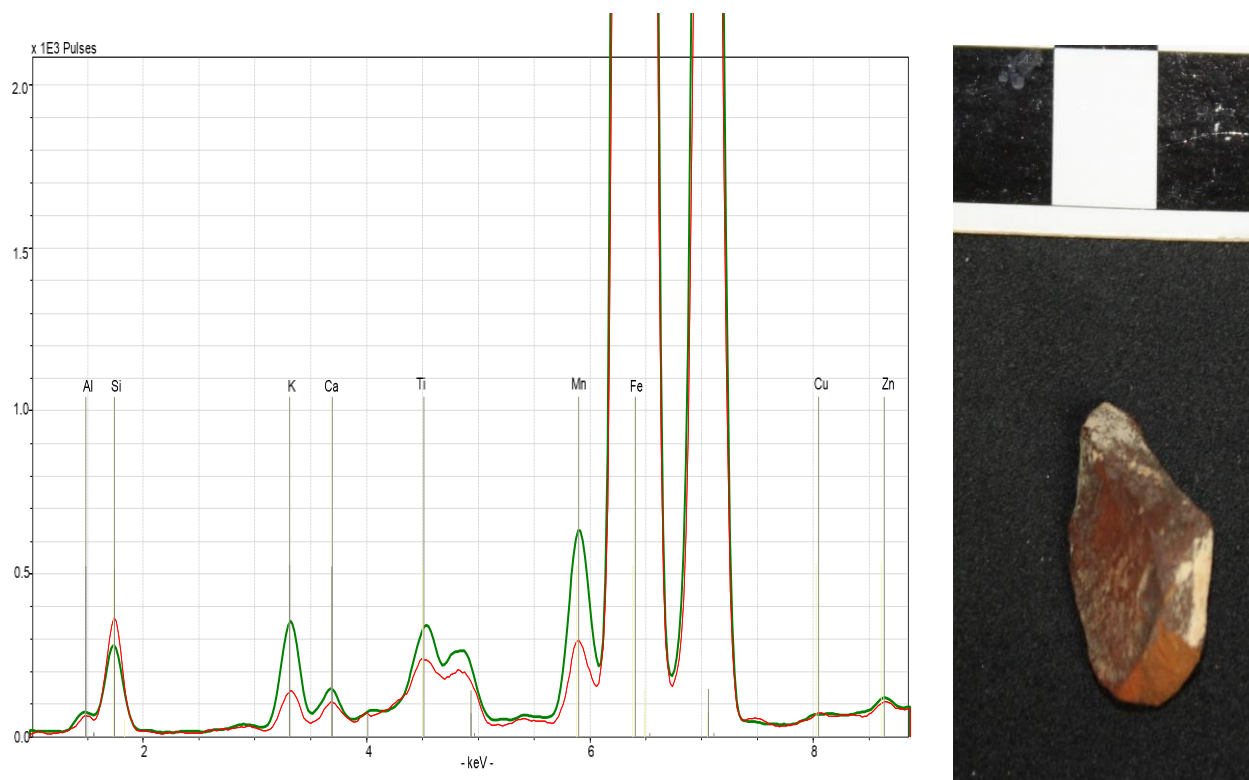


Figure 31: PXRF analysis of a hematite fragment (right) found on the ground surface at the Bay Creek Site.

Buffalo Rock

We analyzed a total of three pictographs, two bare rock controls, and took one measurement on an iron ochre fragment recovered on the floor of the shelter. When we visited the site in 2013 for our PXRF analysis, the bison pictograph showed evidence of recent attempts of refreshing the image by covering it with yellowish mud. This covering sat atop the red paint, presumably to emphasize the original form. As noted above, this image has been refreshed since the 1930s with what appears to be both red and yellow pigment. The original image, however, was red. We took two readings from this pictograph, one on the red underlayer (original) paint and the other on the newly applied yellowish mud. Elements present in the paint include Al, Si, K, Ca, Ti, Fe, Cu, Zn, Sr, and Zr (Table 5). When the red (original) paint is compared to the yellowish mud, the only notable differences are in the quantity of Fe present, with more Fe

identified in the red paint underlayer. The yellowish outermost layer contains higher concentrations of Sr and Zr. The high quantity of Fe in the red paint suggests an iron ochre was used for the original painting of the bison image.

The other pictographs analyzed at Buffalo Rock were a moon motif and a star motif, both executed in red paint. The PXRF analysis indicated the presence of Al, Si, K, Ca, Ti, Fe, Cu, Zn, Sr, and Zr. Both images contain high levels of Fe, which we would expect from ochre paint. However, the moon pictograph also contains high levels of Ca, which could indicate a clay or calcite was used as an additional component to the paint recipe.

Table 5: NPA Results from Buffalo Rock.

PICTOGRAPH DESIGNATION	ELEMENT									
	Al Kα	Si Kα	K Kα	Ca Kα	Ti Kα	Fe Kα	Cu Kα	Zn Kα	Sr Kα	Zr Kα
BUFFALO (ORIGINAL)	324	1166	718	336	1842	82383	13	35	206	393
BUFFALO (COVERING)	399	2044	544	390	1732	32593	46	36	362	1110
MOON #1	238	647	129	1868	1074	3383	38	55	212	512
STAR #1	272	260	44	430	1150	5140	28	41	180	383
ROCK CONTROL #1	401	2887	222	489	1768	2041	34	83	210	628
ROCK CONTROL #2	234	2077	86	425	1207	2075	27	63	180	1610

Parsons Site

Eight pictographs and one rock control were analyzed at the Parsons Shelter (Figure 32). Elements present in the spectra include Al, Si, K, Ca, Ti, Fe, Cu, Zn, Sr, and Zr (Table 6). There are some notable differences among the pictographs from the Parsons Site. First, the legs of the canid pictograph contain sulfur—an element not present in any other glyphs from the site—and the highest concentration of Ca. These two elements are constituents of the mineral gypsum

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which may have been intentionally added to the paint recipe before creating the motif. Again, we see varying amounts of iron, which is directly tied to the visibility of the painted

motifs. Motifs that are thinner and more faded have less Fe and more Si, Sr, and Zr, indicating that the PXRF is analyzing the faded image as well as a substantial portion of the sandstone underlayer. Those images that are more thickly painted contain higher Fe and relatively lower concentrations indicative of the sandstone. Once again, iron ochre appears to be the primary chromophore for the images created at this site.



Figure 32: PXRF analysis at the Parsons Site. Image courtesy Jan F. Simek.

Table 6: NPA Results from Parsons Site.

PICTOGRAPH DESIGNATION	Motif Design	ELEMENT										
		Al K α	Si K α	S K α	K K α	Ca K α	Ti K α	Fe K α	Cu K α	Zn K α	Sr K α	Zr K α
GLYPH #1	Abstract Fringe	274	1947	33	67	552	1292	1228	66	38	233	1569
GLYPH #2	Moon	373	2965	13	151	600	1475	1089	40	72	281	944
GLYPH #3	Bison	253	2390	2	83	445	1240	1592	29	27	154	283
GLYPH #4	Quadruped	415	4133	397	487	4618	1991	6639	45	95	386	1740
GLYPH #5	Letter "A"	303	3214	78	375	1121	1852	8544	49	64	362	3266
GLYPH #6	Enigmatic creature	257	2186	49	134	645	1061	3067	51	45	387	1287
GLYPH #7	Bison Hide	258	3100	40	179	630	1267	6496	41	52	265	1091
GLYPH #8	Bison	259	3416	31	129	835	1288	606	44	72	342	1637
ROCK CONTROL #1		320	3734	66	162	974	1517	1826	49	66	402	2079

Discussion

In determining the elemental composition of paints used to produce the rock art from the sites in southern Illinois, the low-z elements are the primary indicators of recipe variations. For the most part, pre-Contact paint recipes in this region are simple, comprising a primary chromophore. This chromophore likely had water added to produce a liquid paint that was then applied to the rock surface. Reds were created using iron-rich ochre, while black paints were created using wood charcoal as the colorant. Pre-Contact pictographs at the Stewart Site, the Painting Site, and the Buffalo Rock site all contain images created with this basic recipe. The Parsons Site and the Piney Creek Site also contain paintings with this recipe, but some images at these two sites contain additional ingredients.

At least one of the pictographs at the Parsons Site and one at the Piney Creek Site contained gypsum, which could have given the image technical or supernatural enhancements. Although it is not necessary to create effective paint, gypsum can be added to function as a binding agent helping the paint adhere and harden onto a surface (Rowe 2001; Siddall 2018). Both images containing gypsum are of quadrupeds—a dog at the Parsons Site and a deer at the Piney Creek Site. Gypsum is hydrous calcium sulfate ($CaSO_4 \cdot 2H_2O$) that can be found in caves where the air is dry enough to allow it to be deposited and preserved. Pre-Contact cave mining is not unusual in the Southeast. Dating back to the Archaic period, peoples mined and used a range of minerals, especially gypsum (Crothers 2012; Crothers et al. 2002; Munson and Munson 1991; Pritchard 2008; Simek et al. 1998; Watson 1969). While the addition of gypsum may have served to increase the effectiveness of the paint, it may also represent a symbolic addition to the paint.

Additionally, two of the images at Piney Creek—a bowman and a deer that face one another—contain manganese, which can be used to create black paints or to darken a color chromophore. At Piney Creek, manganese was used in combination with iron ochre to produce a deep red color. Three other pictographs on the same panel as the bowman and deer were analyzed but no other pictographs contain manganese. This suggests that the bowman and deer motifs at Piney Creek were produced at the same time, and likely by the same artist as part of a small but separate composition at the shelter.

Relative dating methods can place art within a general chronological framework especially when they are based on a combination of different kinds of evidence. Subject matter like the bow and arrow and bison were introduced into the region at particular times and can provide *terminus pro quo* ages for the art. A similar approach involves comparisons between rock art motifs and similar styles on other, better-dated archaeological media. Lastly, associated surface artifacts present at a site and excavations may also provide some indication of the age of the art. For the sites presented here, a combination of these methods was useful to determine the relative ages of the art, but we cannot know for instance whether the art at a site was produced at a single point in time or if it was the result of multiple visits to a site. Differing paint recipes at sites like Parsons and Piney Creek suggest multiple painting episodes.

In this sample of rock art sites, several individual paintings were historically refreshed. These pictographs always contained higher concentrations of iron, which is what we would expect to see if ochre was used, but it also raises an important consideration for PXRF analysis. While this instrument is sensitive, analyzing faint or faded pictographs can be difficult if the underlying material is not also analyzed *via* measured controls. In all our analyses, measurements were made of the limestone and sandstone rock to assess inter- and intra-site

variability. In many instances, the presence of certain elements in the measurements taken from a pictograph can be directly attributed to the background composition of the shelter itself. We are able to sort this out by examining the net intensities of elements in the paint and control readings. Through our analysis, we were able to distinguish modern paints from pre-Contact ones. As was the case at the Piney Creek Site, the modern paint analyzed contained elements such as barium and lead. In instances where pictographs had been repainted by avocational archaeologists like Irvin Peithmann, however, no elemental differences between the historic repainting and pre-Contact original paint were detected. The materials used for re-freshening were the same as the pre-Contact ones.

Conclusions

The rock art sites selected for this analysis represent different cultural affiliations and contain a wide array of imagery. Late pre-Contact, Mississippian-aged sites contain motifs such as ogees, falcons, horned-serpents, bi-lobed arrows, anthropomorphs, and quadrupeds executed in red and black paint. Proto-historic and Historic sites depict red bison imagery. Given the variation in chronology and subject matter we assumed that paint recipes at these sites would correspondingly differ. The paint recipes, however, are remarkably standardized across our sample. Reds and yellows were created using an iron-rich chromophore and blacks were produced from charcoal. These chromophores were then mixed with water to create a liquid paint that was then applied to the rock surface at each site. This basic recipe was identified in all but four pictographs. At Piney Creek a manganese-iron recipe was used to create two images. The manganese addition likely served a technical function to impart a rich, dark color. Another variation of paint recipe was the addition of gypsum at two pictographs, each from different

sites. This addition could have served strictly as a binder for the paint, or it may have served as a non-utilitarian additive to symbolically imbue the image. These outliers likely represent different art episodes at the sites; however, both sites (Piney Creek and Parsons) display an abundance of art indicative of multiple art making events, the majority of which are produced using the same basic recipe. Even though variances in paint recipes only occurred in four pictographs, they represent cases where the paint recipe was intentionally modified to achieve the artists desired result.

We believe our findings indicate that the basic color/water mixture paint was efficacious, and, in some cases, recipes were modified to either technically or symbolically enhance the paint. While this study examines several sites and images in southern Illinois, many more remain to be investigated with PXRF. As our sample becomes more robust, our knowledge of the materials used to create these artworks will become more comprehensive. This will enable us to view the rock art traditions of southern Illinois within the larger context of their relationship to other similar Native American pictograph sites in the Mississippian world.

Transition from Chapter II to Chapter III

The previous chapter (Chapter II) demonstrated that PXRF can enhance our understanding of how pre-Contact, Proto-Historic, and Historic rock art was made. It is a powerful tool for non-destructively investigating important cultural heritage artifacts. Through this case study, we determined that paint recipes *can* differ with respect to motif design in rock art. It also indicates that if paint recipes can differ within rock art, perhaps recipes will be variable across other archaeological media. Chapter II also highlights a main pitfall in PXRF methodology in that instrument stability is a critical part of obtaining precise compositional data. Methods can further be refined through the instrument settings to examine a wide range of elements and reduce field analysis time, thereby allowing for more specimens to be analyzed. Moving forward, all analytical assays were obtained with the following instrumental settings: 40kV, highest micro amperage, and a vacuum pump. The micro amperage was modified in each case to optimize the raw count rate in the instrument detector as to not over- or under-saturate the specimen with X-rays. The micro amperage must be adjusted to produce accurate compositional data. This combination of instrument settings allows all X-rays from 1keV to 40keV to reach the specimen and excite elements from Magnesium to Plutonium. Without sacrificing compositional data, these settings also significantly reduce the time spent analyzing one specimen. Without the need to adjust the instrument and change filters and take two readings from one spot, the time spent analyzing one specimen is reduced by nearly 3/4ths. By reducing the sampling time, more specimens can be analyzed during a session.

The next chapter I used these methodological changes and explores another archaeological medium, Mississippian stone statuary. I also add another analytical instrument to the analysis, a fiber-optic reflectance spectrometer (FORS). This instrument provides

mineralogical data. As explained in Chapter I, FORS complements the PXRF data and provides a more comprehensive non-destructive analysis of pre-Contact paint recipes.

CHAPTER III: CARVED IN STONE: A COMPOSITIONAL ANALYSIS OF FREESTANDING MISSISSIPPIAN STONE STATUARY

A version of this chapter is being prepared for publication by Sierra M. Bow, Jan F. Simek, Kevin E. Smith, Robert V. Sharp, and Jeffrey E. Moersch as:

Bow, Sierra M., Jan F. Simek, Kevin E. Smith, Robert V. Sharp, and Jeffrey E. Moersch (2020). Compositional Analysis of Mississippian Stone Statuary. *Journal of Archaeological Sciences* (in preparation).

This chapter is a research chapter. The text of this chapter regularly uses the pronouns “we” and “our” to reference the contributions of my co-authors, Drs. Jan F. Simek, Kevin E. Smith, Robert V. Sharp, and Jeffrey E. Moersch. It should be noted, however, that in addition to conducting the analytical research, I am the senior author. This work will be submitted to the *Journal of Archaeological Science*. This peer-reviewed journal provides an international forum for archaeologists and scientists who can advance the development and application of scientific techniques and methodologies to all areas of archaeology. Particular emphasis is placed on methodological innovation and their archaeological significance. The Impact Factor of the *Journal of Archaeological Science* is 3.030 and a CiteScore of 3.35. In this dissertation, the main structure of the paper and the word count are compiled based on the journal guidelines. A typical paper for this journal should not exceed 5,000 words—excluding tables and figures. Complete guidelines for preparing and submitting the manuscript to the journal can be found here: <https://www.journals.elsevier.com/journal-of-archaeological-science>. Apart from the content and word requirements, all remaining formatting in this chapter follows guidelines set forth by the University of Tennessee Graduate School.

Abstract

Since the mid-nineteenth century, many stone statues have been discovered in Mississippian contexts in the Southeast. Much research has been devoted to recording and describing cultural attributes of these enigmatic figures, but little attention has been devoted to the composition of the figurines themselves or the paint often applied to the faces. In large part, this is due to the destructive nature of traditional laboratory instrumentation and techniques, and the inability of such techniques to be used in the field. Here, we report on chemical and mineralogical analyses of Mississippian stone statues from the Tennessee-Cumberland Region of Tennessee using non-invasive Portable X-Ray Fluorescence (PXRF) and Fiber-Optic

Reflectance Spectroscopy (FORS). Results obtained on twenty-eight carved statues indicate that different raw material types were used prehistorically. This suggests that statues were not manufactured in one or a few locations but rather created and used locally. We were also able to determine pre-Contact paint composition on the statues. Our work demonstrates the efficacy of PXRF and FORS for adding to our understanding of pre-Contact religious objects in the region.

Introduction

When explorers began their forays into southeastern North America during the sixteenth and seventeenth centuries, they saw a variety of novel artifacts made and used by pre-Columbian native peoples. Noteworthy among these were idols found in the “temples” or “shrines” of native peoples (Adair 1775; Anghiera 1912:262-267; Beverley 1905; Le Petit 1900; Shelby 1993:299, 301-302; Strachey 1949:90; Swanton 1911:260-261; Varner and Varner 1951:315-325). These figures were sculpted human or anthropomorphic statues most frequently made of wood but occasionally of stone and pottery. While these shrine statues roused enough curiosity to be mentioned in chronicles of these early explorers, they were in search of something more valuable in the form of gold or land. It was not until the farming and cultivation of the fertile southeastern bottomlands in the 18th and 19th centuries that these statues were rediscovered. Since then, precontact freestanding stone figures have attracted the attention of the public, antiquarians, and archaeologists.

One of the earliest documented discoveries of a stone statue was found by an anonymous farmer plowing along the Cumberland River southwest of present-day Lexington, Kentucky (Smith and Miller 2009:1-2). The statue was sent to Thomas Jefferson on July 8, 1790, who described it as “the best piece of workmanship I ever saw from their [Indian] hands” (Jefferson

1791). After this discovery, more statues were uncovered by farmers tilling their land throughout the river valleys of the interior Southeast. By the mid-1800s expanding farms and the emergence of “digging” for antiquities as a new hobby fueled the discovery and interest in these figures. This resulted in a wide range of speculative theories as to who created them (Atwater 1820; Clifford 1820; Haywood 1823:140-141), and their relative rarity made them into highly sought-after objects for elite collectors.

Because the overwhelming majority of statues were discovered by farmers, antiquarians, or collectors, detailed archaeological contexts and associations for these objects are poorly described or altogether lacking. There have been a few attempts to catalogue these figures (Engle 1957; Jones 1869; Myer 1928; Thruston 1897; Webb and DeJarnette 1942), however, Smith and Miller’s *Speaking with the Ancestors* (2009) is the only systematic attempt to bring together and depict all known examples in a comprehensive gazetteer. These authors researched over 88 possible examples of southeastern Mississippian statuary dating back as far as 1,000 years ago, and they measured, analyzed, photographed, and traced the known histories of 42 statues that comprise the Tennessee-Cumberland style statuary corpus (for a tabular summary of statuary characteristics, see Appendix A.1 in Smith and Miller 2009:181-201). From this Smith and Miller concluded that the Tennessee-Cumberland style statues were sculpted from a variety of relatively soft stones that, based on macroscopic observations, are distributed in a broad geographic area of the interior of the southeastern United States. Therefore, it is theorized that these figures were used and deposited in the archaeological record not too distant from their place of manufacture rather than being centrally manufactured and distributed throughout interconnected Mississippian communities (Smith and Miller 2009:32). To test this hypothesis, we use two non-destructive analytical techniques—portable X-ray fluorescence spectrometry

(PXRF) and fiber-optic reflectance spectrometry (FORS)—to examine the material properties of the stone used to create a sample of these statues. The goal of this analysis is not to source the raw material to a geographic location, but to empirically determine the raw material composition and to understand the variability in the resources used to create these figures. We also explore the composition of paints on a few statues. Both of these techniques are completely non-invasive and non-destructive, which are highly advantageous qualities for the analysis of precious archaeological materials.

Mississippian Stone Statue Characteristics

Human figural art in the Southeast dates to at least 3500 years ago, when people of the Poverty Point Culture of the Mississippi Valley (Gibson 2000:151-152) crafted solid, baked loess into small and simplistically portrayed anthropomorph figures. Around A.D. 1-400, evidence for more complex human figural art arose from the cultures within the Hopewell Interaction Sphere (Seaman 2004) but it is not until the Mississippian period, around A.D. 900-1500 that sculpted human figures become larger, and more complex (Smith and Miller 2009). Mississippian cultures spanned hundreds of societies over a large region of the American Midwest and Southeast that flourished by A.D. 1200. While there are some differences among the Mississippian subgroups, they all exhibit similar religious, ceremonial, and technical practices (Brose et al. 1985; Townsend and Sharp 2004). The widespread development of maize agriculture with the ability to cultivate and generate food surplus resulted in population expansion, complex towns and polities, and large-scale spheres of trade and influence. Over time these spheres emerged into complex socio-political systems or chiefdoms with hierarchical organization, centralized religion, and widely produced iconographic art. As artistic traditions

developed and expanded in the Mississippian world, artisans crafted statues that broadly served similar functions as important religious relics within many chiefdom centers. They have long been interpreted as objects of special religious veneration, perhaps supernatural beings, ancestors, or other spiritual personages that were kept and used in religious centers to provide a foundation of chiefly power within Mississippian chiefdoms (Smith and Miller 2009:32).

The densest concentration of these objects lies in the Cumberland River Valley of Tennessee and Kentucky, and in north Georgia, with some found from sites along the periphery of the Cumberland River Valley in Tennessee and in the Ohio and Mississippi valleys. More than forty-eight statues have been catalogued in this area and are collectively referred to as the *Tennessee-Cumberland style statuary* (denoted as CSS). The Tennessee-Cumberland style statues share several common stylistic attributes throughout the corpus. Sculpted features focus primarily on the head detailing the eyes, nose, mouth (some depicting lips, tongue, and teeth), and hairstyles or coiffure (Figure 33). Occasionally, paint is also present on details of the head, or on the body of statues (see Figure 34a and Figure 40). Secondary emphasis is given to the upper torso area. Sex characteristics have been identified, appendages such as hands and feet are sculpted to a varying degree, and a few additional features are sometimes carved, like shoulders, collarbones, and vertebra (Smith and Miller 2009:20-29). A small number of statues from near Nashville, Tennessee, and Etowah, Georgia, have characteristics interpreted as clothing in the form of a waistband accompanied by a line above the knee (suggesting a kilt or skirt, see Figure 33b). Seating positions are also apparent for the statues that have been sculpted below the waist and posture often correlates with identified sex characteristics. The Tennessee-Cumberland style stone statuary typically depict individuals in relatively simple attire.



Figure 33: Features carved on the Tennessee-Cumberland Style statuary listed in Table 7. Image A- CSS-003 (left) and 002 (right) carved limbs and feet; Image B- CSS-089 female statue in seated position C. Hands, limbs, breasts, and clothing are depicted; Image C- CSS-018 with typical male hair knot. Image D- CSS-003 rare hairstyle. Image E- CSS-004 detailing hands and fingers across the abdomen; Image F- CSS-018 male statue in seated position A. Facial features, including the neck, and limbs are detailed. Images courtesy David Dye.

Based on these carved characteristics two broad types of statues have been identified—Ancestral Pairs and a character called “the Old Woman” (Smith and Miller 2009:29-36). The first represents male and female statues that exhibit clusters of sculpted traits suggesting the sculptor originally made them as a set. Male-female paired statues are typically found from the same site and are believed to represent real or mythological lineage ancestors (Figure 34). The Old Woman theme gets its name from a supernatural female figure known across North America by various names (i.e. Old Woman, Old-Woman-Who-Never-Dies, Grandmother, Corn Mother, Earth Mother, among others) (Bowers 1950, 1963; Beckwith 1938; Mooney 1900; Prentice 1986). Statues that fit within this theme display female sex characteristics along with the hands resting on a projecting abdomen (Figure 35). Sculpting of the vulva can also be present on these statues.

Overall, the characteristics of the Tennessee-Cumberland style statuary depict realistic portrayals of human (or spiritual human) figures sculpted from stone, and while the statues have been examined for individual and shared visual characteristics by Smith and Miller (2009), the stone itself and the paint sometimes applied to the faces have yet to be fully inspected. Part of this is due to the dispersed nature of the corpus of Tennessee-Cumberland style statuary. The lack of materials research is primarily due, however, to an understandable reluctance to destroy (even if minutely) parts of these beautiful artifacts for scientific gain. Fortunately, recent technical advancements in spectrometry allow for precise chemical analyses performed non-invasively without affecting the specimen.

Our initial interest in the composition of these stone statues came through a separate research project on revealing the material properties of Mississippian period rock art paint using PXRF (Simek et al. 2020). As part of this research, we analyzed a variety of painted archaeological media including rock and cave art, pottery, and two statues (CSS-003 and 004).

Due to the nature of PXRf analysis, our analysis protocol necessitates a control reading of the bare, unpainted substrate to make interpretations of the true paint ingredients used to impart color. During the analysis of two statues from the Sellars Farm site, CSS-003 and 004, we noticed that despite both statues being carved from a hard, sandstone material the composition of the stone itself was highly variable. We expanded our sample size and analyzed four more statues (CSS-001, 009, 031, and 065). Again, the results suggested different raw material sources were selected to create the statues.

These preliminary results prompted new research questions concerning how these statues reflect their origins and social function—were these statues produced and used locally, or were they manufactured in a few locations and traded through interconnected Mississippian communities? One way to begin to address such questions is through examining the stone from which the statues were made, as variation or lack thereof in the stone sources has implications for how and where these objects were made, distributed, and perhaps venerated. Again, Smith and Miller (2009:32) proposed that for the most part these statues were created and used locally. This theory of production and use of the Tennessee-Cumberland style statuary contrasts with that of “red stone” figures recovered from Mississippian sites like Cahokia, Spiro, Moundville, Shiloh, and a few other locations in the American Bottoms (Emerson 1982, 1989, 1997; Emerson and Hughes 2000; Emerson et al. 2003). The Cahokia style statues are another large corpus of figures with a highly developed and distinctive realistic portrayal of human or mythic figures carrying out specific acts or deeds (Reilly 2004). Compositional analyses of these red stone statues have established they were carved from flint clay sourced in southeastern Missouri, suggesting that these figures were likely manufactured by artisans at Cahokia and then moved at



Figure 34: Example of Tennessee-Cumberland Ancestral Pairs from Table 7. Males are sitting left and females on right. A- Sellars Farm pair, CSS-003 and 002, both with apparent paint; B- Riddleton Pair, CSS- 018 and 019; C- Brentwood pair, CSS-030 and 031, male sex characteristics carved; D- Beasley Mounds pair, CSS-010 and 011. Images courtesy David Dye.



Figure 35: Examples of the Old Woman statuary theme from Table 7. Left to right: CSS-024, 004, and 023. Images courtesy David Dye.

various times through mechanisms of extra-local exchange (Emerson and Hughes 2000; Emerson et al. 2003). If the Tennessee-Cumberland style stone statuary are locally produced and used, then we would expect the raw materials used to create them to be variable. In this paper, we test this hypothesis by conducting a non-destructive compositional analysis through PXRF and FORS to empirically identify the raw materials used to create these figures and examine variability within raw materials used to produce Tennessee-Cumberland statuary. We also examine the paint recipes used to decorate a select few and compare the data to other examples of Mississippian period paint in the region.

Materials and Methods

Samples

In 2015 the Tennessee State Museum in Nashville curated an exhibition entitled *Ancestors: Ancient Native American Sculptures of Tennessee* (Figure 36). This exhibition presented the largest group ever assembled of pre-Contact Mississippian stone statues, with twenty-eight specimens gathered from the institutional collections of various museums and private collections (Table 7). Our analysis took place during the installation (October 2015) and decommission (May 2016) of the exhibition. All of these statues stylistically conform to the Tennessee-Cumberland style stone statuary as described above. Within this group, twenty-six statues originated during the Mississippian period, while two statues are documented 19th century forgeries. We include these folk-art statues in our results to highlight the advantages and pitfalls of using PXRF and FORS to interpret the material properties of archaeological materials. Of the pre-Contact statues, eight are Ancestral Pairs (CSS-002/003; 010/011; 018/019; and 030/031), and five are stylistically characteristic of the Old Woman. The remaining statues do not have apparent traits to securely ascribe them into the Ancestral Pair or Old Woman type as described above.

Methods

Both instruments collect information along the electromagnetic spectrum, the difference is in their detector capabilities and their range. PXRF functions within the x-ray spectral range and FORS within the visible and near-infrared (VNIR) and short-wave infrared (SWIR) wavelength regions. Thus, PXRF produces spectra associated with atoms, giving the elemental composition of a material; FORS produces spectra associated with compounds, i.e. mineralogy.



Figure 36: Ancestors Exhibit. Image courtesy Tennessee State Museum.

Furthermore, both methods are rapid, can be performed *in situ*, and are completely non-invasive. PXRF and FORS have been used on a variety of archaeological applications (Appolonia et al. 2009; Bacci et al. 1992; Cavaleri et al. 2013; Craig et al. 2007; Delaney et al. 2014; Grave et al. 2012; Hunt and Speakman 2015; Picollo et al. 2000; Shackley 2011; Shugar and Mass 2012; Speakman et al. 2011).

Our elemental analysis was performed using a Bruker Tracer III-SD handheld PXRF equipped with a rhodium tube and a silicon drift detector (SDD) that allows for the identification of multiple elements based on how atoms behave when they interact with radiation (Shackley 2010). Resulting data appear as spectral peaks, the sizes of which correspond to elemental concentration or presence within the artifact. For this work, we analyzed each statue as they were being installed into their display case by mounting the instrument on an extending tripod rig

Table 7: Summary of statuary characteristics analyzed by PXRf and FORS. Raw material identifications were informed by the elemental and mineralogical data in addition to visual inspection of the stones. Table adapted from Smith and Miller 2009.

CSS #	THEME	SITE	SEX	SEATING TYPE	HEIGHT (CM)	WIDTH (CM)	THICKNESS (CM)	HAIR TYPE	RAW MATERIAL	CURATION	PHOTO
001	Core	Sellars (40Wi1), Wilson County, TN Plowed up in habitation area June 8, 1922	Male	A?	65	33	23	B	Sandstone	Private Collection	
002	Ancestral Pair, Core	Sellars (40Wi1), Wilson County, TN Plowed up in habitation area Late 1938 or early 1939	Female	C	38	28	25	C	Sandstone	McClung Museum of Natural History and Culture	
003	Ancestral Pair, Core	Sellars (40Wi1), Wilson County, TN Dug up in habitation area December 1939	Male	B	47	*	*	E, F	Sandstone	McClung Museum of Natural History and Culture	
004	Old Woman, Core	Sellars (40Wi1), Wilson County, TN Dug up in habitation area December 1939	Female	C?	48	25	17	C	Sandstone	McClung Museum of Natural History and Culture	

Table 7 Continued

008	Core	Castalian Springs (40SU14) Sumner County, TN Discovered summer of 1888	Female (?)		22 (head only)			C	Sandstone	National Museum of the American Indian Object no. 0035337.000	
009	Core	Castalian Springs (40SU14) Sumner County, TN Discovered after 1923	Male (Penis?)	B	28 (body only)	25	28		Sandstone	Bledsoe's Lick Historical Association	
010	Ancestral Pair, Core	Beasley Mounds (40SM43) Smith County, TN Discovered 1898	Male	A?	36	22	17	B	Sandstone	National Museum of Natural History Object no. A334008	
011	Ancestral Pair, Core	Beasley Mounds (40SM43) Smith County, TN Discovered 1898	Female	C?	33	22	17	C	Sandstone	National Museum of Natural History Object no. A334007	

Table 7 Continued

012	Core	Beasley Mounds (40SM43) Smith County, TN Discovered 1898	Male (?)	A?	31 (body only)	28	19		Sandstone	National Museum of Natural History Object no. A334012	
013	Old Woman, Core	Beasley Mounds (40SM43) Smith County, TN Discovered 1898	Female (Vulva)	C	22 (body only)	15	13		Sandstone	National Museum of Natural History Object no. A334013	
014		Beasley Mounds (40SM43) Smith County, TN Discovered before 1923	?	A?	26 (body only)	29	11		Sandstone	National Museum of Natural History Object no. A334011	
018	Ancestral Pair, Core	Martin Farm/Riddleton Smith County, TN Discovered Spring of 1905	Male	A	38	24	18	B	Sandstone	Private Collection	

Table 7 Continued

019	Ancestral Pair, Core	Martin Farm/Riddleton Smith County, TN Discovered Spring of 1905	Female	C?	33	22	13	C	Sandstone	National Museum of Natural History Object no. A334009	
021	Core	DeKalb County, TN Discovered before 1898	Female (?)	?	48	36		C,D	Calcite (non-speleogenic)	National Museum of Natural History Object no. A334005	
023	Old Woman, Core	Terry Farm Burgess Cove, White County, TN Discovered 1903	Female	C	42	23	18	C,D	Calcite (Speleogenic)	National Museum of Natural History Object no. A334006	
024	Old Woman, Core	Rhea County (reinterpreted by Smith and Miller 2009 to possibly near McMinnville, Warren County, TN)	Female	C?	35			C	Sandstone	National Museum of the American Indian Object no. 0210965.000	

Table 7 Continued

030	Ancestral Pair?, Core	Valley of the Cumberland Williamson County, TN Discovered prior to 1868	Male (Penis?)	B	34				F	Sandstone	National Museum of the American Indian Object no 0007277.000	
031	Ancestral Pair?, Core	Near Jarman Farm (409WM210) Williamson County, TN Discovered 1881	Female ?	B	31	16	20		C	Sandstone	Tennessee State Museum Object no. 82.100.1091	
032	Core	Cheatham County, TN Discovered about 1890	Male?	?	33	23	13		B	Sandstone	National Museum of Natural History Object no. A334010	
035	Core	Wallace Farm Site Christian County, Kentucky Discovered 1887		?	19 (head only)	14	15		C	Calcite (Speleogenic)	Metropolitan Museum of Art Object no. 1979.206.1139	

Table 7 Continued

036	Ancestral Pair?, Core	Link Farm (40HS6) Humphreys County, TN Discovered March 23, 1895	Male	B	67	36	27	E,F	Sandstone	Metropolitan Museum of Art Object no. 1979.206.476	
045	Old Woman, Core	Valley of the Cumberland Williamson County, TN Discovered prior to 1868	Female (Vulva)	C	29			C*	Sandstone	National Museum of the American Indian Object no. 0007276.000	
048	Old Woman (?)	Perry County, TN Discovered prior to 1868	Female (Vulva?)	C	20	10	8	A*	Sandstone	National Museum of Natural History Object no. A19934	
065		Cardwell Mountain (40WR15) Warren County, TN Discovered 1970 or 1971	Male	A				?	Calcite (non-speleogenic)	Tennessee State Museum Object no. 2003.2	

Table 7 Continued

067	"Discovered" Benton County, TN Given to TN Historical Society in 1896 *Fake						Sandstone and Plaster	Tennessee State Museum Object no. 8.714	
068	"Discovered" Benton County, TN Given to TN Historical Society in 1896 *Fake						Sandstone and Plaster	Tennessee State Museum Object no. 8.715	
089	at or near Moss Mound Site Smith County, TN Discovered prior to 1960	Female	C			?	Sandstone	Private Collection	
090	Whitwell's Farm Perry County, TN Discovered prior to 1870	?	?			?	Sandstone	Tennessee State Museum Object no. 4.207	

(Figure 37). With this, we were able to obtain samples at multiple points on the statues with minimal contact with the figures themselves while maintaining stabilization for the analyzer. Settings were optimized at a voltage of 40kV and current of 40 μ A. Additionally, we used a vacuum pump to prevent attenuation of the lighter elements. To keep the analysis completely non-destructive, no statues were cleaned or prepped. Instead, we selected areas for analysis that were free from oxidation, oils, or other surface films and debris. Compositional data were collected for 180 seconds at multiple spots on each statue. Measurements were also collected on any paint that was present.



Figure 37: PXRF set-up during the installation of the statuary exhibit.

Once all data were collected the PXRF spectra data were processed to enable semi-quantitative analysis. Here, a semi-quantitative spectral evaluation was conducted using ARTAX 7. This software converts spectra using Bayesian Deconvolution to determine Net Peak Areas (NPA) estimates for the elements of interest in each analytical spectrum. The software deconvolutes each spectrum through stripping routines that calculate the intensity of each element of interest and “strip” them from overlapping elements to eliminate matrix effects (i.e. mass absorption and overlap effects) that can occur during analysis (Shackley 2011:21; Lachance and Claisse 1994). The resulting NPA calculations represent the net photon count for each element. NPA values provide the means to numerically compare elemental concentrations between specimens without conversion to a more quantitative format (Forster et al. 2011; Grave et al. 2012:1683). NPA results are then normalized against rhodium to remove instrument-introduced variability. The detector in the Tracer III-SD is rhodium and provides a useful constant to measure and correct intensity variations between results. After the data have been processed, elemental identifications can be determined and the relative concentrations of elements from specimen to specimen can be compared.

To collect mineralogical spectral data, we used an ASD FieldSpec4 Standard-Res portable spectroradiometer. This reflectance spectrometer can acquire data across the visible-near infrared (400-1000 nm), and short-wave infrared spectral ranges (1000-2500 nm). Spectral resolution varies from 3 nm at 700 nm and 10 nm at 1400/2100 nm with spectral sampling done at 1.4 nm intervals in the visible and near-infrared and 2 nm in the short-wave infrared range. Software is used to convert the radiant energy into a spectral waveform comprising positive and negative peaks. The negative peaks are the absorption bands, and these features are related to the mineralogy of a sample (Hapke 1993). The VNIR region can detect transition metals such as

iron, while the SWIR region can detect hydroxyls (e.g. hydroxyl ions and rock-forming minerals like clays), carbonates (e.g. calcite), and water content. This instrument is also portable, albeit similar to a one-man band with the spectroradiometer carried as a backpack and laptop carried at the front (Figure 38). This work was completed while the exhibition was being decommissioned using a backpack portable set-up, which enabled us to move around the statues for optimal measurement acquisition. To control for light in the museum we used a muglight with a tungsten quartz halogen light source to minimize measurement errors associated with stray light. We fitted the end of the muglight with a soft, black neoprene sleeve to seal the light source and provide a cushion against the statues during analysis. This cushion did not interfere with any spectral readings. To calibrate the instrument before collecting spectral information a Spectralon reflectance panel was used. This reflectance panel is a thermoplastic resin that is 96-99% reflective in the 250-2500 nm wavelength range. Similar to the PXRF measurements, several readings were taken on each statue with the FORS instrumentation on both the bare and painted surfaces.

The FORS spectral data were interpreted using ENVI image analysis software to compare spectral data to known references from multispectral data (Kokaly et al. 2017). Rather than elements being identified, FORS spectral data comprise a continuum of valleys or absorption bands. Different minerals have characteristic absorption bands that can be identified. Here initial elemental identifications were made with the PXRF data. Then the mineral constituents of the paint were determined by the FORS data. As many of these statues had not been documented in great detail, we also made visual inspections of each statue and took detailed photographs to inform our analytical analyses.



Figure 38: FORS set-up for statuary analysis during the decommission of the exhibit.

Results

Based on the elemental and mineralogical analyses, there are two categories of raw material: sandstone and limestone. We discuss each raw material grouping below in light of the PXRF and FORS data.

A total of twenty-two statues were produced from sandstone. All of the statues contain the following elements: Al, Si, P, S, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, and Zr. However, there is significant variability in these elements among the statues in this group. This variability is also present in mineralogical data. Rocks are aggregates of minerals, which create complex FORS spectra. However, it is possible to determine broad spectral characteristics based on absorption band features. In sedimentary rocks such as sandstone, water absorption bands are

present at 1400 nm and 1900 nm. Clay-shales have an additional feature at 2100-2300 nm. Lastly, iron-oxide staining produces spectral features that extend from 600-1000 nm. Ferric iron in particular shows an absorption band at 870 nm (Figure 39).

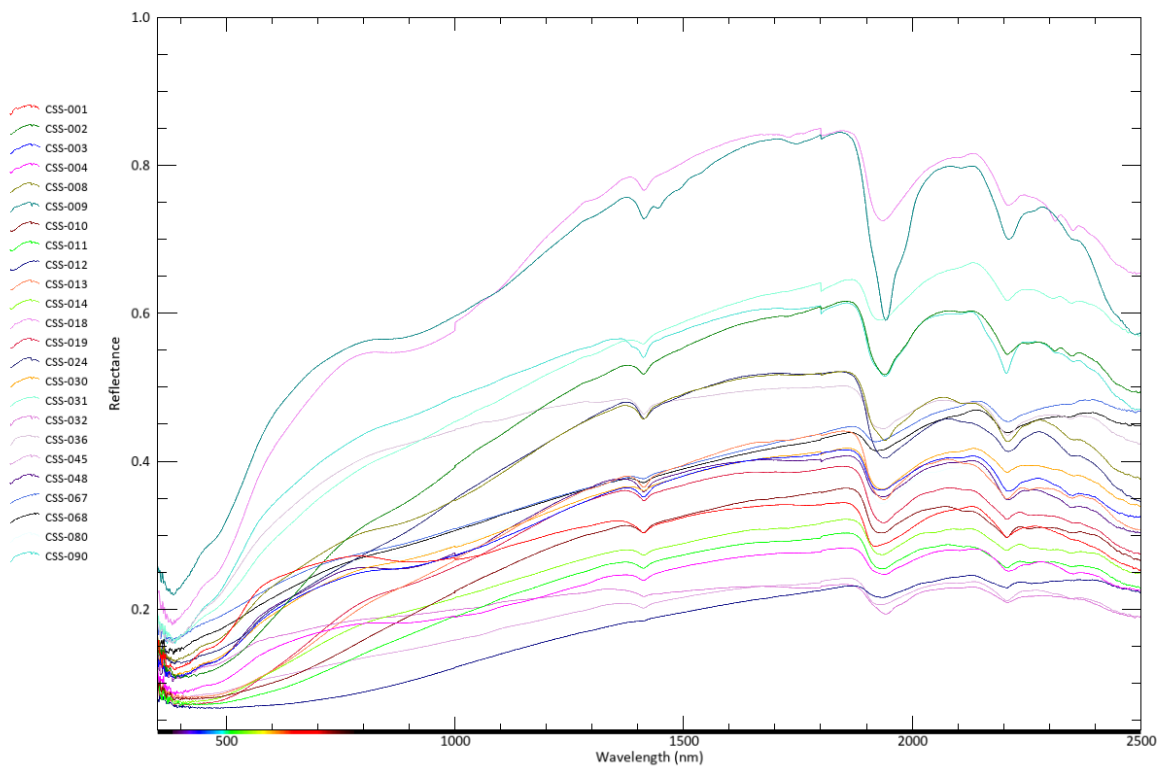


Figure 39: FORS spectral overlays of sandstone raw material statuary group.

This sandstone raw material group also contains the only painted statues. Four statues exhibit paint, and all are from the same archaeological site (Sellars Farm in Wilson County, Tennessee). Statues CSS-002, 003, and 004 all have evidence for pre-Contact paint, while the elemental data from CSS-001 suggests some of the paint was a historic addition after the statue was discovered. It has been recognized for some time that both CSS-003 and 004 were painted. CSS-003 exhibits black pigment across the mid-face and interior of the eyes, red pigment on the lip and mouth, and yellow pigment across the forehead area. CSS-004 only has black pigment

applied to the face. During the installation, however, it was discovered that CSS-002 was also painted prehistorically (

Figure 40). CSS-002 has black paint across the face, similar to CSS-003, with lines running horizontally across the cheeks and vertical lines on either side of the mouth. There is also evidence for pigmentation along the hairline and in the interior of both eyes.

Black pigments can be produced by three chromophores: manganese, bone black, or charcoal. Elevated manganese was not detected in the PXRF data and the elements indicative of bone black (elevated levels of Ca and P) were not present either. The black paint on these statues was therefore likely produced using charcoal as the chromophore. PXRF analysis of the red and yellow paints on CSS-003 indicates that an iron mineral is the primary chromophore. FORS absorption features around the 8700-9000 nm range confirm that red was created with ferric iron in the mineral form of hematite or red ochre, while the yellow was produced using a hydrous iron oxide, or limonite. No other spectral features are present in the FORS or PXRF data to suggest other minerals such as clay were added to the paint recipes used on these statues. The paints used to decorate these statues consisted of simple ingredients: a colorant—charcoal, hematite, or limonite—added to water to produce liquid paint. This basic recipe is the same one we encounter in the region for pre-Contact rock art paintings (Simek et al. 2020).

Our analysis also indicates that some of the paint on CSS-001 is recent in origin rather than prehistoric. This statue displays dark red (almost purple) paint on the lips and mouth area and a whitewash over the entire body of the statue (Figure 41). PXRF analysis indicated high quantities of lead in the dark red paint, which is commonly found in historic era paints and suggests the paint was applied after the statue was recovered from the ground. Other historic additions to this statue include a base, without which the statue would not be able to stand



Figure 40: Profile and frontal views CSS-002 showing presence of black paint across the face and hair.

upright. PXRF compositional data of the whitewash that covers the entire statue is calcium and clay-rich suggesting a clay or limestone wash was used to cover the statue.

Absorption features in the FORS data at 1400 nm, 2200 nm, and 2300 nm are most similar to illite clays. This addition could have been applied historically. Or it may have been part of the original pre-Contact construction of the statue as the whitewash underlays the red paint on the lips. If it was a historic addition, there are no compositional indicators of modern paint. The main body of the statue is comprised of sandstone.

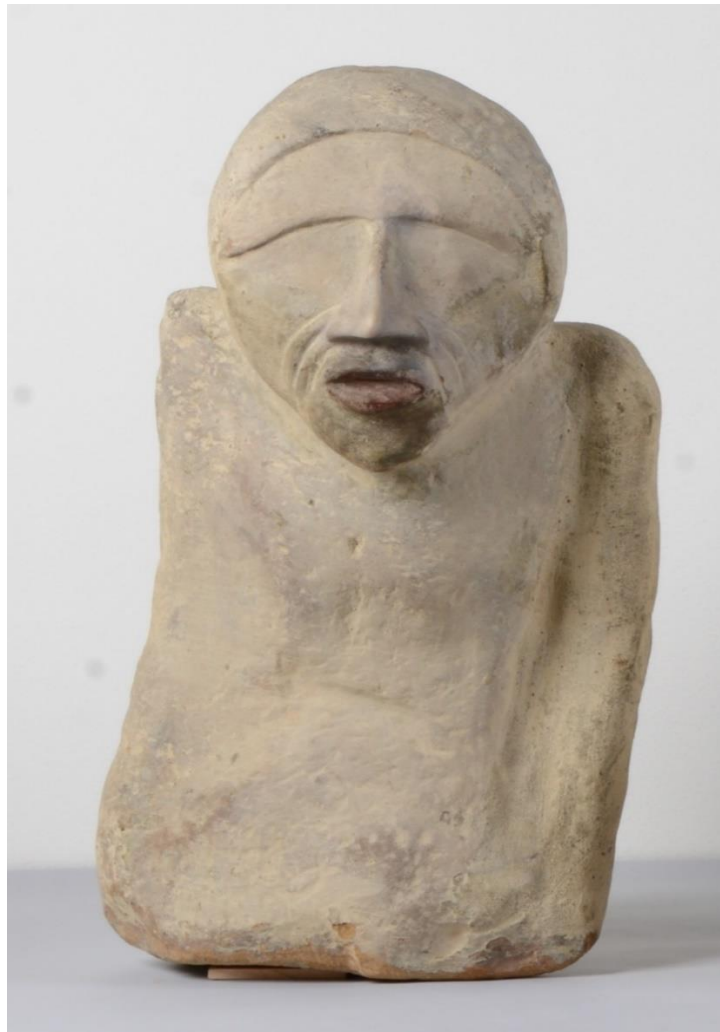


Figure 41: CSS-001 from Sellars Farm. Historic red paint was applied to the lips, mouth, and a whitewash was applied to the statue.

The second raw material group is comprised of statues produced from carbonates. While PXRF and FORS can both distinguish between some types of calcium-rich rocks and minerals, however, those materials that all have the same lattice structure and chemical formula (i.e., CaCO_3) are more difficult to distinguish. For instance, main elemental peaks from the PXRF data from this group of statues indicate relatively high quantities of Ca with minor variations in trace elements. FORS spectral features at 1900 nm and 2350 nm (the latter being more intense) are indicative of a rock consisting of carbonate minerals (Figure 42). Similar features from CSS-023 and CSS-035 were noted at 1900 nm, 2100 nm, and 2350 nm, which are similar to a mixture of calcite and dolomite minerals (Figure 43).

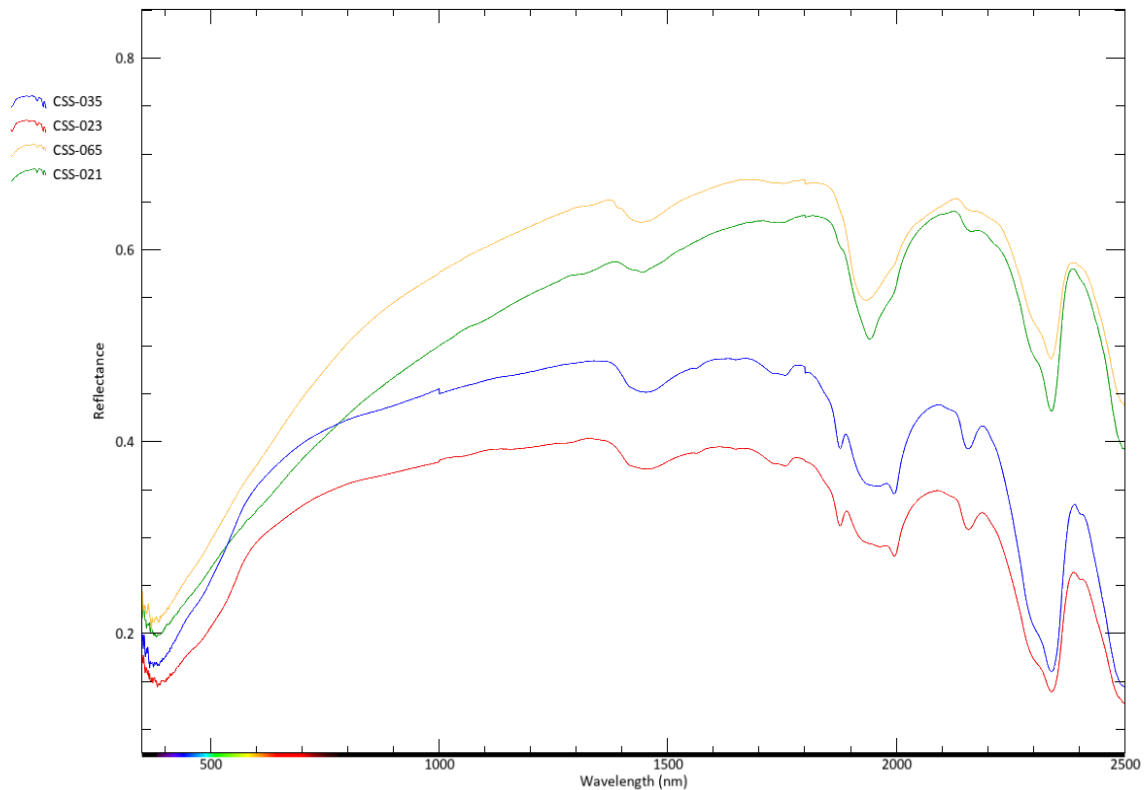


Figure 42: FORS data from CSS-021, 023, 035, and 065. Spectral features at 1900 nm, 2100 nm and 2350 nm are indicative of calcium carbonate.

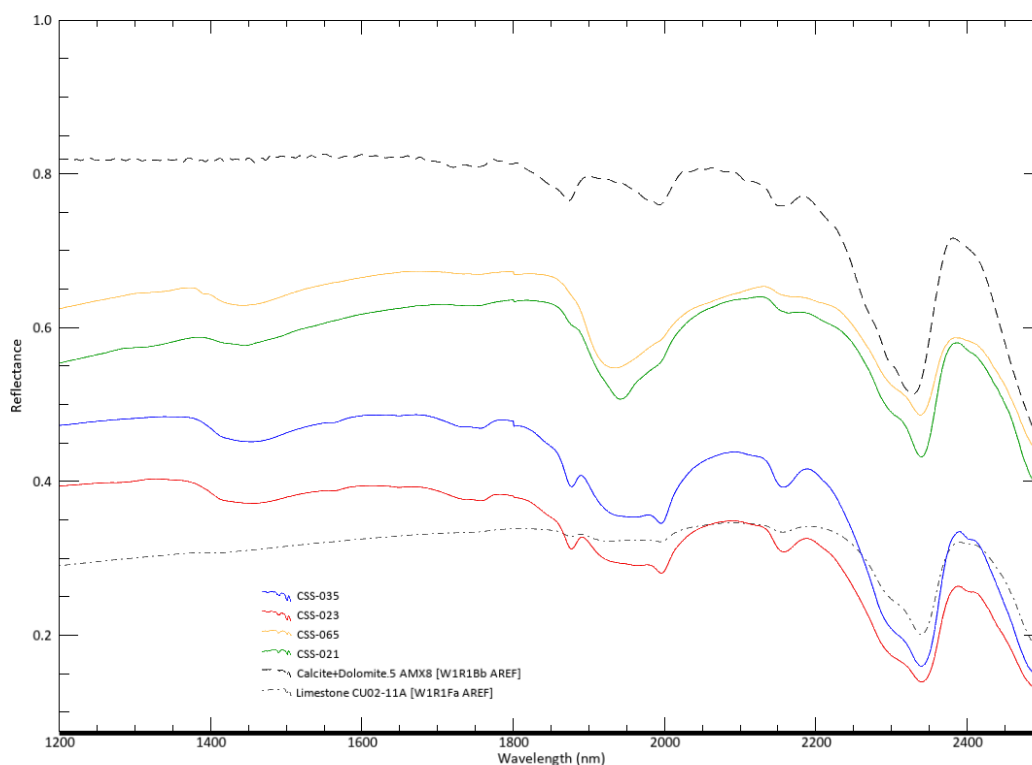


Figure 43: FORS data from CSS-021, 023, 035, and 065 compared to USGS limestone and calcite + dolomite references (Kokaty et al. 2017). Spectral features at 1900 nm, 2100 nm, and 2350 nm are indicative of carbonates.

While the elemental and mineralogical data indicates these statues consist of calcite materials, after a thorough visual inspection, we made further raw material divisions based on the acquisition location of the rock. While all four statues are calcite, we determined that two statues, CSS-021 and 065, were produced from non-speleogenic calcite, while CSS-023 and 035 were produced from speleogenic calcite. Calcite is the most abundant cave mineral in the Appalachian karst region, and a primary constituent of speleothems—a secondary mineral deposit that is formed in caves (Moore 1952). Visual inspection of the mineral grains enabled us to make these divisions (Figure 44). Calcite deposits large enough to produce these two statues could have only been acquired from cave deposits in our region (Hill and Forti 1997).



Figure 44: CSS-035 determined to be speleogenic calcite based on the visual characteristics observed from the underside of the statuary head. Note the red numbering in the photographs is the catalogue number assigned to the piece.

The remaining two statues discussed here are documented forgeries. CSS-067 and 068 were given to the Tennessee Historical Society in 1897 and were accepted as genuine for many decades, even displayed in the Tennessee State Museum. Eventually, in 1987 these objects were inspected more closely and discovered to have marks left by chisels, files or rasps, and other modern metal tools (Brehm 1987). Upon their “discovery”, they were described as being “modeled out of the soft, ball clay” (Myer 1923:644-645). Ball clay has known, extensive deposits in West Tennessee and is described as low organic, low residue with white-firing characteristics due to its high kaolinitic content (Nelson 1911). The FORS data do not confirm ball clay to be the material used based on the absence of kaolinite absorption features. Plaster of Paris is another likely construction material used heavily during the time these statues were discovered; however, gypsum was not detected in either the PXRF (high sulfur and calcium) or FORS (triplet absorption feature between 1400—1600 nm) data. The compositional data from both PXRF and FORS indicate these fakes were carved from likely local sandstones and are simply additions to a broad range of Tennessee folk art whose creation was inspired by stone statuary discovered in the region.

Discussion and Conclusions

Before our analysis, information concerning the raw material of these statues was ambiguous with references to siltstones, sandstone, “compact limestone”, marble, or described as a “soft”, “hard”, or “crystalline” stone (Brown 1799; Dorian 1984: 136; Jones 1873: 432-434; Lewis 1955; Myer 1923: 360, 377; Seever 1897: 141; Willoughby 1932:29). With recent advancements in non-destructive technology, we can gain new insights into the materials of artifacts. Through our compositional analyses, we have demonstrated that Mississippian cultures

who created the Tennessee-Cumberland style statuary chose different raw materials from different geological contexts to create these objects. Smith and Miller (2009:32) suggested that the Tennessee-Cumberland style stone statues likely entered the archaeological record not too far from their place of manufacture. A key concept used in compositional analyses is called the Provenience Postulate, which states that chemical differences within a single source are less than the differences between sources (Weigand et al. 1977). Therefore, if statues were produced in a few locations we would expect the raw material to be compositionally homogeneous. Two different raw material categories were identified by the analytical analyses—sandstone and limestone—indicating that a unitary source was not used to produce the statuary in this region. Further visual identification revealed that sandstone, non-speleogenic calcite, and speleogenic calcite were selected by Mississippian artists as the raw materials. A majority of the statues analyzed here were carved from sandstone and both carved types (Ancestral Pair and Old Woman) are represented. While there is considerable compositional variability within the sandstone group as a whole, this variability could be due to inherent variability within sandstone deposits or could be indicative of different sandstone deposits being quarried on the landscape. Tailored experiments and testing could further clarify these questions.

All of the raw material resources used to create these statues were readily available across the physiographic provinces in which they were found—the Highland Rim and the Central Nashville Basin of Tennessee (Figure 45; Luther 1977; Wilson 1939). Sandstones could have been acquired across the Highland Rim from Pennington-age formations. Non-speleogenic calcites could have been procured from Mississippian age deposits present in the Central Basin or the eastern or western Highland Rim (Luther 1977). Speleogenic calcite formations large enough to sculpt, however, can only be obtained inside caves found in the Highland Rim region.

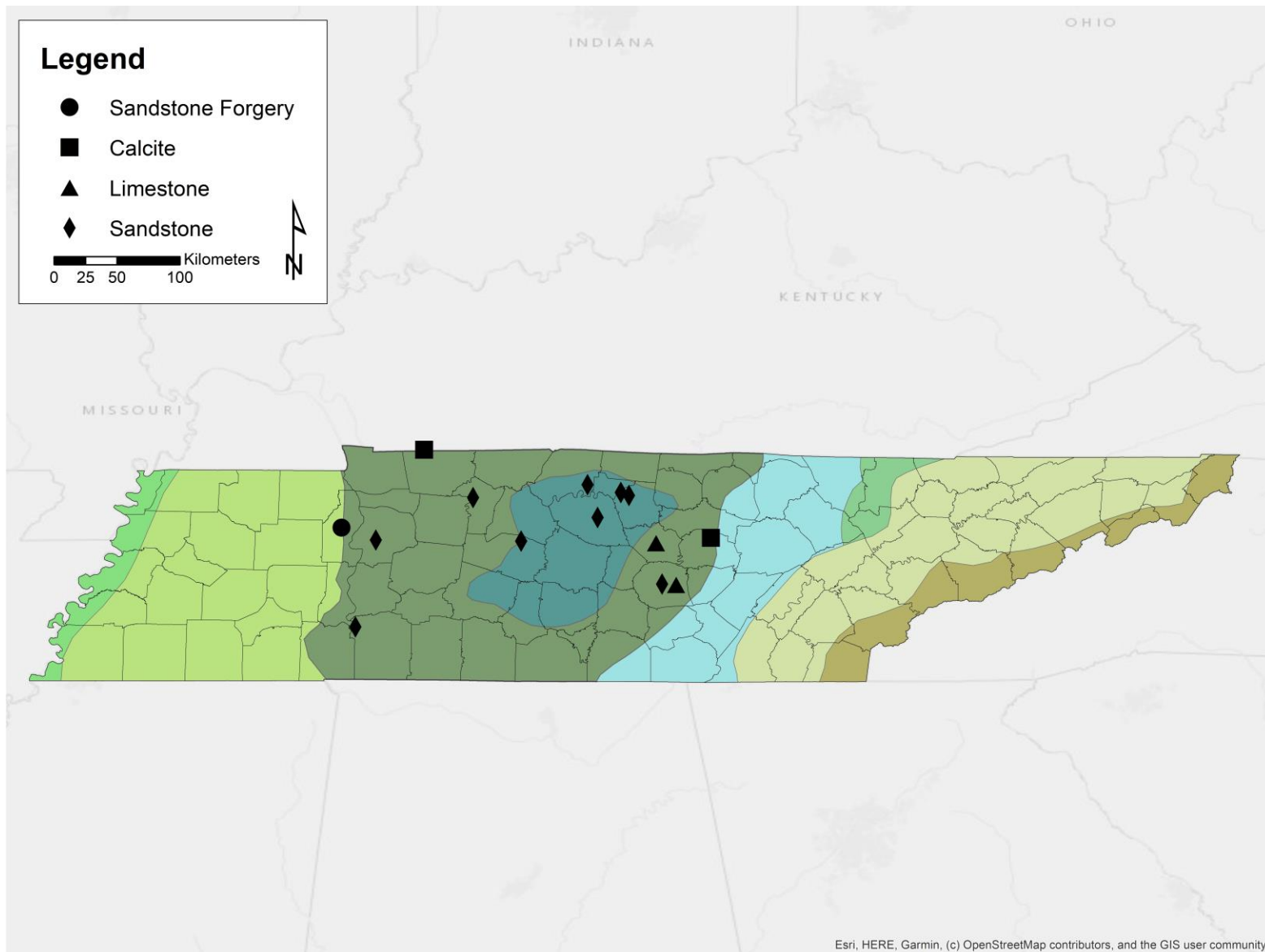


Figure 45: Distribution of Tennessee-Cumberland style stone statuary analyzed.

Speleothems can form large sheets and curtains of calcite deposition, while others can form as smaller formations, more easily acquired through pre-Contact mining practices. The Highland Rim region is entirely underlain by limestone and exhibits mature karst topography with thousands of caves (Barr 1961; Matthews 1971). Southeastern cave archaeology has documented a variety of pre-Contact uses for caves, reaching as far back at the Archaic Period (Simek et al. 2013). In Tennessee specifically, there is a very rich and deeply rooted tradition of cave art (Simek and Cressler 2005; Simek et al. 2001, 2012) as well as resource mining in the Eastern Highland Rim area (Crothers et al. 2002; Franklin and Simek 2008; Pritchard 2008). In short, it is not unusual that pre-Columbian peoples in the region procured calcite from deep within caves to create carved statues.

As we have begun to unravel the composition of these statues, a more nuanced picture of their production and distribution has emerged. Smith and Miller (2009) identified two central types of the Tennessee-Cumberland style stone statuary: (1) males and females created in pairs, representing real or mythological ancestral pairs and (2) the supernatural female figure known as the Old Woman (in addition to others). Some statues, however, are more ambiguous and do not fit into either of these categories. Mississippian sculptors used a variety of raw materials to create these statues as well. Our results do not support that sculptors produced statues in a centralized location and distributed across the region. Instead it appears that characteristics of the stone itself were sought specifically for the intended use of the statue. For instance, individual statuary pairs were always produced from the same raw material and visually exhibit a dichotomy in color schemes. Male statues tend to be carved from darker sandstones, while the females are lighter colored sandstones. Additionally, pre-Contact peoples ventured into caves, into their underworld, to retrieve calcite for sculpted statues depicting the Old Woman. One of these statues, CSS-023,

is carved with specific characteristics of the Old Woman theme, the other is a detached head. Mississippian artisans in the Tennessee-Cumberland region no doubt carved these figures with their intended function in mind. Not only is Mississippian symbolism depicted through the carving of these figures, but it is also reflected in the materials used to create them. Through a materials approach, we can demonstrate that the stone used to produce these figures was an important part of the overall significance of the statues themselves and the role they played within Mississippian society.

Transition from Chapter III to Chapter IV

Chapters II and III demonstrate that while Mississippian period paint recipes across the Southeast are relatively simple and effective, the designs being depicted on rock art and the materials selected for stone statuary are perhaps more important than the paint. Both artifact classes (rock art and statuary) fall within the realm of sacred items within the Mississippian culture. Rock art was produced in a variety of locations; however, the subject matter and nature of the art suggests that its construction and viewing may have been restricted. Likewise, Mississippian stone statues were kept and used within shrines or structures atop large earthen mounds within their communities. While we may never be able to determine what types of rituals or activities occurred in conjunction with rock art or statuary, the artifacts themselves speak to the ceremonial nature of their uses.

In the next chapter, I examine the final case study of this dissertation—painted pottery. Through the previous two chapters, a solid analytical methodology for PXRF and FORS has been established. These instruments will now be used to examine Mississippian painted pottery from the Hiwassee Island Site in Tennessee. This site represents the largest collection of red painted pottery in the region. It was found within household structures, refuse piles, and was consecrated within mound construction episodes.

CHAPTER IV: PAINTED POTS: COMPOSITIONAL ANALYSIS OF PAINTED POTTERY FROM THE HIWASSEE ISLAND SITE, TENNESSEE

This chapter is prepared for publication by Sierra M. Bow as:

Bow, Sierra M. (2020) Compositional Analyses of Late Pre-Contact Painted Pottery from the Hiwassee Island Site, Tennessee. *In preparation*.

This chapter is a research chapter. This work will be submitted to *Southeastern Archaeology*. This journal is a peer-reviewed, academic archaeology journal that publishes works concerning the archaeology and history of southeastern North America and neighboring regions from all chronological time periods. Specific aims and scope of the journal include: articles of a theoretical nature; review articles such as updated regional or topical summaries; technical and methodological reports of regional significance; and field reports whose results in terms of interpretive content are of regional interest. In this dissertation, the main structure of the paper and the word count are compiled based on the journal guidelines. A typical paper for this journal should be no more than 10,000 words. Complete guidelines for preparing and submitting the manuscript to the journal can be found here: <https://www.tandfonline.com/toc/ysea20/current>. Apart from the content and word requirements, all remaining formatting in this chapter follows guidelines set forth by the University of Tennessee Graduate School.

Abstract

The Hiwassee Island Site in Tennessee is well known and has a long history of archaeological investigations dating back to the eighteenth and nineteenth centuries. Large scale excavations conducted as part of a collaboration between the Works Progress Administration and Tennessee Valley Authority during 1937-1939 uncovered significant deposits, the analysis of which laid the foundation for our understanding of Woodland, Mississippian, and early Historic cultural histories in the region. Of particular interest here is the collection of painted pottery from the assemblage dating to the Hiwassee Island phase (A.D. 1000-1300). During this time Hiwassee Island Red-Filmed and Red-on-Buff painted types occur in a variety of contexts throughout the site. While much research has been devoted to temper and surface decorations of

Mississippian period pottery, little attention has been directed at understanding the pigment composition used on these painted ceramic wares. Recent technical advancements of spectrometer instruments have enabled archaeologists to investigate a wide range of artifacts non-destructively. I use portable X-ray fluorescence spectrometry (PXRF) and fiber-optic reflectance spectrometry (FORS) to examine the chemical composition of the paint used to create Hiwassee Island Red-Filmed and Red-on-Buff pottery. Results indicate potters used a very simple paint recipe, one consisting of ochre and water; the paint was not enhanced with non-essential components. This suggests that if these types were intended to be special, non-utilitarian wares then the color and the designs depicted on these wares likely conveyed the particular meaning for people living at Hiwassee Island rather than materials incorporated in the paint.

Introduction

The Mississippian Period (ca. 1000-1600 A.D.) represents the “pinnacle of religio-socio-political complexity” of precontact Southeast societies (Chapman 1985:74). At its peak, the Mississippian was marked by urban centers dependent on maize agriculture; the construction of earthen platform mounds with associated structures on top; the arrangement of villages around a centralized plaza; an increased population; organized chiefdoms; increased territoriality and warfare; an elaborate and well-developed religious ceremonialism; and changes in pottery and a proliferation of ceramic styles (Anderson and Sassaman 2012; Smith 2007). It is also during this time that paint use became widespread in the archaeological record of the Southeast. Paint can be found adorning rockshelters and in the deep recesses of caves (Diaz-Granados and Duncan 2000; Diaz-Granados et al. 2015; Sabo and Sabo 2005; Simek et al. 2013;). It was used to color or

‘paint’ earthen mounds (Anderson 2012; Sherwood and Kidder 2011; Pursell 2004, 2013) as well as to embellish the interior of structures built atop mound summits (Polhemus 1987). It was widely used during the Mississippian period across the region to decorate and/or sanctify a variety of contexts. Of particular importance here was its use on pottery vessels. Much research has been devoted to cataloguing and deciphering painted pottery motifs to understand how they reflected social, religious, or political systems of Mississippian cultures (Hilgeman 2000; Pauketat 2004; Townsend et al. 2004). Some investigations have even examined the material properties of painted vessel clays to address questions of trade and distribution (Peacock et al. 2007; Steponaitis et al. 1996; Thompson et al. 2008). Research involved in the material properties of the paint itself, however, has received little attention (Baumann et al. 2013). Chemical and mineralogical data are particularly important for classifying artifacts, especially if we want to fully understand the role(s) of materials in shaping the archaeological past. Techniques typically used to identify material composition required the removal of samples for laboratory analysis, and researchers were reluctant to conduct large scale analyses out of ethical concerns. The development of non-destructive analytical instruments, however, has given researchers the ability to sample many specimens. Here, I use portable X-ray fluorescence spectrometry (PXRF) and fiber-optic reflectance spectrometry (FORS) to identify the elemental and mineralogical constituents of paint on pottery from the Hiwassee Island site (40MG31) in Meigs County, Tennessee. Hiwassee Island Red-Filmed and Red-on-Buff pottery was produced at the site ca. A.D. 1100-1300 and believed by Lewis and Kneberg (1946:92) to represent the *de luxe* ware of the time at Hiwassee Island. In addition to characterizing the composition of the paint used to create these vessels, a secondary goal of this research is to gain new insights into how these pottery wares figured into the culture at the site.

Cultural Context and Previous Research at Hiwassee Island

The Hiwassee Island Site is located at what was the confluence of the Hiwassee and Tennessee rivers before the Tennessee River inundation (Figure 46; Lewis and Kneberg 1946; Sullivan 2009). The island is today roughly two miles long and a mile wide and contains approximately 781 acres. Early investigations at the site were undertaken by private individuals and the Smithsonian Institution (Harrington 1922; Moore 1915; Thomas 1891), but the largest archaeological excavations at the site were conducted by the University of Tennessee at Knoxville with a Works Progress Administration (WPA) crew as part of the Tennessee Valley Authority (TVA) Chickamauga Reservoir Project from 1937-1939 (Lewis and Lewis 1995). This work was carried out before the inundation of the Chickamauga Reservoir, which was constructed by the TVA in 1939-1940 to provide flood control, electricity, recreational opportunities, and a corridor for barge traffic. More than 3,066 m² of archaeological deposits were excavated during the salvage project, which culminated in a landmark publication that laid a foundation for regional chronology in eastern Tennessee (Lewis and Kneberg 1946).

The site was not revisited until 1987 when limited excavations were undertaken by the University of Tennessee (Hall 1987), and archaeological field schools were conducted at the site from 1997 to 1999 (Claassen et al. 1998; Claassen and Sullivan 1997; Sullivan 1998) to examine archaeological features that were not impacted by inundation and compare them to the WPA excavations. In 2015, a geophysical survey of the island was conducted by New South Associates for the Tennessee Valley Authority to document the extent of intact deposits at the site (Patch et al. 2015), and in 2017 limited test excavations were carried out to ground-truth those results (Pritchard 2017). Suffice it to say that the site is still bearing archaeological information, adding to and refining our understanding of prehistory in the region.

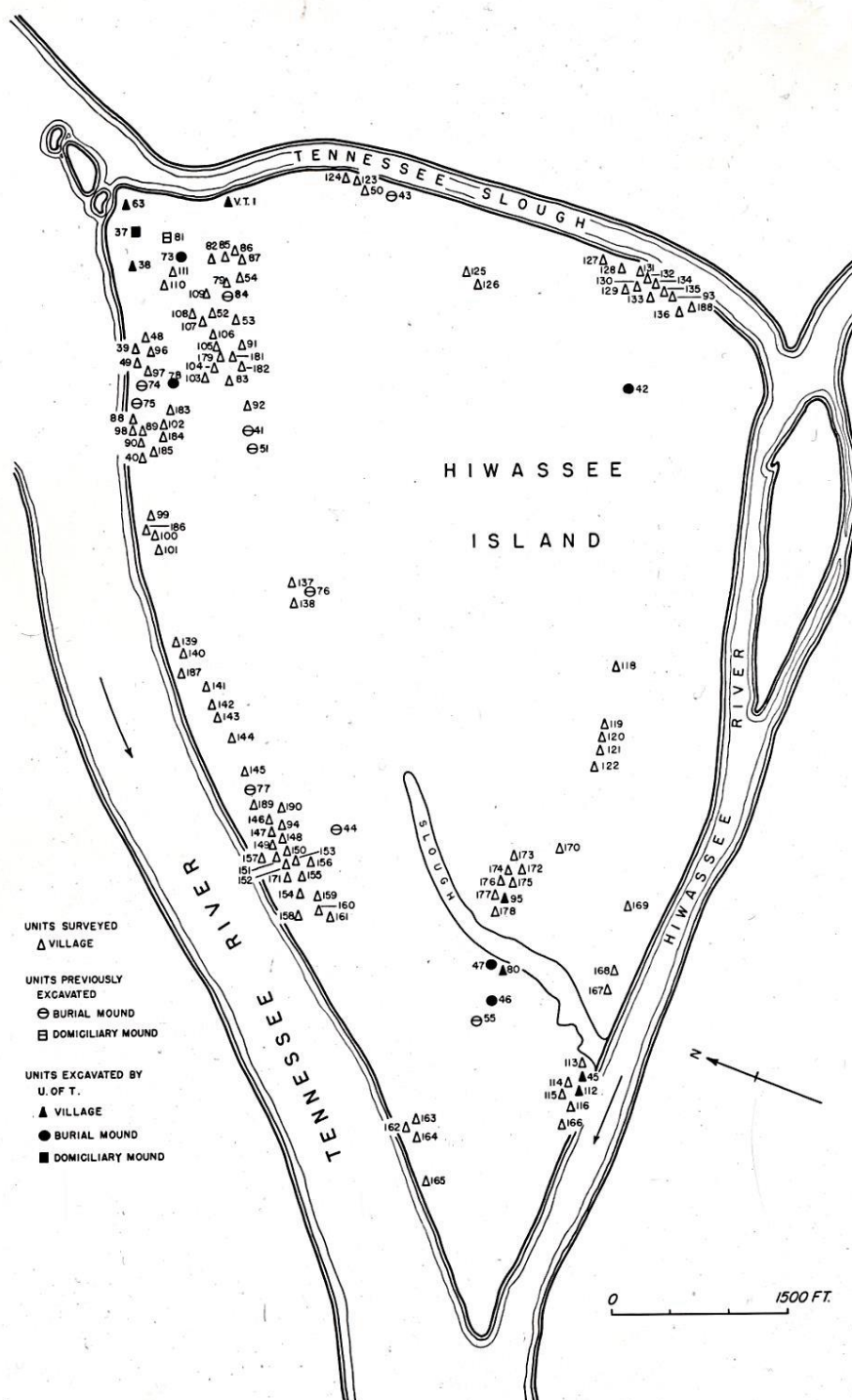


Figure 46: Map of Hiwassee Island, WPA excavation units. Lewis and Kneberg 1946: Map 1. Image courtesy McClung Museum of Natural History and Culture, University of Tennessee.

The Hiwassee Island archaeological deposits are multicomponent with evidence of Woodland conical mounds and shell middens, a Mississippian village with a platform mound and plaza, and historic Native American occupations during the eighteenth and nineteenth centuries (Lewis and Kneberg 1946). The site also has evidence for non-Native historic components. Traditionally, Mississippian cultures have been defined by a set of common characteristics such as chiefdom-level organization, maize-based subsistence, shell-tempered pottery, large population centers, and monumental architecture. These characteristics have roots in the Late Woodland/Emergent Mississippian period, but during the Mississippian, they played a much larger role and influenced everyday life to a much greater extent (Anderson and Sassaman 2012). The Mississippian period occupation at Hiwassee Island included two phases (Table 8). The Hiwassee Island Phase (Mississippian II), A.D. 1000-1300 and the Dallas Phase (Mississippian III), A.D. 1300-1600 are both represented (Lewis and Kneberg 1946; Lewis et al. 1995; Schroedl et al. 1990).

Table 8: Simplified Chronology for the Chickamauga Basin after Sullivan 2015.

PERIOD	PHASE		DATE RANGE
HISTORIC MISSISSIPPIAN	Mississippian IV	Overhill Cherokee	Post A.D. 1600-1838
	Mississippian III	Mouse Creek	A.D. 1450-1550
		Dallas	A.D. 1300-1400
	Mississippian II	Hiwassee Island	A.D. 1100-1300
WOODLAND ARCHAIC	Mississippian I	Martin Farm	A.D. 1000-1100
			900 B.C- A.D. 1000
			7900-900 B.C

The Hiwassee Island phase (Mississippian II) is generally characterized by sedentary agricultural life with settlements ranging from dispersed farmsteads to small villages that were comprised of wall-trench and single-post rectangular architecture and occasionally associated with a mound, plaza, and palisaded enclosure (Schroedl 1998). Subsistence practices focused on diverse flora and fauna coupled with the increased use of maize (Schroedl et al. 1990; Sullivan 2009). This phase also saw a shift in pottery technology to nearly exclusive shell tempering. Ceramic assemblages at sites throughout East Tennessee also become more diverse (Schroedl et al. 1990) with an increase in vessel forms and decorations, including the creation of red-filmed and painted pottery (Kimball 1985). During the second century of the Hiwassee Island Phase (A.D. 1200-1300), the use of burial mounds ceased, and internments were made in platform mounds. This shift in burial customs and new use of Mississippian symbols during this time hint at expanding relationships with regional centers to the south such as Etowah (Lewis and Kneberg 1946; Lewis et al. 1995; Sullivan 2009).

The Late Mississippian period in the Chickamauga Basin is typically divided into the Dallas and Mouse Creek Phases (Mississippian III) and began A.D. 1300. The Dallas Phase (Mississippian III) is marked by pronounced social and political complexity, inferred through public structures, mortuary patterns suggestive of ascribed status, and a large range of house sizes (Schroedl 1998; Sullivan 1995; Sullivan and Harle 2010). Common characteristics that define this phase are a continuation of shell-tempered pottery, and nucleated, often palisaded, villages with mounds topped by a single, large structure. Burials were made in and around houses and in platform mounds. Dallas Phase sites occur throughout most of the Upper Tennessee River Valley. There is, however, considerable subregional variation (Sullivan 2016; Sullivan and Harle 2010). The Mouse Creek phase begins slightly later in time (A.D. 1450-1500)

in the Chickamauga Basin and southern Watts Bar Reservoir area, while the Dallas phase continues elsewhere in East Tennessee (Sullivan 2016:143). Mouse Creek phase towns consisted of densely packed palisaded villages arranged around a central plaza and lacking platform mounds. Burials were located in and around houses and in dedicated cemeteries (Sullivan 1987).

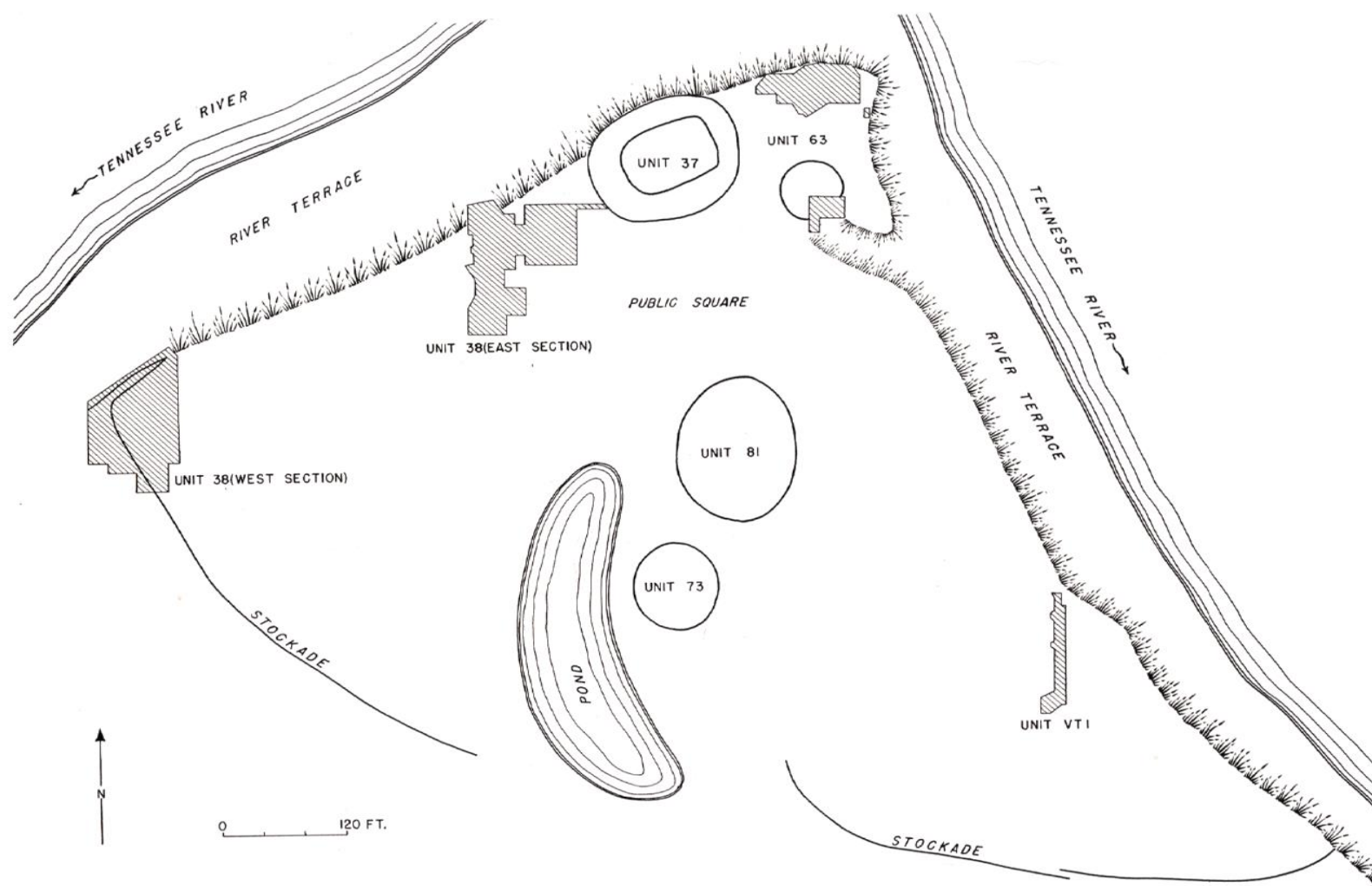
New studies and major archaeological investigations at other sites in the region have added a significant amount of information and encouraged revisions and interpretations of the Hiwassee Island Site since the initial report by Lewis and Kneberg (1946). The earliest stages of occupation at the site shared similarities with contemporary sites in the Chickamauga Basin, notably the Sale Creek and Davis sites (Sullivan 2016). Initial mound construction at Hiwassee Island likely began in the twelfth century and consisted of two low platforms that were later transformed into one mound (Lewis and Kneberg 1946; Lewis et al. 1995:422-430; Sullivan 2009). There is limited evidence of a substantial residential population at this time, and it is unclear if actual habitation was contemporary with the earliest stages of mound construction at the site. During these early stages trading relationships and other interactions with people to the south can be inferred through pottery styles. In the Chickamauga Basin, temper preferences shifted from limestone to shell hybrid wares (limestone and shell mixed temper) with local shell tempering and complicated stamped designs occurring between A.D. 1100-1200. This is also when the Etowah Site in Georgia, a powerful political and religious center, was established (King 2003). By A.D. 1200, Hiwassee Island became a hub of interactions between East Tennessee peoples and those in northern Georgia. The mound created at Hiwassee Island was topped with elaborate buildings by its inhabitants that likely served multiple purposes as temples, homes of religious/civil leaders, and backdrops for ceremonies (Sullivan 2016). Between A.D. 1250-1300, new mounds were being constructed by peoples elsewhere in the Chickamauga

Basin and the use of the Hiwassee Island mound declined (Lewis et al. 1995). After A.D. 1300, the Hiwassee Island Site was being used once again. Evidence suggests that during this phase of occupation, the mound contained one building on its summit and was surrounded by residences (Sullivan 2009:205; 2016:148-149). Similar constructions occur at the Dallas Site, downriver from Hiwassee Island, and at the Citico and Hixon sites, suggesting that the decline of Etowah led to the development of a new social order (Sullivan 2016:163). These changes mark the end of the Hiwassee Island phase and the beginning of the Dallas phase in the region.

Excavations

The major excavations conducted by Lewis and Kneberg remain the primary source of excavated archaeological materials from Hiwassee Island. They identified at least 15 conical mounds, and several small midden areas, as well as a large village with two substructure mounds. WPA crews excavated five of the conical mounds on the south end of the island, but much of their attention was devoted to the large Mississippian town and the large undamaged platform mound at the north end of the site. The excavations of the Mississippian village at Hiwassee Island extended over 3,122 m² and included excavation units 38, 63, VT-1, and 81 (Figure 47). For the village areas, a 0.93 m² (10 ft²) grid system was laid out along a north to south axis through the center of the site. The plow zone was rapidly removed, and subsequent layers were excavated in arbitrary 7.62-cm (3-in) levels. Artifacts were recorded by 15.24-cm (6-in) levels, an arbitrary division that, at the time, had very little interpretative value: “a long period of continuous occupation by several groups of people had resulted in a thorough mixture of the cultural materials”, according to the excavators (Lewis and Kneberg 1946:26). Unit 38 was the largest excavated area and consisted of two sections 61 m apart, west of the large

platform mound. A combined 910 m² were excavated, revealing numerous structure patterns, various features, pits, human burials, and part of a wall trench palisade. There were also two sections of Unit 63, albeit much smaller than Unit 38, with 372 m² of excavation area. This unit is located east of the mound and uncovered wall trench structures, burials, numerous post molds, pits, and other features. VT-1 (Village Test-1) was an exploratory trench that uncovered about 111 m². This trench encountered part of a wall-trench structure, several human burials, and numerous post molds and pit features. Unit 81 was identified as a potential low substructure mound but was ultimately not excavated. The main substructure mound, Unit 37, was excavated using a new method, a horizontal stripping technique that exposed entire summits complete with building patterns. This method enabled researchers to reconstruct how a mound appeared at various points in time (Figure 48). At the time of excavation, the summit of the mound rose ca. 7 m above the adjacent ground level and had a basal diameter of ca. 46 m. Seven major phases of mound construction were identified, each including large public buildings. The mound at Hiwassee Island served as the community center throughout the history of the site. Sullivan (2009) addressed the large chronological issues of Hiwassee Island through analyzing diagnostic attributes of artifacts from the Hiwassee Island and Dallas Phases at the site, radiocarbon dates, and comparisons with nearby sites in the Chickamauga Basin (Dallas, Hixon, and Davis sites). From this work, she proposed that most of the Hiwassee Island platform mound dates to the Hiwassee Island phase, even though there appear to be some hiatuses in its use through time (Sullivan 2016).



Concentrated habitation area at head of island. Included are excavated units and aboriginal pond.

Figure 47: Lewis and Kneberg 1946: Plate 7. Indicating the locations of Units 37 and 63 included in this analysis. From Thomas M.N. Lewis and Madeline Kneberg, *Hiwassee Island: An Archaeological Account of Four Tennessee Indian Peoples*. Copyright © 1946 by The University of Tennessee Press. Reprinted by permission.

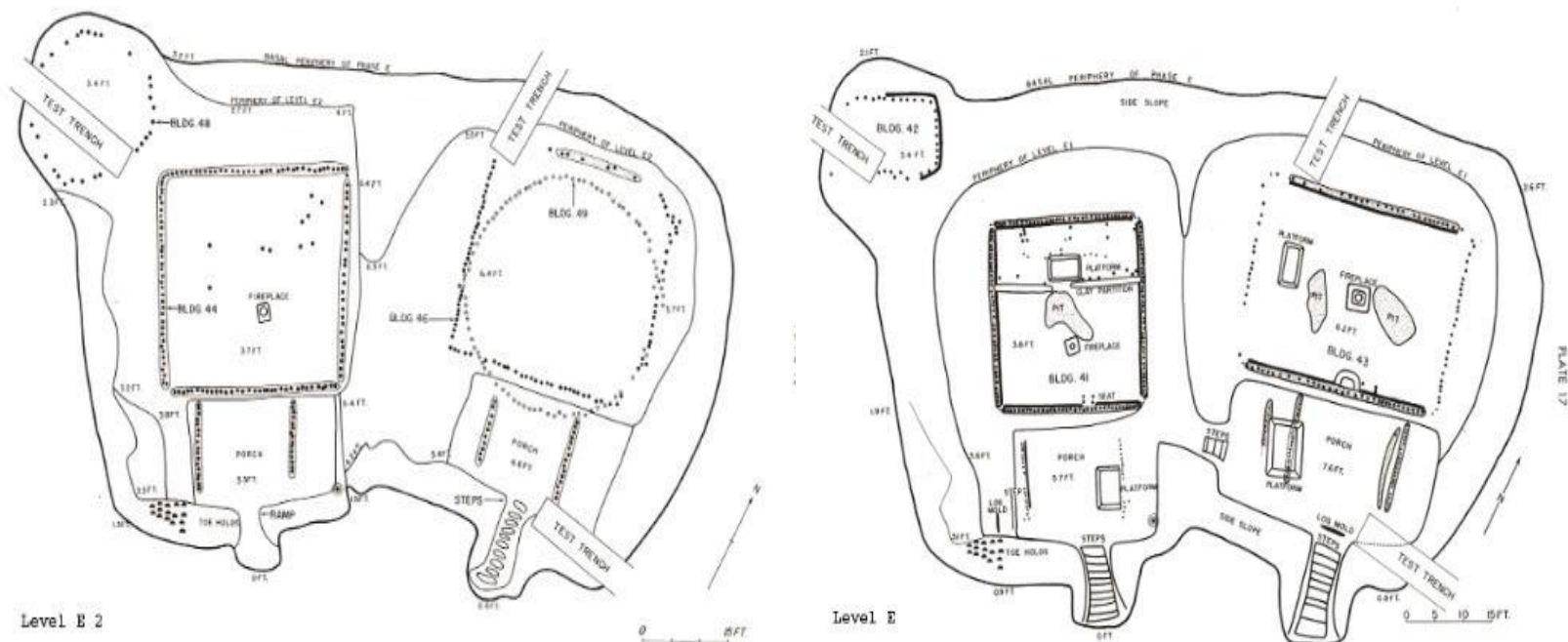


Figure 48: Mound sequence for primary Hiwassee Island phase at the Hiwassee Island site. Source: Lewis and Kneberg 1946: Plates 16 and 17. From Thomas M.N. Lewis and Madeline Kneberg, *Hiwassee Island: An Archaeological Account of Four Tennessee Indian Peoples*. Copyright © 1946 by The University of Tennessee Press. Reprinted by permission.

Hiwassee Island Painted Pottery

Pottery traditions have changed to meet the functional and social needs of pre-Contact cultures throughout the Southeast since their inception in the Late Archaic period (Sassaman 2002). Over time, pre-Contact potters refined their technologies, resulting a beautiful array of functional and ceremonial vessels used by Mississippian peoples throughout the region. One of the hallmarks of the Mississippian period in some parts of the southeast is the shift in pottery tempering practices from limestone to shell temper. In the Chickamauga Basin, this shift occurred ca. A.D. 1000. Although fresh-water mussel shells are heavily exploited for subsistence during the Late Archaic and Woodland periods, preferential pottery tempering agents used during these time periods include grog, fiber, and limestone. In the Chickamauga Basin, shell tempering does not show up in the archaeological record until the Martin Farm phase, from A.D. 1000-1100. This phase was first defined at the Martin Farm Site (40MR20) on the Tellico Reservoir (Schroedl et al. 1985, 1990; Schroedl 2009) and is often referred to as an “emergent Mississippian” phase, marking the transition between the Late Woodland and Early Mississippian periods in the region (Schroedl 1973:10, 1978:193; Schroedl et al. 1990; Sullivan 2007:90, 2016:143). Cultural material indicative of this phase includes shell and limestone-tempered pottery, along with the earliest expressions of Mississippian style structures and platform mounds (Schroedl et al. 2007:185). In particular, the pottery assemblages are characterized by predominantly limestone tempered wares with plain and cord-marked surface treatments and plain, shell tempered wares.

By the Hiwassee Island phase (A.D. 1100-1350), shell tempered pottery dominated assemblages throughout the eastern Tennessee region. The size of shell temper ranges from tiny pulverized particles to large lenticular flakes. Those tempered to a finer paste have better

execution of shape and decoration and generally exhibit characteristics of manufacturing by potters exercising more care and skill in all steps of manufacture. The Hiwassee Island Site, the Hixon Site (Lewis et al. 1995), and early occupations at the Toqua Site (Polhemus 1987) represent some of the large sites in the Tennessee River Valley that show a shift in pottery tempering technology during the Hiwassee Island phase. Pottery from the Hiwassee Island Phase is almost all shell-tempered with surface treatments of plain, cord-marked, textile impressed, complicated stamped, and red-filmed. Limestone tempered pottery is still found in small amounts with plain and cord-marked surface treatments. Increased diversity in pottery types and shapes also occurred during this time (Schroedl et al. 1990). Basic vessel forms include jars, bowls, colanders, salt pans, and bottles. Major surface treatments during the Hiwassee Island phase include plain, cord-marked, fabric-marked, and complicated stamped, incised, and painted wares. It is in this cultural phase that we see the first evidence for “painted” ceramic vessels, classified as red-filmed and red-on-buff.

At Hiwassee Island 82,157 pottery sherds were classified based on their paste, tempering material, surface treatments, decoration, and shape (Lewis and Kneberg 1946:80). Seventy-two whole or restored vessels from the site aided in the overall analysis, many of which were found in direct association with burials or within house floors. Of the total, 70,838 were shell-tempered. Through this analysis, Lewis and Kneberg (1946) arrived at several conclusions for the Hiwassee Island phase at the site. First, pottery was locally manufactured and exclusively shell-tempered. Plain surface treatments were predominant and typically associated with large, loop-handled jars, excurved rims jars, shallow bowls, blank-faced effigy bottles, and short-necked bottles. Cord-marked surfaces were present in minor quantities during the early period and became more frequent over time. The presence of complicated stamped and sand-tempered pottery suggests an

affiliation with the Etowah Site to the south. Decorated pottery wares such as red-filmed were occasionally embellished with molded appliques and were an early ware. Another pottery, red-on-buff, appeared slightly later in time during the Hiwassee Island phase and had two variants: painted motifs on vessel bodies and painted rims. An important subgroup, identified during the excavations at Hiwassee Island, was characterized by the clay itself (Lewis and Kneberg 1946; Lewis et al. 1995). Described as a “buff-firing ball clay”, this ware has little to no shell tempering, and the clay body is particularly fine and compact, producing very thin and hard pottery.

Nothing quite like the painted vessels at Hiwassee Island were created anywhere else in the region at this time (Lewis and Kneberg 1946:9; Lewis et al. 1995:11; Schroedl et al. 2007:188). A total of 577 red-filmed and 599 red-on-buff sherds were identified at the site. Although the frequency of painted pottery from Hiwassee Island seems to be low in light of the seventy-thousand shell tempered sherds from the site, they represent the largest concentration of red-painted wares found at any one site in the Chickamauga Basin (Lewis and Lewis 1995).

Red-Filmed

Red-filmed surface treatments were an early manifestation during the Hiwassee Island phase. Hiwassee Island Red-Filmed pottery is characterized by moderate amounts of crushed mussel shell temper of fine to medium sizes. This resulted in a clay body (clay plus temper) that is fine, medium, or coarse depending on the size of the temper and characteristics of the clay itself. Typical coloring of this ware is pale buff or grey with a well-smoothed surface finish. The “red film” was then applied as an “iron oxide” wash covering the vessel (Figure 49). Sometimes this wash was applied in a thin layer allowing the shell tempering material to be seen. Other

times the wash was thick enough to be classified as a slip, according to Lewis and Kneberg (1946:103). A slip is traditionally defined as a “fluid suspension of clay (and other substances) in water applied to an unfired clay piece to form a thin, nonvitreous coating” (Rice 2015:162). Many times, the iron-rich coating was present on the interior and exterior of the vessel suggesting it was dipped, similar to a slip application (Rice 2015). Vessels with a thick coat application are typically found on the coarser clay bodies. Occasionally vessels were embellished with modeled effigy heads. Vessel shapes included shallow bowls with various types of rim configurations as well as long-necked bottles and blank-face effigy bottle rims (Lewis et. al 1995:108).



Figure 49: Example of a Hiwassee Island Red Filmed pottery sherd from the Hiwassee Island site.

Red-on-Buff

Hiwassee Island Red-on-Buff vessels were also constructed using crushed mussel shell temper of various sizes, similar to red-filmed. The surface finish consisted of a well-smoothed exterior made from a finer buff-colored clay, the so-called “ball clay” (Lewis and Kneberg 1946). Painted designs on the exterior of this ceramic type were created by potters with again a “red oxide” paint. There are two styles of this type, one characterized by painting only on the rims of bowls and the other with painted designs on the body or rim (Figure 50). Shapes associated with red-on-buff are mostly shallow bowls with a few long neck bottles. The designs painted consist of lines and solid elements. Fine lines were used as a hachure or cross hachures to fill in triangles, rectangles, or bands. Large, broad lines were also frequently used. Solid elements were incorporated into larger motifs and consisted of small triangles and rectangles, and occasionally circles. These decorations covered the entire vessel. The red-on-buff pottery type is believed to have developed from red filmed as it appears slightly later in the Hiwassee Island phase sequence (Lewis and Kneberg 1946:104).

Methods

In this study, I used a portable X-ray fluorescence spectrometer (PXRF) and a fiber-optic reflectance spectrometer (FORS) to assess both the elemental and mineralogical composition of the paints used on Hiwassee Island painted pottery. Both of these analytical instruments collect information along the electromagnetic spectrum—PXRF within the X-ray spectral range and FORS within the visible and near-infrared (VNIR) and short-wave infrared (SWIR) wavelength regions. Therefore, PXRF results in elemental data while FORS yields mineralogical data. Both instruments are fast (FORS generates readings in real-time) and can be performed *in situ*.



Figure 50: Example of a Hiwassee Island Red-On-Buff pottery sherd from the Hiwassee Island site.

Both techniques are completely non-invasive. There are no previous benchmark studies to inform the analyses on pre-Contact paint using PXRF and FORS, therefore the settings described below for each instrument were selected to gather a wide range of the elemental and mineralogical constituents of the paint.

To obtain the elemental composition I used a Bruker Tracer III-SD PXRF. This is a handheld energy-dispersive instrument with silicon-based detectors allowing for the identification of multiple elements simultaneously. By selecting the appropriate combination of parameters, elements can be isolated, identified, and important information about the overall composition of the artifact being analyzed can be obtained. PXRF functions on the same basic X-ray principle of traditional benchtop analyzers. When electrons are excited and displaced from their atomic orbital positions by incoming X-rays from the instrument, those vacancies are filled

with higher-orbit electrons, which releases a burst of energy characteristic to a specific element. This fluorescent energy is registered by the instrument detector, which then categorizes those energies by element (Jenkins 1974, 1999). X-ray fluorescence analysis is used in a wide array of disciplines for understanding the elemental makeup of a range of materials in archaeology. It is most frequently used for sourcing materials. The use of this technology has significantly increased with the introduction of non-invasive, field-portable devices. The PXRF instrumental settings were optimized at 40kV and 11.30 μ A with a vacuum pump attached. These settings provide general elemental spectra on both high-z and low-z elements on the periodic table. The instrument was used in a laboratory with a benchtop set-up for stabilization and assays were taken for 180 seconds (Figure 51). For each pottery sherd, one assay was taken from the paint and one from a bare, unadorned area on the sherd. For red-filmed wares that had color on the exterior and interior of the sherd, a control reading was obtained from the cross-section. In all other instances, control readings were taken on the interior of the vessel.

For mineralogical data, an ASD Fieldspec4 Standard-Res spectroradiometer was used. This instrument collects data across the visible-near infrared (400-1000 nm), and short-wave infrared spectral ranges (1000-2500 nm). Reflectance spectroscopy, in general, is the study of light as a function of a wavelength that has been reflected from a solid in this case. Software is used to convert radiant energy into a spectral waveform, the character of which is dictated by the mineral make-up of the sample being analyzed. Light from the visible-near infrared region (VNIR) can identify transition metals such as iron, while light from the short-wave infrared region (SWIR) can detect hydroxyl bearing minerals (e.g., clays), and carbonates (e.g., calcite). Reflectance spectroscopy in the visible region has been applied to the study of art paintings since the 1930s (Barnes 1938). Once spectrometers were equipped with optical fibers to operate in the

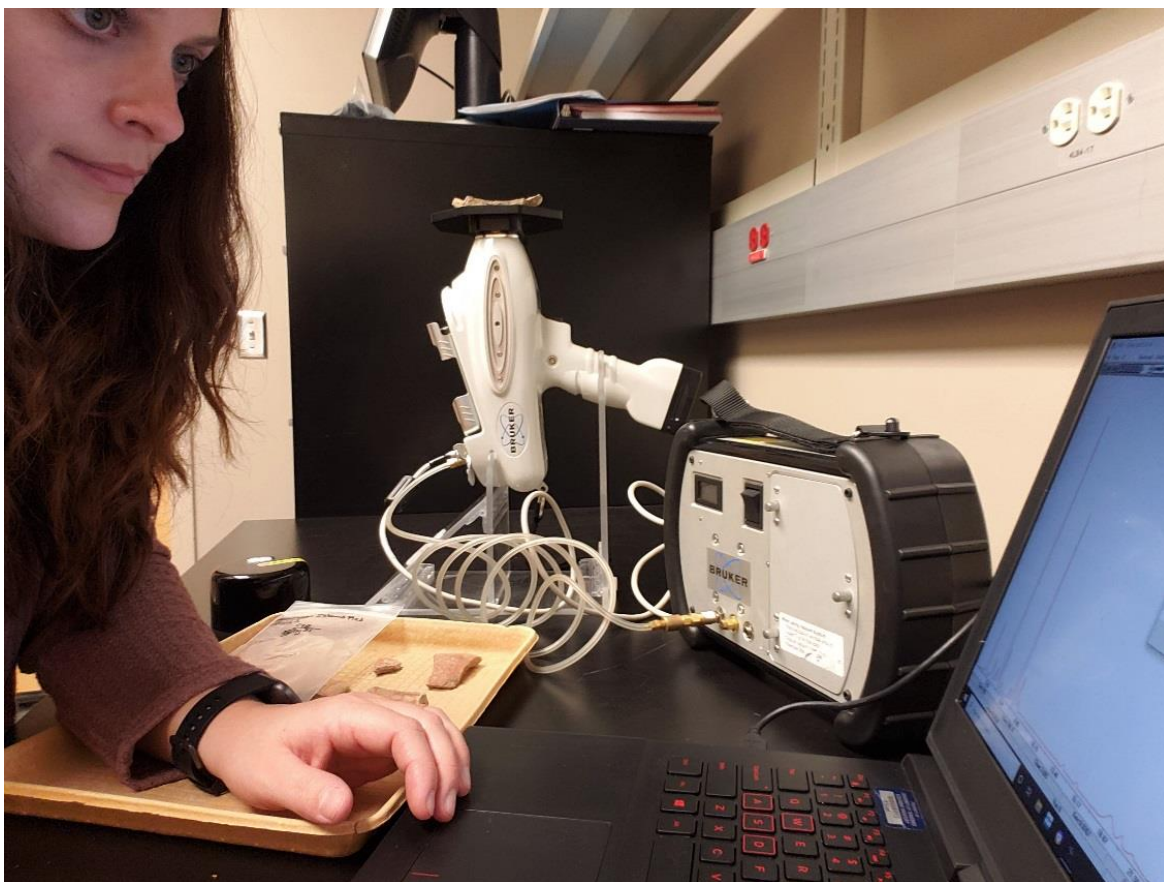


Figure 51: PXRF benchtop set-up.

VNIR in the 1980s, they have been used widely as non-invasive instruments for art conservators and scientists to identify pigments and variations on historic paintings (Bacci et al. 1992; Bacci et al. 1991; Cucci et al. 2013; Leona and Winter 2001). Here, the instrument was also set up on a laboratory benchtop to control spectral data collection. The fiber-optic cable was fitted with a muglight, which provided constant artificial illumination. To this, we added a soft, black neoprene sleeve to create a light sealed environment for the analysis and a soft buffer against the pottery (Figure 52). This sleeve did not interfere with any spectral readings. A 99% Spectralon diffuse reflectance standard was used to calibrate the instrument and convert radiance to

reflectance. As with the PXRF analysis, one reading was taken on paint and one on a bare, unpainted ceramic surface for each analyzed specimen.

During the WPA era excavations, fragments and whole vessels were assigned a field specimen number based on the unit where they were excavated (Lewis et al. 1995:627). Therefore, several pottery fragments have the same field specimen number. WPA era catalog numbers were written on the interior of pottery sherds and sealed with lacquer. In instances

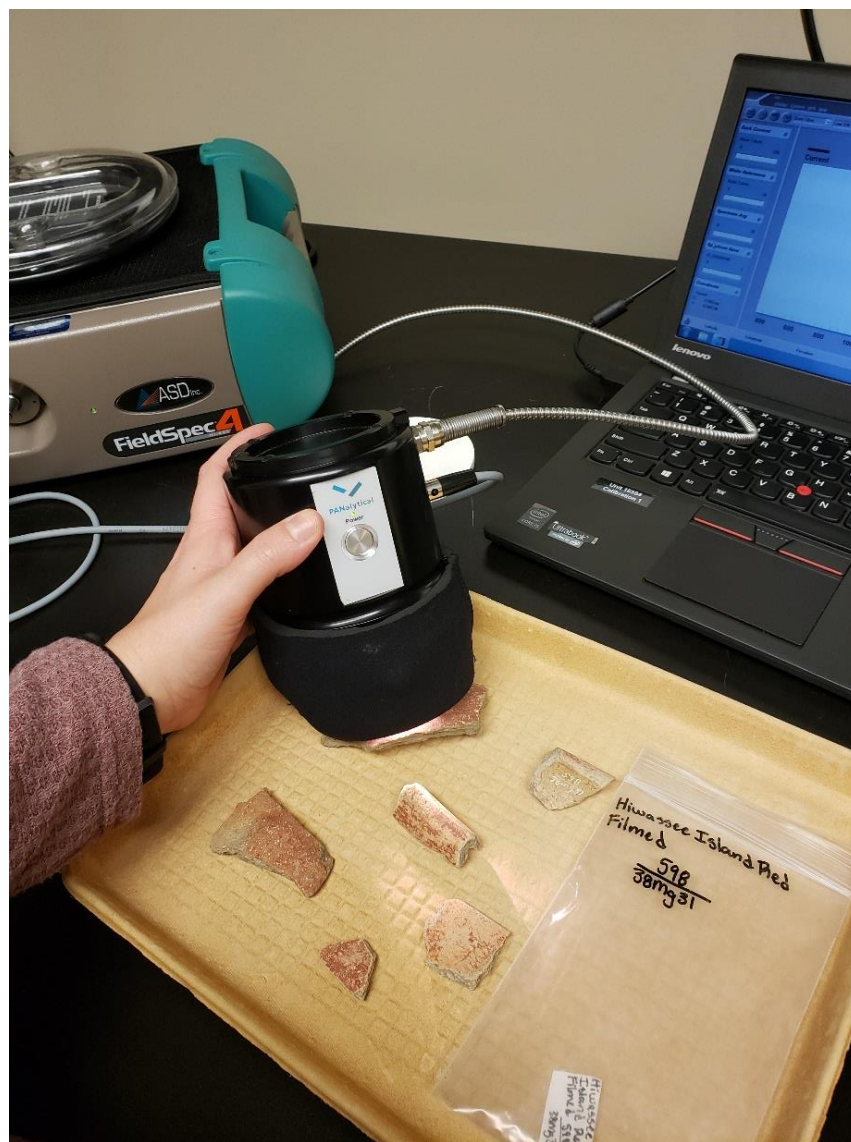


Figure 52: FORS laboratory set-up.

where a secure control reading could not be taken on the interior of the vessel, a reading was obtained in the sherd cross-section or not included in the analysis. Pottery sherds selected for analysis are entirely from the WPA excavation Units 38 and 63 (Figure 53). Sherds were purposefully selected from the village areas to avoid the mound contexts where pottery was likely involved in sacred rituals associated with the mound construction at the site. Additionally, no sherds or vessels were analyzed from any burial contexts. After sherds were selected based on archaeological context, they were selected for the prominence of paint and the overall size of the painted area. Both instruments provide surface/near surface analyses. The PXRF instrument has an aperture of ca. 3x4 mm oval and the FORS has a 25° fiber optic field of view. Therefore, sherds with thinly painted or poorly covered areas were excluded from the analysis.

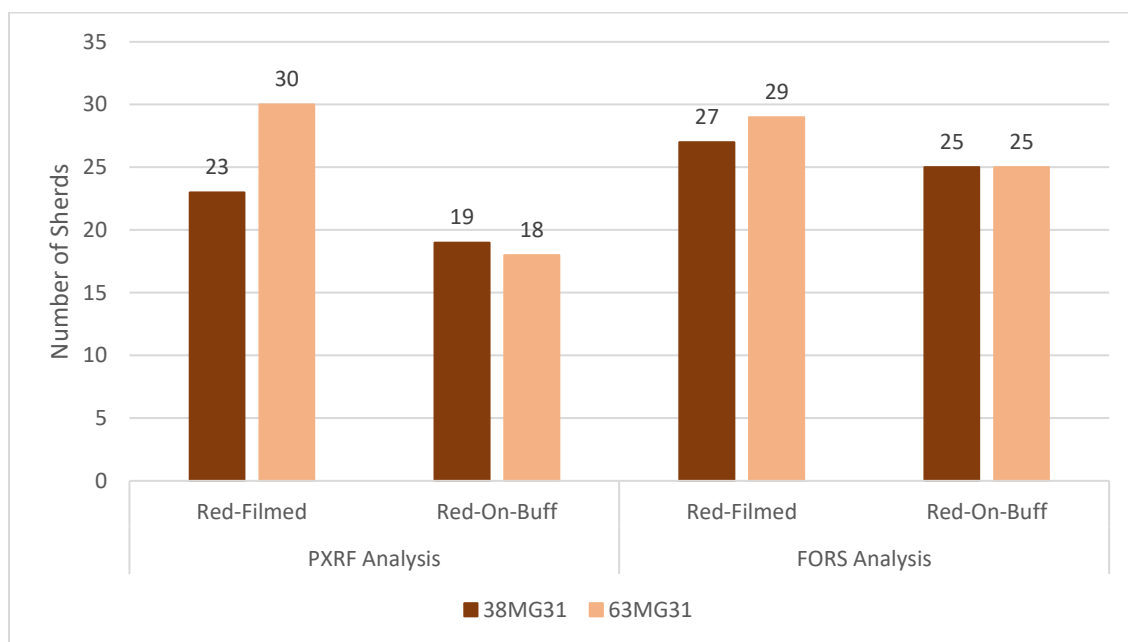


Figure 53: Hiwassee Island pottery sherds selected for PXRF and FORS analysis.

Results

Once all data were collected, the resulting PXRF spectra data were processed to enable semi-quantitative analysis. Here, a semi-quantitative spectral evaluation was conducted using ARTAX 7. This software converts spectra using Bayesian Deconvolution to determine Net Peak Areas (NPA) estimates for the elements of interest in each analytical spectrum. The software deconvolutes each spectrum through stripping routines that calculate the intensity of each element of interest and “strip” them from overlapping elements to eliminate matrix effects (i.e. mass absorption and overlap effects) that can occur during analysis (Shackley 2011:21; Lachance and Claisse 1994). The resulting NPA calculations represent the net photon count for each element. NPA values provide the means to numerically compare elemental concentrations between specimens without conversion to more quantitative format (Forster et al. 2011; Grave et al. 2012:1683). NPA results are then normalized by ratioing against rhodium to remove instrument-introduced variability. The detector in the Tracer III-SD is rhodium and provides a useful constant to measure and correct intensity variations between results. After the data were processed, elemental identifications were determined and the relative concentrations of elements from specimen to specimen were compared.

The FORS spectral data were interpreted using ENVI image analysis software to compare spectral data to known references from multispectral data. Rather than elements being identified, FORS spectral data comprises a continuum with valleys or absorption bands. Different minerals have characteristic absorption bands. Here initial elemental identifications were made with the PXRF data. Then the mineral constituents of the paint were determined by the FORS analysis. A total of 109 red-filmed and 87 red-on-buff pottery sherds were analyzed representing roughly

14% and 12% of the total amount of painted pottery sherds recovered from the Hiwassee Island site during the WPA excavations. No pottery sherds were altered or affected by these analyses.

PXRF Elemental Chemistry

A total of 53 red-filmed and 37 red-on-buff pottery sherds were analyzed by PXRF. Fewer red-on-buff sherds were analyzed due to narrow painted designs. Elements identified during the PXRF analysis of Red-Filmed and Red-on-Buff pottery include Al, Si, P, S, K, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Y, and Zr. All of these elements are present in both the paint and the bare, unpainted pottery matrix (Figure 54).

There is, however, considerable variation. This is not unusual as pottery is by nature an additive process by which potters can introduce variation to enhance efficacy in specific vessels (i.e. mixing clay resources, sieving, etc.). Some broad patterns can be examined. Most notable is the difference in iron between the paint and control readings (Figure 55). While red is visually identifiable on red-filmed and red-on-buff painted surfaces, the PXRF data indicate the red colorant is composed of iron. This is an important distinction as red color can also be imparted by cinnabar (mercury-sulfide, HgS). While sulfur is present in the spectra at 2.3 keV, there are no spectral peaks indicative of mercury (9.98 keV) in either the red-filmed or red-on-buff pottery wares analyzed. Manganese is a mineral that can be added to produce a darker red; however, for both wares, it does not appear that manganese was an additive. The similar variation in manganese among paint and control readings between both pottery types suggests that the variability in this element is due to the clay bodies rather than associated with paint. Likewise, the NPA of other elements typical of clay (i.e. K, Ca, and Sr) vary across the paint and control data. The wide variability in clay elements could suggest that different clay sources were being

used from the landscape. Mussel shell, however, could also be a major contributor to this variability (Peacock 2007; Steponaitis et al. 1996). Attempting to source the pot clays however, is outside the scope of this research.

An interesting element that is present in some of the data (paint and control of both red-filmed and red-on-buff) is barium. Barium is an element found naturally only in combination with other elements (like Sr and Ca) because of its high level of reactivity (Emsley 2011). Barite ($BaSO_4$) is the most common mineral of barium and can occur in a variety of sedimentary rocks that form clay deposits. There are no clear patterns of barium in the data. It is occasionally present in both red-filmed and red-on-buff pottery and is present in the paint and control readings of those sherds. The addition of barium, however, could be due to an enrichment from post-depositional alteration processes (Golitzko et al. 2012). While the thickness of the coating on red-filmed pottery varies, clay was not likely the medium by which the colorant was suspended before decoration. There is no minimum percentage of clay content required to create a slip. Yet on red-filmed vessels with thick coatings, clay elements (i.e. Al, K, Ca, Sr) are not elevated, suggesting that a clay slip was not used to create this pottery ware. In fact, red-filmed coatings contain fewer NPA of clay elements than do the controls. Instead the elemental data suggest that a fluid suspension containing an iron-rich chromophore and water were used to slip these pottery wares. No other elements in the PXRF data suggest any additional ingredients in the paint recipes used to create red-filmed and red-on-buff pottery types at Hiwassee Island.

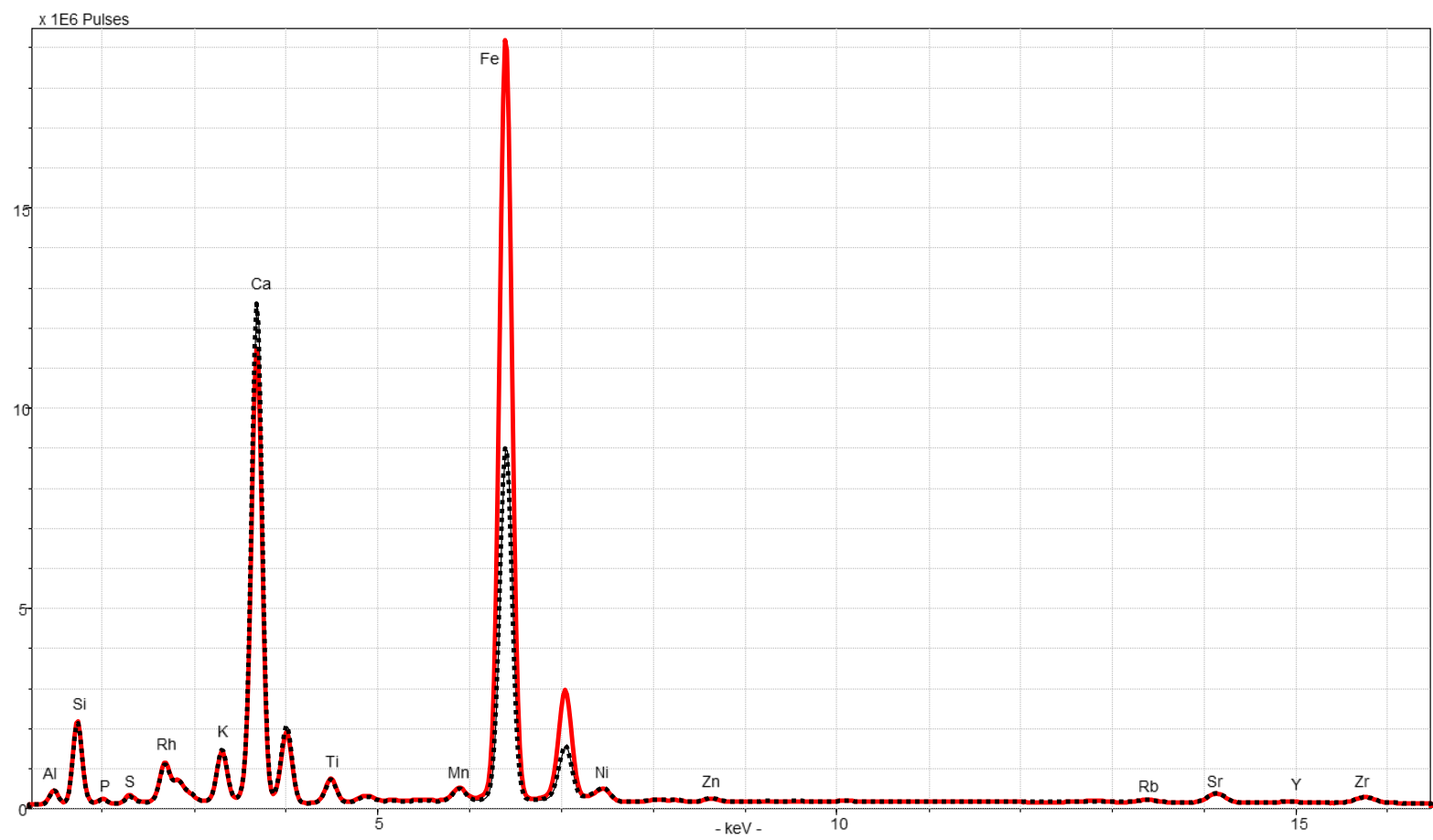


Figure 54: Example of PXRF spectra data from a red-filmed pottery sherd--red denotes the red film, black denotes the unpainted, bare clay body.

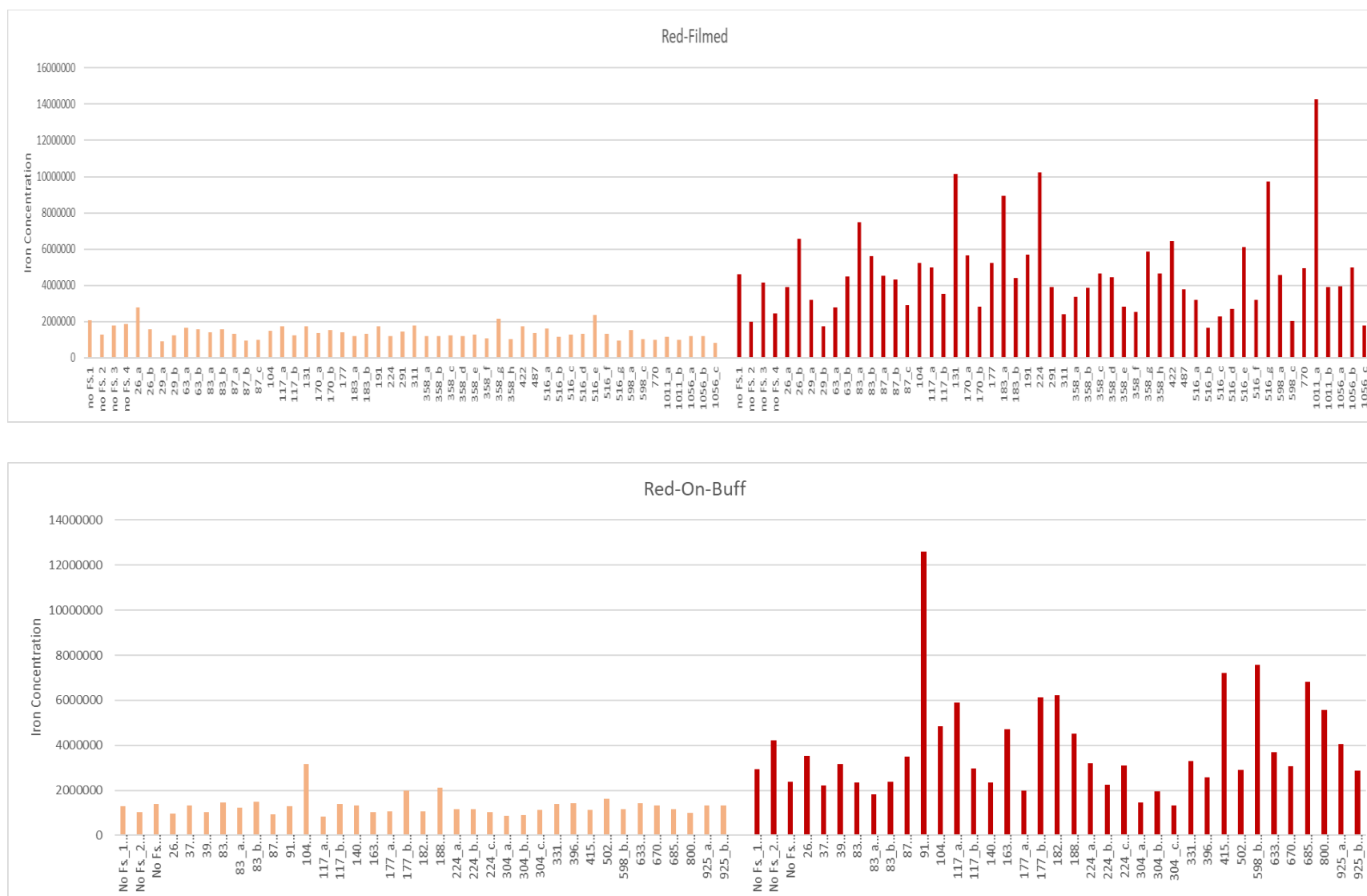


Figure 55: PXRf data of iron concentrations in the paint (red) compared to the control (buff) from red-filmed and red-on-buff pottery sherds.

FORS Mineralogical Chemistry

A total of 56 red-filmed and 50 red-on-buff pottery sherds were analyzed by FORS. Analysis of the FORS data consisted of matching absorption bands to known mineral references (Kokaly et al. 2017). Since this method of analysis is relatively new in archaeology, reference spectra do not yet exist for archaeological materials. Even still, we can use FORS to broadly determine mineral components that are suggested by PXRF results. All spectra collected from the pottery were compared to different types of clays as well as to major mineral compounds which could not be determined by PXRF alone, such as hematite, goethite, limonite, and calcium carbonate.

Similar to the PXRF spectra, FORS data appear as a continuum comprising hills and valleys, and slopes. Figure 56 depicts the major spectral features identified in the paint and controls from both red-filmed and red-on-buff pottery wares. Absorption bands, or the negative peaks in the spectra, are present at ca. 850 nm, 1400 nm, 1900 nm, 2200 nm, and 2300 nm. Hematite is identified by the broad feature at 800 nm that rises at 700 nm, then makes a steep drop towards visible blue. Absorption features located at 1400 nm and 1900 nm are due to water molecules. Broad water molecule peaks mean that they occur in unordered positions, while sharp peaks imply well-defined loci (Gupta 2003:41). Variability in these peaks occurs throughout the data set and is likely the result of technological practices e.g., making the clay body and then drying and firing, as well as how the paint was produced and applied. The remainder of the SWIR region consists of spectral features related to hydroxyls and carbonates. In particular, the ratio of broad bands at 1550-1750 nm and 2200 nm is useful in identifying clay mineral assemblages (Abrams et al. 1977). When referencing pottery control spectra to known spectra of illites, muscovites, and kaolinite clays, no clear matches could be made (Figure 57).

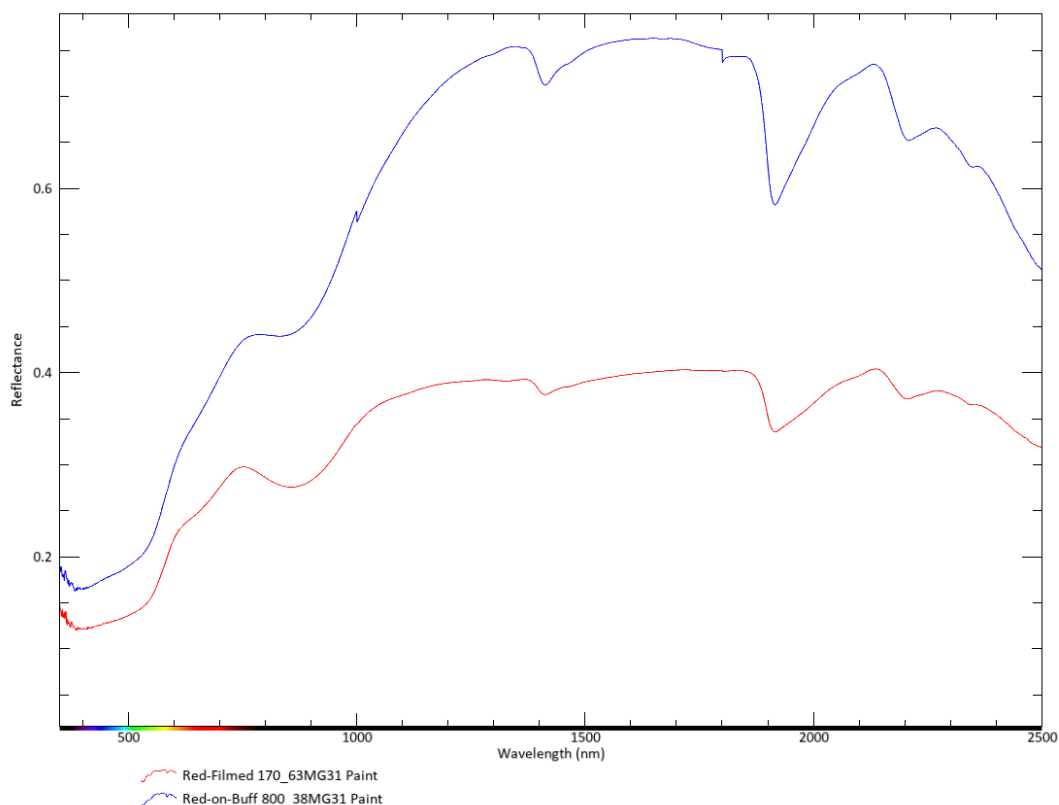


Figure 56: FORS spectra of paint from red-filmed (solid blue line) and red-on-buff pottery (solid red line).

Other features worth mentioning include a small absorption band at 450 nm that suggests trace quantities of manganese. When compared to the control spectra, however, this feature is virtually identical. This supports the PXRF data findings that manganese is part of the clay body, but it was not intentionally added as an ingredient to the paint.

Hematite absorption features within the red-filmed painted pottery sherds are widely similar, with attributes as described above at 800 nm. However, the hematite absorption features within the red-on-buff group show some variability. Figure 58 shows three primary groups of hematite spectral features identified during the analysis. The first group, depicted in the dot-and-line spectra, exhibits a relatively low and broad absorption feature at 850 nm, with a sharp rise at 750 nm followed by an immediate decline to 500 nm. This group often displays an additional

small shoulder feature at 600 nm. The second group depicted by a dashed line in the figure has a much less pronounced feature at 800 nm and a more general sloping from 600-500 nm. The last group, shown with a dotted line, has very low spectral features with a moderate peak at 700 nm and a small decline to 500 nm.

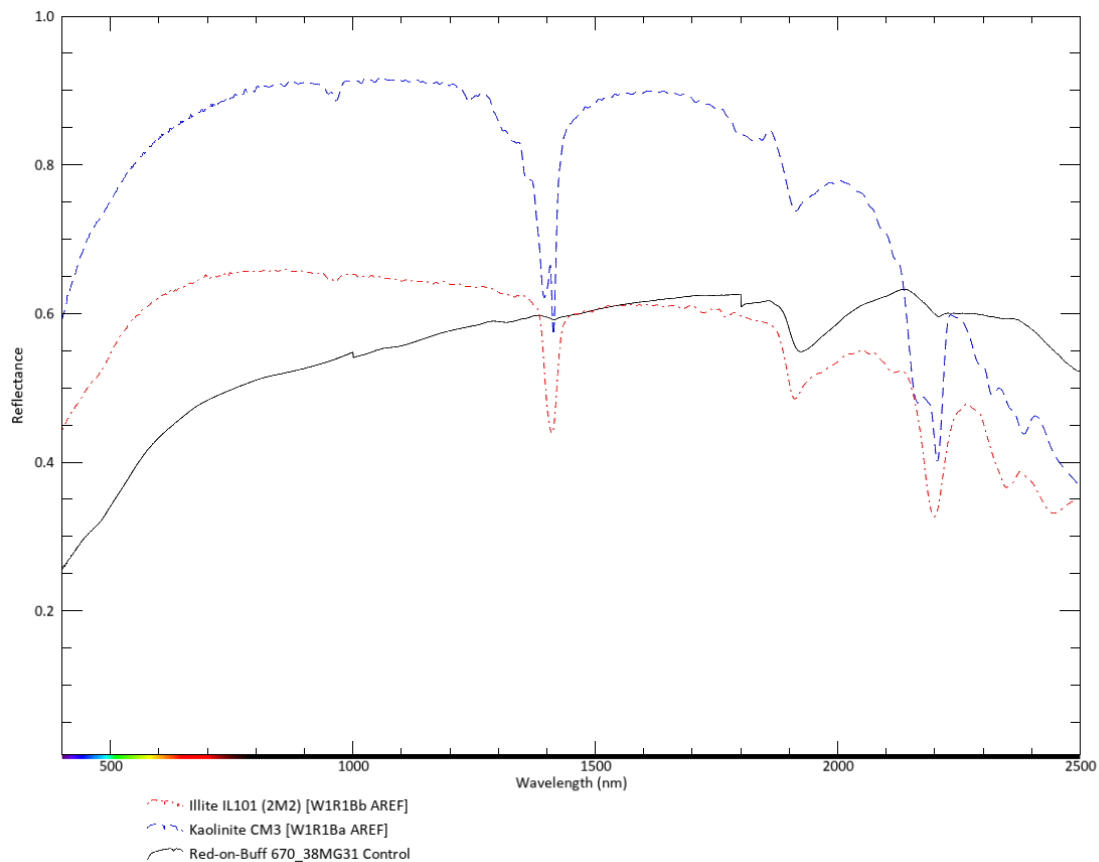


Figure 57: Comparison of pottery control to illite and kaolinite clays from the USGS spectral library (Kokaly et al. 2017). Note that spectral features beginning at 2000 nm to 2500 nm are markedly different.

While FORS cannot distinguish hematite sources per se, these data do suggest that a variety of hematite sources was likely used in the production of paint. Hematite can vary in appearance and occur in many forms including micaceous, oolitic, and others (Klein and Hurlbut 1999:379-380). In sedimentary deposits, hematite forms by inorganic or biological precipitation

in a body of water. During this process, clay minerals can be added to the iron oxide. This results in considerable variation in composition by source (Misra 2000). Thus, while we cannot source the hematites, we can suggest that several sources might have been used.

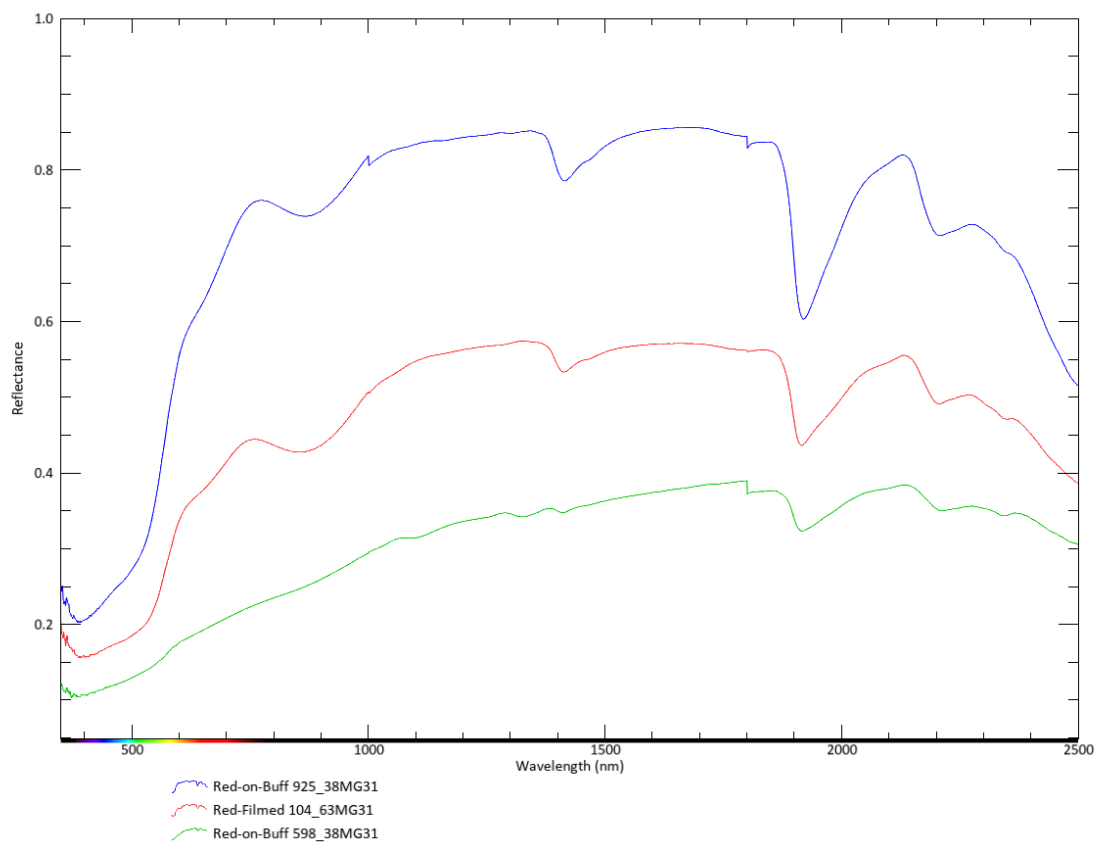


Figure 58: Variability of hematite absorption features among red-on-buff paint spectra.

FORS data also support the idea that clay was not an ingredient in paint recipes used to produce red-filmed and red-on-buff pottery. Generally, clay absorption features are less pronounced in paint spectra than in the controls. Also similar to the PXRF data, FORS is susceptible to preservation issues. Painted sherds with lighter paints are more often spectrally similar to their control readings (Figure 59), those sherds with faint paint have more prominent clay absorption features than those with prominent or thicker paint. Therefore, similar to the

PXRF results, sometimes the resulting spectra are influenced by the internal artifact surface stratigraphy.

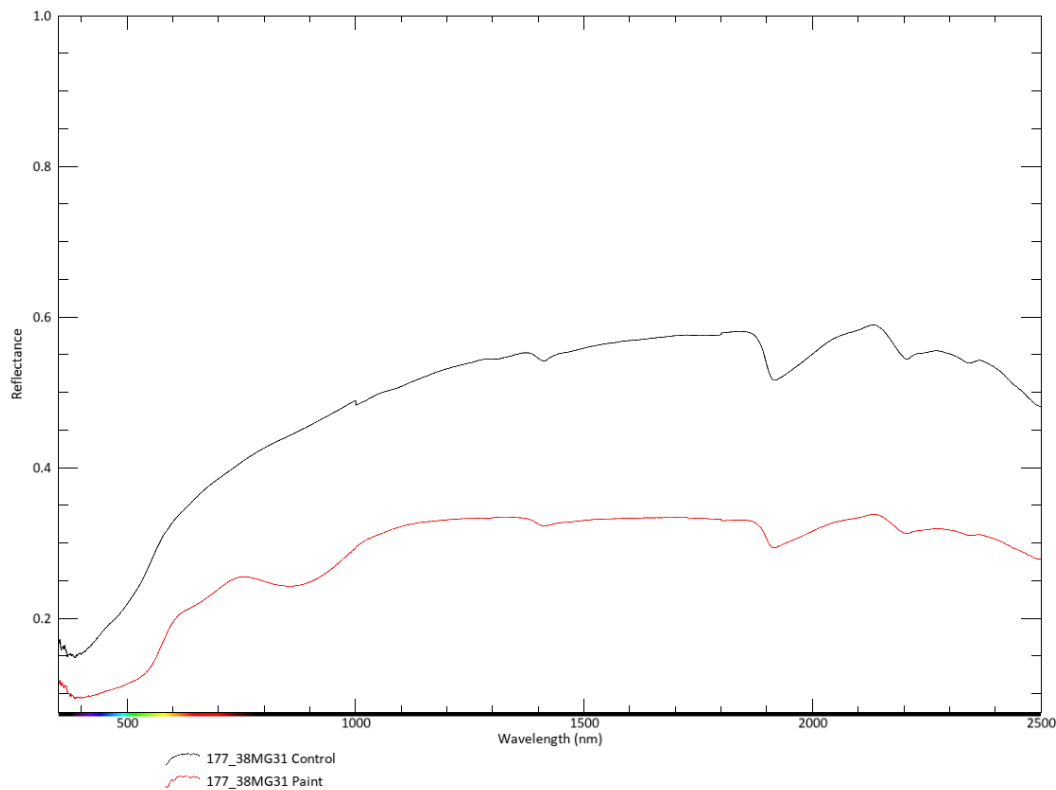


Figure 59: Red-filmed sherd, 177-38MG31 depicting paint (red) and control (readings). Very minor spectral differences are noted at 800 nm for the hematite, based on the poor preservation of the paint.

Conclusions

Through PXRF and FORS analyses several conclusions can be drawn concerning painted pottery from the Hiwassee Island Site. For application on pottery, paints were usually mixed with a chromophore or colorant, fine clay, water, and a binder (Rice 2015:160). It is argued that clays can enhance the adhesion of the pigment to the clay body although other vehicles for the mixture can include water or other organic substances (i.e. resins, fats, oils, wax, urine, etc.). However, this may not be necessary. At the Angel Site, Baumann et al. (2013) used a variety of traditional

analytical instruments, including X-ray fluorescence (XRF) and X-ray diffraction (XRD) to examine black on red negative painted pottery. They concluded that the red pigment was applied by using ground hematite and goethite mixed with water to create a low viscosity wash, not a slip (Baumann et al. 2013:241). While this example is geographically and temporally distinct from that at Hiwassee Island, it underscores the idea that paints applied to pottery do not necessarily need an added binder to create a successful product. Both PXRF and FORS datasets in this study indicate that the paints used to produce red-filmed and red-on-buff pottery consisted of hematite and water. This simple, yet effective recipe would have made for a quick and easy method for producing paint in large enough quantities to apply as coverings or washes for red-filmed pots or the painted designs exhibited on red-on-buff wares. While organic components could have been added, signatures of these would not have survived the firing process.

The data also highlight preservation concerns and the reliability of data acquisition. For surficial analytical techniques like those used in this research, sampling methods must be rigorous. Our data showed that thin or faded paint did not produce a good chemical or mineralogical signature. Another important aspect of methodology highlighted here is the necessity of taking numerous control readings.

The differences in water molecules in the FORS data suggest there may have been differences in firing practices at Hiwassee Island. Vessels that were adequately dried and fired in optimal conditions would, in theory, contain fewer water molecules (Rice 2015:102-104). Drying vessels before firing is a critical step in the production process of pottery that functions to remove water added during the construction of the vessel (i.e. coiling, smoothing, etc.). This step also removes interlayer and crystal lattice water that is inherent to the clay, since clays are a “hydrous” alumina silicate (Grimshaw 1971:443-449; Rice 2015:89). Drying can reduce the

water content of vessels, but the elevated temperatures introduced during firing are what cause progressive and irreversible physical modifications. Physical structures change and plasticity is lost, which creates a hardened and durable vessel. For Hiwassee Island, there are no clear-cut patterns in the FORS data concerning the water content to suggest differences in drying or firing practices. There is, however, clearly a potential for future investigations into firing practices using FORS with tailored experiments and increased sample size.

While the goal of this work was primarily to characterize paint recipes rather than to source clay or hematite, the variability in clay among both painted pottery groups suggests that potters at Hiwassee Island may not have used single clay sources to acquire their pot clays. Once clay was collected for pottery production, there can be multiple iterations of sieving or removing impurities and adding clay as well as puddling clays together. Therefore, the variability in clay minerals shown in the FORS data is not surprising. While clay mixing was undoubtedly practiced by potters in the region, the data do not indicate a difference between clay bodies used to produce red-filmed or red-on-buff pottery.

Lewis and Kneberg (1946) referenced Hiwassee Island Red-on-Buff pottery as being made with ball clay. This particular clay has extensive known deposits in West Tennessee and is described as low organic, low residue with white-firing characteristics due to its high kaolinitic content (Nelson 1911). Smith and Roger's (2011) survey of historic Tennessee-made pottery includes a reference to “ball clay” as being an important commercial material, found in West Tennessee (Floyd 1965:31). Other important studies of Tennessee clays include Eckel (1903), Ries (1903-1908), and Hollenbeck and Tyrrell (1969). Figure 60 shows the major Tennessee

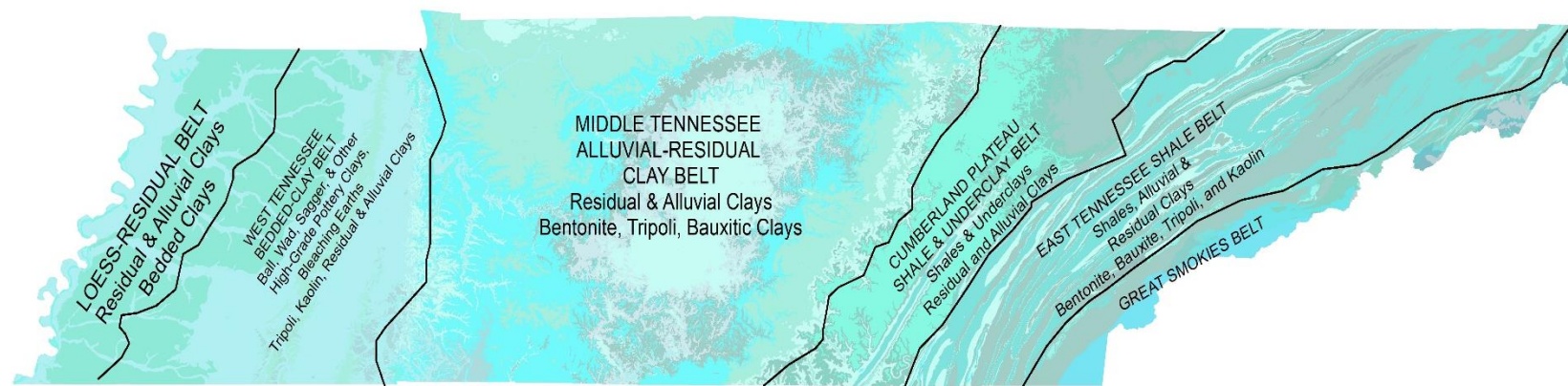


Figure 60: Tennessee clay belts and ceramic resources (adapted from Whitlatch 1940: Plate1). Ball-grade clays labeled for West Tennessee. East Tennessee, where Hiwassee Island is located, contains shales, alluvial and residual clays.

clay belts and ceramic resources found in each major geological province of Tennessee. Even today Tennessee is the leading producer of ball clay in the United States. Based on FORS data, the clay used to create red-on-buff vessels was not in fact ball clay based on the absence of features consistent with kaolinite. Additionally, the PXRF also indicates ball clay was not used based on the relative low iron content (see Figure 55). Clay sources could have still held significance for the potters at Hiwassee Island. Lyle (2017) used PXRF to examine compositional differences in the clay bodies of several different pottery wares from Hiwassee Island, including red-filmed and red-on-buff. Her work showed distinct groupings of paste composition for red-filmed and red-on-buff clays, suggesting that different clay sources may have been used. A larger data set, including pottery types from other chronological associations, can elucidate these findings.

While temper types shifted from limestone to crushed mussel shells during the Hiwassee Island phase, vessel construction methods, sizes, and shapes did not change substantially. Even when new pottery types such as red-filmed, red-on-buff, and complicated stamped were introduced, potters at Hiwassee Island continued to use the same basic technological practices. If these pottery wares were special and non-utilitarian as Lewis and Kneberg (1946:92) suggested, then it appears that the color and decoration of these vessels conveyed more meaning than the materials used to produce them. Likewise, paint recipes used to decorate these vessels were created using a simple recipe with readily available materials. Pottery “is an exciting combination of art, science, painting, and sculpture... it embodies geology, chemistry, physics, artistry, and more than a little alchemy” (Hopper 2009:247). With advances in analytical instruments, we can shed new light on pottery traditions in the region. Hiwassee Island was repeatedly used during a time that was charged with ritual symbols and ceremonies, but it was

more likely the designs, colors, and placement of these symbols that imparted powerful meaning rather than the construction of the items themselves.

CHAPTER V: CONCLUSIONS

In this dissertation, I examined the composition of late pre-Contact period paints in the American Southeast from three archaeological contexts. Bringing the results of these studies together to address the major questions raised in Chapter I, three main points emerge that address our understanding of Mississippian period paints in the region:

1. Pre-Contact paint recipes were largely created using minimal ingredients—a chromophore mixed in water.
2. This basic recipe was consistently found in all archaeological media analyzed. There are, however, some cases where additional ingredients were incorporated to paint recipes. These additional ingredients may have served technical functions to aid in adherence of the paint to the media surface or may have served as a culturally significant, symbolic ingredient. In any case, such added components are rare.
3. Contextual differences related to the intended use of a painted object are perhaps more significant indicators of Mississippian period religious manifestations than are the constituents of paint recipes.

One of the primary questions I sought to answer in this dissertation was “what are the constituents of late pre-Contact period paints?” The nature of pigment material used to adorn archaeological media have often been overlooked, but I have shown that by scientifically examining the material properties of paint we can begin to understand pre-Contact paint manufacture. The techniques I used specifically inform on a paint’s chromophore that was used to make a liquid paint. They can also identify additives that may have been used to contribute to

the performance of the paint or to imbue some kind of additional cultural significance into the paint itself. While destructive analytical techniques have heretofore been used to ascertain this information about pre-Contact paint use, the research presented in this dissertation shows that non-destructive techniques *can* contribute towards our overall understanding of how Mississippians and later native peoples made and used materials.

The analysis of rock art paints provided the most variation in paint recipes presented in this dissertation. Pictographs produced in southern Illinois were created by native peoples using either an iron-rich ochre to create reds and yellows, while a vegetal carbon was used to create black paints. Artists then mixed these chromophores with water and used the resulting paints to create a wide array of images such as ogees, quadrupeds, anthropomorphs, and geometric shapes at Mississippian, Proto-Historic, and Historic period rock art sites. In a select few cases, native painters added additional ingredients to this paint recipe. The first differing recipe I identified consisted of an iron-rich chromophore, manganese, and water. The second contained an iron-rich chromophore, gypsum, and water. Interestingly, these recipes are present in pictographs from the same site. Differing paint recipes at the same rock art locale could be indicative of idiosyncratic artists' recipes (i.e. paint made by different people, temporal differences (i.e. paint made at different art making episodes at the site), or be an indication of symbolic/ritualistic differences (i.e. paints made for specific motifs or use). As I argued, however, there is some reason to believe that different groups of people made pictographs in southern Illinois during the late Precontact and Contact periods. In any case, a variety of theories exist for why rock art was created by indigenous peoples (David and McNiven 2019) and in the absence of direct ethnographic records, we may never truly understand the meaning behind these images. For the

rock art presented here, the imagery itself appears to be the primary transmitter, while the paint provides the medium for expression of that information.

In the case of Mississippian stone statuary, artisans applied paints in only a few cases. The recipes analyzed indicate, again, a very simple paint recipe with chromophore ingredients including hematite, goethite (or limonite), and charcoal to create reds, yellows, and blacks, respectively. Interestingly, the analytical techniques indicate that sculptors selected different stone raw materials to create these figures. This variability suggests that, while the figures constitute a *style* of artifact used within several Mississippian communities across the Southeast, they were manufactured and used locally by individual communities. This contrasts with the Cahokia-style statuary produced from a localized flint-clay resource, made centrally, then dispersed across regional Mississippian communities. The variability in the Tennessee-Cumberland style statuary indicates the purposeful acquisition of certain raw materials, likely reflective of religious narratives about the identity of the characters, to create these figures. One of these acquisition locales includes traversing into the underworld, natural caves in the region, to acquire calcite large enough to carve a freestanding statue.

Mississippian painted pottery from the Hiwassee Island Site represents the largest data set of paint analyzed in this dissertation. Paints used on this archaeological medium, however, were ubiquitously consistent. All of the red paints were created *via* hematite as the chromophore with water as the suspension medium that potters then applied to the vessel. Despite red-on-buff being described as the *de luxe* ware at Hiwassee Island (and its relative rarity in relation to red-filmed wares in the region), the paint recipes were not different.

There are, however, some matters to consider when adopting these analytical techniques for the analysis of paints (and archaeological materials more generally). First, one must consider

the paint's structure—its support or underlayer, thickness, and pigment heterogeneity (McGlinchey 2012:131). Each of these will influence how much useful information PXRF and FORS can provide. As was highlighted in earlier chapters, when thin or eroded paint was analyzed, the information collected was not highly dependable. If the analyzed layer is thinly applied or heavily weathered, the spectral reading will reflect the underlying material rather than the actual paint. Both PXRF and FORS take surficial measurements and whatever the nose of each instrument is pointed at will become part of the overall spectral reading. Therefore, prioritizing suitable areas to analyze must be taken into consideration and specifics concerning the instrument analysis window must be understood. Ideal conditions for spectral readings on paint are those made on paint that is thick and consistently applied to the artifact.

Thickness measurements should consider horizontal thickness, or width of the paint, in addition to how thickly the layer of paint is applied to the surface of the artifact. Even under the most ideal conditions, PXRF spectra will include varying amounts of the underlayer in the overall creation of the waveform. This is due to the physics behind how the instrument operates and to what degree the emitted X-rays penetrate the material matrix. In the cases presented in this dissertation, underlayer matrices are heterogeneous and therefore X-rays will penetrate the specimen at varying depths depending on what it comes into contact with inside that matrix (i.e. in pottery this could be temper, clay, or other mineral inclusions naturally or culturally in the clay body). To mitigate these issues control readings are crucial. As has been said numerous times throughout this dissertation, these readings serve to help determine the presence or absence of elements and relative concentrations of elements within the paint and substrate layer. This is especially important in dealing with red paint colors as the primary chromophore is likely to be comprised of iron, which is also present in various rock formations and clays.

To examine the extent to which the underlying substrate can influence paint readings with the PXRF instrument, I conducted an exploratory principal component analysis (PCA) and canonical discriminant analysis (CDA) on some of the painted media data sets using the NPA results (see Appendices D and E). PCA essentially is a data reduction technique to reduce the number of variables, while maintaining most of the information found in the original data in the first several components. Conversely, a discriminant analysis is generally a statistical technique used to classify observations into non-overlapping groups, based on scores on one or more quantitative predictor variables (Tinsley and Brown 2000). It is a dimension-reduction technique related to (PCA). This type of statistical test, however, derives *canonical variables* (linear combination of the interval variables) that summarize between-class variation in much the same way that principle components summarize total variation. Therefore, it contrasts to that of PCA in that it extracts a new set of variables that maximize the differences between two or more groups rather than maximizing the total variance of the data set (Glascock 1992:18). The strengths of CDA are that it can be used to make predictions about group membership outcomes, and it can be used to describe the nature of differences between groups (Warner 2013:728).

The PCA results for the rock art revealed primary components that comprised the underlying rock or pottery substrate, rather than the paint constituents themselves.

For instance, four-component solution derived principle components such as Ca, Rb, Sr, K, and Ti for the Illinois rock art dataset (see Appendix D). A Varimax orthogonal rotation was employed to aid interpretability, however, the solution was a complex structure that could not be directly attributed clusters of paint recipes and controls. The elements identified and spread can be directly attributed to the sandstone and limestone rockshelter substrate upon which the paints were applied. Based on this exploratory analysis, a PCA was attempted on the painted pottery

from Hiwassee Island, however the dataset violated several basic PCA assumptions. Most notable among these were the Kaiser-Meyer-Olkin measure of sampling adequacy, which was ‘unacceptable’ based on Kaiser’s (1974) classification of measure values.

While statistical analyses of the paint layers were unsatisfying, the Tennessee-Cumberland style stone statuary provided more compelling results. To further explore the composition of raw materials artisans used to create the stone statuary, I conducted a CDA using the NPA results from the PXRF analysis. Specific to my research, this test allowed for a further understanding of how the elements interrelate in distinguishing raw material groupings of the statues analyzed.

For this analysis a total of 28 statues were analyzed with 93 cases included in the statistical analysis (Appendix, Table E. 1). Wilk’s Lambda is significant ($p < 0.05$), indicating that functions 1 through 2 significantly explain the variance (Appendix, Figure E. 1). Within these, function 1 is explained primarily by the element Ca, whereas function 2 is mainly driven by the elements Sr and Zn (Appendix, Figure E. 2).

The standardized plot in Figure 61 indicates two very distinct clusters of raw materials, with the sandstone statues differing from calcite statuary (Appendix, Figure E. 3). Interestingly, the statues visually determined to be speleogenic calcite, from cave sources, cluster slightly apart from those designated as non-speleogenic calcite statues. While the group size of each are relatively small (limestone N=6; calcite N=8) and the group centroids are relatively close to one another, analyzing more calcite statuary may reveal better defined clusters. With respect to the sandstone group, the data clusters very tightly, suggesting perhaps that the variability in sandstone outcrops that artisans used to carve these figures is more closely related to the trace elemental variation. This can be further explored by examining the elemental variability in

sandstone outcrops in the region. With the standardized plot, we can observe that function 1 (explained primarily by Ca) is driving the differences among statues. The clustering of speleogenic and non-speleogenic calcite suggest that Ca does vary, however, the biggest variation exists among the sandstone statuary compared to calcite raw materials. While this distinction can be made through a visual inspection of the statues, this statistical analysis displays the robusticity of the PXRF data in making these classification determinations also.

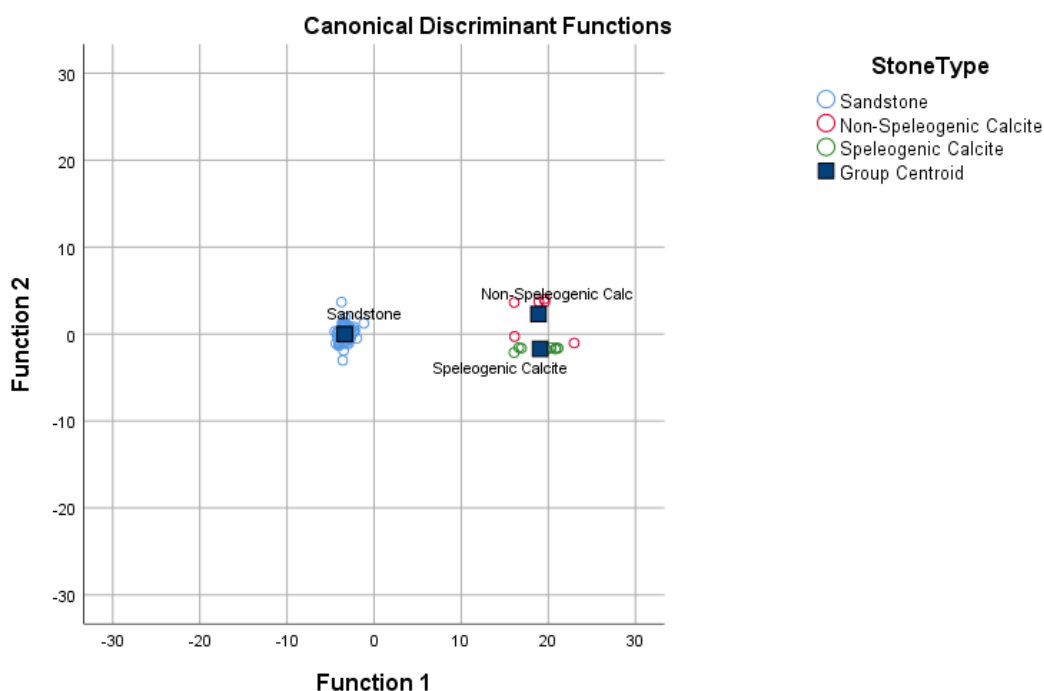


Figure 61: Canonical discriminant function plot for Tennessee-Cumberland style stone statuary.

With regards to FORS analysis specifically, the largest hurdle facing archaeological applications is the need for extensive, accessible spectral libraries that include a range of natural objects and cultural artifacts. Unlike PXRF, which gives relatively straight-forward element identifications, mineralogical identifications based on FORS spectra are much more complex.

The amalgamation of the main absorption features with combination and overtone features that comprise a FORS waveform could be due to several different minerals in the archaeological specimen. There are large spectral libraries for a range of geological samples, and while they are extremely useful, they are not wholly representative of cultural materials. As FORS progresses into mainstream archaeology, these reference spectral libraries will be crucial for accurate interpretations of mineralogical constituents of artifacts. One way this issue is mitigated in the short term, as I have done in this dissertation, is to compare the mineralogical data to the elemental data. For example, iron is identified elementally with the PXRF, but it does not tell us whether that iron comes from the mineral goethite, limonite, or hematite. All three are iron-rich ochres, but mineralogically their absorption bands differ.

A secondary avenue for studying mineral forms of ochre is the effects of firing. Yellow goethite ochres can be heated to convert them to red ochre of various shades when exposed to temperatures in excess of ca. 250°C. This conversion results in structurally disordered hematite, which could be evidence for primitive heat treatment (David et al. 2001; Hradil et al. 2003). In the cases analyzed in this dissertation, hematite identified by FORS is variable. Experiments on controlled modification of color through heating ochres should be undertaken and examined by FORS to expound on the manufacturing process of red paints.

It would be also worthwhile to analyze a range of organic materials that could be used in the creation of cultural materials. While we cannot discount the possibility of organic elements being added to the paints analyzed in this dissertation, especially for rock art, organic components, often the focus of bacterial attack, break down resulting in a deterioration of the paint over time. The sheer durability and subsequent induration of Southeast Mississippian paint into the substrate layer suggest that organic components were not added. Horn (2018)

successfully identified binder ingredients like egg, oils, and fats *via* FORS from experimental paints. After simulated age-progression, however, some of these binders could not be identified spectrally (Horn 2018). This offers another avenue of potential research to expand on with FORS.

The color itself seems to take preference in the creation of paints presented in this dissertation. We know through various ethnographies that color symbolism was deeply entrenched in a variety of Native societies including major linguistic groups such as Caddoan (e.g., the Pawnee Arikara, Wichita, and Caddo) (Dorsey 1904; Weltfish 1965), Siouan (e.g. the Osage and Winnebago (Bailey 1995; Radin 1915), Algonkian (e.g. the Shawnee) (Trowbridge 1939), Muskogean (e.g. Choctaw and Chickasaw) (Swanton 1928), and Iroquoian speakers (e.g. the Cherokee (Hudson 1976; Mooney 1970). Although the specific details and meaning associated with colors vary among different tribes, the colors are semiotic codes meaning they are deeply engaged in social relations and in the creation of cultural order (Sahlins 1976). So, while the paints described in this research are *technically* simplistic, they are certainly not *culturally* simplistic. For instance, vegetal carbon to create blacks could have been acquired from special hearths or created using certain types of woods like cedar. Likewise, pre-Contact artists may have selected specific hematite locations on the landscape.

Continued work on the pictographs that line the Cumberland Plateau from Kentucky, Tennessee, and Alabama also indicates that paints were prepared simply and were created with two ingredients—chromophore and water (Bow 2015, 2016a, b; Bow and Simek 2014; Simek et al. 2012, 2020). In addition to the motif, or design, color adds a layer of signaling of symbolic behavior. Certain motifs are depicted strictly based on their location on the landscape as was the selection of color to create these images (i.e. rock art vs. cave art, see Simek et al. 2013).

Collecting a chromophore, turning it into a powder or paint, and applying it on a surface to express meaning to others is a multistep process, done with the intent to convey information to another individual or individuals (who possess the ability to understand the signal). We may not ever fully understand *what* these painted symbols mean, or understand what, or if, rituals associated with them occurred.

The primary colorants found in the Mississippian period consist of black, red, yellow, and white. Black can be produced in three ways: using the mineral manganese, carbon from charcoal, or by firing and grinding bone. As we saw in Chapter III, black can be identified quite easily through PXRF analysis alone through looking at the presence/absence and relative concentrations of manganese, calcium, and phosphorus between black pictograph and control analytical readings. Red, yellow, and orange are all produced with ochres, or iron oxides (of which the mineral constituents vary). These are relatively common in many natural geological and soil formations. And while they are perhaps best known for their use in creating art or in mortuary contexts, ancient and historic peoples also widely used them as both internal and external medications, food or wood preservatives, insect repellents, tanning for hides, and for a range of other purposes (Basedown 1925:65; Berndt and Berndt 1964:99; Flood 1990:241; Level 1966:290; Peile 1979; Roper 1991:296).

Each of these chromophores used to create paints analyzed in this dissertation could be obtained with relative ease in the Mississippian world. Ochre pieces both small and large can be found across the landscape and could have easily been gathered. Black chromophores could have easily been obtained in large quantities from charcoal in the numerous hearths within Mississippian villages. Furthermore, these may have been culturally specific hearths, or certain types of wood may have been selected for by native peoples. Each of these colors requires very

little effort to acquire; from that point they simply needed to be finely ground and added to water before they could be used as functional paint. In the cases presented in this dissertation, materials used to create paints required the least-cost effort of acquisition.

Artists generally produced paints in the Southeast with the most practical and expediently acquired materials possible. This does not, however, mean that the selection of chromophores was not without meaning. Colors—red, yellow, and black—were purposefully selected for by artists to produce these paints. Except for a few specific examples of additional mineral additives, paints were produced for a variety of purposes using the same basic recipe. The primary recipe revealed in this dissertation is simple, a colorant plus water.

As the technological capabilities of non-destructive analytical techniques continue to advance, our application of these techniques will continue to provide hard scientific answers to the questions associated with cultural materials. In this instance, it appears the artistic choices of color, motif, and spatial context were of far greater consequence and meaning than the ways the paints themselves were made. This dissertation demonstrates the value that non-destructive materials analysis can bring to archaeological interpretations. Although only three cases were presented, there is a large avenue for future research in pre-Columbian paint studies in the region.

There are a range of tailored experiments that could be conducted. On a very basic level, creating experimental paints with a variety of organic binders. While few studies have been conducted on organics, these kinds of tests could empirically shed light on the decomposition process and aid in the comprehending the full detection capabilities of PXRF and FORS. One Cherokee ritual describes using deer tallow, or fat, mixed with dried and pounded white clay to form a white paint (Fradkin 1990:358). Investigations into a range of organic ingredients must be

conducted. Other experiments could be tailored around reliability and replicability of handholding the PXRF instrument. Lastly, experiments should be conducted on the effects of paint thickness and how to isolate PXRF and FORS readings from the underlying substrate. Another research avenue is the creation of a FORS spectral reference library. Specifically, one that is tailored to cultural materials and local material sources such as hematite, clays, and sedimentary rocks. The creation and availability of such a database would greatly inform future archaeological studies using FORS. Once these basic experiments have been conducted, varying painted archaeological media should be added to the dataset. While a basic recipe was identified in the three cases presented here, variable paint recipes could certainly exist on other painted media or on those from different Mississippian cultures in the Southeast. As with all archaeological research, there is always more to be done but XRF and FORS provide an exciting new avenue to travel down.

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APPENDICES

Appendix A: DStretch Image Enhancing Software

DStretch is a rock art digital enhancement tool created by Jon Harmon that used to bring out faint pictographs that can be invisible to the naked eye. DStretch stands for decorrelation stretch, which was first used in remote sensing to enhance multispectral images. For archaeologists, and rock art researchers in particular, it has been modified and implemented as a plugin to ImageJ (<http://rsb.info.nih.gov/ij/index.html>) which is a full-featured imaging program written in Java. Pictographs can be enhanced using DStretch to bring out subtle differences in hue. A full explanation of how the algorithm can be found at www.DStretch.com.

Appendix B: Data Availability Statement

The datasets generated during and/or analyzed during this dissertation are not publicly available herein. Instead, datasets are subject to availability determined by the corresponding institutions or museums listed below in Table B.1.

Table B.1: Data availability of analyzed materials in this dissertation.

ARCHAEOLOGICAL SPECIMEN ANALYZED		CURATION INSTITUTION/MUSEUM
Rock art	Illinois Sites	Southern Illinois University, Carbondale and the Center for Archaeological Investigations
Statuary	CSS-001; 018; 089	Individually Owned/Private Collections
	CSS-002; 003; and 004	The McClung Museum of Natural History and Culture
	CSS-008	National Museum of the American Indian Object no. 0035337.000
	CSS-009	Bledsoe's Lick Historical Association
	CSS-010; 011; 012; 013; 014; 019; 021; 023; 032; 048	National Museum of Natural History Object no. A334008, A334007; A334012; A334013; A334011; A334009; A334005; A334006; A334010; A19934
	CSS-024; 030; 045	National Museum of the American Indian Object no. 0210965.000; 0007277.000; 0007276.000
	CSS-031; 065; 067; 068; 090	Tennessee State Museum Object no. 82.100.1091; 2003.2; 8.714; 8.715; 4.207
Pottery	CSS-035; 036	Metropolitan Museum of Art Object no. 1979.206.1139; 1979.206.476
	Hiwassee Island Red-Filmed and Red-on-Buff pottery	The McClung Museum of Natural History and Culture

Appendix C: Inventory of Hiwassee Island Pottery Analyzed by PXRF and FORS.

Table C. 1: Hiwassee Island pottery sherds analyzed by PXRF

FULL PROVENIENCE	SHERD	UNIT	TYPE	# OF SHERDS ANALYZED
38MG31	no FS.	38MG31	Red Filmed	4
26-63MG31	26	63MG31	Red Filmed	2
29-63MG31	29	63MG31	Red Filmed	2
63_63MG31	63	63MG31	Red Filmed	2
83-63MG31	83	63MG31	Red Filmed	2
87-63MG31	87	63MG31	Red Filmed	3
104-63MG31	104	63MG31	Red Filmed	1
117-63MG31	117	63MG31	Red Filmed	2
131-63MG31	131	63MG31	Red Filmed	1
170-63MG31	170	63MG31	Red Filmed	2
177-38MG31	177	38MG31	Red Filmed	1
183-63MG31	183	63MG31	Red Filmed	2
191-63MG31	191	63MG31	Red Filmed	1
224-63MG31	224	63MG31	Red Filmed	1
291-63MG31	291	63MG31	Red Filmed	1
311-38MG31	311	38MG31	Red Filmed	1
358-63MG31	358	63MG31	Red Filmed	8
422-38MG31	422	38MG31	Red Filmed	1
487-38MG31	487	38MG31	Red Filmed	1
516-38MG31	516	38MG31	Red Filmed	7
598-38MG31	598	38MG31	Red Filmed	2
770-38MG31	770	38MG31	Red Filmed	1
1011-38MG31	1011	38MG31	Red Filmed	2
1056-38MG31	1056	38MG31	Red Filmed	3
63MG31	No Fs.	63MG31	Red on Buff	1
38MG31	No Fs.	38MG31	Red on Buff	2
26-63MG31	26	63MG31	Red on Buff	1
37-63MG31	37	63MG31	Red on Buff	1
39-63MG31	39	63MG31	Red on Buff	1
83-63MG31	83	63MG31	Red on Buff	1
83-38MG31	83	38MG31	Red on Buff	2
87-63MG31	87	63MG31	Red on Buff	1
91-63MG31	91	63MG31	Red on Buff	1
104-63MG31	104	63MG31	Red on Buff	1
117-63MG31	117	63MG31	Red on Buff	2
140-63MG31	140	63MG31	Red on Buff	1

Table C.1 Continued

163-63MG31	163	63MG31	Red on Buff	1
177-38MG31	177	38MG31	Red on Buff	2
182-63MG31	182	63MG31	Red on Buff	1
188-38MG31	188	38MG31	Red on Buff	1
224-63MG31	224	63MG31	Red on Buff	3
304-38MG31	304	38MG31	Red on Buff	3
331-63MG31	331	63MG31	Red on Buff	1
396-63MG31	396	63MG31	Red on Buff	1
415-38MG31	415	38MG31	Red on Buff	1
502-38MG31	502	38MG31	Red on Buff	1
598-38MG31	598	38MG31	Red on Buff	1
633-38MG31	633	38MG31	Red on Buff	1
670-38MG31	670	38MG31	Red on Buff	1
685-38MG31	685	38MG31	Red on Buff	1
800-38MG31	800	38MG31	Red on Buff	1
925-38MG31	925	38MG31	Red on Buff	2
TOTAL				90

Table C. 2: Hiwassee Island pottery sherds analyzed by FORS.

FULL PROVENIENCE	SHERD	UNIT	TYPE	# OF SHERDS ANALYZED
38MG31	No Fs.	38MG31	Red Filmed	3
26_63MG31	26	63MG31	Red Filmed	2
29_63MG31	29	63MG31	Red Filmed	2
63_63MG31	63	63MG31	Red Filmed	1
83_63MG31	83	63MG31	Red Filmed	2
87_63MG31	87	63MG31	Red Filmed	3
117_63MG31	117	63MG31	Red Filmed	2
131_63MG31	131	63MG31	Red Filmed	1
170_63MG31	170	63MG31	Red Filmed	3
177_38MG31	177	38MG31	Red Filmed	5
183_63MG31	183	63MG31	Red Filmed	2
191_38MG31	191	38MG31	Red Filmed	1
224_63MG31	224	63MG31	Red Filmed	1
291_63MG31	291	63MG31	Red Filmed	1
311_38MG31	311	38MG31	Red Filmed	1
358_63MG31	358	63MG31	Red Filmed	8
422_38MG31	422	38MG31	Red Filmed	1

Table C.1 Continued

516_38MG31	516	38MG31	Red Filmed	7
598_38MG31	598	38MG31	Red Filmed	3
770_38MG31	770	38MG31	Red Filmed	1
1011_38MG31	1011	38MG31	Red Filmed	2
1056_38MG31	1056	38MG31	Red Filmed	4
63MG31	No. Fs	63MG31	Red on Buff	3
26_63MG31	26	63MG31	Red on Buff	1
37_63MG31	37	63MG31	Red on Buff	1
39_63MG31	39	63MG31	Red on Buff	1
83_38MG31	83	38MG31	Red on Buff	1
83_63MG31	83	63MG31	Red on Buff	1
87_63MG31	87	63MG31	Red on Buff	1
91_63MG31	91	63MG31	Red on Buff	1
104_63MG31	104	63MG31	Red on Buff	1
117_63MG31	117	63MG31	Red on Buff	1
140_63MG31	140	63MG31	Red on Buff	1
158_63MG31	158	63MG31	Red on Buff	1
163_63MG31	163	63MG31	Red on Buff	1
177_38MG31	177	38MG31	Red on Buff	2
182_63MG31	182	63MG31	Red on Buff	1
188_38MG31	188	38MG31	Red on Buff	1
224_63MG31	224	63MG31	Red on Buff	5
280_63MG31	280	63MG31	Red on Buff	1
304_38MG31	304	38MG31	Red on Buff	5
331_63MG31	331	63MG31	Red on Buff	2
371_63MG31	371	63MG31	Red on Buff	1
374_36MG31	374	36MG31	Red on Buff	1
396_63MG31	396	63MG31	Red on Buff	1
415_38MG31	415	38MG31	Red on Buff	1
502_38MG31	502	38MG31	Red on Buff	2
598_38MG31	598	38MG31	Red on Buff	3
633_38MG31	633	38MG31	Red on Buff	3
670_38MG31	670	38MG31	Red on Buff	1
800_38MG31	800	38MG31	Red on Buff	1
856_38MG31	856	38MG31	Red on Buff	1
925_38MG31	925	38MG31	Red on Buff	2
685_38MG31	685	38MG31	Red on Buff	1
TOTAL				106

Appendix D: Exploratory Principal Component Analysis (PCA) Results for the Illinois Rock Art Dataset.

This section contains the statistical results of the exploratory principal component analysis on Illinois rock art. All statistics were performed using IBM SPSS Statistics, version 26 software.

For the Illinois rock art dataset, a PCA was run on 16 elements that were identified in 56 paint and control samples. The suitability of PCA was assessed prior to the analysis. Inspection of the correlation matrix showed that all variables had at least one correlation coefficient greater than 0.3. The overall Kaiser-Meyer-Olkin (KMO) measure was 0.723, with all individual elements except Fe and Zn possessing an individual KMO > 0.5 (Kaiser 1974). In the second iteration of the PCA, Fe and Zn were removed. This improved the KMO measure to 0.776. Bartlett's test of sphericity was statistically significant indicating that the data was likely factorizable.

PCA revealed four components that had eigenvalues greater than one and which explained 39.1%, 29.2%, 14.4%, and 5.3%, of the total variance respectively. Visual inspection of the scree plot indicated that four components should be retained (Cattell 1966). A Varimax orthogonal rotation was employed to aid interpretability. The rotated solution exhibited a relatively complicated structure with several elements comprising each component and some elements comprising two components (Thurstone 1947). The interpretation of the data suggests that the underlying rock substrate cannot be statistically separated from the paint layer. When viewing the component plot in rotated space, one cluster of Ba, Pb, and Mn can be identified, and perhaps represent the 'outliers' of paints analyzed. High quantities of Ba and Pb were found in the 'Historic Paint #1' paint and elevated amounts of Mn were identified in two prehistoric glyphs. The spread of the remaining elements suggests, however, that statistically the paint

recipes cannot confidently be separated from the control readings. This suggests that the PXRF detects the underlying substrate in all paint readings.

Correlation Matrix

		Al	Si	S	K	Ca	Ti	Mn	Fe	Cu	Zn	Rb	Sr	Y	Zr	Ba	Pb
Correlation	Al	1.000	.277	-.067	.411	.048	.264	-.108	.602	.466	.575	.029	.042	.002	.014	-.092	-.094
	Si	.277	1.000	-.251	-.095	-.275	.081	.078	-.050	.137	.024	-.277	-.217	-.290	.550	.083	-.025
	S	-.067	-.251	1.000	.576	.748	.069	.064	-.046	.104	.410	.719	.723	.743	-.117	.124	.162
	K	.411	-.095	.576	1.000	.766	.071	-.079	.478	.403	.712	.795	.529	.806	-.087	-.088	-.073
	Ca	.048	-.275	.748	.766	1.000	-.112	-.146	-.039	.285	.602	.983	.721	.964	-.127	-.103	-.061
	Ti	.264	.081	.069	.071	-.112	1.000	.788	.301	.023	-.033	-.112	.492	-.124	.114	.898	.910
	Mn	-.108	.078	.064	-.079	-.146	.788	1.000	-.016	-.267	-.306	-.138	.406	-.139	.168	.877	.868
	Fe	.602	-.050	-.046	.478	-.039	.301	-.016	1.000	.370	.401	-.035	-.095	-.036	-.189	-.039	-.028
	Cu	.466	.137	.104	.403	.285	.023	-.267	.370	1.000	.498	.265	.142	.239	.082	-.166	-.170
	Zn	.575	.024	.410	.712	.602	-.033	-.306	.401	.498	1.000	.593	.339	.579	-.011	-.261	-.233
	Rb	.029	-.277	.719	.795	.983	-.112	-.138	-.035	.265	.593	1.000	.697	.988	-.111	-.097	-.057
	Sr	.042	-.217	.723	.529	.721	.492	.406	-.095	.142	.339	.697	1.000	.688	-.010	.515	.569
	Y	.002	-.290	.743	.806	.964	-.124	-.139	-.036	.239	.579	.988	.688	1.000	-.113	-.098	-.057
	Zr	.014	.550	-.117	-.087	-.127	.114	.168	-.189	.082	-.011	-.111	-.010	-.113	1.000	.174	.077
	Ba	-.092	.083	.124	-.088	-.103	.898	.877	-.039	-.166	-.261	-.097	.515	-.098	.174	1.000	.981
	Pb	-.094	-.025	.162	-.073	-.061	.910	.868	-.028	-.170	-.233	-.057	.569	-.057	.077	.981	1.000

Figure D. 1: PCA correlation matrix for the first iteration on the Illinois rock art PXRF dataset. All elements contain at least one correlation coefficient greater than 0.3.

KMO and Bartlett's Test		
Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.723
Bartlett's Test of Sphericity	Approx. Chi-Square	1310.113
	df	120
	Sig.	.000

Figure D. 2: KMO and Bartlett's test for the first iteration on the Illinois rock art PXRF dataset. The overall Kaiser-Meyer-Olkin (KMO) measure is 0.723, considered 'middling' to 'meritorious' according to Kaiser (1974). Bartlett's test of sphericity is statistically significant, indicating that the data is factorizable.

Anti-image Matrices

	Al	Si	S	K	Ca	Ti	Mn	Fe	Cu	Zn	Rb	Sr	Y	Zr	Ba	Pb
Anti-image Correlation	.585 ^a	-.124	.083	-.215	-.085	-.608	-.013	.301	-.098	-.321	.103	-.016	.042	.305	.071	.371
	-.124	.523 ^a	-.097	-.399	-.145	-.030	.051	.440	-.150	-.149	.052	.270	.219	-.302	-.205	.077
	.083	-.097	.861 ^a	.058	-.185	.145	.005	-.191	.127	-.125	.312	-.332	-.283	.061	-.121	.026
	-.215	-.399	.058	.706 ^a	.289	-.001	-.353	-.713	.094	.105	-.088	-.330	-.519	.097	-.229	.313
	-.085	-.145	-.185	.289	.767 ^a	.172	-.114	-.312	-.034	-.048	-.755	-.547	.185	.136	-.151	.154
	-.608	-.030	.145	-.001	.172	.665 ^a	.126	-.522	.044	-.046	-.207	-.302	.240	-.329	-.065	-.599
	-.013	.051	.005	-.353	-.114	.126	.858 ^a	.103	.223	.106	-.016	.095	.243	-.202	-.007	-.300
	.301	.440	-.191	-.713	-.312	-.522	.103	.374 ^a	-.223	-.157	.196	.552	.210	.155	.174	.076
	-.098	-.150	.127	.094	-.034	.044	.223	-.223	.853 ^a	-.029	-.028	-.145	.015	-.121	-.051	.009
	-.321	-.149	-.125	.105	-.048	-.046	.106	-.157	-.029	.917 ^a	-.024	.022	-.093	-.155	.151	-.061
	.103	.052	.312	-.088	-.755	-.207	-.016	.196	-.028	-.024	.759 ^a	.253	-.687	.006	.040	.037
	-.016	.270	-.332	-.330	-.547	-.302	.095	.552	-.145	.022	.253	.736 ^a	.006	-.128	.283	-.251
	.042	.219	-.283	-.519	.185	.240	.243	.210	.015	-.093	-.687	.006	.778 ^a	-.133	.094	-.268
	.305	-.302	.061	.097	.136	-.329	-.202	.155	-.121	-.155	.006	-.128	-.133	.383 ^a	-.298	.482
	.071	-.205	-.121	-.229	-.151	-.065	-.007	.174	-.051	.151	.040	.283	.094	-.298	.781 ^a	-.683
	.371	.077	.026	.313	.154	-.599	-.300	.076	.009	-.061	.037	-.251	-.268	.482	-.683	.659 ^a

a. Measures of Sampling Adequacy(MSA)

Figure D. 3: The Anti-image Matrices indicates individual KMO measures for each element. Those highlighted in yellow were retained for the second PCA iteration. Two elements highlighted in red, Fe and Zr, were removed for the second PCA iteration for having a KMO < 0.5.

Correlation Matrix

		Al	Si	S	K	Ca	Ti	Mn	Cu	Zn	Rb	Sr	Y	Ba	Pb
Correlation	Al	1.000	.277	-.067	.411	.048	.264	-.108	.466	.575	.029	.042	.002	-.092	-.094
	Si	.277	1.000	-.251	-.095	-.275	.081	.078	.137	.024	-.277	-.217	-.290	.083	-.025
	S	-.067	-.251	1.000	.576	.748	.069	.064	.104	.410	.719	.723	.743	.124	.162
	K	.411	-.095	.576	1.000	.766	.071	-.079	.403	.712	.795	.529	.806	-.088	-.073
	Ca	.048	-.275	.748	.766	1.000	-.112	-.146	.285	.602	.983	.721	.964	-.103	-.061
	Ti	.264	.081	.069	.071	-.112	1.000	.788	.023	-.033	-.112	.492	-.124	.898	.910
	Mn	-.108	.078	.064	-.079	-.146	.788	1.000	-.267	-.306	-.138	.406	-.139	.877	.868
	Cu	.466	.137	.104	.403	.285	.023	-.267	1.000	.498	.265	.142	.239	-.166	-.170
	Zn	.575	.024	.410	.712	.602	-.033	-.306	.498	1.000	.593	.339	.579	-.261	-.233
	Rb	.029	-.277	.719	.795	.983	-.112	-.138	.265	.593	1.000	.697	.988	-.097	-.057
	Sr	.042	-.217	.723	.529	.721	.492	.406	.142	.339	.697	1.000	.688	.515	.569
	Y	.002	-.290	.743	.806	.964	-.124	-.139	.239	.579	.988	.688	1.000	-.098	-.057
	Ba	-.092	.083	.124	-.088	-.103	.898	.877	-.166	-.261	-.097	.515	-.098	1.000	.981
	Pb	-.094	-.025	.162	-.073	-.061	.910	.868	-.170	-.233	-.057	.569	-.057	.981	1.000

Figure D. 4: PCA correlation matrix for the second iteration on the Illinois rock art PXRF dataset. All elements contain at least one correlation coefficient greater than 0.3.

KMO and Bartlett's Test		
Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.776
Bartlett's Test of Sphericity	Approx. Chi-Square	1169.146
	df	91
	Sig.	.000

Figure D. 5: KMO and Bartlett's test for the first iteration on the Illinois rock art PXRF dataset. The overall Kaiser-Meyer-Olkin (KMO) measure is 0.776, considered 'middling' to 'meritorious' according to Kaiser (1974) but is improved from the first iteration PCA. Bartlett's test of sphericity is statistically significant, indicating that the data is factorizable.

Anti-image Matrices

	Al	Si	S	K	Ca	Ti	Mn	Cu	Zn	Rb	Sr	Y	Ba	Pb
Anti-image Correlation	.628 ^a	-.211	.130	-.091	-.047	-.516	.016	-.009	-.266	.056	-.171	.026	.122	.278
	-.211	.474 ^a	.027	-.012	.082	.158	-.097	-.107	-.162	-.054	-.081	.081	-.535	.310
	.130	.027	.866 ^a	-.150	-.288	.086	.047	.098	-.149	.367	-.262	-.242	-.063	-.003
	-.091	-.012	-.150	.762 ^a	.044	-.588	-.360	-.072	.032	.087	.203	-.519	-.058	.456
	-.047	.082	-.288	.044	.805 ^a	.074	-.045	-.096	-.079	-.755	-.446	.314	-.041	.110
	-.516	.158	.086	-.588	.074	.669 ^a	.157	-.120	-.202	-.138	-.105	.392	-.076	-.616
	.016	-.097	.047	-.360	-.045	.157	.881 ^a	.240	.098	-.043	-.012	.197	-.108	-.239
	-.009	-.107	.098	-.072	-.096	-.120	.240	.888 ^a	-.080	.014	-.053	.050	-.046	.079
	-.266	-.162	-.149	.032	-.079	-.202	.098	-.080	.922 ^a	.004	.102	-.088	.148	.016
	.056	-.054	.367	.087	-.755	-.138	-.043	.014	.004	.750 ^a	.177	-.775	-.003	.040
	-.171	-.081	-.262	.203	-.446	-.105	-.012	-.053	.102	.177	.867 ^a	-.188	.155	-.269
	.026	.081	-.242	-.519	.314	.392	.197	.050	-.088	-.775	-.188	.755 ^a	.003	-.242
	.122	-.535	-.063	-.058	-.041	-.076	-.108	-.046	.148	-.003	.155	.003	.784 ^a	-.664
	.278	.310	-.003	.456	.110	-.616	-.239	.079	.016	.040	-.269	-.242	-.664	.680 ^a

a. Measures of Sampling Adequacy(MSA)

Figure D. 6: The Anti-image Matrices indicates individual KMO measures for each element on the second PCA iteration. All elements were retained. Si, highlighted in orange is slightly under the acceptable KMO of 0.5. It was kept in the final analysis.

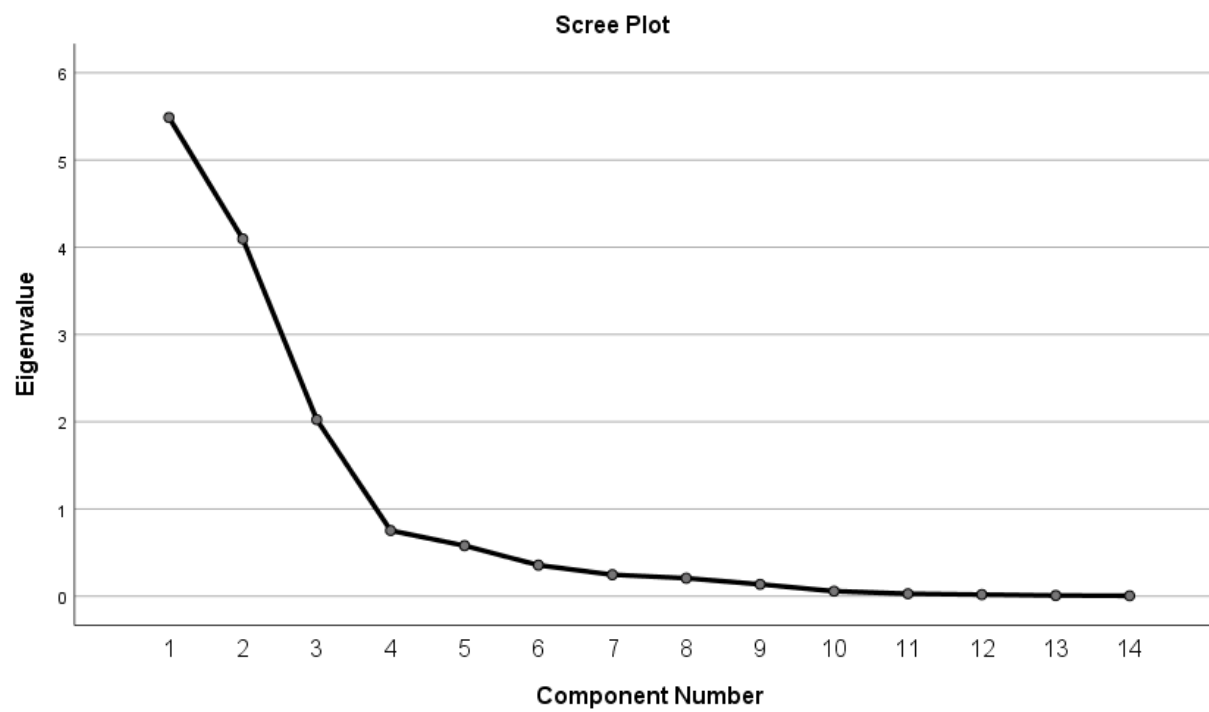


Figure D. 7: Scree plot from the second PCA iteration. A main inflection point is identified at Component 4. Therefore, four components were retained.

Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.487	39.196	39.196	5.487	39.196	39.196	5.049	36.064	36.064
2	4.095	29.248	68.444	4.095	29.248	68.444	4.035	28.818	64.882
3	2.024	14.458	82.902	2.024	14.458	82.902	2.282	16.302	81.183
4	.753	5.377	88.279	.753	5.377	88.279	.993	7.095	88.279
5	.579	4.136	92.415						
6	.356	2.540	94.954						
7	.246	1.760	96.714						
8	.206	1.475	98.189						
9	.136	.973	99.162						
10	.058	.415	99.577						
11	.028	.200	99.777						
12	.019	.133	99.910						
13	.008	.057	99.966						
14	.005	.034	100.000						

Extraction Method: Principal Component Analysis.

Figure D. 8: Total variance explained by each component for the final PCA analysis.

Rotated Component Matrix^a

	Component			
	1	2	3	4
Y	.969			
Rb	.964			
Ca	.962			
S	.846			
Sr	.766	.551		
K	.761		.489	
Pb		.980		
Ba		.974		
Ti		.956		
Mn		.903		
Al			.909	
Cu			.733	
Zn	.539		.692	
Si				.959

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.^a

a. Rotation converged in 5 iterations.

Figure D. 9: Rotated component matrix indicating which elements are comprising the components.

Component Plot in Rotated Space

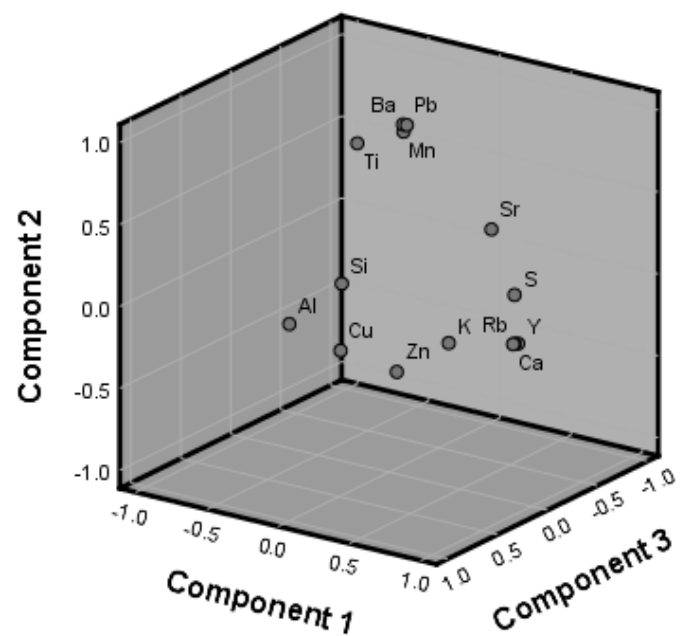


Figure D. 10: Final PCA for the Illinois rock art data set. A Varimax orthogonal rotation was employed.

Appendix E: Discriminant Analysis (DA) Results

This section contains the statistical results of the discriminant analysis that was conducted on the Tennessee-Cumberland style stone statuary. All statistics were performed using IBM SPSS Statistics, version 26 software.

Table E. 1: Tennessee-Cumberland style stone statuary used in the Discriminant Analysis.

CSS #	ANALYSIS LOCATION	RAW MATERIAL
001	Nose	Sandstone
001	Bottom, bare rock	Sandstone
001	Eye, right	Sandstone
001	Chest, left side	Sandstone
001	Eye, left	Sandstone
001	Eye, right	Sandstone
002	Arm, left	Sandstone
002	Ear, left	Sandstone
002	Scapula, right	Sandstone
002	Nose	Sandstone
003	Fingers, right side	Sandstone
003	Scapula, Right	Sandstone
003	Head, left helmet circle	Sandstone
004	Bottom, left side	Sandstone
004	Bottom	Sandstone
004	Shoulder, left	Sandstone
004	Arm, right	Sandstone
008	Head	Sandstone
008	Ear, left	Sandstone
008	Cheek, right	Sandstone
009	Sternum	Sandstone
009	Arm, upper left	Sandstone
009	Back, upper left	Sandstone
010	Bottom	Sandstone
010	Arm, right	Sandstone
010	Cheek, right	Sandstone
011	Chin	Sandstone
011	Foot, left	Sandstone
011	Nose	Sandstone
012	Arm/Chest, right	Sandstone

Table E.1 Continued

012	Bottom	Sandstone
012	Bottom knee, right	Sandstone
013	Bottom, left feet	Sandstone
013	Arm, right	Sandstone
013	Chest, right side	Sandstone
014	Bottom, ride side	Sandstone
014	Chest, right side	Sandstone
014	Shoulder, right	Sandstone
018	Forehead	Sandstone
018	Cheek, right	Sandstone
018	Shoulder, right	Sandstone
019	Cheek, left	Sandstone
019	Shoulder, left	Sandstone
019	Chin	Sandstone
021	Bottom	Limestone
021	Forehead	Limestone
021	Arm, right	Limestone
023	Bottom	Calcite
023	Arm, left	Calcite
023	Cheek, left	Calcite
024	Forehead	Sandstone
024	Hand, left	Sandstone
024	knee, left	Sandstone
030	Forehead	Sandstone
030	knee, left	Sandstone
030	Knee, right	Sandstone
031	Head, left side	Sandstone
031	Nose	Sandstone
031	Back, upper area	Sandstone
032	Bottom, flat underside	Sandstone
032	Bottom, left side	Sandstone
032	Cheek, left	Sandstone
035	Ear, below left	Calcite
035	Bottom	Calcite
035	Chin, right side	Calcite
035	Ear, right	Calcite
035	Head, top	Calcite
036	Foot, left	Sandstone
036	Foot, right	Sandstone
036	Knee, right	Sandstone

Table E.1 Continued

045	Forehead	Sandstone
045	knee, left	Sandstone
045	Cheek, right	Sandstone
045	Knee, right side	Sandstone
048	Bottom	Sandstone
048	Back	Sandstone
048	Head	Sandstone
065	beneath crossed arms	Limestone
065	Arm, left lower	Limestone
065	Nose	Limestone
067	Bottom	Sandstone
067	Head	Sandstone
067	Shoulder, left	Sandstone
068	Cheek, left	Sandstone
068	bottom	Sandstone
068	Arm, left	Sandstone
068	Side, right bottom	Sandstone
068	Cheek, right	Sandstone
089	Shoulder, left	Sandstone
089	Hand, right	Sandstone
089	Neck, upper left side	Sandstone
090	Cheek, left	Sandstone
090	Cheek, right	Sandstone

Eigenvalues				
Function	Eigenvalue	% of Variance	Cumulative %	Canonical Correlation
1	65.957 ^a	99.1	99.1	.993
2	.611 ^a	.9	100.0	.616

a. First 2 canonical discriminant functions were used in the analysis.

Wilks' Lambda				
Test of Function(s)	Wilks' Lambda	Chi-square	df	Sig.
1 through 2	.009	381.475	36	.000
2	.621	38.845	17	.002

Figure E. 1: Eigenvalues and Wilks' Lambda tables for the Canonical Discriminant Analysis (CDA). Eigenvalues indicate the ratio of between-groups variability to within-groups variability for a function. The larger the eigenvalue, the better at accounting for the group differences are the discriminator variables loading on the function. Wilks' Lambda, the ratio of within-group variability to total variability on the discriminator variables, is an inverse measure of the importance of the functions. Values close to 1 indicate that almost all of the variability in the elements (discriminator variables) is due to within-group differences. Values close to 0 indicate that almost all of the variability in the elements is due to group differences.

Standardized Canonical Discriminant Function Coefficients		
	Function	
	1	2
Al	.369	.232
Si	-.118	.116
P	-.291	-.085
S	-.204	.217
K	-.355	-.302
Ca	1.150	-.029
Ti	-.416	-.275
Cr	.275	.226
Mn	-.024	.067
Fe	-.098	.459
Cu	.063	-.472
Zn	.406	.727
Rb	-.209	-.225
Sr	-.141	1.146
Y	-.279	.083
Zr	-.014	.154
Nb	.331	-.339
Pb	-.066	-.589

Structure Matrix		
	Function	
	1	2
Ca	.790*	-.044
Rb	-.220*	-.088
Si	-.140*	-.011
K	-.126*	-.057
Fe	-.120*	-.013
Al	-.114*	-.015
Nb	-.097*	.002
Y	-.080*	.030
Zr	-.068*	-.012
Mn	-.056*	-.030
Ti	-.022*	-.021
Sr	-.002	.644*
Zn	.004	.238*
Cu	-.023	-.176*
P	-.041	-.070*
S	-.011	-.054*
Cr	-.004	-.042*
Pb	-.006	.017*

Pooled within-groups correlations between discriminating variables and standardized canonical discriminant functions

Variables ordered by absolute size of correlation within function.

*. Largest absolute correlation between each variable and any discriminant function

Figure E. 2: Standardized Canonical Discriminant Function Coefficients and Structure Matrix tables. These identify which elements comprise each function in the discriminant analysis. The Standardized Canonical Discriminant Function Coefficients are used to plot out where individuals fall. The Structure Matrix identifies what is explaining the functions. These are the correlation coefficients.

Functions at Group Centroids

StoneType	Function	
	1	2
Sandstone	-3.363	-.002
Non-Speleogenic Calcite	18.868	2.296
Speleogenic Calcite	19.061	-1.707

Unstandardized canonical discriminant functions
evaluated at group means

Figure E. 3: Group centroids of the CDA analysis. These represent the mean discriminant score of the members of a group on a given discriminant function. These specifically reveal how much and in what ways the groups are differentiated on each function. Function 1 discriminates limestone and calcite from sandstone. Limestone and calcite scored at the positive end on the bipolar function and sandstone at the negative end of the function. Function 2 discriminated limestone from calcite and sandstone statuary. For this function, limestone at the positive end of the function and sandstone and calcite at the negative end of the function.

VITA

Sierra May Bow received a Bachelor of Science in Psychology with a concentration in behavioral neuroscience in 2008 from East Tennessee State University and a Master of Arts in Anthropology with a concentration in archaeology in 2012 from the University of Tennessee, Knoxville. Her M.A. thesis investigated the chemical composition of a Late Woodland pottery assemblage from a rock-art rockshelter along an escarpment in Franklin County, Tennessee. After entering the graduate program in Anthropology at the University of Tennessee, Knoxville in Fall 2009 she worked as a Graduate Research Assistant in the Analytical Archaeology Laboratory and subsequently as a Graduate Teaching Associate in the Department of Anthropology. In 2016 she began working as an adjunct faculty member at East Tennessee State University teaching online courses through the Sociology and Anthropology Department. Sierra completed her PhD in Anthropology in May 2020. When she is not working, she enjoys spending all her time with family, outside, exploring the natural world.