REFLECTANCE SPECTROSCOPY AS A CHERT SOURCING METHOD

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Abstract

The non-destructive application of reflectance spectroscopy within chert provenance studies is evaluated and the implications of archaeological source determination of chert artifacts are discussed. The combined use of Visible Near-infrared (VNIR) and Fourier Transform Infrared (FTIR) reflectance spectroscopy demonstrate the accurate, fast and relatively low cost potential for the characterization of geologic deposits of chert and the identification of source for chert archaeological materials. Reflectance spectroscopy gathers data on the trace and minor mineral components within a sample as identified by subtle absorption peaks and slope changes. The variable range of spectral features per sample, per deposit, per geologic formation is potentially diagnostic for a geographically isolated deposit of chert. A chert sample database consisting of 2,430 samples from the Midwestern and Southeastern United States is utilized to illustrate the potential application of reflectance spectroscopy at characterizing chert deposits for archaeological use.

1. Introduction

1.1. Chert Sourcing

The objective of the study is to assess the application of reflectance spectroscopy as a chert provenance technique. The accurate determination of source for raw materials utilized by past peoples provides a proxy for modeling a wide range of human behaviors. The source or provenance of the raw material utilized in the manufacture of the particular artifact allows researchers to study human behavior relating to both group and environmental interactions. Obsidian provenance research continues as a reliable methodology for reconstructing past behavior (Ericson and Glascock 2004; Glascock et al. 1998; Glascock et al. 2010; Shackley 1988; Shackley 1992; Shackley 2009). Chert provenance research arguably lags behind obsidian provenance research due to complications relating in part to the heterogeneity of chert and the resulting difficulties associated with accurately differentiating one deposit from another. However, the significant contribution chert provenance research has in archaeology cannot be overlooked and remains a viable means of investigating past human behavior.

Current chert provenance research involves many methodologies and techniques (Church, 1994; Pollard et al. 2007). The multitude of chert sourcing techniques can be organized into three main groups, macroscopic attribute analysis, petrographic and geochemical. Petrographic techniques examine mineral, textural, and fossil inclusions at magnification. Geochemical analysis involves the gathering of compositional trace element and rare earth element data. However, one of the most popular methods in chert provenance research is the visual analysis of "characteristic" physical properties including color, texture, luster, fossil inclusions and tractability. Limitations including high cost, destructiveness, lengthy analysis, data management,

reliability and precision are routine issues confronting chert provenance techniques (Frahm, 2012, Crandell, 2006). Arguably, the most critical issue limiting the use of chert provenance data in explaining prehistoric behavior is accuracy; the ability of the technique to identify the 'true' source of the material used to manufacture the artifact in question. Accuracy, or sometimes referred to as "archaeological accuracy" (Hughes, 1998), is often difficult to achieve due to overlapping visual, petrographic, and geochemical variables. A narrow geologic and geographic perspective of tool stone availability solely focusing upon well documented 'type' locations further limits our anthropological applications of chert provenance data.

A successful chert provenance study must characterize all possible sources at a geographic scale which matches the anthropologic question and geologic reality. In other words, a study assessing Paleoindian mobility in a tool stone poor region must sample, characterize, and differentiate chert types by formation possibly over a large region. However, a study concerned with the distribution of Hopewell blades from a particular procurement site might have a more spatially restricted sampling universe to various deposits within a singular geologic formation. Therefore, the anthropologic question in part determines the spatial scale of the provenance study in addition to the geologic setting and geographic distribution.

A successful chert provenance study must also be able to characterize a potential source through large geologic sample sets and be able to differentiate the sampled source from other deposits. The Provenance Postulate as originally articulated by Weigand et al., (1977) stands as the overarching theoretical premise behind provenance studies. The Provenance Postulate stipulates that variation must be greater between sources than within a source location. Additionally, a provenance study must characterize the range of variation within an unknown artifact and match it to a particular range of variation at the source location (Harbottle, 1982). Therefore, the "fingerprint" analogy within provenance research is often a misnomer as singular diagnostic attributes rarely exist but rather source determinations are performed statistically using potential characteristic ranges of variation (Luedtke, 1979). The current study examines the use of reflectance spectroscopy to gather spectral data upon a large number of geologic chert samples to specifically address the ability of the method in differentiating one chert type (chert bearing formation) from another, one deposit from another within the same chert bearing formation, and to differentiate sub-sections within the same deposit.

1.2. Reflectance Spectroscopy

Spectroscopy is the study of the interaction of light (electromagnetic radiation) with matter (Hollas, 2002). A spectrometer is an instrument that measures this interaction (Smith, 2011). Two spectrometers are used in the current study, Visible Near-Infrared (VNIR) and Fourier Transform Infrared (FTIR), measuring radiation in the visible, near, and middle infrared regions respectively. Reflectance spectroscopy encompasses a wide range of techniques that gather electromagnetic data which is reflected or emitted from matter. The reflected electromagnetic radiation contains information related to atomic and chemical functional groups within a

compound. The incident radiation in the visible portion of the spectrum (350 – 750 nm) stimulates vibration of particular atoms whereas dipole bonded molecules are stimulated in the near and middle infrared (751 – 25,000 nm) regions. The induced vibrations correspond to the energy state of the particular atom or molecule causing them to bump up to a higher energy state. Absorption of the incident radiation is wavelength dependent meaning absorption occurs at the wavelength frequencies corresponding to particular vibration energy states of the atom or molecule present. Therefore, the absorption of the incident radiation at certain frequencies gives the researcher information regarding atomic and molecular structure and composition of the material. The reflected electromagnetic radiation signal is weaker due to these key absorption and transmission features within the sample.

In a crystalline lattice, such as chert, the compounds vibrate and rotate when struck with a particular frequency causing absorption of that portion of the signal and bumps the molecule up to a higher energy state. The resulting absorption at a particular wavelength or wavelength region may be diagnostic for a particular mineral group. The raw data generated is an arbitrary reflectance intensity number between 0 and 1 for each measured unit of radiation (i.e. wavenumber or wavelength). A spectrum measuring reflectance in a portion of the middle infrared (2,500 – 16,000 nm) would produce 13,500 reflectance intensity numbers, one per each wavelength recorded. Low reflectance intensity numbers signify absorption of particular atomic or molecular components which can be used to identify micro-mineral groups in the chert sample. Quantitative compositional data can be gathered using Beers Law and the transformation of a reflectance spectrum to absorbance. Both qualitative and quantitative relationships can be made on spectra using various mathematical functions, a subset of analytical chemistry termed chemometrics (Morin, 2012).

Our human eyes are an example of a reflectance spectrometer capable of gathering reflectance spectra in the visible portion of the electromagnetic spectrum (350 – 750 nm). Incident radiation from the sun is differentially absorbed, reflected, and transmitted through various materials. The signal that is reflected and gathered by our eyes allows us to 'see' color. The electromagnetic spectrum is divided into different portions based upon wavelength. Wavelength throughout is reported in nanometers (nm) though wavenumbers (cm^{-1}) are a common unit of measurement. The reflectance spectroscopy techniques utilized in the current study generate a composite spectrum for chert in the visible, near-infrared and middle-infrared regions. When graphically portrayed, the reflectance values per wave unit produce a line graph composed of Gaussian and Lorentzian curves (Figure *). The spectrum of chert in the visible, near-infrared and middle-infrared regions is largely redundant from sample to sample as subtle spectral features are overshadowed by larger stretch and bend fundamental vibration features related to quartz and inter-granular water. However, slight features and imperceptible slope changes in the chert's spectrum related to micro-mineral impurities are proving to be diagnostic for particular chert bearing formations and deposit locations. These subtle features have to be

augmented through spectral processing techniques and statistical analyses as discussed below in section 2.2 *Spectral Analysis*.

The diagnostic micro-mineral groups causing particular spectral features maybe directly related to the paleodepositional environment of the parent geologic formation and the diagenetic processes influencing chert formation. Other researchers, using geochemical data, have speculated that chert diagnosis imparts a variable range of diagnostic characteristics (Foradas, 1994, 2003; Malyk-Selivanova, 1998) but the lengthy and costly analysis of large sample sizes have previously restricted efforts to tease out the geologic and geographic relationships on a large scale.   More of this discussion is found in section, 3. *Results and Discussion*.

1.1.1. Previous Research

Reflectance spectroscopy continues to be used in a variety of fields from industry to space exploration. Spectral data in manufacturing is applied to assess quality control. Reflectance spectroscopy in remote sensing is used to study land use and climate change. Additionally, geologic samples of unknown mineral composition can be rapidly identified using peak matching software within spectral libraries of known minerals. The use of reflectance spectroscopy also varies with scale. The use of reflectance spectroscopy ranges from analysis of the structure of an individual cell to the composition of entire planets. Continuing research is uncovering the causes of spectral shifts and natural variation allowing for the increasingly detailed analysis of chemical variability. A commonly stated disadvantage of reflectance spectroscopy is that it is too sensitive to slight chemical and structural changes (Clark, 1999). However, the sensitivity of reflectance spectroscopy is also a powerful tool in detecting subtle spectral differences. The analysis of chert benefits from extreme analytical sensitivity as the mineral, chemical and structural differences are often minor.

The archaeological material science community has been relatively slow in applying reflectance spectroscopy for broad applications despite the success of early studies (Beck, 1986; Beck et al., 1965). The trend is quickly changing as a variety of materials and methodologies are demonstrating the potential application of spectroscopy (Emerson et al., 2013; Hubbard et al., 2005; Hubbard, 2006; Morin, 2012; Wisseman et al., 2002). Currently researchers are using spectral data to identify prehistoric residues, pigments, soil, masonry stone, thermal alteration, patina formation and various artifact compositions. Archaeology provenance studies include those examining the source of amber, soapstone, flint-clay, nephrite, chert and clay.

The studies specifically related to the current one are those chert provenance applications of both reflectance and transmission spectroscopy (Hassler et al., 2013; Hawkin et al., 2008; Hubbard et al., 2005; Long et al., 2000; Parish, 2011; Parish et al., 2013). Previous research on the chert provenance applications of reflectance/transmission spectroscopy demonstrate that particular diagnostic spectral features related to micro-mineral groups differentiate one chert type or deposit from another. The studies listed above both outline the basic methodologies and give

positive case studies but can be described as preliminary and explore smaller sample sizes within restricted geographic regions. It is the objective of the current study to expand the application scope of reflectance spectroscopy and to convey a broader use in differentiating various chert resources over a large geographic region.

1.1.2. *How Reflectance Spectroscopy Differs from Previous Techniques*

Reflectance spectroscopy as a chert source technique differs from current methodologies in four significant ways; 1) data acquired, 2) speed, 3) level of destructiveness, and 4) cost. As discussed above in section 1.1 *Chert Sourcing*, existing chert sourcing methodologies gather attribute, petrographic, and geochemical data. Spectral data exists as arbitrary percent reflectance decimal numbers between 0 and 1 per wave frequency. Depending on the wavelength region analyzed, reflectance numbers ranging in the thousands may collectively represent a single spectrum. Each reflectance value is a potentially 'diagnostic' variable relating to a possibly unique atomic or molecular composition, though this is rarely the case as the range in variability is necessary when characterizing materials. Therefore, reflectance spectroscopy is not attribute information derived from empirical observations, nor is it purely geochemical data in the form of trace or rare earth element quantities. The reflectance data gives information directly related to the atomic and molecular presence, composition and structure of chert. The application of reflectance spectroscopy when coupled with an appropriate sampling methodology, spectral processing techniques, and chemometric analysis is proving to be a viable means to differentiate chert tool-stone resources.

2. Methods
2.1. *Experiment design*

The application of reflectance spectroscopy to chert provenance research is assessed through three accuracy tests. The accuracy tests are designed to quantify the ability of reflectance spectroscopy in characterizing variation and differentiating ranges of variation both between and within chert bearing formations. The first test examines the accuracy of reflectance spectroscopy in distinguishing chert type, or deposits of chert within different geologic formations over hundreds of kilometers in lateral extent. The second test refines the spatial scale of accuracy through characterization and differentiation of multiple chert deposits within a single geologic formation. The third and final test explores intra-deposit variability as the accuracy of reflectance spectroscopy is examined by differentiating sub-set samples of chert within a single deposit.

The accuracy assessment tests use randomly selected ten percent sample populations treated as having 'unknown' provenience within the chert database to internally evaluate the accuracy of provenance assignments. Archaeological materials were not included as these truly have unknown provenance and would not make a good control for assessing accuracy. Accordingly, additional experiments beyond those already conducted (Parish 2009; 2013a) will have to be

performed in order to examine the effects that thermal alteration and outer surface weathering (i.e. patina) has on non-destructive analysis of cultural materials. Through these additional experiments, the viability of reflectance spectroscopy to chert artifacts will be further refined. However, the necessary first step is to examine to what extent spectral variance in chert can be quantified in a meaningful way so that accurate artifact source can be possible. By conducting internal tests within the chert database of known provenance, the accuracy of source assignment at different levels is assessed. Conducting internal tests also helps the construction of appropriate anthropological questions. These anthropological questions are tailored to the ability of the source technique to quantify and differentiate variation at various spatial scales. Primarily, in order to quantify variation, potentially discriminate one source from another, and test provenance accuracy a robust geologic sample database must be assembled.

2.2. *Sampling*

Arguably the first step in any provenance study is to identify potential sources and assemble a representative database of those sources. The objective of any sampling strategy is simply to obtain a representative sample which most accurately describes the population. Sampling in the framework of a chert provenance study is dictated by the spatial scale of the study. The spatial scale of the study is outlined by a combination of the anthropologic question, geologic setting, and physiographic region. The anthropologic question outlines the realm and extent of possible chert resources. The geologic setting identifies both the quantity and surficial distribution of some potential chert material types. The physiographic region further refines the potential number of chert resources and their possible existence within secondary and tertiary deposits (e.g. alluvium and fluvial deposits). The number of samples to obtain per chert bearing formation or deposit largely depends on the amount of variability present in the properties being analyzed.

Luedtke and Myers (1984) present an equation to assess the geochemical variability present in any particular chert deposit and the subsequent number of samples needed to quantify variation. Chert provenance studies utilizing geochemical data indicates a great deal of variation is often present (Eley and von Bitter, 1989; Foradas, 1994; Gauthier et al., 2012; Luedtke, 1979; Malyk-Selivanova, 1998). The heterogeneity of trace elemental data in chert has traditionally frustrated our abilities to differentiate material types even at the formation level, the coarsest spatial scale (Cackler et al., 1999; Evans et al., 2007). Positive results by Speer (2014a; 2014b) are demonstrating that larger sample sizes, the high elemental resolution of LA-ICPMS, and use of multivariate statistics allows for the successful differentiation of Ft. Edwards, Alibates, Georgetown, and possibly other chert types. An experiment by the author regarding sample size and accuracy in which chert geologic samples were removed from the training database in randomly selected groups of 10%, 20% and 30% demonstrated that source accuracy within the three test groups diminished with diminishing sample sizes in the database (Parish, 2013a). Therefore, judgmental samples of only a few specimens per deposit are almost certainly not enough to characterize the variation at the geologic formation or the individual outcrop.

Additional factors affecting sample size, other than internal variability, include cost and speed of analysis.   The high cost of geochemical analysis prohibits the processing of large chert sample sets. Even the relatively less expensive cost of creating thin sections would inflate a budget needing to characterize multiple chert types and deposits. The speed of analysis negatively affects the incorporation of large chert sample sets. Multiple samples require many hours of lab preparation and analysis prohibiting the characterization of potential sources. The limitations imposed by cost and speed promote the choice sampling of only a few specimens.

Reflectance spectroscopy allows for a fast cost efficient method in chert analysis. These advantages promote the acquisition and analysis of large chert type datasets. An ambitious sampling strategy is adopted for the current study in which 30 samples are selected across the lateral and vertical breadth of the chert deposit. Multiple deposits and outcrops are sampled per chert bearing geologic formation. In two instances 60 samples were collected from two deposits in different deposit sub-sections to assess intra-deposit heterogeneity. All deposits sampled were marked using a handheld GPS unit. Additional, field notes and photographs were taken in order to document the chert deposits.

Geologic chert samples were obtained from three main location types; 1) prehistoric procurement/quarry sites, 2) in situ outcrops, and 3) secondary/tertiary deposits such as fluvial gravels. Recorded prehistoric procurement/quarry sites are ranked as locations of the highest priority with both natural and modern exposures of in situ outcrops being second. Finally, chert deposits in secondary (alluvium) and tertiary (stream gravels) were ranked the lowest priority. However, the objective of the sampling strategy is to sample any and all potential sources of chert exploited in prehistory and the incorporation of secondary and tertiary sources is necessary and desirable. The selection of chert samples out of their original geologic context must be done with care when building a type database within which artifacts of unknown provenance are to be characterized. Secondary and tertiary chert deposits should be assigned with consideration to the surrounding surficial geologic setting and the transportation processes present. Tentative geologic provenience assignments for displaced chert materials should be avoided as the type database will be constructed to assign unknowns to type formations.

The total number of samples analyzed for the study is 2,430 from 81 deposits/outcrops collectively representing seven chert types present in the Midwestern and Southeastern United States. An additional 2,040 from 68 deposits/outcrops awaits analysis and may provide spectral differentiation of nine chert types from these regions. It is noted here that much more sampling needs to be conducted as chert resources are rich and diverse in these regions. The need for baseline data is an immediate need as our views regarding the 'lithic landscape' are broadening beyond a few type site locations.

2.3 *Sample Preparation*

All samples obtained were fractured conchoidally by direct hard hammer percussion using quartzite hammerstones. Six flakes were retained per sample so that the chert type collection can be duplicated six times. Flake diameter ranges from 3 to 6 cm with relatively flat expansive ventral surfaces. Flake thickness ranges from just under one to 3 cm. Thirty sample bags each containing six flakes collectively represent a chert deposit. Just prior to analysis, lens tissue was used to lightly wipe the analyzed surface. No other treatments were used in preparing samples for spectral analysis.

2.3. Spectral Analysis

2.3.1 VNIR

Two reflectance spectrometers were used in the study. A FieldSpecPro® manufactured by ASD Inc. was used to collect spectral data in the visible and near-infrared regions (350 – 2,500 nm). The spectral resolution of the device from 350 to 1,000 nm is 4 nm and from 1,001 to 2,500 nm is 10 nm. A single spectrum contains 2,150 reflectance values. The device is portable but all measurements were taken in an atmosphere controlled laboratory environment. The fiber optic detector probe was mounted on a metal stand perpendicular to and approximately five centimeters above the samples surface. The probe to sample surface distance minimized signal loss due to atmospheric interference and provided an approximate two centimeter diameter field of view on the sample. The radiation (light) source, a quartz-halogen bulb, was mounted nearby illuminating the sample tray below the detector. The spectrometer was given time to initialize and the white reference material, Spectralon ®, was used to calibrate the device and standardize all subsequent measurements. A white reference reading was taken every 10 samples to minimize instrument drift and atmospheric interference.

Each chert sample was placed directly under the detector probe with the ventral surface facing up perpendicular to the probe. The 90 degree sample surface to probe angle was maintained as much as possible as sample to probe angle effects alter the reflected spectra intensity. However, the angle effects are largely eliminated during spectral processing. The sample's spectrum was recorded in less than 0.1 seconds producing a composite spectrum of the area of the specimen within the two centimeter diameter field of view. All 2,430 samples were analyzed in this manner. Approximately, 100 samples were analyzed each hour. The spectral raw data was exported as ASCI text files.

2.3.2 FTIR

A Bio-Rad FTS 40 spectrometer collected spectra in the middle infrared region (2,500 – 25,000 nm). However, detector limitations excluded long wavelengths beyond 16,000 nm. The device was given time to initialize and a background measurement was taken upon a gold standard both to calibrate and to minimize atmospheric interference. Spectral resolution was set at 4 cm^{-1} (12 nm), a compromise between noise and detail. Total number of scans per analysis was set at 64 further eliminating noise through multiple readings upon a single spot. Samples

were placed under the spectrometer's optical scope and a spot drawn into focus prior to rotating the IR detector into place. The location on the sample chosen for analysis is a relatively flat surface perpendicular to the detector probe. The spot being analyzed is small, in the order of 250 microns, therefore three measurements in different locations were taken upon each sample and later averaged to provide a more representative spectrum per sample. Analysis time for each spectrum was approximately one minute. Ten samples were analyzed in just under an hour. A total of 1,867 reflectance values collectively represent a single spectrum in the middle infrared.

2.3.3 Spectral Processing

All of the raw spectral data were processed using conventional techniques in order to eliminate or reduce atmospheric interference, instrument noise, sample surface to probe angular effects, and standardize measurements for comparison. In addition to spectral processing, the reflectance spectra were converted to absorbance and first derivative transformed. Both absorbance and first derivative transforms provide a more robust means for quantitative analysis as well as highlighting subtle spectral slope changes.

Two spectral software suits facilitated both processing and spectral transforms. The software used included GRAMS® by Thermo Scientific and Unscrambler® X by CAMO. The VNIR spectra were imported directly into Unscrambler® X as ASCI text files whereas the FTIR spectra were first processed in GRAMS®. Initial processing of the FTIR spectra consisted of background correction using the gold standard spectrum, averaging the three analyses per sample, and changing wavenumbers (cm^{-1}) to nanometers (nm). The FTIR spectra were then uploaded into Unscrambler® X.

Both VNIR and FTIR spectra were further processed using three transform functions, spectroscopic, normalization, and derivative. The spectroscopic transform function converted the reflectance spectra of the samples into absorbance giving the absorbed incident radiation at specific wavelengths. Next, the normalization function was used to standardize differences in absorbance peak heights. Normalization minimizes spectral differences inherent between measurements obtained under slightly different conditions (e.g. viewing geometry) (Smith, 2011:77). Finally, the first derivative for each spectrum was calculated using the GAP algorithm with a moving kernel value of 1. Selection of a GAP value of one is a compromise between noise and spectral resolution. The use of a derivative algorithm on spectral data is an established technique in spectral analysis (Kemper and Luchetta, 2003; Smith, 2011). A derivative is a plot of the slope of a function versus its X axis values (Smith, 2011:184). The GAP algorithm with a value of 1 calculates the slope difference between every other reflectance value. A derivative algorithm is useful in spectral analysis as it removes any multiplicative effects while highlighting absorbance features (Kemper and Luchetta, 2003).

In a first derivative transformed spectrum the point at which the spectrum crosses the X axis at zero reflectance directly corresponds to the wavelength of peak absorbance in the original

spectrum. Derivative transforms are used to aid peak matching of unknown spectra within a spectral library. A derivative transform is useful in the current study as it highlights subtle slope changes due to electronic and molecular influences within a particular chert type at a particular geographic location. Slope changes are important as the major spectral absorption features of chert are relatively homogenous. The first derivative transform also highlights smaller features with the elimination of noise using the derivative GAP value.

The final stage in spectral processing was the combining of the VNIR dataset to the FTIR dataset as seamless integration is possible since the VNIR spectra ends at 2,500 nm and the FTIR spectra begins at 2,500 nm. The composite spectral database provides potentially diagnostic reflectance values in the visible, near-infrared, and middle infrared regions. Each chert sample's spectrum consists of 4,017 reflectance values. Therefore, multivariate statistical techniques are needed to characterize spectral variation at various levels (i.e. geologic formation, deposit or outcrop, sub-deposit section) and differentiate one sample set from another. If the characterization of chert samples can be distinguished from others in the sampled population then the sourcing of unknown chert artifacts is possible.

2.4. Statistical Analysis

All statistical analysis of the spectra was performed using the Statistical Package for the Social Sciences (SPSS) manufactured by IBM. Both the VNIR and FTIR chert spectral database spreadsheets were individually uploaded into SPSS. The X-axis wavelength positions were coded as individual integer variables and positioned as column headings. Chert sample names were placed as the row headings. Individual cells contained the first derivative transformed reflectance values at corresponding wavelength position. A grouping variable was created in the first column in order to designate sample classes. The samples classes and grouping variables changed according to the three accuracy assessment experiments whose aim was to test the discriminatory accuracy of reflectance spectroscopy in characterizing deposits of chert at various spatial scales. Therefore, the grouping variable was an integer ranging in value and represented the provenience of the sample within the parent geologic formation, individual deposit within a particular geologic formation, or sampling section within a particular deposit. In the initial experiment the grouping variables $(1-7)$ designated chert samples whose provenience is from seven specific geologic formations, Lower St. Louis, Ft. Payne, Tuscaloosa, Upper St. Louis, Ste. Genevieve, Leipers and Catheys, and Burlington Formations.   In the next analysis focusing on deposits within the Upper St. Louis formation, the grouping values were changed to 1 through 12 representing 30 samples from each of the 12 sampled deposits. In the final experiment, the grouping variable (1 and 2) represented two sample sections within a single chert deposit.

A stepwise canonical discriminant analysis was conducted on portions of the VNIR and FTIR spectral datasets. The determination of which portions of the dataset to analyze was controlled by a priori explorative data analysis and software limitations. Preliminary examination of spectra identified portions of noise. Usually, areas dominated by noise are

located at the shortest wavelength ends of both the VNIR and FTIR datasets. Also, the longest wavelength end of the spectral datasets contained higher noise due to low detector sensitivity. Therefore, the 350-399 nm and 2,495-2,500 nm sections were excluded from analysis in the visible and near-infrared dataset. The noise dominated region of 2,500-2,577 nm and 14,399-25,000 nm was not analyzed in the middle-infrared dataset. The potentially diagnostic regions in the VNIR data include most of the visible and a portion of the near-infrared sections. Exploratory data analysis and previous research by Hassler (2011) and Hassler et al. (2013) identified the 2,600 to 7,500 nm region of the middle-infrared spectral data as containing potentially diagnostic information. Specific diagnostic wavelength positions are reported in Parish et al. (2013). The middle-infrared range includes numerous smaller features located at shorter wavelength positions before the spectra are dominated by the large quartz reststrahlen band fundamentals. Most of the diagnostic variables used in the study were selected from the 2,600 to 7,500 nm region; however, additional portions of the middle-infrared signal were also included.

The stepwise canonical discriminant function analysis evaluates each wavelength variable and enters or removes it from the discriminant model depending on its probability of F value. An entry value of 0.5 and a removal value of 1.0 are used to independently assess the significance level of each variable's F value. Only the most discriminatory variables (reflectances/wavelengths) falling between the entry and removal value are used to construct the model. Additionally, the groups were weighted to account for differences in group size when assessing the characterization and discriminatory power of reflectance spectroscopy at the formation level. Group weighting was not necessary in differentiating deposits within a formation as each deposit consists of 30 samples.

The data reduction capabilities of discriminant function analysis are helpful in dealing with large spectral datasets. One limitation with assigning classification to unknown samples is that each unknown is assigned to a class within the chert database. Sample classification for unknown cases is based upon the calculated Mahanolobis distance measurement from the unknown sample to the nearest group centroid. However, the 'forced' classifications of unknown samples is suitable given the probability that some chert deposits exploited for tool-stone material may never be sampled or otherwise no longer exist. The characterization of artifact to deposit methodology also justifies assigning class to all unknown samples.

The inclusion of more diagnostic reflectance values at corresponding wavelengths is deemed the optimal analytical strategy. The use of multiple diagnostic variables partially alleviates the problem of alteration of the spectral signature by weathering of soluble mineral groups. The absence of 3 to 4 diagnostic variables in one portion of the sample's spectrum might harm the source determination. However, a suite of variables may provide enough diagnostic information to make an accurate source determination. The use of the combined VNIR and FTIR dataset is presented as a case study illustrating this point.

3.   Results and Discussion

The results of three experiments are presented below. In the first experiment, all 2,430 chert samples were organized according to parent geologic formation. The experiment assessed the ability of both the spectral variance recorded by reflectance spectroscopy and the discriminatory power of the multivariate statistical technique to accurately differentiate chert by parent geologic formation. The second experiment focused on differentiating 12 individual chert deposits within the Upper St. Louis Formation sampled over a 400 km lateral extent. The third and final experiment examined the spectral differences within a single deposit of Ste. Genevieve chert as samples were obtained in two sectors within a prehistoric procurement site. In each experiment a base discriminant function model was generated with all samples having known provenience followed by a second model where a random ten percent of the samples were treated as having unknown provenience by removal of their grouping variable. In this manner chert provenance accuracy at various geographic spatial scales is quantified for the given sample by recording the number of correct source assignments within the ten percent unknown sample group.

3.1. Characterizing chert by formation (type)

The dual application of reflectance spectroscopy and multivariate statistical analysis in differentiating chert by parent geologic formation (type) returned 2,395 correct source assignments out of 2,430 (99% correct classification). A total of 35 samples were misclassified to other geologic formations. The majority of the samples misclassified (17) were of the Tuscaloosa Formation a Cretaceous gravel deposit mainly consisting of secondary Fort Payne chert infused with various iron oxides giving them a distinct tri-colored, red, yellow, and black appearance referred to regionally as Horse Creek or Pickwick chert.

Upon removal of a randomly selected ten percent sample (n = 243), the discriminant function model was run a second time with a reduced training set of samples to quantify spectral variation by formation and assign source to each sample. A total of 228 (94% correct classification) unknown samples were corrected assigned to their subsequent geologic formations. Fifteen samples were misclassified to geologic formations other than their correct provenience.

3.1. Characterizing chert by deposit

The accuracy of intra-formation chert provenance was assessed in the Upper St. Louis Formation among 360 Upper St. Louis chert samples from twelve individual deposits. The base model successfully classified all 360 samples (100% correct classification) into their source deposits. A 10 percent (n = 36) random sample of specimens had their grouping variable removed, and the discriminant function model was rerun. All 36 unknown samples (100% correct classification) were correctly assigned to their source deposits.

3.2. Characterizing chert within a deposit

Prehistoric site 40Pm103 is a recorded quarry site of unknown cultural affiliation located in Putnam County, Tennessee. The site is approximately 2,330 square meters and is situated on a north facing ridge spur. Numerous tested nodules and debitage of Ste. Genevieve chert are scattered throughout limestone bedrock exposures and young growth timber. Initially, 30 samples of chert were collected from the northern section of the site followed by a collection of 30 samples of chert from the southern section at a later date. The two groups of samples were treated as sub-samples within the single deposit of Ste. Genevieve chert and run in the discriminant function model. A third group consisting of 30 samples of Ste. Genevieve chert from a prehistoric quarry further to the south (40Wr48) was included in the analysis as a control. The resulting intra-deposit assessment of the base discriminant function model correctly classified all 90 samples (100% correct classification) successfully differentiating chert samples from both the north and the south portions of the deposit in addition to those samples from the control group. A randomly selected 10% sample (n=6) from the 60 obtained from the 40Pm103 deposit were treated as having unknown provenience. The discriminant function model correctly identified the sub-deposit source of five of the six samples (83% correct classification). The single misclassification identified the unknown sample as being from the control group location.

3.3. Archaeological Implications

The results of the three accuracy assessment tests demonstrate the potential application of reflectance spectroscopy in chert provenance research. The continuing research and development of these techniques and analytical methods is warranted. Primarily, further examination of analysis upon an altered chert artifact's outer surface will be a crucial step in assessing the viability of reflectance spectroscopy in archaeological provenance research. The ability of reflectance spectroscopy to characterize variation within chert at various spatial scales and discriminate between sources is shown at the inter-formation, intra-formation, and intra-deposit levels. The findings show that slight spectral differences exist within the sampled deposits of chert investigated in this study which can be used collectively to separate one source from another.

The broad archaeological implication illustrated in the study is that reflectance spectroscopy may be a viable method for identifying the source of chert for unknown artifacts. The ability of reflectance spectroscopy to do so quickly, economically, and potentially non-destructively makes it a desirable method in provenance research. Priceless curated specimens maybe analyzed quickly without sacrificing the integrity of the piece through ablation, abrasion, irradiation, crushing, and slicing. Additionally, the analysis of multiple specimens within an assemblage may shift focus from possible long distance acquisition relations to local lithic economies. The analysis of debitage in addition to curated bifaces will almost certainly provide researchers with a more complete understanding of the entire sequence of tool-stone consumption. The relationships between source, technology, availability, cultural interactions,

procurement strategies, population movements, and many others can be more thoroughly explored.

4. Conclusions

The identification of chert source is often performed through the identification of macroscopic attributes which often fails to quantify the range of variability between and within chert types and deposits. Large error rates are observed in the visual provenance of chert resources (Boisvert and Williams, 2014; Calogero, 1991, 1992; Hess, 1996; Perry, 1992; Price et al., 2012; Spielbauer, 1984). The aid of type collections in the identification process is potentially limiting as the few samples representing a specific type (parent formation) of chert constrains the analyst's ability to adequately characterize variation. Additionally, type collections limit identification of the chert artifact to fixed type locations on the landscape. A sampling strategy which assembles a large range of materials from specific deposits, multiple deposits within a geologic formation, and secondary and tertiary sources is necessary but unmanageable as a type collection.

The use of analytical techniques such as geochemical methods is limited in terms of the cost of analysis and the level of destructiveness. The advent of portable geochemical techniques such as portable X-ray florescence (pXRF) is promising but due to lower elemental resolution may not adequately quantify slight trace elemental differences. However, the benefits of developing a viable chert provenance technique(s) and methodology outweigh the associated difficulties.

Reflectance spectroscopy's application within chert provenance research is shown in the current study as promising. The spectral variance within a deposit of chert due to the structural arrangement and composition of molecular compounds is patterned. The patterned spectral variability within a chert bearing formation, between deposits within a formation, and within a single deposit is able to be characterized and differentiated to a high degree of accuracy. The results of the accuracy assessment tests demonstrate the ability of reflectance spectroscopy coupled with multivariate statistical analysis to correctly assign source greater than 90% of the time by formation and deposit and above 80% of the time by sub-deposit.

The accuracy of reflectance spectroscopy is in part due to the techniques' ability to record and identify a range of diagnostic spectral variables but also to the speed and low cost of analysis. A sample of 2,430 samples from seven geologic formations and 81 deposits is used in the study to test the chert provenance application of reflectance spectroscopy. Currently, another 2,040 samples obtained from 68 deposits await analysis. The speed of analysis and economic cost of such analysis directly promotes the construction of large representative databases of chert resources. The characterization of chert deposits necessitates large sample sizes in order to bracket variability at various scales of resolution. It is quite probable that the inability of previous studies to distinguish source are due to small unrepresentative sample sizes (Cackler et

al., 1999; Evans et al., 2007; Parish, 2013). Additionally, the non-destructive application of reflectance spectroscopy is vital from a preservationist perspective. In the current study, all analysis is conducted upon interior material surfaces and additional controlled experiments need to be conducted upon patinated archaeological materials.

The prehistoric use of chert as tool-stone material across broad regional and temporal spans makes the application of chert source programs of paramount interest. The range of human behavioral questions which could be addressed through chert source research illustrates the need for reliable methods. The appropriate scale of the chert provenance study as defined by the anthropologic question being asked is crucial when deciding which sources to include. The application of reflectance spectroscopy and multivariate statistical analysis allows for large representative samples and the fast processing of multiple spectral attributes. The ability of reflectance spectroscopy to accurately assign chert source is illustrated by the study and has the potential to track the movement and interaction of prehistoric people via their consumption of tool-stone resources.

Acknowledgements

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