# 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 for the characterization of geologic deposits of chert and the potential 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 2430 samples from the Midwestern and Southeastern United States is utilized to illustrate the accuracy of reflectance spectroscopy at characterizing chert deposits for archaeological use.

**Keywords:** reflectance spectroscopy, chert, provenance research, Southeastern United States, VNIR, FTIR

## Introduction

### *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. Chert provenance research has produced varied results. However, the significant contribution chert provenance research has in archaeology cannot be overlooked and remains an important mechanism in studying past human behavior.

Current chert provenance research involves many methodologies and techniques (Church, 1994). The multitude of chert sourcing techniques can be organized into three main groups, macroscopic attribute analysis, petrographic and geochemical. 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 is accuracy; the ability of the technique to identify the 'true' source of the material used to manufacture the artifact in question. Furthermore, a narrow geologic and geographic perspective of tool stone availability 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 resource base. A 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. In addition, 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 (Luedtke 1979). The current study examines the use of reflectance spectroscopy to gather spectral data within a chert samples database to specifically address the ability of the method in differentiating chert by parent formation, one deposit from another within the same formation, and to differentiate sub-sections within the same deposit.

### *Reflectance Spectroscopy*

Spectroscopy is the study of the interaction of light (electromagnetic radiation) with matter. A spectrometer is an instrument that measures this interaction (Smith 2011). 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. 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. When graphically portrayed, the reflectance values per wave unit produce a line graph composed of Gaussian and Lorentzian curves (Figure 1). 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. Both qualitative and quantitative relationships can be studied using various mathematical functions, a subset of analytical chemistry termed chemometrics (Morin 2012).

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 diagnesis imparts a variable range of diagnostic characteristics (Foradas 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. A variety of provenance studies are demonstrating the potential application of spectroscopy in archaeology (Beck 1965; Emerson *et al.*, 2013; Hubbard 2006; Morin 2012). The studies specifically related to the current one are 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).

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. Spectral data exists as arbitrary percent reflectance decimal numbers between 0 and 1 per wave frequency. Each reflectance value is a potentially 'diagnostic' variable relating to an atomic or molecular composition. 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.

## Methods

### *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. The second test refines the spatial scale of the provenance study through characterization and differentiation of multiple chert deposits within a single geologic formation. The third and final test explores intra-deposit variability by differentiating sub-set samples of chert within a single deposit. By conducting internal tests within the chert database of known provenance, the accuracy of source assignment at different levels is quantified.

### *Sampling*

Arguably the first step in any provenance study is to identify potential sources and assemble a representative database of those sources. 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 are sampled per chert bearing geologic formation. In two instances 60 total samples were collected from a deposit in separate 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. The total number of samples analyzed for the study is 2430 from 81 deposits/outcrops collectively representing seven chert types in the Midwestern and Southeastern United States (Figure 2) (Table 1).

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. Thirty sample bags each containing six flakes collectively represent a single 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.

### *Spectral Analysis*

#### VNIR

Two reflectance spectrometers were used in the study. A FieldSpecPro® manufactured by ASD Inc. was used to collect 2150 reflectance values in the visible and near-infrared regions (350 – 2500 nm) (Figure 3). The probe to sample surface distance provided an approximate two centimeter diameter field of view upon the sample. The radiation (light) source, a quartz-halogen bulb, was mounted nearby illuminating the sample tray below the detector. The sample was placed under the detector and a spectrum was recorded in less than one second producing a composite spectrum of the area of the specimen. A white reference reading was taken every ten samples to minimize instrument drift and atmospheric interference. All 2430 samples were analyzed in this manner. Approximately, 100 samples were analyzed each hour.

### FTIR

A Bio-Rad FTS 40 spectrometer collected spectra in the middle infrared region (2500 – 25,000 nm) (Figure 4). 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. Samples were placed under the spectrometer’s optical scope and a spot 20 microns in diameter was drawn into focus prior to rotating the IR detector into place. 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 1867 reflectance values collectively represent a single spectrum in the middle infrared.

### 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 highlight subtle spectral slope changes. A more detailed discussion regarding spectral processing may be found in Parish (2013:176-178). The final stage in spectral processing was the combining of the VNIR dataset to the FTIR dataset. Each chert sample's composite spectrum consists of 4017 reflectance values.

### *Statistical Analysis*

A stepwise canonical discriminant function analysis was conducted on portions of the VNIR and FTIR spectral datasets. The potentially diagnostic regions in the VNIR data include most of the visible and a portion of the near-infrared sections. Most of the middle-infrared diagnostic variables used in the study were selected from the 2600 to 7500 nm region; however, additional portions of the middle-infrared signal were also included. Specific diagnostic wavelength positions are reported in Parish (2013:278-285). The discriminant function analysis evaluates each wavelength variable and enters or removes it from the discriminant model. Additionally, the groups were weighted to account for differences in group size.

## **Results and Discussion**

The results of three experiments are presented below. In the first experiment, all 2430 chert samples were grouped according to parent geologic formation assessing inter-formation provenance. The second experiment focused on differentiating 11 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.

### *Characterizing chert by formation (inter-formation)*

The accuracy assessment by parent geologic formation (type) returned 2395 correct source assignments out of 2430 (99% correct classification). A total of 35 samples were misclassified to other geologic formations. 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. A total of 228 (94% correct classification) unknown samples were correctly assigned to their subsequent geologic formations. Fifteen samples were misclassified to geologic formations other than their correct provenience (Figure 5a) (Table 1).

### *Characterizing chert by deposit (intra-formation)*

The accuracy of intra-formation chert provenance was assessed in the Upper St. Louis Formation among 330 Upper St. Louis chert samples from eleven individual deposits. Lower St. Louis chert samples (n=180 from 6 deposits) were included as a control. The base model successfully classified all 330 samples (100% correct classification) into their source deposits. A 10 percent (n = 33) random sample of specimens had their grouping variable removed, and the discriminant function model was rerun. All 33 unknown samples (100% correct classification) were correctly assigned to their source deposits (Figure 5b) (Table 1).

### *Characterizing chert within a deposit (intra-deposit)*

Prehistoric site 40Pm103 is a recorded quarry site of unknown cultural affiliation located in Putnam County, Tennessee. 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 sample group 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). A randomly selected 10% sample (n = six) 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 (Figure 5c) (Table 1).

## Conclusions

Chert source is often assigned through the identification of macroscopic attributes often failing to quantify the range of variability between chert deposits with large associated error rates (Calogero 1991). The aid of type collections as a methodology is potentially limiting. The few samples representing a specific type of chert constrains the analyst's ability to adequately characterize variation. Additionally, type collections limit identification of the chert artifact to a few locations on the landscape. It is quite probable that the inability of previous studies to distinguish source are due to small unrepresentative sample sizes (Parish, 2013:214). A sampling strategy which assembles a large range of materials is necessary but unmanageable as a type collection.

The use of analytical techniques such as geochemical methods is restricted by the cost of analysis and the level of destructiveness. The results of the current study demonstrate that reflectance spectroscopy's application within chert provenance research is a viable methodology. The spectral variance within a deposit of chert due to the atomic structural arrangement and composition of molecular compounds is patterned. The results of the accuracy assessment tests demonstrate the ability of reflectance spectroscopy to correctly assign source greater than 90% of the time by formation and deposit and above 80% of the time by sub-deposit (Table 1).

The analysis of 2430 samples from seven geologic formations and 81 deposits illustrates the reflectance spectroscopy's ability to identify a range of diagnostic spectral variables, speed of analysis, and low cost. Currently, another 2040 samples obtained from 68 deposits await analysis (Figure 2). The positive attributes of reflectance spectroscopy promotes the construction of large representative databases of chert resources necessary in order to bracket variability at various scales of resolution. Additionally, the non-destructive application of reflectance spectroscopy is vital from a preservationist perspective. Future research will focus on controlled experiments of 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 addressed through chert source research illustrates the need for reliable methods. The capability 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

The authors acknowledge the time and advice of * anonymous reviews. The significant assistance and permission given by multiple property owners and flint knappers are also gratefully recognized here without whose help much of the sampling could not have been accomplished. The author appreciates the invitation to contribute to the volume of Archaeologia Polona.  Funding for portions of this research was graciously provided by a National Science Foundation, Dissertation Improvement Grant (#1261385) and a National Park Service, Preservation Technology and Training Grant (#P14AP00142). The authors accept responsibility for any deficiencies found throughout.

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## Figure and Table captions

Figure 1. A typical chert reflectance spectrum in the visible near-infrared and middle infrared with some spectral features labeled.

Figure 2. All chert deposits sampled within the Midwestern and Southeastern United States. Deposits analyzed in the study are solid dots whereas sampled deposits needing analysis are circles.

Figure 3. An ASD Inc. FieldSpec® spectrometer used to obtain spectra in the visible and near-infrared regions.

Figure 4. A BioRad FTS-40 FTIR spectrometer used to obtain spectra in the middle infrared region.

Figure 5. Discriminant function analysis scatter plot showing; (a) delineation of chert by type/parent geologic formation, (b) by deposit within the Upper St. Louis Formation, and (c) by sub-section within prehistoric procurement site 40Pm103.

Table 1. Chert deposits analyzed in the study and the results of the three accuracy assessment tests.

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**Inter-formation accuracy test**

| Geologic Formation | *Deposits* | *# of samples* | Base Model misidentified | *10% test set misidentified* |
|---|---|---|---|---|
| ***Lower St. Louis*** | 6 | 180 | 8 | 2 |
| ***Fort Payne*** | 47 | 1410 | 3 | 4 |
| ***Tuscaloosa*** | 4 | 120 | 17 | 2 |
| ***Upper St. Louis*** | 11 | 330 | 2 | 2 |
| ***Ste. Genevieve*** | 11 | 330 | 4 | 5 |
| ***Leipers and Catheys*** | 1 | 30 | 1 | 0 |
| ***Burlington*** | 1 | 30 | 0 | 0 |
| **Total** | **81** | **2430** | **35** | **15** |

**Intra-formation accuracy test**

| Geologic Formation | *Deposit* | *# of samples* | Base Model misidentified | *10% test set misidentified* |
|---|---|---|---|---|
| ***Lower St. Louis*** | *control* | *control* | *control* | *control* |
| ***Upper St. Louis*** | Adams, KY | 30 | 0 | 0 |
|  | Cook 1, TN | 30 | 0 | 0 |
|  | Dot, KY | 30 | 0 | 0 |
|  | DVD, KY | 30 | 0 | 0 |
|  | Port Royal, TN | 30 | 0 | 0 |
|  | St. Louis 1, KY | 30 | 0 | 0 |
|  | St. Louis 2, KY | 30 | 0 | 0 |
|  | St. Louis 3, KY | 30 | 0 | 0 |
|  | St. Louis 4, KY | 30 | 0 | 0 |
|  | St. Louis 5, KY | 30 | 0 | 0 |
|  | WFDC 1, KY | 30 | 0 | 0 |
| **Total** | **11 deposits** | **330** | **0** | **0** |

**Intra-deposit accuracy test**

| Geologic Formation | *Deposit* | *# of samples* | Base Model misidentified | *10% test set misidentified* |
|---|---|---|---|---|
| ***Ste. Genevieve*** | 40Pm103a | 30 | 0 | 1 |
|  | 40Pm103b | 30 | 0 | 0 |
|  | 40Wr48 | *control* | *control* | *control* |
| **Total** | **2 deposits** | **90** | **0** | **1** |

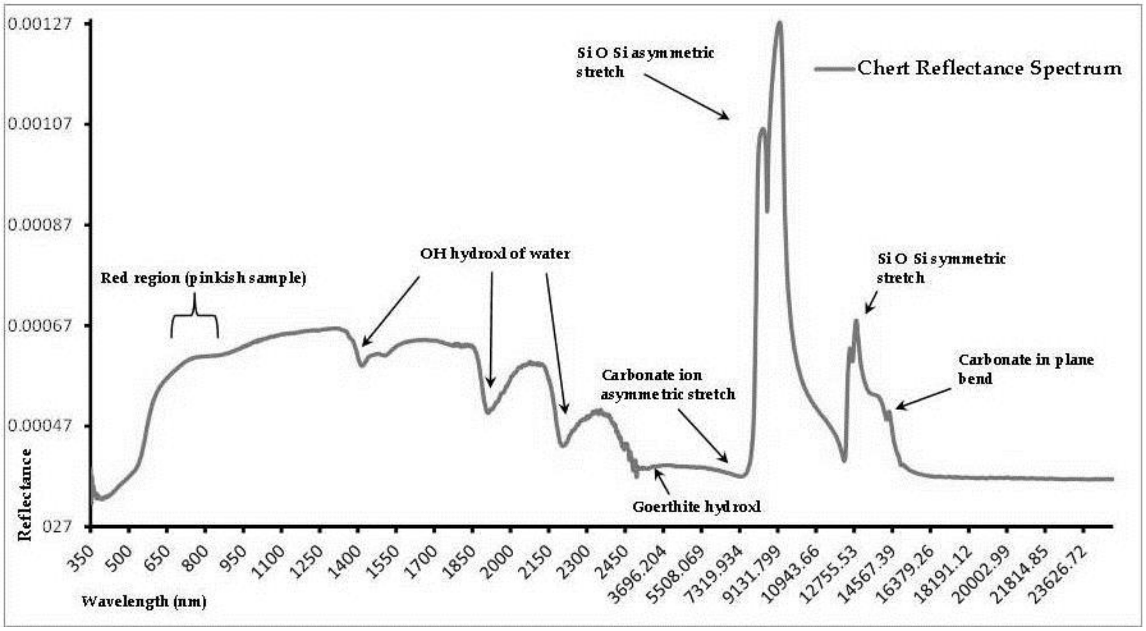

**Figure 1.** A typical chert reflectance spectrum in the visible near-infrared and middle infrared with some spectral features labeled.

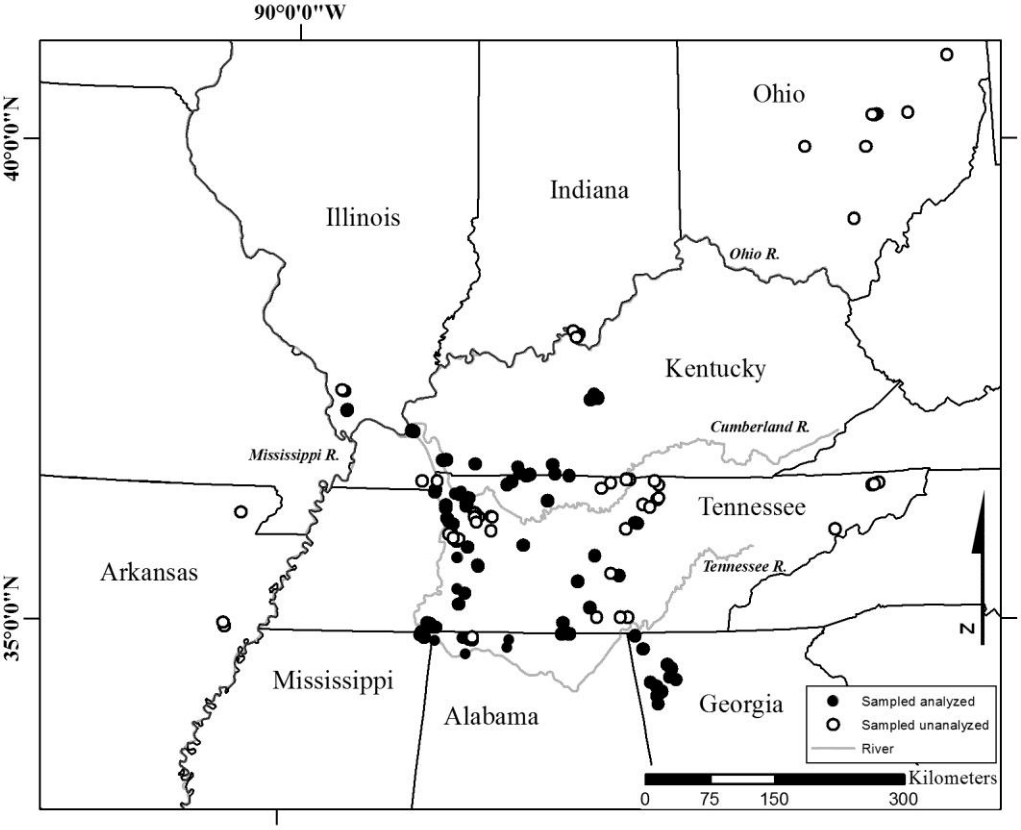

**Figure 2**. All chert deposits sampled within the Midwestern and Southeastern United States. Deposits analyzed in the study are solid dots whereas sampled deposits needing analysis are circles.

**Figure 3**. An ASD Inc. FieldSpec® spectrometer used to obtain spectra in the visible and near-infrared regions.

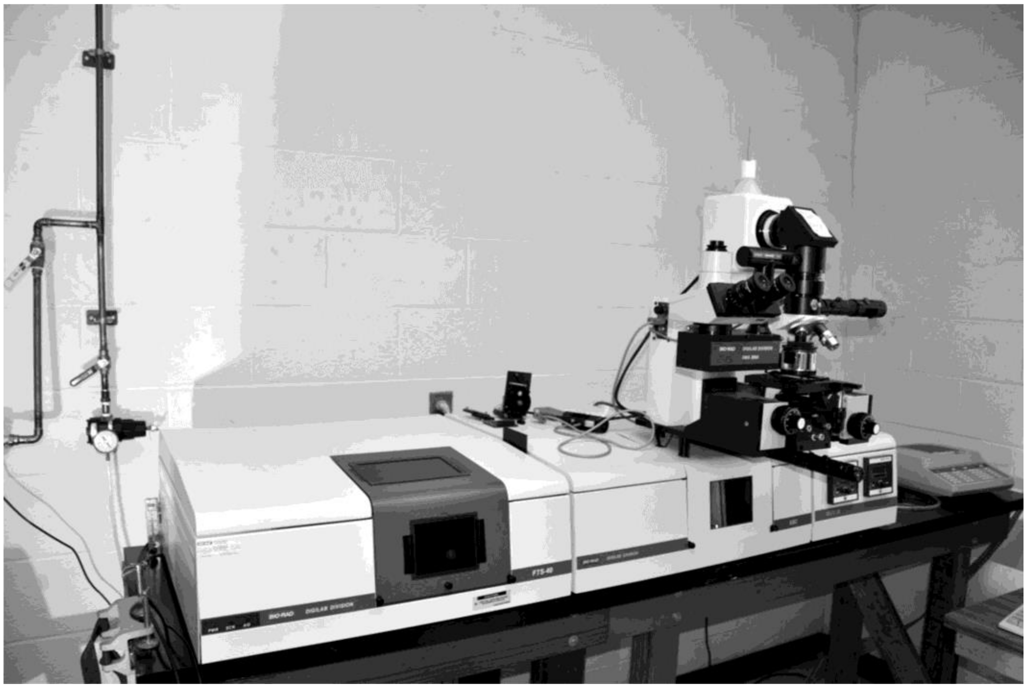

**Figure 4.** A BioRad FTS-40 FTIR spectrometer used to obtain spectra in the middle infrared region.

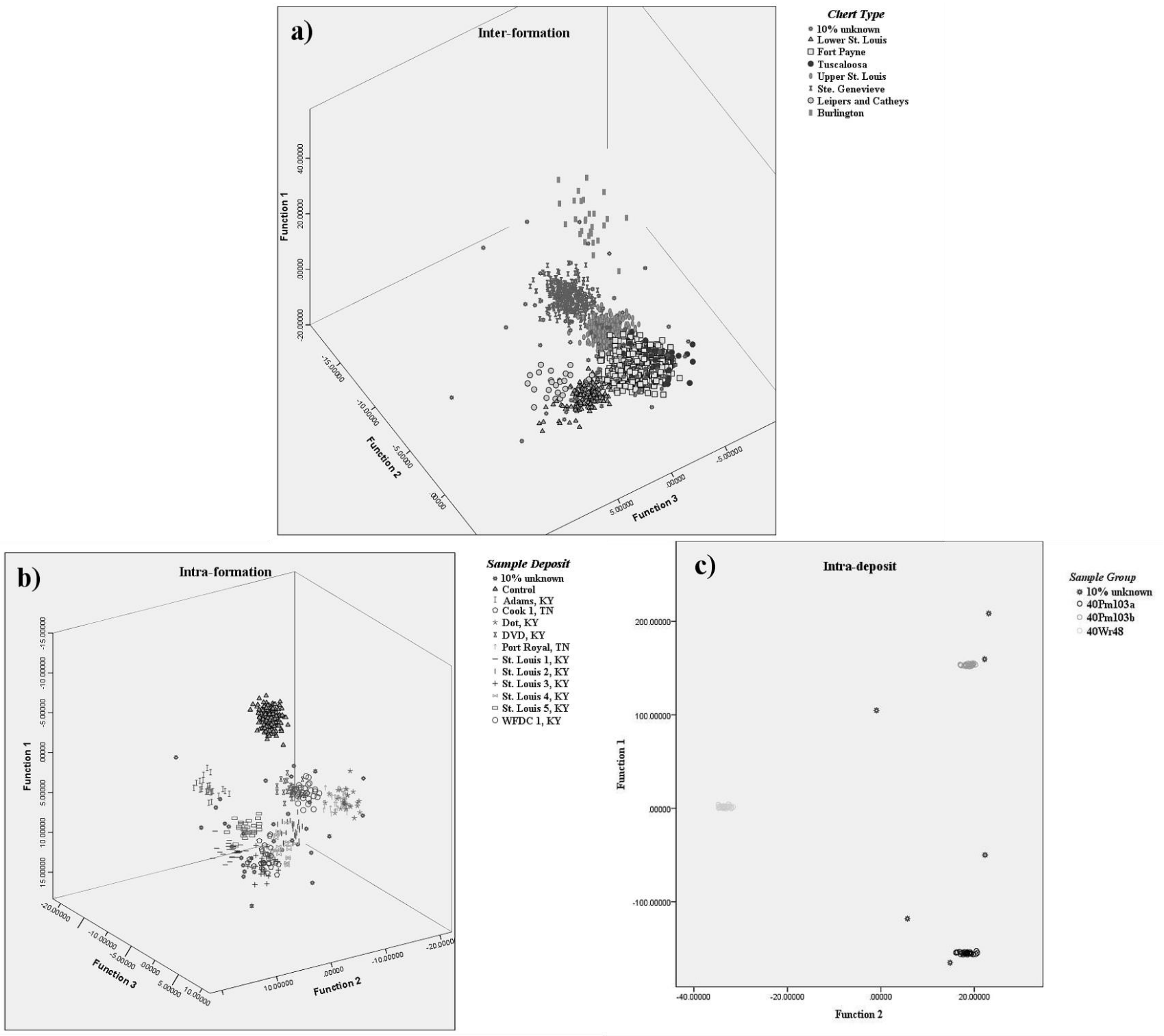

**Figure 5**. Discriminant function analysis scatter plot showing; (a) delineation of chert by type/parent geologic formation, (b) by deposit within the Upper St. Louis Formation, and (c) by sub-section within prehistoric procurement site 40Pm103.