

# APPLICATION OF VIS/NIR SPECTRAL REFLECTANCE IN SOURCING AND RECOGNITION OF HEAT-TREATMENT IN CHERTS

## Introduction

Lithic material is ubiquitous and durable, sometimes comprising the only remains found at archaeological sites. The provenance of this lithic material holds the key to many archaeological questions. Traditional lithic sourcing methods have many drawbacks including extensive sample preparation time, cost and destructiveness. These drawbacks have severely limited sample sizes in lithic sourcing studies. This increases the probability of underestimating the true variability of a source and is probably the most common lament among lithic sourcing experts.

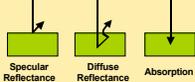
We present here a method for sourcing lithic materials using diffuse reflectance spectroscopy (DSR) in the visible and near-infrared portions of the spectrum. To our knowledge this method has not been utilized in lithic sourcing. Although, Long et al. (2001), reported promising results using Fourier-transformed spectroscopy in the mid-infrared.

## What is DSR?

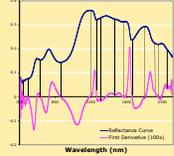
When incident light hits a sample's surface it interacts differentially with each of the sample's constituents. Depending on the wavelength of light, specific electronic and vibrational processes of the molecules present and crystal orientations all combine to produce the recorded spectra.

DSR can be used to identify mineral spectra (e.g. Hunt and Salisbury, 1970). Source/pattern matching can be accomplished entirely qualitatively and the exact chemical composition is unnecessary. Indeed, many factors which are considered confounding variables in quantitative studies may actually add information to qualitative analyses and increase material discrimination.

However, there is one confounding factor which is quite problematic in diffuse reflectance, that of specular reflectance. The specular ("mirror-like") component of reflectance occurs at the air/rock interface. Although it does contain information about surface texture, it does not contain any compositional signatures of the specimen.



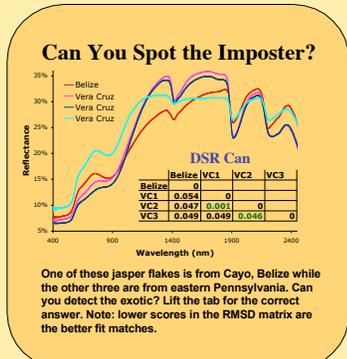
## Absorption Features in Conklin Jasper



This spectrum demonstrates the strong amorphous iron features (400-1000 nm) characteristic of many jaspers. The absorption bands at ~1400, 1900 and 2400 nm are typical of the -OH bonds in water and the large band around 2300 nm is probably associated with carbonates and/or clay minerals. We have refrained from identifying all the features since it was unnecessary for our statistical approach.

## Advantages to using DSR in lithic sourcing

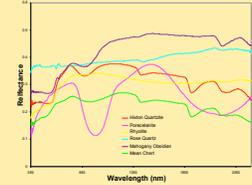
- Non-destructive, samples need no special preparation, sample is not altered.
- Cheap. Instruments are fraction of the cost of other sourcing methods.
- Fast. The instrument takes approximately 10 seconds to take 100 measurements on a sample.
- Widely available in commercial labs and universities.
- Safe, no waste products or radioactivity are produced or toxic substances used.
- Instrument can be used with minimal training.
- Portable, whole apparatus weighs less than 20 pounds.
- Samples as small as 3mm may be measured.
- Multiple attributes are simultaneously measured.



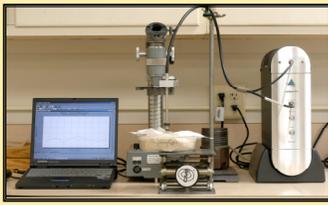
One of these jasper flakes is from Cayo, Belize while the other three are from eastern Pennsylvania. Can you detect the exotic? Lift the tab for the correct answer. Note: lower scores in the RMSD matrix are the better fit matches.

## Non-Chert Lithics

While an objective method for sourcing chert is sorely needed, there is something to be said for a method that can easily and objectively differentiate between chert and non-chert artifacts. In a double-blind study, Calogero (1991) found that archaeologists in New England were only able to visually discriminate between rhyolite and chert a surprising 40% of the time. Rhyolites and cherts are sufficiently distinct in their reflectance characteristics that it is unlikely the two could be confused spectroscopically. Below are a few examples of spectra of some common lithic materials. Note their differences from the mean chert spectrum.



## THE INSTRUMENT



## LabSpec Pro FR 350 nm - 2500 nm



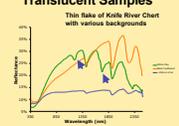
## Materials

| Chert                                  | N     |
|--|-------|
| Burlington Chert, MO                   | 34    |
| Conklin (Limerock) Jasper, Conklin, RI | 10    |
| Flint Ridge Flint, Licking Co., OH     | 25    |
| Upper Mercer Chert, East-Central, OH   | 23    |
| Knife River Flint, ND                  | 30    |
| Arizona Chert, AZ                      | 5     |
| Mexican Jasper                         | 11    |
| Antelope Jasper, ID                    | 4     |
| Massachusetts Chert, Netherlands       | 15    |
| Arizona Chert, AZ                      | 5     |
| Vera Cruz Jasper, Reading Prong, PA    | 12    |
| Arkansas Novaculite, AK                | 45    |
|  | N=221 |

The cherts used in this project were collected by one of the authors (MLJ). The sample was never intended for such a project and does not represent the diversity of samples needed from a quarry. In some cases the measurements were taken on only one or two hand samples from each locality. In other cases a larger sample was available.

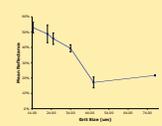
HUBBARD, Michael J., Department of Anthropology, Kent State Univ, Lowry Hall, Kent, OH 44240, mhubbard1@kent.edu; WAUGH, David A., Department of Geology, Kent State Univ, Kent, OH 44242, and ORTIZ, Joseph D., Geology, Kent State Univ, Lincoln and Summit Streets, Kent, OH 44242

## Effect of Background on Translucent Samples



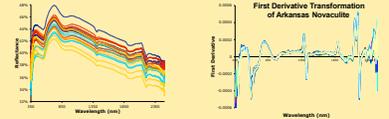
This graph shows the effects of sample background taken on a thin translucent chert sample. Note the cyan and black contours increased the reflectance of the sample. Blue arrows indicate examples of major spurious features that could have been assigned to the chert spectra had the effects of background materials not been noted.

## Effects of Surface Polish



Any number of post-discard or use-related processes can induce changes to surface texture. Here we show how various polishing grits can change mean reflectance values. The intensity of spectral features can also be altered.

## Within Sample Variability of Spectra

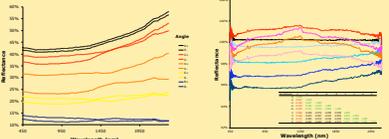


This graph shows the spectra taken at five separate locations on a sample of Arkansas Novaculite. Each color represents a series of four spectra taken at 90 degree rotations at the same point. Note the similarity in shape is retained, but that there is a multiplicative effect ranging from 2.6% reflectance at a single point to about 6% for the whole sample. This benefit must be corrected before analysis. We opted to use the first derivative transformation to accomplish this.



This graph shows first derivative transformation for the repetitive measurements of the Arkansas Novaculite (data from graph on left). The similarity in the graphs show that features are retained despite the baseline shift caused by changes in the probe-to-surface geometry.

## Effect of Angle

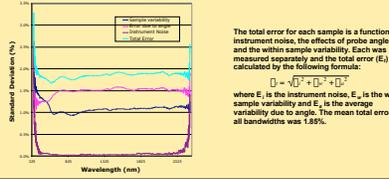


Here an Upper Mercer Chert blank which had been ground flat with 600 grit paper was mounted on a universal stage. Measurements were taken on the same spot with the stage tilted sequentially in two degree increments, first in one direction and then the other (i.e. 180° orthogonal). The nearly linear drop-off in reflectance values with increasing angle was expected. What appears to be the complete inversion of the whole spectrum between matched angle pairs was not. Needless to say, such inversions in the sourcing analysis could seriously distort our ability to predict matches between similar materials.

To explore the potential causes of the observed inversions we swapped the chert blank with a BaSO<sub>4</sub> calibration standard on the assumption that the chert's crystal orientation could be the culprit. The most obvious feature that is only a net deviation of about 4.5% reflectance with the standard as compared to about 20% with the chert blank.

To illustrate how this might affect the data analysis a correlation matrix is provided. A typical r<sup>2</sup> score for samples from the same source were usually above 0.8. Note the gross inversions of spurious features and curvilinear trending due to the subtle differences in surface-to-probe angle which combine to produce scores well below what should be expected.

## Instrument Error



The total error for each sample is a function of instrument noise, the effects of probe angle, and the within sample variability. Each was measured separately and the total error (E<sub>T</sub>) was calculated by the following formula:

$$E_T = \sqrt{E_I^2 + E_A^2 + E_S^2}$$

where E<sub>I</sub> is the instrument noise, E<sub>A</sub> is the within sample variability and E<sub>S</sub> is the average variability by angle. The mean total error for all bandwidths was 1.85%.

## References

Calogero, B. 1991. *Macroscopic and Petrographic Identification of the Rock Types for Stone Tools in Central Connecticut*. Unpublished Ph.D. dissertation, University of Connecticut.

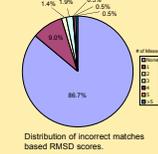
Hunt, G. R. and Salisbury, J. W. 1970. Visible and near-infrared spectra of minerals and rocks: I. silicate minerals. *Modern Geology* 1:333-300.

## Acknowledgements

We thank the Kent State Department of Geology for providing facilities to conduct this research. We especially thank Marisa Keatts for help in printing this poster. Eric Katz helped proofread this poster, all errors are solely his.

## Search Match

The final data set consisted of just over a half million points. Several methods were explored to compare these spectra. We present here just the results from Pearson's correlation and the Root Mean Square Deviation (RMSD) on both the reflectance data and its first derivative. Regardless of method we scored a comparison as a "hit" if its highest score (r<sup>2</sup> or RMSD) was with another sample of the same material (excluding spectra from the same sample). Otherwise we counted the number of false positives before a legitimate match occurred.



## Results

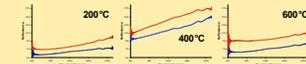
The derivitized data was consistently more reliable and though correlation and the RMSD produced approximately the same number of direct matches (82.8% versus 82.6%), the RMSD was much more likely to predict a match within the top five scores. Throughout the analysis the number of misses also gave us an indication of problem samples. More often than not samples which did not have a proper match within the top few scores could be justifiably culled from the final analysis on the basis of obvious sampling flaws (e.g. spectra was of cortex or an inclusion rather than the chert).

After removing 11 samples that should not have been included in the first place, the final result for the RMSD on derivitized data was an 86.7% match rate and 99.0% within the top five scores. Closer examination of the misses that persist suggests that visual inspection of the unknown spectrum with its closest matches will in many cases allow the researcher to rule out spurious matches, further increasing accuracy.

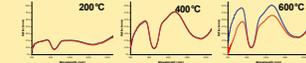
## Heat Treatment

The following experiment was designed to test whether significant spectral changes occur as a result of heat-treatment. One sample of each material was buried in an aluminum pan with about 10cm of sand and placed in an oven. The temperature was raised gradually at 50°C/hour for each batch until the desired temperature was reached (200°C, 400°C, or 600°C) and was then maintained at this temperature for four hours. We used the existing oven temperature gauge rather than a more accurate thermocouple. The samples were re-measured at the same spot before and after heating.

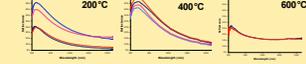
## Upper Mercer Chert



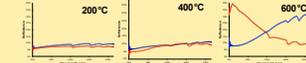
## Porcelonite



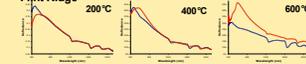
## Arkansas Novaculite



## Knife River Chert



## Flint Ridge



## Heat-treatment Results

Most heat-treatment was probably accomplished in the temperature range of 200-500°C. Only the white novaculite showed no apparent visual changes at any temperature, but it should be noted that all the color changes that did occur could very easily fall within the normal range of variation for their material type. The heat-damaged samples would be the only truly reliable visual indicator of heat-treatment in the field. The series of graphs to the right shows representative spectra for each material both before and after heat-treatment. Spectral changes are readily apparent at higher temperatures. However, by subtracting one spectrum from another and rescaling, it is apparent even for what appear to be unaltered spectra that small, potentially diagnostic changes, have occurred.

— Heat-treated  
— Un-heated spectra

## Conclusions

Our results suggest that DSR is a useful addition to the lithic source analyst's toolbox both as a stand-alone application or in conjunction with other sourcing methods.

Potential sources of error that were identified in this study include backscattering of underlying substances with thin or translucent samples and unpredictable spectral effects due to surface texture and probe angle. There is reason to believe that a few simple modifications to the experimental set-up, sample selection and the way the data is processed can significantly reduce these errors. More sophisticated pattern-matching algorithms capable of extracting and weighing "signature" features, detrending data, and removing baseline drift exist and will be explored in the near future.

We have shown that heat-treatment of cherts can alter the spectral characteristics of chert. We believe that some materials and temperatures may produce a reliably detectable signature, which falls outside the source material's normal range of variation, allowing DSR to detect heat-treatment in archeological artifacts.