



C 23rd Conference on Application of Accelerators in Research and Industry, CAARI 2014

Ion Beam Analysis of Microcrystalline Quartz Artifacts from the Reed Mound Site, Delaware County, Oklahoma

S. B. Younger-Mertz^{a,b*}, J. E. Manuel^c, T. Reinert^c, S. Z. Szilasi^c, S. W. Hammerstedt^d,
G. A. Glass^c

^a*Department of Anthropology, University of Oklahoma, Norman, Oklahoma, USA*

^b*Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, USA*

^c*Ion Beam Modification and Analysis Laboratory, Department of Physics, University of North Texas, Denton, Texas, USA*

^d*Oklahoma Archaeological Survey, University of Oklahoma, Norman, Oklahoma, USA*

Abstract

Ion beam analysis (IBA) has been a powerful, non-destructive tool for archaeological research worldwide for over four decades, yet its full potential is seldom realized in North American archaeology. Herein the potential of particle induced X-ray emission spectrometry (PIXE) as a tool for future Ozarks chert provenance studies is evaluated based on its ability to facilitate (1) discrimination of Ozarks chert materials from different geological formations and (2) identification of discrete groups of artifacts from the same geological formation. In addition, PIXE was also used to evaluate the elemental heterogeneity of Ozarks chert materials. Thirty chert (microcrystalline quartz) artifacts were visually sorted and classified according to macroscopic features characteristic of certain chert resources from particular Ozarks geological formations. The elemental concentrations obtained from PIXE analysis underwent multivariate statistical analyses in order to gain insight from the data. The results indicate that PIXE could be a useful tool for assigning Ozarks chert materials to their respective geological formations, and possibly for determining regional or sub-regional provenance.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Selection and peer-review under responsibility of the Organizing Committee of CAARI 2014

Keywords: IBA; PIXE; archaeometry; Mississippian Archaeology; chert provenance; microcrystalline quartz

* Corresponding author. Tel.: 214-326-5828.

E-mail address: stewart.b.youngermertz-1@ou.edu

1. Introduction

Elemental analysis is an invaluable tool for archaeological research, particularly because it is an objective, non-destructive process that can be used to determine the provenance of archaeological materials. Provenance studies can greatly increase our understanding of prehistoric peoples by providing valuable insight regarding their patterns of resource procurement, material preferences, and exchange networks. However, establishing the origin of microcrystalline quartz artifacts (chert, flint, chalcedony, etc.) has proven rather cumbersome, especially chert materials from the Ozarks physiographic province of the United States [1-2]. Objects crafted from chert and other lithic materials represent the only remains for many prehistoric societies, particularly those with pre-metallurgical and pre-ceramic industries. In many cases, lithic technology is the only channel available for reconstructing prehistoric societies, and the knowledge gained from chert provenance studies provides a foundation for further research concerning resource procurement, mobility, trade, and technology.

Dozens of analytical techniques commonly used by chemists, physicists, and geologists can be used to characterize archaeological materials such as chert [3], yet only a handful have been used in studies concerning Ozarks chert materials, including energy-dispersive X-ray fluorescence spectrometry (EDXRF), instrumental neutron activation analysis (INAA), and laser ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS). Of these three techniques, LA-ICP-MS has shown the most promise for determining the source of particular Ozarks chert varieties [4-5]. Bulk techniques such as INAA and EDXRF have proven to be relatively ineffective for assigning sources to Ozarks materials [6-7], which is likely due to the compositional heterogeneity of Ozarks chert sources. For these bulk techniques to be effective, especially INAA, the compositional variability *between* sources must be greater than the compositional variability *within* sources [1], which essentially is not the case for the Ozarks. The heterogeneous nature of most archaeological materials necessitates the use of micro-analytical techniques in order to address difficult archaeological questions, and in this respect, accelerator-based microbeam methods such as ion beam analysis (IBA) and synchrotron radiation X-ray fluorescence spectrometry (SRXRF) are leading the way [3].

Though the potential of PIXE as a tool for Ozarks chert research has been discussed in the past [2], ion beam analysis has yet to be applied to materials from this region, despite the fact that ion beam methods such as particle induced X-ray emission spectrometry (PIXE) [8], particle induced gamma emission spectrometry (PIGE) [9], nuclear reaction analysis (NRA) [10], Rutherford backscattering spectrometry (RBS) [11], and elastic recoil detection (ERD) [12], have been used successfully in archaeological research for decades. PIXE has proven to be a very valuable tool for determining the provenance of various archaeological materials in many regions throughout the world, including North American native copper [13], ancient Indian coins [14], Middle Age jewels [15], lithics [16], ceramics [17], emeralds set on Visigothic royal crowns [18-19], rubies inlaid in a Mesopotamian statuette [19-20], obsidian [21], pigments [22-24], and glass [9]. Nevertheless, PIXE is rarely used to source chert artifacts. Studies of chert and flint from the Paris Basin using PIXE at the AGLAE facility (Accélérateur Grand Louvre d'Analyses Élémentaires-Center de Recherche et de Restauration des Musées de France-C2RMF, Paris) have yielded promising results that demonstrate PIXE can be used to identify chert materials from different geographical locations, but belonging to the same geological formation [16]. These positive results provided incentive to apply PIXE analysis to Ozarks chert materials, and evaluate its potential for future Ozarks provenance research. The potential of the method was evaluated based on its ability to facilitate (1) successful discrimination of chert materials from different geological formations and (2) successful identification of discrete groups of artifacts from the same geological formation. In addition, PIXE was used to investigate the elemental heterogeneity of Ozarks chert.

2. Archaeological Background

The Ozarks physiographic province has been inhabited and exploited by humans for over 13,000 years [1]. This region has arguably more chert per unit area than any other region in North America (and perhaps the entire world) [1], and it is so abundant that it “covers the roads, chokes the stream beds, and in many places all but obliterates the soil” [25]. Until the 19th and 20th centuries, chert was a primary resource for the inhabitants of the region, and it was crafted into tools such as projectile points, axes, blades, hide scrapers, and even ceremonial sword bifaces [1]. The Ozarks chert artifacts chosen for this study derive from the Reed archaeological site, a multi-mound community center located in northeastern Oklahoma [26]. This site was inhabited during the Mississippian period of the

southeastern United States, which lasted from approximately A.D. 900-1500 [27]. It is located on the northwestern limit of the Caddo Mississippian cultural area between the Neosho/Grand and Cowskin rivers (Fig. 1). Radiocarbon data suggest that the site was occupied primarily during the Harlan phase (A.D. 1000-1250) [26-28], a period of immense socio-cultural change [29]. An unprecedented increase in mound construction and interregional exchange along the Arkansas, Poteau, Illinois, and Neosho rivers occurred during this phase, and it is unclear whether these phenomena represent local innovations, or if a new group of people moved into the area [28]. Platform mounds and conjoined burial mounds are defining characteristics of this period, and are exemplified at the Harlan, Spiro, Norman, and Reed sites [28].

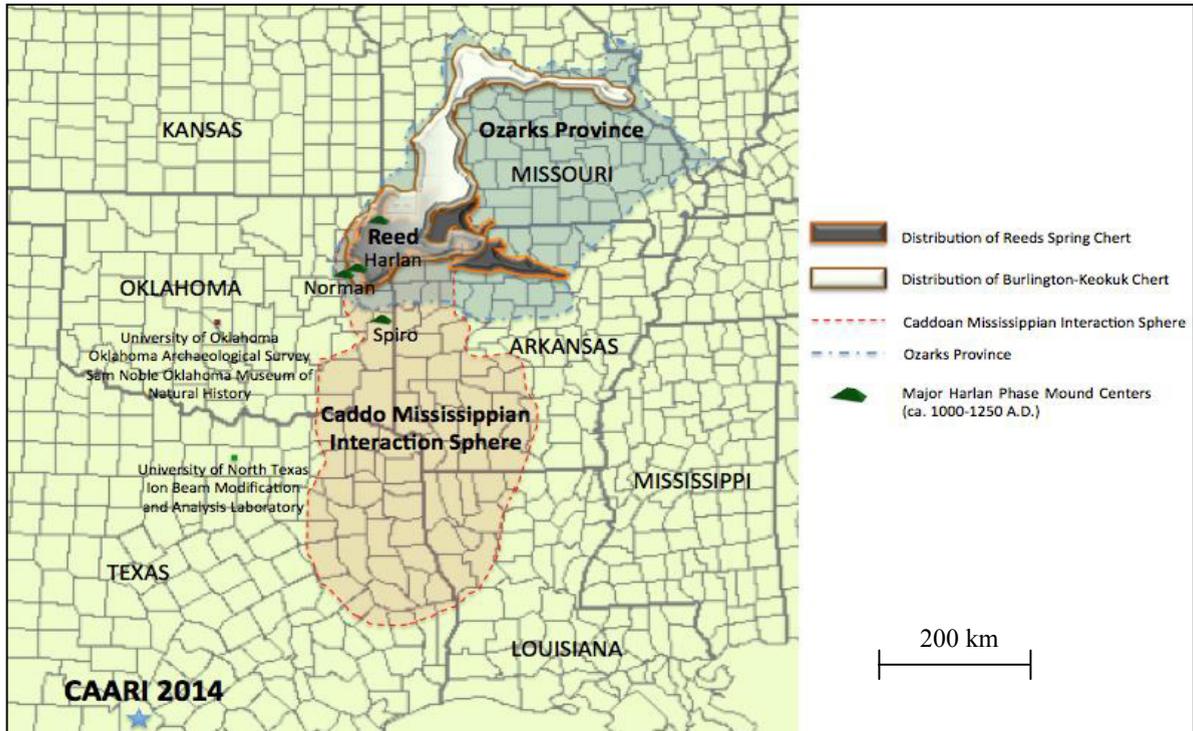


Fig. 1. Map illustrating the geographical extent of the Ozarks province and the Caddo Mississippian interaction sphere. The geographical distribution of Reeds Spring and Burlington-Keokuk chert resources is also featured, along with the locations of the major community mound centers that were active during the Harlan Phase, ca. 1000-1250 A.D. Note that the Burlington-Keokuk formation is superimposed upon the Reeds Spring formation to indicate their stratigraphic positions relative to one another.

The Reed site is located in the Springfield Plateau sub-region of the Ozarks province, which features 24 chert-bearing formations and at least 59 different chert varieties, many of which are of very high quality [1]. The Reeds Spring and Keokuk formations, which belong to the Osagean stratigraphic series of the Mississippian geological system (Fig. 2), provided the primary chipped-stone resources for the prehistoric inhabitants of the area [1]. The site originally featured a platform mound (36 m x 35 m, 2.5 m tall), a conjoined burial mound, and an associated village that encompassed approximately 15-20 hectares [27]. The thirty artifacts (27 projectile points and three bifaces) analyzed in this study were obtained from the platform mound during the first major excavations at the site, which took place in 1937 under the auspices of the Works Progress Administration (WPA) [30]. The artifacts now reside in the archaeological collections of the Sam Noble Oklahoma Museum of Natural History.

Classifying chert materials according to their respective geological formations (or geological age) is an important first step towards identifying their sources because chert-bearing formations occur in discrete geographical locations. In many cases this can be readily achieved through visual inspection, and the range of possible source areas can be reduced significantly as a result. In some cases, however, light colored cherts from several Ozarks formations, such as the Reeds Spring and Keokuk formations, are virtually indistinguishable, and can only be

distinguished visually by the most experienced eyes, if at all. Yet, chert resources that seem identical macroscopically may in some cases prove to be readily distinguishable when analyzed at the atomic level using instrumental methods of analysis. Dr. Don Wyckoff, an archaeologist with expertise in archaeological geology and lithic technology, visually classified the thirty artifacts included in this analysis. Relying on decades of experience working with Ozarks chert materials, he used various macroscopic features such as color, texture, and the presence/absence of inclusions to categorize the artifacts. His visual sorting concluded that the chert materials in the artifact sample derived from the Reeds Spring (20 artifacts), Keokuk (7 artifacts), Upper Illinois River Boone (1 artifact), and Cotter Dolomite (1 artifact) geological formations. One artifact was left unclassified.

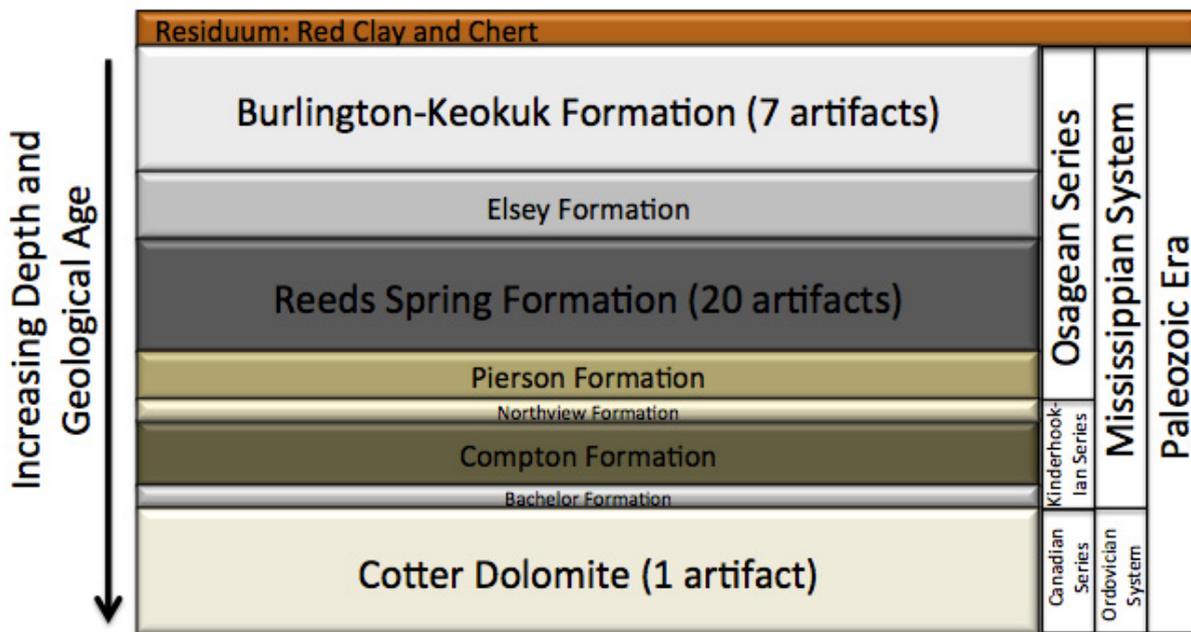


Fig. 2. Idealized stratigraphic representation of the Springfield Plateau sub-region of the Ozarks.

3. PIXE Analysis

The elemental compositions of the Reed Mound artifacts were determined using particle induced X-ray emission spectrometry (PIXE) at the Ion Beam Modification and Analysis Laboratory (IBMAL) at the University of North Texas. PIXE spectra were obtained using a 2.0 MeV proton beam generated by a National Electrostatics Corporation 3.0 MV 9SH Pelletron® accelerator. The artifacts were analyzed in a specimen chamber under vacuum, and carefully oriented on a rotating sample holder so that the incident proton beam irradiated the smoothest surfaces available on the artifacts. Sample preparation and carbon coating of artifacts was prohibited for these experiments. However, the use of low beam currents prevented excess charge build-up on the samples, and the quality of the spectra obtained from these non-conductive materials was preserved. Each spectrum was acquired for approximately five minutes, with an accumulated charge of 2.0 μC using a proton beam current of approximately 3-5 nA, and a spot size of approximately one millimeter in diameter. An upstream grid was used for charge integration. Since the beam current could not be measured accurately while samples were being irradiated, the accumulated charge on the samples was determined indirectly by first measuring the current collected from an upstream grid and calibrating with a Faraday cup in the sample position. It was determined that the Faraday cup current was 3.8 times the grid current. The grid current was monitored during PIXE acquisition, and this multiplier was used to calculate the accumulated charge on each sample. X-rays were detected using an Amptek XR-100 silicon-drift X-ray detector,

placed 40 mm from the sample surface at an angle of 45° (Fig. 3). A 75-micron Kapton filter was used to prevent backscattered protons from entering the detector. The XR-100 was connected to a PX5 digital pulse processor.

Silicon was the only major element observed in any of the spectra, which was expected given the fact that chert is microcrystalline quartz (SiO_2). Though oxygen cannot be detected using PIXE, it was clearly seen in all RBS spectra (note that RBS data were not processed or quantified, and spectra were only observed during PIXE data acquisition). Considering the stoichiometry of silicon dioxide, it is reasonable to assume that the artifacts are approximately 53.3% oxygen by weight. Taking this assumption into consideration, the remaining elements can further be assumed to comprise the remaining 46.7%, and therefore can be scaled accordingly.

The PIXE spectra were analyzed using GeoPIXE software (version 6) [31]. Using variables and experimental parameters defined by the PIXE yield equation [32], elemental concentrations can be obtained from the X-ray yields acquired from the experiments. When quantifying the PIXE spectra, the total charge accumulated on each artifact was scaled to account for variations in the solid angle of the X-ray detector since the sample-detector distance could not be kept constant due to varying sample heights. The differences in sample heights were measured with respect to the sample holder for which the detector solid angle was calibrated. Elemental concentrations obtained from GeoPIXE analysis were normalized based on the stoichiometry of silica (SiO_2), as discussed above. The composition of each artifact was assumed to be that of SiO_2 , i.e. 53.3% oxygen by weight, and the concentrations for the remaining major, minor, and trace elements were scaled to equal 46.7% by weight, yielding a total of 100%. Excluding silicon, the average minimum detection limit (MDL) at 99% confidence was approximately 16 parts per million (ppm). However, the average MDL for first row transition metals (Ti, V, Cr, Mn, Fe, Ni, and Cu) was 4 ppm. *d*-block elements overall (Zn and Zr in addition to first row transition metals) had an average MDL of 14 ppm, while *s*-block (K, Ca, Ba) and *p*-block (S, Cl, Bi) elements had average MDL's of 11 ppm and 28 ppm, respectively. The average analytical uncertainty overall was about 10 ppm, while the uncertainty for first row transition metals was about 5 ppm, *d*-block elements 8 ppm, *s*-block elements 12 ppm, and *p*-block elements 15 ppm.

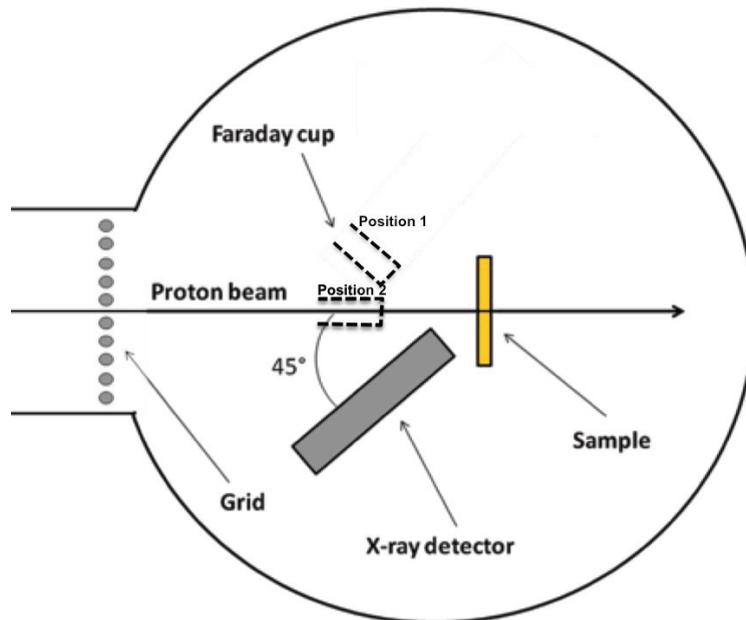


Fig. 3. Schematic of the experimental setup inside the specimen chamber.

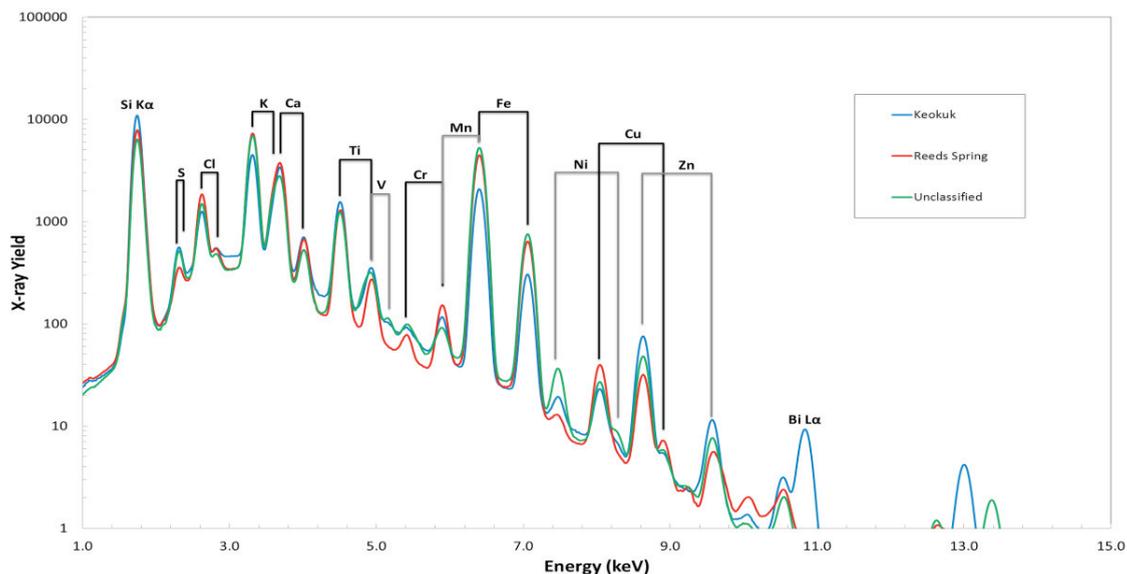


Fig. 4. GeoPIXE spectra representative of the Reeds Spring and Keokuk groups, as well as the unclassified artifact.

The results of the GeoPIXE analysis (Fig. 4) showed that the average composition of the artifacts was 98% silicon dioxide. Aside from silicon, six minor elements (1 - 0.1%) and nine trace elements (< 0.1%) were detected in this set of artifacts. The minor elements observed included iron (average 0.67%), potassium (average 0.50%), chlorine (average 0.27%), calcium (average 0.23%), sulfur (average 0.16%), and titanium (average 0.09%). These ubiquitous elements were present in every artifact, with the exception of four artifacts classified as Reeds Spring chert, which lacked any detectable amounts of sulfur. The nine trace elements detected in this set of artifacts included vanadium, chromium, manganese, nickel, copper, zinc, zirconium, barium, and bismuth. Zinc was the most abundant trace element (average 150 ppm), and was present in all but four artifacts. Manganese (average 92 ppm), copper (average 77 ppm), barium (average 122 ppm), vanadium (average 43 ppm), and chromium (average 33 ppm), were also detected in several artifacts. Nickel, zirconium, and bismuth were the least abundant trace elements in the set. Nickel was present in three artifacts (74 ppm, 40 ppm, and 101 ppm), zirconium was present in two artifacts (279 ppm and 758 ppm), and bismuth was present in two artifacts (274 ppm and 49 ppm). The average number of trace elements present in each artifact was approximately three, and ranged from zero trace elements (artifact classified as Upper Illinois River Boone chert) to seven trace elements (unclassified artifact). Including minor elements, each artifact on average included 10 elements, ranging from six elements (artifact classified as Upper Illinois River Boone chert), and 14 elements (unclassified artifact).

4. Multivariate Statistical Analyses

The elemental concentrations obtained from the GeoPIXE analysis were log-transformed and subject to multivariate statistical analyses using JMP 11[®] analysis and visualization software from SAS [33]. The purpose of the statistical analyses was to determine if the differences between the chert categories identified by Dr. Wyckoff could be modeled with respect to elemental data obtained for the members of these groups using PIXE analysis. Additional statistical methods were also employed for exploratory purposes to see if any structures could be discerned in the elemental data that could potentially represent particular chert varieties, regional sources, or sub-regional sources. The complex, multivariate nature of the question of provenance requires the use of statistical tests that employ linear combinations of variables to gain insights from large amounts of data, such as linear discriminant analysis (LDA) and principal components analysis (PCA).

Linear discriminant analysis was used to model the difference between Dr. Wyckoff's chert categories with respect to the elemental data obtained from PIXE analysis. The purpose of using LDA is to find a linear combination

of variables (in this case elements) that characterizes and discriminates between classes of artifacts. To achieve this, each artifact is plotted along one of several discriminate functions calculated using co-variances derived from the elemental data [34]. As a result, groups may or may not form according to the nominative categories defined for the sample. The distance between groups is critical for evaluating their significance. The results of the LDA clearly modeled the difference between the unclassified artifact, the Upper Illinois River Boone artifact, and the rest of dataset (Fig. 5). The unclassified artifact had a distinct green color and a unique trace element composition including vanadium (48 ppm), chromium (43 ppm), manganese (72 ppm), nickel (101 ppm), copper (94 ppm), zinc (271 ppm), and barium (839 ppm). This artifact exhibited the greatest compositional diversity in the dataset (15 elements), however, the other outlier (the Upper Illinois River Boone artifact) exhibited a low degree of elemental diversity (eight elements-silicon, sulfur, chlorine, potassium, calcium, titanium, manganese, iron), as well as the lowest silica concentration (92.5%), and the highest iron and potassium concentrations (about 3.0% and 1.7%, respectively). A subsequent iteration, which excluded the unclassified, Upper Illinois River Boone, and cotter dolomite artifacts, clearly modeled the compositional difference between the Keokuk and Reeds Spring groups (Fig. 6). As is clearly seen in the LDA plots below, iron and potassium were the most significant variables used to differentiate the Keokuk and Reeds Spring groups. Based on the elemental data and the results of the LDA (assuming that the groups identified actually derive from their associated geological formations), it appears that the groups identified by Dr. Wyckoff are significant with respect to their elemental compositions. The 96% correspondence between the chert categories and the data support this assertion, and it seems that only one artifact was misclassified. This artifact was classified as Reeds Spring chert, however, the results of the LDA suggested that its elemental composition was more similar to the Cotter Dolomite artifact than the Reeds Spring group. It is also possible that the artifact did not come from either formation, and it may derive from an entirely different formation.

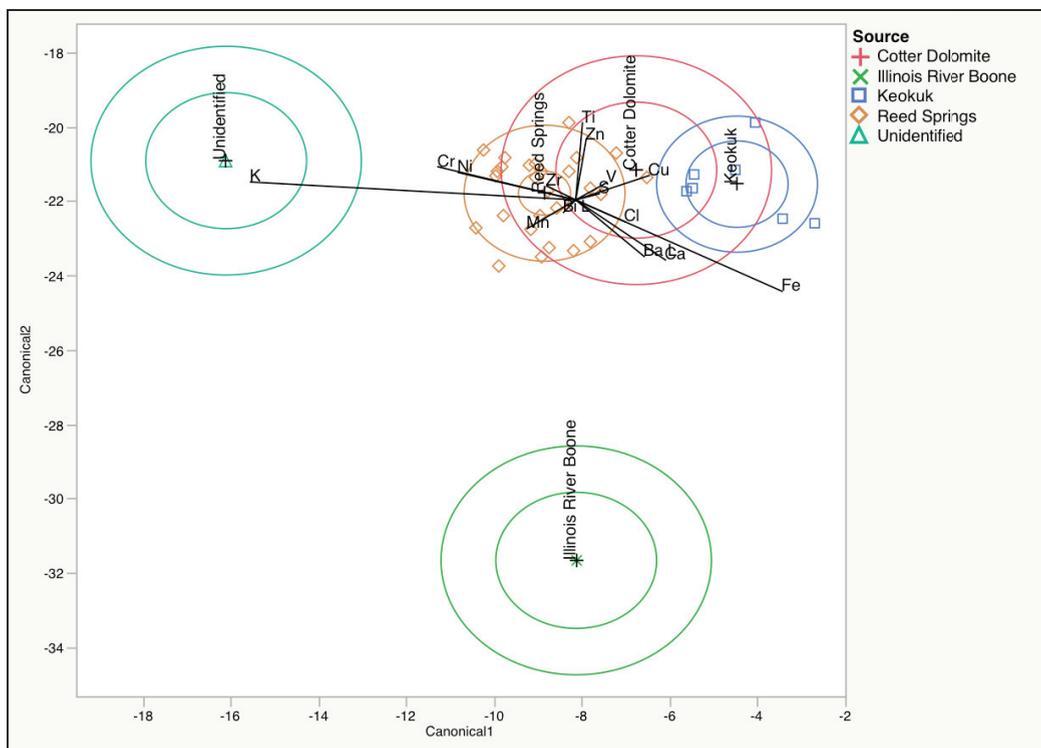


Fig. 5. The results of the linear discriminate analysis (LDA) modeling the differences between the unclassified artifact, the Upper Illinois River Boone artifact, and the rest of the artifacts, with respect to the elemental data acquired using PIXE. Note the large magnitude of the iron (Fe) and potassium (K) vectors compared to the rest of the elemental variables, which is representative of their relative importance for modeling the visually identified classes of chert materials.

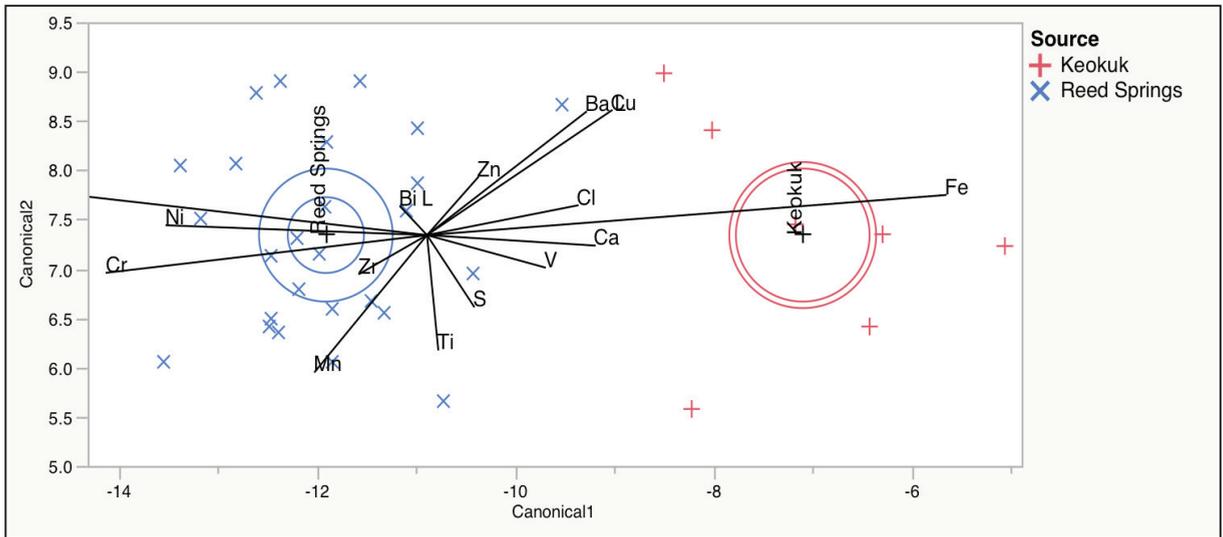


Fig. 6. The results of the LDA modeling the difference between the Reeds Spring and Keokuk groups. Again, Fe and K are the dominant variables for modeling the distinction between the Reeds Spring and Keokuk chert classes.

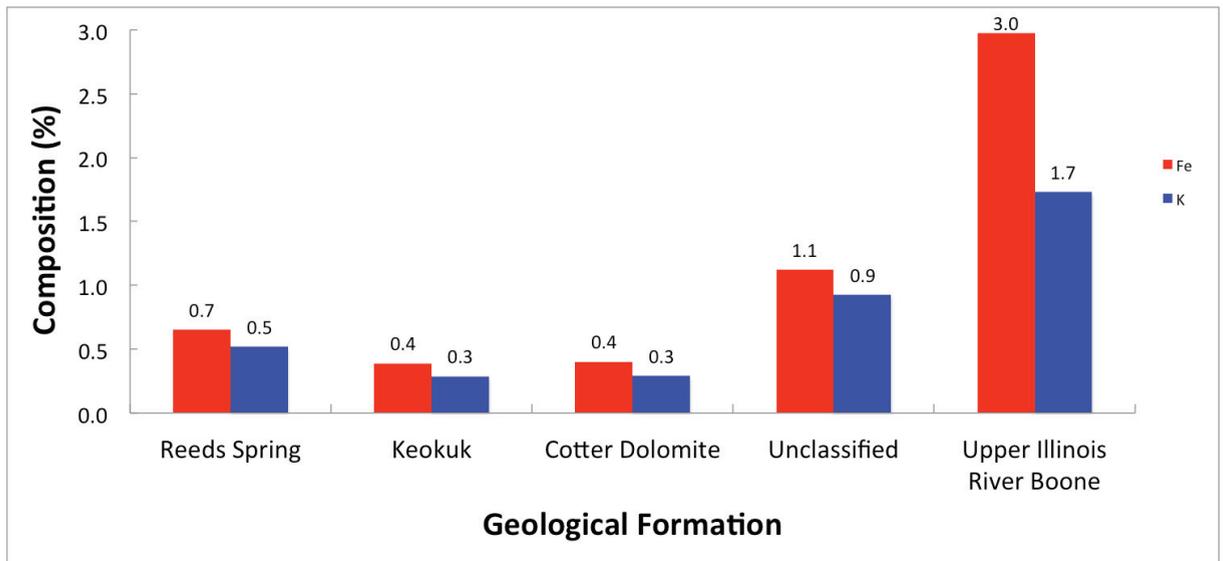


Fig. 7. Comparison of iron and potassium content for each material category.

As the results of the LDA suggest, two-thirds (20 out of 30) of the artifacts analyzed belong to the group associated with the Reeds Spring formation. This group was the subject of additional statistical tests in order to discern potential sub-groups that could possibly represent particular chert varieties, or possibly regional or sub-region chert sources. The subset was first analyzed using an eigenvector-based method known as principal components analysis (PCA). The data underwent an orthogonal linear transformation to a new coordinate system, thereby transforming the set of potentially correlated variables into a set of linearly uncorrelated variables known as principal components [34]. In other words, the data were transformed into a new coordinate system so that the most

variance is on the first coordinate (or principal component), the second most variance is on the second coordinate, the third most is on the third coordinate, etc. The first principal component obtained from the test encompassed the most variance in the dataset (31.2%), the second component encompassed the second most variance (19.3%), and so on. Four components were necessary to account for approximately 70% of the variance in the data, which is typically sufficient to adequately model the variance in the data. Fig. 7 shows the PCA biplot that was obtained when the artifacts were plotted with respect to the first and second principal components. The biplot seems to have some structure, though it is not well-defined. Cluster analysis was applied to the data obtained from the PCA in order to search for clusters, and define sub-groups within the Reeds Spring subset.

The data were partitioned with respect to the first four principal components using a connectivity-based clustering method known as Ward's method of hierarchical agglomerative clustering (HCA). This method uses the Euclidean distance between groups of points to define clusters and evaluate their dissimilarity [34]. Initially, each member of the set is defined as its own cluster. Subsequently, each member is successively grouped together based on their relative degrees of similarity. The product of hierarchical cluster analysis is a dendrogram that represents the agglomerative clustering process. The dendrogram obtained from the analysis of the Reeds Spring subset shown below suggests there are at least three unique groups (colored red, green, and blue) within the sample of artifacts associated with the Reeds Spring geological formation. These groups are marked and colored in the PCA biplot.

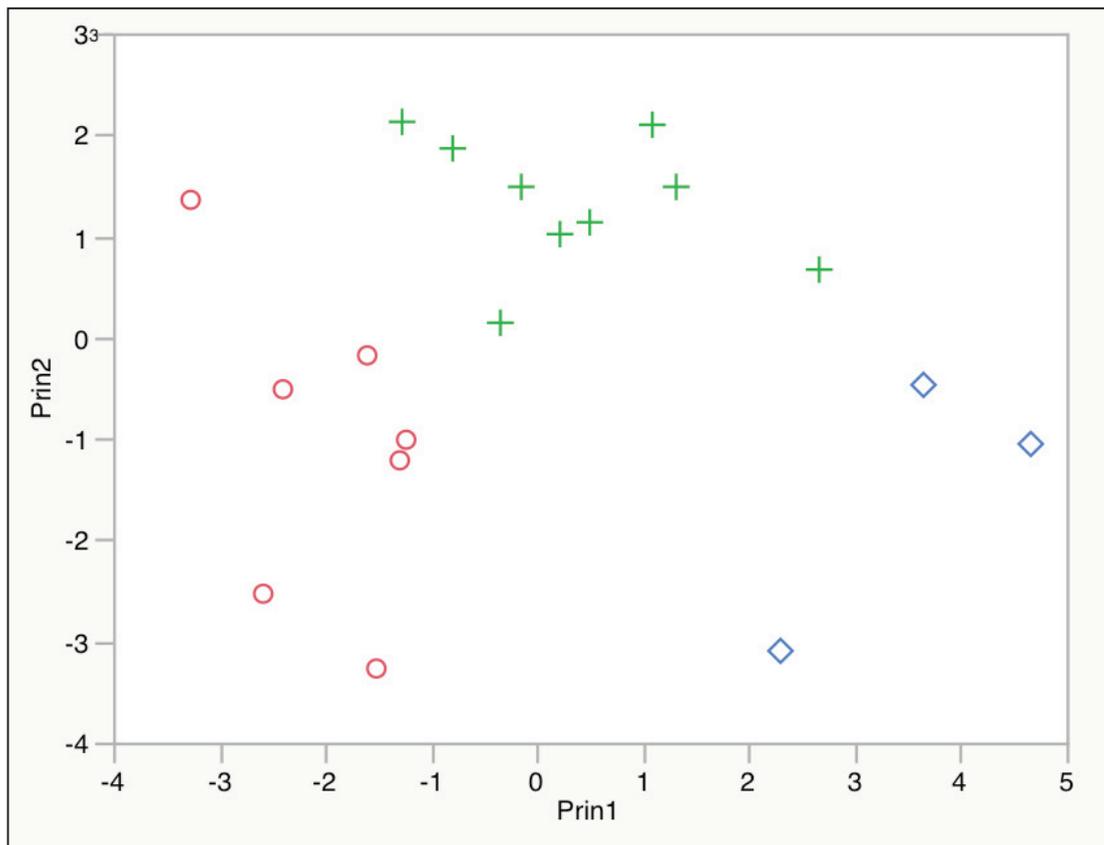


Fig. 8. The results of the principal components analysis (PCA) of the Reeds Spring subset. In this biplot, the artifacts are plotted with respect to the first two principal components obtained from the PIXE data (which underwent orthogonal linear transformation).

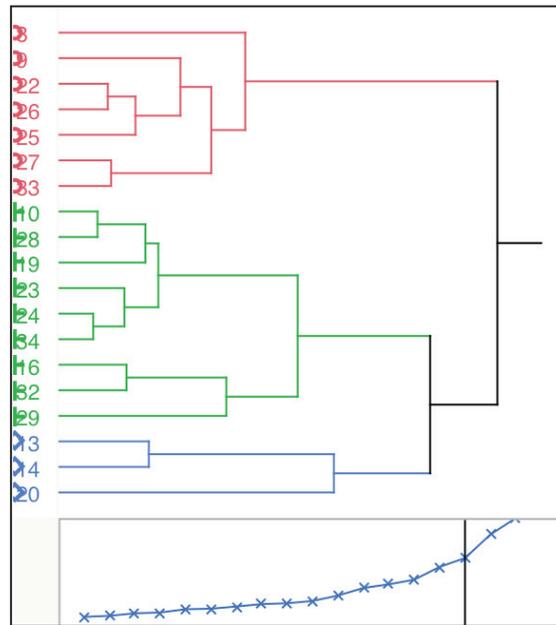


Fig. 9. The results of the hierarchical cluster analysis (HCA). This dendrogram represents the process of identifying clusters in the data (with respect to the first four principal components) by first considering each artifact as its own cluster (the far left of the dendrogram), and then successively agglomerating the artifacts into groups based on their similarities (Euclidean distance), until all the artifacts are agglomerated into a single cluster (far right of the dendrogram). The plot below the dendrogram indicates that a large increase dissimilarity, represented by a large increase in slope, occurs after the artifacts are agglomerated into three clusters.

5. Elemental Heterogeneity of Ozarks Chert

Perhaps one of the greatest challenges that continuously faces archaeological scientists, especially those pursuing questions concerning provenance, is the heterogeneity of individual artifacts. Lithic and ceramic artifacts are particularly inhomogeneous, which is why they are some of the most difficult materials to source. However, this challenge also presents the opportunity to develop innovative research methodologies to address issues that arise when dealing with inhomogeneous archaeological materials. Microanalytical techniques such as PIXE and electron probe microanalysis (EPMA) are particularly well suited for characterization of heterogeneous materials because they irradiate samples with millimeter and/or micrometer scale beams that can be used to identify and characterize mineral inclusions, which can either be (1) avoided in order to obtain a more accurate average composition for the primary matrix or (2) used as a diagnostic feature for elucidating provenance. As a first step towards understanding the degree of compositional variability within individual Ozarks chert artifacts, spectra were acquired from multiple locations for five artifacts. Fig. 9 and Fig. 10 display the trace element concentrations obtained for Reeds Spring Artifact A (RSA) and Reeds Spring Artifact B (RSB). Both RSA and RSB exhibited a significant amount of trace element variability. Three distinct zones are visually discernable for RSA, with the upper and lower portions featuring a reddish-pink color, and the middle portion featuring a gray color. The reddish-pink regions possess trace levels of nickel and copper, and no vanadium. Interestingly, trace levels of vanadium are present in the gray region, but nickel and copper are absent. RSB also exhibits a significant degree of variability, and an inverse relationship seems apparent between barium and *d*-block element concentrations. For RSA, it seems quite reasonable to attribute the elemental variability to the presence of unique phases in the artifact, with certain areas possessing different frequencies and different types of mineral inclusions. This is likely the case for RSB as well, however, it is unclear

to what extent environmental contamination contributed to the observed trace element variability. Fig. 11 shows a backscattered electron image of a raw Reeds Spring chert sample acquired using an electron microprobe. The micrograph clearly illustrates the compositional heterogeneity characteristic of Ozarks chert.

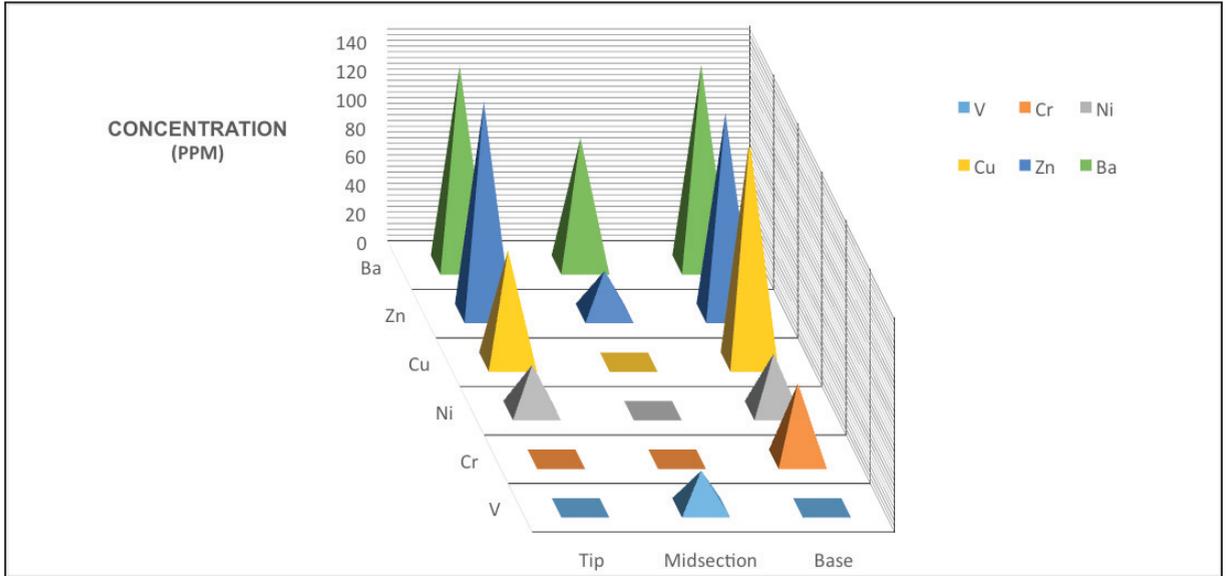


Fig. 10. Trace element concentrations for Reeds Spring Artifact A. X-ray spectra were obtained from three different locations on this artifact.

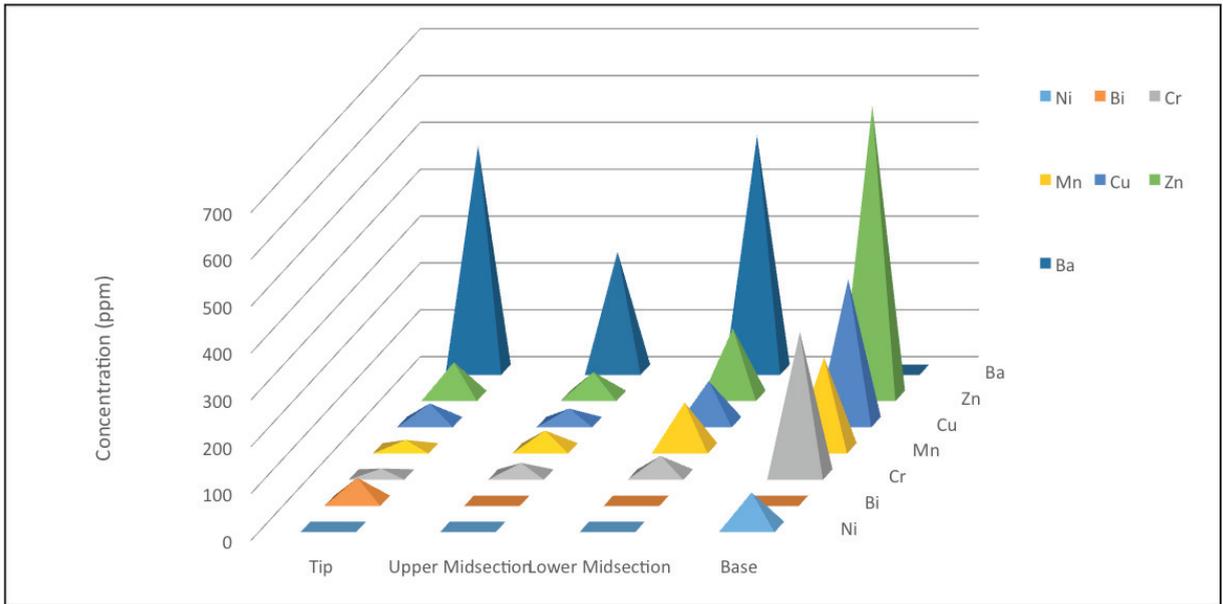


Fig. 11. Trace element concentrations for Reeds Spring Artifact B. X-ray spectra were obtained from four different locations on this artifact.

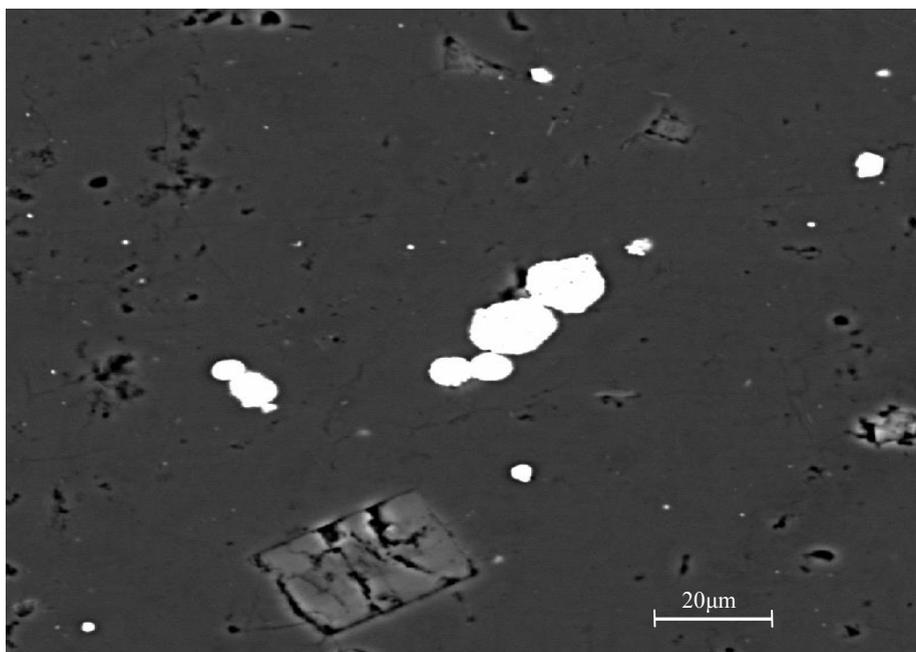


Fig. 12. Backscattered electron image (19.9 KeV, 19.75 nA) of a raw Reeds Spring chert sample. Image was acquired using a Cameca SX50 electron microprobe at the University of Oklahoma Electron Microprobe Laboratory. This image clearly displays mineral inclusions commonly found in chert. The dark gray background is silica (SiO₂), the primary constituent of chert. The bright white inclusions are pyrite (FeS), which is likely the primary contributor of iron and sulfur in the PIXE spectra. The light gray rhombohedral inclusion at the bottom of the micrograph is dolomite (CaMg(CO₃)₂), which is likely a contributor to much of the calcium observed in the PIXE spectra.

6. Results

The intentions of this pilot study were threefold: to evaluate (1) the potential for using PIXE as a tool for discriminating Ozarks chert materials deriving from different geological formations, (2) the potential for using PIXE as a tool for identifying particular varieties of chert from the same geological formation, and (3) the elemental heterogeneity of Ozarks chert. Linear discriminate analysis (LDA) and principal components analysis (PCA) were used to accomplish the first and second objectives, respectively. The results of the LDA suggest that the elemental PIXE data and chert classes identified by Dr. Wyckoff correspond with a high degree of accuracy (> 95%). Assuming that these classes in fact represent materials from different geological formations, it seems that PIXE is a useful tool for differentiating Ozarks chert materials deriving from different geological strata. This has important implications for archaeologists studying Ozarks chert, because visual classifications with this degree of accuracy are certainly not typical, and depend significantly on the skills of the individual performing the classifications. Only after years of familiarity with the chipped-stone resources of a particular region can an archaeologist achieve the skill level necessary to correctly identify chert materials visually with a high degree of accuracy, and it is especially difficult for novices in the field to correctly assign chert materials to their respective geological formations with any degree of reliability. PIXE could therefore be an extremely valuable tool for assigning Ozarks chert artifacts to their respective geological formations, especially for those with minimal exposure to Ozarks materials. In addition, PIXE would also be a useful tool for experts in lithic technology by allowing them to refine their material assignments. Nobody is perfect, everyone makes mistakes when analyzing lithic artifacts, especially when dealing with light colored Ozarks chert varieties that derive from the Osagean stratigraphic series.

PCA and HCA were used to evaluate the potential of PIXE as a tool for identifying particular varieties of chert that derive from the same geological formation. Assuming that all the materials assigned to the Reeds Spring group in fact derive from the same geological formation (which is supported by the results of the LDA), the results of the

PCA and HCA suggest that PIXE could potentially be used to identify unique subgroups within sets of artifacts associated with the same Ozarks formation. These subgroups could potentially represent particular varieties of chert from the same formation, or possibly even regional or sub-regional sources. At least three distinct groups were identified in the Reeds Spring subset, which correspond roughly to the chert colors observed, with one group consisting of dark gray materials (perhaps the Lower Reeds Spring variety [1]), another consisting of light gray materials, and the last consisting of a variety of gray, brown, and reddish materials. However, the significance of these groups needs to be further explored, and further research will be necessary to fully evaluate the potential of PIXE as a tool for identifying particular varieties of Ozarks chert from the same geological strata, and for assigning sources to individual artifacts.

The elemental heterogeneity of Ozarks chert poses a challenge for provenance studies. The results of this study highlight the danger of acquiring only one spectrum from one location on an artifact, which was the case for most of the artifacts in this study. The degree of variability in the trace element compositions of RSA and RSB shown in Fig. 9 and Fig. 10 suggests that acquiring spectra from even three or four locations is inadequate for obtaining a statistically significant average composition for an artifact. Spectra should be acquired from at least 10-20 locations on an artifact in order to minimize statistical uncertainty. It is quite possible that clearer results would have been obtained from the multivariate statistical analyses if 10-20 spectra had been acquired for each artifact, and if the statistical tests had been performed on average values instead of data from singular locations for each artifact. Future studies would be well advised to take this into consideration

7. Discussion

The results of this study warrant further research using PIXE for Ozarks chert research. However, in order to conduct successful provenance research, meticulous and innovative research strategies must be developed that address the idiosyncrasies of Ozarks materials. These strategies must also evolve to keep pace with insights that will be gained and technological developments that will be made in the future, which adds an intrinsic experimental flavor to provenance research. Such strategies should include systematic collection of statistically adequate samples of as many Ozarks chert sources as possible, and full characterization of these sources using PIXE, other IBA methods such as PIGE, RBS, and NRA, and other complementary methods such as EPMA, LA-ICP-MS, X-ray diffraction [35], μ -Raman [36], and electron paramagnetic resonance spectroscopy [37]. This will result in the creation of a database containing the fingerprints, or genetic codes, for Ozarks chert sources, built from data obtained from complementary methods of analysis.

Research strategies involving PIXE must improve in efficacy and efficiency by continually refining experimental procedures. Of particular importance when analyzing Ozarks chert, and other inhomogenous materials, is the minimization of statistical uncertainty by acquiring data from multiple locations (preferably 10-20) on each sample. Such measures improve the efficacy of subsequent multivariate statistical analyses of the data. Complications arising from environmental contamination should also be avoided when analyzing raw chert samples by analyzing freshly broken or ground surfaces. When possible, artifacts should also undergo minimal sample preparation to eliminate ambiguities arising from surface contamination. Many stone artifacts feature broken surfaces that are very amenable to sample preparation through minimal grinding, which doesn't compromise the integrity of the object. Nevertheless, it must be accepted that sample preparation will be forbidden for many archaeological materials, and steps must be taken to account for uncertainties arising from surface contamination. The efficacy and efficiency of data acquisition could also potentially be optimized by (1) experimenting with other projectiles such as alpha particles and deuterons (to reduce X-ray bremsstrahlung background for example), (2) using multiple beam energies, multiple high energy and low energy X-ray detectors, and various filters and absorbers in order to maximize detection of as many elements as possible, (3) reducing the turnover rate of analysis by analyzing samples in air using an external beam, thereby increasing analytical efficiency (by increasing the speed and maneuverability of analysis) and eliminating charge build-up on samples, and lastly (4) correcting X-ray attenuation caused by surface roughness (perhaps this could be achieved by analyzing the sample surface using an interferometer, and subsequently applying the straightforward procedure outlined by Campbell et al. [32] for correcting X-ray attenuation caused by surface roughness in PIXE analysis).

IBA could also be used to address other research questions involved in Ozarks chert research besides those concerning provenance. μ -PIXE has been used to investigate stone tool function by using elemental maps of the use-edges of stone tools that feature trace-element patterns characteristic of the material that was worked [38]. This methodology has not yet been applied to Ozarks materials. The nuclear microprobe that has recently been constructed at IBMAL would be well suited for this task. RBS has been used to investigate the relationship between the presence of uranium and the UV fluorescence properties of various types of chert [11]. The RBS data obtained suggested that the presence of uranium in chert is responsible for causing the fluorescence of chert under UV radiation; however, the fluorescence properties did not appear to be correlated with the concentration of uranium, and other elements seem to be responsible for the amplification or attenuation of the fluorescence response [11]. Though UV fluorescence has shown little promise for Ozarks chert provenance studies [1], perhaps UV fluorescence could evolve into a complementary technique that can be used to help identify and classify various chert resources once a better understanding of their fluorescence properties is attained. Nuclear reaction analysis (NRA) has also been used for chronometric chert studies involving fluorine diffusion [10, 39-40]. Silicon and fluorine form extremely strong chemical bonds, and over time fluorine reacts with the surface of microcrystalline quartz (chert) and gradually penetrates into the material. When a chert tool is made, fresh surfaces are exposed to the environment that are free of fluorine. However, fluorine gradually penetrates into the material over time, and as a result, the fluorine diffusion profile of a chert artifact can be used as a relative, chronometric indicator. The elemental profile for fluorine can be obtained using NRA by analyzing the gamma rays and charged particles emitted as products of the resonant nuclear reactions resulting from the penetration of fluorine nuclei by protons, in conjunction with step-wise increases in beam energy. Though this method is rarely used and has received relatively little interest from the archaeological community (most likely due to relatively esoteric status of ion beam methods in North American archaeology), this method holds great potential for Ozarks chert research, especially in conjunction with carbon-14 dating using accelerator mass spectrometry (AMS), thermoluminescence dating, electron paramagnetic resonance spectroscopy (EPR), as well as sites with well-defined stratigraphy, and seriated collections of chert artifacts with well-defined artifact types and reliable provenience information. Fluorine diffusion dating would be particularly interesting for the artifacts in this study because the point types represented in the set of artifacts are characteristic of archaeological contexts ranging from several millennia B.C. to 1200 A.D. It would be intriguing to see if the artifacts could be ordered chronologically based on their fluorine diffusion profiles.

8. Conclusion

PIXE is ideal for chert provenance studies because of its non-destructive nature, low detection limits, and high accuracy. In this preliminary study, the potential of the method as a tool for research concerning Ozarks materials was evaluated. Thirty chert artifacts from the central platform mound of the Reed archaeological site were visually inspected and classified into groups according to macroscopic features characteristic of certain types of Ozarks chert materials. Elemental data were acquired for these thirty artifacts using PIXE analysis, which subsequently underwent multivariate statistical tests in an attempt to mathematically model the differences between the chert types identified. The Reeds Spring subset of the elemental data was analyzed further in order to determine if discrete groups within the subset could be identified. The results of this study indicate that the groups identified by Dr. Wyckoff are distinct with respect to the elemental data, which suggests that PIXE would likely be a very useful method for classifying Ozarks chert artifacts with respect to their associated geological formations. In addition, three discrete subgroups were identified within the Reeds Spring subset, which indicates that PIXE could potentially be useful for identifying chert varieties deriving from the same geological formation, and perhaps for assigning artifacts to regional or sub-regional sources. The elemental heterogeneity of individual artifacts was also investigated, and it was determined that multiple spectra must be acquired from multiple locations on an artifact in order to obtain its *average* elemental composition for subsequent statistical analyses. In conclusion, the results of this study indicate that PIXE could potentially be a powerful tool for future Ozarks chert research. However, this conjecture is not decisive, and further research will be necessary to fully evaluate the suitability of PIXE as a tool for Ozarks provenance research. Nevertheless, there is little doubt that PIXE will continue to be very powerful tool for elucidating the past throughout the world.

Acknowledgements

The authors thank the Ion Beam Modification and Analysis Laboratory (Department of Physics, University of North Texas) for participating in this research, and the Sam Noble Oklahoma Museum of Natural History for providing the artifacts used in this study. We also thank Dr. Don Wyckoff for participating and visually classifying the artifacts, Dr. Patrick Livingood for assisting with JMP[®] statistical software, Dr. Mark Levine for providing access to the artifacts, and Shelia Savage for her past and ongoing contributions to Reed Mound studies. We also thank Dr. Bonnie Pitblado for her valuable guidance and encouragement during the course of this research. The authors also thank the National Science Foundation, as this work was supported in part by NSF grant DMR-0960222.

References

- [1] J. H. Ray, *Ozarks Chipped-Stone Resources: A Guide to the Identification, Distribution, and Prehistoric Use of Cherts and Other Siliceous Raw Materials*. Missouri Archaeological Society Special Publications No. 8. Missouri Archaeological Society, Springfield (2007).
- [2] L. D. Banks, *From Mountain Peaks to Alligator Stomachs: A Review of Lithic Sources in the Trans-Mississippi South, the Southern Plains, and Adjacent Southwest*. Memoir No. 4. Oklahoma Anthropological Society (1990).
- [3] G. Artioli, *Scientific Methods and Cultural Heritage: An introduction to the application of materials science to archaeometry and conservation science*. Oxford University Press, New York (2010).
- [4] R. J. Speakman, M. Glascock, and J. H. Ray, The White and the Gray: Geochemical Analysis of Midwestern Chert. Paper presented at the 66th Annual Meeting of the Society for American Archaeology (2001).
- [5] R.J. Speakman, H. Neff, M. D. Glascock, and B. J. Higgins, Characterization of Archaeological Materials by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. In *Archaeological Chemistry: Materials, Methods, and Meaning*, edited by Kathryn A. Jakes, pp. 48-63. ACS Symposium Series 831. American Chemical Society, Washington, D.C. (2002).
- [6] M.D. Glascock, A Report of the Analysis of Chert from the Western Ozarks Using Instrumental Neutron Activation Analysis. In *Lithic Sourcing Studies: An Assessment of Current Techniques on a Collected Sample of Cherts from the Western Ozarks*, by Gregory J. Maggard, pp. 70-77. Unpublished Masters thesis, Department of Anthropology, University of Tulsa (1998).
- [7] G.J. Maggard, *Lithic Sourcing Studies: An Assessment of Current Techniques on a Collected Sample of Cherts from the Western Ozarks*. Unpublished Masters thesis, Department of Anthropology, University of Tulsa (1998).
- [8] G.E. Coote, N.E. Whitehead, G.J. McCallum, A rapid method of obsidian characterisation by inelastic scattering of protons. *J. Radioanal. Chem* (1972) 491-496.
- [9] Z. Smit, P. Pelicon, G. Vidmar, B. Zorko, M. Budnar, G. Demortier, B. Gratuze, S. Turm, M. Neemer, P. Kump, and M. Kos. Analysis of medieval glass by X-ray spectrometric methods. *Nucl. Instr. Meth. B* 161/163 (2000) 718.
- [10] J.Y. Jin, D.L. Weathers, F. Picton, B.F. Hughes, J.L. Duggan, F.D. McDaniel, and S. Matteson, A Nuclear Reaction Analysis Study of Fluorine Uptake in Flint. *AIP Conference Proceedings* 475 (1999) 554-557.
- [11] S. Matteson, M.J. Avara, C.V. Nguyen, S.H. Kim, RBS characterization of uranium in flint and chert. *Nucl. Instr. Meth. B* 465 (2005) 465-469.
- [12] T. Calligaro, Y. Coquinot, I. Reiche, J. Castaing, J. Salomon, G. Ferrand, Y.L. Fur, Dating study of two rock crystal carvings by surface microtopography and ion beam analyses of hydrogen. *Appl. Phys. A* 94 (2009) 871-878.
- [13] J.W. Palmer, M.G. Hollander, P.S.Z. Rogers, T.M. Benjamin, C.J. Duffy, J.B. Lambert, and J.A. Brown, Pre-Columbian Metallurgy: Technology, Manufacture, and Microprobe Analyses of Copper Bells from the Greater Southwest. *Archaeometry* 40 (1998) 361-382.
- [14] M. Hajivaliei, M.L. Garg, D.K. Handa, K.L. Govil, T. Kakavand, V. Vijayan, K.P. Singh, I.M. Govil, PIXE analysis of ancient Indian coins. *Nucl. Instr. Meth. B* 150 (1999) 645-650.
- [15] T. Calligaro, S. Colinart, J.-P. Poirot, and C. Sudres, Combined external-beam PIXE and μ -Raman characterization of garnets used in Merovingian jewellery. *Nucl. Instr. Meth B* 189 (2002) 320.
- [16] S. Consigny and P. Walter, Flint origin and ion beam analysis: archaeological results in the Paris Basin, France. In *Man and Flint: Proceedings of the VIIth International Flint Symposium, September 1995*, edited by R. Schild and Z. Sulgostowska, pp. 337-42. Institute of Archaeology and Ethnology, Polish Academy of Sciences, Warszawa (1997).
- [17] H.J. Fischbeck, J.D. Rogers, S.R. Ryan, F.E. Swenson, Sourcing Ceramics in the Spiro Region: a Preliminary Study Using Proton-Induced X-ray Emission (PIXE) Analysis. *Midcontinental Journal of Archaeology* 14 (1989) 3-17.
- [18] T. Calligaro, J.-C. Dran, J.-P. Poirot, G. Querré, J. Salomon, and J.-C. Zwaan, PIXE/PIGE characterization of emeralds using an external micro-beam. *Nucl. Instr. Meth. B* 150 (1999) 622.
- [19] T. Calligaro, J.-C. Dran, and J. Salomon. Ion beam microanalysis. In *Non-Destructive Microanalysis of Cultural Heritage Materials*, edited by K. Janssens and R. V. Grieken, pp. 227-276. Comprehensive Analytical Chemistry Vol. XLII, edited by D. Barcelo. Elsevier, Amsterdam (2004).

- [20] T. Calligaro, A. Mossman, J.-P. Poirot, and G. Querré, Provenance study of rubies from a Parthian statuette by PIXE analysis. *Nucl. Instr. Meth. B* 136/138 (1998) 846.
- [21] G. Poupeau, F.-X. Le Bourdonnec, T. Carter, S. Delerue, M.S. Shackley, J.-A. Barrat, S. Dubernet, P. Moretto, T. Calligaro, M. Milić, K. Kobayashi, The use of SEM-EDS, PIXE, and EDXRF for obsidian provenance studies in the Near East: a case study from Neolithic Catalhöyük (central Anatolia). *Journal of Archaeological Science* 37 (2010) 2705-2720.
- [22] M. Sánchez del Río, P. Martinetto, C. Solís, C. Reyes-Valerio, PIXE analysis on Maya blue in Prehispanic and colonial mural paintings. *Nucl. Instr. Meth B* 249 (2006) 628-632.
- [23] P. Nel, P.A. Lynch, J.S. Laird, H.M. Casey, L.J. Goodall, C.G. Ryan, R.J. Sloggett, Elemental and Mineralogical study of earth-based pigments using particle induced X-ray emission and X-ray diffraction. *Nucl. Instr. Meth A* 619 (2010) 306.
- [24] L. Beck, Recent Trends in IBA for cultural heritage studies. *Nucl. Instr. Meth. B* 332 (2014) 439-444.
- [25] C.O. Sauer, *The Geography of the Ozark Highland of Missouri*. University of Chicago Press, Chicago (1920).
- [26] D.G. Wyckoff, *Caddoan Adaptive Strategies in the Arkansas Basin, Eastern Oklahoma*. Unpublished Ph.D. dissertation, Department of Anthropology, Washington State University, Pullman (1980).
- [27] D.G. Anderson and K.E. Sassaman, *Recent Developments in Southeastern Archaeology: From Colonization to Complexity*. SAA Press, Washington, D.C (2012).
- [28] S.W. Hammerstedt and S. B. Savage, Late Prehistoric Mortuary Behavior in Northeastern Oklahoma: A View from the Reed Site. Paper Presented at the Annual Meeting of the Southeastern Archaeological Conference. Baton Rouge, LA (2012).
- [29] R.E. Bell, Arkansas River Caddoan: The Harlan Phase. In *Prehistory of Oklahoma*, edited by Robert E. Bell, pp. 221-240. Academic Press, New York.
- [30] B.L. Purrington, *The Prehistory of Delaware County Oklahoma: Cultural Continuity and Change on the Western Ozark Periphery*. Unpublished Ph.D. dissertation, Department of Anthropology, University of Wisconsin, Madison (1971).
- [31] C.G. Ryan, Developments in dynamic analysis for quantitative PIXE true elemental imaging. *Nucl. Instr. and Meth B* 181 (2001) 170-179.
- [32] J.L. Campbell, R.D. Lamb, R.G. Leigh, and B.G. Nickel, Effects of Random Surface Roughness in PIXE Analysis of Thick Targets. *Nucl. Instr. Meth. B* 12 (1985) 402-412.
- [33] B. Jones and J. Sall, JMP statistical discovery software. *Wiley Interdisciplinary Reviews: Computational Statistics* 3 (2011) 188-194.
- [34] M. Baxter, *Statistics in Archaeology*. Oxford University Press, New York (2003).
- [35] J.P. Pretola, A Feasibility Study Using Silica Polymorph Ratios for Sourcing Chert and Chalcedony Lithic Materials. *Journal of Archaeological Science* 28 (2001) 721-739.
- [36] V. Hernández, S. Jorge-Villar, C. Capel Ferrón, F.J. Medianero, J. Ramos, G.-C. Weniger, S. Domínguez-Bella, J. Linstaedter, P. Cantalejo, M. Espejo, and J.J. Durán Valsero, Raman spectroscopy analysis of Palaeolithic industry from Guadalteba terrace river, Campillos (Guadalteba county, Southern of Iberian Peninsula). *J. Raman Spectrosc.* 43 (2012) 1651-1657.
- [37] M. Brilli, L. Conti, F. Giustini, M. Occhiuzzi, P. Pensabene, M. De Nuccio, Determining the provenance of black limestone artifacts using petrography, isotopes and EPR techniques: the case of the monument of Bocco. *Journal of Archaeological Science* 38 (2011) 1377-1384.
- [38] Z. Šmit, G.W. Grime, and S. Petru, Usewear studies on archaeological stone tools. In *Ion beam study of art and archaeological objects*, edited by G. Demortier and A. Adriaens, pp. 67-71. A contribution by members of the COST G1 Action, European Commission, EUR 19218, Brussels (2000).
- [39] R.E. Taylor, Fluorine Diffusion: A New Dating Method for Chipped Lithic Materials. *World Archaeology* 7 (1975) 125-135.
- [40] Ph. Walter, M. Menu, and J.C. Dran, Dating of Archaeological Flints by Fluorine Depth Profiling: New Insights into the Mechanism of Fluorine Uptake. *Nucl. Instr. and Meth B* 64 (1992) 494-498.