INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF CHERT FROM THE WILLIAMSON AND BOLSTER'S STORE SOURCES, DINWIDDIE COUNTY, AND THE MITCHELL PLANTATION SOURCE, SUSSEX COUNTY, VIRGINIA

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Introduction

Provenance studies through trace element characterization are widely applied throughout the world as a means of reconstructing trade/exchange networks, territorial ranges, and interaction spheres. Research along this line has used materials where the chemistry is indicative of geographical origin and include obsidian (Yacobaccio et al. 2004), soapstone (Truncer et al. 1998), jade (Kovacevich et al. 2005), metals (Zedeno et al. 2005), and cryptocrystalline rocks, such as jasper, flint, and chert (Blades et al. 1997; Cackler et al. 1999; Hoard et al. 1992; Morrow et al. 1992). Statistical discrimination between material sources at high levels of confidence is usually achieved with materials that have high intra-source chemical homogeneity and large inter-source variability with respect to chemistry. Obsidians and some metal deposits meet these criteria, while cryptocrystalline artifacts frequently do not and may require additional assessments, such as petrographic analysis (Malyk-Selivanova et al. 1998) or fluorescence (Lyons et al. 2003). Because of the large ranges for chemical constituents within cherts and flints, it cannot be assumed that individual chert sources will have unique signatures useful for investigating past behavior. It is often necessary to carefully evaluate the potential for lithic provenance studies within a region of interest.

Within the eastern region of Virginia there are numerous chert, jasper and chalcedony sources that are located in the vicinity of the geological Fall Line, which defines the boundary between the coastal plain and the piedmont region to the west (Figure 1). There are no cryptocrystalline sources to the east of this fault. We are aware of eight sources to the west of the Fall Line, of which seven are recorded as quarry locations (i.e. Bolster's Store (44DW18), Bonifant 44PO84), Bourne (44HN198), Brook Run (44CU122), Feldspar Quarry (44HN102), Mitchell Plantation (44SX140), Williamson (44DW1), and two reported as regions where sources are suspected (i.e., Brunswick County and Hanover County), based upon high densities of these materials at archaeological sites. In this preliminary study, we have selected the Bolster's Store, Mitchell Plantation, and Williamson sources to determine if they can be differentiated on the basis of their trace element chemistry.

Lithic Source Descriptions

Geographically, the chert outcrops are located approximately 25-45 km south-southwest of Petersburg, Virginia and within 25 km of one another (Figure 2). The northernmost chert outcrop is located in Dinwiddie County at the Williamson site along the west-to-east flowing Little Cattail Creek. The southernmost chert outcrop is located on the Mitchell Plantation in Sussex County along the Nottoway River. The Bolster's Store outcrop is
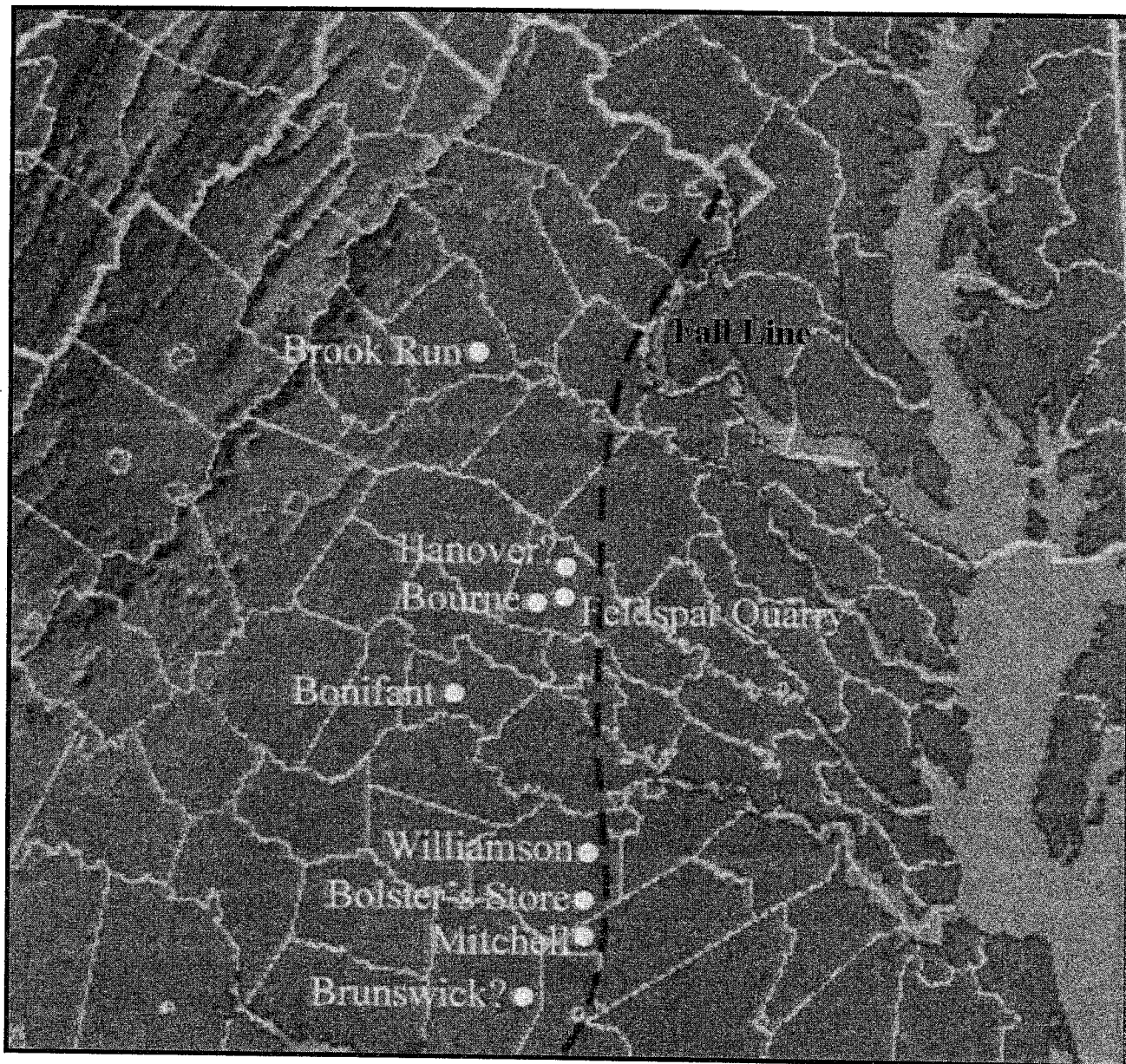
Figure 1. The Location of Eastern Virginia Chert and Jasper Sources in Relation to the Geological Fall Line that Separates the Coastal Plain from the Interior Piedmont.

located in Dinwiddie County near the Dinwiddie-Sussex County line about 5 km north of the Mitchell Plantation and roughly 20 km south of the Williamson site.

The Williamson nodule source and an associated Paleoindian site (44DW1) are positioned along Little Cattail Creek at the juncture of the Petersburg Granite and the Bacons Castle Formation (see Figure 2). The Petersburg granite ranges from a true granite to a granodiorite and contains many accessory minerals, such as magnetite, zircon, pyrite, and apatite. The Bacons Castle forma-

tion is a surface deposit of gray, yellowish-orange, and reddish brown sand, gravel, silt, and clay, which dates to the Upper Pliocene (Johnson 1993). The cherts have been previously described as being highly variable in color and texture: "Colors range from white and translucent to opaque black, but cream, gray, blue and brown in variegated forms predominate. Textures range from grainy, like quartzite, to smooth and waxy, and while several varieties are translucent, most are subtranslucent" (McAvoy 1992:25). A portion of the material also contains impurities of yellow and brown jasper.
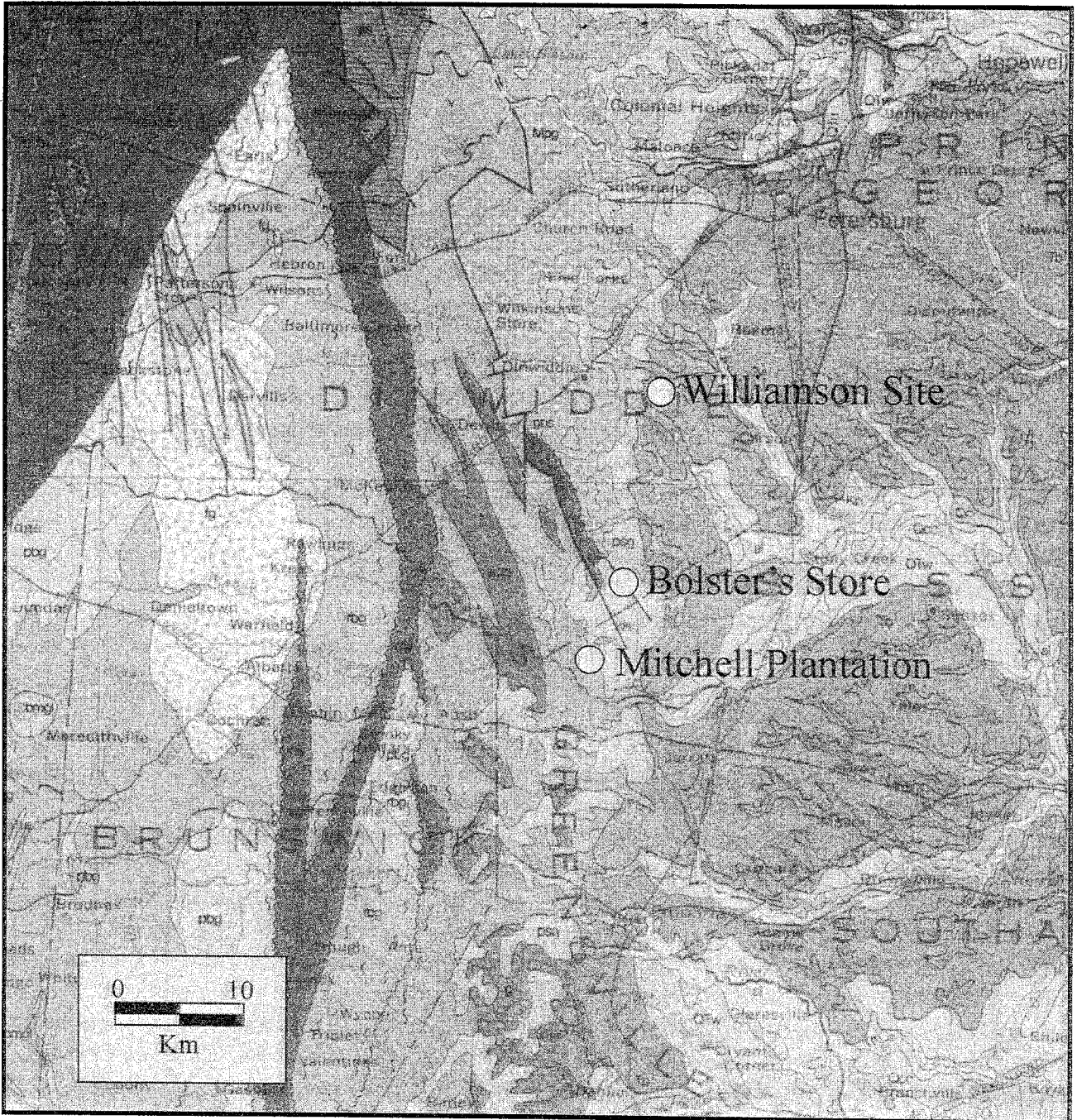
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Figure 2. Portion of the Geological Map of Virginia Showing Locations for the Williamson Site (44DW1), the Bolster's Store Source (44DW18), and the Mitchell Plantation Source (44SX140).

The Bolster's Store source (44DW18) is located near the source area of Hardwood Creek and erodes out from the red clay as nodules. Here the surface geology is a Pliocene sand and gravel (Johnson 1993). The quarry is situated directly on a geological fault (see Figure 2), which likely exposed the deposit. The chert is grainy in texture and occurs in colors of red, brown, cream, yellow, and blue-gray. Pyrite crystals within the chert are visible to the naked eye and oxidize to a red-brown color over time (McAvoy 1992).

The Mitchell Plantation source (44SX140) is located within a region of mafic and felsic metavolcanic rocks that date from the late Proterozoic to Cambrian (Johnson 1993). McAvoy (1992) reports that it consists of at least four

outcroppings located within a mile of the Nottoway River (see Figure 2). This lithic source is a replacement chert formed by precipitation within a quartz vein (McCary and Bittner 1979) and, as such, had to be physically removed by percussion by prehistoric peoples. The color of the chert is extremely variable with white, cream, gray, blue, violet, pink, and dark brown surfaces represented in the quarry assemblage (McAvoy 1992).

A few samples from each source were chemically analyzed by energy dispersive x-ray spectroscopy for their major, minor, and trace elements (McAvoy 1992:32). These semi-quantitative analyses provided some valuable preliminary assessments of composition even if they were not suitable for reliable provenance studies. It was observed that Bolster's Stone had the lowest silica concentration range (90-98%) while the concentration of silica in the other two sources was equal to 98% or greater. The Bolster's Store cherts also had the highest concentrations of iron (1.2-6.6%) and sulphur (0.0-4.4%) in comparison to the Williamson and Mitchell Plantation cherts (0.0-0.75%). The Mitchell Plantation had the greatest number of minor element impurities with Ti, Al, Fe, and Ca all represented. Heavier elements, such as W, Hg, Tl, and Th, were present but their concentration levels were not specified. Based upon this information it appeared that iron might be a potentially useful discriminating element.

Sample Selection and Preparation

A total of 48 chert specimens from three sources were analyzed in the Archaeometry Lab at the University of Missouri Research Reactor (MURR) by instrumental neutron activation analysis (INAA). Sixteen samples were obtained from each of the source outcrops either by site visitation or from the reference collections at the Virginia Department of Historic Resources (DHR), Richmond. The chert specimens were assigned individual analytical identification numbers: Bolsters Store samples (DHR148 to DHR163); the Williamson samples (DHR164 to DHR179); and the Mitchell Plantation samples (DHR180 to DHR195).

All samples were initially washed to remove adhering dirt and other loose particles from the surface. The samples were prepared by placing the source specimens between two tool steel plates and crushing them with a Carver Press to obtain a number of small 50-100 mg fragments. The fragments were examined with a magnifier to eliminate those fragments with metallic streaks or crush fractures that could possibly contain traces of contamination. Several grams of clean fragments were obtained from each sample and stored in plastic bags.

Two analytical samples were prepared from each source specimen. The first sample, used for short irradiations, was made by placing about 200 mg of fragments into clean high-density polyethylene vials. A second sample, used for long irradiation and weighing about 800 mg, was placed in clean high-purity quartz vials. Individual sample weights were recorded to the nearest 0.01 mg using an analytical balance. Both irradiation vials were sealed prior to irradiation. Standards made from the National Institute of Standards and Technology (NIST) certified standard reference materials SRM-1633a (Coal Fly Ash), SRM-278 (Obsidian Rock), and SRM-688 (Basalt Rock) were similarly prepared.

Irradiation and Gamma-ray Spectroscopy

Instrumental neutron activation analysis of archaeological materials at MURR, which consists of two irradiations and a total of three measurements of emitted gamma rays, constitutes a superset of the procedures employed at most other INAA laboratories. As discussed in detail in Glascock (1992), a short irradiation is carried out through the pneumatic-tube irradiation system at MURR. Samples and standards in polyethylene vials are sequentially irradiated, two at a time, for five seconds by a thermal neutron flux of 8×10^{13} n cm^{-2} s^{-1}. Following irradiation, the samples are allowed to decay for 25 minutes so that radioactivity from the short-lived radioisotope ^{28}Al (half-life = 2.24 min) can decline to acceptable levels. Sample vials are mounted in sample holders at a distance of 10 cm from the face of separate high-purity germanium (HPGe) detectors. The sample holders are designed to continuously rotate the samples during a 12-min counting period in order to compensate for slight differenc-

es between individual sample shapes. The short-count, gamma-ray spectra for each day are stored and later analyzed in batches to determine the concentrations of elements in the unknown archaeological samples relative to the standard reference materials. The short-lived elements measured in chert characterization studies are usually aluminum (Al), calcium (Ca), dysprosium (Dy), potassium (K), manganese (Mn), sodium (Na), titanium (Ti), and vanadium (V).

The long irradiation samples and standards in high-purity quartz vials are wrapped in bundles of approximately 32 unknowns and six standards each. Two sample bundles are placed inside an aluminum can and irradiated for a total of 70 hours by a thermal neutron flux of 5×10^{13} n cm^{-2} s^{-1}. Following irradiation, the sample bundles are unwrapped and the quartz vials are washed in aqua regia to remove possible surface contamination. Two gamma measurements are performed on the individual samples from each bundle using a pair of HPGe detectors coupled to automatic sample changers with rotating sample holders. The first count for 2,000 seconds each (i.e., the "middle count") is usually made about one week after the end of irradiation to allow ^{24}Na (half-life = 15 hr) to decay to a safe handling level. The middle count yields data for the determination of several medium half-life elements, including arsenic (As), barium (Ba), lanthanum (La), lutetium (Lu), neodymium (Nd), samarium (Sm), uranium (U), and ytterbium (Yb). After an additional three- or four-weeks of decay, a final measurement of approximately four hours each (i.e., the "long count") is carried out. The latter measurement yields the data for a number of long-lived elements, including cerium (Ce), cobalt (Co), chromium (Cr), cesium (Cs), europium (Eu), iron (Fe), hafnium (Hf), nickel (Ni), rubidium (Rb), antimony (Sb), scandium (Sc), strontium (Sr), tantalum (Ta), terbium (Tb), thorium (Th), and zinc (Zn). More details about gamma-ray spectroscopy, neutron activation analysis, and standardization can be found in Glascock (1998).

Interpreting Compositional Data

The interpretation of compositional data obtained from the analysis of archaeological materials is discussed in detail elsewhere (e.g., Baxter and Buck 2000; Bieber et al. 1976; Bishop and Neff 1989; Glascock 1992; Harbottle 1976; Neff 2000) and is only summarized here. The main goal of data analysis is to identify distinct homogeneous groups within the analytical database. Based on the provenance postulate of Weigand et al. (1977), different chemical groups may be assumed to represent geographically restricted sources. For lithic materials such as obsidian, basalt, and cryptocrystalline silicates (e.g., chert, flint, or jasper), raw material samples are frequently collected from known outcrops or secondary deposits and the compositional data obtained on the samples is used to define the source localities or boundaries.

Compositional groups are viewed as "centers of mass" in the compositional hyperspace described by the measured elemental data. Groups are characterized by the locations of their centroids and the unique relationships (i.e., correlations) between the elements. Decisions about whether to assign a specimen to a particular compositional group are based on the overall probability that the measured concentrations for the specimen could have been obtained from that group.

Potential compositional groups can be hypothesized initially by using non-compositional information (e.g., archaeological context, visual attributes, etc.) or by application of one or more different pattern recognition techniques to the multivariate chemical data. Some of the pattern recognition techniques that have been used to investigate archaeological data sets are cluster analysis (CA), principal components analysis (PCA), and discriminant analysis (DA). Each of the techniques has it own advantages and disadvantages for data interpretation, which may depend upon the types and quantity of data available.

The variables (measured elements) in archaeological and geological data sets are often correlated and frequently large in number. This makes handling and interpretation of patterns within the data more challenging. It is often advantageous to transform the original variables in the data set into a smaller set of uncorrelated variables in order to make data interpretation easier. Of the above-men-

Table 1a. Descriptive Statistics for Chert from the Bolster's Store Source.

Element	Mean	St. Dev.	% St. Dev.	No. Obs.	Minimum	Maximum
AS	1.678	1.516	90.355	15	0.175	5.313
BA	132.107	109.742	83.070	14	21.100	338.400
LA	2.230	2.829	126.861	16	0.076	10.729
LU	0.045	0.066	146.221	16	0.003	0.268
ND	2.562	3.555	138.745	14	0.169	12.624
SM	0.505	0.701	138.777	16	0.040	2.552
U	0.515	0.361	70.013	16	0.070	1.212
YB	0.296	0.445	150.561	14	0.015	1.721
CE	3.032	3.105	102.410	16	0.192	9.893
CO	0.573	0.731	127.565	16	0.032	2.339
CR	1.568	1.861	118.633	16	0.207	6.511
EU	0.156	0.233	149.564	15	0.006	0.850
FE	12560.863	16086.025	128.065	16	731.900	53919.800
HF	0.166	0.210	126.273	11	0.015	0.612
SB	1.327	1.233	92.938	16	0.028	5.165
SC	0.361	0.265	73.482	16	0.069	0.951
TB	0.095	0.157	165.227	13	0.004	0.577
TH	0.105	0.137	131.175	15	0.010	0.424
ZN	1664.242	5479.859	329.271	16	0.800	21942.460
AL	1524.860	465.794	30.547	15	872.000	2336.800
CA	396.500	370.071	93.335	7	116.900	1192.800
MN	69.546	136.018	195.581	16	1.650	417.460
NA	83.106	31.990	38.493	16	57.500	181.300

tioned pattern recognition techniques, PCA is the technique that transforms from the data from the original correlated variables into uncorrelated variables most easily.

Principal components analysis uses all of the variables measured in the sample (in this case element concentrations) and calculates the variation among those variables. The individual principal components (PCs) are measures of the magnitude of variation, each describing a decreasing amount of variance. The first PC subsumes the greatest amount of variance in the data set and is aligned along the direction of greatest variation. The second PC is orthogonal to the first PC and also a linear combination of the variables analyzed. The second PC subsumes the greatest amount of variation after removal of the first PC and is aligned along the direction of greatest remaining variation. The third PC is orthogonal to the first two PCs and subsumes the greatest amount of remaining variation after the first two PCs, and so forth. The number of PCs calculated will be equal to the number of original variables measured.

PCA creates a new set of reference axes arranged in decreasing order of variance subsumed. The individual PCs are linear combinations of the original variables. The data can be displayed on combinations of the new axes, just as they can be displayed on the original elemental concentration axes. PCA can be used in a pure pattern-recognition mode, i.e., to search for subgroups in an undifferentiated data set, or in a more evaluative mode, i.e., to assess the coherence of hypothetical groups suggested by other criteria. Generally, compositional differences between specimens can be expected to be larger for specimens in different groups than for specimens in the same group, and this implies that groups should be detectable as distinct areas of high point density on plots of the first few components.

It is well known that PCA of chemical data is scale dependent (Mardia et al. 1979), and analyses tend to be dominated by those elements or isotopes for which the concentrations are relatively large. As a result, standardization methods are common to most statistical packages. A common ap-

Table 1b. Descriptive Statistics for Chert from the Williamson Source.

Element	Mean	St. Dev.	% St. Dev.	No. Obs.	Minimum	Maximum
AS	0.915	1.094	119.501	14	0.122	4.512
BA	111.533	136.066	121.996	15	6.000	354.700
LA	1.236	1.162	94.000	16	0.167	4.415
LU	0.028	0.028	100.245	15	0.003	0.090
ND	1.235	1.085	87.905	14	0.182	4.178
SM	0.251	0.271	108.232	16	0.029	1.075
U	0.602	0.707	117.412	14	0.045	2.611
YB	0.185	0.188	101.647	16	0.028	0.615
CE	1.568	1.567	99.936	16	0.198	5.837
CO	0.864	1.413	163.626	16	0.043	5.052
CR	2.324	2.411	103.754	16	0.402	8.429
EU	0.079	0.084	105.545	16	0.009	0.318
FE	7359.875	18401.894	250.030	16	77.200	64448.800
HF	0.013	0.011	80.197	12	0.003	0.036
SB	0.268	0.148	55.177	16	0.088	0.597
SC	0.182	0.146	79.994	16	0.019	0.530
TB	0.044	0.040	90.481	15	0.006	0.153
TH	0.026	0.032	120.813	14	0.006	0.130
ZN	1.961	1.709	87.136	15	0.320	6.920
AL	1194.464	255.163	21.362	14	882.300	1769.400
CA	2903.045	5349.972	184.288	11	236.200	16561.500
MN	411.153	1129.786	274.785	16	2.550	4282.260
NA	100.079	54.668	54.625	14	54.500	255.000

proach is to transform the data into logarithms (to base 10). As an initial step in the PCA of most chemical data at MURR, the data are transformed into log concentrations to equalize the differences in variance between the major elements, such as Al, Ca, and Fe, on one hand and trace elements, such as the rare-earth elements (REEs), on the other hand. An additional advantage of the transformation is that it appears to produce more normal distributions for the trace elements.

A frequently exploited strength of PCA, discussed by Baxter (1992), Baxter and Buck (2000), and Neff (1994, 2002), is that it can be applied as a simultaneous R- and Q-mode technique, with both variables (elements) and objects (individual analyzed samples) displayed on the same set of principal component reference axes. A plot using the first two principal components as axes is usually the best possible two-dimensional representation of the correlation or variance-covariance structure within the data set. Small angles between the vectors from the origin to variable coordinates indicate strong positive correlation; angles at 90

degrees indicate no correlation; and angles close to 180 degrees indicate strong negative correlation. Likewise, a plot of sample coordinates on these same axes will be the best two-dimensional representation of Euclidean relations among the samples in log-concentration space. Displaying both objects and variables on the same plot makes it possible to examine the contributions of specific elements to group separation. Such a plot is commonly referred to as a "biplot" in reference to the simultaneous plotting of objects and variables. The variable inter-relationships inferred from a biplot can be verified directly by inspecting bivariate elemental concentration plots.

Whether a group can be discriminated easily from other groups can be evaluated visually in two dimensions or statistically in multiple dimensions. A metric known as the Mahalanobis distance (or generalized distance) makes it possible to describe the separation between groups or between individual samples and groups on multiple dimensions. The Mahalanobis distance of a specimen from a group centroid (Bieber et al. 1976; Bishop and

Table 1c. Descriptive Statistics for Chert from the Mitchell Plantation.

Element	Mean	St. Dev.	% St. Dev.	No. Obs.	Minimum	Maximum
AS	0.396	0.394	99.592	12	0.126	1.537
BA	84.581	99.951	118.171	16	15.600	388.300
LA	0.670	0.514	76.741	16	0.175	1.960
LU	0.166	0.116	70.223	16	0.032	0.436
ND	1.241	0.789	63.620	16	0.293	2.899
SM	0.611	0.393	64.324	16	0.108	1.441
U	0.566	0.567	100.145	16	0.071	2.102
YB	1.117	0.776	69.451	16	0.220	3.024
CE	1.556	1.085	69.700	16	0.381	3.763
CO	0.258	0.307	118.962	16	0.047	1.092
CR	0.382	0.305	79.977	12	0.103	1.196
EU	0.187	0.119	63.615	16	0.034	0.437
FE	278.931	173.971	62.371	16	60.100	736.000
HF	0.025	0.018	71.617	14	0.007	0.074
SB	0.335	0.132	39.523	16	0.154	0.670
SC	0.614	0.481	78.458	16	0.188	1.780
TB	0.248	0.166	67.007	16	0.046	0.661
TH	0.031	0.019	62.682	16	0.009	0.069
ZN	1.759	0.873	49.631	16	0.610	3.370
AL	2127.844	382.683	17.985	16	1697.000	2912.800
CA	521.408	444.856	85.318	12	180.600	1719.400
MN	17.874	14.449	80.834	16	7.010	66.360
NA	124.344	19.469	15.657	16	90.000	154.500

Neff 1989) is defined by:

$$D^2_{y,X} = [y - \overline{X}]^t I_x [y - \overline{X}]$$

Where y is the 1 x m array of logged elemental concentrations for the specimen of interest, X is the n x m data matrix of logged concentrations for the group to which the point is being compared with $\overline{X}$ being it 1 x m centroid, and I_x is the inverse of the m x m variance-covariance matrix of group X. Because Mahalanobis distance takes into account variances and covariances in the multivariate group, it is analogous to expressing distance from a univariate mean in standard deviation units. Like standard deviation units, Mahalanobis distances can be converted into probabilities of group membership for individual specimens. For relatively small sample sizes, it is appropriate to base probabilities on Hotelling's T^2, which is the multivariate extension of the univariate Student's t.

When group sizes are small, Mahalanobis distance-based probabilities can fluctuate dramatically depending upon whether or not each specimen is assumed to be a member of the group to which it is being compared. Harbottle (1976) calls this phenomenon "stretchability" in reference to the tendency of an included specimen to stretch the group in the direction of its own location in elemental concentration space. This problem can be circumvented by cross-validation, that is, by removing each specimen from its presumed group before calculating its own probability of membership (Baxter 1992; Leese and Main 1994). This is a conservative approach to group evaluation that sometimes excludes true group members.

Small sample and group sizes place further constraints on the use of Mahalanobis distance. When there are more elements than samples, the group variance-covariance matrix is singular, thus rendering calculation of I_x (and D^2 itself) impossible. Therefore, dimensionality of the groups must be reduced. One approach would be to eliminate elements considered irrelevant or redundant. The problem with this approach is that the investigator's preconceptions about which elements should

Table 2. Principal Components Analysis of SE Virginia Cherts (Bolster's Store, Williamson, and Mitchell Plantation) with Eigenvalues and Percentage of Variance Explained.

Eigenvalue	%Variance	Cum.%Var.
2.462	38.42	38.42
1.602	25.00	63.42
0.5084	7.934	71.35
0.4264	6.655	78.01
0.3100	4.838	82.85
0.2378	3.712	86.56
0.1984	3.096	89.65
0.1467	2.290	91.94
0.1271	1.984	93.93
0.1058	1.651	95.58
0.06135	0.9574	96.54
0.05443	0.8494	97.38
0.04541	0.7087	98.09
0.03898	0.6084	98.70
0.02538	0.3960	99.10
0.01661	0.2591	99.36
0.01377	0.2148	99.57
0.008784	0.1371	99.71
0.006759	0.1055	99.81
0.004634	0.07231	99.89
0.004276	0.06673	99.95
0.001657	0.02587	99.98
0.001315	0.02052	100.0

be discriminating may not be valid. It also squanders the main advantage of multielement analysis, namely the capability of measuring a large number of elements. An alternative approach is to calculate Mahalanobis distances using the principal component scores. This approach entails only the assumption, entirely reasonable in light of the above discussion of PCA, that most group-separating differences should be visible on the first several PCs. Unless a data set is extremely complex, containing numerous distinct groups, using enough components to subsume 90% of the total variance in the data is generally assumed to yield Mahalanobis distances that approximate Mahalanobis distances in full elemental concentration space.

Lastly, Mahalanobis distance calculations are also quite useful for handling missing data (Sayre 1975). When many specimens are analyzed for a large number of elements, it is almost certain that a few element concentrations will be missed for some of the specimens. This occurs most frequently when the concentration for an element is near the detection limit. Rather than eliminate the specimen or the element from consideration, it is possible to substitute a missing value by replacing it with a value that minimizes the Mahalanobis distance for the specimen from the group centroid. Thus, those few specimens that are missing a single concentration value can still be used in group calculations.

Results and Discussion

In this particular investigation, we know that the samples were collected from three different locations (i.e., Bolster's Store, Williamson, and Mitchell Plantation). Therefore, our primary goal is to determine if the specimens at each location group in such a way as to enable successful differentiation of the chert from each location from one another. If the source groups are different, how well does this differentiation hold for the individual source samples and how do the chert source(s) in this study compare to other regional lithic sources? The nearest source that has been studied by INAA is the Brook Run (44CU122) jasper from Culpeper County, Virginia (Carr et al. 2004; Fernandez-Sardina et al. 1999; Monaghan et al. in press).

Analysis of the chert samples from Dinwiddie and Sussex counties in this study produced concentrations for up to 32 elements in the samples. A few elements, especially Cs, Rb, Sr, Ta, and Dy, were below the detection limit in a majority of the samples. These elements were therefore dropped from consideration during statistical analysis of the data set.

A Comparison of the SE Virginia Sources

Tables 1a, 1b, and 1c list the descriptive statistics for the three chert outcrops in this study, including the sample means, standard deviations, percent standard deviation, and minimum and maximum sample values. The large percent standard deviations observed for most of the elements are not surprising but are rather typical of many varieties of chert. The Mitchell Plantation chert is least variable and has lower concentrations for Fe and higher con-

centrations for the heavy REEs (i.e., Tb, Lu, and Yb) than chert samples from Bolster's Store or the Williamson source. One of the more interesting findings occurs for a few samples from Bolster's Store. The measured concentration for zinc in sample DHR158 (Zn = 2.19%) and to a lesser degree zinc in samples DHR153 (Zn = 958 ppm), DHR155 (Zn = 3512 ppm), and DHR160 (Zn = 139 ppm) are several orders of magnitude above all other samples. An inspection of gamma-ray spectra for these samples also finds them to have measurable concentrations for silver and gold (i.e., low ppm). This is supported by a visual inspection of the samples, which confirms the presence of a vein of metallic droplets–undoubtedly the cause of higher Zn, Ag, and Au concentrations. What is most clear from the tables is that if one examines elemental data for chert in a univariate fashion (i.e., one element at a time), it can be very difficult to differentiate samples from another. Obviously, more powerful multivariate methods are needed.

The first step in the multivariate analysis was to perform a log base-10 transformation on the 27 elements remaining after elimination of the five elements cited above. Any remaining missing values for individual samples were replaced using the Mahalanobis distance minimization routine mentioned earlier. Next, the log base-10 data for all three chert outcrops were merged into a single data set so that a PCA could be performed. Table 2 presents the PCA results, including the eigenvectors, amount of variance subsumed by the individual PCs, and the cumulative variance. One notes that the first eight components account for about 92 percent of the variance in the data set.

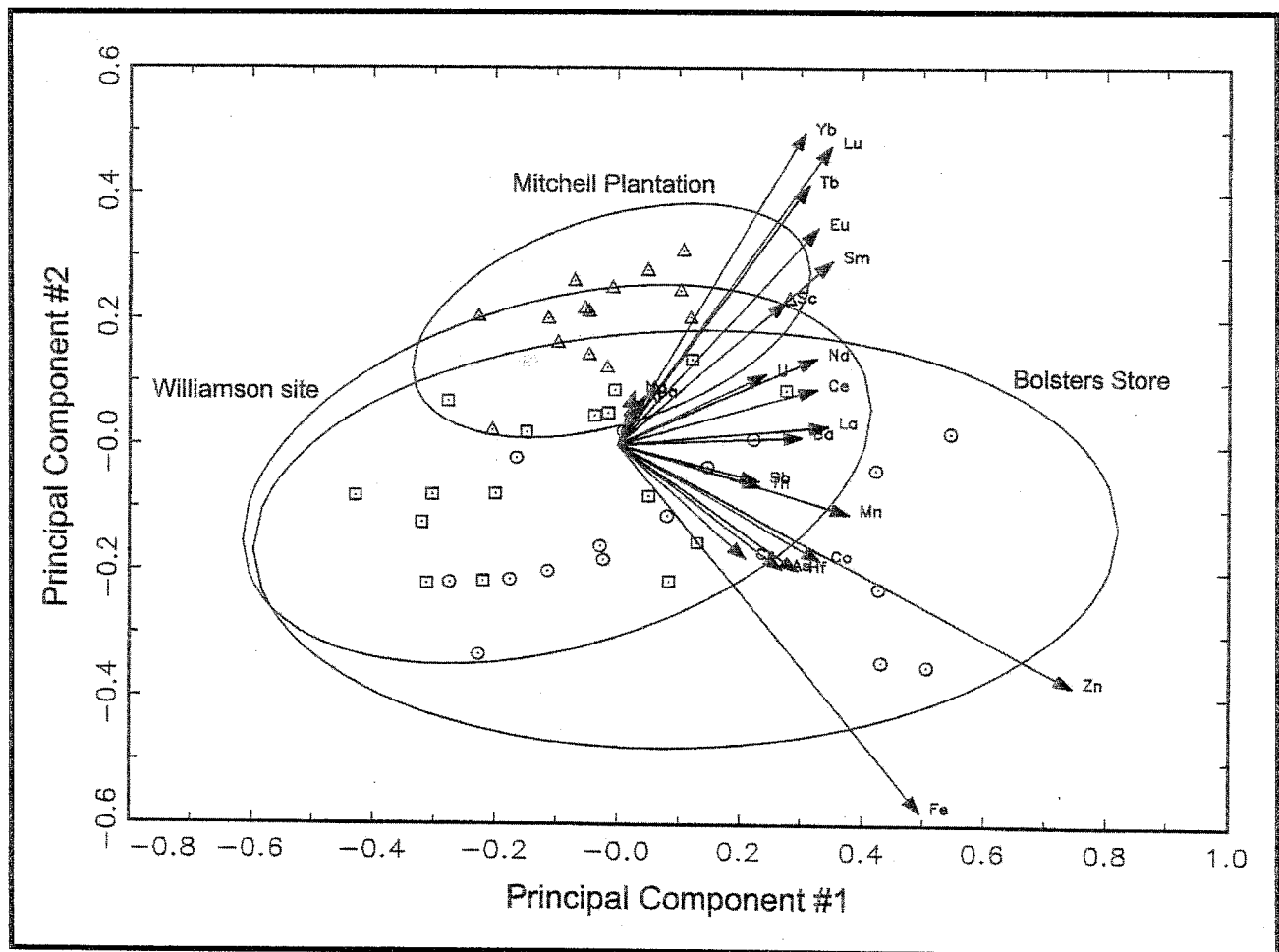Biplots of the first and second PCs and the

Figure 3. Biplot of the First Two Principal Components for SE Virginia Chert. The vectors show the direction of increasing concentration for each element. Longer vectors indicate a greater contribution to the overall variance. The ellipses are plotted at the 90% confidence level for each outcrop.

first and third PCs are shown in Figures 3 and 4, respectively. The plots indicate that there are some differences between the locations of the group centroids and the group dispersion and the relative orientation of the groups to one another. The elements Fe and Zn are higher in chert from Bolster's store than the Mitchell Plantation. The heavy REEs have higher concentrations in the chert samples from Bolster's Store and Mitchell Plantation than in samples from Williamson. A plot of the elements Zn versus Yb shown in Figure 5 is the best two-dimensional plot for showing the differences between the Mitchell Plantation and Williamson chert samples.

As a test of posterior classification of the source samples, Mahalanobis distance calculations were performed on the three groups using the first eight PCs, which subsume almost 92% of the variance. The jackknifing option was used (i.e., remov-

ing the sample under consideration before calculating its membership probability). The results in Tables 3 and 4 indicate that chert from the Williamson site can be differentiated from both other sources without error; chert from the Bolster's Store has only one erroneous assignment out of 16; and chert from the Mitchell Plantation has four errors out of 16 samples.

A Comparison of SE Virginia Sources and Brook Run Jasper

The 15 specimens of Brook Run jasper analyzed earlier had missing values for Hf, Ni, Ca, K, and Ti in a majority of the samples. Therefore, these elements had to be deleted along with the five elements mentioned earlier from the Brook Run and SE Virginia cherts before other statistical testing was possible. Both data sets were log base-10 trans-
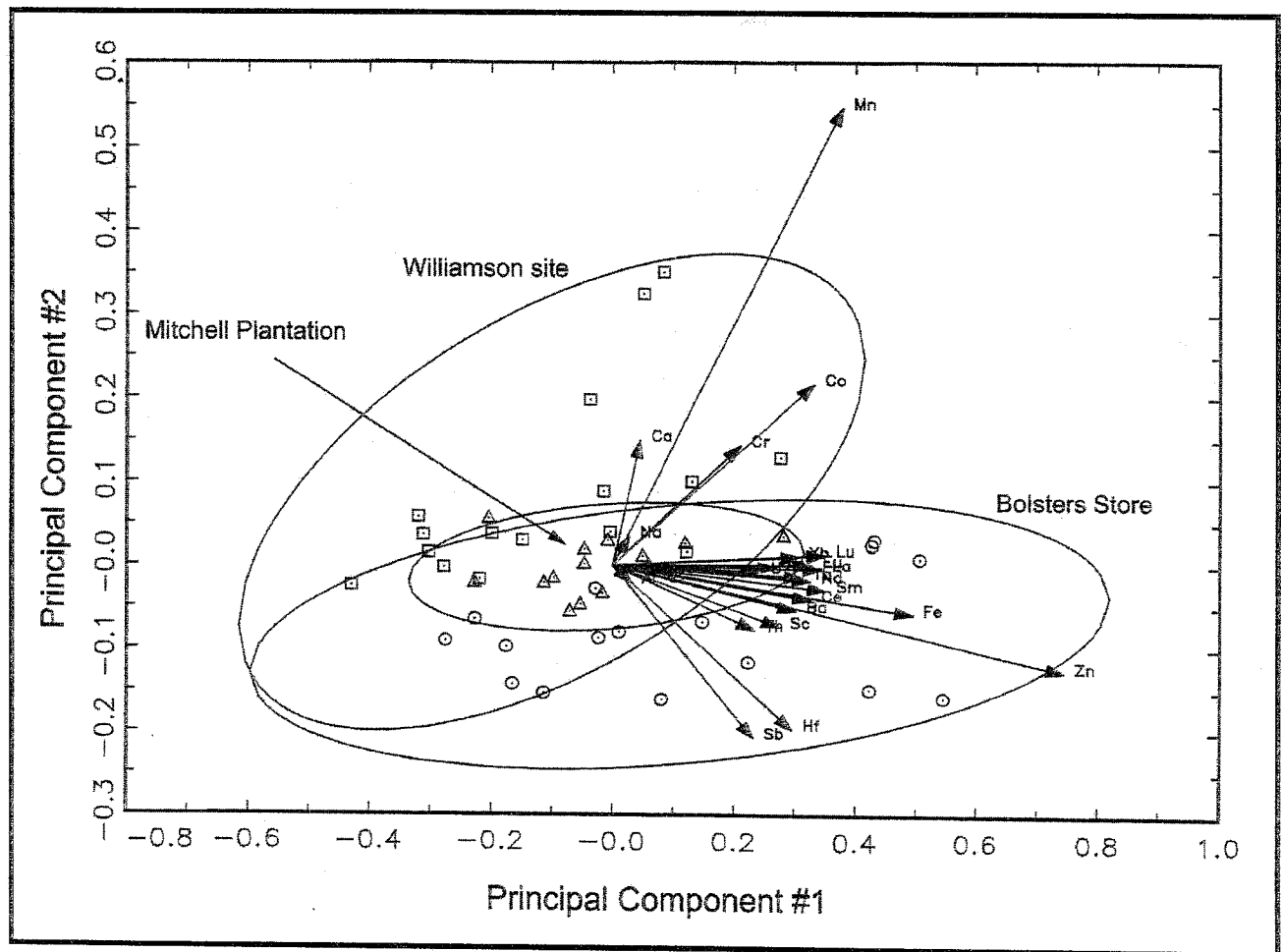

Figure 4. Biplot of the First and Third Principal Components for SE Virginia Chert. The ellipses are plotted at the 90% confidence level for each outcrop.

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Table 3. Mahalanobis Distance Calculations and Posterior Classification for Williamson, Bolster's Store, and Mitchell Plantation.

ID.NO.	PC-CMS1	PC-CMS2	PC-CMS3	From:	Into:
DHR148	67.971	5.016	0.051	1	1
DHR149	57.235	4.639	0.031	1	1
DHR150	9.170	7.839	0.002	1	1
DHR151	78.783	9.758	0.070	1	1
DHR152	37.395	1.525	0.024	1	1
DHR153	22.358	0.208	0.001	1	1
DHR154	92.163	1.961	0.003	1	1
DHR155	9.830	0.153	0.000	1	1
DHR156	99.982	13.092	0.163	1	1
DHR157	9.607	20.248	4.290	1	2
DHR158	1.502	0.064	0.000	1	1
DHR159	62.588	41.023	0.189	1	1
DHR160	30.926	2.018	0.019	1	1
DHR161	82.839	15.413	3.377	1	1
DHR162	42.164	1.717	0.081	1	1
DHR163	78.192	4.616	0.035	1	1
DHR164	10.720	95.621	0.435	2	2
DHR165	0.673	88.350	0.046	2	2
DHR166	0.738	8.194	0.041	2	2
DHR167	2.587	53.454	0.309	2	2
DHR168	0.209	75.949	0.267	2	2
DHR169	3.017	52.840	1.544	2	2
DHR170	6.136	68.357	0.050	2	2
DHR171	15.569	78.392	0.409	2	2
DHR172	4.472	79.011	2.279	2	2
DHR173	0.421	27.464	0.377	2	2
DHR174	0.092	9.976	0.007	2	2
DHR175	2.242	3.018	2.293	2	2
DHR176	3.464	84.078	0.011	2	2
DHR177	0.450	44.349	0.220	2	2
DHR178	0.083	34.930	0.004	2	2
DHR179	0.177	9.155	0.002	2	2
DHR180	7.517	6.231	1.246	3	1
DHR181	11.089	3.930	80.407	3	3
DHR182	6.899	7.400	71.316	3	3
DHR183	32.335	24.894	1.248	3	1
DHR184	9.040	1.416	37.824	3	3
DHR185	8.872	7.104	72.942	3	3
DHR186	12.761	10.176	38.887	3	3
DHR187	16.710	9.963	78.934	3	3
DHR188	12.761	9.825	54.775	3	3
DHR189	6.109	1.783	70.045	3	3
DHR190	13.082	5.970	93.973	3	3
DHR191	16.383	27.580	25.705	3	2
DHR192	30.654	16.064	25.356	3	1
DHR193	17.018	9.825	99.485	3	3
DHR194	5.625	4.722	11.152	3	3
DHR195	6.682	4.240	42.338	3	3

Groups are:1, PC-CMS1 - Bolster's Store; 2, PC-CMS2 - Williamson Site; and 3, PC-CMS3 - Mitchell Plantation.

Table 4. Summary of Classification Success Classified into Group.

Group	PC-CMS1	PC-CMS2	PC-CMS3	Total
PC-CMS1	15	1	0	16
PC-CMS2	0	16	0	16
PC-CMS3	3	1	12	16
Total	18	18	12	48

formed and any remaining missing values from the few specimens were replaced by Mahalanobis minimization as before. A new PCA was performed on the data and the results show that the first seven PCs subsume in excess of 90% of the variance. Figure 6 shows the SE Virginia and Brooks Run jasper specimens plotted against the first and third PCs. Tables 5 and 6 report the results of the posterior classification comparing the Brook Run jasper and SE Virginia cherts to each other. The classification

yields a perfect differentiation. These results, along with the near perfect discrimination between the three chert sources, are very encouraging. They suggest that lithic provenance studies may have a solid grounding in eastern Virginia. The characterization of the remaining lithic sources needs to be completed in the near future to finish the evaluation process and lay the groundwork for interpretive archaeological studies.
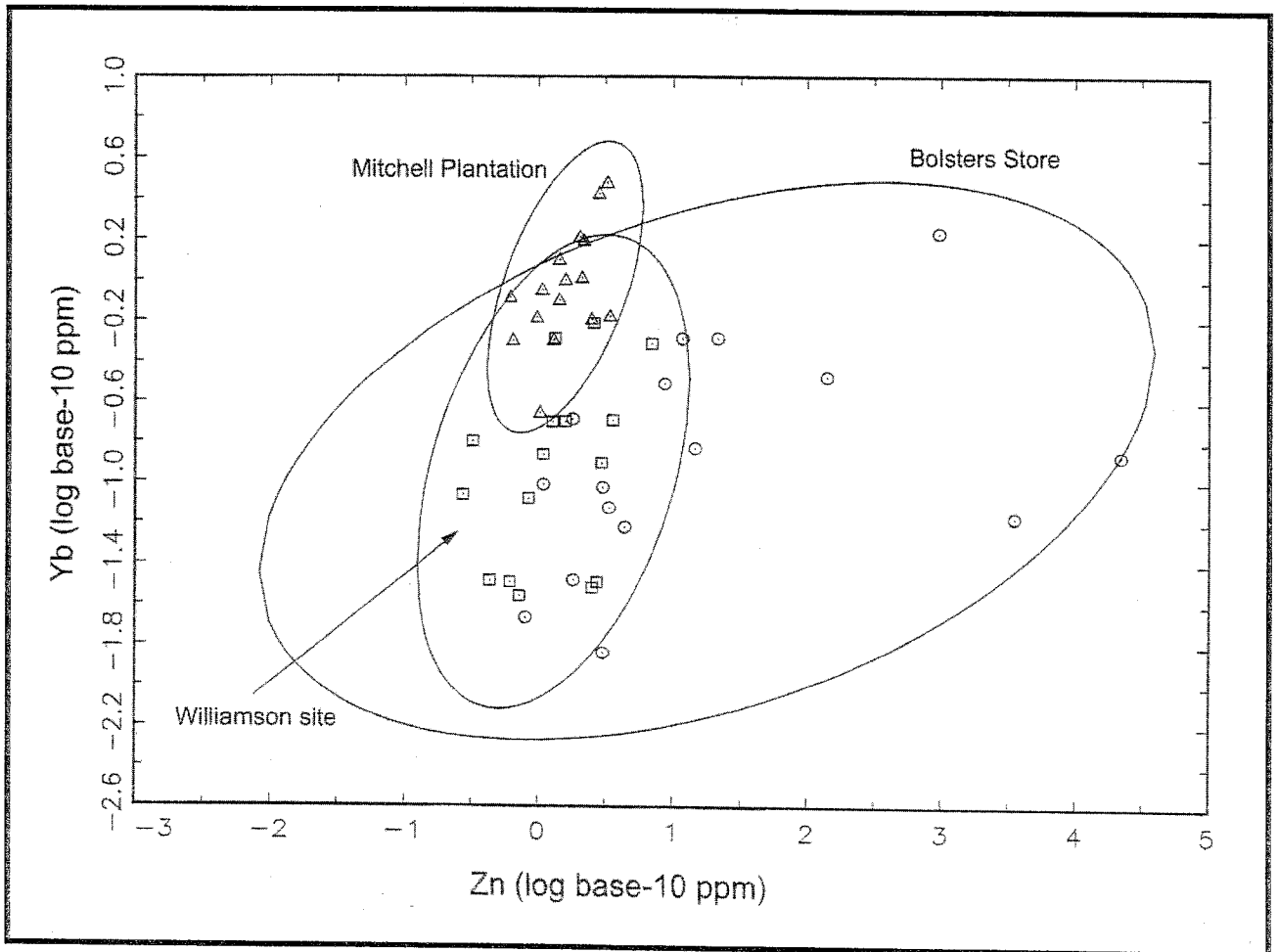
Acknowledgements

Figure 5. Bivariate Plot of Yb Versus Zn for Chert from Three Outcrops in SE Virginia. The ellipses are plotted at the 90% confidence level for each outcrop.

Table 5. Mahalanobis Distance Calculation and Posterior Classification for SE Virginia Cherts and Brook Run Jasper.

ID.NO.	PC-DHR	PC-BRVA	From:	Into:	ID.NO.	PC-DHR	PC-BRVA	From:	Into:
DHR148	30.197	0.000	1	1	DHR180	83.686	0.000	1	1
DHR149	47.072	0.000	1	1	DHR181	67.246	0.000	1	1
DHR150	9.093	0.000	1	1	DHR182	50.593	0.000	1	1
DHR151	65.107	0.000	1	1	DHR183	98.680	0.000	1	1
DHR152	15.846	0.000	1	1	DHR184	80.470	0.000	1	1
DHR153	1.818	0.000	1	1	DHR185	70.052	0.000	1	1
DHR154	40.746	0.000	1	1	DHR186	89.487	0.000	1	1
DHR155	3.659	0.000	1	1	DHR187	91.645	0.000	1	1
DHR156	85.128	0.000	1	1	DHR188	79.737	0.000	1	1
DHR157	93.082	0.000	1	1	DHR189	66.146	0.000	1	1
DHR158	0.025	0.000	1	1	DHR190	91.717	0.000	1	1
DHR159	88.222	0.000	1	1	DHR191	81.265	0.000	1	1
DHR160	11.672	0.000	1	1	DHR192	78.922	0.000	1	1
DHR161	99.770	0.000	1	1	DHR193	94.187	0.000	1	1
DHR162	29.797	0.000	1	1	DHR194	65.143	0.000	1	1
DHR163	34.530	0.000	1	1	DHR195	79.755	0.000	1	1
DHR164	50.918	0.000	1	1					
DHR165	65.654	0.000	1	1	CHR001	0.000	50.025	2	2
DHR166	32.555	0.000	1	1	CHR002	0.000	78.068	2	2
DHR167	56.561	0.000	1	1	CHR003	0.000	85.996	2	2
DHR168	55.666	0.000	1	1	CHR004	0.000	9.829	2	2
DHR169	67.501	0.000	1	1	CHR005	0.001	15.051	2	2
DHR170	25.791	0.000	1	1	CHR006	0.006	50.632	2	2
DHR171	0.965	0.000	1	1	CHR007	0.000	85.079	2	2
DHR172	90.521	0.000	1	1	CHR008	0.000	52.616	2	2
DHR173	22.298	0.000	1	1	CHR009	0.000	67.497	2	2
DHR174	0.040	0.007	1	1	CHR010	0.003	16.136	2	2
DHR175	89.614	0.000	1	1	CHR011	0.000	16.489	2	2
DHR176	69.186	0.000	1	1	CHR012	0.000	83.491	2	2
DHR177	42.516	0.000	1	1	CHR013	0.002	64.126	2.	2
DHR178	14.481	0.000	1	1	CHR014	0.000	21.600	2	2
DHR179	19.484	0.001	1	1	CHR015	0.000	59.730	2	2

Groups:1, PC-DHR - SE Virginia; 2, PC-BRVA - Brook Run.

Table 6. Summary of Classification Success.

Group	PC-DHR	PC-BRVA	Total
PC-DHR	48	0	48
PC-BRVA	0	15	15
Total	48	15	63

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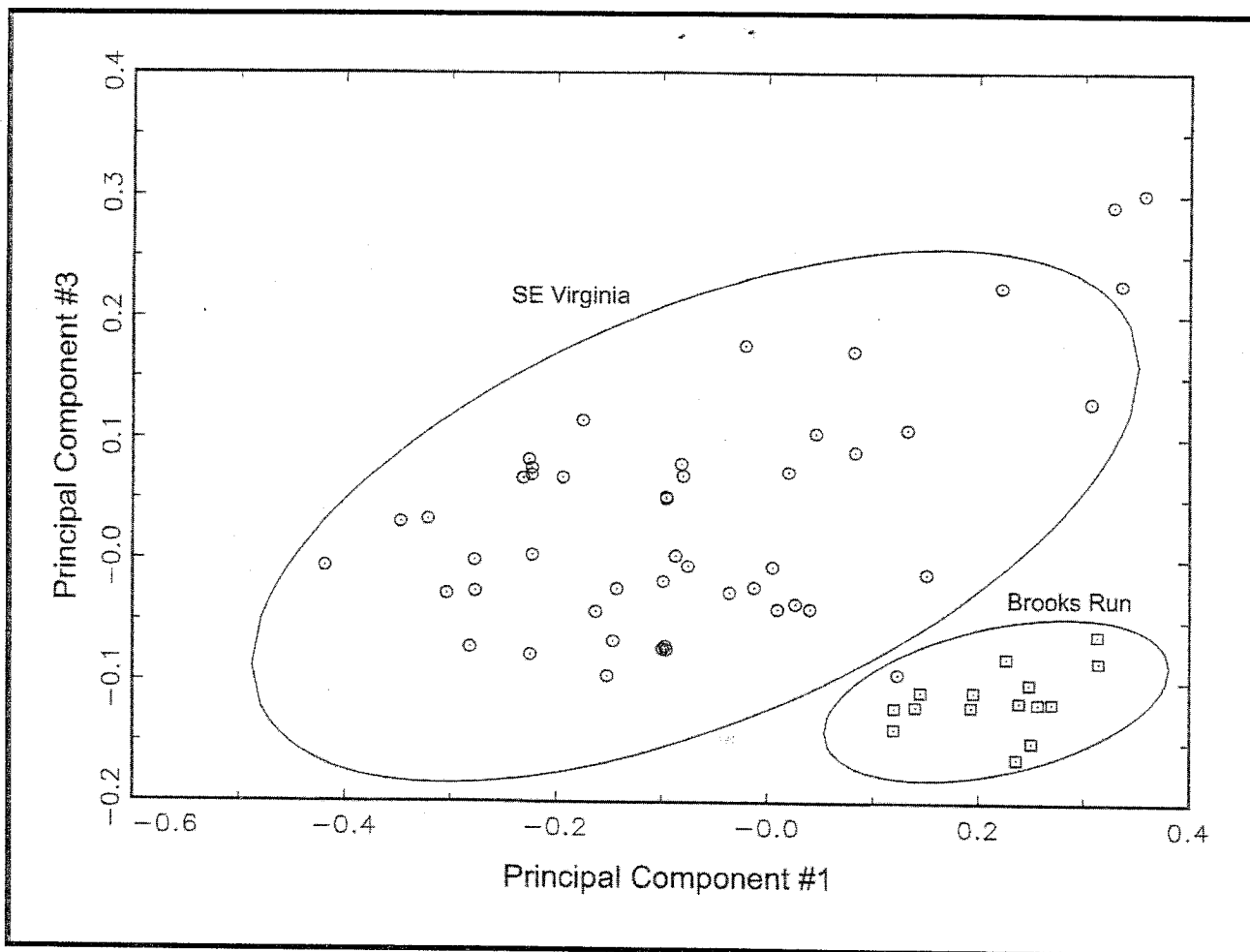
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