Instrumental Neutron Activation Analysis of Afro-Caribbean Ware Pottery from Brimstone Hill Fortress, St. Kitts, West Indies

Report Prepared by:
Robert J. Speakman and Michael D. Glascock
Archaeometry Laboratory
Missouri University Research Reactor
University of Missouri
Columbia, MO 65211

Report Prepared For:

Todd Ahlman
Department of Anthropology
The University of Montana
Missoula, MT 59812-4918

March 29, 2006

Introduction

Forty-five Afro-Caribbean pottery and clays from Brimstone Hill Fortress National Park, St. Kitts, West Indies were analyzed by instrumental neutron activation analysis (INAA) at the University of Missouri Research Reactor Center (MURR). Here, we describe sample preparation and analytical techniques used at MURR and report the subgroup structure identified through quantitative analysis of the ceramic compositional data set.

Sample Preparation

Pottery samples were prepared for INAA using procedures standard at MURR. Fragments of about $1cm^2$ were removed from each sample and abraded using a silicon carbide burr in order to remove glaze, slip, paint, and adhering soil, thereby reducing the risk of measuring contamination. The samples were washed in deionized water and allowed to dry in the laboratory. Once dry, the individual sherds were ground to powder in an agate mortar to homogenize the samples. Archival samples were retained from each sherd (when possible) for future research.

Two analytical samples were prepared from each source specimen. Portions of approximately 150 mg of powder were weighed into clean high-density polyethylene vials used for short irradiations at MURR. At the same time, 200 mg of each sample was weighed into clean high-purity quartz vials used for long irradiations. Individual sample weights were recorded to the nearest 0.01 mg using an analytical balance. Both vials were sealed prior to irradiation. Along with the unknown samples, Standards made from National Institute of Standards and Technology (NIST) certified standard reference materials of SRM-1633a (coal fly ash) and SRM-688 (basalt rock) were similarly prepared, as were quality control samples (e.g., standards treated as unknowns) of SRM-278 (obsidian rock) and Ohio Red Clay (a standard developed for in-house applications).

Irradiation and Gamma-Ray Spectroscopy

Neutron activation analysis of ceramics at MURR, which consists of two irradiations and a total of three gamma counts, constitutes a superset of the procedures used at most other NAA laboratories (Glascock 1992; Neff 1992, 2000). As discussed in detail by Glascock (1992), a short irradiation is carried out through the pneumatic tube irradiation system. Samples in the polyvials are sequentially irradiated, two at a time, for five seconds by a neutron flux of 8×10^{13} n cm^{-2} s^{-1} The 720-second count yields gamma spectra containing peaks for nine short-lived elements aluminum (Al), barium (Ba), calcium (Ca), dysprosium (Dy), potassium (K), manganese (Mn), sodium (Na), titanium (Ti), and vanadium (V). The samples are encapsulated in quartz vials and are subjected to a 24–hour irradiation at a neutron flux of 5×10^{13} n cm^{-2} s^{-1}. This long irradiation is analogous to the single irradiation utilized at most other laboratories. After the long irradiation, samples decay for seven days, and then are counted for 1,800 seconds (the "middle count") on a high-resolution germanium detector coupled to an automatic sample changer. The middle count yields determinations of seven medium half-life elements, namely arsenic (As), lanthanum (La), lutetium (Lu), neodymium (Nd), samarium (Sm), uranium (U), and ytterbium (Yb). After an additional three- or four-week decay, a final count of 8,500 seconds is carried out on each sample. The latter measurement yields the following 17 long half-life elements: 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), zinc (Zn), and zirconium (Zr).

The element concentration data from the three measurements are tabulated in parts per million using the EXCEL spreadsheet program. Descriptive data for the archaeological samples were appended to the concentration spreadsheet. The data are also stored in a dBASE/FOXPRO database file useful for organizing, sorting, and extracting sample information. The data file enclosed with this report contains the sample database in EXCEL format.

Interpreting Chemical Data

The analyses at MURR described previously produced elemental concentration values for 32 or 33 elements in most of the analyzed samples. Data for Ba, K, Ni, and U was below detection limits in many and were subsequently removed from consideration during the analysis. Statistical analysis was subsequently carried out on base-10 logarithms of concentrations on the remaining 32 elements. Use of log concentrations rather than raw data compensates for differences in magnitude between the major elements, such as calcium, on one hand and trace elements, such as the rare earth or lanthanide elements (REEs). Transformation to base-10 logarithms also yields a more normal distribution for many trace elements.

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. 1975; Bishop and Neff 1989; Glascock 1992; Harbottle 1976; Neff 2000) and will only be 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. The locations of sources can also be inferred by comparing unknown specimens (i.e., ceramic artifacts) to knowns (i.e., clay samples) or by indirect methods such as the “criterion of abundance” (Bishop *et al*. 1992) or by arguments based on geological and sedimentological characteristics (e.g., Steponaitis *et al*. 1996). The ubiquity of ceramic raw materials usually makes it impossible to sample all potential “sources” intensively enough to create groups of knowns to which unknowns can be compared. Lithic sources tend to be more localized and compositionally homogeneous in the case of obsidian or compositionally heterogeneous as is the case for most cherts.

Compositional groups can be 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.

Initial hypotheses about source-related subgroups in the compositional data can be derived from non-compositional information (e.g., archaeological context, decorative attributes,

etc.) or from application of various pattern-recognition technique 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 which may depend upon the types and quantity of data available for interpretation.

The variables (measured elements) in archaeological and geological data sets are often correlated and frequently large in number. This makes handling and interpreting patterns within the data difficult. Therefore, it is often useful to transform the original variables into a smaller set of uncorrelated variables in order to make data interpretation easier. Of the above-mentioned pattern recognition techniques, PCA is a technique that transforms from the data from the original correlated variables into uncorrelated variables most easily.

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 approach it to transform the data into logarithms (e.g., 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 nearly normal distributions for the trace elements.

One frequently exploited strength of PCA, discussed by Baxter (1992), Baxter and Buck (2002), 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 (if the PCA was based on the variance-covariance matrix) or standardized log-concentration space (if the PCA was based on the correlation matrix). Displaying both objects and variables on the same plot makes it possible

to observe the contributions of specific elements to group separation and to the distinctive shapes of the various groups. 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. [Note that a bivariate plot of elemental concentrations is not a biplot.]

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 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 1994; Leese and Main 1994). This is a conservative approach to group evaluation that may sometimes exclude true group members.

Small sample and group sizes place further constraints on the use of Mahalanobis distance: with more elements than samples, the group variance-covariance matrix is singular thus rendering calculation of I_x (and D^2 itself) impossible. Therefore, the dimensionality of the groups must somehow 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 be discriminate may not be valid. It also squanders the main advantage of multielement analysis, namely the capability to measure a large number of elements. An alternative approach is to calculate Mahalanobis distances with the scores on principal components extracted from the variance-covariance or correlation matrix for the complete data set. 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 at least 90% of the total variance in the data can be 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 which are missing a single concentration value can still be used in group calculations.

Results and Conclusions

Four compositional groups were identified, and Mahalanobis distance probabilities based on the first nine principal components (>96% of the cumulative variation) support the proposed subgroup structure. The six figures included at the end of this report illustrate the basic group structure identified during this analysis. PCA scores, descriptive information, group assignments, raw data, and Mahalanobis distance probabilities are included in the attached spreadsheet.

The differences between Groups1 and 2 are subtle, but exist nonetheless, indicating that NAA studies of pottery have the potential to contribute to understanding Afro-Caribbean pottery production and distribution. Clay samples 41 and 42 have clear affiliation with Group-1 (Table 1) whereas none of the clays suggest an affinity with Group-2. However, given that the differences between Groups 1 and 2 are so subtle, it seem likely that Group-2 also represents pottery production on St. Kitts. Group-3 contains two samples that are distinct in most projections of the data. Group-4 also contains two samples that also are distinct from the other samples in the dataset. At present, it is unclear if Groups-3 and 4 represent nonlocal production, or if they simply represent variation in the locally available raw materials on St. Kitts. Additional analyses seem justified to further explore chemical variability and Afro Caribbean pottery production/distribution in the West Indies.

Acknowledgments

We acknowledge Jonathon Dake, Mark Hammond, Nicole Little, Tessa Schut, and Corinne Rosania for their roles in preparing the samples for irradiation. This project was supported in part by NSF grant BCS-0504015 to the Archaeometry Laboratory of the Research Reactor, University of Missouri.

References Cited

Baxter, Michael J.

1992 Archaeological uses of the biplot—a neglected technique? In *Computer Applications and Quantitative Methods in Archaeology, 1991*, edited by G. Lock and J. Moffett. BAR International Series S577, 141–148. Tempvs Reparatvm, Archaeological and Historical Associates, Oxford.

1994a *Exploratory Multivariate Analysis in Archaeology*. Edinburgh University Press, Edinburgh.

1994b Stepwise discriminant analysis in archaeometry: a critique. *Journal of Archaeological Science* 21:659–666.

Bieber, Alan M. Jr., Dorothea W. Brooks, Garman Harbottle, and Edward V. Sayre

1976 Application of multivariate techniques to analytical data on Aegean ceramics. *Archaeometry* 18:59–74.

Bishop, Ronald L. and Hector Neff

1989 Compositional data analysis in archaeology. In *Archaeological Chemistry IV*, edited by R. O. Allen, pp. 576–586. Advances in Chemistry Series 220, American Chemical Society, Washington, D.C.

Bishop, Ronald L., Robert L. Rands, and George R. Holley

1982 Ceramic compositional analysis in archaeological perspective. In *Advances in Archaeological Method and Theory*, vol. 5, pp. 275–330. Academic Press, New York.

Glascock, Michael D.

1992 Characterization of archaeological ceramics at MURR by neutron activation analysis and multivariate statistics. In *Chemical Characterization of Ceramic Pastes in Archaeology*, edited by H. Neff, pp. 11–26. Prehistory Press, Madison, WI.

Harbottle, Garman

1976 Activation analysis in archaeology. *Radiochemistry* 3:33–72. The Chemical Society, London.

Leese, Morven N. and Peter L. Main

1994 The efficient computation of unbiased Mahalanobis distances and their interpretation in archaeometry. *Archaeometry* 36:307–316.

Loose, Richard W.

1977 Petrographic notes on selected lithic and ceramic materials. In *Settlement and Subsistence Along the Lower Chaco River*, edited by C. Reher, pp. 567–571. University of New Mexico Press, Albuquerque.

Lynott, Mark J., Hector Neff, James E. Price, James W. Cogswell, and Michael D. Glascock

2000 Inferences about prehistoric ceramics and people in Southeast Missouri: Results of ceramic compositional analysis. American Antiquity, 65(1): 103–126.

Neff, Hector

1992 Introduction. In *Chemical Characterization of Ceramic Pastes in Archaeology*, edited by H. Neff, pp. 1–10. Prehistory Press, Madison, WI.

1994 RQ-mode principal components analysis of ceramic compositional data. *Archaeometry* 36:115–130.

2000 Neutron activation analysis for provenance determination in archaeology. In *Modern Analytical Methods in Art and Archaeology*, edited by E. Ciliberto and G. Spoto, pp. 81–134. John Wiley and Sons, Inc., New York.

2002 Quantitative techniques for analyzing ceramic compositional data. In Ceramic *Source Determination in the Greater Southwest*, edited by D. M. Glowacki and H. Neff. Monograph 44, Cotsen Institute of Archaeology, UCLA, Los Angeles.

Rautman, Marcus L., Basil Gomez, Hector Neff, and Michael D. Glascock

1993 Neutron Activation Analysis of Late Roman Ceramics from Kalavasos-Kopetra and the Environs of the Vasilikos Valley. In *Report of the Department of Antiquities, Cyprus 1993*. Pp. 233–265.

Robinson, David G.

2004 Petrographis Analysis of Prehistoric Ceramics from two sites in La Junta Archaeological District, Presidio County, Trans-Pecos, Texas. In The Arroyo de la Presa Site: A Stratified Late Prehistoric Campsite Along the Rio Grande, Presidio County, Trans-Pecos Texas. Reports in Contract Archaeology 9. Center for Big Bend Studies, Sul Ross State University, Texas.

Sayre, Edward V.

1975 Brookhaven Procedures for Statistical Analyses of Multivariate Archaeometric Data. Brookhaven National Laboratory Report BNL-23128. New York.

Steponaitis, Vincas, M. James Blackman, and Hector Neff

1996 Large-scale compositional patterns in the chemical composition of Mississippian pottery. *American Antiquity* 61:555–572.

Weigand, Phil C., Garman Harbottle, and Edward V. Sayre

1977 Turquoise sources and source analysis: Mesoamerica and the southwestern U.S.A. In *Exchange Systems in Prehistory*, edited by T. K. Earle and J. E. Ericson, pp. 15–34. Academic Press, New York.

Table 1. Mahalanobis distance and posterior classification based on PC01-PC09 which account for more than 94% of the cumulative variation in the dataset.

Anid	Group-1	Group-2	Assigned Group
TMA021	31.86	0.02	Group-1
TMA023	98.09	0.00	Group-1
TMA024	14.38	0.00	Group-1
TMA025	80.87	0.07	Group-1
TMA027	67.15	0.00	Group-1
TMA028	94.80	0.00	Group-1
TMA031	18.97	0.01	Group-1
TMA032	82.04	0.00	Group-1
TMA033	19.98	0.00	Group-1
TMA034	52.20	0.00	Group-1
TMA036	87.30	0.00	Group-1
TMA038	1.98	0.00	Group-1
TMA041	57.68	2.14	Group-1
TMA042	35.35	0.09	Group-1

Anid	Group-1	Group-2	Assigned Group
TMA001	0.02	4.30	Group-2
TMA002	0.28	25.79	Group-2
TMA003	1.33	94.68	Group-2
TMA004	2.70	88.79	Group-2
TMA005	3.03	55.32	Group-2
TMA006	0.86	62.99	Group-2
TMA007	0.06	86.12	Group-2
TMA008	1.87	80.23	Group-2
TMA009	1.20	52.99	Group-2
TMA010	0.60	76.36	Group-2
TMA011	0.07	1.88	Group-2
TMA012	0.96	98.61	Group-2
TMA013	0.26	77.15	Group-2
TMA014	0.07	0.67	Group-2
TMA015	0.45	95.76	Group-2
TMA017	0.33	56.94	Group-2
TMA018	1.69	97.01	Group-2
TMA022	0.13	96.03	Group-2
TMA026	0.12	34.10	Group-2
TMA029	0.07	5.50	Group-2
TMA037	0.37	0.89	Group-2
TMA039	1.16	85.21	Group-2

Anid	Group-1	Group-2	Assigned Group

TMA020	0.00	0.00	Group-3
TMA040	0.00	0.00	Group-3

Anid	**Group-1**	**Group-2**	**Assigned Group**
TMA030	0.00	0.00	Group-4
TMA035	0.00	0.00	Group-4

Anid	**Group-1**	**Group-2**	**Assigned Group**
TMA016	30.79	36.57	Unassigned
TMA019	0.01	0.00	Unassigned
TMA043	0.11	0.06	Unassigned
TMA044	0.44	0.09	Unassigned
TMA045	0.28	0.02	Unassigned

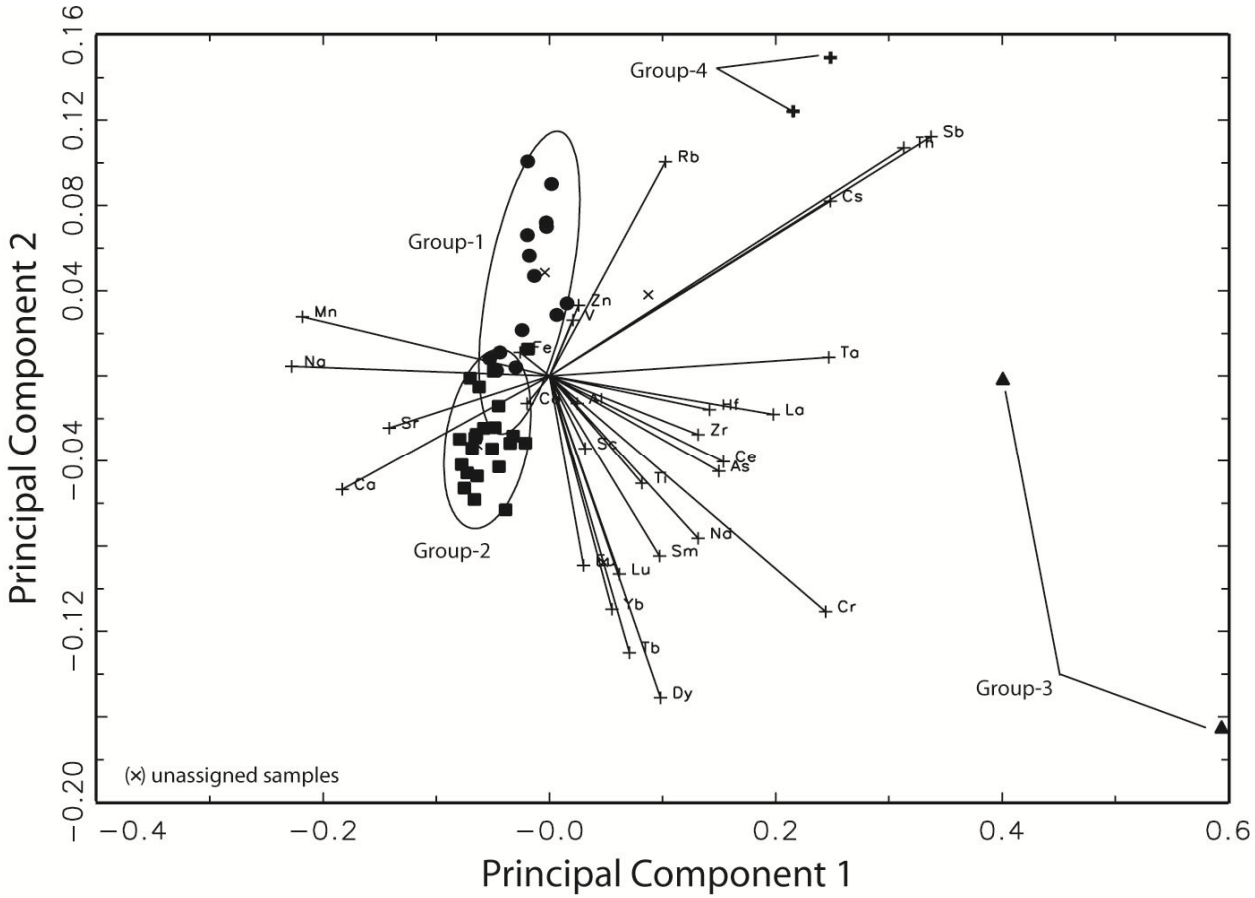


Figure 1. Biplot derived from PCA of the variance-covariance matrix of the St. Kitts pottery and clays. Ellipses represent 90% confidence level for membership in the groups.

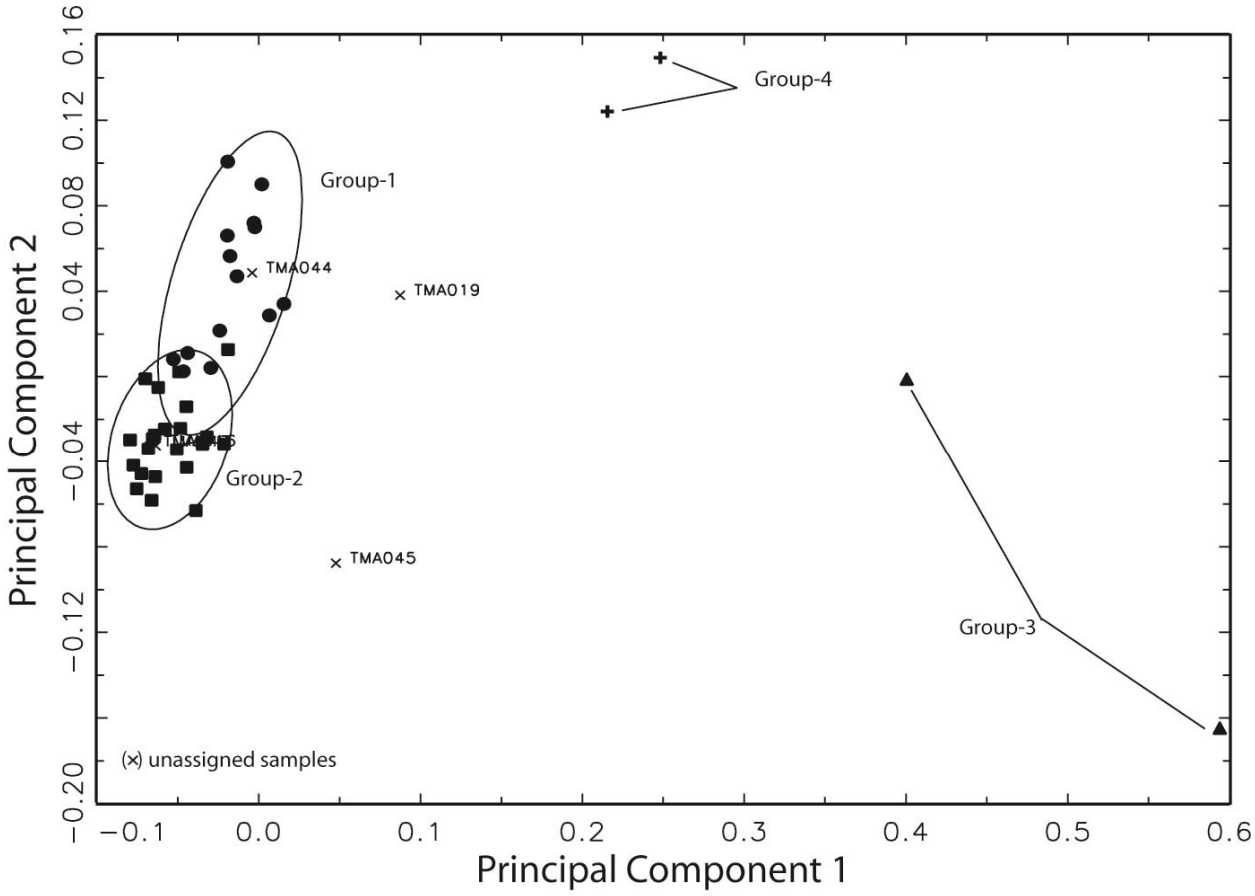


Figure 2. Same as Figure 1, but without vectors and with individual samples labeled. Ellipses represent 90% confidence level for membership in the groups.

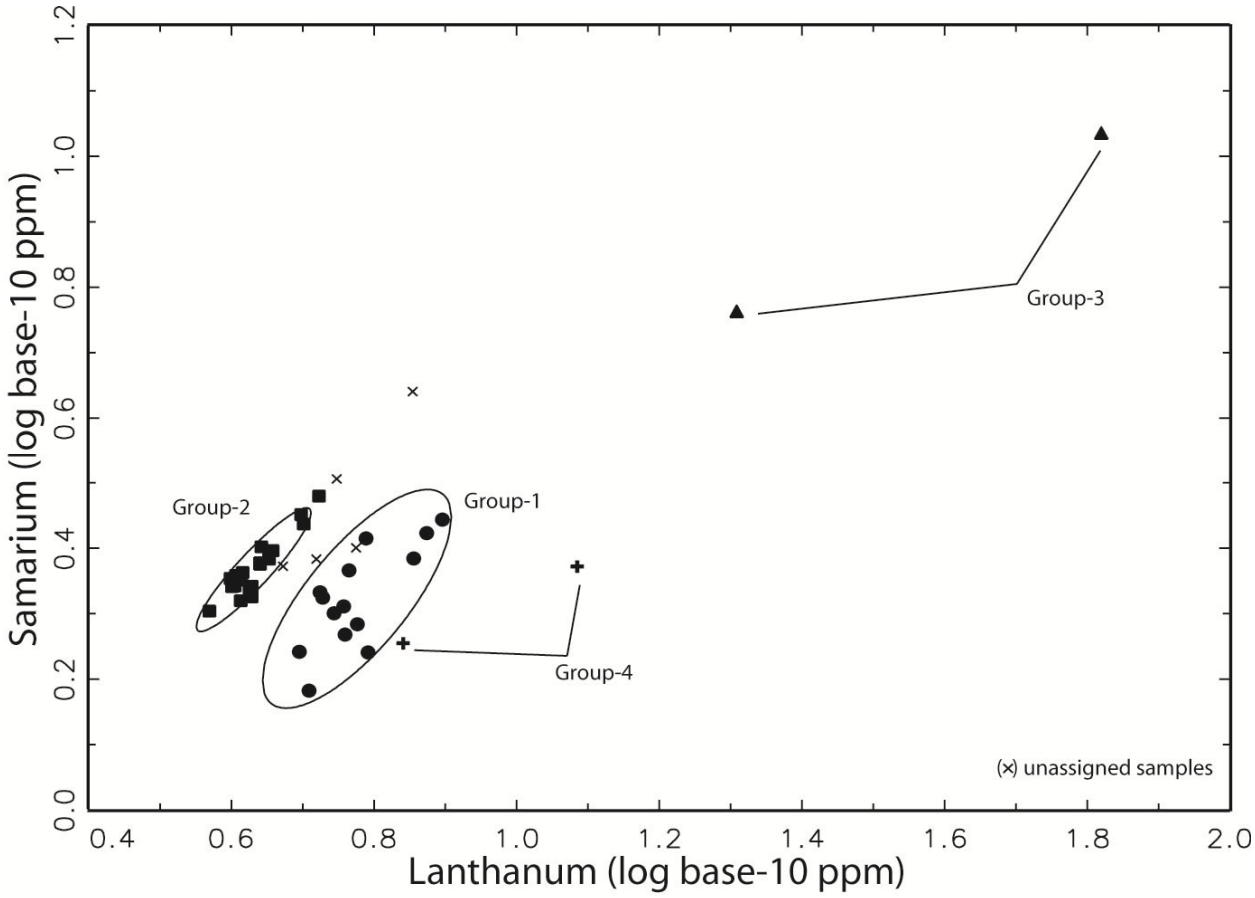


Figure 3. Bivariate plot of lanthanum and samarium base-10 logged concentrations showing the separation of the St. Kitts pottery groups. Ellipses represent 90% confidence level for membership in the groups.

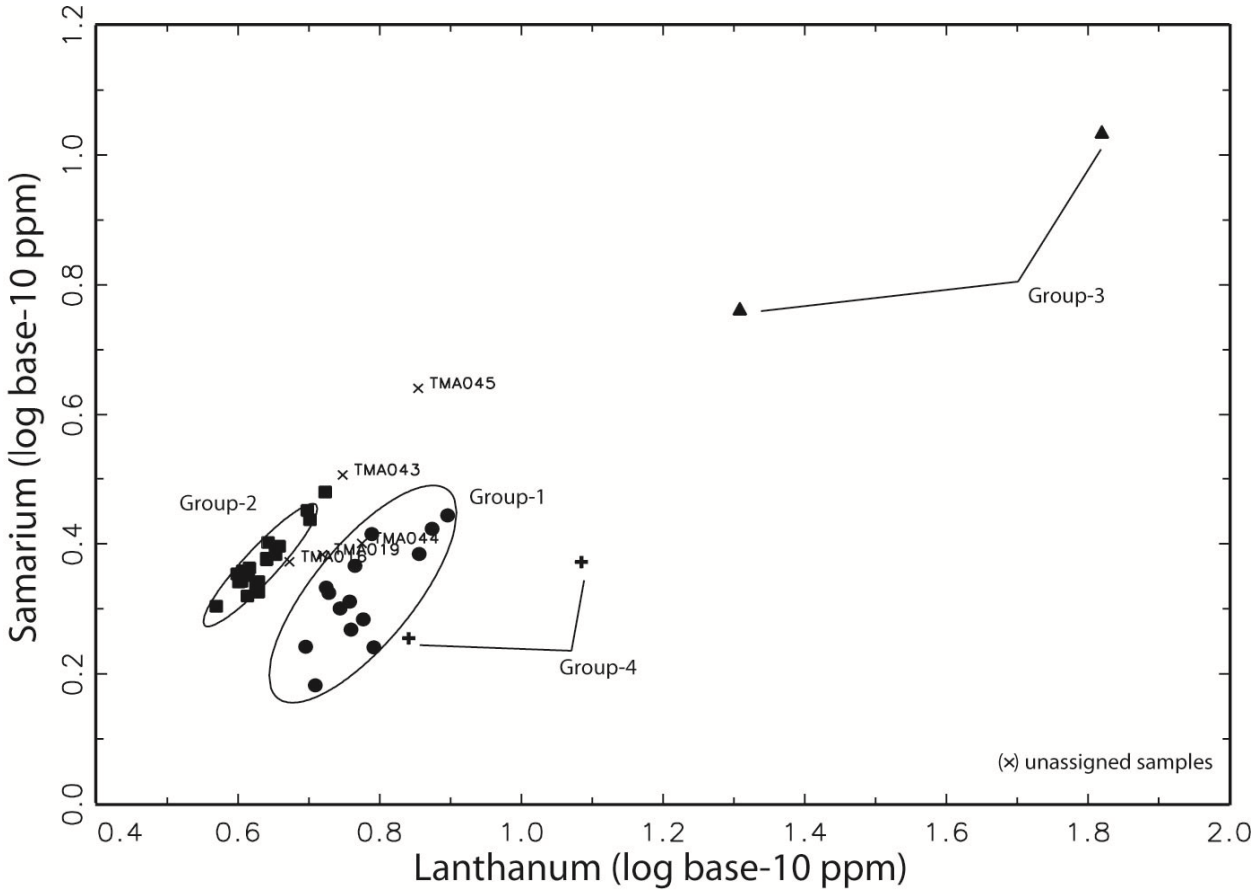


Figure 4. Same as Figure 3, but with unassigned samples labeled.

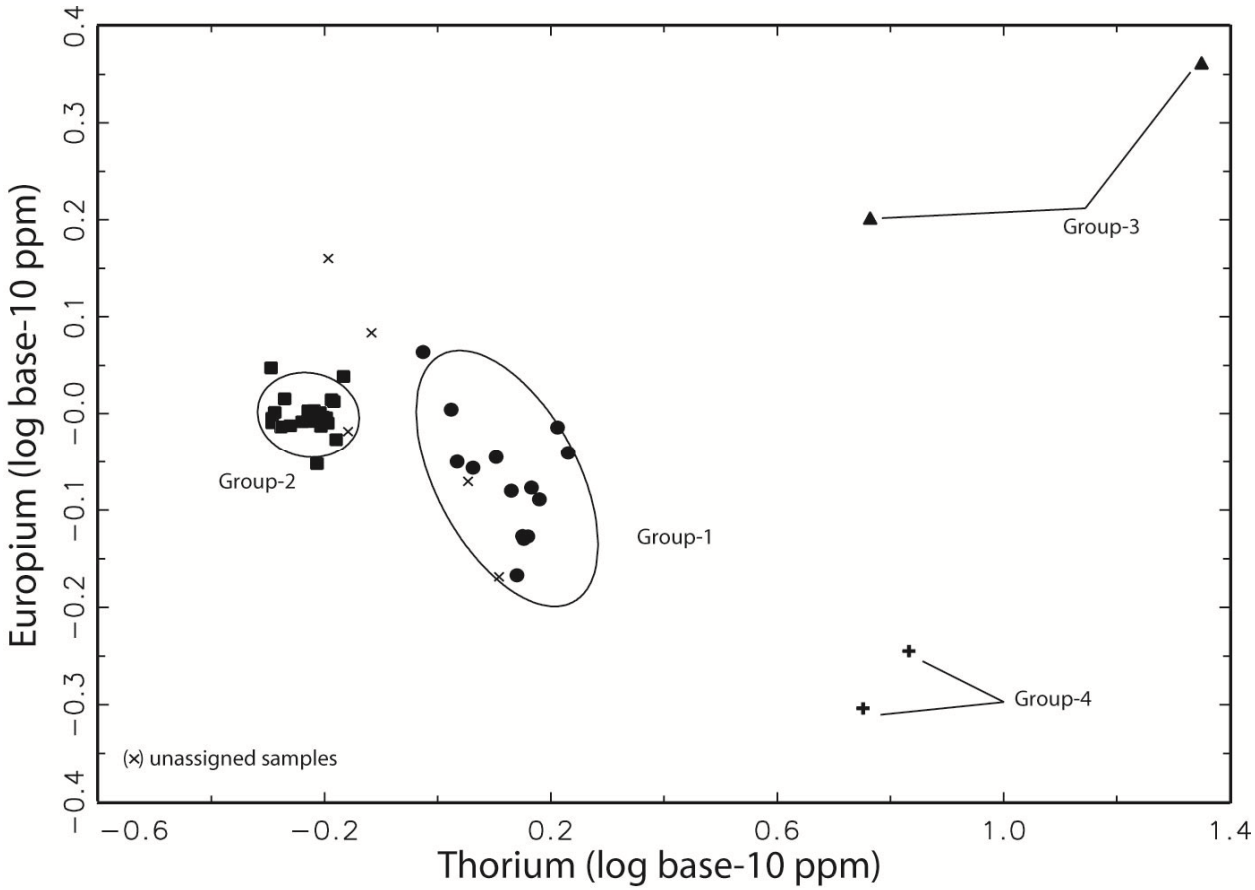


Figure 5. Bivariate plot of thorium and europium base-10 logged concentrations showing the separation of the St. Kitts pottery groups. Ellipses represent 90% confidence level for membership in the groups.

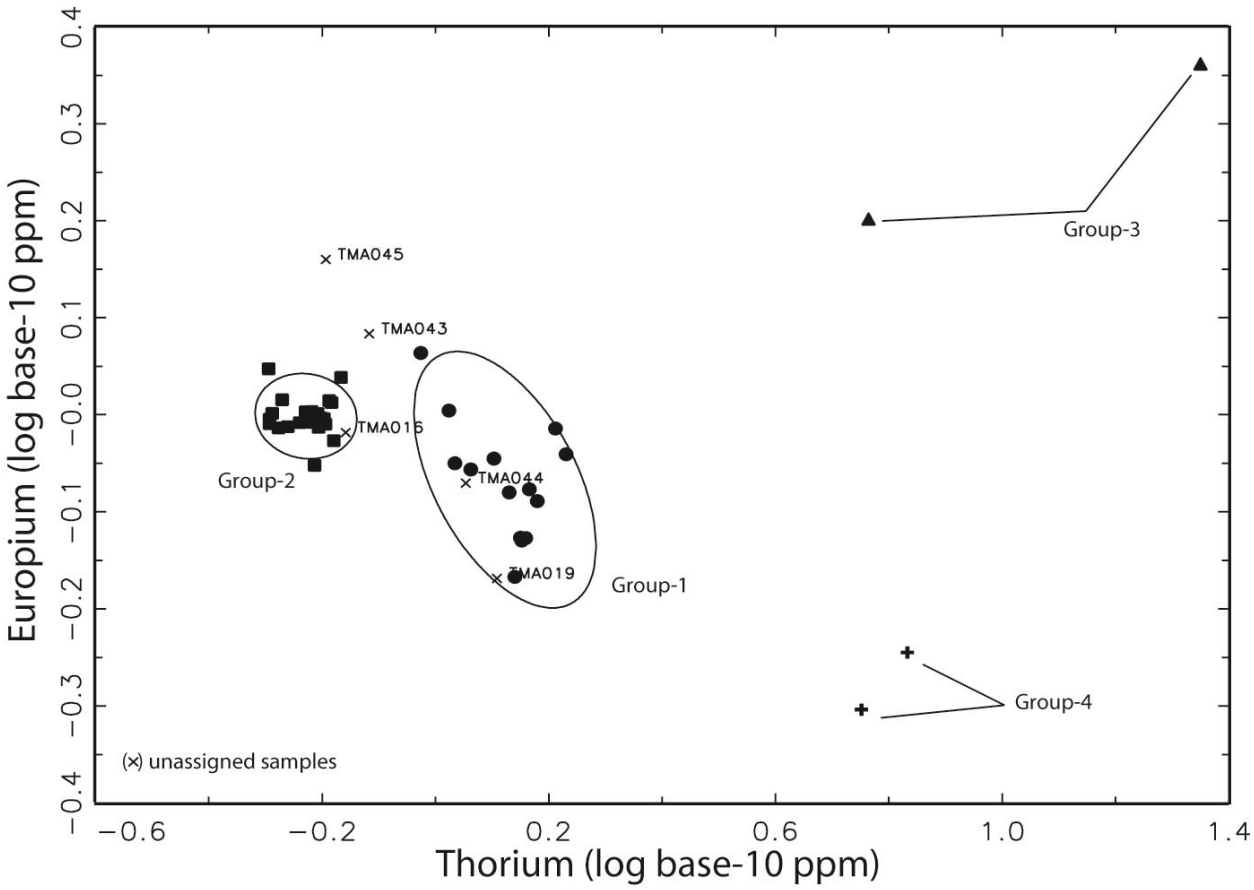


Figure 6. Same as Figure 5, but with unassigned samples labeled.