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Provenance determination of Bronze Age pottery using neutron activation analysis

Debra Ann Kipler-Koch

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PROVENANCE DETERMINATION OF BRONZE AGE POTTERY

USING NEUTRON ACTIVATION ANALYSIS

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April, 1989
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Many thanks to Dr. Robert Johnston, Dean of the College of Fine and Applied Arts, Rochester Institute of Technology, The Buffalo Materials Research Center; and The Department of Energy Sharing Grant Program for their strong support. I would also like to thank my husband and family for their love and understanding. Most of all, I would like to thank my advisor, Dr. Laura Ellen Tubbs, for all her help and guidance throughout my work.
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ABSTRACT:

Neutron activation analysis has been used for provenance determinations of Bronze Age pottery from two cities in the Jordan River and Dead Sea areas. A pottery shard group believed to represent the local clay composition of one of the sites based on statistical clustering procedures was used with a dilution factor method developed by H. Mommsen and colleagues (1) to determine the origin of the shards. Based on the dilution factor method, a provenance determination has been established for three of the thirty-two shards analyzed. Irradiations of 30 min, 1 hr, and 4 hr duration were performed using a two megawatt nuclear reactor. Isotopes observed were Ag 110m, La 140, Sc 46, Nb 95, Mn 56, K 40, K 42, Na 24, and Br 82. The overall error in the isotopic concentrations is taken to be 8%. This includes an estimate for the natural inhomogeneity in clay (1). In addition, mudbrick originally assumed to be representative of the local clay composition of the two cities was studied. The intent was to use these samples to form known clay composition groups. Mudbrick was shown not
to provide an accurate representation of the local clay composition.
INTRODUCTION:

The purpose of this project is to determine the provenance (origin) of ancient pottery recovered from Bronze Age cities surrounding the Dead Sea and Jordan River areas using neutron activation analysis. Provenance determination of pottery recovered during evacuation of a site provides information regarding possible contact between that site and sites of other geographical locations. In principle, pottery or clay samples of known provenance are analyzed to characterize concentrations of elements present in materials native to that site. A comparison of trace element concentrations of "known" samples with the concentrations found in pottery shards of interest provides an analysis of their possible sources. For this type of determination, clay samples of known origin are highly desirable.

Clay samples of known origin are rarely available. A frequently used method is to analyze a number of pottery samples from the same site and then separate them into groups with different elemental compositions (2). When one
group is predominant at a site, it can then be taken to represent the local clay composition. This assumption however, becomes more problematic when two or more composition types are present in approximately equal amounts at one site. Elemental compositions of clays and shards expected to be of the same origin should be essentially the same. If however, the composition of a shard has been proven to differ from the composition characteristics of a particular site of interest, it may be concluded with some confidence that the shard did not originate from that site. A positive identification of a shard's geographical origin is often difficult and is only possible if the elemental compositions for all of the sites of interest have been established.

A common problem in attempting to compare shards with the local clay composition is the potter's treatment of the clay, i.e., the addition of tempers. The addition of tempers in varying amounts to the same clay will change the concentrations of the elements present. Sand and lime have been commonly added to clay to act as a diluent. In such tempers, most trace elements have very low concentrations compared with clay (2). Samples that are diluted in this manner are not usually recognized as group members in common multivariate statistical analyses.

Another problematic factor considered in the past, is any change that might occur in the clay as a result of
environmental interaction during burial at ambient temperatures. The results of U.M. Franklin and V. Vitali's study on the environmental stability of ancient ceramics show this not to be a problem (3). In their study, samples of ceramics of known elemental compositions were subjected to a variety of aqueous solutions designed to simulate a broad range of soil environments. By monitoring the ceramic plus solution system as a function of time at two different temperatures, they obtained an overview of the corrosive effect on the ceramics over a wide range of conditions. The results of this experiment show remarkable uniformity in the response of the ceramics over a wide range of simulated soil environments. As a result, it was proven that exposure of the ceramics to the varying soil environments has little effect on their elemental compositions.

Analytical techniques that have been used in the past and are presently used to analyze clay compositions are neutron activation (NA), proton induced x - ray emission (PIXE), x - ray fluorescence (XRF), and scanning electron microscopy (SEM) (4). Neutron activation was the most suitable technique for this work due to its high sensitivity for trace elements. Although many elements were available for neutron activation, trace constituents are the focus of this project. It has been shown that the most useful elements probably vary with the geochemistry.
of the area of interest and with the natures and preparation of the pottery (2). The best preliminary approach is to analyze as many elements as possible. One element alone can be used to distinguish different claybeds, however, more accurate results involve comparison of a number of elements. The elements chosen should show a variation of concentrations in pottery of different provenance, and small variations of concentrations in pottery of the same provenance. For a successful analysis, the concentrations of the elements to be analyzed must be greater than the detection limits of the detector system used so that good analytical precision may be reached.

There is no uniform method of estimating the required number of pottery samples or elements for a provenance determination, since there are no apriori guidelines for the number of samples and the kinds of elements for which data would be useful (2).

The samples for neutron activation were provided by Dr. Robert Johnston, Dean of the College of Fine and Applied Arts at the Rochester Institute of Technology. The samples, classified as mudbrick or pottery, have been recovered from a total of five different cities in the Dead Sea area, two of these cities, Bab edh Dhra and Numeira are the focus of this project (see Figure 1). The location of the recovery site of each sample was to remain
unknown until after the analysis was performed and results were obtained.

The mudbrick samples obtained from Bab edh Dhra and Numeira were originally assumed to be representative of the "local clay" of these areas. Having determined the elemental concentrations of both the mudbrick and pottery samples, it was the goal of this project to 1) identify the composition types that can be distinguished for mudbrick of known provenance, 2) match pottery of unknown provenance to the mudbrick groups and identify the origin of the pottery as either being a product of the Bab edh Dhra or Numeira areas or of another geographical location.
Figure 1 (5). Location of Archaeological Sites

SETTLEMENT IN THE SOUTHEASTERN DEAD SEA PLAIN
Neutron activation is an analytical technique for determining elemental composition in a wide variety of materials. Neutron activation is a method of measuring concentrations of constituent isotopes in a given sample by observing the characteristic radiation emitted by radioactive nuclides produced when the sample is exposed to a high flux of neutrons. The radioactive nuclides result from nuclear transformations.

In 1936, Hevesy and Levi produced neutrons by reacting radium with carbon-13 (6). In the reaction, they used beryllium to produce carbon-13 (see Figure 2). Following their production of neutrons, the two scientists used the technique of neutron activation to determine the concentration of dysprosium in impure yttrium. At this time, applications of the technique were limited due to the difficulty of producing large fluxes of neutrons. In 1942 the first nuclear reactor was constructed. After the advent of intense sources of neutrons from nuclear reactors, many technical developments took place. Among these were the development of the multichannel analyzer.
Figure 2. Hevesy and Levi First Source of Neutrons

\[ ^9\text{Be} + ^4\alpha \rightarrow ^{13}\text{C} \]

\[ ^{13}\text{C} + ^{226}\text{Ra} \rightarrow ^{239}\text{Pu} + ^0\text{n} \]
and neutron generators. Neutron activation is now a major analytical tool for trace element analysis.

As previously mentioned, radioactive nuclides are produced when the sample is subjected to a high flux of neutrons. Irradiations of this type can be produced by nuclear reactors and neutron generators. The nuclear reactor used in this work is located at the Buffalo Materials Research Center, the State University of New York at Buffalo. This reactor is an open tank type two megawatt reactor. The present core became critical on June 22, 1964. What this essentially means is that at this point, the reactor began to produce enough neutrons to sustain a chain reaction. The fuel in the reactor is $^{235}\text{U}$ enriched $^{2}$oria (uranium dioxide) clad with zircaloy.

Cooling is provided with light water. The core reflection may consist of light water, graphite, aluminum or a combination of these. The core of the reactor is at rest in the center of a seven foot diameter tank.

$^{235}$

(a) The enrichment is in $^{235}\text{U}$.

(b) Light water is due to the covalent bonding of hydrogen, $H_2(1p, 1e)$, with oxygen. This is opposed to heavy water, $D_2O$, where deuterium, $D(1p, 1n, 1e)$ replaces hydrogen.
Neutron activation can be applied to any type of sample - solid, liquid, or gas. Solid samples are easiest due to the availability of solid standards. To produce a more uniform irradiation, the solid samples should be in the powder form. The powder form also allows the sample to be in the same physical state as the standard. Powders can be made by grinding the solid with an electric metal grinder, or a conventional mortar and pestle. The latter is the preferred method because the electric metal grinder may contaminate the sample with metal impurities.

After being ground, the powder samples are placed in a small plastic vial, and heat sealed to prevent sample contamination. The vials are then placed in a rabbit. A rabbit is a polyurethane container used as a carrier in the pneumatic system of the reactor. In the pneumatic system, the rabbit travels through the pipeline until it is at rest next to the core. After the desired irradiation, the rabbit is forced back through the pipeline and recovered. The activity emitted by the samples following the irradiation decays for a period of time until it is reduced to a point where the samples can be handled appropriately. A maximum of three sample vials and one standard vial are placed in a rabbit.

Standards that are used in this analysis are the National Bureau of Standards Coal Fly Ash, and G - 2 Geological Survey Standard. Each standard contains a known
amount of selected trace elements. Certified elemental values provided for each standard are a result of several methods of analytical instrumental analyses. Examples of methods used to analyze the composition of the standards are: atomic absorption spectrometry, flame emission spectrometry, isotope dilution mass spectrometry, neutron activation, and polarography. Although both G - 2 Geological Survey Standard and National Bureau of Standards Coal Fly Ash are both acceptable standards for neutron activation analysis, G - 2 is the preferred standard for this work. There are a greater number of elements available for a quantitative analysis in the G - 2 standard, and all of the elemental concentration values documented from this standard are certified.

Selection of the length of irradiation is an essential parameter in neutron activation analysis. In order to fully understand the nature of selection of irradiation times, the concept of cross section must first be understood. The probability of a nuclear process occurring is expressed in terms of cross section, which has the dimensions of area. The probability of a reaction between a nucleus and an impinging particle is proportional to the cross sectional target area exhibited by each nucleus. Each element has different nuclear cross sections for a particular reaction. The total cross section of the collision of a fast particle with a nucleus
is never greater than twice the geometrical cross sectional area of the nucleus. Fast particle cross sections are rarely greater than $1 \times 10^{-24} \text{ cm}^2$. This value has been named the barn, and represents the standard unit of nuclear cross sections. The nuclear cross section of sodium for thermal neutron absorption of 0.51 barns is an example of a high cross section. Lithium for the same reaction, has a nuclear cross section of 28 millibarns. This is an example of a low cross section. More sodium isotopes will react during a given irradiation with thermal neutrons. A longer irradiation would be required for analysis of the same amount of lithium than for sodium.

Sample analysis following high flux neutron irradiation involves the use of computer automated analytical instrumentation. The instrument used to view the characteristic energy peaks from the emitted radiation is the multichannel analyzer. The multichannel analyzer displays pulses received by the radiation detector. The multichannel analyzer used in this work was the Canberra (Meriden, CT) Series 8100 multichannel analyzer. This instrument displays 1024 energy channels. The screen on the instrument horizontally displays the individual channels, and vertically displays the channel intensities. The detector used was an Ortec EG&G (Oak Ridge, TN) lithium drifted germanium detector [Ge(Li)] (see Figure
3). In this type of detector, the lithium fills the germanium crystal lattice intrinsically. The [Ge(Li)] detector consists of $p$ - $n$ type reversed bias semiconductor material.

When radiation energy emitted by the radioactive sample is absorbed by the germanium crystal, electron pairs are created. A collection of these "charged carriers" produce an output signal which is proportional to the amount of energy absorbed by the detector from the radioactive sample. For ionization to take place, the germanium crystal requires a small charge of 2.8 eV. This provides very high resolution which is an advantage of this type of detector. Although high resolution is a crucial advantage in this type of analysis, a disadvantage of this type of detector is that it must be kept at liquid nitrogen temperature to prevent damage to the crystal. The detector is surrounded by a cave of lead blocks. The lead blocks shield the detector from outside radiation so it will only "see" the radiation from the sample, i.e. they decrease the background radiation.

Prior to sample analysis, the counting system is calibrated with a standard which emits characteristic isotopic gamma ray energy peaks. The standard used for this process is the Marinelli - 2 beaker standard. This standard produces characteristic energy peaks of the following isotopes:
Figure 3 (7). Lithium Drifted Germanium Detector
Cd 109 at 88keV
Cs 137 at 662.2 kev
Co 60 at 1173.2 and 1332.5 kev

To analyze a sample, the sample is placed in the lead
cave over the detector at a distance which produces
anywhere between 1 - 5% dead time. Dead time is expressed
as the amount (in %) of radiation pulses not being
accurately responded to by the detector. Samples exceeding
5% dead time are too "hot" for the detector to accurately
analyze. By increasing the distance between the sample and
the detector, the detector receives fewer $\gamma$ rays and is
able to respond to a higher percentage of them.

After the gamma - ray spectrum is viewed on the
multichannel analyzer, and each desired elemental peak is
identified, activity intensity measurements are then made
at the full - width at half maximum (FWHM) value of each
peak. The computer automated system provides an output of
this intensity data in units of counts - per - minute
(cpm).

To successfully analyze this data, corrections must
be made on the intensity values. The first correction is a
direct result of the Compton effect, named after A. H.
Compton. In the Compton effect, a gamma photon emitted by
the radioactive sample collides with an outer shell
electron from the germanium crystal. In this interaction,
the electron appears to the gamma photon as a "free electron". This free electron is commonly called the Compton free electron. Upon collision, the primary gamma photon loses part of its energy to the Compton free electron which is scattered at a 90° angle from the Compton scattered photon $\gamma'$. As a result of this elastic collision, the Compton free electron and the Compton scattered photon share the energy of the incident gamma photon. The interaction of a $\gamma$ photon and an outer shell electron from the germanium crystal produces a broad continuum, referred to as the Compton Continuum. A correction called the Compton Corrected Count is performed on each sample photopeak. This correction subtracts the background activity intensities from each selected photopeak arising from Compton distributions (see Appendix 1).

As part of a routine analysis, a correction for background radiation in the detector must also be included. To do this correction, an empty detector cave must be counted for a known amount of time. Background intensity values for each selected elemental isotope peak must be obtained. The background intensity values are Compton corrected, and subtracted from the Compton corrected sample intensities. The background correction ensures that the sample counts obtained in the analysis are primarily due to radiation emitted from the sample,
and not from any radiation naturally present in the detector cave.

The final stage of the sample analysis is the application of the calculations necessary to determine the quantity of each isotope present. Appendix 2 contains a brief review of some nuclear chemical units, as well as a review of the concept of radioactive half-life and elementary kinetics used in this calculation. In the first step of the quantitative analysis, isotopic activity values in units of counts - per - minute are converted to units of microCuries - per - milligram (uCi/mg). Using the first order rate equation, the initial activity of each desired isotope can be obtained in units of microCuries - per - milligram (uCi/mg). By setting up a proportion between these calculated values and the known isotope concentration values of the standard, concentration values of each elemental isotope in the sample can be obtained.

Very few chemical analysis techniques are as sensitive as neutron activation analysis. Some trace elements have been detected with concentrations of 1 in 10^15 (8). Maximum sensitivity from the technique is obtained when a high neutron flux is used and the time between irradiation and counting is appropriate depending on whether short - lived or long - lived nuclides are being measured.
EXPERIMENTAL:

All irradiations were performed at the S.U.N.Y. Buffalo two megawatt nuclear reactor. A preliminary trial irradiation was performed on mudbrick samples in the powder form and mass range of approximately 10 - 15 mg. The samples were subjected to a neutron flux of $3 - 5 \times 10^2$ thermal neutrons/cm sec for 30 min. The irradiated samples were then allowed to decay for approximately 16 hr. The only available isotopes from an irradiation of this timing were the K 42, K 40, Na 24 isotopes and one trace isotope, Mn 56. It was apparent at this point that a longer irradiation would be needed to make available a greater number of trace elements, which are the focus of this project.

To modify the previous procedure, 10 - 15 mg of mudbrick, pottery, and Geological Survey standard G-2 in the powder form were subjected to a neutron flux of $3 - 5 \times 10^2$ thermal neutrons/cm sec for an irradiation time of 60 min. The irradiated samples were allowed to decay for approximately 16 hr. After the decay period, the samples
were analyzed by gamma ray spectroscopy using the Canberra series 8100 multichannel analyzer and the Ortec EG&G lithium drifted germanium detector system. The data was analyzed as described in the Methodology section. Error analysis was also performed (see Appendix 3).

A 4 hr trial irradiation was performed on a single mudbrick sample. The sample was subjected to a neutron flux under the same conditions as the 60 min irradiated samples. The 4 hr irradiation was requested primarily for a qualitative analysis. The analysis was performed to determine if a longer irradiation time would provide a greater number of useful radioactive isotopes.
RESULTS:

Table 1 lists the isotopes observed in this project as a result of a 1 hr irradiation and their half-lives. Table 2 lists the mudbrick and pottery samples analyzed with their relative isotopic concentration values in ppm.

In short irradiations, the only elements that can be determined with high precision are sodium (Na) and manganese (Mn) (2). This is due to their short lifetime, high abundance and high cross sections in comparison to the other elements available from a sixty minute irradiation.

The total percent error in the isotopic concentration values as determined from the propagation of errors program (see Appendix 3) was shown to be approximately 3.2% for all samples. In the work of Mommsen et al. (1), it was mentioned that natural element inhomogeneity in clay is generally between 5 and 8%. The total percent error for each isotopic concentration was increased from 3.2% to 8% to account for clay inhomogeneity.

A 4 hr neutron irradiation did not provide additional useful isotopes. The gamma-rays observed from this
irradiation were shown to be repetitious of the isotopes observed from the 60 min neutron irradiation.
## Table 1. Observed Isotopes and Their Half-Lives

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<th>HALF-LIFE</th>
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<td>Ag 110m</td>
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<td>Mn 56</td>
<td>$1.55 \times 10^3$ min</td>
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<td>Nb 95</td>
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<tr>
<td>Sc 46</td>
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<tr>
<td>La 140</td>
<td>$2.43 \times 10^2$ min</td>
</tr>
<tr>
<td>Na 24</td>
<td>$9.00 \times 10^{14}$ min</td>
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<tr>
<td>K 40</td>
<td>$6.73 \times 10^3$ min</td>
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<tr>
<td>Br 82</td>
<td>$2.12 \times 10^3$ min</td>
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Table 2.

MUDELICE/POTTERY ISOTOPIC CONCENTRATIONS - PPM

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<td>284</td>
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<td>7.61</td>
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<td>0.078</td>
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<td>------</td>
<td>36.5</td>
<td>7.91</td>
<td>------</td>
<td>24.3</td>
<td>17.8</td>
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<td>47.4</td>
<td>11.2</td>
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<td>25.4</td>
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<td>0.266</td>
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<td>144</td>
<td>0.733</td>
<td>65.1</td>
<td>-----</td>
<td>0.388</td>
<td>0.743</td>
<td></td>
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<tr>
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<td>62.8</td>
<td>3.54</td>
<td>0.169</td>
<td>16.8</td>
<td>0.13</td>
<td>-----</td>
<td>0.150</td>
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<tr>
<td>252/187</td>
<td>0.722</td>
<td>45.7</td>
<td>------</td>
<td>1.03</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>0.324</td>
</tr>
</tbody>
</table>

* concentration listed in %
DATA ANALYSIS AND DISCUSSION:

Bromine and potassium in the form of KBr are sometimes added to clay before firing. Most of the bromine added to clay is lost during the firing process (8). It was pointed out in the same work that bromine composition is extremely variable and is believed to be sensitive to firing conditions. Although the potassium content is not known to be sensitive to firing conditions like bromine, following a 60 minute neutron irradiation the potassium isotope was not observed in many of the samples. The amount of this isotope that is detectable in the samples may vary as a result of treatment of the clay by the potter. Since prior treatment of the samples of this project are unknown, it cannot be determined whether the potassium being analyzed in this work is due to the natural composition of the clay or to the addition of tempers before firing. Therefore, the Br 82 and K 40 isotope values will not be used for the provenance determination in this project.

Three multivariate statistical analyses were
performed to try to establish a representative chemical composition for the samples. All of the statistical analyses were performed with the use of a statistical computer software system called SAS. The three SAS programs that were applied to the data were the average linkage cluster analysis, the principal components procedure, and the standard procedure.

The cluster analysis constructs similarity coefficients from the multivariable matrix. Similarity coefficients are used in archaeometry to construct dendrograms from the elemental composition data of the clay samples. A similarity coefficient is a measure used to quantify the similarity or dissimilarity between two samples. The similarity coefficient can be represented mathematically as the mean interpoint euclidian distance (ED) where:

\[
ED = \left[ \frac{1}{m} \sum_{i}^{m} (P_{1i} - P_{2i})^2 \right]^{1/2}
\]

In this equation, \( P_{1} \) is the composition of sample 1 and \( P_{2} \) the composition of sample 2, \( m \) indicates the number of isotopic concentrations available in the particular sample, and \( i \) represents the vectorial direction. The closer the euclidian distance, the more similar the two sample's chemical composition. Sample clusters are formed based on the similarity levels of the chemical composition.
data for the sample. Similarity levels up to approximately 0.80 are considered to represent reasonably matching compositions in the average cluster analysis (2).

The principal components procedure is a multivariate technique for examining relationships among several quantitative variables. The function of the principal components procedure is to reduce the number of variables in clustering. Given a data set with n numeric variables, n principal components may be computed. Each of the principal components constructed represents a linear combination of the original variables with coefficients equal to the eigenvectors of the correlation matrix. All principal components are presented by descending order of the eigenvalues, which in turn are equal to the variances of the components. By observing the correlations resulting from this procedure, any one of two elements having high correlation may be eliminated, thus reducing the number of variables to be used in the cluster analysis.

The standard procedure functions to standardize all variables in a data set producing a new data set containing values of a standardized mean and standard deviation. Standardizing is a technique for removing scale attributes from a set of data. By using this procedure, all isotope concentration values are centered to a mean of zero and a standard deviation of one. An advantage to this procedure is that it excludes all null values from the
standardization. This differs from the previous procedures where null data is interpreted by the program as a "zero" value.

A. Data Analysis of Mudbrick

The original intent of this project was to establish a provenance determination of recovered pottery shard samples from Bronze Age cities based on local mudbrick compositions. The standardization was applied to the mudbrick isotope concentration data. The newly standardized data was then analyzed using the principal components procedure, and the average linkage cluster analysis. The result is that the Bab edh Dhra clay is indistinguishable from the clay of Numeira (see Figure 4).

Since the mudbrick samples show no dissimilarity based on the two recovery sites, a cluster analysis was applied to the mudbrick data of the individual sites. Several clusters were formed within each city (see Figure 5). Following this analysis, a map illustrating the recovery sites for each mudbrick within both Bab edh Dhra and Numeira was provided by Dr. Johnston. The clusters formed within each city matched the mudbrick recovery site with the exception of mudbricks 26, 6, 5, and 3 (see Figure 6). Noting that mudbrick 26 is very different from the other mudbrick samples, and upon further discussion
Figure 4. Average Linkage Cluster Analysis of All Mudbrick Samples

**MUDBRICK ORIGIN**

- MB 1: Nebi
- MB 2: Nebi
- MB 3: Bab enh Dhra
- MB 4: Bab enh Dhra
- MB 5: Bab enh Dhra
- MB 6: Bab enh Dhra
- MB 7: Bab enh Dhra
- MB 8: Bab enh Dhra
- MB 9: Bab enh Dhra
- MB 10: Bab enh Dhra
- MB 11: Nebi
- MB 12: Bab enh Dhra
- MB 13: Nebi
- MB 14: Nebi

**NAME OF OBSERVATION OR CLUSTER**

- 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27

**AVERAGE DISTANCE BETWEEN CLUSTERS**

- 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0
Figure 5. Average Linkage Cluster Analysis Within Each Site
AVERAGE LINKAGE CLUSTER ANALYSIS

NAME OF OBSERVATION OR CLUSTER

AVERAGE DISTANCE BETWEEN CLUSTERS

Bab edh Dhra

5C
Figure 6 (10). Mudbrick Recovery Locations Within Numeira (6A, 6B) and Bab edh Dhra (6C)
Topographic Survey
Numeira, 1977
with Dr. Johnston it was determined that mudbrick sample 26 is not a mudbrick sample but a vat shard. Reanalysis without sample 26 gives clusters matching the recovery sites for samples in the Numeira area.

B. Discussion of Mudbrick Data

Following the analysis of the mudbrick data, discussions with Dr. Johnston on how mudbrick is formed provided the following information. Tempers such as straw, hay and dung are mixed with moist clay to give it a more rigid and workable texture. The elemental concentrations determined are then those naturally present in the tempers and the clay rather than just the natural composition of the clay. Due to this factor, it is evident that the mudbrick do not provide a valid representation of the local clay composition of Bab edh Dhra or Numeira. Mudbricks 6, 5 and 3, although from different sites within Bab edh Dhra may have been constructed with tempers of similar chemical composition. The observation that mudbrick of different cities cannot be distinguished by neutron activation is rational since the natural composition of straw, hay, grass etc., which was used to make the mudbrick, will cause the composition of trace elements to vary in unknown ways.
C. Data Analysis of Pottery

1) Method

The primary goal of this project, as previously stated, is to determine the provenance of recovered Bronze Age potshards as being a product of the Bab edh Dhra or Numeira areas or of another geographical location. In the original proposal, the shard composition was to be compared to the composition of the mudbrick to determine provenance. This was not done since the temper used in the mudbrick contributed to the trace element content. The common tempers in forming pottery do not vary the trace element content on their concentrations. Since the addition of these tempers to the clay changes the isotopic concentration as compared to the raw clay values, the data analysis applied must be able to account for diluted materials and recognize them as being the same as the undiluted materials. A method taking dilutions into account [Mommsen et al. 1987 (1)] was chosen for this task. In this method, shard samples of unknown provenance are directly compared to compositions of clay of known provenance by applying a dilution factor. The Dilution Factor method is a suitable method since it not only corrects for null data, it takes into account the addition of tempers to a clay. This method can only account for
tempers that do not effect elemental composition such as those used in the pottery making process rather than tempers such as straw which do effect the composition.

2) Establishment of Core Group

Since mudbrick is not appropriate to be used as a local composition group of Bab edh Dhra and Numeira, a clay composition "core" group needed to be established for the two cities. Following consultation with Dr. Johnston, it was discovered, only two of the measured shard samples were recovered in Numeira. Since two shard samples are simply not enough to accurately determine the overall chemical composition of the Numeira region, a core group representing Numeira was unable to be established. Of the remaining shards analyzed, the majority were recovered in Bab edh Dhra with two samples from Ezion Geber, another Bronze Age city, and four samples from Salona, Pennsylvania, U.S.A.. Table 3 is a listing of the analyzed shards and their recovery sites.

A Bab edh Dhra shards "core" group with a similarity level of 0.60 based on atomic absorption analysis was provided by Dr. Johnston (11). The core group provided (see Table 4) was taken to represent the Bad edh Dhra local clay composition and used in Mommsen's Dilution Factor method. Since there is no Numeira core group
<table>
<thead>
<tr>
<th>SITE</th>
<th>RECOVERED SHARD SAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bab edh Dhra</td>
<td>327/180, 328/135, 329/136, 112, 331/450,</td>
</tr>
<tr>
<td></td>
<td>332/158, 100/56, 326/132, 330/181,</td>
</tr>
<tr>
<td></td>
<td>251/186, 334, 260/195, 256/191, 253/188,</td>
</tr>
<tr>
<td></td>
<td>255/190, 249/184, 250/185, 254/189,</td>
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<td></td>
<td>257/192, 265/200, 264/199, 259/194,</td>
</tr>
<tr>
<td></td>
<td>261/196, 252/187</td>
</tr>
<tr>
<td>Numeira</td>
<td>66/23, 68/25</td>
</tr>
<tr>
<td>Ezion Geber</td>
<td>ez11,021, ez817</td>
</tr>
<tr>
<td>Salona</td>
<td>sler, slbr, slsc, slbo</td>
</tr>
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Table 3. Recovery Sites of Analyzed Shards
<table>
<thead>
<tr>
<th>Identification Numbers of Bab edh Dhra Core Group Shards</th>
</tr>
</thead>
<tbody>
<tr>
<td>327/180</td>
</tr>
<tr>
<td>328/135</td>
</tr>
<tr>
<td>330/181</td>
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<tr>
<td>251/186</td>
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<td>260/195</td>
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<td>256/191</td>
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<td>253/188</td>
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<td>264/199</td>
</tr>
<tr>
<td>261/196</td>
</tr>
<tr>
<td>252/187</td>
</tr>
</tbody>
</table>
available, a provenance determination was made identifying the origin of the pottery as a product of Bab edh Dhra or of another geographical location.

3) Results

Using Mommsen's Dilution Factor method, a dilution factor was obtained for all isotopes (see Appendix 4). The provenance determination was based primarily on a "Goodness of Fit" parameter also obtained from Mommsen's method. Table 5 is a listing of each shard sample and their "Goodness of Fit" value with respect to the chosen core group.

Mommsen and colleagues consider "Goodness of Fit" values in the range of 0.6 - 1.3 to be a sample match. Based on Mommsen's criteria [Mommsen et al. 1987 (1)], shards included in the matching range are 331/450, 332/158, and 259/194. The Numeria samples fall below the acceptable matching range with "Goodness of Fit" values ranging from 0.09 - 0.31. The Ezion Geber samples "Goodness of Fit" values range from 1.33 - 1.90, and the Salona sample values range from 1.91 - 3.06. The Salona shard samples were included in the neutron activation analysis as "test" samples. These samples were analyzed to see if the Salona clay appeared different from the other analyzed clay. Both sites are outside the acceptable
Table 5. Goodness of Fit Values For Shard Samples

<table>
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<tr>
<th>SHARD SAMPLE</th>
<th>GOODNESS OF FIT $\chi^2$</th>
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<tr>
<td>329/136</td>
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<td>112</td>
<td>0.09</td>
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<tr>
<td>331/450</td>
<td>1.22</td>
</tr>
<tr>
<td>332/158</td>
<td>0.55</td>
</tr>
<tr>
<td>100/56</td>
<td>0.13</td>
</tr>
<tr>
<td>326/132</td>
<td>0.35</td>
</tr>
<tr>
<td>334</td>
<td>2.25</td>
</tr>
<tr>
<td>249/184</td>
<td>0.41</td>
</tr>
<tr>
<td>250/185</td>
<td>0.47</td>
</tr>
<tr>
<td>265/200</td>
<td>0.22</td>
</tr>
<tr>
<td>259/194</td>
<td>1.23</td>
</tr>
<tr>
<td>66/23</td>
<td>0.09</td>
</tr>
<tr>
<td>68/25</td>
<td>0.31</td>
</tr>
<tr>
<td>ez11,021</td>
<td>1.91</td>
</tr>
<tr>
<td>ez817</td>
<td>1.33</td>
</tr>
<tr>
<td>slsr</td>
<td>3.06</td>
</tr>
<tr>
<td>slbr</td>
<td>2.26</td>
</tr>
<tr>
<td>also</td>
<td>2.60</td>
</tr>
<tr>
<td>slbo</td>
<td>1.91</td>
</tr>
</tbody>
</table>
matching range. The remaining samples range from 0.09 - 2.25. Those that fall within the matching range are assumed to have originally been from the Bab edh Dhra site, and those outside are suspected to have originated from elsewhere.
CONCLUSION:

A provenance assignment has been established for Bronze Age pottery shards as being a possible product of the Bab edh Dhra area or of another geographical site. A Bab edh Dhra pottery core group based on atomic absorption data was provided by Dr. Robert Johnston (11). The core group was assumed to represent the profile of the local clay in the Bab edh Dhra area. Based on a dilution factor method, the Numeira samples "Goodness of Fit" values fall below the accepted matching range of 0.6 - 1.3. The "Goodness of Fit" values for the Ezion Geber and Salona samples fall above the accepted matching range. The "Goodness of Fit" values for the remaining samples fall both above and below the accepted matching range. These samples are assumed to be from another geographical location.

Uncertainty in the provenance assignment for a shard sample depends on the accuracy of the atomic absorption data provided by Dr. Johnston (11). Further uncertainty in the provenance results is due to the isotopes selected for
the analysis. Elements most useful for provenance studies are unknown prior to analysis, so it is not certain whether the elements chosen will provide the most accurate profile of the clay composition. Additional research to examine the reliability in the previous provenance results was unattainable in this work due to restrictions in irradiation and reactor time. Another approach would be to irradiate samples for 8 - 16 hr selecting additional isotopes for the analysis. Increasing the number of isotopes in the analysis would provide a more accurate compositional profile of the analyzed clay. Irradiations greater than 4 hr is suggested since additional isotopes are unavailable under the conditions of this work. Irradiations of 8 hr or greater are standard for an analysis of this type (4).

The provenance results are the best available based on the isotopes that have been measured in this work.
APPENDIX 1

Isotopic Quantitative Analysis Calculations
Activity intensity values obtained from the radioactive samples via the multichannel analyzer, [Ge(Li)] detector, and computer automated system are expressed in units of counts - per - minute (cpm). These values along with the background activity values must be corrected for Compton distributions. The following equation corrects for the Compton Continuum on each selected photopeak.

\[ \text{CCC} = \text{Imax} - \left( \frac{\text{I1} - \text{I2}}{2} \right) \times Z \quad \text{[eq. 1]} \]

where:

\( \text{CCC} \) = Compton corrected activity counts

\( \text{Imax} \) = activity intensity at the peak maximum

\( \text{I1} \) = activity intensity at first peak channel

\( \text{I2} \) = activity intensity at last peak channel

\( Z \) = the number of channels in region of interest
After the background corrected activity counts are subtracted from the sample corrected activity counts, the activity values are converted from units of counts per minute to units of microCuries per milligram (uCi/mg):

\[
A \text{ (uCi/mg)} = \frac{\text{BCC}}{t} \times \frac{1}{\text{ab}} \times \frac{6}{2.22 \times 10^6} \text{ uCi/mg} \text{ [eq. 2]}
\]

where:

\[
A = \text{the final isotopic activity}
\]

\[
\text{BCC} = \text{background corrected counts}
\]

\[
t = \text{the counting time in minutes}
\]

\[
\text{ab} = \text{isotopic abundance}
\]

\[
\text{m} = \text{sample mass in milligrams}
\]

By calculating back to the time \( t = 0 \) (the time the sample was recovered from the reactor), and by substituting in for the time between sample recovery and sample counting, the initial isotopic activity in uCi/mg may be obtained where:
\[ A = A_0 e^{-\lambda t} \]  
[eq. 3]

Note that this expression is equivalent to the first order rate equation since \( A \), the activity, is proportional to \( N \), the number of atoms.

Once the initial activities of each isotope in the samples and standards are obtained, a simple mathematical proportion to convert the activity values in uCi/mg to concentration values in parts - per - million (ppm) is employed where:

\[
\frac{\text{uCi/mg STD}}{\text{uCi/mg SAMPLE}} = \frac{\text{ppm STD}}{\text{ppm SAMPLE}} \quad [\text{eq. 4}]
\]

By substituting in the initial activities of the desired isotopes from the standard and the samples, and the concentration of each isotope in the standard in units of parts - per - million, the concentration of the isotopes in the samples can be obtained in units of parts - per - million. A reference table is available for the G - 2 Geological Survey standard listing each elemental component along with the concentration values in parts - per - million.
APPENDIX 2

Nuclear Chemical Concepts
The following is a review of the nuclear chemical concepts applied to this work.

The rate of decay of all radioactive isotopes has been found to be first order and independent of temperature. The rate of decay is therefore dependent only on the amount of radioactive material present. The number of atoms of a radioisotope, $N$, remaining at a particular instant of time is proportional to $A$, the activity:

$$A \propto N \quad [\text{eq. 5}]$$

If $dN$ is the number of atoms that disintegrate in a time interval, $dt$, and $\lambda$ is the rate constant, the instantaneous rate of change in the number of atoms is given by:

$$\frac{dN}{dt} = -\lambda N \quad [\text{eq. 6}]$$

If there are $N$ atoms at a time $t = 0$, the instantaneous change in the number of atoms with time can be expressed as:

$$\frac{dN}{N} = -\lambda dt \quad [\text{eq. 7}]$$
This equation states that the fraction lost \((dN/N)\), in a given time interval \((dt)\), is directly proportional to the decay constant. Integration of both sides of the equation

\[
\int_{N_0}^{N_t} \frac{dN}{N} = - \int_0^t dt \quad \text{[eq. 8]}
\]

\[
\ln \left( \frac{N}{N_0} \right) = - \lambda t \quad \text{[eq. 9]}
\]

\[
\frac{N}{N_0} = e^{-\lambda t} \quad \text{[eq. 10]}
\]

\[
N = N_0 e^{-\lambda t} \quad \text{[eq. 11]}
\]

yields a first order decay equation where:

\[
\lambda = \frac{0.693}{t_{1/2}}
\]

and

\[
t_{1/2} \quad \text{is the radioactive half-life.}
\]

The unit used to measure radioactivity is the Curie \((\text{Ci})\). The Curie is based on the disintegration rate of one gram of radium. One Curie is defined as \(3.7 \times 10^{10}\) disintegrations - per - second \((\text{dps})\). In SI units, the Becquerel \((\text{Bq})\) has been named the unit of measure of radioactivity where:

\[
1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq.}
\]
APPENDIX 3

Error Analysis
A computer program was written in BASIC to execute the following error analysis for each sample's isotopic concentration values:

\[
\% \text{ error} = \pm \left[ (X/dA)^2 + (X/dT)^2 \right]^{1/2} \times 100\%
\]

\[x = \text{isotopic concentration in ppm}\]
\[dA = \text{error in the analytical balance} = \pm 0.1 \text{ mg}\]
\[dT = \text{error in the decay time} = \pm 5.0 \text{ min}\]

The error in the reactor system was also accounted for in the following manner. According to the Buffalo Materials Research Center, the total error in the reactor system (neutron flux, irradiation time, pneumatic system, multichannel analyzer, and detector systems etc.) has been experimentally determined to be \(\pm 3.0\%\). The total error in the sample isotope concentrations is then represented by:
\[ \text{total \% error} = \left| \% \text{ error} + 3.0\% \right| \]
APPENDIX 4

Dilution Factor Method
For each sample \( x \) with concentration values \( x_i \) \( (i = 1 \) to \( m) \) where \( m = \) the number of isotopic concentrations in the particular sample, an average dilution factor can be calculated as:

\[
f = \frac{1}{m} \sum_{i=1}^{m} f_i
\]

where:

\[
f_i = \frac{c_i}{x_i}
\]

\( c_i = \) known clay group mean isotope concentration

\( x_i = \) shard sample mean isotope concentration

If sample \( x \) is from the same clay workshop, i.e. same origin, the dilution factors for each element measured will be approximately the same. If no dilution has been made, however, this value will be equal to unity. If on the other hand, \( x_i \) has a different composition than \( c_i \),
the single f values will be widely scattered. The size of this scatter can be calculated by the dilution factor spread given below.

\[ \sigma_f = \left\{ \frac{1}{m-1} \sum_{i=1}^{m} (\bar{f} - f_i)^2 \right\}^{1/2} \]

It has been found in past work that the dilution factor spread is a very sensitive measure (1). Samples with small dilution factor spreads are possible further members of the group. The error in the dilution factor is given by the following equation.

\[ \Delta f_i = \left\{ \left( \frac{\Delta c_i}{c_i} \right)^2 + \left( \frac{\Delta x_i}{x_i} \right)^2 \right\}^{1/2} \times f_i \]

For improved results, a weighted calculation for the dilution factor can be made as follows.

\[ f_w = \frac{\sum_i \{f_i/(\Delta f_i)^2\}}{\sum_i \{1/(\Delta f_i)^2\}} \]
The error in the dilution factor spread is then:

\[ \sigma_{f_w} = \left[ \frac{1}{m-1} \sum_i \frac{(f'_w - f_i)^2}{(\Delta f_i)^2} \right]^{1/2} \frac{1}{\left\{ \frac{1}{m} \sum_i \frac{1}{(\Delta f_i)^2} \right\}} \]

The final and most crucial measure that will be calculated is the "Goodness of Fit" measure. The "Goodness of Fit" equation is:

\[ \chi^r_v = \frac{\sum_i \{f_i/(\Delta f_i)^2\}/\sum_i \{1/(\Delta f_i)^2\}}{1/\left\{ \frac{1}{m} \sum_i \frac{1}{(\Delta f_i)^2} \right\}} \]

This measure is simply the weighted average dilution factor divided by the variance in the weighted average dilution factor spread. For a matching sample, the "Goodness of Fit" parameter should be approximately unity. Mommsen and colleagues consider "Goodness of Fit" values
in the range of 0.6 - 1.3 to be a sample match (1). A correction for null data is obtained by simply reducing the number of terms in the number of isotopic concentrations available in the particular sample (m value). This correction was made to produce more accurate results in the pot shard match determination.
REFERENCES


