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Chemical characterization of ancient pottery from the greater Accra region of Ghana using neutron activation analysis

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A B S T R A C T

Archaeology in Ghana has a long and respectable tradition. Despite this encouraging situation, significant gaps still exist in our understanding of the history of some early societies in Ghana. Accumulated evidence revealed that the Ga (Ayawaso), Dangme-Shai and the Wullf had trade and other cultural contacts with their Akan and Guan neighbours as well as the various European factors that traded and established footholds in the Accra coast. In an attempt to reconstruct the early history of the Ga, Dangme-Shai and Wullf, the archaeological material remains recovered from these communities during excavation have been studied. In all, 15 trace elements were determined in 40 pottery shards using instrumental neutron activation analysis. The elemental concentrations were processed using multivariate statistical methods, such as cluster, factor and discriminant analyses. The results revealed patterns of trade between these communities and also classified the 40 samples into two major groups based on variations in elemental compositions. The groupings suggested a clear separation between the shards from Shai and Ayawaso. The shards from Wullf scattered amongst the two groups, consistent with the archaeological findings that the Wullf community never produced their own pots.

1. Introduction

Archaeology in Ghana has a long and respectable tradition especially in relation to other areas in the West African sub-region. Despite this encouraging situation, significant gaps still exist in our understanding of the history of some early societies in Ghana. The need to apply an archaeological research approach supported by scientific analytical tools for reconstructing the general and broad history of some ancient Ghanaian societies to fill in the gaps cannot be overemphasized.

The analytical techniques commonly used in archaeological studies with regards to pottery characterization include atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), inductively coupled plasma-optical emission (ICP-OES) and mass spectrometry (ICP-MS) and instrumental neutron activation analysis. Among these, instrumental neutron activation analysis (INAA) has become the widely used technique due to its high precision, accuracy, sensitivity coupled with the ease of sample preparation [1,2].

In pottery characterization studies using INAA, vast amount of data is frequently generated on a large number of specimens. The volume of data is so substantial and the relation between elements and specimens are so complex that more advanced methods for data handling and data evaluation are required in order to elucidate the major variations in the set of compositional data. The main objective of compositional characterization of a pottery assemblage is to identify pottery types or groups that can be clearly differentiated from other groups to reveal a meaningful archaeological interpretation. It is important to employ Multivariate Statistical methods that use the correlations between elemental concentrations as well as absolute concentrations to characterize sources of pottery samples. The Multivariate Statistical Analyses commonly used for such studies include Cluster Analysis (CA), Principal Component Analysis (PCA) and Discriminant Analysis (DA) and these methods have subsequently been used in this work.

The chemical composition of pottery is strongly related to the source of clay and the recipe of the fabrication. INAA focuses more on the chemical composition of the pottery which is related to the sources of raw materials used for their production. The concentration levels of a number of major elements, such as Al, Fe, Mn and Si, are usually similar for different samples of sand or clay. The clay, sand and other natural materials from which the pottery were

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fashioned can have a chemical composition which is unique and which may serve as a diagnostic of the local source from which the ceramics were taken [3–8]. This makes it necessary to consider the chemical composition and concentration levels of trace elements like the rare earth elements in the materials from which the pottery was manufactured [9].

The accumulated evidence revealed that the Ga (Ayawaso), Dangme-Shai (Shai) and the Wullf who lived in the ancient Ghana had trade and other cultural contacts with one another; the Akan and the Guan neighbours, as well as the various European factors who established footholds in the Accra coast. Ayawaso was the ancient capital of the Ga community on the Accra coast. It served as the centre for political, social and economic activities. The Dangme-Shai, settling in the Accra plains, first settled on the rocky hills of Shai. Hioweyu, Adwuku and Mlayo were abandoned towns on the Shai Hills where the excavation was done. The Wullf community was a non potting town named after one Wullf, a Danish official. The vestiges of these activities are the material remains that form the archaeological data recovered during excavation. The archaeological data from here, therefore, might serve as a representative basis for the reconstruction of the early history of the Ga, Dangme-Shai and the Wullf [10]. This research considered these three towns (Ayawaso, Shai Hills and Wullf) in relation to their potteries to provide a corpus archeological data for the reconstruction of the past life patterns of these towns using neutron activation analysis. The Wullf community is geographically located in between Ayawaso and Shai communities which are the main potting towns in the Greater Accra Region. During the excavation in the Wullf community, pottery shards of various forms were found. The big question confronting us is "Where did those pottery shards come from?" since the Wullf community never produced their own pots. Did they receive those pots from Ayawaso which was the closer potting town or Shai which was further away from the Wullf community?

In spite of the importance of INAA in archaeological studies, its application in Ghana has received little attention. To the best knowledge of the authors, the only available literature is the trace element fingerprinting of pottery shards from Jenini (a slave camp in the Brong Ahafo region of Ghana) conducted by Nyarko et al. [11]. In this study, the chemical profile of 40 pottery shards excavated from Shai, Ayawaso and Wullf have been determined using INAA. The work is aimed at characterizing the pottery shards on the basis of their trace elemental concentrations and to use multivariable statistical methods to define one or more compositional groups, which presumably would represent one or more production sites.

2. Materials and methods

2.1. Sample collection

The main objective of sampling was to analyse a representative portion of the original assembly of pottery from the settlement of Shai, Ayawaso and Wullf, all in the Greater Accra region, Ghana (Fig. 1).

Forty pottery samples were taken from different trenches and depths, all in the form of shards. Samples from Shai were excavated in 1982, those from Ayawaso in 1988 and 1989, and Wullf in 1999 and 2004. Shards excavated from Wullf and Ayawaso sites used in this analysis were coded with prefixes Wu and Aya, respectively. Samples excavated from Shai were prefixed HWO and ADW with reference to Hioweyu and Adwuku, respectively. The samples were excavated by the Archaeological Department, University of Ghana, Legon, at different trenches and depths from the soil surface to about 8 m deep down the soil profile. These specimens were selected and collected from the department in pre-cleaned polythene bags and stored in a contamination free area.

2.2. Sample preparation

Sample preparation was done in the A. Chatt Chemical Laboratory at the Ghana Research Reactor-1 (GHARR-1) Centre. Each shard was handled with a fresh pair of sterile disposable gloves. A small portion was taken off each sample, cleaned with acetone and oven dried for 48 h at 105 °C to remove any moisture in the sample.

The individual shards were then ground and homogenized to fine powder with the Laboratory Mortar Grinder (Pulverisette 2). Three replicate samples, about 100 mg each, were weighed and sealed into polythene bags. Equal weights of GBW07106 and IAEA Soil 7 reference materials were also weighed and sealed into polythene bags for the quantitative analysis of the elements in the shards samples and validation of the analytical tool, respectively. The sealed bags were then packed into plastic rabbit capsules labeled by a marker, and heat sealed using a soldering iron.

2.3. Irradiation and counting

Samples and standard reference materials were irradiated in the inner pneumatic irradiation sites of the Ghana Research Reactor-1 (GHARR-1) facility, operating at half full power of 15 kW with corresponding thermal neutron flux of 5.0×10^{11} n cm^{-2} s^{-1}. Irradiation times ranged from 10 s to 1 h according to the half-lives of the elements of interest. For elements with relatively short half-lives such as Ba, Ca, Dy, Mn, Sm, Sr, Ti, U and V, with half-lives between 2 min and 15 h, irradiation time was 10 s and counting time was 10 min.

The detector used in this work was an n-type high purity germanium (HPGe) detector Model GR 2518 (Canberra Industries Inc.) with a resolution of 0.85 KeV (FWHM) and 1.8 KeV (FWHM) for ^{60}Co gamma-ray energies of 1332 KeV. The detector operated on a bias voltage of (−ve) 3000 V with relative efficiency of 25% to NaI detector. A Microsoft Soft window based software MAESTRO was used for the spectrum analysis.

The analytical photopeaks used for the determination of the various elements have been summarized in Table 1.

2.4. Multivariate statistical analysis

The application of multivariate statistical analysis allowed for the rigorous inspection and evaluation of variability present in the voluminous data produced by the chemical characterization. Several methods were applied to process the variability between the potteries. The elemental concentration values were first transformed to log base 10 values before performing multivariate statistical analysis on the data. This compensated for the differences in magnitude between minor and trace elements, and normalized element distribution [12]. Visual inspection of the log transformed data was made and binary scatter plots were generated among some of the elements. Cluster analysis (CA), Principal component analysis (PCA) and Discriminant analysis were thereafter employed using SPSS 16.0 Statistical package.

2.4.1. Cluster analysis

Cluster analysis is an efficient statistical technique for investigating the complicated relations between analysed specimens, in the process distance between the individual specimens are calculated. Cluster analysis attempts to earmark individual specimens to groups so that each specimen group is distinct from every other group. The results of cluster analysis are in most circumstances presented in the form of dendrograms which show the order and levels of specimen clustering. Visual inspection of dendrograms is useful as a method of identifying preliminary groups.