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Chemical Characterization of Ancient Pottery from Dixcove, Ghana, Using Instrumental Neutron Activation Analysis (INAA)

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Introduction

Pottery constitutes the most abundant and ubiquitous cultural material recovered at most archaeological sites. Its most admirable feature is its durability. It does not wear easily and in the event of breakage, each sherd still retains much of its physical and chemical attributes. Like molluscs shells, their hardy nature makes them almost resistant to bushfires and vagaries of tropical weather conditions. Scientifically, analyzing pottery can play a central role in reconstructing cultural lifeways of ancient societies. For example, it can reveal probable source areas of the clay used for their manufacture, ancient trade networks, culinary and gustationary patterns. It is also the most important yardstick for establishing technological and stylistic developments of ancient societies. Their study is thus of immense importance in archaeological research.

Pottery analysis occurs in two forms: physically and chemically. The former, which is inexpensive and the more popular of the two, involves the scientific study of the shape, size, thickness of body fabric, and tempering materials (grog, mollusc shells etc.) used for their manufacture. It is very helpful in establishing vessel function, identifying the manufacturers (potters) and sometimes place of manufacture of vessels (Sharer and Ashmore 1985: 104). Physical analysis of sherds can sometimes be unreliable because of the small sample sizes used and their fragmented nature, some of which measure less than 1cm^2 across their longest axis.

Chemical analysis of sherds however is reliable because it scientifically establishes concentrations of the various trace elements, rare earth chemicals, and other microscopic properties unique to specific geographical regions. It is the most accurate method currently available to archaeologists intending to establish the origin of clays used for manufacturing vessels recovered from the archaeological record. This is because chemical constituents of pottery are directly related to the recipe of fabrication and the clay source. Their origins can thus be easily established (Peisach *et al.* 1991).

The main chemical characterizing methods commonly used in analyzing potsherds recovered from archaeological contexts include Atomic Absorption Spectrometry (AAS), X-ray Fluorescence (XRF), Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Plasma-Optical Emission (ICP-OES) and Mass Spectrometry (ICP-MS). Of the five methods named above, INAA is currently the most popular because of its high precision rate, accuracy, sensitivity and ease of preparing the pottery samples to be analyzed.

In Ghana, the use of the above named applications for archaeological research, especially to establish mineral and chemical compositions in sherds came into usage after 2006, primarily because of the absence of qualified personnel and the requisite equipment necessary to undertake these experiments. To date, the application of INAA to establish chemical characterization in archaeologically recovered pottery is still at an infant stage and more education needs to be rolled out to popularize its usage among archaeologists. Two of the earliest to have been undertaken include those by Nyarko *et al*. (2007) to establish the chemical profiles of 40 sherds recovered from archaeological excavations at Jenini, an ancient slave camp located in the Brong Ahafo Region of Ghana. The second by Tandoh *et al*. (2009) established the chemical profiles of 40 sherds recovered from Ayawaso, Shai and Wulff, all in the Greater Accra Region of Ghana.

This paper presents results of INAA analysis of 31 potsherds recovered from archaeological excavations conducted at Dixcove during the 2014/15 annual field school of the Department of Archaeology and Heritage Studies, University of Ghana, Legon. The objective of the study was to use the INAA method to establish/differentiate the various chemical constituents associated with the Dixcove pottery assemblage to shed light on probable source area of the clay used for their manufacture and facilitate meaningful archaeological interpretations for the area.

The Research Area and People

Dixcove (N4°48′ W1°57′) is located in the Western Region of Ghana (Figure 1) and is occupied by the Ahanta ethnic group. It is underlain with the *P*recambian Upper Birimian rock series. The predominant mineral types associated with this rock system are phyllite, limestone, schist, quartzite and hornstone. Others include andesite, hornblendite, actinolite, biotite granite and periditite (Kesse 1985: 12-16).

Much of the Dixcove coastline is also characterized by large rocky boulders composed of granite and gneiss which jut into the sea to create promontories. The topography consists of several small hills rising averagely to 20-70masl (Ghana Survey Department 2005: Sheet No. 0402A1). Top soils are generally thin but loamy and rich in humus. The soils consist mainly of red laterite and dark grey clayey soils underlain by the above named rock types. Several small streams such as Mawu, Busua and Nfuma can also be found in the neighbourhood of Dixcove.

There are two seasons in the research area: a main maximum which occurs from mid-March and peaks in mid-July, followed by an "August break" from mid-July to August, and a lesser maximum in October to November. Mean annual rainfall averages about 1875mm. The inflow of the southwest winds all year round is responsible for this high amount of rainfall. The dry season starts from December to mid-March, and is characterized by strong dry Harmattan winds. Temperatures and humidity levels are also high all year round with an average of 30˚C and 80% humidity respectively (Dickson and Benneh 1973: 38).

Much of the original vegetative covers have been decimated due to tree felling for fuel and heavy reliance on shifting cultivation which is the principal farming method used by the indigenes of the study area. The current vegetation consists of mostly climbers and creepers interspersed with occasional patches of thick shrubs. The predominant tree types are coconut (*Cocus*), few immature Neem trees (*Azadirachita indica*), Kyenkyen (*Antiaris toxicaria*) and Acacia (*Acacia sp.*).

The Ahanta constitute one of seven ethno-linguistic groups settled along Ghana's expansive coastline. The indigenes of the research area were also one of the earliest to have had regular culture contact with European traders who visited the Gold Coast. It is uncertain when this occurred. Lawrence

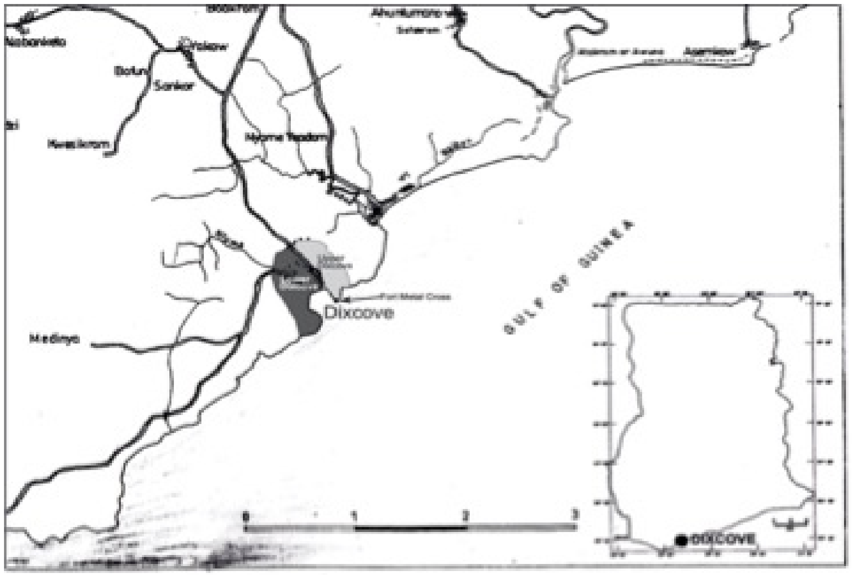

Figure 1: Map of the research area showing Upper and Lower Dixcove.

(1963: 292) has postulated that it probably preceded the construction of Fort Metal Cross, built in 1692, by some two hundred years. The fort located in the heart of *Ntwarkro,* (Upper Dixcove) one of two suburbs of Dixcove was the social and commercial epicenter of Euro-Ahanta interactions during the period.

Prior to the advent of Europeans to Dixcove, it was called Efiema, and comprised two small chiefdoms, each governed by its own paramount chief who was independent of the other (Bosman 1705: 12-13). The name change occurred sometime in the early 17th century when Europeans began referring to the Dixcove coastline as "Dick's cove," after Dick, a prominent English trader who operated along that stretch of the Dixcove coastline. Dick is also reputed to have facilitated and played a key role in the construction of Fort Metal Cross. The name was later corrupted to "Dick's cove" and "Dickies cove" by European seafarers.

European traders were attracted to the Dixcove coastline primarily because it had abundant reserves of gold (Samuel Swan, quoted in Bennett and Brooks 1965: 50). It was also linked directly by pathways to Sewfi and Wassa which also had abundant reserves of quality gold. According to van Dantzig (1980: 45), another reason why Europeans were attracted to Dixcove was that the traditional ports of trade along the Gold Coast were no longer able to supply sufficient quantities of gold as previously, and therefore came to Dixcove to procure supplies. Early European records posit that fishing, gold mining, palm oil and salt production constituted the major lynch-pins of the local economy. Other natural resources unique to the Dixcove area included palm oil, lime, gneiss, granite and timber required for the refurbishment of ships and English trade factories on the Gold Coast (Lawrence 1963: 294, 298 and 308).

Materials, Methodology and Sample Preparation of the Dixcove Sherds

All of the 31 pottery samples used for the study were recovered from archaeological excavations. After removal of surface soil and dirt, the potsherds were first dried for two days in an oven at 60º C, and crushed in an agate mortar to homogenize them into a fine powder. The powdered samples were then oven-dried for 24 hours and sieved, using a fine 0.5mm size mesh. After this, individual samples were prepared for short, medium and long irradiations by weighing three replicate samples of each portion of 200mg into small polythene vials. All weights were recorded to the nearest 0.01mg. The polythene vials were then wrapped and heat-sealed, using an electric soldering iron. After heat-sealing of the polythene vials, the samples were encapsulated in appropriate plastic containers/capsules for irradiation. An IAEA 'Soil 7' reference material was also prepared in the same way along with the samples.

Sample Irradiation

All samples and standard reference materials were irradiated in the inner sites of the GHARR-1 facility at a thermal neutron flux of 5.0 x 10^{11}ncm^{-2} s^{-1} at half-full power of 15kW. Irradiation and counting of samples using the Ghana Research Reactor-1 facility has been described earlier. Each of the capsules containing the samples was sent into the reactor for irradiation by means of a pneumatic transfer system operating at a pressure of 65Psi. The irradiation scheme adopted for the irradiation of the samples is given as follows:

For the short-lived elements such as Dy, Ca, Mn, Sm, Sr, U, V, and Al with half-lives between two minutes to 10 hours, the samples were irradiated for 30 seconds, delayed or cooled for 10 minutes, and counted for 10 minutes.

With the medium-lived elements such as Na, La, and As with half-lives between 13 to 45 hours, the samples were irradiated for two hours, delayed for between one to three days, and counted for 10 minutes.

For the long-lived elements such as Ce, Co, Cr, Eu, Gd, Hf, Lu, Sc, Th, and Zn with half-lives greater than two days, two hours of irradiation time between three to 16 days cooling time, and two hours counting time were chosen. Tables 1 to 3 show the nuclear data for the elements of interest measured.

Sample Counting

Counting of the samples was done on a PC-based gamma-ray spectroscopy system. The spectroscopy system consists of an N-type High Purity Germanium (HPGe) detector model GR 2518, a high voltage (HV) power supply model 3105, a spectroscopy Amplifier model 2020 (all manufactured by Canberra Industries Inc.), an 8k ORTEC EMCAPLUS Multi-Channel Analyzer (MCA) Emulation software card, and a 486 micro-computer for data evaluation and analysis. The detector operates on a negative bias voltage of 3000 V, and has a resolution of 0.85keV and 1.8keV for ^{57}Co and ^{60}Co of gamma-ray energies of 122keV and 1332keV respectively. The relative efficiency of the detector is 25%.

The quantitative analysis was done by converting the counts (area) under the photo peak of the radionuclides by the INAA comparator method (Glascock 1982). All of the samples and the comparator standard reference material were counted at a distance of 7.2cm from the top of the detector surface to quantify the elements.

Results of the INAA Experiment and Discussion

The trace element data set of this work consisted of 31 samples with 20 elements making a total of 620 data points. Table 4 shows the elemental concentrations in the varieties of pottery excavated from Dixcove. The results presented are the average of the three-analyzed samples prepared from each sample with their standard deviations, and the precision of all of the 20 elements was better than 10%. The results of the analysis of the samples were validated using IAEA "Soil 7" reference materials. The mean elemental concentrations, ranges, and standard deviations for the potsherds are listed in Table 4. The elements identified were Al, As, Ba, Ca, Ce, Co, Cr, Cs, Dy, Eu, Fe, Hf, La, Mn, Na, Sc, Sm, Th, U, and V. With the exception of Al, which is reported in percentage (%), all other values are given in part per million (ppm).

Statistical Treatment of the Analytical Data

Most of the elemental concentrations were above detection limits. Five elements: As, Cs, Dy, Hf and

Element	Target Isotope	Formed Nuclide	Isotopic abundance (%)	Thermal cross section σ_{th} (barns)	Half-life	Gamma-ray energy keV	g-yield (%)
Al	^{27}Al	^{28}Al	100	0.226	2.24 min	1778.99	100
Ba	^{138}Ba	^{139}Ba	71.70	0.405	84.63min	165.85	22.05
Ca	^{48}Ca	^{49}Ca	0.187	1.12	8.72 min	3084.54	92.10
Mn	^{55}Mn	^{56}Mn	100	13.2	2.58 h	1810.72	27.19
Sm	^{154}Sm	^{155}Sm	22.70	7.74	22.3 min	104.18	28.82
U	^{238}U	^{239}U	99.27	2.75	23.47min	74.66	50.0
V	^{51}V	^{52}V	99.75	4.79	3.75 min	1434.08	100

Source: IAEA/TECDOC - 564, 1990

Table 1: Nuclear data of short-lived nuclides

Element	Target Isotope	Formed Nuclide	Isotopic Abundance (%)	Thermal cross section σ_{th} (barns)	Half-life	Gamma-ray energy keV	g-yield (%)
As	^{75}As	^{76}As	100	3.86	26.32h	559.10	44.60
La	^{139}La	^{140}La	99.91	53.0	40.27h	487.02 1596.27	44.27 95.40
Na	^{23}Na	^{24}Na	100	0.513	14.96 h	1368.6, 2754	100 99.94

Source: IAEA/TECDOC-564, 1990

Table 2: Nuclear data of medium-lived nuclides.

Element	Target Isotope	Formed Nuclide	Isotopic abundance (%)	Thermal cross section σ_{th} (barns)	Half-life	Gamma-ray energy keV	g-yield (%)
Ce	^{140}Ce	^{141}Ce	88.48	0.575	32.5d	145.44	48.20
Co	^{59}Co	^{60}Co	100	37.13	5.27y	1173.2 1332.5	99.99 99.98
Cr	^{50}Cr	^{51}Cr	4.25	15.2	27.7d	320.01	10.08
Eu	^{151}Eu	^{152}Eu	47.80	5900	13.33y	964.10 1408.0	14.62 20.85
Fe	^{58}Fe	^{59}Fe	30.83	0.28	44.5d	1099.25	56.50
Lu	^{176}Lu	^{177}Lu	2.60	2100	6.71d	208.36	11.0
Sc	^{45}Sc	^{46}Sc	100	26.3	83.81d	889.28	99.98
Th	^{132}Th	^{233}Pa	100	7.26	26.97d	312.0	36.00
Zn	^{64}Zn	^{65}Zn	48.6	0.726	243.9d	1115.55	50.70

Source: IAEA/TECDOC-564, 1990

Table 3: Nuclear data of long-lived nuclides.

Element	Range	Mean ± SD
Al (%)	5.69-11.62	8.16 ± 0.05
Ba	16.28-474.71	276 ± 14
Ca	2582-22425	8231 ± 326
Ce	98-1186	818 ± 159
Co	5.78-12.45	9.54 ± 1.15
Cr	9.58-246.20	93.46 ± 10.35
Eu	0.75-3.96	2.03 ± 0.12
Fe	31450-58270	41504 ± 2248
La	15.20-44.46	28.45 ± 3.07
Mn	234-2760	687.3 ± 20.8
Na	5562-17393	11336 ± 35
Sc	5.39-12.59	10.32 ± 0.35
Sm	0.52-4.01	2.23 ± 0.14
Th	0.39-8.82	4.92 ± 0.24
V	71-179	103.3 ± 5.6
As	0.57-1.92	1.06±0.13
Cs	2.38-4.15	3.79 ± 0.23
Dy	0.49-1.27	0.96±0.06
Hf	3.94-7.27	5.11 ± 0.31
U	0.72-2.30	1.37±0.08

Table 4: Range, mean and standard deviation of elemental concentrations (ppm) for the potsherds.

U, however had three or more values missing or below the detection limits across a sample set. These elements were subsequently excluded in the statistical analysis as it is crucial to consider only elements with fewest missing values in such studies. Based on this screening criterion, 15 elements namely: Al, Ba, Ca, Ce, Co, Cr, Eu, Fe, La, Mn, Na, Sc, Sm, Th and V were used in subsequent data analyses.

Since INAA measures both bulk and trace elements, elemental concentrations were converted to log base 10 values to compensate for the large difference of magnitudes between major and trace elements (Davis 1986). Cluster analysis (CA) and Discriminant analysis were thereafter employed using SPSS 16.0 statistical package.

Cluster Analysis

Cluster analysis is a multivariate statistical technique that has a main objective to group the similar samples in accordance with their characteristics (Johnson and Wichern 1992). Cluster analysis was performed on the log-transformed variables using Euclidean distance and Ward's linkage method. The data were then standardized by Z-score approach. The dendrogram of the results of the cluster analysis is shown in Figure 2, and as can be seen, the preliminary classification showed the existence of three groups that are very well defined. The number of samples contained in each cluster group is also shown in Table 5.

Discriminant Analysis

In order to confirm the assumption obtained from the results of the cluster analysis, the data were further subjected to discriminant analysis. After the identifications of clusters within samples, discriminant analysis was used to isolate those variables which can most effectively reveal the differences between clusters and establish a discriminant function for this purpose. The plots obtained by the discriminant analysis of the samples are presented in Figures 3 and 4. The plots also revealed three main chemical groups that are well separated from one another showing that the samples are clearly different in their chemical composition. Samples with similar elemental chemistry fell in the same group and elemental concentrations of different signatures or chemistry were also not well correlated. The plots also tend to reveal that significant variations existed in the elemental compositions of the pottery from Dixcove.

Conclusions

The study revealed that the INAA facility at the Ghana Research Reactor-1 Centre at the Ghana Atomic Energy Commission is suitable for analyzing chemical and mineral constituents of archaeologically excavated potsherds. The INAA technique proved useful in characterizing ancient potsherds from Dixcove into their real geochemical groups. The statistical analytical procedures and cluster and discriminant analyses also revealed trace elements, variability and differences in the geochemical signatures of the potsherds.

The statistical analyses revealed that at least three potter groups using different fabrication methods and operating from different locations were responsible for producing the pottery recovered from Dixcove. Each of the three potter groups sourced their clay raw material from different geographical locations, thus accounting for the different mineral constituents in the sherds. Whether they were settled nearby or lived far from Dixcove will become clearer

Results by class:						
Class	1	2	3	4	5	6
Objects	9	13	1	6	1	1
Sum of weights	9	13	1	6	1	1
Within-class variance	1.080	1.143	0.000	1.324	0.000	0.000
Minimum distance to centroid	0.541	0.783	0.000	0.809	0.000	0.000
Average distance to centroid	0.909	1.011	0.000	1.044	0.000	0.000
Maximum distance to centroid	1.814	1.419	0.000	1.149	0.000	0.000
	T1-A7	T1-A13	T1-A16	T2-A6	T2-B6	T2-B8
	T1-B5	T1-A14		T2-A8		
	T1-B11	T1-A23		T2-B4		
	T1-B13	T1-B4		P1-A2		
	T1-B14	T1-B7		P1-A5		
	T1-B20	T2-A1		P1-B7		
	T1-B22	T2-A2				
	T2-A9	T2-A17				
	P1-B4	T2-B3				
		T2-B10				
		T2-B11				
		T2-B15				
		P1-B9				

Table 5: Table showing cluster analysis of pottery groupings from Dixcove.

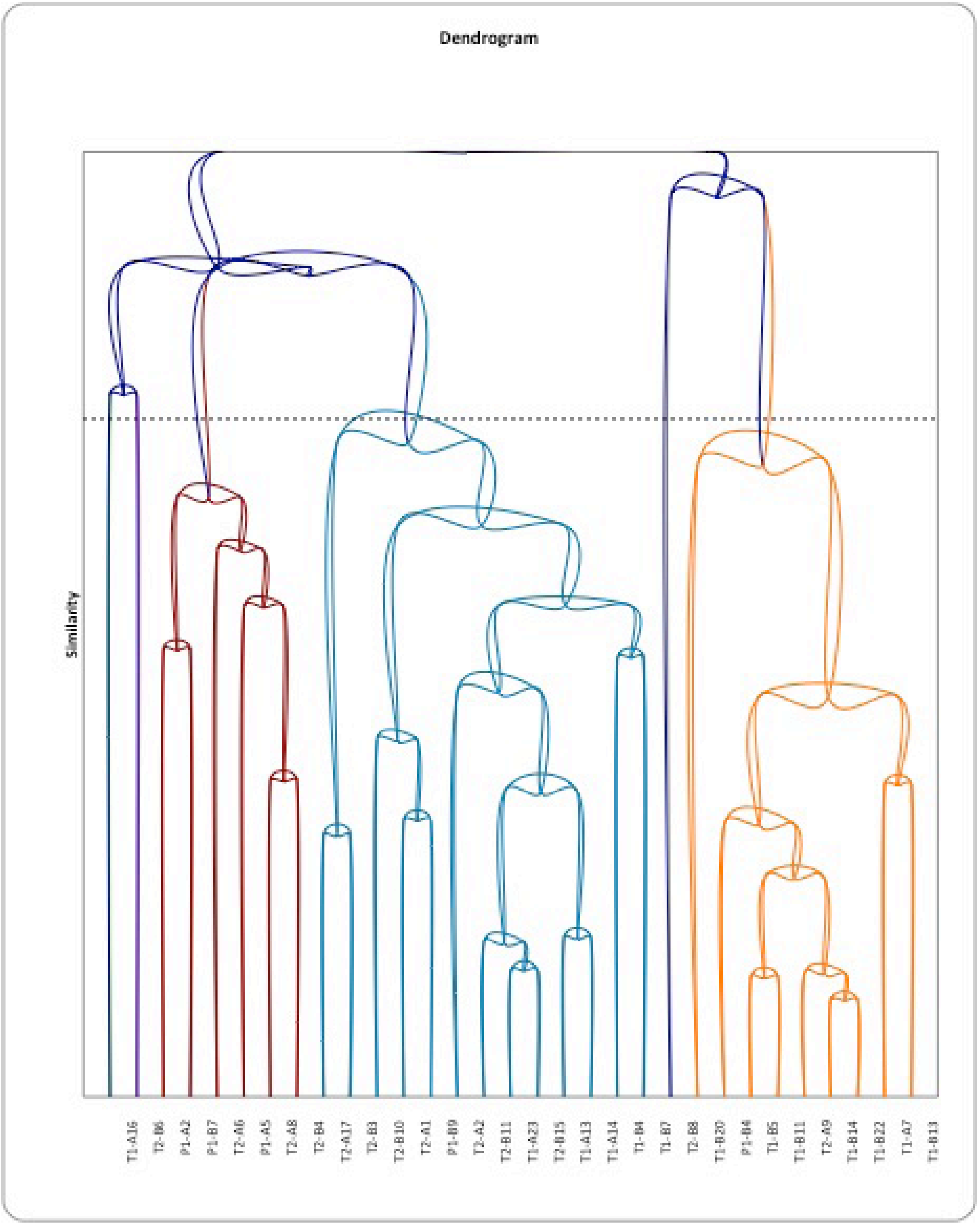

Figure 2: Cluster analysis dendrogram showing groupings of pottery from Dixcove.

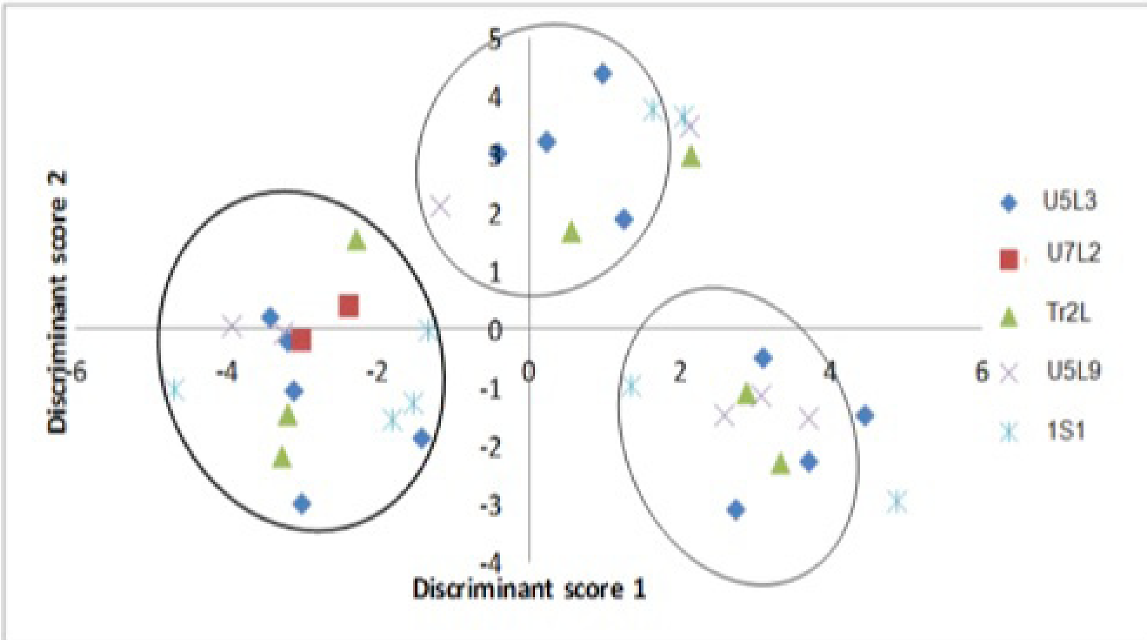

Figure 3: A plot of the first and second discriminant function of potsherds from Dixcove.

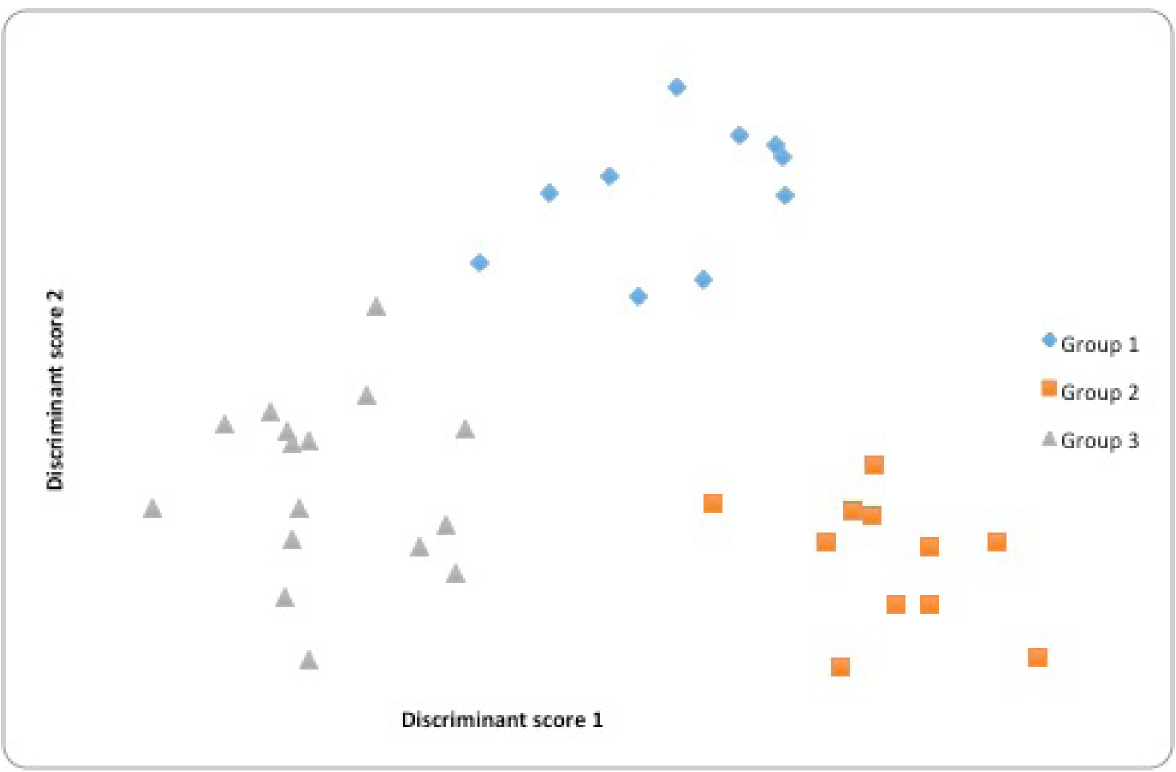

Figure 4: A plot of discriminant analysis showing groupings of pottery sherds from Dixcove.

after systematic clay analyses of the region have been undertaken in the near future. The above view appears to support ethno-historical assertions of the people of Dixcove that fishing and crop farming constituted their main vocations in the past and that their ancestors procured their pottery from elsewhere probably via trade.

Acknowledgments

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