2017 International Nuclear Atlantic Conference - INAC 2017
Belo Horizonte, MG, Brazil, October 22-27, 2017
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN

Agência Brasileira do ISBN
ISBN 978-85-99141-07-6

CHEMICAL CHARACTERIZATION OF ANCIENT POTTERY FROM THE SOUTH-WEST AMAZONIA USING NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The analyzes carried out in this work aims to contribute to the discussion about the ceramic objects founded in Monte Castelo's sambaqui located at south-west Amazonia. The first study accomplished by Miller in 1980 suggests that this archaeological site is inserted in the old contexts of production of ceramics in the Amazon. Until today, there are not any physical and chemical analysis studies in this ceramics and this kind of studies may help archaeological studies performed at the sambaqui. With this purpose, this work presents a preliminary study of chemical characterization of eighty-seven ceramic samples using the Neutron Activation Analysis (NAA). The analyzed elements were: As, K, La, Lu, Na, Nd, Sm, U, Yb, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Tb, Th. With the purpose to study the similarity/dissimilarity between the samples cluster and discriminant analysis were used. The results showed the existence of three different chemical groups that are in agreement with the archaeological studies made by Miller which found a sequence of cultural development, with three main occupational components whose dating ranging from 8.400 to 4.000 b.P. In this way, the results of this work are in agreement with miller's studies and suggest Bacabal's phase as the oldest ceramist culture in the Southwest of the Amazon.

1. INTRODUCTION

The Amazon system is the largest and most complex terrestrial ecosystem. Its area includes nine Latin American countries, due to its large size, this area can be seen as a demographic void [1, 2]. However, archaeological research in the region has shown a very different picture. Archaeological remains found in different areas indicate an age-old history of human occupation of 14000 years old. With this perspective, some archaeological currents concentrate on the search of traces of human occupation to prove that before the arrival of the Europeans to the continent, the Amazon was dense and diversely occupied [3].

One of the focuses of these searches has been the study of pottery, which are one of the materials most produced and are especially well suited to derive archaeological information and help understanding the way of life of the populations due to its abundance and variety [4].

In the Amazon, the older contexts of pottery production are always associated with sambaquis. The Monte Castelo's sambaqui is one of the old context of pottery production in the Amazon and is located in the alluvial plain of the Rio Branco, about 20 km from its confluence with the Rio Guaporé (Figure 1) [5].

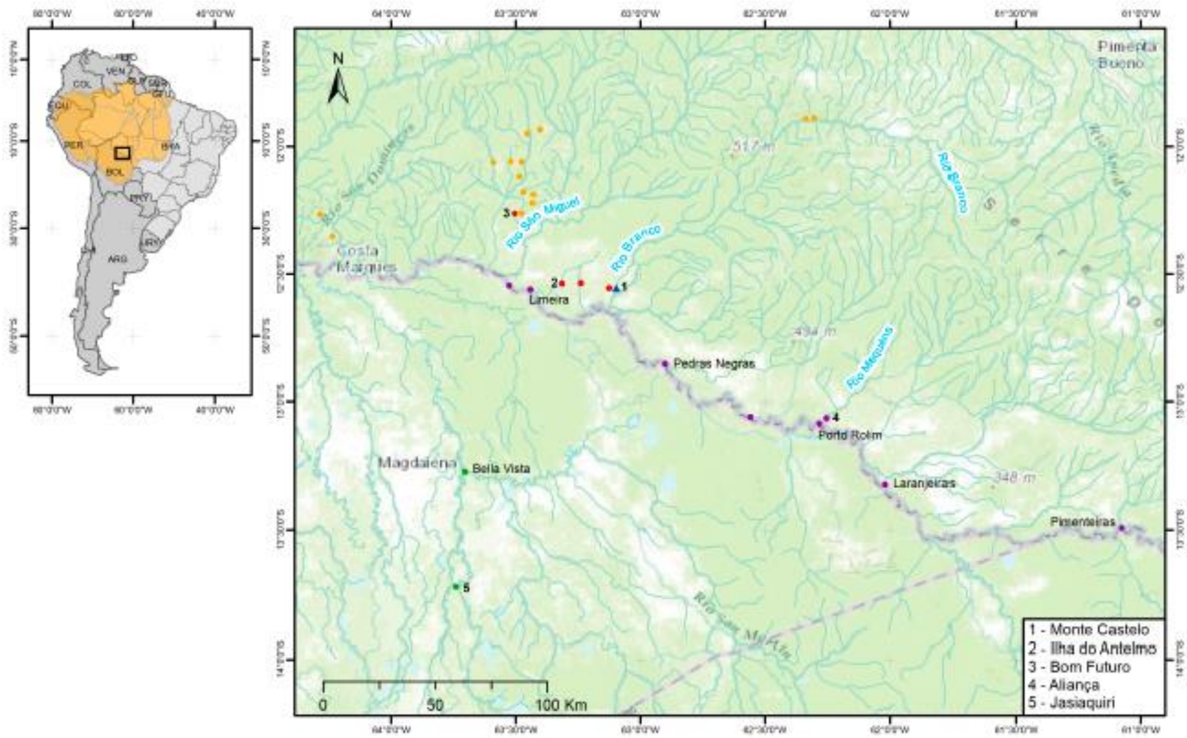

Figure 1. Monte Castelo archaeological site in the alluvial plain of the Rio Branco.

The first intervention at this sambaqui was made by Miller in 1980 and indicated large quantities of ceramic fragments, lithic artifacts, plant remains, and abundant wildlife including snail of the genus *Pamacea* that constitute the matrix of sambaqui. The dates of Monte Catelo's sambaqui (at total 22 dates of ^{14}C) allow the reconstruction of a sequence of cultural development, that identifies a long pre-ceramic occupation of 8400 years old called as Cupim's phase, followed by the Sinimbu's phase of 7100 years old, and the sudden appearance of Bacabal's phase of 4000 years old. Miller was unable to continue his work at the sambaqui due to a malaria attack and has not returned the excavations. However, his preliminary experience demonstrate a high potential for this to be one of the oldest known settlement systems in the Amazon.

Currently, the researches at the Monte Castelo archaeological site were taken up with the objective of performing detailed stratigraphic analyzes, collection of samples for dates and physicalchemical analysis that will help in the search for information about the prehistoric Amazon.

The physicochemical study of archaeological ceramics has reached a large number of publications in the field of archaeology in recent years [6]. Those studies fragments can be used provenance characterization study of exchange and manufacturing of ceramics [6, 7].

Different techniques can be applied to determine the sample composition, including AAS, ICP, PIXE and NAA. The neutron activation analysis comprises a multielement nondestructive nuclear analytical technique able to perform analysis of inorganic chemicals major, minor and trace elements [8, 9], and is based in the measurement of induced radioactivity in sample. [10]. The particle emitted by nuclei of radioactive isotopes can be measured using gamma spectroscopy [11]. In short, it has advantages such as high levels of precision, accuracy and reproducibility [9]. In this context, NAA has been widely used in basic studies of ceramics material because with this analytical technique it is possible to interpret and associate its life cycle to the behavior of the people involved, assessing patterns of exchange and trade [8-15].

This work presents a preliminary study of chemical characterization of eighty-seven bacabal's pottery samples using the Neutron Activation Analysis (NAA). The results of the chemical compositional study will help archaeological studies performed at the Monte Castelo's sambaqui.

2. METHODOLOGY

2.1. Sample Collection

The samples analyzed in this work were collected during the reopening of excavations at the Monte Castelo's sambaqui and were provided by the Museum of Archeology and Ethnology of the University of São Paulo (MAE / USP).

Up to the present time, the reopening of excavations has carried out prospects surveys every 10 cm until 800 cm depth. The excavation of the first 80 cm was one of the more complex contexts, since it contained considerable amount of pottery material, lithic material, and artifacts in bones and bivalve shells mixed up by the work done in the past by Miller. Thus, although 10 by 10 cm sections were cut, some stratigraphic profiles were not possible to be well delimited. The stratigraphic delimitation without interference, originating from the previous excavation done by Miller, was only initiated after these 80 cm.

However, the 87 samples of pottery fragments whose typological studies claim that the fragments belong to the Bacabal's phase were selected from the following stratigraphy's (Table 1).

Tables 1. Relation of the selection of samples and the stratigraphy.

Samples quantities	Stratigraphy
10 samples	Level 30 - 40 cm
10 samples	Level 0 - 80 cm
10 samples	Level 0 - 90 cm
9 samples	Level 20 - 90 cm
20 samples	Level 80 - 90 cm
10 samples	Level 90 - 100 cm
10 samples	Level 100 - 110 cm
3 samples	Level 120 - 130 cm
5 samples	Level 130 - 140 cm

2.2. Sample Preparation and irradiation

The ceramic fragments selected were analyzed by INAA in order to obtain their elemental composition. The external surface was removed with a fine bristle brush. After this procedure, holes were made on the samples with a tungsten carbide rotary file, attached to a variable speed drill. Around 500 mg of powdered sample was obtained from three to eight holes on the side surface of the ceramic fragment, preventing the drill from crossing over the walls.

This powder is then collected, dried for 24 h in an oven at 100 °C and stored in desiccators [16], until it is cold enough for weighing. Around 100 mg of each sample were weighed in polyethylene involucres and sealed with sealing iron. Each involucre was wrapped in aluminum foil. Groups of up to seven ceramic powdered samples and two reference materials were wrapped in another aluminum foil, in order to group them in a parallel fashion to receive approximately the same neutron flux inside the nuclear reactor. The Standard Reference Material – NIST - SRM 1633b was used as standard for analysis and a sediment that is a candidate to reference material analyzed by 38 NAA laboratories from Wageningen University (Wepal), was used for the analytical quality control.

The samples were irradiated in the swimming pool research reactor IEA-R1 of the Nuclear and Energy Research Institute (IPEN-CNEN/SP), at a thermal neutron flux of 1.10^{11} $cm^2.s^{-1}$ for 8 h. The gamma-ray spectrometry was carried out with a hyperpure germanium detector (model GX 2519 from Canberra), with a resolution of 1.90 keV at the 1332 keV gamma peak of ^{60}Co. The spectra were collected by a Canberra S-100 MCA with 8,192 channels. The software Genie-2000 NAA Processing Procedure, developed by Canberra, was used to analyze the gamma-ray spectra. Two measurement series were carried out. The elements As, K, La, Lu, Na, Nd, Sm and Yb were measured after 7 days of decay. The elements Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Tb, Th and Zn were measured after 25–30 days of decay [17].

3. RESULTS AND DISCUSSION

One of the basic premises underlying the use of chemistry in ceramic analysis is that clay sources can be differentiated if an adequately precision analytical technique is used. If an element is not measured with good precision it can obscure real differences in concentration and the discriminating effect of other well-measured elements tends to be reduced. These differences can be used to form ceramic compositional groups because vessels manufactured from a given clay source will be more similar to each other than to other type of vessels which were manufactured from a different source [16].

In this work the precision was studied using a candidate to reference material analyzed by 38 NAA laboratories from Wageningen University (Wepal). For that, were made 10 independent determinations. The mean, the standard deviation (SD) and the relative standard deviation (RSD) were calculated. These results were compared with the values presents at the report (Table 2).

Table 2. Results for precision study, in µg/g, unless otherwise indicated.

Sample	Mean ± SD	RSD (%)	Report
Na (%)	4,68 ± 0,14	3,02	4,69 ± 0,34
K (%)	13,45 ± 0,62	4,60	12,87 ± 0,67
As	18,23 ± 0,88	4,82	17,56 ± 1,93
La	21,12 ± 0,88	4,17	19,46 ± 1,72
Nd	20,02 ± 6,08	30,37	18,91 ± 2,96
Sm	3,71 ± 0,13	3,59	--------
Yb	1,51 ± 0,36	23,54	--------
Lu	0,26 ± 0,05	19,05	--------
Sc	5,44 ± 0,25	4,67	5,67 ± 0,37
Cr	74,96 ± 7,52	10,04	70,98 ± 7,31
Fe (%)	25,33 ± 1,29	5,10	25,39 ± 1,42
Co	7,95 ± 0,55	6,96	8,14 ± 0,75
Zn	380,09 ± 42,81	11,26	391,50 ± 25,00
Rb	66,86 ± 14,89	22,27	61,38 ± 5,02
Cs	4,03 ± 0,64	15,88	3,77 ± 0,36
Ce	40,56 ± 2,03	5,00	39,99 ± 5,03
Eu	0,72 ± 0,06	8,79	--------
Tb	0,53 ± 0,16	30,65	--------
Hf	7,97 ± 1,30	16,37	--------
Ta	0,867 ± 0,23	26,268	--------
Th	5,90 ± 0,35	5,886	5,69 ± 0,62

As can be seen at the Table 2 the relative standard deviation (RSD) of Na, K, La, As, Sm, Sc, Fe, Co, Ce, Eu and Th was less than 10% and are similar to those from the report. Elements that have low precision can reduce the discriminating effects of other well measured elements. In this study all the elements with precision of less than 10% were considered for interpretation of the results. This precision is considered appropriate by several authors for the choice of the chemical elements for studies of archeological objects using multivariate statistical methods [18].

Although Co had RSD around 7%, was not included in the data set because the concentration can be affected by tungsten carbides files [19]. The precision of As was better than 10%; however, they were not included because they presented 15% of missing values.

Besides that, Na and K present’s anomalies in their mass fractions as can be observed in the projection of the first two main components obtained by principal component analysis based on the covariance matrix (Figure 2).

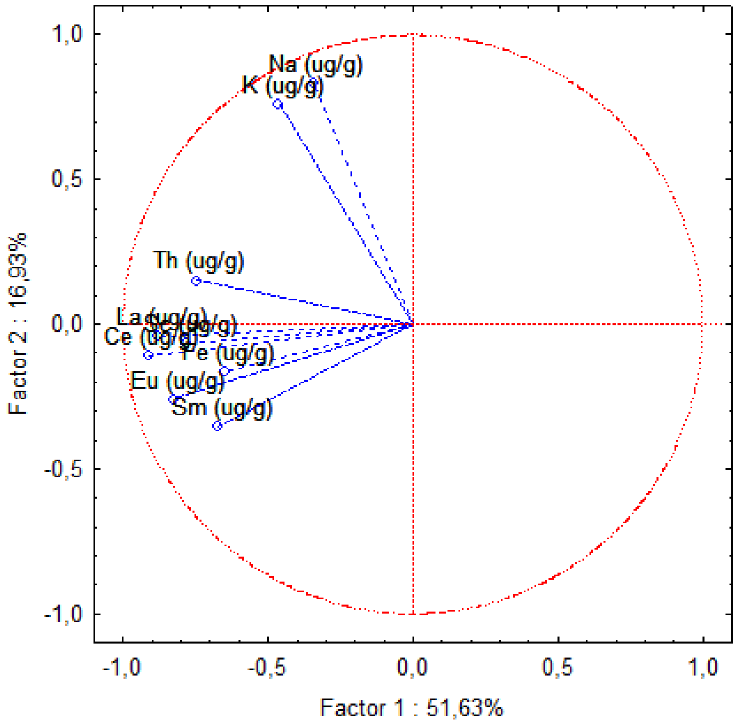

Figure 2: Projection of the vectors of the variables of the two main components.

The dominance of the elements Na and K in the first two components is evident by visualizing the size of the projection of the vectors relative to Na and K in Figure 2. These effect can be explained according to literature data [20], that there is a tendency of high enrichment of Na and K in the clays of the Sambaqui region. Therefore, it was decided to exclude these elements in multivariate analyzes.

Based on these screening criteria, 7 elements: La, Sm, Sc, Fe, Ce, Eu and Th were used in subsequent data analyses. None of these elements considered contained missing values. The description values (values of maximum, minimum, mean e RSD) of ceramic chemical elements are presented in Table 3.

Table 3. Elemental description for Monte Castelo archaeological sites

	La (μg/g)	Sm (μg/g)	Sc (μg/g)	Fe (%)	Ce (μg/g)	Eu (μg/g)	Th (μg/g)
Minimum	14,75	2,72	2,75	3,01	11,61	0,27	1,65
Maximum	62,88	25,25	18,67	36,07	117,36	2,04	16,74
Mean	34,05	6,74	12,17	16,60	63,62	1,06	10,39
RSD (%)	27,19	51,91	20,88	29,66	31,33	36,07	23,38

Initially, at the data of elementary mass fraction of the ceramic samples was made a transformation to compensate for the difference in magnitude among elements given in percentages and at trace level. In archaeometric studies, the elemental concentrations are frequently logarithmically transformed, based on the assumption that the trace elements have a natural lognormal distribution [21-23]. In the present work, the elemental concentrations were rescaled to base-10 logarithms.

After being transformed, the data set was submitted to two multivariate statistical analysis: cluster and discriminant analysis. The multivariate statistical analysis techniques are designed to determine the existence of groups in the data set according to similar or distinct chemical groups [24].

Cluster analysis is a multivariate statistical technique used to produce behavioral patterns in experimental results through the formation of homogeneous groups of samples [24]. The results of cluster analysis are commonly presented in the form of dendrograms which show the order and levels of specimen clustering. In this work, the statistical program R was used to perform the cluster analysis as a preliminary classification of the results, adopting the squared Euclidean distance and Ward's method as the clustering algorithm, thus generating the dendrogram of the Figure 3.

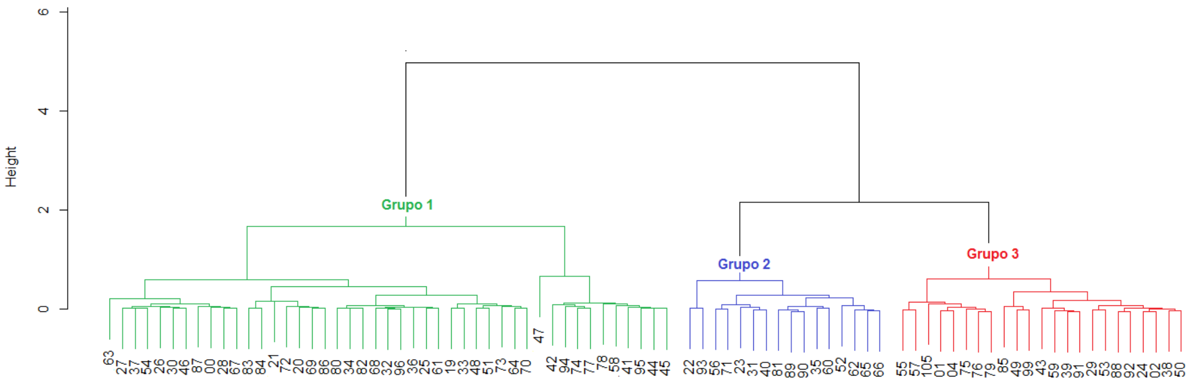

Figure 3: Dendrogram of the ceramic samples using squared Euclidean distance and Ward's method, (n = 87).

As can be seen in the figure the preliminary classification showed the existence of three groups very well defined.

After the clustering procedure, a discriminant analysis was carried out in order to verify the data structure. The basis for all multivariate analyses is that all the elements included are independent variables. This is not necessary true, but it can be tested using the pooled within-groups correlation matrix provided by discriminant analysis [24]. After identifying the cluster 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 plot obtained by the linear discriminant function 1 versus the linear discriminant function 2 is presented in Figure 4.

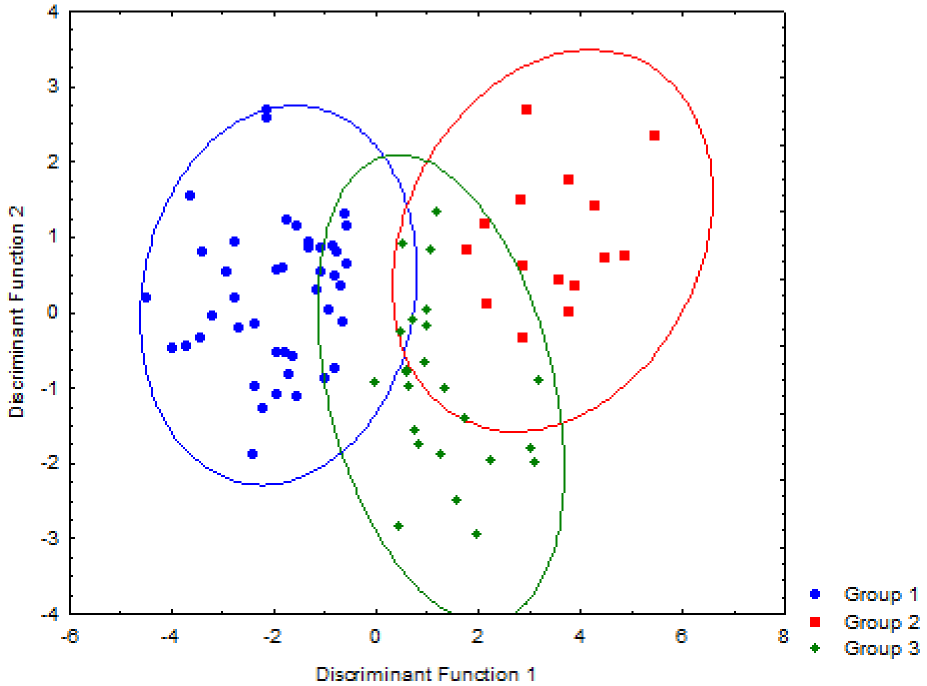

Figure 3: Plot of the linear discriminant function 1 *vs* linear discriminant function 2.

As shown in the Figures 3 and 4, the plot reveals three chemical groups, showing that the samples are different in their chemical composition. As can be seen in the figures, three different row material in the ceramics production in the Monte Castelo archaeological site was used.

4. CONCLUSIONS

The preliminary study made in the Monte Castelo's sambaqui showed differences exist in the elements concentrations and a simple inspection of the data cannot be used to differentiate the chemical groups.

Therefore, two multivariate methods, cluster and discriminant analysis, were applied for examining the chemical composition data. The combination of the associated cluster and discriminant analysis proved to yield useful results for the elemental concentration data sets used in this work. Until the present moment, three different compositional groups can be assigned to Monte Castelo archaeological site.

Our preliminary results provide evidence that the Monte Castelo ceramic were manufactured from a least three different clay sources that are in agreement with the archaeological studies made by Miller which found a sequence of cultural development, with three main occupational components whose dating ranging from 8.400 to 4.000 b.P.

In this way, the results of this work corroborate with miller's studies and suggest a high possibility that the Bacabal's phase is the oldest ceramist culture in the Southwest of the Amazon. These results will become clear by the future dating analysis.

ACKNOWLEDGMENTS

The authors wish to thank Comissão Nacional de Energia Nuclear (CNEN), for the financial support.

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