The Archaeometry study of the Chemical and Mineral composition of Pottery from Brazil's Northeast

J. O. Santos[1, 2], C. S. Munita[2], R. G. Toyota[2], C. Vergne[3], R. S. Silva[3], P. M. S. Oliveira[4]

1. Centro Federal de Educação Tecnológica de Sergipe, CEFET-SE, Aracaju – SE, Brazil

2. Instituto de Pesquisas Energéticas e Nuclerares, IPEN/CNEN-SP, São Paulo, BRAZIL

3. Universidade Federal de Sergipe, UFSE, São Cristóvão-SE, BRAZIL

4. Instituto de Matemática e Estatística da Universidade de São Paulo, IME/USP, São Paulo, BRAZIL

In this study, chemical and mineralogical analyses were performed on ceramics and clay samples from Barracão archaeological site located in Baixo São Francisco River. The chemical and mineral analysis was performed by INAA and by means differential scanning calorimetry (DSC). The data set was studied by means of cluster analysis and discriminant analysis. The results showed that the raw material used in ceramics is not local. By using DSC it was possible to discover that the principal minerals in the samples are quartz, feldspars, mica and kaolinite. The existence of kaolinite denotes that the firing temperature of the pottery analyzed was lower than 500 °C. The results obtained in this study, in association with archaeological information, allowed for the identification of the ceramic groups relative to the ceramists occupations at Xingó area.

Introduction

Nowadays Archaeology has used a variety of methods and tools to reconstruct ancient cultures through environmental analysis, sociology, scientific and historical dating methods, historic and iconographic sources, and material analysis of artifacts that have been found, in addition to other methods. The use of an adopted method from the natural sciences is currently subsumed under the term Archaeometry. Archaeometry is an interdisciplinary field of research that covers aspects of analytical chemistry and spectroscopy, electrochemistry, physics, electrochemistry, anthropology, among other fields.[1]

Since ceramics represents a sophisticated merging of previously separate domains of human knowledge and experience, these objects are intensely studied by means of archaeometric methods.[2] In addition to its abundance and durability, ceramics has several macroscopic and microscopic attributes of interest to archaeologists.[3] Visual properties such as shape and surface decoration are frequently used as cultural and chronological indicators. Most especially used is the compositional study of the clay, sand and other natural material from which the pottery were taken, due to the fact that the chemical composition of these materials can be unique.[4, 5]

It has been an integral approach to archaeological pottery studies most often has been provided information about the provenance of raw materials and ancient technologies, such as firing conditions of raw materials during the manufacturing process.[6] Evaluating the original firing temperature is one of the most intriguing aspects of the technological studies of ancient ceramics. The firing process of ceramics plays a fundamental role in ceramic production, like time, temperature and the firing atmosphere, which contributes to the final properties of the obtained items. The traditional studies of the firing temperatures have been estimates. This has been achieved through the study of the minerals and the new-formed minerals which has resulted from firing process. The study has been achieved by means of x-ray diffraction (XRD) and differential scanning calometry (DSC).[7]

In recent years, a multidisciplinary research program has begun between the Federal University of Sergipe (UFS) and the Nuclear and Energy Research Institute (IPEN/CNEN-SP) to study the ancient ceramic cultures of the Xingó region, situated in Canindé do São Francisco, in Northeastern Brazilian. Recent studies conducted in the area have shown the existence of an independent ceramist group without relation to the well established ceramist groups in the Brazilian Northeast.[8] Dating obtained by means of carbon-14 analysis, from skeletons, has indicated that there was evidence of human occupation 9,000 years before present in "Xingó" region.

Archaeometric studies on possible clay sources contribute in determining a "fingerprint" of raw materials used to manufacture of ceramics, so, in this project, instrumental neutron activation analysis (INAA) was utilized to determine the elemental composition of pottery fragments and clays from the Barracão archaeological site, situated in Canindé do São Francisco, to establish a categorization of these ceramics and the raw material sources. Additional studies about mineral composition of clay and ceramic samples from Xingó were done through the DSC technique in order to characterize their mineral contents and to determine their equivalent firing temperature. In addition, the hypotheses for the analyzed clay samples, which would be used as raw material for the ceramic paste of ceramics from Barracão archaeological site were verified.

Experimental

Sample preparation and standard

In this study, 103 samples, 73 ceramic fragments and 30 clay samples, from the Barracão archaeological site were analyzed by means of INAA. The clays samples were collected near to Barracão site from three places, called Clay A, B and C. Although several chemical methods have been employed to analyze ceramics and clays, the analytical technique that has dominated pottery provenance research from the late 1960s up to the present day has been INAA.[9-12] According to archaeological studies, the ceramist occupation in the Xingó area was one of the most ancient in the Brazilian Northeast.[13]

Ceramic powder samples were obtained by cleaning the outer surface and drilling to a depth of 1-2 cm using a tungsten carbide rotary file attached to the end of a flexible shaft, using a variable speed drill. Depending on the thickness, 3 or 5 holes were drilled as deep into the core of the fragment as possible without drilling through the walls. Clay samples were ground in an agate mortar until a granulometry of 100-200 mesh was achieved. Finally, the powered samples were dried in an oven at 105^{o}C for 24 hrs and stored in desiccators.

Constituent Elements in Coal Fly Ash - NIST-SRM-1633b, were used as standards in all analysis. The standard reference material Brick Clay - NIST-SRM-679 was used to check the analytical quality of the results. The standards and the samples were dried in an oven at 105^{o}C, the standards for 4 hrs and samples for 24 hrs and stored in a desiccator until weighing.

Irradiation and radioactivity

About 100 mg of ceramics samples, and NIST-SRM-1633b were weighed in polyethylene bags and wrapped in aluminum foil. Groups of 8 ceramic samples and two reference materials were packed in aluminum foil and irradiated in the swimming pool research reactor, IEA-R1m (IPEN/CNEN – SP) at a thermal neutron flux of about 5 x 10^{12} $n \cdot cm^{-2} \cdot s^{-1}$ for 8hrs.

Two measurement series were carried out using Ge (hyperpure) detector, model GX 2020 from Canberra, with a resolution of 1.90 keV at the 1332.49 keV gamma peak of ^{60}Co, with S-100 MCA of Canberra with 8192 channels. As, K, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days cooling time and Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, and Zn after 25-30 days. Gamma ray spectra analysis was carried out using the software Genie 2000 NAA Procedure from Canberra.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out in an automatic thermal system (model DSC-50 - Shimadzu). Samples of about 3 mg were packed into an aluminum crucible and it was thermally treated at a heating rate of 10°C.min^{-1} in an air flow, with an ambient temperature up to 600°C. The equivalent firing temperature was estimated by comparing the measurement on the original shred (1° cycle) with the measurement data on the same shred, re-firing at an increasing temperature (2° cycle).

Statistical method

To identify outlying cases, the robust Mahalanobis distance (RD) based on the minimum covariance determinant (MCD)[14 -17], was utilized. It was possible construct the ellipse corresponding to squared Mahalanobis distance (often called a tolerance ellipse) for each group. The observation found outside of the tolerance ellipse, in the space established for the first two principal components, was considered an outlier.[18]

In general, cluster analysis is used to identify initial groups after which other techniques for group refinement and classification are subsequently applied.[19,20] To identify initial groups of ceramics from Barracão site, a cluster analysis using Ward's Method and squared Euclidian distance was performed.[21]

Discriminant analysis is a multivariate statistical technique used in Archaeometry to identify elements which are most useful in discriminating between groups and graphically displaying the chemical distinction between these groups.[22] In this study, discriminant analysis was used to identify the groups of samples.

Results and Discussion

To evaluate the analytical process and to establish the chemical elements which can be used in the data interpretation, the elemental concentrations for reference material Brick Clay - NIST-SRM-679 were statistically compared with the data found in our laboratory. The precision of several elements (La, Th, Sc, Fe, Eu, Ce, Zn, Hf, and Co) was better than 5%. Some elements presented a RSD (Relative Standard Deviation) of less than 10% (Nd, Rb, Sm, Ba, Sb, Ta, and Tb) and are similar to those from the literature.[23]

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 (Na, Lu, Yb, La, Th, Cr, Cs, Sc, Ce, Fe, Eu, Zn, Co, Ta, U and Hf).[24] The Zn presented RSD better than 10% but was excluded from the data set because its determination suffers strong gamma ray interferences of ^{46}Sc and ^{182}Ta. The elements Co and Ta were eliminated because their concentrations can be affected by tungsten carbides drills.[25] The K and Sb were better than 10%, however they were excluded because they presented 15% of missing values. Based on these screening criteria 13 elements: Na, Lu, Yb, La, Th, Cr, Cs, Ce, Sc, Fe, Eu, U and Hf were used for the interpretation of the results.

The results were transformed to $\log_{10}$ to compensate for the large magnitude difference between the measured elements at the trace level and the larger ones. One reason for this is the belief that, within manufacture raw materials, elements have a natural lognormal distribution, and that data normalization is desirable. After logarithmic transformation the data set was submitted to outlying tests by means of robust Mahalanobis distance, using a minimum covariance determinant, where critical values were obtained $\chi^2_{2;0.98}$. Only one sample was considered an outlier.

Hierarchic cluster analysis, HCA, was used to study the clusters of the pottery samples. Figure 2 shows the cluster using as similarity measured the square Euclidean distance and the Ward's method among the 13 chemical elements to pottery samples. The Figure shows the separation of the pottery in four groups. The groups are named A, B, C and D.

In order to confirm the compositional groups, the data were submitted to discriminant analysis (DA). According with results from HCA *'a priori'* to pottery samples was defined. Figure 3 presents a bivariate plot of discriminant functions showing seven main groups, three groups of clay samples (Clay A(19), clay B (10) and clay (10)) and four groups of potteries (Pottery A(10), Pottery B (12), Pottery C(9) and Pottery D(32)). In addition, the results from DA indicated that raw materials used in the manufacture of the analyzed ceramics are distinct and the clay samples investigated were not used to obtain a ceramic paste from Barracão site. Since investigated clay samples were available near to Barracão archeological site, it can be inferred that potters, who lived at Barracão area searched their raw material far from this site. Therefore, the search for clay of appropriate properties to manufacture the ceramics, perhaps, has induced craftsman to seek raw materials far from place where they lived.

Figure 1

Figure 2

Equivalent firing temperature

In order to verify the equivalent firing temperature of the ceramics from Barracão archaeological site a mineralogical study was accomplished by using differential scanning calorimetry. The Figure 4 shows DSC typical curves for all the samples from Barracão site. It has been found that the mineral composition of the most of the studied shreds is quartz, feldspars, mica and kaolinite. According to our thermal results, we can affirm that all the samples have a similar mineral composition, which is represented in Figure 4. The DSC curve (BV05, BV31, BV56 and BV17), which corresponding to 1° cycle of heating, shows three main endothermic peaks: the first peak around 100°C corresponding to a loss of adsorbed and interlayer water; the second peak around 500°C corresponding to a deyhidroxilation of the kaolinite; and the peak at 573°C is related to a transformation from α – quartz to β – quartz[26]. The curve corresponding to 2° cycle in Figure 4, all the samples present, only peak at 573°C, once the transformation from α – quartz to β – quartz is reversible. The existence of kaolinite denotes that the equivalent firing temperature was lower than 500°C. According to our results, we can infer that the calculated firing temperature should be grouped around only one temperature (500 °C), which in turn reflects the organization production at the Barracão archaeological site.

Figure 3

Conclusion

The INAA of ceramics from the Barracão site was successful in identifying distinct compositional groups. There were four groups of ceramics and three groups of clay identified. The results from DA showed that the clay samples analyzed in this study were not used to prepare ceramic pastes at the Barracão archaeological site. Therefore, it can be inferred that the raw materials for the manufacture of potteries at the Barracão site was not from there. Thermal analysis shows that the equivalent firing temperature of potteries from Barracão site was around 500°C. The results provided information about the occupational dynamic of ceramist groups in the Xingó area, during the pre-historical period.

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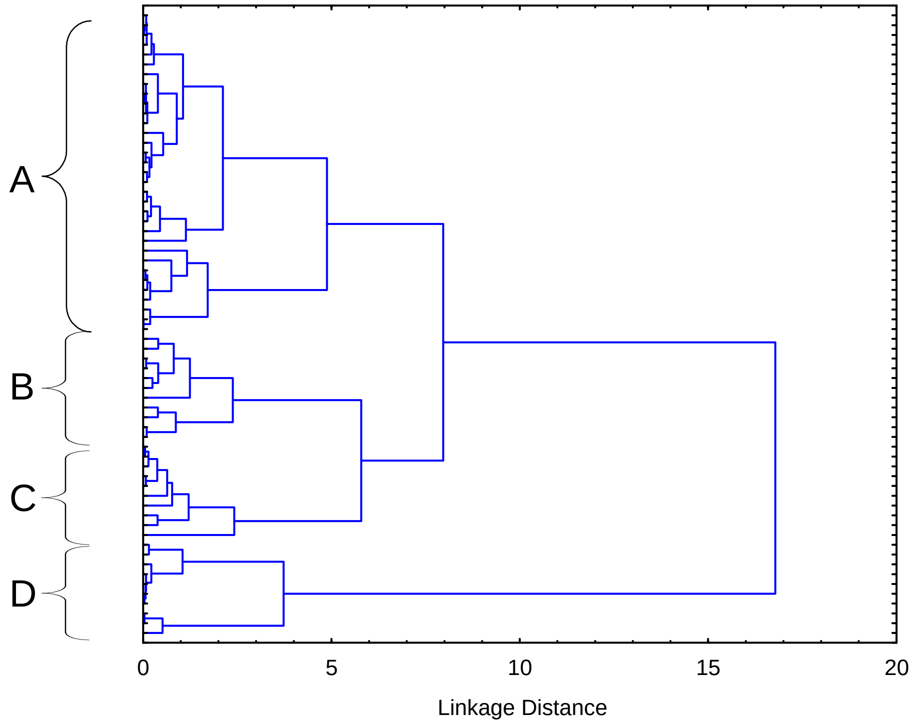

Figure 1

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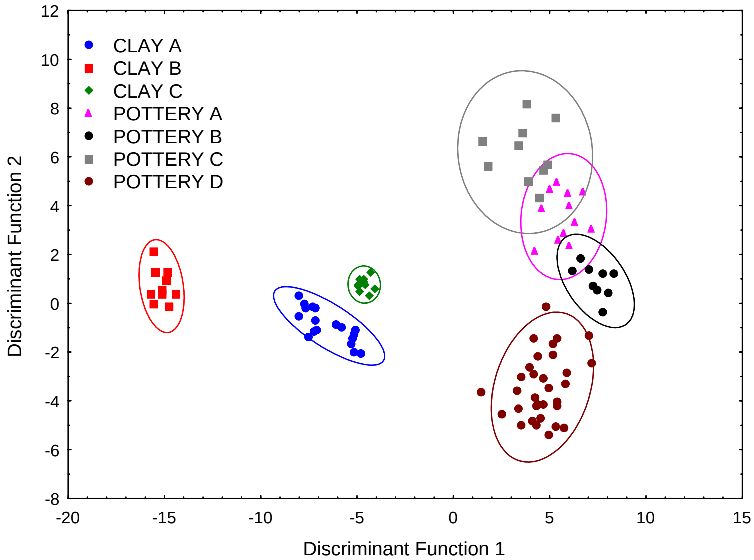

Figure 2

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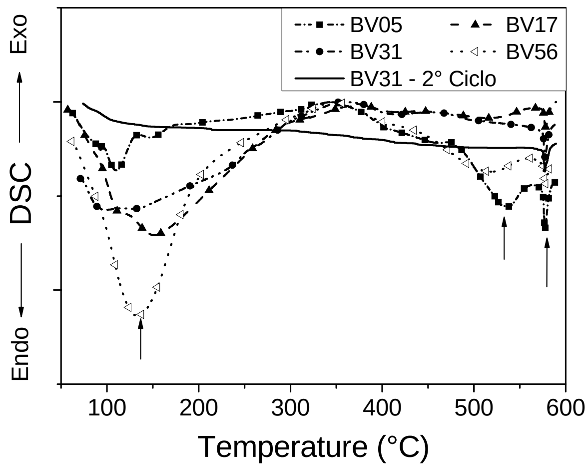

Figure 3

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Captions to Figure

Figure 1 – Dendrogram for pottery samples from square Euclidean distance and cluster analysis.

Figure 2 – Linear discriminant analysis of ceramic and clay samples from the Barracão archaeological site. Ellipses represent a 95% confidence level.

Figure 3 – The DSC results to the Barracão archaeological site