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Major and trace element characterization of prehistoric ceramic from Rezende archaeological site

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Forty one ceramic fragment samples from Rezende archaeological site, Centralina city, Minas Gerais State, Brazil, were analyzed using INAA to determine the concentration of 24 chemical elements: As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn. Three multivariate statistical methods, cluster, discriminant and principal components analysis were performed on the data set. The results showed that the large majority of the samples (94%) can be considered to be manufactured using the same source of raw material.

Introduction

Compositional analysis has gained widespread use as a tool for sourcing of archaeological artifacts over the last two decades.[1] Much of the information for judging provenience lies in the trace elements[2–8] to make reasonable association of prehistoric and early historic finds with likely sources origin. Ceramic is one of the fundamental tools used to derive archaeological information and help understanding the way of life of different civilizations due to its abundance and variety. The characterization involves numerous studies since the sample typology (i.e., the study of shape, color, presence of drawings, texture of the material and decoration)[8] to chemical composition determination.

Typology has been very useful when applied to whole or reconstructed objects. However, it was proved to be less helpful for materials in fragmented condition.

As ceramics compose a large portion of the materials recovered from excavations and appear to be closely similar even under microscopic examination, the clay, sand, and other natural materials from which they were fashioned can have a chemical composition which is unique and diagnostic of the local source from which they were taken.[8,9]

The natural raw material constituents from ceramics are complex and include a variety of items such as sand and granule sized igneous minerals, sand and granule sized calcareous grains, sedimentary rock sourced sand, granule mineral grains such as quartz, mica, magnetite, chalcedony.[10] The concentration levels of a number of major elements, notably Si, Al and Fe are usually similar for different samples of sand or clay. For this reason it is necessary to consider the chemical composition and concentration levels of trace elements in the materials from which the pottery was manufactured.[11–15]

Different techniques can be applied to determine the sample composition, including AAS,[6] ICP,[11] PIXE,[12] and INAA.[6,8,13,16,17] Among the various techniques INAA employing gamma-ray spectrometry seems to be the most suitable analytical technique because it does not require mineralization of samples and provides the determination of numerous elements simultaneously with high sensitivity, accuracy and precision. Sample preparation is relatively easy and fast.

The aim of this study was to characterize by means of As, Ce, Cr, Eu, Fe, Hf, La, Na, Nd, Sc, Sm, Th, and U contents the pre-historical ceramic raw material source from Rezende archaeological site.

Experimental

Archaeological background[18]

Rezende archaeological site is located in the farm Paiolão, in Piedade, Parnaíba valleys, 7 km from Centralina city, Minas Gerais State, Brazil. Archaeological studies evidenced two occupation: the most recent one is represented by ceramic occupation and was dated 1190±60 year before present. It begins in the surface and goes up to 35/40 cm in depth. The archaeological studies demonstrated that the population lived in oval huts forming villages, and made use of the fire for light, heat and cooking. They also had an incipient agriculture – the horticulture. The ceramic produced was plain, utilitarian and funerary. The oldest one is pre-ceramic occupation (or pure lithic) that is 90/130 cm in depth and was dated 7300±80 years before present. They represent the first and the oldest inhabitants of the Minas Gerais area, called “the Mineiro Triangle”. This population consisted of hunter-collector nomads that made their living by fishing, hunting and collecting.

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Sample preparation

Powder samples were obtained by cleaning the outer surface and drilling to a depth of 2–3 mm using a tungsten carbide rotary file attached to the end of a flexible shaft, variable speed drill. Depending on the thickness, 3 or 5 holes were drilled as deep into the core of the sherd as possible without drilling through the walls. Finally, the powered samples were dried in an oven at 105 °C for 24 hours and stored in a desiccator.

Standard and check sample preparation

Buffalo River Sediment (NIST-SRM-2704) and Coal Fly Ash (ICHTJ-CTA-FFA-1) were used as standards, and Brick Clay (NIST-SRM-679) and Ohio Red Clay were used as check samples in all analysis. These materials were dried in an oven at 105 °C for 24 hours and stored in a desiccator until weighing.

Irradiation and measurements

About 100 mg of ceramic samples, Brick Clay, Ohio Red Clay, Buffalo River Sediment and Coal Fly Ash were weighed into polyethylene bags and wrapped in aluminum foil. Groups of 6 samples and one of each reference material were packed in aluminum foil and irradiated in the swimming pool research reactor IEA-R1m at a thermal flux of about $5\cdot10^{12}$ $n\cdot cm^{-2}\cdot s^{-1}$ for 8 hours. Two measurement series were carried out using a Ge (hyperpure) detector, model GX 2020 from Canberra, resolution of 1.90 keV at the 1332.49 keV gamma-peak of ^{60}Co. Spectra were collected with a Canberra S-100 MCA with 8192 channels. As, Ba, K, La, Lu, Na, Nd, Sm and Yb were measured after 7-day cooling time and Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, Zn and U after 15 days. Gamma-ray spectrum analyses were carried out using the Vispect II software, developed by Dr D. Piccot, Saclay, France.

Results and discussion

To evaluate the analytical process the elemental concentrations for Brick Clay (NIST-SRM-679) and Ohio Red Clay (new bag) were statistically compared with data obtained from BISHOP[19] for over a 17 year period (1982 to 1999) for Brick Clay and a period of over 10 year (1989 to 1999) for Ohio Red Clay. For both materials 15 independent determinations were carried out. The precision for most elements (As, Ce, Co, Cr, Cs, Eu, Fe, Hf, Na, Sc, and Th) was better than 5% and agreed with the precision obtained by Bishop and it is comparable to those from the literature.[20]

For elements with RSD around 10% or more the results obtained in this work are in agreement with the ones obtained by Bishop and are also similar to those from the literature[20] except to Sm and Zn. The determination of Zn is not reliable due to the strong gamma ray interferences of ^{46}Sc and ^{182}Ta. The interference of ^{235}U fission in the determination La, Ce, and Nd was negligible because U concentration did not exceed 5 ppm and the rare earth elements were not extraordinarily low.[16]

One of the basic premises underlying the use of chemistry in a 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 one another than to vessels, manufactured from a different source. In this work all the elements with precision less than 10% were considered. Although Co and Ta have RSD around 3% for both materials, it was not included in the data set because the concentration can be affected by tungsten carbides files.[21] The precision of Cs, K and Rb was better than 10%, however, they were not included because they presented 15% of missing values.

Based on these screening criteria, 13 elements: As, Ce, Cr, Eu, Fe, Hf, La, Na, Nd, Sc, Sm, Th and U were used in subsequent data analyses. None of these elements considered contained missing values. Eight samples were eliminated by evident outliers. Range, mean and standard deviation are presented in Table 1. Elemental concentrations were converted to log base-10 values to compensate the large difference of magnitudes between major and trace elements. Cluster, discriminant and principal component analysis were used in order to study the similarities among samples.

The statistical studies were made using two programs: Statistical Package for Social Sciences (SPSS) and Statistica. To perform the hierarchical cluster analysis the squared Euclidean distances was used to calculate dissimilarities between samples. In the resulting dendrogram were evidenced only two clusters: one cluster containing 31 samples and one isolated cluster with 2 samples (named 7–2 and 10–1). From the results of cluster analysis it is apparent that some basic discriminations were possible within the data but the large size of group (94% of the samples) needed further investigation on whether it could be split up. Also despite the fact that the other group seemed to be separable from each other in the dendrogram, they were refined by multivariate analysis. It has been shown elsewhere[22] that cluster analysis alone is not the most reliable technique for grouping, especially when there are strong interelemental correlations in the data.

Table 1. Range, mean and standard deviation for ceramic samples from Rezende archaeological site (in µg·g^{-1}) unless indicated

Element	Range	Mean ± SD*
As	0.05 – 3.0	1.87 ± 0.55
Ce	52.5 – 135	81.9 ± 20.6
Cr	150 – 303	217.8 ± 27.9
Eu	2.4 – 4.6	3.2 ± 0.4
Fe, %	7.17 – 16.24	10.9 ± 2.4
Hf	10.5 – 12.8	11.5 ± 0.7
La	26.2 – 54.5	37.8 ± 6.7
Na	92 – 271.1	161.3 ± 43.8
Nd	35 – 71	52.1 ± 8.8
Sc	37.2 – 50.9	44.2 ± 3.2
Sm	7.5 – 14.1	10.5 ± 1.5
Th	4.8 – 7.7	6.4 ± 0.8
U	0.9 – 1.9	1.4 ± 0.2

* Mean and standard deviation of 33 individual samples.

In order to confirm the latter assumption the data were submitted to discriminant and component analysis. The basis for all multivariate analyses is that all the elements included are independent variables. This is not necessarily true, but it can be tested using the pooled within-groups correlation matrix provided by discriminant analysis. When the cluster within samples have been identified, discriminant analyses was used to isolate those variables which could most effectively reveal the differences between clusters and establish a discriminant function for this purpose. The plot obtained by canonical discriminant function 1 is presented in Fig. 1. As it can be seen, only two samples 7–2 and 10–1 (indicated as 2 in the plot) are separated and the other samples are included in the group of 31 samples.

PCA of the variance-covariance matrix of the data set showed that the first three components account for 70% of the variance. A bivariate plot of the first two components (Fig. 2) shows that the samples form a very tight chemically homogeneous group, providing a high degree of chemical similarity between the samples.

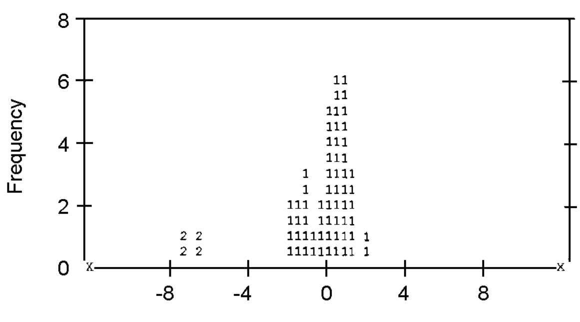

Fig. 1. Canonical discriminant function 1

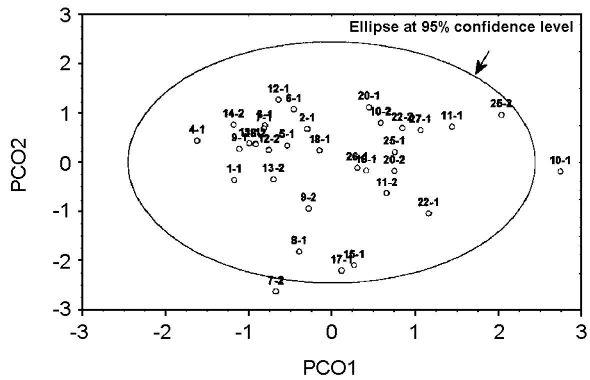

Fig. 2. Plot of the first two principal components

Conclusions

Regarding the question of the raw material of the ceramic fragment, inspection of the chemical data by three multivariate statistical method demonstrated, clearly, that almost all the samples (94%) found at Rezende archaeological site were made using the same source of clay.

Statistically all ceramics present the same elemental chemical composition, except for two samples referenced as cases 7–2 and 10–1, even though a visual inspection of data do not reveal any significant difference in the chemical composition. Besides, the samples showed no visible temper or gritty texture differences in their manufacture. This suggests that a single type of raw material was used in the manufacturing of most of the ceramic analyzed. Samples 7–2 and 10–1 could have been made from a different raw material or the composition of the original raw material could have been altered during the overall ceramic manufacturing process by washing or by adding temper or coloring agent. On the other hand, anomalous samples could be imported from another area. In this case, since the imported to local production ratio is small, an idea of an autonomous development without much contact with its neighbors would be supported.

Finally the results provided persuasive evidence that Rezende ceramics used at least two different clay sources. Whether these sources are local or not, it will only become clear by means of a systematic local clay analysis.

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