

## Determination of trace elements in archaeological ceramics and application of Kernel Density Estimates: Implications for the definition of production locations

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Chemistry fingerprint of materials helps determine provenance and technological production techniques, and, therefore, is useful way to study interaction between prehistoric people. In this work 38 ceramic fragments from Justino and São José sites, in Brazilian northeast, were analyzed using instrumental neutron activation analysis (INAA). The recognition of the compositionally homogeneous group within of the database was performed by means of principal component (PC). The PC scores were calculated on the matrix covariance of the log base 10 transformed concentration values, and grouping was sought in the PC scores using Kernel Density Estimates (KDE). By using KDE from PC scores two chemically different groups were found. Discriminant analysis was performed to assess the groups' validity. Despite of the pottery from Justino and São José sites present same technical profile, different of the Tupiguarani and Aratu traditions, it was obtained that Justino and São José samples are constitute of distinct ceramic pastes. This result can be understood in terms of the cultural influences in the preparation of the ceramic past and that potteries analyzed are originate locally.

### Introduction

The chemical analysis of pottery is an important aspect of prehistoric and historic archaeology.<sup>1–3</sup> Pottery was probably the first synthetic material made by humans, and thus broken pottery fragment are among the most common artifacts found at archaeological sites around the world. As a consequence, pottery is one of the materials most often studied by archaeologists. Several studies have showed the efficiency of archaeometric techniques based on physiochemical properties of the raw material that composes the ceramic.<sup>4–7</sup> The application of archaeometric techniques has aided in determining the provenance and technology of ceramic production, and, therefore, are useful techniques for reconstructing trade habits and interaction between prehistorical people.<sup>8</sup>

In Northeast areas of Brazil several regional traditions according to morphological or stylistic criteria of ceramic artifacts were identified, without explanation of the socioeconomic characteristics of groups' ceramist and its ethnic affiliations.<sup>9</sup> In agreement with these criteria two traditions widely present in the area were established – the Tupiguarani and Aratu traditions. Recent study, however, has suggested the existence of independent groups, without relation with these two main traditions, thus demanding more studies to support existence of the unknown, independents traditions in the area.<sup>10</sup>

In this work, 38 ceramic fragments from São José and Justino archaeological sites in the Brazilian Northeast were analyzed using instrumental neutron activation analysis (INAA) and the concentration of 24 chemical elements was determined. Justino and São José sites are located in Canindé of São Francisco city, in the area of Baixo São Francisco about 150 km from Aracaju, capital of Sergipe State, Brazil. The archeological studies based on the ceramic typology have showed that the pottery from these sites has same technical profile.<sup>11</sup> The local pottery found at sites Justino and São José was used basically for storage and cooking of food, as well as funereal urns. In this work, 17 samples were collected at depth of 150 cm (phase 15, each 10 cm of the depth corresponds one phase) of depth in Justino site and 21 samples from São José site (several depths).

In order to interpret data set PCA, DA and KDE<sup>12</sup> were used with the purpose to supply more information in support of a new hypothesis about the penetration of different prehistoric groups, which were neither the Tupiguarani nor the Aratu traditions, in the Northeast of Brazil.

### Experimental

#### *Instrumental neutron activation analysis*

Although several chemical methods have been employed to analyze pottery and clays, including atomic absorption spectroscopy (AAS), X-ray fluorescence

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(XRF), proton induced X-ray emission (PIXE), etc., the analytical technique that has dominated pottery provenance research from the late 1960s up to the present time is instrumental neutron activation analysis (INAA).<sup>13–15</sup> The main advantages of the method for pottery analysis are: (a) high precision, accuracy and sensitivity for many elements; (b) need for small sample (50–150 mg); (c) low nuclear activities for the major constituents (Si, Al, O, Mg) comparative to majority of the trace elements; (d) instrumental technique capable of measuring 30 elements or more simultaneously, and (e) demonstrated potential for inter-calibrating between measurements made in different NAA laboratories.<sup>16</sup>

#### *Sample preparation and standard*

Ceramic powder samples were obtained by cleaning the outer surface and drilling to a depth of 1–2 cm with 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 fragment as possible without drilling through the walls. The powdered samples were dried in an oven at 105 °C for 24 hours and stored in desiccators.

The clay samples were prepared by manually grinding in an agate mortar and pestle, until a sufficiently fine granulometric powder was obtained, in order to pass through a 100–200 mesh sieve. The samples became more homogenous, considering that it would be predominantly used in a trace analysis. The large contamination of Si, which can originate from agate, was not a serious problem, since this element was not determined. All clay samples were dried in an oven at 105 °C for 24 hours and stored in desiccators.

Constituent elements in Coal Fly Ash, NIST SRM 1633b, was used as standard, throughout this work. The standard was also dried in an oven at 105 °C for 4 hours and stored in desiccators until weighing. Analytical details and precision of the described sample and standard preparation are published elsewhere.<sup>17,18</sup>

#### *Description of the method*

About 100 mg of ceramics samples and NIST SRM 1633b were weighed in polyethylene bags and involved in aluminum foil. Groups of 8 ceramic samples and one standard were packed in an aluminum foil and simultaneously irradiated in the swimming pool research reactor IEA-R1m at a thermal neutron flux of about  $5 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  for 8 hours.

Two measurement series were carried out using hyperpure Ge detector (model GX 2020, Canberra, with resolution of 1.90 keV at the 1332.49 keV gamma-peak of <sup>60</sup>Co), connected to the S-100 MCA (Canberra) with 8192-channels. As, K, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days of cooling time, while Ba,

Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, and Zn were measured after 25–30 days. The isotopes determined in this work emit gamma-rays with discrete energies that are uniquely characteristic of the elements.<sup>19</sup> Gamma-ray spectra analysis was carried out using the software Genie 2000 NAA Procedure from Canberra.

#### *Statistical method*

PCA is a commonly used technique in the ceramics compositional studies since it reduces the dimensionality of the data set and makes no assumptions on the number of groups in the data set.<sup>20</sup> On the other hand, KDEs are used to aid in the interpretation of the principal components scores since they are mathematical ways of finding the structure and overall pattern in a data set. KDEs have been extensively used by statisticians and their applications in other fields is growing.<sup>21</sup> While these two methods can be used to find grouping in the chemical data, the discriminant analysis is done to assess group validity and to see which variables separate groups the best. The purpose of LDA is to find linear combination of observed variables that have the most power for submitted groups. LDA maximizes the ratio inter-group over intra-group variance.<sup>22</sup> The validity of the groups in this work was assessed using LDA. LDA with all the log-transformed variables entered at once resulted in 100% of the cases being correctly classified. LDA with cross-validation resulted in 96% of the cases being correctly classified. The cross-validation was done by discriminant analysis, so that more realistic classification rule was obtained.<sup>23</sup>

DA, PCA and KDE were used in order to study the similarities among the samples. The statistical analysis was done with three programs: Statistical Package for Social Sciences (SPSS), Statistica and JMP.

### **Results and discussion**

To evaluate the analytical process the elemental concentrations of Brick Clay (NIST-SRM-679) were statistically compared with values certified by NIST. The precision of several elements (Na, La, Th, Cs, Sc, Fe, Eu, Ce, Hf and Co) was better than 5% and agreed with precision obtained by other authors.<sup>24</sup> Some elements presented relative standard deviation (RSD) worse than 10% (Nd, Sm, Ba, Sb, and Tb) and are similar to those from the literature.<sup>25</sup> The interference of <sup>235</sup>U fission in the determination of La, Ce and Nd was negligible because U concentrations did not exceed 5 ppm and the rare earth concentrations were not very low.<sup>26</sup>

One basic requirement for the composition characterization of the archeological pottery is that the analytical technique used has appropriate precision.

Elements measured with low precision can reduced the discriminating effects of other elements, which can be measure with higher precision. In this work only elements measured with RSD below 10% were considered for interpretation of the results. In addition, Zn presented RSD better than 10% but was excluded from database, because its determination suffered strong gamma-ray interferences from  $^{46}\text{Sc}$  and  $^{182}\text{Ta}$ . Similarly, Co and Ta were eliminated because their concentrations can be affected by tungsten carbides drills, although the precision has been better than 10%. The RSD of K, Rb and U was better than 10%, however, they were excluded because they presented 15% of missing values (i.e., not detected).

Based on these screening criteria, 11 elements: Yb, La, Th, Cr, Cs, Rb, Sc, Fe, Eu, Ce and Hf were used for interpretation of the results. Three samples were eliminated because of evident outliers. The elemental concentrations were standardized by log base-10, reducing the differences of magnitudes of the obtained concentrations.

The PCs were obtained in order to calculate the KDEs. The PCA indicated that the first four components account for the majority of the total variance in the data set, 80.7% of the total variance. The screen test was conducted to estimate the number of principal components. In agreement with the screen plot (Fig. 1), four components can be assumed to explain significantly the variability of the database.

KDEs can be used as an informal means of cluster analysis. It is known that  $k$ -means cluster has a tendency to produce spherical cluster that can be avoided by clusters suggested by KDEs. An attraction of using KDEs is that they can be used as a basic for producing contour plot of the data and this leads to graphical

representations of data of a kind that archaeologists should find familiar. Assuming that the distribution of points is normal the scores of principal components was used to determine KDEs. The contour maps and surface of the space formed by the scores of principal components and KDEs (Fig. 2) showed that the chemical compositions of the samples from the studied archaeological sites tend to form two groups. In Fig. 2 it is possible to observe that there is clearly one main concentration of data, which correspond to Justino site, and the second more widespread data set that correspond to the pottery samples collected at the São José site.

In order to confirm existence of only two different groups of ancient pottery fragments excavated at Justino and São José sites based on their chemical composition, a LDA of the concentration of the 38 samples was accomplished. Figure 3 presents a bivariate plot of discriminant function 1 versus discriminant function 2 showing that two main data groups were separate functions. Figure 3 illustrates that the pottery samples from each São José and Justino sites are chemically homogeneous, since they each concentrate in an ellipse with a significance of 90%. These results indicate that clay collected from the ceramics fragments at two sites, originated from two distinct raw materials or the chemical composition of clay paste was modified during its preparation by ancient potters using a specific processing recipe.<sup>27</sup> Despite of the geographical proximity between these two sites, about to 2 km, the discriminant analysis showed that the ceramic from both archaeological sites are different and according with "criterion of abundance", which states that artifacts probably originate where they are most common, these potteries were locally produced.<sup>28</sup>

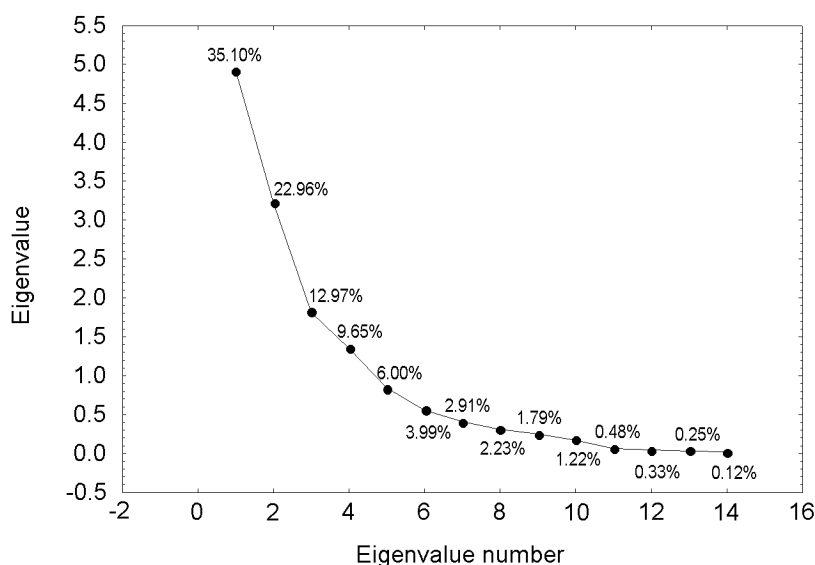


Fig. 1. Screen plot for selecting the number of components

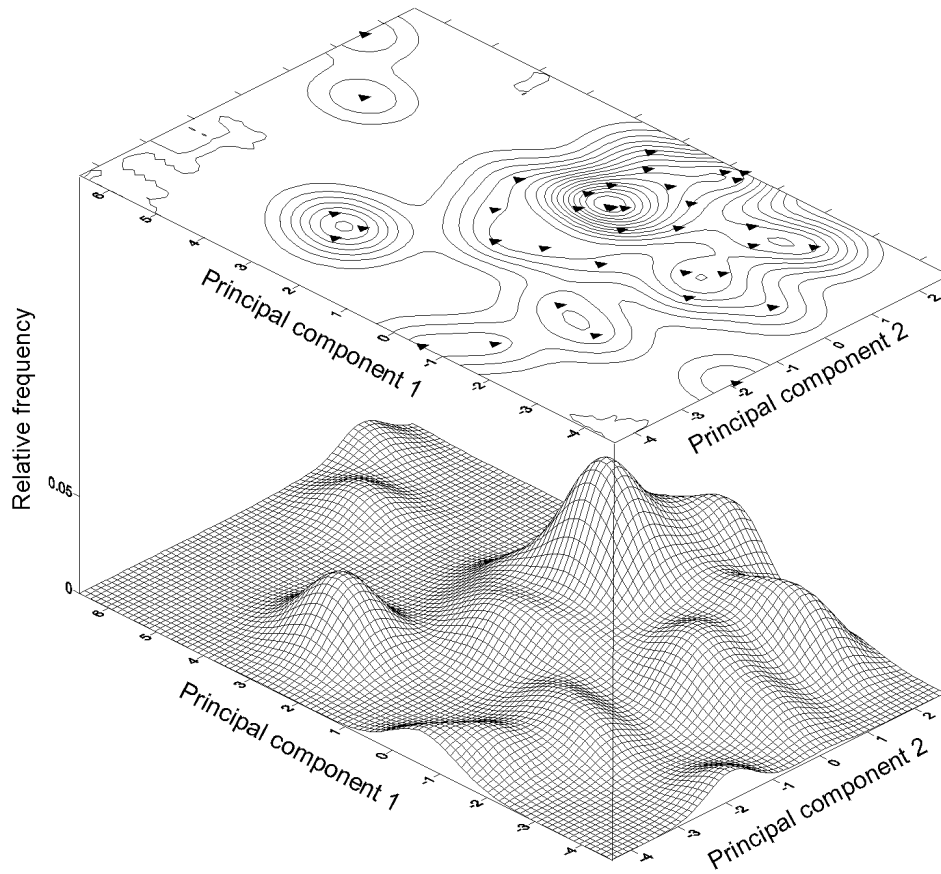


Fig. 2. Surface and contour plots from principal components of the Justino and São José samples

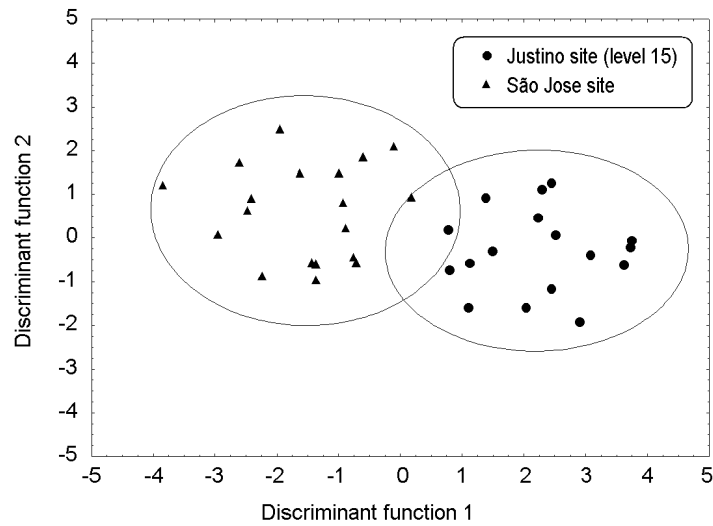


Fig. 3. Linear discriminant analysis of the archaeological pottery samples from Justino and São José showing that two main potteries are clearly separate on Discriminant Function 1 vs. Discriminant Function 2

## Conclusions

The results presented in this work provide evidence for chemical comparison of pottery fragments collected at the Justino and São José sites in Brazil. The discriminant functions scores of the clay elemental concentration showed that the sources of raw material from two archaeological sites studied are different with separation of 96% or were changed by ancient potters during the production. The KDE also showed that chemical composition of the samples formed two groups, one with strong homogeneity and the other one, which is more dispersed (Fig. 2). Although the styles and morphology of pieces display no significant difference, the results obtained in this work provided grounds to confirm the existence of a local tradition, without relation with the Tupiguarani and Aratu traditions, due the locality of the potteries studied.

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