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ARCHEOLOGY AND WORKS OF ART

Contribution of neutron activation analysis to archaeological studies

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Abstract: Thirty-four ceramic fragment samples from the Prado archaeological site, Perdizes city, Minas Gerais State, Brazil, were analyzed using INAA to determine the concentration of 15 chemical elements, namely, As, Ce, Cr, Cs, Eu, Fe, Hf, La, Na, Nd, Rb, Sc, Tb, Th, and U. Two multivariate statistical methods, cluster and discriminant analysis were performed on the data set. Discriminant analysis confirms that 82.4% of the ceramic samples classified by cluster analysis are correctly classified. The results show that a large majority of samples (94%) can be considered to have been manufactured using the same source of raw material.

Key-words: Neutron activation analysis, ceramics, cluster analysis, discriminant analysis, trace elements.

Abbreviations: AAS, atomic absorption spectrometry; ICP, inductively coupled plasma; INAA, instrumental neutron activation analysis; PIXE, particle induced X-ray emission; RSD, relative standard deviation; SD, standard deviation; SPSS, statistical package for social sciences.

INTRODUCTION

Pottery is especially well suited to derive archaeological information and help understanding the way of life of the different civilizations due to its abundance and variety. Such studies are of particular interest to archaeologists [Ochsenkuhn *et al.*, 1999; Gunneweg *et al.*, 1991], anthropologists [Rossini *et al.*, 1993], ethnoarchaeologists [Redmount and Morgenstein, 1996] as well as to physicists, chemists and geologists. The characterization involves numerous studies from sample typology (i.e. study of the shape, color, presence of drawings, texture of the material and decoration [Punyadeera *et al.*, 1999]) to chemical composition determination. Typology has been useful especially when applied to whole or reconstructed objects, but much less for fragmented materials. The pottery shards, which constitute a large part of the materials recovered from excavations, appear to be closely similar even under microscopic examination, but the clay, sand, and other natural materials from which they were fashioned can have a chemical composition which is unique and which may serve as diagnostic of the local source from which they were taken [Punyadeera *et al.*, 1999; Peisach *et al.*, 1991].

The natural raw material constituents from ceramics are complex and include a variety of items: sand and granule-sized igneous minerals, calcareous grains, sedimentary rock sourced sand and granule mineral grains such as quartz, mica, magnetite, chalcedony [Redmount and Morgenstein, 1996]. 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 [Kilikoglou *et al.*, 1997; Kuisma-Kursula and Raisanen, 1999; Hughes *et al.*, 1999; Mommsen *et al.*, 1988; Burton and Simon, 1993]. Different techniques can be applied to determine the sample composition, including AAS [Rotunno *et al.*, 1997], ICP [Kilikoglou *et al.*, 1997], PIXE [Kuisma-Kursula and Raisanen, 1999], and INAA [Punyadeera *et al.*, 1999; Hughes *et al.*, 1999; Rotunno *et al*, 1997; Glascock, 1992; Cogswell *et al.*, 1996]. Among the various techniques INAA employing γ-ray spectrometry seems to be the most suitable analytical technique because it does not require mineralization of samples and allows the determination of numerous elements simultaneously with high sensitivity, accuracy and precision. Moreover, sample preparation is relatively easy and fast.

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

MATERIALS AND METHODS

The Prado archaeological site is located in Perdizes city, Minas Gerais State, Brazil. The few whole pottery vessels collected and those partially reconstructed do not present plastic decoration or painting, with predominance of medium to large granularity and a bad selection of grains. 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 shard as possible without drilling through the walls. Finally, the powered samples were dried in an oven at 105°C for 24 h and stored in a desiccator. 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 analyses. These materials were dried in an oven at 105°C for 24 h and stored in a desiccator until weighing.

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 foils. Groups of 6 samples and one of each reference material were packed in aluminum foils and irradiated in the swimming pool research reactor IEA-R1m at a thermal neutron flux of about 5×10^{12} $n \cdot cm^{-2} \cdot s^{-1}$ for 8 h. Two measurement series were carried out using a Germanium (hyperpure) detector, model GX 2020 from Canberra, resolution of 1.90 keV at the 1332.49 keV γ-peak of ^{60}Co. Spectra were collected with a Canberra S-100 multi-channel analyzer 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 assess the analytical process the elemental concentrations measured with Brick Clay (NIST-SRM-679) and Ohio Red Clay were statistically compared with data obtained by Bishop (personal communication). 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 around 5% or less, i.e. comparable with that obtained by Bishop and that found in the literature [Kuleff and Djingova, 1990]. For the elements determined with a precision of 10% or more, apart from Sm and Zn, our results are also in agreement with those by Bishop (personal communication) or found in the literature [Kuleff and Djingova, 1990]. The determination of Zn is not reliable as a consequence of a strong γ-ray interference by ^{46}Sc and ^{182}Ta. The interference by the ^{235}U fission in the determination of La, Ce, and Nd was negligible because the U concentration did not exceed 5 ppm and the rare earth elements were not extremely low [Glascock, 1992]. In this work we have considered only the elements determined with a precision better than 10%. Although Co has a RSD close to 3% for both materials, it was not included in our data set because the concentration can be affected by tungsten carbides files [Attas *et al.*, 1984].

Based on these screening criteria, 15 elements (As, Ce, Cr, Cs, Eu, Fe, Hf, La, Na, Nd, Rb, Sc Tb, Th and U) were used in the subsequent data analyses. None of these elements contained missing values. Range, mean and standard deviation are presented in Table 1. The elemental concentration data were converted to base log 10 to normalize element distributions and to reduce the impact of the differences in the concentrations of some of the major elements. Cluster and discriminant analysis were used in order to assess similarities among samples. Hierarchical clustering is a useful technique to evidence clusters. It measures the distance between all points (Euclidean distance), finds

TABLE 1
Range, mean and standard deviation for ceramic samples from the Prado archaeological site, in $\mu g \cdot g^{-1}$, unless otherwise indicated

Element	Range	Mean ± SD[a]
Na	302 - 2017	676 ± 347
Sc	26.11 - 33.88	29 ± 2
Cr	96 - 186	138 ± 23
Fe (%)	1.72 - 3.84	3.0 ± 0.5
As	1.08 - 2.6	1.7 ± 0.3
Rb	58 - 128	81 ± 18
Cs	9 - 14.1	11 ± 1
La	27.2 - 52.6	34 ± 5
Ce	67.5 - 137.2	113 ± 12
Nd	26 - 57	38 ± 8
Eu	1.01 - 2.23	1.5 ± 0.3
Tb	0.52 - 1.6	1.1 ± 0.2
Hf	7.6 - 11	8.8 ± 0.7
Th	9.6 - 19.5	17 ± 2
U	1.8 - 6.3	4.0 ± 0.9

[a]Mean and standard deviation of 34 individual samples

the closest pair, combines them into a single point half-way in between, recalculates the distances from this new point and then seeks the next closest pair of points. The process is repeated until all points in the space have been combined. The Statistical Package for Social Sciences (SPSS) was used to perform the hierarchical cluster analysis. Squared Euclidean distances were used to calculate dissimilarities between samples [Glascock *et al.*, 1998]. In the resulting dendrogram showed in Fig. 1 three clusters are evidenced containing 28, 4 and 2 (case 7 and case 8) samples, respectively.

In order to confirm the latter assumption the data were submitted to discriminant 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. 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 canonical discriminant function 1 is presented in Fig. 2. As can be seen, only samples 7 and 8 (indicated as 2 in the plot) are separated while the other 4 samples (cases 1, 3, 5 and 6) were included in the group of 28 samples.

CONCLUSION

Two multivariate methods, cluster and discriminant analysis, were applied for examining the chemical composition data. Statistically apart from the two samples 7 and 8 all ceramics present the same elemental chemical composition and the potteries showed

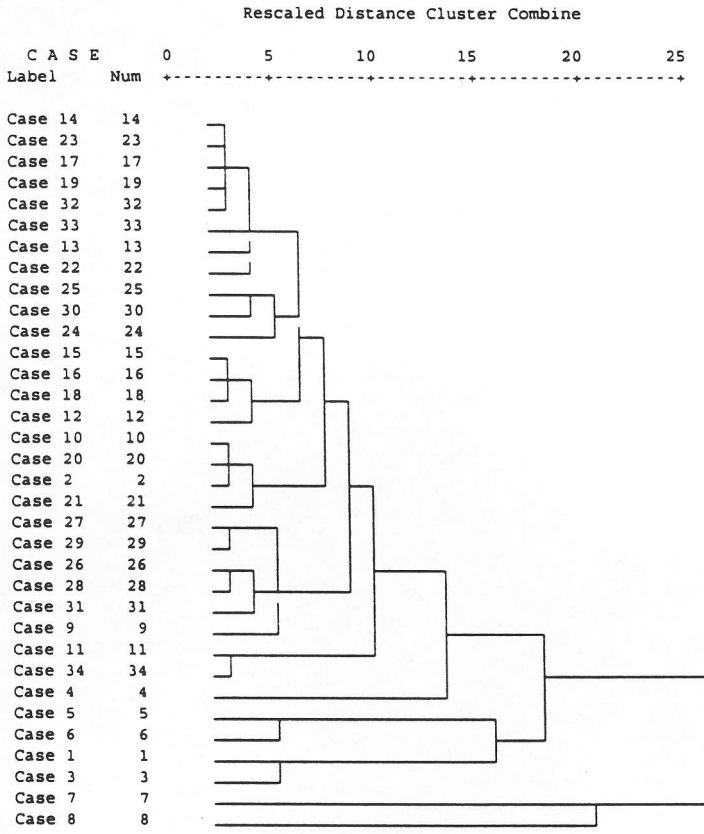

FIG. 1. Dendrogram of 34 samples from the Prado archaeological site, square mean Euclidean cluster analysis.

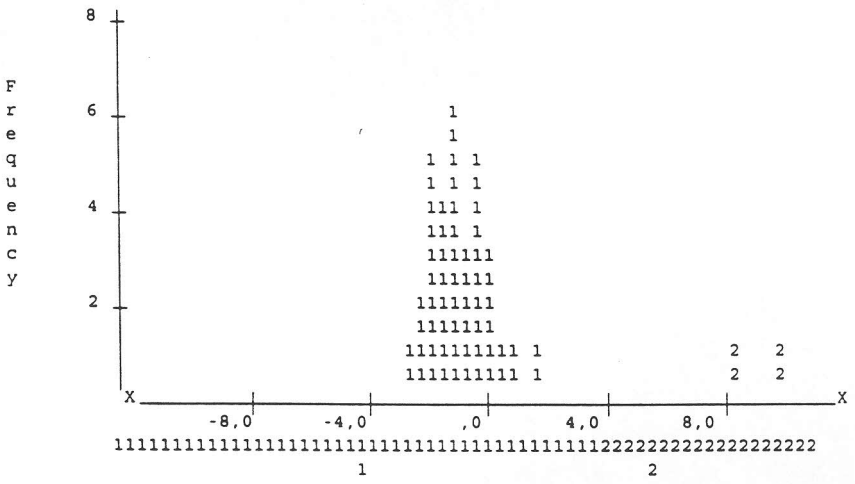

FIG. 2. Canonical discriminant function 1.

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 pottery analyzed. Samples 7 and 8 might have been made using a raw material different from that for the other samples or the composition of the original raw material might have been altered during the ceramic manufacturing process as a consequence of washing or of the addition of temper or coloring agents. As an alternative anomalous samples might have been imported from another area. In this case, since the imported to local production ratio is small, this would be consistent with the hypothesis that the local population would have developed without much contact with its neighbors.

Finally our results provide evidence that the Prado ceramics were manufactured from at least two different clay sources. Whether these sources are local or not will become clear by systematic local clay analysis.

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