

INAA of archaeological ceramic for provenance study

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One hundred forty nine ceramic fragment samples from three archaeological sites were analyzed using instrumental neutron activation analysis (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. A multivariate statistical method, discriminant analysis, was performed on the data set. Discriminant analysis identified three compositional grouping and derived two discriminant functions that account for 100% of the variance between groups. The results show, at a confidence level of 98%, that ceramics of each separate site are statistically similar among them and it can be said that a common source of raw material was used independently in each of these sites.

Introduction

Over the last three decades, ceramic analyses have become central to derive archaeological information and to help understand the way of life of the different civilizations due to its abundance and variety. The delineation of past systems of production and exchange lies at the core of these research.¹

The characterization involves numerous studies from sample typology i.e. the study of shape, color, presence of drawings, texture of material and decoration² 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. On the other hand, the ceramic fragments constitute a large part of materials recovered from excavations, these materials it seem to be closely similar even under microscopic examination. The raw material constituents from ceramics are complex and include a variety of items: sand and granule-sized igneous minerals, calcareous grain, sedimentary rock, sourced sand and granule mineral grains such as quartz, mica, magnetite, chalcedony.³ The concentration levels of a number of major element, such as Al, Fe and Si are usually similar for different samples of sand or clay. The clay, sand, and

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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.^{2,4} 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.⁵⁻⁹

Different techniques can be applied to determine the sample composition, including AAS¹⁰, ICP⁵, PIXE⁶, and INAA.^{2,7,10,11} 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. Sample preparation is relatively easy and fast.¹²

The aim of this study was to characterize by means of inorganic elements, the Brazilian prehistoric ceramic from three archaeological sites as potential indicators of the Indian culture. The data obtained helped archaeological studies already made in the region with the objective of making spatial, temporal and cultural reconstruction of this time. Samples from Água Limpa, Prado and Rezende were studied.

Experimental

Archaeological background

The technique of excavation was Wide Surfaces adapted to tropical conditions of the Brazilian soil.^{13,14} The ceramics found in these sites were associated to food preparation, funeral urns and decorative uses. The three sites are superficially located in the intermediary part of a hill with a water course in its inferior part.¹⁵ The locations are indicated in Figure 1.

Água Limpa site

The Água Limpa site is located in the confluence of three small farms, in Monte Alto city in the North of São Paulo State, 21°15'40" S - 48°29'47" W. The site has been divided in two excavations zones. In zone 1, the village is formed by only two dark spots. An area of primary burials of extended and semiflexed youths and adults has been detected. Ten other burials have been exhumed besides the exhumation of a secondary burial of an adult inside a globular urn with lid.¹⁶ There was one hearth on the spot, dated 1524 years B.P. All other hearths were external. In internal and external hearths there were ceramics vessels related to flakes, scrapers, mammalian bones, reptiles, fishes and shells with indications of preparation and consumption of food obtained through

hunting, collecting and, in a smaller scale, fishing.¹⁷ In zone 2, the village is formed by eight dark spots and several hearths, most of them inside houses. Only a secondary burial of a child was found and exhumed.

The ceramic are of two types: plain and painted. The painting is in red and white, without slipping the painted fragments and the few whole painted sherds that were collected have no forms. The selection of grains is good with predominance of thin and medium grains.

Prado site

Prado site is located at Engenho Velho Farm, in Perdizes city, State of Minas Gerais, Brazil, 19°14'25" LS - 47°16'00" LW. It is formed by seven dark spots (housing structures); three hearths (one internal and two external to the spot); two concentrations of lithic remains and one primary burial inside a pyreform urn covered with a lid. Three stratigraphic profile were executed indicating one single stratum: the litho-ceramic.

The archaeological vestiges collected are represented by two kinds of documents: ceramic and lithic (polished and unpolished).

The few whole ceramic vessels collected and those partially reconstructed in field or laboratory are smooth, without plastic decoration or painting, with predominance of medium to large granularity, with bad selection of grains. They were produced with utilitary and funerary objectives, according to the archaeological evidence.¹⁸⁻²¹ Their most expressive forms are globular vases and pots, spherical bowls, and pyreform urns.

Rezende site

Rezende site is located in Paiolão farm, in Piedade, Paranaíba Valley, 7 km from Centralina city, Minas Gerais State, Brazil, 18°33' LS, 49°13' LW. Archaeological studies evidenced two occupation: the most recent one is represented by ceramic occupation and was dated 1190 ± 60 year B.P. 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 year B.P. 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.^{15,22}

Multivariate statistical analyses

In order to elucidate the major variations in the set of compositional data obtained using INAA, it is indispensable to employ multivariate statistical that use the correlation between element concentrations as well as absolute concentrations to characterize the sources of the samples. 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.

Discriminant function analysis is a multivariate technique and is based on the assumption that the pooled variance-covariance matrix is an accurate representation of the total variance and covariance of the data set.²³ Bivariate plots of discriminant functions are useful for visually displaying group separation.

The statistical studies were made using three programs: SPSS, Statistical Package for Social Sciences version 8, Statistica version 5 and Excel version 97.

Sample preparation and standard

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 powdered 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 analysis. These materials were dried in an oven at 105°C for 24 h and stored in a desiccator until weighing. Analytical details and precision were published elsewhere.²⁴⁻²⁶

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. In this work all the elements with RSD less than 10% were considered.²⁵ Although Co and Ta had RSD around 3%, it was not included in the data set because the concentration can be affected by tungsten carbides files.²⁷ The precision of Cs, K and Rb was better than 10%; however, they were not included because they presented 15% of missing values. The determination of Zn is not reliable due to the strong gamma ray interferences of ⁴⁶Sc and ¹⁸²Ta. The interference of ²³⁵U 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.¹¹

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. The entire data set consisted of all 149 samples (Água Limpa: 82, Prado:34 and Rezende:33). Eight samples were eliminated by evident outliers. Since INAA measures both bulk and trace elements, elemental concentrations were converted to log base-10 values to compensate the large difference of magnitudes between major and trace element.^{28,29}

In order to examine questions of exchange and socio political interaction among the prehistoric cultures of these three sites, the similarities among samples were studied by means of discriminant analysis. Since differences in chemical composition are typically interpreted as evidence for distinct productions locations, our main purpose was to identify and distinguish the similarities among the samples analyzed with the aim to define one or more compositional groups, which presumably would represent one or more production places. Such information helps the range of compositional variation that might be expected from a single production context. A bivariate plot obtained by canonical discriminant functions is presented in Figure 2.

As it can be seen, the results show that the samples of each site form a very tight chemically homogeneous group, showing a high degree of chemical similarity among them. The results showed that clay from ceramics fragments collected and analyzed from three sites were originated from three distinct raw material. From the samples studied at least three center of production may be identified in the area. Whether these sources are local or not, it will only become clear by means of a systematic local clay analysis. The idea of an autonomous development without contact with its neighbors could be supported.

By the other hand, when the data set of each site are interpreted separately, two sample from Prado and Rezende and three samples from Água Limpa proved to be different from the group. However, when the data set are studied together, they become similar to the other samples of each site. This means that the difference that occurs is not important. In other words this proves the

hypotheses that the raw material of the ceramics studied comes from the same source. This all suggests that at these sites a single type of clay material was used in the manufacturing vessel analyzed in this study. This does not necessarily mean that a single clay source was used, since there is the possibility that similar raw material may have been available at a number of different locations.

Conclusions

Inspection of the chemical data of ceramic fragment by discriminant analysis method demonstrated, clearly, that all the samples found in each of the archaeological sites were manufactured with the same sources of raw material.

Statistically all ceramics of each site present the same elemental chemical composition, even though a visual inspection of data does not show any significant difference in their composition. In addition, the samples showed no visible temper or gritty texture differences in their manufacturing.

This suggests that a single type of raw material was used in the manufacturing of all of the ceramics analyzed of each site 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 agents. An idea of an autonomous development without contact with its neighbors could be supported.

Finally, INAA studies have provided important contribution in ceramic production and distribution in the prehistoric era. This information confirms previous hypotheses. The use of NAA has allowed ceramic analysis to reach a higher level of resolution, and allowed as to sharpen our understanding of the past.

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References

1. A. J. CARPENTER, A. J., G. M. FEINMAN, *J. Archaeol. Sci.*, 26 (1999) 783.
2. C. PUNYADEERA, A. E. PILLAY, L. JACOBSON, G. WHITELAW, *J. Trace Microprobe Techn.*, 17 (1999) 63.
3. C. REDMOUNT, M. E. MORGENSTEIN, *J. Archaeol. Sci.*, 23 (1996) 741.
4. M. PEISSACH, C. A. PINEDA, L. JACOBSON, J. H. N. LOUBSER, *J. Radioanal. Nucl. Chem.*, 151 (1991) 229.

5. V. KILIKOGLU, Y. BASSIAKOS, R. C. DOONAN, J. STRATIS, *J. Radioanal. Nucl. Chem.*, 216 (1997) 87.
6. P. KUISMA-KURSULA, J. RAISANEN, *Archaeometry* 41 (1999) 71.
7. M. J. HUGHES, K. J. MATHEUS, J. PORTAL, *Archaeometry* 41 (1999) 287.
8. H. MOMMSEN, A. KRAEUSER, J. WEBER, *Archaeometry* 30 (1988) 47.
9. J.H. BURTON, A. W. SIMON, *American Antiquity* 58 (1993) 45.
10. T. ROTUNNO, L. SABBATINI, M. CORRENTE, *Archaeometry* 39 (1997) 343.
11. M. D. GLASCOCK, in: *Chemical Characterization of Ceramic Paste in Archaeology*, Monographs in World Archaeology, H. NEFF. (Ed.), Prehistory Press, Section 1, 1992, p. 11.
12. R. L. BISHOP, V. CANOUTS, P. L. CROWN, S. P. DE ATLEY, *American Antiquity* 55(3) (1990) 537.
13. A. LEROI-GOURHAN, *Fuilles de pincevent. Essai d'analyse ethnographique d'un habitat magdalénien (La section 36)*, CNRS, Paris, Vocabulaire, Annexe IV, 1972, p. 321.
14. L. PALLESTRINI, *Coleção Museu Paulista, São Paulo, Série Arqueologia, n° 1*, 1975.
15. M. A. ALVES, *Rev. do Museu de Arqueologia e Etnologia, São Paulo*, 2 (1992) 27.
16. M. A. ALVES, L. M. MACHADO, *Coleção Arqueológica 1, Porto Alegre, EDIPUCRS, Vol.2*, 1995, p. 295.
17. M. A. ALVES, M. E. V. CALLEFFO, *Rev. do Museu de Arqueologia e Etnologia, São Paulo*, 6 (1996) 123.
18. M. A. ALVES, *Rev. do Museu Paulista, São Paulo*, 19, (1983), 169.
19. M. A. ALVES, *Rev. do Museu de Arqueologia e Etnologia, São Paulo*, 1, (1991), 71.
20. M. A. ALVES, *Rev. Museu de Arqueologia e Etnologia, São Paulo*, 4 (1994) 39.
21. M. A. ALVES, *Rev. de Arqueologia*, 8(2), (1994), 133.
22. M. A. ALVES, *Coleção Arqueológica 1. Porto Alegre, EDIPUCRS, Vol. 1*, 1995, p. 255.
23. M. D. GLASCOCK, G. E. BRASWELL, R. H. COBEAN., in: *Archaeological Obsidian Studies. Method and theory*, M. S. SHACKLEY (Ed.), Plenum Press, New York 1998, p. 29.
24. C. S. MUNITA, R. P. PAIVA, M. A. ALVES, E. F. MOMOSE, M. SAIKI, *J. Radioanal. Nucl. Chem.*, 244(3) (2000) 575.
25. C. S. MUNITA, R. P. PAIVA, M. A. ALVES, P. M. S. OLIVEIRA, E. F. MOMOSE, *J. Trace Microprobe Techn.*, 18(3) (2000) 381.
26. C. S. MUNITA, R. P. PAIVA, P. M. S. OLIVEIRA, E. F. MOMOSE, R. PLÁ, M. MORENO, O. ANDONIE, F. FALABELLA, L. MUÑOZ, I. KOHNENKAMP, *J. Trace Microprobe Techn.*, 19(2) (2001) 189.
27. M. ATTAS, J. M. FOSSEY, L. YAFFE, *Archaeometry* 26(1) (1984) 104.

28. G. HARBOTTLE, in: *Radiochemistry: A Specialist Periodical Report*, Vol. 3, G. W. A. NEWTON (Ed.), The Chemical Society, London, 1976, p. 33.
29. A. M. POLLARD, in: *Fitch Laboratory Occasional Papers 1*, R. E. JONES (Ed.), British School of Archaeology, Athens, 1986, p. 56.

Captions for Figures

FIG. 1. Map showing the location of sites

FIG 2. Canonical discriminant functions for all samples studied. Ellipses represent 98% confidence level for samples inclusion into clusters



