Chapter 5

CHEMICAL CHARACTERIZATION OF BRAZILIAN PREHISTORIC CERAMICS BY INAA

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Abstract

One hundred and forty-nine ceramic fragment samples from three archaeological sites were analysed 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 groupings and derived two discriminant functions that account for 100% of the variance between groups. The results show, at a confidence level of 98%, that the ceramics from each separate site are statistically similar so that it can be concluded that a common source of raw material was used independently at each of these sites.

5.1. INTRODUCTION

Over the last three decades, ceramic analyses have become central in deriving archaeological information and in helping to understand the way of life of different civilizations on the basis of the abundance and variety of the ceramics. The delineation of past systems of production and exchange lies at the core of this research [5.1].

The characterization involves numerous studies of sample typologies, i.e. from the study of shape, colour, presence of drawings, texture of material and decoration [5.2] to determination of the chemical composition. Typology has been very useful when applied to whole or reconstructed objects. However, it has proved to be less helpful for materials in fragmented condition as, although ceramic fragments constitute a large part of the materials recovered from excavations, these fragments happen to be very 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 grains, sedimentary rocks, sourced sand and granule mineral grains such as quartz, mica, magnetite and chalcedony [5.3]. The concentration levels of a number of major elements, such as Al, Fe and Si, are usually similar for different samples of sand or clay. The clay, sand and other natural materials from which the ceramics were fashioned can have a chemical composition which is unique and which may serve as a diagnostic of the local source from which the ceramics were taken [5.4–5.9]. 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 [5.5–5.9].

Different techniques can be applied to determine the sample composition, including atomic absorption spectrometry (AAS) [5.4], ICP [4.5], proton induced X ray emission (PIXE) [4.6] and instrumental neutron activation analysis (INAA) [5.2, 5.7, 5.10, 5.11]. Among the various analytical techniques, INAA employing gamma ray spectrometry seems to be the most suitable 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 [5.12].

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

5.2. ARCHAEOLOGICAL BACKGROUND

The wide surface excavation technique was adapted to the tropical conditions of the Brazilian soil [5.13, 5.14]. The ceramics found in these sites were associated with 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 interior part [5.15]. The locations are indicated in Fig. 5.1.

The Água Limpa site is located at the confluence of three small farms, in the city of Monte Alto in the north of São Paulo state (21°15′40″S, 48°29′47″W). The site has been divided into two excavation zones. In zone 1, all that remains of the village is two dark spots. An area of primary burials of extended and semi-flexed youths and adults was detected. Ten other burials were exhumed, besides the exhumation of a secondary burial of an adult inside a globular urn with a lid [5.16]. There was one hearth on the spot, dated 476 A.D. All other hearths were external. In the internal and

FIG. 5.1. Map showing the location of the excavation sites.

external hearths there were ceramic vessels related to flakes, scrapers, mammalian, reptile and fish bones and shells, with indications of the preparation and consumption of food obtained through hunting, collecting and, on a smaller scale, fishing [5.17].

In zone 2, eight darks spots and several hearths, most of them inside houses, form the remains of the village. Only a secondary grave of a child was found and exhumed.

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

The Prado site is located at Engenho Velho farm, in the city of Perdizes, in the state of Minas Gerais (19°14′25″S, 47°16′00″W). It is formed of 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 pyriform urn covered with a lid. Three stratigraphic profiles were excavated and indicate a single stratum: the litho-ceramic.

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

The few whole ceramic vessels collected and those partially reconstructed in the field or the laboratory are smooth, without plastic decoration or painting, with a predominance of medium to large granularity, and with a poor selection of grains. They were produced for utilitarian and funerary objectives, according to the archaeological evidence [5.18–5.21]. Their most expressive forms are globular vases and pots, spherical bowls and pyriform urns.

The Rezende site is located at the Paiolão farm at Piedade in the Paranaíba valley, 7 km from the city of Centralina in the state of Minas Gerais. Archaeological studies have found evidence of two occupations: the more recent one was ceramic production and was dated 810 ± 60 years A.D. The remains begin at the surface and go down to 35–40 cm in depth. The archaeological studies have demonstrated that the population lived in oval huts forming villages and made use of fire for light, heat and cooking. They also had an incipient agriculture–horticulture. The ceramics produced were plain, utilitarian and funerary. The oldest one is a pre-ceramic (or pure lithic) that is at a depth of 90–130 cm and was dated as 7300 ± 80 years B.P. (before present). They represent the first and 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 [5.15, 5.16].

5.3. MULTIVARIATE STATISTICAL ANALYSES

In order to elucidate the major variations in the set of compositional data obtained using INAA, it is necessary to employ multivariate statistics that use correlations between element concentrations as well as absolute concentrations to characterize 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 [5.22]. 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.

5.4. EXPERIMENTAL TECHNIQUE

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, three or five 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 105ºC 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 reference samples in all analyses. These materials were dried in an oven at 105ºC for 24 h and stored in a desiccator until weighed. Analytical details and the precision attained have been published elsewhere [5.23–5.25].

5.5. RESULTS AND DISCUSSION

One of the basic premises underlying the use of analytical chemistry for ceramic analysis is that clay sources can be differentiated if a highly precise analytical technique is used. If an element is not measured with good precision real differences in concentration can be obscured 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 types of vessels which were manufactured from a different source. In this work all the elements with a relative standard deviation (RSD) of less than 10% were considered [5.24]. Although Co and Ta have RSDs around 3%, they were not included in the data set as their concentrations could have been affected by the tungsten carbide files [5.26]. The precision to which Cs, K and Rb concentrations were measured was better than 10%; however, they were not included because of missing values. The determination of Zn is not reliable due to the strong gamma ray interference from ^{46}Sc and ^{182}Ta. The interference of ^{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 extraordinarily low [5.11].

On the basis of 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 the elements considered contained missing values. The entire data set consisted of all 149 samples (Água Limpa, 82; Prado, 34; Rezende, 33). Eight samples were eliminated by evident outliers. Range, mean and standard deviation are presented in Table 5.1. Since INAA measures both bulk and trace elements, elemental concentrations were converted to log base 10 values to compensate for the large difference of magnitudes between major and trace elements [5.27, 5.28].

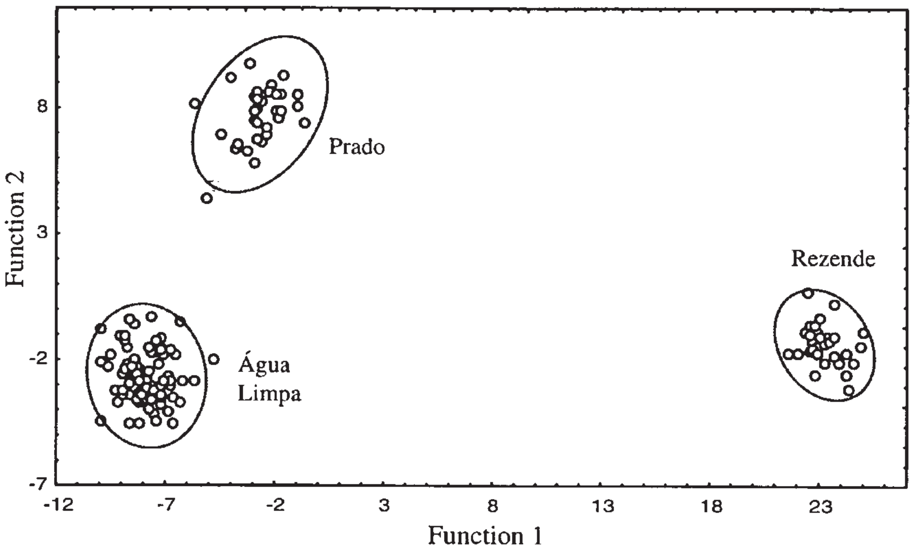

FIG. 5.2. Canonical discriminant functions for all the samples studied. The ellipses represent 98% confidence levels for sample inclusion in the clusters.

In order to examine questions of exchange and sociopolitical 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 production locations, our main purpose was to identify and distinguish the similarities among the samples analysed with the aim of defining one or more compositional groups, which presumably would represent one or more production sites. 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 Fig. 5.2.

As can be seen the samples from each site form a very tight chemically homogeneous group, showing a high degree of chemical similarity among themselves. The results show that clay from ceramic fragments, which was collected and analysed from three sites, originated from three distinct raw materials. From the samples studied at least three centres of production may be identified in the area. Whether these sources are local or not will only become clear by means of a systematic local clay analysis. The idea of autonomous development without contact with neighbours could be supported.

On the other hand, when the data from each site are interpreted separately, two samples from Prado and Rezende and three samples from Água Limpa proved to be different from the group. However, when the data sets 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 hypothesis that the raw material of the ceramics studied came from the same source, all suggesting that at these sites a single type of clay material was used in the manufacture of the vessels that have been analysed in this study. This does not necessarily mean that a single clay source was used, since there is the possibility that similar raw materials were available from different locations.

5.6. CONCLUSION

Inspection of the chemical data from ceramic fragments by the discriminant analysis method has demonstrated clearly that all the samples found in each of the archaeological sites were manufactured from a site specific raw material.

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

This suggests that a single type of raw material was used in the manufacturing of all of the ceramics analysed from each site or that the composition of the original raw material could have been altered during the overall ceramic manufacturing process by washing or adding temper or colouring agents. There is support for the idea of an autonomous development without contact with neighbours.

Finally, INAA studies have provided important contributions to the study of 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 us to sharpen our understanding of the past.

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