Chemical Study of Some Ceramics from Brazilian Northeast

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In this work 80 ceramic fragments from six archaeological sites were studied considering two main aspects: - mineralogical/petrographic examination to identify the compounds and minerals present, and elemental analysis via INAA to determine the concentration of 24 elements. Petrographic analysis showed that the samples from the all sites are quite similar in general paste characteristics. The paste is rich in sand, mica and opaque minerals, especially iron and titanium oxides. Principal components analysis was carried out using the log transformed concentrations of determined elemental concentrations. Three components with eigenvalues greater than 1 had been extracted from the variance-covariance matrix that explained 74% of the

total variation. Bivariate plot of the first two principal components showed a high degree chemically homogeneous group, providing a high degree of chemical similarity between the samples.

Introduction

Archaeometric provenance determination by mineralogical investigations, petrography, INAA, etc., use different information stored in the ceramics. They can be considered as complementary and are recommended to obtain an additional subclassification and/or an independent verification of the chemical results. They also might be helpful to explain the reasons for the chemical differences in ceramic groups.[1,2] However, an advantage of elemental analysis is that it produce "hard" quantitative data the interpretation of which does not depend on acquired expertise in recognizing inclusions.[3]

A basic aim of compositional characterization of archaeological ceramics is to isolate ceramic groups of similar chemical profiles and statistically to test the validity of those groups. The emerging compositional patterns can be further evaluated through comparison with typological and/or mineralogical data and used to address different aspects of ancient ceramic production and distribution.

To meet the above objectives, a battery of instrumental techniques has been used throughout the past three decades. These include atomic absorption spectrometry (AA)[4], X-ray fluorescence (XRF)[5], instrumental neutron activation analysis (INAA)[6-12] and, inductively mass spectrometry (ICP-MS).[5] The technique most often used has been INAA, primary because of its ability to provide the required levels of precision and accuracy, large sample throughput and simultaneous elemental determinations.[7]

In this paper contains 80 ceramic fragments from 6 archaeological sites (Justino, São José I and II, Alcobaça, Vitória Régia I and II) located in the Brazilian Northeast as shown in Fig. 1, which were analyzed using INAA to determine the concentration of 24 elements. The results were compared with petrographic studies already made in the samples.

Archaeological considerations

The archaeological sites Justino, São José I and II, Vitória Régia I and II, are located in alluvial terraces in the canyon of the São Francisco river, in the Xingó region, between the states of Alagoas and Sergipe. The area is inserted in a semi-arid region of the Brazilian Northeast, characterized by brush vegetation and climate, according to the classification of Köppen[13] of the BSh type, it is located in a dry rain deficient environment. From a geo-morphological point of view, the area is found on a plateau of lower São Francisco and the geographic units that directly effect

the located archaeological sites correspond to: New Type Granite Sites, Xingó Type Granites and the Tacaratu Formation, this last one pertains to the Tucano-Jatobá Sedimentary basin.

Through the geo-environmental context one can observe that the clay, the raw material for ceramic, is not found in the canyon area, thus in the alluvial terraces, which lead us to raise the hypothesis that the clay used in the preparation of ceramic objects comes from the plateau region (Pediplano) or from the distant watershed areas.

Recently, people have done a dozen radiocarbon datings, which situate the occupation of these alluvial terraces before the years 8950 to 1280 BP. Within this chronology, all inserted in the Holocene period, one can observe, preliminarily, two modes of terrace occupation, which we characterize by the presence or lack of ceramic remains. The first, which encompasses dates prior to the year 8950 before 5570 BP, are related to hunter-gatherer groups, as demonstrated by the archaeological material found in the deepest layers of the Justino site, here the presence of stone fragments, hearths, fauna remains and 23 skeletons were registered. The second mode of occupation refers to groups that already had ceramic technology, and according to indirect indications, such as the presence of moss and grinding stones, those would be groups which already used vegetable resources intensively, partially planted and partially collected. In the second period, which goes from the years 5570 to 1280 BP, the archaeological remains which were found are ceramics, stone fragments and

the majority of complete skeletons rescued, which were located as much in the Justino site (140) as in the São José II site (28), totaling 168 individuals, hearths, fauna remains and ornaments made from shells, stones, palm tree seeds and bone.[14]

The Alcobaça site is located in the district of Buíque, Pernambuco state, a distance of close to 100 km in a straight line from the Xingó region. It is situated at an altitude of 650-800 m sea level, forming a swamp area. It forms a sandstone shelter, with panel rock paintings approximately 70 meters in length. From an geo-environmental point of view, the Alcobaça site is also inserted in a semi-arid region, being situated geomorphologically in the Tucano-Jatobá Sedimentary Basin.

The archaeological excavations made up until this moment, allows us to identify three periods of occupation. The first, between the years 4851 to 2690 BP, correspond to temporary occupations, with the presence of structured hearths, fauna and vegetable remains, stone fragment material and ceramics. The second, between the years 2466 to 1561 BP, related to occupations where the use of the shelter as a cemetery predominated, where secondary cremated burials were evidenced, accompanied by funerary treatments (ceramics, stone fragments, baskets, fauna and vegetable remains); and the third period, between the years 1234 to 888 BP, characterized by intense occupations which left large amounts and diversity of archaeological remains such as hearths, fauna and vegetable remains,

stone fragment and ceramic material, baskets blocks with pictures among others.

Beginning with the analysis of the remains found, mainly the fauna and vegetable, it can be concluded that the groups based at the site, in different periods, had their economy based on hunting and gathering, possibly having developed an incipient agriculture.

The presence of ceramics in the three periods of occupation means that the groups who habitated the shelters had already the ceramic knowledge and the technical and morphological characteristics show the continuity of their technical profile.[15]

Experimental

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 fragment 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 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.[9-11]

Description of the method

About 100 mg of ceramic samples, Buffalo River Sediment and Coal Fly Ash were weighed in polyethylene bags and involved in aluminum foil. Groups of 6 ceramic 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 neutron flux of about 5 x 10^{12} $n \cdot cm^{-2} \cdot s^{-1}$ for 8h.

Two measurement series were carried out using Ge (hyperpure) detector, model GX 2020 from Canberra, resolution of 1.90 keV at the 1332.49 keV gamma peak of ^{60}Co, with S-100 MCA of Canberra with 8192 channels. As, Ba, K, La, Lu, Na, Nd, Sm and Yb were measured after 7 days cooling time and Ce, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Tb, Th, Zn and U after 15 days. Gamma ray spectra analysis was carried out using the Vispect II software developed by Dr. D. Piccot, Saclay, France.

Results and discussion

Petrographic analysis showed that ceramic samples from six sites are quite similar in general paste characteristics. The paste is rich in sand-sized zoned calcium plagioclase crystal, hornblende, and opaque minerals, especially iron and titanium oxides. Volcanic rock fragments, pyroxene, and quartz are present in lesser amounts.[15]

Based on petrographic observation clays contains at least 25-35% clay minerals i.e., at least one-half to two-third of the matrix comprises clay minerals. The chemical data showed that the pastes are relatively low in Ca, Fe, and K; the bulk of these elements must be contained within the rock fragment and mineral phases. For instance, nearly all calcium would be needed to account for the high proportion of plagioclase and hornblende found in the sand-sized fraction of the paste.[15] Thus, the dominant clay minerals in the are likely to be kaolinite and halloysite, which lack cations such as Ca, Fe, and K, and are the expected products of soil formation on volcanic parent materials under tropical climate conditions.[16]

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 analysis is that all the elements included are independent

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

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.[10] 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.[17] The determination of Zn is not reliable due to the strong gamma ray interference 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.[6]

Based on these screening criteria, 16 elements: As, Ce, Cs, Cr, Eu, Fe, Hf, K, La, Na, Nd, Rb, Sc, Sm, Th and U were used in subsequent data analysis. None of these elements considered contained missing values. The entire data set consisted of all 80 samples (Justino: 16; Alcobaça: 23; São José I: 6; São José II: 7; Vitória Régia I: 16; and Vitória Régia II: 8). Fourth

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.[18,19]

In order to examine questions of exchange and socio political interaction among the prehistoric cultures of these six sites, the similarities among samples were studied by means of principal component 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 analyzed with the aim to define one or more compositional groups.

The plot is useful for visually displaying group separation. A bivariate plot of two first principal components is presented in Fig. 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 six sites were originated from same raw material.

Whether these sources are local or not, it will only become clear by means of a systematic local clay analysis. The idea of development with contact with its neighbors could be supported.

In other words, it proves the hypothesis that the raw material used to make the ceramic fragments studied presents the same chemical

composition. It doesn't mean that the same raw material was used to make the ceramic from the distinct sites. The similarity between the clays can be explained by their geological position from the archaeological sites, situated in part of the same sedimentary basin.

The fact that the pre-historic groups having used clay with the same composition, means that the knowledge of an ideal choice of an adequate type of clay to make their ceramic objects, probably indicates the same technological origin of ceramic making techniques.

Conclusions

Inspection of the chemical data of ceramic fragment by PC analysis showed, clearly, that all the samples found in 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 in the sites. By means experimental studies, through petrography and elemental analysis (via

INAA) we were able to show that the ceramic fragments from the six archaeological sites were manufactured with the same raw material.

Finally, INAA studies have provided important contribution in ceramic production and distribution in the prehistoric era. This information can be an indication that the origin of the ceramic making technique was the same in these two areas. The use of INAA has allowed ceramic analysis to reach a higher level of resolution, and allowed as sharpening our understanding of the past.

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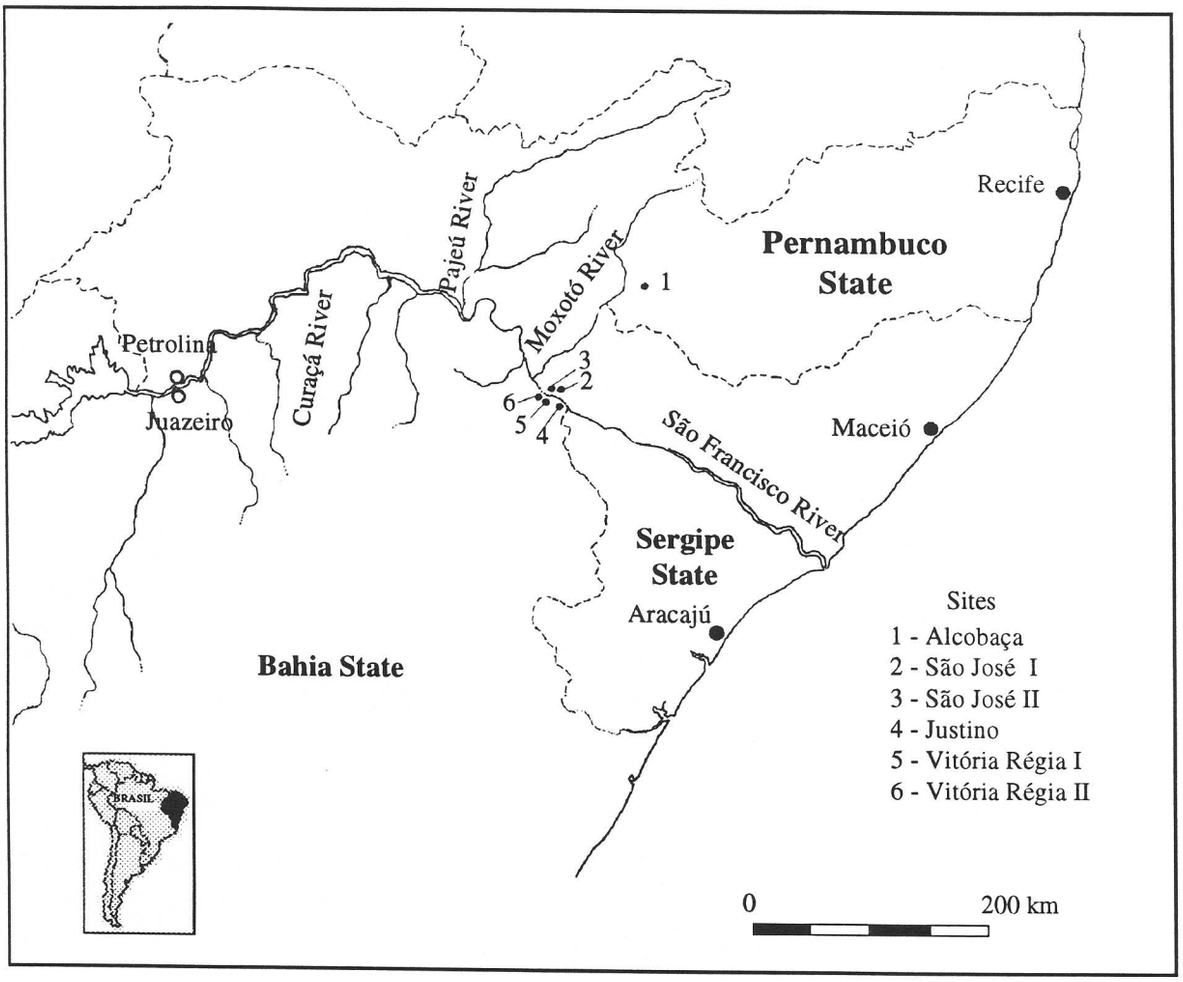
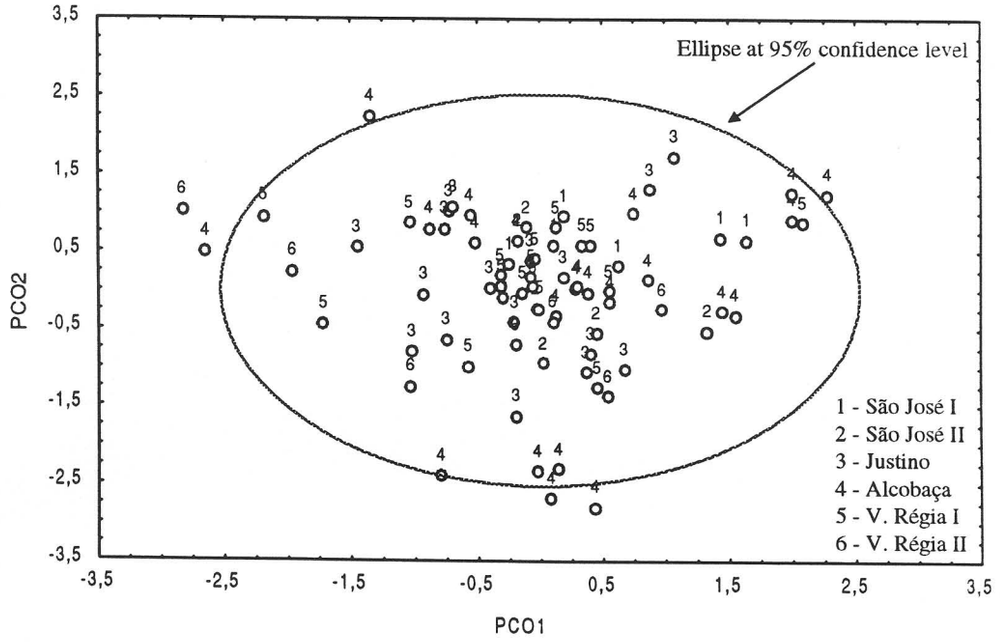
Captions of Figures

Fig. 1. Map showing the location of sites

Fig. 2 . Plot of the first two principal components (PCO1 vs PCO2) from six sites


Recife
Pernambuco State
Pajeú River
Moxotó River
1
Petrolina
Juazeiro
Curaçá River
3
2
6
5
4
São Francisco River
Maceió
Sergipe State
Aracajú
Bahia State
BRASIL
Sites
1 - Alcobaça
2 - São José I
3 - São José II
4 - Justino
5 - Vitória Régia I
6 - Vitória Régia II
0
200 km


Ellipse at 95% confidence level
1 - São José I
2 - São José II
3 - Justino
4 - Alcobaça
5 - V. Régia I
6 - V. Régia II
PCO1
PCO2
3,5
2,5
1,5
0,5
-0,5
-1,5
-2,5
-3,5
-3,5
-2,5
-1,5
-0,5
0,5
1,5
2,5
3,5