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The archaeometry study of the chemical and mineral composition of pottery from Brazil's Northeast

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Abstract Chemical and mineralogical analysis was performed on ceramics and clay samples from Barracão archaeological site located in Baixo São Francisco River by means of instrumental neutron activation analysis (INAA) and by differential scanning calorimetry (DSC). The data set was studied by means of cluster analysis (CA) and discriminant analysis (DA). The results showed that the raw material used in ceramics is not local. By using DSC it was possible to discover that the principal minerals in the samples are quartz, feldspars, mica and kaolinite.

Keywords Archaeometry · Firing temperature · Provenance study

Introduction

Nowadays archaeology has used a variety of methods to reconstruct ancient cultures through environmental analysis, sociology, scientific and historical dating methods, historic and iconographic sources, and material analysis of artifacts that have been found, in addition to other methods [1]. Since ceramics represents a sophisticated merging of previously separate domains of human knowledge and experience, these objects are intensely studied by means of archaeometric methods [2]. In addition to its abundance and durability, ceramics have several macroscopic and microscopic attributes of interest to archaeologists [3]. It has been an integral approach to archaeological pottery studies most often has been provided information about the provenance of raw materials and ancient technologies, such as firing conditions of raw materials during the manufacturing process [4–6].

In this work, INAA was applied to determine the elemental composition of pottery fragments and clays from the Barracão archaeological site, situated in Canindé do São Francisco, to establish a categorization of these ceramics and the raw material sources. Additional studies about mineral composition of clay and ceramic samples from Xingó were done through the DSC technique, in order to characterize their mineral contents and to determine their equivalent firing temperature [7].

Experimental

In this study, 73 ceramic fragments and 30 clay samples from the Barracão site were analyzed by means of INAA. The clay samples were collected near to Barracão site from three places, called Clay A, B and C. Ceramic powder samples were obtained by cleaning the outer surface and drilling to a depth of 1–2 cm using a tungsten carbide rotary file attached to the end of a flexible shaft, using a variable speed drill. Depending on the thickness, three or five holes were drilled as deep into the core of the fragment as possible without drilling through the walls. Clay samples were ground in an agate mortar until a granulometry of 100–200

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mesh was achieved. Finally, the powered samples were dried in an oven at 105 °C for 24 h and stored in desiccators.

Constituent Elements in Coal Fly Ash (NIST-SRM-1633b) was used as standard in all analysis. The standard reference material Brick Clay (NIST-SRM-679) was used to check the analytical quality of the results. The standards and the samples were dried in an oven at 105 °C, the standards for 2 h and samples for 24 h, and stored in a desiccator until weighing. About 100 mg of ceramic samples and NIST-SRM-1633b were weighed in polyethylene bags and wrapped in aluminum foil. Groups of eight ceramic samples and two reference materials were packed in aluminum foil and irradiated in the swimming pool research reactor, IEA-R1 m (IPEN/CNEN-SP) at a thermal neutron flux of about 5×10^{12} n cm^{-2} s^{-1} for 8 h.

Two measurement series were carried out using Ge (hyperpure) detector, model GX 2519 from Canberra, with a resolution of 1.90 keV at the 1332.49 keV gamma peaks of ^{60}Co, with S-100 MCA of Canberra with 8,192 channels. As, K, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days cooling time and Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, and Zn after 25–30 days. Gamma ray spectra analysis was carried out using the software Genie 2000 NAA Procedure from Canberra.

Differential scanning calorimetry (DSC) was carried out in an automatic thermal system (model DSC-2010—TA Instruments). Samples of about 10 mg were weighed into a sample capsule pan, which were sealed hermetically and placed in the calorimeter samples capsule holder. An empty reference capsule was placed in the calorimeter reference capsule holder. The measurements were done with a heating rate of 30 °C min^{-1} in an air flow, with an ambient temperature up to 600 °C. The equivalent firing temperature was estimated by comparing the measurement on the original shred (1st heating cycle) with the measurement data on the same shred, re-firing at an increasing temperature (2nd heating cycle).

To identify outlying cases, the robust Mahalanobis distance (RD) based on the minimum covariance determinant (MCD) [8–11], was utilized. It was possible construct the ellipse corresponding to squared Mahalanobis distance for each group. The observation found outside of the tolerance ellipse, in the space established for the first two principal components, was considered an outlier [12]. Hierarchical cluster analysis was used to identify initial groups using Ward's method and squared Euclidean distance[13, 14] and discriminant analysis (DA) to identify the groups of samples.

Results and discussion

To evaluate the analytical process and to establish the chemical elements which can be used in the data interpretation, the elemental concentrations for reference material Brick Clay (NIST-SRM-679) were statistically compared with the data found in our laboratory. The precision of several elements (La, Th, Sc, Fe, Eu, Ce, Zn, Hf, and Co) was better than 5%. Some elements presented a RSD (Relative Standard Deviation) of less than 10% (Nd, Rb, Sm, Ba, Sb, Ta, and Tb) and are similar to those from the literature [15].

Elements that have low precision can reduce the discriminating effects of other well measured elements. In this study all the elements with precision of less than 10% were considered for interpretation of the results (Na, Lu, Yb, La, Th, Cr, Cs, Sc, Ce, Fe, Eu, Zn, Co, Ta, U, Hf). The Zn presented RSD better than 10% but was excluded from the data set because its determination suffers strong gamma ray interferences of ^{46}Sc and ^{182}Ta. Co was eliminated because their concentrations can be affected by tungsten carbides drills [16, 17]. K and Sb were better than 10%, however, they were excluded because they presented 15% of missing values. Based on these screening criteria 13 elements: Na, Lu, Yb, La, Th, Cr, Cs, Ce, Sc, Fe, Eu, U and Hf were used for the interpretation of the results.

Table 1 shows the means, standard deviations, minimum and maximum values of the elemental concentrations for ceramic and clay samples. Initially, the results were transformed to $\log_{10}$ to compensate for the large magnitude difference between the measured elements at the trace level and the larger ones. One reason for this is the belief that,

Table 1 Means, standard deviations, minimum and maximum values for pottery and clay samples, in μg g^{-1} unless otherwise indicated

Element	Mean	Ceramic			Mean	Clay		
		SD	Min	Max		SD	Min	Max
Ce	115.24	31.04	56.40	189.10	81.18	16.24	50.30	99.10
Co	19.88	3.51	11.80	28.90	8.94	1.36	6.50	11.30
Cr	42.72	21.82	6.10	97.50	52.09	5.92	38.80	66.60
Cs	4.61	1.61	2.00	7.70	3.24	0.64	2.10	5.00
Eu	2.37	0.75	0.90	4.80	1.31	0.28	0.80	1.80
Fe	4.54	1.13	2.10	6.30	2.34	0.35	1.70	2.90
Hf	9.37	1.82	1.10	12.00	14.93	1.44	12.40	18.20
La	61.48	18.90	32.90	97.10	41.90	7.95	26.50	54.40
Lu	0.55	0.17	0.20	0.98	0.53	0.09	0.40	0.70
Na	2.12	0.35	1.23	2.90	0.85	0.34	0.32	1.30
Rb	72.89	16.46	26.00	152.60	64.88	17.73	28.70	115.10
Sc	13.70	3.94	5.10	23.90	7.48	1.32	5.20	9.50
Ta	2.07	0.81	0.50	4.10	1.72	0.44	0.80	2.40
Tb	1.23	0.36	0.40	1.80	0.80	0.22	0.20	1.20
Th	12.44	3.95	4.90	30.30	11.68	2.05	7.30	14.70
U	3.16	0.85	0.90	4.90	2.78	0.56	1.60	3.80
Yb	4.10	1.50	0.90	7.70	3.27	0.51	2.40	4.20
Zn	62.92	15.46	32.40	95.70	42.98	13.69	4.60	63.20

within manufacture raw materials, elements have a natural lognormal distribution, and that data normalization is desirable. After logarithmic transformation the data set was submitted to outlying tests by means of robust Mahalanobis distance, using a minimum covariance determinant, where critical values were obtained $\chi^2_{2;0.98}$. Only one sample was considered an outlier.

Figure 1 shows the cluster of the samples and the separation in four groups (A, B, C and D), with a statistical significance level of 4/5 of maximal linkage distance (Fig. 1).

In order to confirm the compositional groups, the data were submitted to DA. Figure 2 shows the plot of discriminant function 1 versus discriminant function 2 where is possible to see seven groups: three groups of clay samples (Clay A(19), Clay B(10) and Clay C(10)) and four groups of potteries (Pottery A(10), Pottery B(12), Pottery C(9) and Pottery D(32)). DA indicated that raw materials used in the manufacture of the analyzed ceramics are distinct and the clay samples investigated were not used to obtain a ceramic paste. Since investigated clay samples were available near the archeological site, it can be inferred that potters, who lived at Barracão area searched their raw material far from this site. Therefore, the search for clay of appropriate properties to manufacture the ceramics, perhaps, has induced craftsman to seek raw materials far from place where they lived.

In order to verify the equivalent firing temperature of the ceramics a mineralogical study was accomplished by using DSC. Figure 3 shows DSC typical curves for all the samples from Barracão site. It has been found that the mineral composition of the most of the studied shreds is quartz, feldspars, mica and kaolinite. According to our thermal results, we can affirm that all the samples have a similar mineral composition, which is represented in Fig. 3. The DSC curve (BV05, BV31, BV56 and BV17), which corresponding to 1st heating cycle, shows three main endothermic peaks: the first one around 100 °C corresponding to a loss of adsorbed and interlayer water; the second peak at about 500 °C corresponding to a deyhidroxilation of the kaolinite; and the last peak at 573 °C is related to α-SiO_2 to β-SiO_2 phase transition [18]. Additionally, during the 2nd heating cycle all the samples presented, only the peak at 573 °C. Thus, the existence of kaolinite denotes that the equivalent firing temperature was lower than 500 °C. According to our results, we can conclude that the calculated firing temperature should be grouped around at about only one temperature (500 °C), which in turn reflects the organization production at the Barracão archaeological site.

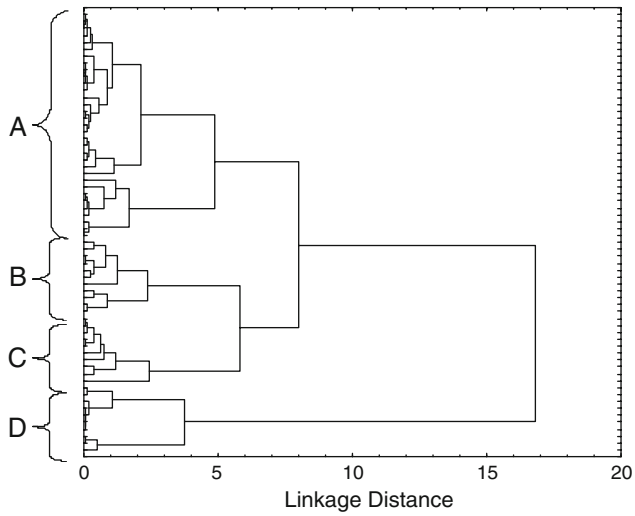

Fig. 1 Dendrogram for pottery samples using Ward's method and squared Euclidean distance

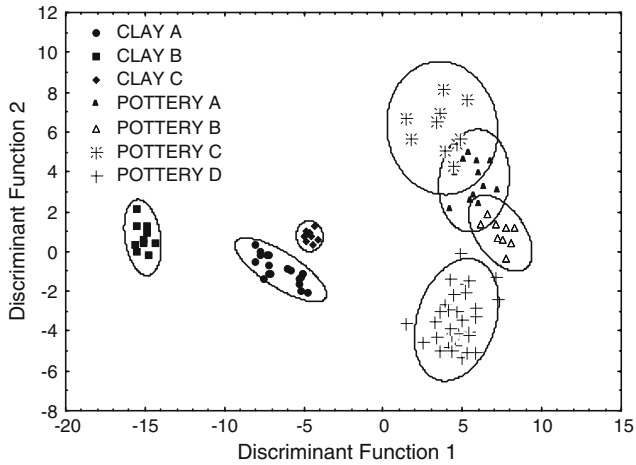

Fig. 2 Linear discriminant analysis of ceramic and clay samples. Ellipses represent a 95% confidence level

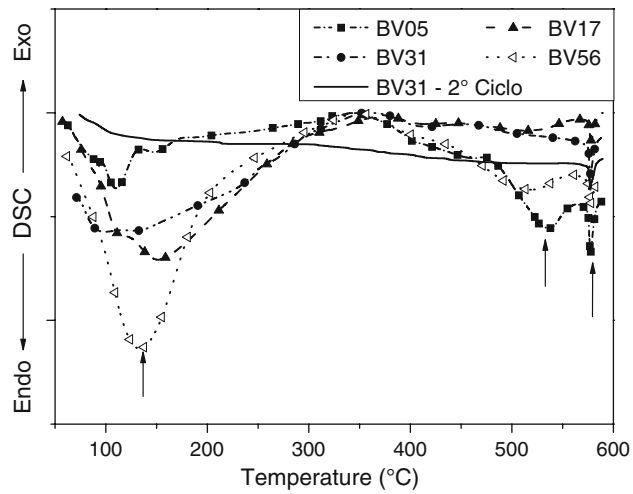

Fig. 3 The DSC results to the archaeological site

Conclusions

INAA of ceramics from the Barracão site was successful in identifying distinct compositional groups. There were four groups of ceramics and three groups of clay identified. The results from DA showed that the clay samples analyzed in this study were not used to prepare ceramic pastes. Therefore, it can be inferred that the raw materials for the manufacture of potteries at the Barracão site was not from there. Thermal analysis shows that the equivalent firing temperature of potteries was around 500 °C. The results provided information about the occupational dynamic of ceramist groups in the Xingó area, during the pre-historical period.

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