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Nuclear and non-nuclear analytical techniques applied to pre-colonial archaeological ceramics from the upper Madeira River/Brazil (940 to 760 B.P)

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1.Introduction

The present study integrates different analytical techniques in order to generate quantitative and qualitative data on chemical composition of pottery samples from the upper Madeira River/southwestern Amazon, and to contribute to the discussion on the process of raw material choice (clay sourcing) and firing techniques used for the production of archaeological vessels. Research carried out in the area indicates the coexistence of three distinct ceramic technologies dating from 940 to 760 B.P [1]. These artifacts were associated with distinct cultural groups that were cohabiting along the Madeira riverbanks and islands [2]. In order to contribute towards the classification and differentiation of pottery making within the region, neutron activation analysis (INAA) was carried out to determine the chemical composition of the ceramics. It was possible to determine the mass fraction of Na, K, La, Sm, Yb, Sc, Cr, Fe, Cs, Ce, Eu, Hf, and Th. The data set was analyzed by two statistical methods: cluster and discriminant analysis. Next, the samples were analyzed by X-ray diffraction (XRD) to determine the mineralogical composition of each group, allowing the observation of variations in the proportions of clay minerals in the samples. With this technique, phengite, quartz, alunogen and schaurteite were refined. Finally, electron paramagnetic resonance (EPR) was applied to identify the firing temperature and determine whether there were similarities or differences in the firing processes. The results indicated a temperature range between 450-550°C, suggesting that firing was done in an oxidizing atmosphere, similar to that identified in Bacabal ceramics [3]. The dates used are all radiocarbon dates, obtained from material associated with the same archaeological layers from which the ceramics were collected. The use of these analytical techniques has allowed us to advance in the characterization of the clay sources of the artifacts ceramics in the upper Madeira River.

2.Methodology

In this work, 118 pottery samples were analyzed by INAA. Sample were recovered during stratigraphically controlled excavations at seven archaeological sites located along the upper Madeira River: 1) Ilha de Santo Antônio, 2) Do Brejo, 3) Teotônio, 4) Ilha das Cobras, 5) Coração, 6) Ilha do Japó and 7) Ilha Dionísio [2]. XRD and EPR analyses were applied, to 6 of these samples.
To perform INAA, the first step involves cleaning the surface of the ceramic with a rotating tungsten carbide

file adapted to a variable speed drill, in order to avoid any contamination. After this procedure, holes were drilled on the side of the ceramic with a tungsten carbide drill (diameters of 1.5 and 2.2 mm), without drilling through the wall. About 500 mg of each sample was collected in the form of powder and left to dry in an oven at 104 ° C for 24 h [4]. To perform the analysis, about 100 mg of dry powder of each ceramic sample was used. It was weighed and packed in polyethylene wrappings, and sealed in a sealpack. Each envelope was wrapped in aluminum foil. Then, a set of 8 samples was assembled with approximately 100 mg of Standard Reference Material NIST-SRM 1633b (Constituent Elements in Coal Fly Ash) and the Sediment candidate certified reference material, (RM), from Wageningen University, the Netherlands. After grouping the samples in parallel to receive the same neutron flux, they were irradiated for 8 hours in the IEA-R1 reactor of IPEN-CNEN / SP, under a thermal neutron flux in the order of 10^{12} $cm^{-2} \times s^{-1}$ [5].

The measurements were performed in two stages, one after 7 days of decay to determine Na, K, La, Sm, Yb, Lu and U mass fractions elements concentrations, and other after 25 to 30 days to determine Sc, Cr, Fe, Co, Zn, Rb, Cs, Ce, Eu, Fe, Hf, Ta and Th. All measurements were performed using the Ge hyperpure detector, model GX 1925 from Canberra, which has a resolution of 1.90 keV at the 1332.49 keV gamma peak of 60Co, with S-100 MCA of Canberra with 8192 channels. The Genie-2000 Gamma Acquisition & Analysis software, v. 3.1.a, developed by Canberra, was used to analyze the gammaray spectra [5].

For XRD analysis, approximately 50mg of ceramic powder was, with particle size of 80 micrometers was used. The sample was placed in the center of a glass sample holder with dimensions of 20 x 20 x 0.5mm and a swab was carried out to remove excess material and to obtain a uniform and smooth distribution. Then, the sample holder was coupled to the goniometer of the diffractometer. The XRD measurements were made in a RIGAKU X-ray diffractometer, model SmartLab SE. The X-rays used in the measurements were those from the Kα band of copper that have wavelengths ((λ) of 1.5418 Å. Using 0.01° step with 1.0 second of reading for each step, starting at 10° and ending at ^{60}Co. The diffractogram data was analyzed using the HighScore Plus software, version 4.9 (2019) [3].

For EPR analysis, approximately 25mg of ceramic powder was distributed in 12 aliquots for each sample. The aliquots were then transferred to porcelain crucibles and fired in a muffle furnace, starting at 350°, with 50°C increments, up to 1000°C, for 30 min. For the EPR analysis and to determine the firing temperature, a Bruker MiniScope MS5000 EPR spectrometer was used. Measurements were performed with 25-mg aliquots of each ceramic powder sample, placed in 4.3cm diameter quartz tubes, with the following spectrometer experimental parameters: magnetic field modulation frequency of 0.1 mT, microwave power of 3.991 mW, scanning range of 150 to 550 mT, and scan time of 60 seconds [3].

3. Results and Discussion

Eighteen samples of the reference material were analyzed in this research, to determine the mass fractions of the following elements: Na, K, La, Sm, Yb, Lu, Sc, Cr, Fe, Co, Zn, Rb, Cs, Ce, Eu, Hf, Ta and Th. The aim of this analysis was to assess the quality control of the analytical meth-od. In order to examine the homogeneity on the observations of the RM, it was used the rmax and rmin criteria [6,7]. These experimental values were compared with the values tabulated for a level of significance of 0.05 and with n-2 degrees of freedom [6]. After verifying the precision for each element, the results showed that most elements presented a RSD ≤ 10%. Elements such as Lu, and Ta were removed because they had precision of > 10%. The determination of Zn was not reliable as a consequence of strong gamma-ray interference by 46Sc and 182Ta. Although Co has a RSD less than 10 %, it was not included in the data set because the determination can be affected by tungsten carbides files. So, the elements used in the interpretation of data set were Na, K, La, Sm, Yb, Sc, Cr, Fe, Cs, Ce, Eu, Hf, and Th. After this step, the elementary concentrations of each were normalized by the transformed log10, which is a common procedure in archaeometric studies, whose function is to compensate for the large differences in magnitude between elements that are at higher level and those at trace level [6]. Subsequently, it was calculated the average, standard deviation, maximum and minimum values for each ceramic fragment. After removing the discrepant samples using the *Mahalanobis* distance and the Lambda Wilks criteria, the results of the elementary concentrations of 118 samples were subjected to

statistical analysis. First, cluster analysis was applied to search for the presence of homogeneous groups of samples [8], adopting the criteria of similarity to the quadratic *Euclidean* distance and as a clustering algorithm *Ward*, thus generating a dendrogram. Next, the discriminant analysis was performed to confirm the number of groups defined by cluster analysis. The discriminant analysis technique function is maximizing the differences between two or more groups, extracting new variables from the original variables [9]. The results showed the presence of three compositional groups, indicating different clay sources of raw material in the manufacture of ceramic artifacts (Figure 1).

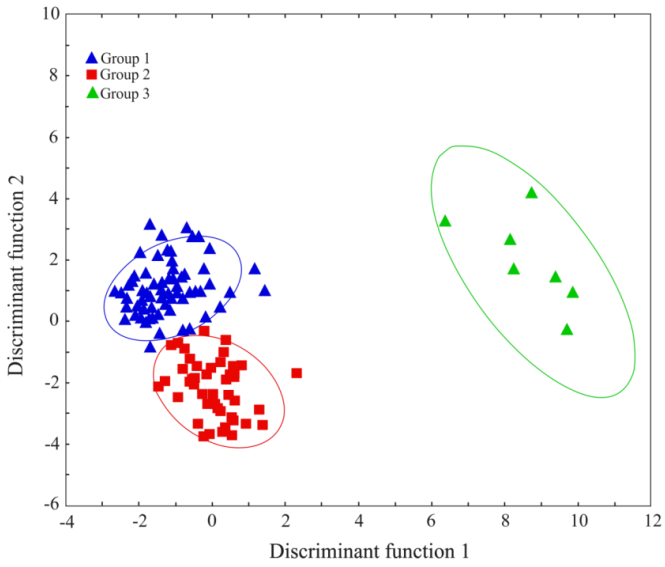

Figure 1: Discriminant function 1 versus discriminant function 2. Ellipses represent a confidence level of 85%.

Samples from each group identified in the discriminant analysis were selected to determine their mineralogical structure. The criteria in this case were fragments from radiocarbon-dated archaeological layerfrom the period between 940 and 760 B.P. For this analysis we selected fragments from the Santo Antônio ceramic assemblage collected at the Ilha de Santo Antônio and Do Brejo archaeological sites, fragments from the Dionísio assemblage collected at the Ilha Dionísio site, and fragments from the Polychrome Tradition assemblage collected at the Coração site.

The XRD results show the presence of Mg-phengite, quartz, alunogen and schaurteite. The Mg-phengite phase is present in all groups. It is noted in all samples a relative concentration of K, Fe and rare earths (REEs) characteristic of the chemical composition of the Mg-phengite phase. Group 2 highlights the absence of the student phase. Group 3 presents the highest concentration of Fe, K and REEs when compared to the other groups and this characteristic may be related to a greater presence of Mg-phengite Type 2 and 3 (hydrothermal origin and well-crystallized lath form).

The EPR results show that the firing temperature is in the 450-550°C range, indicating that the firing of all pottery samples was carried out in open fires, in an oxidizing environment. The same firing temperature range was observed in the Bacabal ceramics from southern Rondônia [10]. Ceramic samples from the Amazon Polychrome Tradition, which are associated with Group 1 (FC128), were fired at 450±50ºC. Ceramic samples from Santo Antônio (FC56 and FC58) and Do Brejo (FC78), assembled in Groups 1 and 3, are in the 500-550ºC range. The Dionísio ceramic sample FC01, which belongs to Group 2, was fired at 500±50ºC. Sample FC02 from the Dionísio site showed a high concentration of Fe^3, making it impossible to determine the firing temperature.

4. Conclusions

The nuclear and non-nuclear analytical techniques used in this work showed that the indigenous communities that produced the Santo Antônio pottery and inhabited Ilha de Santo Antônio and Do Brejo archaeological sites [1], as well as the indigenous groups that produced Amazon Polychrome Tradition pottery and inhabited the Coração site [1], produced their artifacts using mainly the Group 1 clay source. The firing temperature of this material varies between 450-550°C. In addition to the Group 1 clay source, they were also exploiting a second clay source assembled in Group 3 rich in Fe. In relation to the indigenous group that produced Dionísio pottery and inhabited the Ilha Dionísio site [11], it was found that the pottery producers used another clay source of Group 2, characterized by the absence of alunogen. The firing temperature of this material varies between 500-550°C. This approach possible understand technological choices linked to the selection of certain clay sources [12], and the results suggest that different indigenous group that inhabited the upper Madeira River region in the period between 940-760 B.P selected three sources of clay for the production of vessels.

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