

# PXRF and multivariate statistics analysis of pre-colonial pottery from northeast of Brazil

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Portable system of energy dispersive X-ray fluorescence was used to determine the elemental composition of 68 pottery fragments from 'Sambaqui do Bacanga', an archeological site in São Luis, Maranhão, Brazil. This site was occupied from 6600 BP until 900 BP. By determining the element chemical composition of those fragments, it was possible to verify the existence of engobe in 43 pottery fragments. Obtained from two-dimensional graphs and hierarchical cluster analysis performed in fragments of stratigraphies from surface and 113-cm level, and 10 to 20, 132 and 144-cm level, it was possible to group these fragments in five distinct groups, according to their stratigraphies. The results of data grouping (two-dimensional graphics) are in agreement with hierarchical cluster analysis by Ward method. Copyright © 2011 John Wiley & Sons, Ltd.

**Keywords:** portable X-ray fluorescence (PXRF); hierarchical cluster analysis (HCA); archeological pottery; archeometry

## Introduction

In Brazil, almost all written documentation related to human occupation, before the contact with Europeans, is difficult to be accessed; in that way, the study of material culture is an important means for understanding the pre-colonial history of this country.<sup>[1,2]</sup>

A pioneer research project about the occurrence of pottery in archeological record has been developed in São Luis (Maranhão). Pre-colonial civilizations that inhabited that territory were characterized by being fishing populations – catchers – hunters and ceramists, who settled down in the region around 6600 years ago and remained inhabiting the place till the year 900 of our era.<sup>[1,2]</sup>

Amidst all such material culture, ceramics are highlighted as objects of highly archeological value because they are extremely resistant to weather and environment conditions.<sup>[3]</sup>

With the energy dispersive X-ray fluorescence (EDXRF) technique, making chemical characterizations of pottery fragments and obtaining important information about the origin of raw materials, quality of the revetment and trace of paintings, among others, in a multi-elemental, simultaneous, fast and non-destructive way has been made possible. The principles of the EDXRF method are well established<sup>[4–6]</sup>, and the EDXRF method is one of the important analytical techniques that is used for the study of pre-colonial pottery.<sup>[7–28]</sup>

The pottery fragments obtained from Sambaqui do Bacanga were analyzed with the use of a portable system of EDXRF aiming to verify the existence of any type of different treatment on faces (concave and convex) related to the ceramic paste. The multivariate statistics analysis was employed to verify the similarity between the chemical elements in fragments with equal stratigraphy and also with different ones; this was achieved by two-dimensional graphs and hierarchical cluster analysis (HCA).<sup>[29]</sup>

## Experimental

### Description of the archeological site

The pottery fragments were collected in site Sambaqui do Bacanga, located in Bacanga State Park, in the island of São Luis – MA/BR. This site is located in the center-west area of the island

of São Luis and in part of the central area of São Luis city and, also, located near the region of the equator.

Sambaqui do Bacanga is located in the island of São Luis (river's mouth) on the river borders whose name it bears. This river is protected by an environmental conservation organization called Bacanga State Park.

### Description of samples

Stratigraphic samples of 68 pottery fragments were collected, deriving from the following sectors: Exploratory Trench, Profile 1, Excavation Area 1 and Profile 2, as shown in Tables 1 to 4. Samples sizes varied from 3.5 × 2.5 cm to 11.0 × 6.5 cm.

### Portable system of EDXRF

The portable system of EDXRF (PXRF-LFNA-02) utilized for irradiation/detection of the fragments consists of a 4-W X-ray mini-tube with Ag anode and 50- $\mu$ m Ag filter (Moxtek, Inc., Orem, UT, USA); a Si-PIN detector with pre-amplifier XR-100CR (AMPTek Inc., Bedford, MA, USA), 221-eV full width at half maximum (FWHM) for the 5.9-keV Mn line, 25- $\mu$ m Be window and thermoelectric cooling system by Peltier Effect; PX2CR conjugated high-tension source module and amplifier (AMPTek Inc.); multichannel analyzer model MCA8000A (AMPTek Inc.); an excitation–detection system positioning module with freedom degrees XYZ and rotation in relation to the analyzed sample; and a notebook for data acquisition and storage.

Measurement conditions were 28 kV and 5  $\mu$ A in the X-ray mini-tube, and acquisition time was 500 s.

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Table 1. Information about fragments in sector Exploratory Trench		
Sample	Quantity of fragments	Stratigraphic levels
Sample 03	01	Surface
Sample 09	02	Surface
Sample 20	11	Surface
Sample 15	02	125 cm
Sample 05	01	128 cm
Sample 12	03	128 cm
Sample 17	03	135 cm
Sample 18	02	138 cm
Sample 07	08	144 cm
Sample 01	01	150 cm
<b>Total</b>	<b>34</b>	<b>07</b>

Table 2. Information about fragments in sector Profile 1		
Sample	Quantity of fragments	Stratigraphic levels (cm)
Sample 04	01	0–8
Sample 14	02	10–20
Sample 06	01	80
Sample 22	04	113
Sample 21	07	125
Sample 19	06	132
Sample 08	03	140
<b>Total</b>	<b>24</b>	<b>07</b>

Table 3. Information about fragments in sector Excavation Area 1		
Sample	Quantity of fragments	Stratigraphic levels
Sample 02	01	Surface
Sample 10	03	Surface
Sample 11	02	Surface
<b>Total</b>	<b>06</b>	<b>01</b>

Table 4. Information about fragments in sector Profile 2		
Sample	Quantity of fragments	Stratigraphic levels (cm)
Sample 13	02	30–35
Sample 16	02	40
<b>Total</b>	<b>04</b>	<b>02</b>

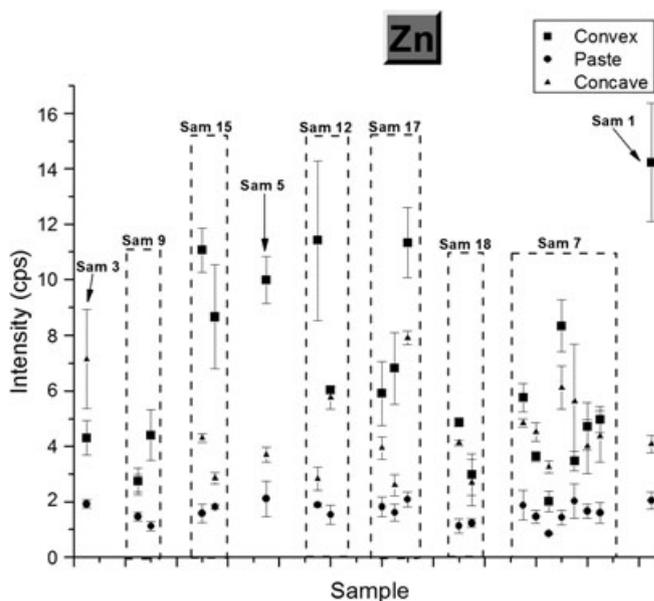
Taking into account that both X-ray tube and detector form a fixed (pre-established) geometry, we can position the sample in a desirable area for analysis. A region with a diameter of about 5 mm was studied for each point measured.

In average, nine measurements were made in different points of each fragment: three of them in the concave face, three in the convex one and three in the ceramic paste. The three points of each group were scattered equally throughout the area of the considered region.

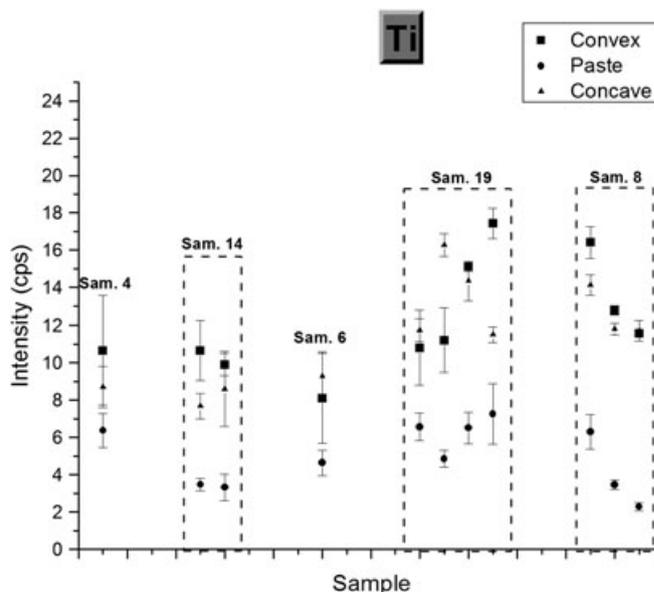
The analysis of the spectra was conducted by using the software Quantitative X-ray Analysis (AXIL),<sup>[30]</sup> distributed by the International Atomic Energy Agency (IAEA).

For the analyses of the data obtained with AXIL, only the intensities of the chemical elements whose net areas were threefold higher than their standard deviations were considered.

The average intensity for each chemical element (obtained from three measures of each concave and convex faces) was estimated. This evaluation was also carried out for the ceramic paste. So, these averages represent three regions of 5-mm diameter each.



**Figure 1.** Graph of Zn intensity for the samples in the Exploratory Trench, in which the samples are separated in different stratigraphies and the number of fragments is in brackets: surface [samples 3(1) and 9(2)], 125 cm [sample 15(2)], 128 cm [samples 5(1) and 12(2)], 135 cm [sample 17(3)], 138 cm [sample 18(2)], 144 cm [sample 7(7)] and 150 cm [sample 1(1)].



**Figure 2.** Graph of Ti intensity for samples from Profile 1, in which the samples are separated in different stratigraphies and the number of fragments is in brackets: 0 to 8 cm [sample 4(1)], 10 to 20 cm [sample 14(2)], 80 cm [sample 6(1)], 132 cm [sample 19(4)] and 140 cm [sample 8(3)].

## Results and discussions

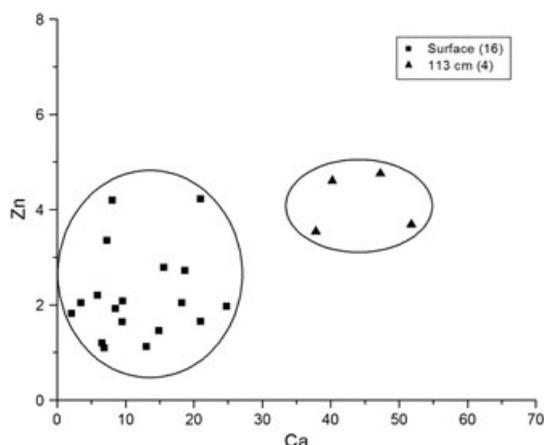
### Qualitative analysis

With the results obtained from these measures, it was possible to observe elements K, Ca, Ti, Mn, Fe, Zn, Br, Rb, Sr, Y, Zr and Pb in different analyzed fragments. The statistical deviations of each measurement, obtained by AXIL, were generally of 1.0% for Fe, 5.0% for Ca, 2.5 to 10.0% for Sr, Zr, Mn, Ti and Zn, and 20.0 to 25.0% for K, Br, Rb, Y and Pb.

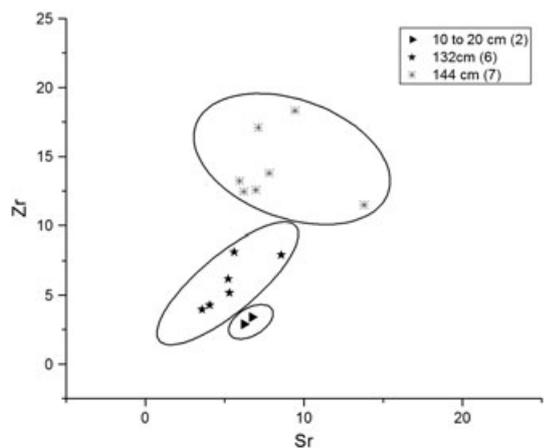
The elements Ca, Ti, Mn, Fe, Zn, Sr and Zr were observed in the ceramic paste of all 68 pottery fragments analyzed, indicating that these elements are present in the composition of the clay used in manufacturing of these ceramics.

Data representing the average intensity for both chemical elements of the concave and convex faces and ceramic paste obtained from each analyzed fragment were displayed on graphs (a visual representation of a relationship between intensity and samples) for each chemical element previously mentioned.

The elements Fe, Sr, Mn, Ti and Zn presented systematically higher intensities in the faces in relation to the ceramic paste in 43 out of the 68 analyzed fragments, indicating that there is a treatment in the faces, with enriching for those elements, which is the engobe. This



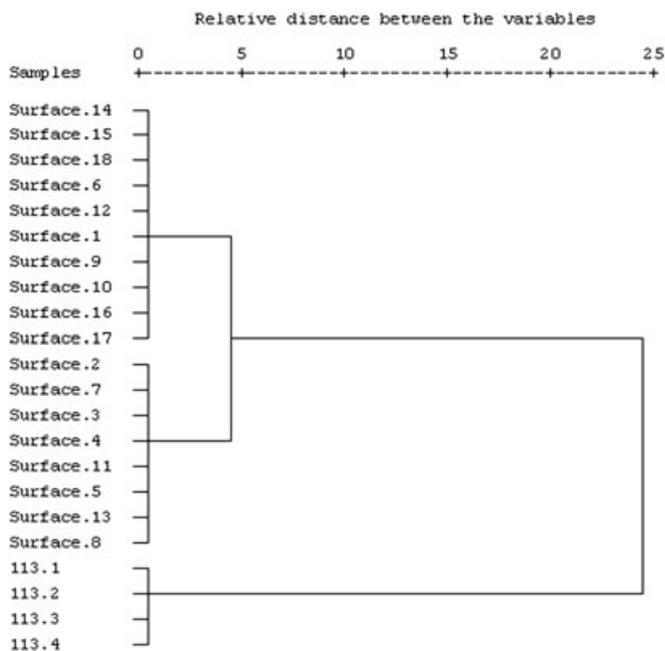
**Figure 3.** Two-dimensional graphs of the X-ray intensities of Ca versus Zn with pottery fragments excavated in two stratigraphies, surface and 113 cm.



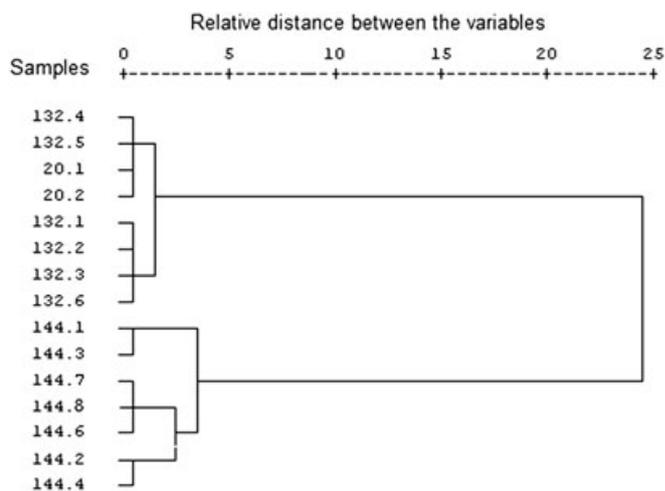
**Figure 4.** Two-dimensional graphs of the X-ray intensities of Sr versus Zr with pottery fragments excavated in three stratigraphies, 10 to 20, 132 and 144 cm.

behavior is shown in Figs 1 and 2, which refer to element Zn in the Exploratory Trench and Ti of Profile 1, respectively.

While analyzing each chemical element graph, it turns out that standard deviation bars are larger than statistical deviation ones, considering each individual measure, indicating the existence of a variability in concentrations of the chemical elements in the fragments. This behavior is shown in Figs 1 and 2. The range of statistical deviations of the individual measures for Ti and Zn ranged from 2.5 to 4.5% and from 4.5 to 6.5%, respectively, whereas, considering all samples, the average of three points in each region for these elements ranged from 3.5 to 30.0% and



**Figure 5.** Dendrogram of hierarchical cluster analysis with pottery fragments excavated in two stratigraphies, surface and 113 cm; the last algarism from left to right in the sample code represents the sample number.



**Figure 6.** Dendrogram of hierarchical cluster analysis with pottery fragments excavated in three stratigraphies, 10 to 20 (represented as 20 cm), 132 and 144 cm; the last algarism from left to right in the sample code represents the sample number.

from 5.0 to 38.0%, illustrating a heterogeneity of the order from 1.0 to 25.5% and 0.5 to 31.5%, respectively.

### Grouping analysis

Two-dimensional graphs were generated (element vs element) for 68 previously referred as analyzed fragments, therefore considering only their stratigraphies, to verify which chemical elements or which chemical combinations of elements group better the pottery fragments according to their chemical similarities. The graphs of intensities Ca versus Zn and Sr versus Zr were the ones, which grouped better the fragments from the surface and 113-cm level, and from the 10 to 20cm, 132 and 144-cm levels, as shown in Figs 3 and 4.

In Fig. 3, the formation of two distinct groups may be verified. These groups consist of fragments from the surface and 113-cm level. From Fig. 4, separation of fragments of stratigraphies 10 to 20, 132 and 144 cm may be visualized. Sample 7.5 was not included in this graph, although a measurable intensity has ever been observed for Sr. These results suggest that the chemical elements Zn, Ca, Sr and Zr characterize the clays used in the manufacturing of fragments of each stratigraphy, and also, the analyzed fragments were manufactured with clays from five different sources.

As shown in Figs 3 and 4, each set of fragments of stratigraphies from the surface and 113-cm level, and from the 10 to 20, 132 and 144-cm levels were grouped separately, suggesting that these groups were obtained from different clays. By aiming to present a more accurate evaluation of the sets of fragments obtained from these five stratigraphies, two HCAs were performed, as shown in Figs 5 and 6.

It is observed that the fragments of stratigraphies from the surface and 113-cm level are divided in two clusters (Fig. 5). In the HCA of Fig. 6, the formation of three groups was observed. The first group includes samples 20.1, 20.2, 132.4 and 132.5; the second one includes samples 132.1, 132.2, 132.3 and 132.6; and the third one includes samples 144.1, 144.2, 144.3, 144.4, 144.6, 144.7 and 144.8. This result proves the separation and the grouping of stratigraphies from the surface and 113-cm level, and from the 10 to 20, 132 and 144-cm levels observed in HCA, except for samples 132.4 and 132.5, which are related to samples 20.1 and 20.2 (same group). The separation between these groups of samples with same stratigraphy indicates that each group of fragments was manufactured with different clays.

Two-dimensional graphs and HCA were also performed with the use of all the stratigraphies where studied fragments were excavated. Even so, it was impossible to identify any type of separation between samples with same stratigraphies, except for the groups presented in this study. Possibly, somehow, a mixture of stratigraphies could have occurred, which explains those fragments not grouped together.

### Conclusions

With the use of a portable system of EDXRF for the analysis of pottery fragments collected in site Sambaqui do Bacanga, it was verified that the basic chemical elements in the composition of the clay used in the manufacture of these fragments are Fe, Ca, Sr, Zr, Mn, Ti and Zn. It was also possible to verify that the fragments are heterogeneous, because the standard deviations of the average are larger than the statistical deviations of each individual measurement.

Out of the 68 pottery fragments analyzed, 43 presented a different treatment on the faces in relation to the ceramic paste. It

means that on these 43 fragments, engobe was applied, which is a kind of clay enriched with the elements Fe, Sr, Mn, Ti and Zn. This more refined material is characterized by forming a concentration increase of such elements in the faces when the ceramics are burnt in the manufacturing process.

From two-dimensional graphs of the X-ray intensities of Ca versus Zn and Sr versus Zr and two hierarchical cluster analyses of the pottery fragments from the surface and 113-cm level, and from the 10 to 20, 132 and 144-cm levels, the formation of five groups was observed. This result indicates that the chemical elements Ca, Zn, Sr and Zr characterize the clays as used to manufacture the pottery of each stratigraphic level, and the fragments analyzed were manufactured with clay from five different sources.

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