AMAZON CERAMICS AND THEIR COLOR PALETTE – THE USE OF ION BEAM ANALYSIS TO DETERMINE THE PIGMENTS

S. C. LIMA, E. G NEVES, R. ALMEIDA*
University of São Paulo, Museum of Archeology and Ethnology,
São Paulo, Brazil
*ARQUEOTROP São Paulo
São Paulo, Brazil

M. A. RIZZUTTO, P. H. O. V. CAMPOS, C. L. RODRIGEUS, T. F. SILVA,
University of São Paulo, Physics Institute São Paulo/São Paulo, Brazil
Email: rizzutto@if.usp.br

Abstract

Despite the knowledge and discussion of archaeological polychrome ceramics in the Amazon for more than half a century, their material characterization still needs further studies and analysis. The description of these ceramics continues to be guided, in most cases, exclusively by the aesthetic aspect (macroscopic) and not by their technological and material characteristics (microscopic). In other words, despite the wide geographical distribution and variability of ceramic style, descriptions of polychrome ceramics are often restricted to observing the presence or absence of engobes and paints with colors mainly determined as white, red, and black. This work aimed to characterize the pigments and their use in ceramic decoration to collaborate with heritage conservation and archaeology in identifying specific technological choices. And investigate the variability of materials present that are so characteristic of Amazonian ceramics and their polychromies. Therefore, archaeometry analyses: binocular magnifying glass, Particle Induced X-ray Emission (PIXE) and Scanning Electron Macroscopic (SEM) were used to characterize a set of polychrome fragments from five archaeological sites in the Central and Northern Amazon region associated with the Polychrome Tradition of the Amazon – Tauary [1,2], Conjunto Villas [1,3], Vila Nova II [4], São João [5] and Hatahara [6,7,8] (spanning a broad spectrum from 100 BC. to 1300 A.D). The proposed analysis with ion beams comes from the better capability to separate the pictorial layers and thus better study the decoration technology of this set of ancient ceramic fragments. Measurements were performed with proton beams in the particle accelerator of the Institute of Physics of the University of São Paulo. Elements such as P, K, Ca, Ti, Fe and Mn were identified in different pigments, and their correlations will be discussed.

1. INTRODUCTION

Ceramics with polychrome decoration are commonly associated with the Amazon Polychrome Tradition and refers to a set of great technological diversity of elements that are dispersed over more than 6400km of distance, in more than 300 scientific sites and a chronology that spans over 1000 years [4,8,9,10]). The presence of black and/or red paint on the white engobe and fluted are techniques highlighted as recognisable elements of polychrome ceramic, despite its known regional variability [1].

When polychromies are discussed, every time refer to the presence of a pictorial layer, of some coating that covers the object. Whichever coating is used, a great deal of technical knowledge is required to handle behaviour differences between the clay body and coat which might lead to shrinkage, melting, etc., during the drying and firing of the artefact. The pictorial layers of the polychrome`s ceramics are white or red material (engobe), in direct contact with the ceramic body and completely covering it. And a layer of white and/or red and/or brown paint forming motifs with well-defined borders on the previous layer or directly on the ceramic paste, partially covering it.

Although we find studies that talk about the use of hematite for red colouring [11], such studies rarely address the variation of shades. The red paint can be made from rich iron clays or enriched with iron oxide. Several factors might influence the chromatic variation that the red engobe or painted motifs can present after firing, from orange to brownish and black. This variation can occur due to differences in composition and the firing atmosphere and temperature or the relationship with the thickness of the applied engobe layer. About the white pigment, usually applied as a thick coating layer, recurrent in Amazonian ceramics. Generally, the term 'tabatinga' is used generically to describe white clays or engobes with varying compaction, gloss and colour after fire treatment.

The description of the colour appears to be not enough to understand the complexity of materials and techniques involved in the polychrome surface finish of Amazonian ceramics. The dark brown painted motifs, often described as black, reveal the inaccuracy of such descriptions, which do not benefit from observing other physical features such as thickness, granulometry, or the transparency, for instance. And they also proved not to be sufficient for discussion of possible degradation and conservation processes [12] that can affect differently varied raw materials and techniques used in the manufacturing of ceramics

2. SAMPLE SET AND ANALYSIS PROCEDURE

Due to the immensity of polychrome ceramic sets and the scope of debates on archaeological cultural traditions in the Amazon, the sample set selected for this research is still restricted to feed broad discussions and does not have this intention. However, through a set of archaeometry analyses, we sought to see, on a new scale, the pictorial layer of ceramics associated with the Polychrome Tradition, searching for possible indicators of technological differences which could help in future studies of archaeological ceramics.

The archaeometry study was carried out with a set of 53 shards of polychrome ceramics from five archaeological sites – Tauary and Conjunto Vilas, located on Lake Tefé and São João on Lake Caiambé, all located in the middle of Solimões River; Vila Nova II, on the Negro River; and Hatahara, on the confluence of Negro and Solimões River, state of Amazonas, Brazil, shown in figure 1. The choice of the sample set was made in collaboration and with the support of researchers from the Laboratory of Archaeology of the Tropics - ARQUEOTROP, from the Museum of Archeology and Ethnology of USP to characterize the diverse colors of polychromies, as can see in figure 2.

FIG.1. Location of the archaeological sites in Amazonas State, Brazil.

The analysis of these fragments was firstly performed with macroscopic scale observation with a binocular magnifying glass, then with Particle Induced X-ray Emission (PIXE) and Scanning Electron Macroscopic (SEM)). The visible view used a binocular glass and a digital microscope Dino-Lite. The chemical element identifications in the paste and paint layers were performed using the external beam setup at LAMFI (Laboratory of Material Analysis by Ionic Beams) of the University of São Paulo, Physics Institute. The PIXE-LAMFI setup comprises

[13] two XR-100CR Si-PIN Amptek X-Ray Detectors [14] with 12.5μm thick beryllium window and a 4.4mm2 active area, 500μm depletion depth and 145eV resolution at the $Mn - K\alpha$ line.

The PIXE technique with an external proton beam setup was chosen due to the non-destructive characteristic, penetration depth, measurements without any sample preparation, greater flexibility in positioning the fragment in relation to the detectors and the beam, and the possibility of using millimeter beams, and the reduction of thermal effects. The 2.4 MeV proton energy has an approximately 30-40 um depth profile. This low penetration is valuable for pigment analysis, allowing a better understanding of the materials that overlap forming the pictorial layer, that is, to see the ceramic stratigraphy. About 6 to 7 points were performed in different regions of the fragments, with areas of the paste, outer face (pigments and shadows) and inner face.

Scanning Electron Macroscopic (SEM) images were obtained in the Laboratório de Filmes Finos of the University of São Paulo, Physics Institute, using a system Jeol model 6460LV. The goal was to investigate the composition variability and thickness of pictorial layers and determine the formation of the engobe fusion with the ceramic mass during firing.

Engobe melting means that this fluid clay layer transforms during firing into a well-agglomerated and resistant coating, with a decrease in porosity that results in increased compaction and surface gloss. The sintering of the engobe might occurs as a function of the granulometry (thin and homogeneity) and/or the composition and/or high temperatures maintained for a sufficient period during firing.

FIG. 2. Ceramics fragments from different cultures with color and shade variations

3. RESULTS AND DISCUSSIONS

The analysis of SEM and PIXE allows a better understanding of the adhesion of the engobe to the ceramics body and enables the identification of the element present in the colours and the mixture of them to produce the shadows.

3.1. Scanning Electron Microscopic

As an example of the visible image, figure 3 shows a binocular magnifying glass and SEM images. The ceramics Vila Nova II (VN111.11) presents brown and white polychrome thin layers of approximately 100□m thickness. Ceramics Vilas (CV991) also white and brown polychrome presents ~50-80µm.

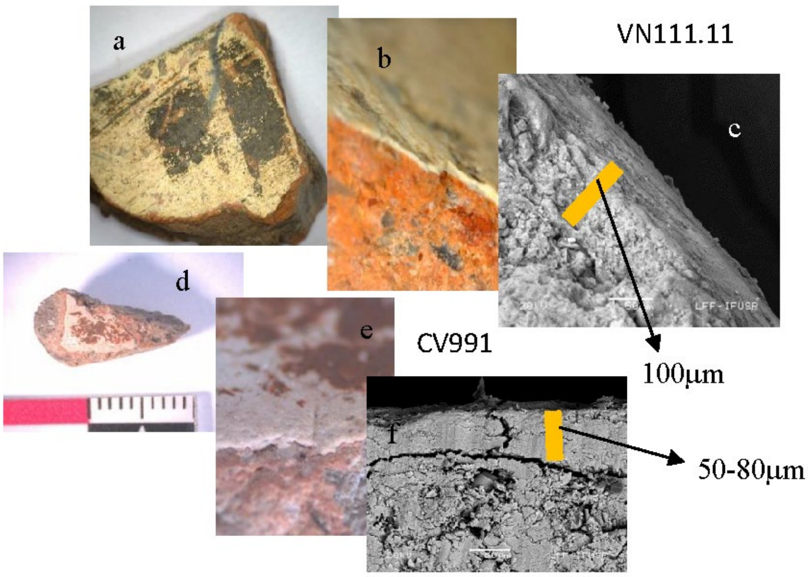

FIG. 3. Superior: Vila Nova II ceramic fragment (VN111.11) image with (a) visible, (b) binocular magnifying glass and (c) SEM with 20kV. Inferior, image with: (d) visible, (e) binocular magnifying glass, (f) SEM with 20kV.

3.2. White Pigments

It is common to observe that the polychromic ceramics of different cultures from Amazonia present a significant variability of texture and sintering of the pictorial layer, especially regarding the white engobe layer. Sometimes it is observed partial melting of the engobe, or semi-vitrification, with a resistant (sintered) final layer on the outer surface, but with a powdery texture in the layer just below, at its interface with the ceramic mass. Identifying this characteristic can be decisive for defining the adequate cleaning processes for the material since removing the external layer can expose the underlying layer of the engobe, which can solubilize it with water.

By characterizing major elements carried out by PIXE, it was possible to identify and differentiate the white engobe present in the fragments from the five archaeological sites. We observed a variation in thickness, compaction, and gloss related to the variability in the chemical composition of these engobes.

At the Vila Nova II archaeological site, we observed white engobes with clays rich in potassium and titanium, with varying proportions between these elements (figure 4 – VN111.11).

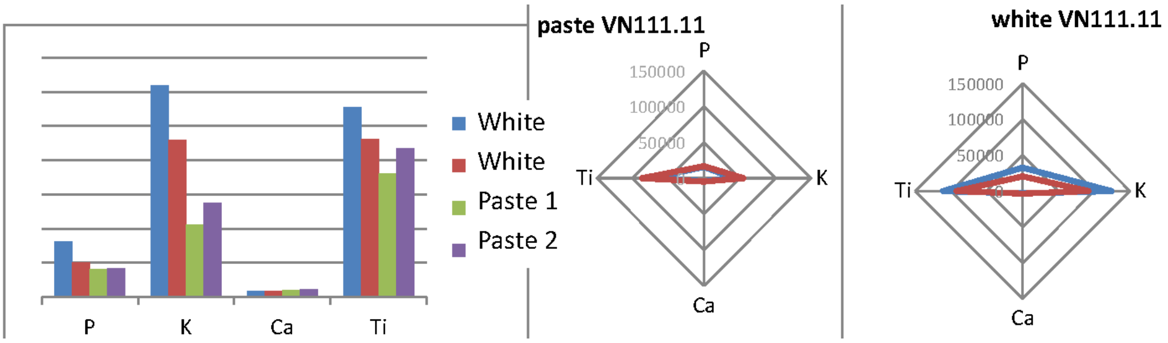

FIG. 4. Bar and star graphics showing the relative variation of the normalized integrated area of each element present in the PIXE spectra of each fragment from Vila Nova II

At the Conjunto Vilas archaeological site, we observed a clear difference between the white engobe of the fragments from the most superficial levels of the site stratigraphy (for example, the fragment CV991), rich in potassium and calcium, and titanium (figure 5) in the deeper levels, also with an inverse proportion relationship between calcium and phosphorus related with the ceramic paste. This same difference between white engobes of fragments from superficial and deep levels of the archaeological context was also observed in the fragments from the São João site.

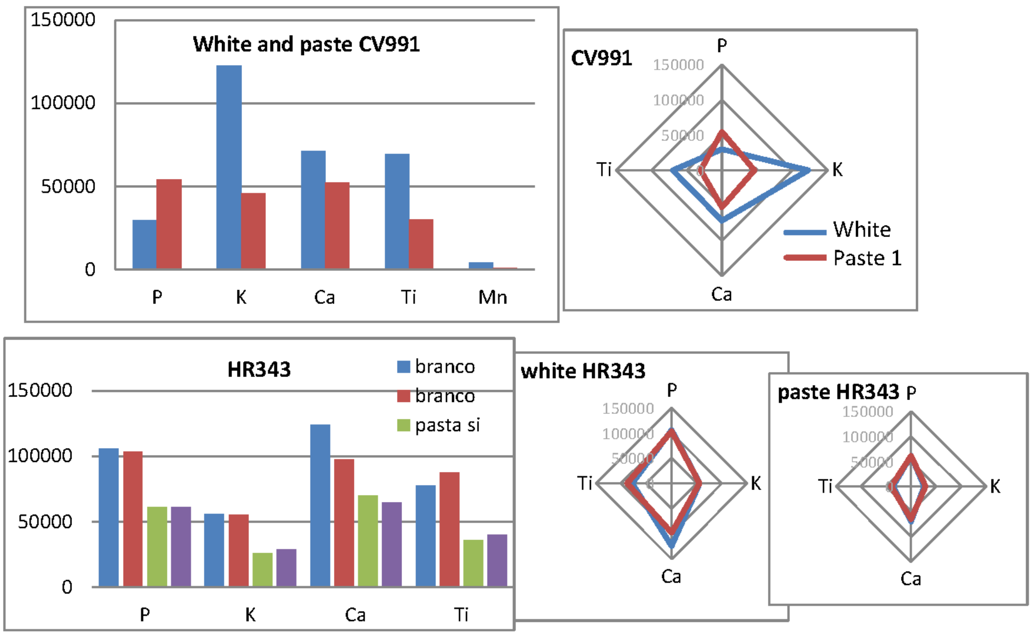

FIG. 5. Bar and star graphics showing the relative variation of the normalized integrated area of each element present in the PIXE spectra of each fragment. Upper: Conjunto Vilas (CV991). Lower: Hatahara (HR343)

The high calcium/phosphorus ratio in Hatahara samples is evident in the composition of the engobe (figure 5), and different from the composition of the paste (measurements were performed on the surface and ceramic core, which led to the exclusion of the hypothesis of contamination from the archaeological context, since the proportionality between these elements is only repeated in the measurements of the white engobe). Suggest the possibility of using hydroxyapatite in the composition of white engobe. From a physical-chemical point of view, this technological choice would make sense as hydroxyapatite acts as a strong fluxing material, considerably lowering the melting temperature of this engobe, which would then result in a more cohesive and less porous layer without changing other features.

3.3. Red, brown and black pigments

The red engobe can be made from rich clays and/or enriched with iron oxide and clayey ocher. Several factors influence the chromatic variation that the red engobe can present after firing, from orange to brownish and black. This variation can occur due to differences in composition but also due to the firing temperature, the relationship with the thickness of the applied layer, as well as the low presence of oxygen (in a reducing or partially reducing atmosphere), which can cause the transformation of the red to dark brown or black due to the transformation of ferric oxide (hematite) into ferrous-ferric oxide (magnetite) [15,16].

The analyses of the brown and red pigments of the same fragments analysed before are present in figure 6 below.

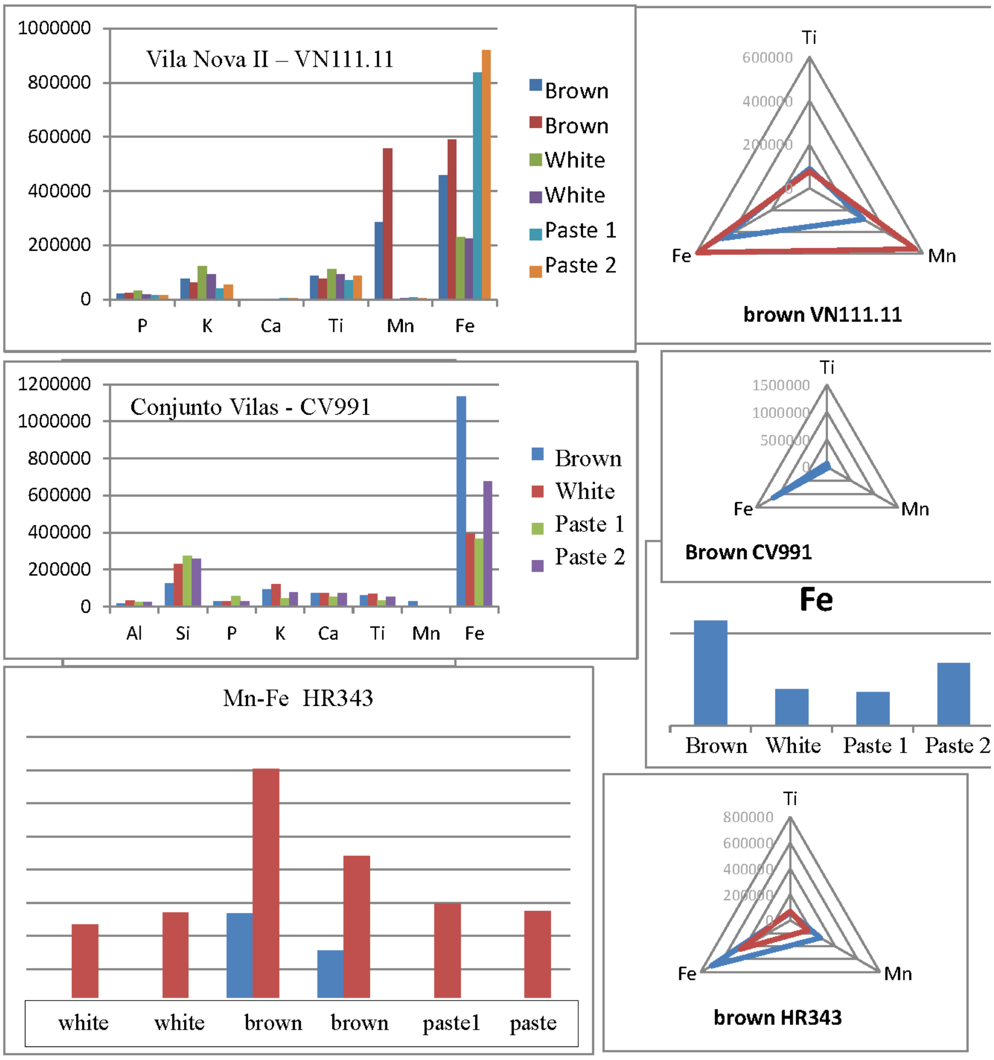

FIG. 6. Bar and star graphics show the relative variation of the normalized integrated area of each element present in the PIXE spectra of each fragment. Upper: Conjunto Vila NOVA II (VN111.11). Medium Vilas (CV991). Lower: Hatahara (HR343).

4. CONCLUSIONS

The different white measures by PIXE allow determine the relationship between some elements and allow to make some groups based on significant associations between the major elements, such as white composed with Ca + P, white with K and less quantity of Ti, Ca, P, white with the equality of Ti and K and finally white pigment with Ti > K. Nevertheless, it will be necessary to expand the set of fragments with the presence of white engobe analyzed to be able to infer more precisely about these relationships. It is essential to point out that due to the penetration and precision characteristics of the archaeometry analysis used (PIXE) and the thickness of these engobes, the results of the measurements carried out in the white engobe, and the ceramic paste are visibly different, that is, the paste does not have the same correlation proportionality between the same elements.

The same characteristics allow differentiating the brown pigment mainly into two groups, composed majoritarian of Fe, and another with a significant value of Mn. This difference in the chemical composition was correlated to macroscopic physical differences in compaction (fusion), gloss, and appearance of the paint layer. The brown layer with enrichment of iron present cast and good coverage, the layer with Mn is commonly grainier and more fragile.

ACKNOWLEDGEMENTS

This work was partially supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazilian research funding agencies. This work is a part of the projects: FAPESP No. 2014/01968-1 and No. 2018/12191-9 and INCT-FNA Proc. CNPq No. 464898/2014-5.

REFERENCES

[1] BELLETTI, J. S., "*A Arqueologia do Lago Tefé e a Expansão Polícroma"*. Dissertação de Mestrado em Arqueologia do Museu de Arqueologia e Etnologia da Universidade de São Paulo, 2015. doi: 10.11606/D.71.2015.tde-13102015-153201.

[2] OLIVEIRA, E., "*Potes que encantam: estilo e agência da cerâmica polícroma da Amazônia Central"*. Dissertação de Mestrado em Arqueologia, Museu de Arqueologia e Etnologia, Universidade de São Paulo, 2016. doi: 10.11606/D.71.2016.tde-21072016-152452.

[3] OLIVEIRA, L.S.S., ABREU, C.M., FERREIRA, F., LOPES, R., ALMEIDA, F., TAMANAHA, E., BELLETTI, J.S.,

[4] MACHADO, R., RIZZUTTO, M., SOUZA, D. "Archeometric study of pottery shards from Conjunto Vilas and São João, Amazon". *Radiation Physics and Chemistry, vol 167.* (2020) 10.8303.doi: 10.1016/j.radphyschem.2019.04.053.

[5] NEVES, E. G., "Sob os tempos do equinócio: oito mil anos de história na Amazônia central (6.500 ac – 1.500 dc)". Tese apresentada para Concurso de Título de Livre-Docente, Museu de Arqueologia e Etnologia, Universidade de São Paulo, São Paulo, 2012.

[6] LOPES, R.C.D.A. "A tradição policroma da Amazonia no contexto do Médio Rio Solimões (AM)". Dissertação de Mestrado em Arqueologia. Universidade Federal de Sergipe. 2018.

[7] MACHADO, J. "Montículos artificiais na Amazônia Central: Um estudo de caso do sítio Hatahara". Dissertação de Mestrado. Museu de Arqueologia e Etnologia, Universidade de São Paulo, São Paulo. 2005

[8] LIMA, H. P. "História das caretas: A Tradição Borda Incisa na Amazônia Central". Tese de Doutorado em Arqueologia. Museu de Arqueologia e Etnologia, Universidade de São Paulo, São Paulo. 2008. doi:10.11606/T.71.2008.tde- 22092008-125315

[9] TAMANAHA, E. K. "Ocupação Polícroma no Baixo e Médio rio Solimões, Estado do Amazonas". Dissertação de Mestrado em Arqueologia do Museu de Arqueologia e Etnologia da USP, 2012. doi: 10.11606/D.71.2012.tde-05062012-104830

[10] TAMANAHA, Eduardo K. & NEVES, Eduardo Góes. "800 anos de ocupação da Tradição Polícroma da Amazônia: um panorama histórico no Baixo Rio Solimões". Anuário Antropológico/2013, Brasília, UnB, 2014, 39 (2): 45-67.

[11] BELLETTI, J.S. "A Tradição Policroma da Amazonia", in BARRETO, C.; LIMA, H.P. & BETANCOURT, C. J. (eds) Cerâmicas arqueológicas da Amazônia: rumo a uma nova síntese. Belém, IPHAN: Ministério da Cultura, 2016.

[12] LEAL, R. S., "Estudo Arqueométrico de Cerâmicas Arqueológicas Marajoara", Dissertação de Mestrado, Universidade Federal do Piauí, Teresina, 2005.

[13] LIMA, S. L., "Conservação Arqueológica: uma reflexão a partir de estudos de caso no Brasil", Projeto FAPESP 2014/01968-1, 2014, Universidade de São Paulo

[14] Silva T, Rodrigues C, Added N, Rizzutto M, Tabacniks M, Mangiarotti A, Curado J, Aguirre F, Aguero N, Allegro

[15] P. et al. "Elemental mapping of large samples by external ion beam analysis with sub-millimeter resolution and its applications", Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 422, (2018) 68–77 doi:10.1016/j.nimb.2018.03.006

[16] XR-100CR SI-PIN X-ray detector. https://www.amptek.com/internal-products/ , Acess april, 2022.

[17] DI CAPRIO, N.C. "Ceramica in Archeologia 2: antiche tecniche di lavorazione e moderni metodi di indagine". Roma: L'Erma di Bretschneider, 2007.

[18] SHEPARD, A. "Ceramics for the archaeologist". Washington: Carnegie Institution of Washington. 1985.