Applied Clay Science 86 (2013) 70–75

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Evaluation of archeothermometric methods in pottery using electron paramagnetic resonance spectra of iron

G.M. Mangueira [a], R. Toledo [a], S. Teixeira [b], R.W.A. Franco [a,*]

[a] Laboratório de Ciências Físicas, Universidade Estadual do Norte Fluminense (UENF), Av. Dr. Alberto Lamego, 2000, CEP: 28013-602 Campos dos Goytacazes, RJ, Brazil
[b] Laboratório de Estudo do Espaço Antrópico, Universidade Estadual do Norte Fluminense, Av. Dr. Alberto Lamego, 2000, CEP: 28013-602 Campos dos Goytacazes, RJ, Brazil

ARTICLE INFO

Article history:
Received 5 December 2012
Received in revised form 4 October 2013
Accepted 7 October 2013
Available online 6 November 2013

Keywords:
Archeological pottery
Electron paramagnetic resonance
Firing temperature
Fe^{3+}
Archeothermometry
Archeometry

ABSTRACT

Knowing the techniques mastered by ancestors in their production of pottery can help understand their habits and skills, therefore increasing the understanding about their culture. In this work, we study pottery from an archeological site located in the city of Campos dos Goytacazes, state of Rio de Janeiro, Brazil, in order to appraise the firing temperature, atmosphere and time during pottery production. For this purpose, electron paramagnetic resonance spectroscopy (EPR) is used to analyze the signals of iron (Fe^{3+}). Methods for obtaining the firing temperature were assessed, comparing archeological pottery with clay and changes caused by heat treatment in archeological pottery. In addition, potteries were prepared in laboratory, finding changes in the EPR spectra resulting from changes in the parameters of pottery making. The observation of colors profiles can provide information about temperature, time and firing atmosphere, but it is not accurate. From these findings, it was considered that the archeological pottery studied were prepared in a single firing, at temperatures up to 650 °C in an open pit firing with semi-oxidizing atmosphere during a short time of approximately 0.5 h.

1. Introduction

The study of production methods of archeological pottery (AP) can provide important information about the culture of ancient peoples that inhabited in a particular region. In some cases, the most accurate information about a civilization comes from archeology, through the study of materials produced by the ancestors. Aspects related to the preparation of archeological pottery, such as the materials used, temperature, atmosphere and time of firing allow the identification of social groups (Kirch, 2004).

Conceptually, archeology deals with the dimensions of space and time for analysis and interpretation. One conceptual category is the notion of tradition, defined as a group of elements or techniques with temporal persistence. Traditions can be divided into stages, which are sets of cultural elements that describe local aspects of any tradition, which may be pottery, lithic, or housing standards, related to time and space in one or more places (Prous, 1992).

AP samples analyzed in this study were donated by the History Museum of Campos dos Goytacazes and they are from the archeological site of Caju (RJ-MP-8) (Dias, 1997). During excavation in the 1980s, the materials collected were dated by Carbon-14 method as being between 800 and 1500 years old, and classified as belonging to Una Tradition from the Mucuri phase (Dias, 1997). Una Tradition spread from central Brazil to the coast between the Una and Paraíba do Sul Rivers, lasting about 2000 years (Fausto, 2005; Prous, 1992). The Mucuri phase (Dias, 1997) was identified through the pottery artifacts, which are normally produced by a technique known as spiral coiling, which consists of making rolls of clay and their subsequent superposition in order to make vessels. The wall formed by the rolls is pressed and the vessel is smoothed in order to reduce undulations caused by the method and also to make thickness homogeneous (Lima, 1987; Prous, 1992). The high plasticity of clay mass can cause deformation of the parts during the drying and fissures during firing. In order to make them more resistant, it is common to add certain substances, named temper, which can be organic or inorganic substances (Lima, 1987). In pottery characterized as Una from the Mucuri phase, most common substances used were grains of quartz or feldspar. The smoothing of the parts is frequent in order to fix the roughness produced by the grains. Decorations as painting or roughness are not usually seen. The fragments under study are parts of a set of funerary urns (Dias, 1997), which in this site have the form of monkey pot fruit (*known as* '*sapucaia*' *in Brazil*) (*Lecythis ollaria*) (Prous, 1992). This particular type of pottery is very convenient in order to study the firing temperature, because it retains the characteristics of initial firing as it is not reheated later as pottery used in cooking.

The aim of this study was to make pottery with thickness and color profiles similar to that of AP. Subsequently, methods for estimating the firing temperature were tested in this current pottery (CP) and data were compared to data from AP.

The methods for estimating the firing temperature of archeological materials (archeothermometry) using electron paramagnetic resonance (EPR) consist of monitoring the intensity and area of Fe^{3+} signals and the effects of heat treatments. The relative areas of Fe^{3+} (EPR spectra)

* Corresponding author. Tel.: +55 22 27486497.
E-mail address: franco@uenf.br (R.W.A. Franco).

0169-1317/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.clay.2013.10.008

in arbitrary units were obtained by double integration of the set of lines. This intensity is directly proportional to the number of spins in resonance and therefore, directly proportional to the concentration of Fe^{3+}. The estimation of firing temperature can be done by comparing the spectra of an AP fragment with the spectra of clay from the region where the pottery was found (Rice, 2005). The firing temperature can also be determined by comparing the spectra of fragments from a single pottery, subjected to heat treatment at various temperatures, when the firing temperature is one in which the signal is altered (Dobosz and Krzyminiewski, 2007; Rice, 2005; Warashina et al., 1981).

2. Experimental

2.1. Samples

AP fragments studied were donated by the History Museum of Campos dos Goytacazes and were discovered in the archeological site of Caju (RJ-MP-8), located in the city of Campos dos Goytacazes, state of Rio de Janeiro, Brazil (longitude: 41°34′11″; latitude: 21°74′21″) (Dias, 1997).

AP was classified as AP1 and AP2 and had similar profiles: wall thickness of 14 mm bounded by light reddish edges — named as inner (7.5YR6/6 for AP1 and 5YR6/6 for AP2) and outer (7.5YR6/4 for AP1 and 5YR6/6 for AP2) — about 2 mm thick and dark gray interior (7.5YR4/1 for AP1 and 5YR4/1 for AP2), with a thickness of 10 mm. The dark color of the inside wall is known as black core. It is associated with the firing of organic matter and is observed in pottery fired at temperatures lower than 750 °C during its making (Rice, 2005). It was possible to observe grains of quartz as temper in both pottery pieces.

In order to make a comparison with AP, CP was made by using clay collected in deposits of commercial extraction which are located 7 km from the archeological site (latitude: 41°22′10″, longitude: 21°47′38″). CP was made with the same thickness of archeological fragments. The firing process was based on information related to temperature ranges, time and firing atmosphere, obtained in a previous study using AP1 (Mangueira et al., 2011). The purpose was to reproduce in CP the color and layer thickness profiles of each color portion of AP.

2.1.1. Samples preparation

CP samples were made with 14 mm thick, 45 mm wide and 75 mm long, using a 2:1:1 ratio of clay volume, sand and water (Rice, 2005). After a period of 10 days drying at room temperature (25 °C) they were subjected to heating at 600 °C for time intervals from 0.5 to 72 h, to obtain the thickness and color similar to those of the light layer of AP (2 mm). Then, CP was made at 500 °C, 550 °C, 600 °C, 650 °C, and 700 °C during 0.5 h and named CP followed by its temperature. Different drying times (3, 6, 15, 20, 25, and 30 days) were tested for the samples prepared at temperatures between 500 °C and 700 °C.

Some pottery cultures perform firing followed or preceded by ember (Rice, 2005). In order to simulate this possibility, CP was fired at 400 °C for 2 h (ember's average temperature) followed by 600 °C for 0.5 h, and another CP was made with reverse treatment.

In order to analyze the samples, they were separated into parts defined by color (Maritan et al., 2006). The color fractions of AP were classified according to the fragment curvature as inner, middle and outer. In the CP samples, the separation was made only into dark (middle part in AP) and light parts (inner or outer parts in AP). Due to the size and shape of CP, it was not possible to distinguish inner and outer parts.

The sand grains of both samples were collected using a ZEISS Stemi DVA optical microscope and were studied separately. For all analyses, the samples were studied in powder form with grain sizes smaller than 0.063 mm.

2.2. Methodology

2.2.1. Heat treatment

The heat treatments of clay consisted in isothermal heating for 0.5 h. The firing was processed in a kiln (reducing atmosphere) in three ways: a) in an alumina crucible (10 cm long and 1 cm wide), with direct exposition to oxygen during cooling; b) in an open quartz tube (3 mm internal diameter and 10 cm long) with indirect exposure to air during cooling; and c) in a covered quartz tube, simulating cooling in reducing atmosphere. According to the archeologists that explore the Caju site (Dias, 1997), traces of open pit firings with pits of various sizes have been found.

CP and AP were subdivided into many parts and each one was subjected to isothermal reheating in a different time and/or temperature in open quartz tubes. All treatments were performed using an EDG 3P-S muffle-type furnace.

2.2.2. Chemical treatment of quartz grains

Chemical treatment was performed in order to reduce the signal intensity of EPR spectra of Fe^{3+} in the sand grains and quartz used as temper for the CP. These grains could contain Fe^{3+} in their chemical structure due to isomorphic substitutions or impurities on their surface. If the grains contained Fe^{3+}, this signal could overlay the EPR signal of the clay and alter the analysis of the firing temperature of pottery.

The treatment consists of putting 0.7 g of sample in 6 mL of hydrochloric acid for 40 min, then rinsing with deionized water to completely remove the acid for subsequently repeating the procedure with 2 mL nitric acid and 2 mL hydrogen peroxide separately (Watanabe et al., 2008).

2.2.3. Chemical analysis

The chemical composition of clay and the AP samples were compared to assess the possibility of using clay to produce CP similar to AP. This analysis was performed by energy dispersive X-ray spectroscopy (EDX) using a Shimadzu EDX 700 spectrometer with a 10 mm collimator and Rh Kα radiation was applied at 15 kV and 216 μA (Na–Sc) and 50 kV and 33 μA (Ti–U).

2.2.4. Color

The colors were identified using Munsell Soil Color Charts (Munsell, 2009). The colors are shown in notation, which are defined by hue, value and chroma. Hue is the name of a color and is represented by a set of numbers and letters shown first in the notation. Chroma is the strength of a color, the quality by which we distinguish a strong color from a weak one. This number varies from 0 to 8 and is denoted by the first number after the hue. Value is the quality by which we distinguish a light color from a dark one and varies from 0 to 10. It is shown by the number after a bar; the lower the number the darker the color. Further information can be found in Munsell (1907).

2.2.5. EPR spectroscopy

Analyses were carried out at the State University of Norte Fluminense (UENF) using a Bruker Elexsys E500 EPR spectrometer, operating in X band (9.7 GHz) with 1.0 mW microwave power, 37 dB receiver gain, 100 kHz modulation frequency and 1 G modulation amplitude. The spectra were obtained at room temperature (25 °C) using 30 mg of each sample. The areas of spectra were obtained by double integration of signals using Xepr program [Xepr software, 2010], considering the entire spectra. Differences in base line can induce an error of 5% in area of the spectra. The intensities are the distances between the minimum and maximum of the signals. The areas and intensities of spectra, expressed in arbitrary units, correspond to relative values between samples.