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Fe^{3+} in pottery: Distinction of the use for cooking and production parameters

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ABSTRACT

The estimated firing temperature and atmosphere in which a piece of pottery was produced can be identified by comparing the concentration of Fe^{3+} between the piece of pottery and clay with a similar chemical composition that were subjected to identical thermal treatments. This procedure was applied to modern pottery donated by indigenous people and to a set of archaeological pottery. The modern pottery that was used for cooking for two years exhibited higher Fe^{3+} concentrations than the clay that was fired at any temperature; thus, the parameters of production were not identified in this pottery. The same procedure can be used to identify the use of a piece of pottery as a pan. Of the set of 14 pieces of archaeological pottery examined in this study, 12 were able to have their production parameters identified, and 2 fragments were identified with Fe^{3+} concentrations that were higher than that of the fired clay, suggesting that these pieces were used as pans. The results of this study indicate that the concentration of Fe^{3+} can be used to determine if a piece of pottery was used for cooking; additionally, if a piece of pottery was not used for cooking, then the proposed method can identify the parameters of the piece of pottery's production.

1. Introduction

Archaeological pottery can be studied using Electron Paramagnetic Resonance (EPR) spectroscopy because these materials may contain unpaired electrons of transition metal ions or free radicals, which are caused by heating and/or natural radiation. The production parameters of archaeological pottery can be obtained from the EPR spectra of the free radicals (Mangueira et al., 2011) and from Fe^{3+} (Mangueira et al., 2013). The shape of the Fe^{3+} spectra is strongly influenced by thermal treatments and their location in a crystalline structure (Bensimon et al., 2000; Bartoll and Tani, 1998). The heating of clays can oxidize Fe^{2+} into Fe^{3+}, increasing the signal strength associated with this ion (Presciutti et al., 2005). This oxidation depends on the temperature, time and environment in which the firing is performed (Mangueira et al., 2011).

The area of a line in the EPR spectrum is directly proportional to the concentration of the detected paramagnetic species. Thus, the coincidence of the area of the Fe^{3+} lines in two pottery materials of the same chemical composition indicates that these pieces of pottery were subjected to the same process of Fe^{2+} oxidation and therefore subjected to the same firing conditions. The method for determining a piece of pottery's production parameters using EPR consists of heating a sample of clay with a chemical composition that is identical to that of a piece of archaeological pottery and compare it with the pottery's spectrum (Dobosz and Krzyminiewski, 2007; Rice, 2005; Bensimon et al., 1998; Warashina et al., 1981; Mangueira et al., 2013). The coincidence of the intensity of the Fe^{3+} signals in the archaeological pottery and the clay fired at a given temperature in a given environment allows the parameters used for the production of the archaeological pottery to be identified.

In this study, two groups of samples were analysed using EPR: a group of modern pottery that was donated by indigenous people and a group of 14 pieces of archaeological pottery. The production parameters of the pottery pieces were obtained, and the effect of successive firings of a piece of pottery that was used as a pan was analysed.

2. Experimental

2.1. Samples

The set of modern pottery was made by the indigenous Asurini people of Xingu (03°53′S; 52°27′W) in the state of Pará, Brazil. These indigenous people are from the Amazon, speak the Tupi-Guarani language and have a population of 140 individuals (Silva, 2008). The set of samples examined in this study was composed of a pottery material that was used as a pan for two years; a piece of pottery material of the same size and shape that was not used as a pan; and the clay used in

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manufacturing these samples. The clay is rich in sand, which acts as a natural antiplastic.

The set of archaeological pottery was composed of 14 fragments from the Goytacá people, who are associated with the Una Tradition (Dias, 1996); the set was donated by the Historical Museum of Campos dos Goytacazes; and originated from the archaeological site of Caju (21°74′S; 43°34′W) in Campos dos Goytacazes in the state of Rio de Janeiro, Brazil. The samples were approximately 1000 years old (Dias, 1996). The fragments had wall thickness between 4 and 14 mm; 11 samples (A, B, C, E, F, G, H, J, L, M and N) had three colours (i.e., a dark grey interior bounded by light reddish edges) and 3 samples (D, I and K) had two colours (i.e., dark grey and light reddish). The clay used as a reference was collected 7 km from the archaeological site from a commercial extraction site.

The coiling technique was used to create Asurini pottery (Silva, 2008) and Goytacá funeral urns (Mangueira et al., 2013); this technique consists of mixing clay with water and moulding the dough in the form of a rope (i.e., cylinders), which is superimposed and smoothed to form the piece of pottery. Their firing processes are also similar: each piece was held in a semi-oxidizing environment at a temperature between 500 and 800 °C for approximately 30 min (Mangueira et al., 2013; Silva, 2008). The fragments had wall thickness between 8 and 11 mm.

2.2. Methodology

2.2.1. Heat treatment

The procedure to heat-treat the clay was the same as that used in a previous study (Mangueira et al., 2013): isothermal heating for 30 min. A given portion of the clay was heated to each temperature. The firing was conducted in three ways in a kiln with a reductive atmosphere: a) in an alumina crucible (10 cm long and 1 cm wide) with direct exposure 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 a reductive atmosphere. All treatments were performed with an EDG 3PS muffle-type furnace.

2.2.2. X-ray fluorescence and X-ray diffraction

The chemical composition of the samples was determined 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 at 50 kV and 33 μA (Ti–U). The identification of mineral phases was carried out by XRD, using a Shimadzu XRD 7000 X-ray diffractometer with CuKα ($\lambda = 1.5418$ Å) radiation, at 30 mV and 40 kV, working step-by-step at 0.03°/2 s. The crystalline phases were identified by comparing the XRD patterns with the PDF files from the JCPDS program (PCPDFWIN, 2000)

2.2.3. Pottery production in laboratory

A piece of pottery was produced in the laboratory with a 45 mm width and a 75 mm length using a ratio of two volumes of clay to one volume of sand, which provided antiplastic properties to the finished piece, to one volume of water (Rice, 2005). The mass was then dehydrated for 10 days at a temperature of 25 °C and then fired at 600 °C for 30 min in a semi-oxidizing atmosphere to produce the pottery material.

2.2.4. EPR spectroscopy

Analyses were performed using a Bruker EleXsys E500 EPR spectrometer, operating in the X band (9 GHz) with a 1.0 mW microwave power, a 100 kHz modulation frequency and a 1 G modulation amplitude. The spectra were measured at room temperature (25 °C) using 30 mg of each sample, which were analysed in powder form with grains sizes smaller than 0.063 mm.

For each archaeological pottery sherd, the spectra of each of its different coloured layers were obtained separately. The intensities of these signals were added by considering the contribution of each layer's thickness so that the intensity of the Fe^{3+} signal from each sample represents the contribution of all of the colours of the sample in their due proportion.

3. Results and discussion

Table 1 shows the chemical composition of the clays and of the pottery from the Campos dos Goytacazes regions and from the Asurini indigenous people. The similarities between the chemical composition of the clays and the pottery material suggest that the heat treatments of each piece of clay can be compared to the heat treatment applied in the production of the pottery from their respective region.

The following mineral phases were identified by the X-ray diffraction in the set of pottery from Campos dos Goytacazes: kaolinite, illite, and quartz. These minerals were also identified in the clay indicating a similar mineral composition of clay and this set of pottery. Albite, hematite, kaolinite, illite, and quartz were identified in the samples from Asurini people.

Fig. 1 shows the intensities of the Fe^{3+} signals of the pottery and clays from the Asurini people. The heat treatment of the clay increases the intensity of the Fe^{3+} signal for all firing atmospheres that were investigated. Two samples were taken from each piece of pottery: one from the base and another from the edge. Both pieces of pottery that were used as pans for cooking exhibited stronger signals than those that were not used as pans for cooking; the successive heating of the pottery during the 2 years that it was used for cooking resulted in an increase in the Fe^{3+} signal of that sample. The intensity of Fe^{3+} in the unused pottery pieces indicates that a firing temperature between 200 and 700 °C had been used; however, it was not possible to distinguish the atmosphere in which the sample was produced. The base of the pottery used as a pan exhibited a signal 3 times stronger than the highest intensity of the fired clay (i.e., 1000 °C in a semi-oxidizing atmosphere), while the edge exhibited an intensity that was equal to the clay fired at 900 °C in a semi-oxidizing atmosphere; these findings suggest that it is not possible to determine the production parameters of pottery used as pans for cooking by comparison with fired clay. Conversely, this result indicates that this method can be used to identify whether the pottery

Table 1
Chemical composition of clay and archaeological pottery from Campos dos Goytacazes, and clay and pottery from the Asurini indigenous people (wt.%).

Origin	Campos dos Goytacazes															Asurini		
Sample	Clay	A	B	C	D	E	F	G	H	I	J	K	L	M	N	Clay	NU	U
AlO_3	38.2	39.5	36.4	37.4	35.1	38.5	38.8	38.8	38.6	38.9	37.5	36.3	40.0	40.9	38.2	28.1	23.4	27.0
SiO_2	46.5	48.6	47.2	46.5	49.3	47.6	48.0	47.7	46.4	47.6	49.7	47.0	47.4	46.4	46.5	52.7	56.3	56.2
Fe_2O_3	6.4	4.6	6.4	6.5	5.8	4.9	4.7	5.7	6.5	4.5	5.2	5.6	4.3	5.5	6.4	11.1	12.9	10.0
TiO_2	1.7	1.6	1.7	1.4	1.7	1.7	1.7	1.7	1.9	1.7	1.6	1.6	1.6	1.7	1.7	1.8	2.0	1.2
SO_3	2.3	2.3	2.3	3.2	2.6	2.7	2.3	2.2	3.0	2.0	2.3	2.4	2.6	1.8	2.3	2.4	1.5	1.7
K_2O	1.0	1.1	1.8	1.1	1.6	1.8	1.8	1.1	1.1	1.7	1.0	2.0	1.6	1.0	1.0	2.1	1.3	3.4
CaO	3.6	1.9	3.7	2.9	3.7	2.2	2.5	2.4	2.4	2.5	2.3	4.0	2.3	2.5	3.6	1.6	2.4	–