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The Role of Ceramics in Xingó History: An Archaeometric Approach

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Abstract
This work aims to contribute to the understanding of the archaeological contexts of the Xingó subregion, located on the lower São Francisco River. Ceramic fragments from six archaeological sites in the region were studied using archaeometric techniques. The proposal is to extend the archaeometric analysis of small sites located upstream, which have been the subject of little research. The Justino site was used as a reference because the one is the best studied in the region to date. To this end, the regional context, already covered, is investigated further, and the activities carried out at the sites studied are described. X-ray diffractometry (XRD), X-ray fluorescence (XRF), Fourier-transform infrared (FTIR), and scanning electron microscopy (SEM) were some of the techniques used in this study. FTIR and thermal analysis suggest that pottery was fired above 500 °C. FTIR/SEM analysis indicated the macroscopic presence of minerals in the clays from different sites. This study also expands on the possibility that added temper containing organic matter in the Justino ceramics may indicate the presence of caraipé (tree bark) in the Xingó region. The presence of this typical Amazonian and Brazilian Cerrado (savannah) temper in Lower São Francisco would provide a framework for understanding precolonial connections between the regions.

Keywords Archaeometry · Archaeological contexts · Archaeological sites · Ceramic sherds

1 Introduction

The Xingó subregion, located on the lower São Francisco River, is one of the most archaeologically studied areas in northeastern Brazil. Most of the research relates to material obtained during the archaeological rescue activities that took place during the implementation of the Xingó Hydroelectric Project, which began in the late 1980s. Since then, many academic papers, master's theses, doctoral dissertations, books, and articles have been published on the archaeology and bioarchaeology of the region [1, 2], albeit there is still much to be understood about its past human occupation in that location.

Until now, the Justino archaeological site is one of the most important locations for the precolonial period in Sergipe state [3–6]. Although many studies have been carried out, questions about Justino's archaeological aspects remain. The site contains a cemetery where 167 burials were excavated and 185 skeletons identified. It has been supposed that Justino began around 8900 years before the present (BP) and ended around 1200 years BP [2, 7]. However, there is evidence of mortuary activity during the contact period [8, 9].

Additionally, due to problems with the direct dating of archaeological remains, especially the burials from the Justino site, its classification into four cemeteries needs to be revised in future archaeological studies.

Other large sites in the region have received attention, including Carvalho and Vergne [10] and Oliveira et al. [11],

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but this has not been the case for small sites. An exception is the study of lithic technology by Fagundes [12], wherein the author attempted to carry out inter-site analyses in a regional context, including small settlements, which were considered temporary camps. However, the archaeological relationships between large persistent sites [12, 13] and those with reduced dimensions need to be better understood. It is believed that the Xingó region, with dozens of excavated sites larger than 10 m^2, provides a unique context for this type of discussion.

Another branch of study is based on the analysis of ceramics found in archaeological sites. The Xingó region has a local ceramic industry, that is part of Xingó culture or tradition. The ceramics found there are the oldest on the South American continent, with dates reaching up to 5500 years BP [3]. Their analysis [14, 15] revealed a homogeneity of production, with a limited number of vessels of simple shape (i.e., without angles), produced mainly with mineral antiplastic (mainly quartz, feldspar, and mica) by the reducing firing of brown pastes to reddish or dark brown. The ceramics are characterized by reduced surface treatment, with a predominance of plastic finishes such as brushing and incisions. Their spatial and temporal variability has been little studied. Recently, the analysis of ceramic artifacts from the Cipó site led to an increase in studies of a larger universe of sites [16]. Luna and Nascimento [17] found that fragments from the lower levels of the Justino site had undergone more surface treatment than those from the upper levels. The authors' efforts contributed to an attempt to map the technological similarities and differences between the oldest and most recent ceramics, including the vases currently produced by the indigenous potters of Xocó [13, 16].

Recent studies have brought a more humanistic, anthropological view to the archaeology of Xingó, taking into account the long-term history of indigenous communities. At the same time, there has been a movement toward the exact sciences, seeking to use the analytical techniques on offer. For example, in studies on archaeological dating coordinated by Prof. Shigueo Watanabe (whom we honor with this article), thermoluminescence (TL) and optically stimulated luminescence (OSL) techniques have been used to date archaeological artifacts and paleontological and geological samples from certain regions of America do Sul [18, 19]. In some of the studies coordinated by the professor, electronic paramagnetic resonance (EPR) spectroscopy and X-ray fluorescence (XRF) techniques were used to examine the composition of the samples [20, 21]. In one of his first works on dating, Prof. Watanabe's group studied ceramic artifacts from precolonial archaeological sites in the state of Bahia [22]. These artifacts probably bear similarities to those analyzed in the present study. The professor's interest in dating extends beyond his own life, as can be seen in the papers published by his group since the 1980s onwards, including Oliveira et al. [23] and Matsuoka et al. [24].

The use of archaeometric techniques to help clarify archaeological questions has great potential. One such technique is instrumental neutron activation analysis (INAA). Luna [14] used INAA to identify the chemical composition of ceramic pastes from the Justino and São José I and II sites and found them to be similar. Subsequently, Santos and Munita [25] identified the use of different chemical "recipes" in the production of ceramics from the Justino site. The authors (also using INAA) identified three different raw material sources and four chemical groupings for ceramics from the Barracão site. The composition of the raw material sources was different from those of the ceramics, indicating that materials from an external source were used to produce the vases. Santos and Munita [25] noted that the firing temperature of the ceramics was around 500 °C.

The present study aims to contribute to the understanding of regional archaeological contexts using archaeometric techniques to study ceramics. Using the Justino site as a reference, the best studied in the region to date, the proposal is to extend the archaeometric analysis of small sites located upstream, which have been the subject of little research. For this purpose, the regional context, already mentioned in the introduction, is investigated further, and the activities carried out at the sites studied are described.

The ceramic fragments studied were chosen from six archaeological sites in the Xingó region. The choice of this type of archaeological artifact is based on its high resistance to temporal conditions and the environment that surrounds it, which makes it possible to preserve information about the societies that produced the ceramics for a long time. This resistance to weathering means that large quantities of these archaeological artifacts are found at sites. The analysis of ceramic fragments can provide data on manufacturing techniques and the type of material used and help resolve anthropological questions about the social environment and customs that prevailed in past civilizations [26–28]. This is followed by a presentation of the methods employed, the data obtained, and a discussion of their possible meanings.

2 The Archaeological Context

2.1 The Xingó Region

The predominant vegetation in Xingó is the hyperxerophic caatinga, a shrub that grows on sandy soils and, in the river terraces where most of the sites are located, on sandy-silty sediments deposited by the São Francisco River [29]. Within this vegetation, there is a recurrent correlation of archaeological sites with species of faveleira (*Cnidoscolus phyllacanthus*), quixabeira (*Bumelia sartorum*), pau-ferro (*Caesalpinia ferrea*), angico (*Pidtademia* sp. and *Anadenanthera* sp.), species of jurema (*Mimosa melacocentra*), black jurema (*Mimosa hostilis*), white jurema (*Mimosa melacocentra*), hawthorn (*Mimosa* sp.), craibeira (*Tabebuia caraiba*), facheiro (*Cephalocereus piauhyensis*), juazeiro (*Zizyphus joazeiro*), and hawthorn (*Mimosa* sp.).

Except for rock sites, archaeological occupations in the Xingó region are always found on terraces [30, 31]. These areas are currently the preferred sites for human occupation in the region. The spatial outline in the present study defines one of the most enclosed areas of the Xingó Canyon, where the terraces, before being submerged by the Xingó Lake, would be more scarce and smaller in size compared with (for example) the segment downstream of the Justino site, which is the most downstream of the São Francisco River in our analysis. It is on these small terraces that most of the sites studied herein are located. The data of the archaeological ceramics were obtained by [12], except for those from the Cipó site [16] (Table 1). The C14 dates were provided from charcoal samples identified in cultural layers of the cited sites and the TL dates from their ceramic fragments.

As was noted above, the archaeological chronology in the region begins at 8900 years BP for the Justino site and extends to the contact period, with the most recent date of 300 years BP obtained for the Cipó site [16]. Apart from the Justino site, none of the sites analyzed herein currently has a date (Table 1). The dating techniques used were radiocarbon (C-14) and thermoluminescence (TL).

2.2 The Sites Studied

The materials analyzed in the present study come from six sites: Caraíbas, Fronteira, Lamarão, São Francisco II, Poço Verde, and Justino (Fig. 1). The sites are located in the tri-border area between the states of Sergipe, Alagoas, and Bahia.

The sites are all located between existing Paulo Afonso and Xingó Hydroelectric Power Plants (HPPs) and are flooded by the lake of these HPPs. Those farthest from each other are the Caraíbas and Justino sites (around 31 km). The closest to each other are Lamarão and Poço Verde (around 1.2 km). None of the sites (except the Justino site, which covers an area of approximately 1500 m^2) has defined areas.

At the Justino site, excavations were carried out in units of 5 m×5 m, with artificial levels of 10 cm. The other sites were excavated in units of 1 m×1 m, with artificial levels of 20 cm.

The Caraíbas site is located near the banks of the Igarapé Recantinho and the São Francisco River, on a terrace 12.7 m above the river, in the municipality of Paulo Afonso (BA). The excavation, in the form of a trench parallel to the São Francisco River, measured 2 m × 10 m and 3.5 m deep. Ceramic fragments and six lithic pieces were identified [32].

The Fronteira site is located in the municipality of Paulo Afonso, on an elevated terrace 9.75 m upstream of the São Francisco River, at its confluence with the Xingozinho stream. Its location, at the entrance of a small ravine, gives

Table 1 Dates of the archaeological ceramics collected from different sites of Xingó, according to [12] and [16]

Sites	Method	Level	Laboratory	Conventional Age AP	Reference
Cipó	C14	C5	Beta-509965	300 ± 30	[16]
Porto Belo 1	TL	1		342 ± 51	[12]
Justino	C14	F3	Univ. Lyon	1280 ± 45	[12]
Justino	C14	F6	Univ. Lyon	1780 ± 60	[12]
Saco da Onça	TL	F6		1491 ± 210	[12]
Curituba	TL	F9		1588 ± 140	[12]
Justino	TL	F8	Geo-UFS	1800 ± 150	[12]
Porto Belo 1	TL	F9		2003 ± 195	[12]
Justino	TL	F8	LAB-DAT-UFS	2010 ± 430	[12]
Justino	TL	F10	Geo-UFS	2050 ± 140	[12]
Justino	TL	F4	LAB-DAT-UFS	2191 ± 76	[12]
Vitória Régia I	TL	F6		2240 ± 389	[12]
Justino	C14	F8	UFBA	2530 ± 70	[12]
Justino	C14	F10	UFBA	2650 ± 150	[12]
Justino	TL	F10	LAB-DAT-UFS	2700 ± 720	[12]
Justino	C14	F13	Univ. Lyon	3270 ± 135	[12]
Justino	TL	F15	LAB-DAT-UFS	3865 ± 398	[12]
Justino	TL	F13	LAB-DAT-UFS	4310 ± 800	[12]
Justino	TL	F20	Geo-UFS	4496 ± 225	[12]
Justino	C14	F20	Beta	4790 ± 80	[12]
Justino	TL	F20	LAB-DAT-UFS	5500 ± 980	[12]
Justino	C14	F30	Beta	5570 ± 70 E1	[12]
Justino	C14	F40	Beta	8950 ± 70	[12]

C14 radiocarbon dating, *TL* thermoluminescence

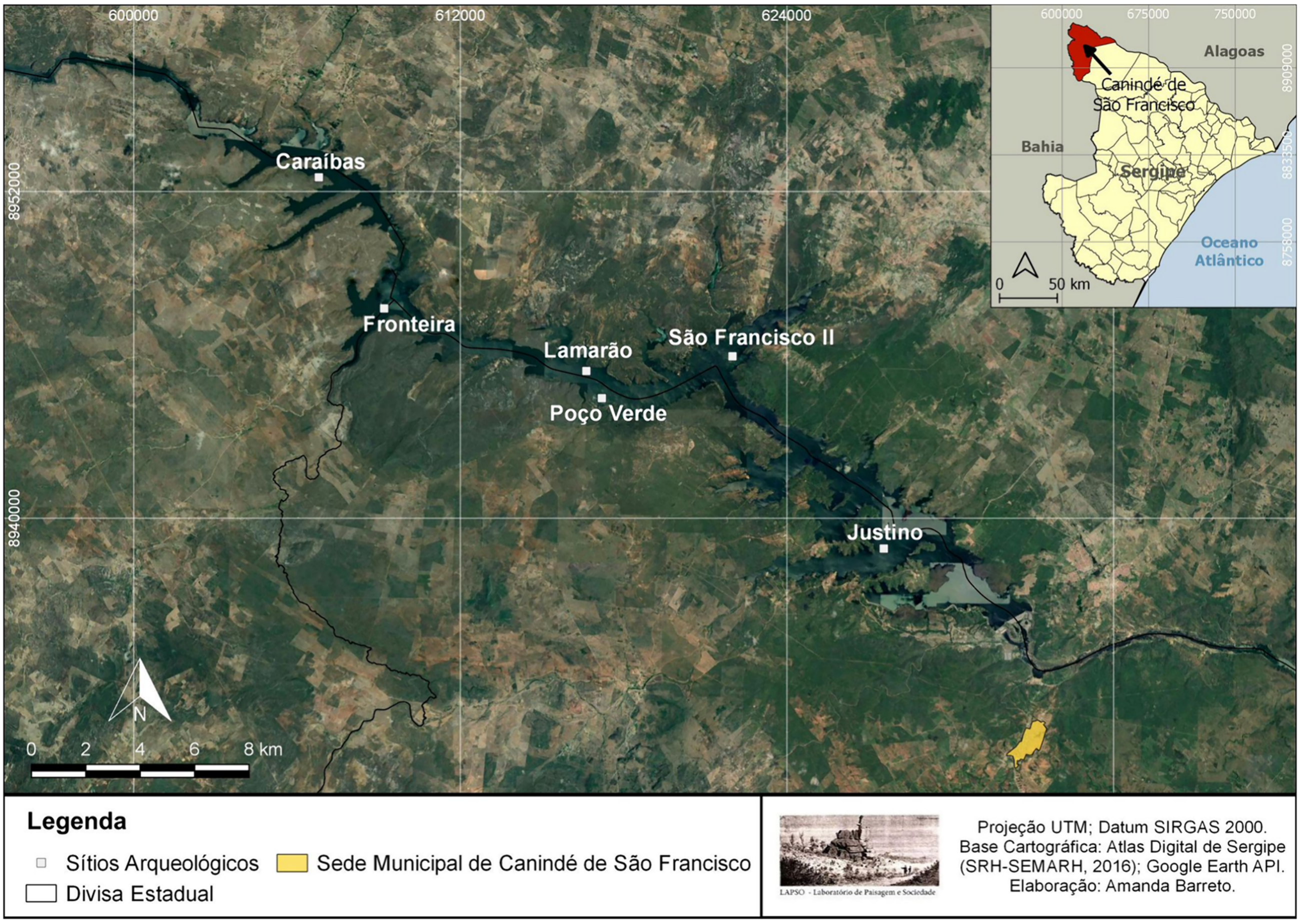

Fig. 1 Location of the sites analyzed (Caraíbas, Fronteira, Lamarão, São Francisco II, Poço Verde, and Justino)

the site protection. The interventions at the site are limited to an area of 2 m × 5 m and 3.5 m deep. Ceramic fragments and six lithic pieces were identified [32].

The Lamarão site is located in the state of Alagoas, in the municipality of Delmiro Gouveia. It is located on the banks of the confluence of the homonymous stream with the São Francisco River, on a terrace 7.9 m above the river. Excavations at this site were limited to the excavation of an area measuring 2 m × 15 m and 2.85 m deep. Ceramic fragments and five lithic pieces have been identified. Also in Delmiro Gouveia, 7.1 m above where the Talhado Creek meets the São Francisco River, the São Francisco II site was identified. This is the same terrace as the São Francisco I site. Two trenches were opened across the São Francisco River, measuring 2 × 12 m and 2 × 10 m, both with a depth of 2.45 m. In addition to ceramics, 32 lithic pieces were identified [32].

In the municipality of Canindé do São Francisco, in Sergipe, the Poço Verde site was identified, on a terrace 6.6 m above the São Francisco River, at its confluence with the Poço Verde stream. A trench was opened near the São Francisco River, this time across the river. An area measuring 2 m × 13 m and 3 m deep was excavated. The document [32] does not make clear the measure used to excavate the artificial levels, but it is assumed that levels of 20 cm were maintained. The Justino site, the most emblematic and studied, is also located in Canindé de São Francisco. This site, located at the confluence of the Cabo de Nego stream and the São Francisco River, had approximately 85% of its area excavated. This area was subdivided into approximately 50 units.

The material density of these sites, with less than 1 ceramic fragment per cubic meter excavated, suggests either a very limited and random use of the available space or simply that these populations produced ceramics in small quantities compared with (for example) sites on the coast [33]. At most of the sites, with the exception of the Justino site, the material of archaeological interest is concentrated in the surface layers.

Table 2 The analyzed ceramic sherds

Sherds	Layer	Site	Regional location
F05	Surface	Fronteira	Paulo Afonso (BA)
25,870–4	10 cm	Caraíbas	Paulo Afonso (BA)
L46	Surface	Lamarão	Delmiro Gouveia (AL)
SFII02	Surface	São Francisco II	Delmiro Gouveia (AL)
25,808	20 cm	Poço Verde	Canindé de São Francisco (SE)
4852	20 cm	Justino	Canindé de São Francisco (SE)

3 Methods and the Presentation of Data

The samples in the present study were ceramic fragments taken from archaeological pieces belonging to the collection of the Museu de Arqueologia de Xingó (MAX), which is located in Canindé do São Francisco (SE). The samples were analyzed at the Federal University of Sergipe (UFS) using microscopy techniques, XRF, X-ray diffractometry (XRD), Fourier-transform infrared (FTIR), and differential thermal and thermogravimetric analysis (DTA/TG). Table 2 lists the samples studied, the respective layers in which they were found, their locations, and municipalities.

In total, approximately 34 archaeological ceramic sherds were collected for the present study (Fig. 2). In total, approximately 34 archaeological ceramic sherds were collected for the present study (Fig. 2), with at least five samples from each site. From each site, three samples were analyzed. As can be seen, the physical aspects of the ceramics are completely different. Those from the Bahia sites have a scratched and darker appearance on the outside, while those from the other sites are a mixture of smooth (Lamarão and Justino) and heterogeneous (Poço Verde and São Francisco II).

In the initial phase of the archaeometric characterization, microscopy techniques (optical microscopy and scanning electron microscopy (SEM)) were chosen because of their non-destructive nature. The optical microscopies were carried out with a magnification of × 1000, while in the SEM, the magnification reached up to × 20,000. For the SEM measurements, the ceramic sherds were covered with a thin layer of gold and examined under a JEOL microscope, model JSM-6510LV.

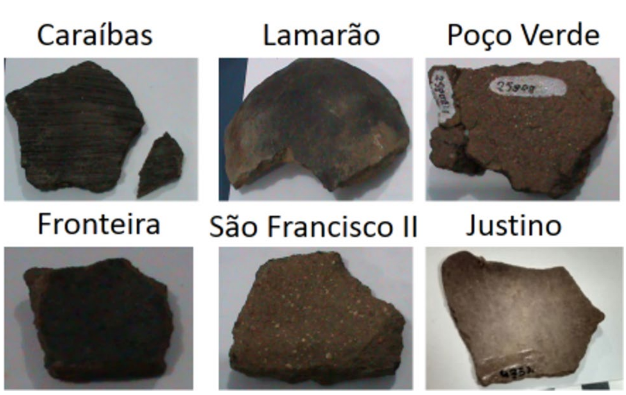

Fig. 2 Photographs of the analyzed ceramic fragments

During the preparation phase for XRF and XRD analysis, portions of the ceramic sherds were crushed with an agate mortar and sieved, resulting in powders with particle sizes less than 75 µm.

For the XRF analyses, 3-cm-diameter pellets were prepared, each being the result of mixing 0.6 g of archaeological material with 2.4 g of boric acid (H_3BO_3), a total of 3 g. The instrument used was a Bruker, S4 Pioneer spectrometer, which monitored the kα fluorescence lines using a rhodium (Rh) target (20–50 kV, 5–100 mA, and 4 kW maximum) regime. This spectrometer works sequentially, adapting the optical settings for each spectral line.

XRD analyses were performed on a Rigaku RINT 2000/PC instrument using Cu Kα radiation in the continuous scan mode at a rate of 2°/min with a 0.02° step and in the 2θ range between 5° and 80°. For the qualitative analysis, the Match and X′Pert HighScore programs were used in conjunction with the JCPDS database (Joint Committee on Powder Diffraction Standards, Swarthmore, USA).

For the FTIR analysis, samples were prepared in the form of small pellets with a diameter of 7 mm using a mixture of ceramic powder and potassium bromide (KBr) in a ratio of 1:3. Infrared spectra were obtained in the 4000–400 cm^{-1} range on a Varian 640 instrument, with a resolution of 4 cm^{-1}, in 64-scan mode.

DTA/TG thermal analysis was performed in a controlled oven of the SDT 2960 instrument (TA Instruments) using 10 mg of ceramic powder from each sample. The samples were heated from room temperature to 1200 °C at a rate of 10 °C/min under an airflow of 100 ml/min.

4 Results and Discussion

Figure 3 shows images taken with a light microscope at × 1000 magnification to better visualize the surface of the ceramic sherds and evaluate their grain size. It is possible to observe different grain sizes. The ceramics from the Justino site have the largest grains.

To analyze the surface of the ceramics in more depth and detail, SEM measurements were performed. Figure 4 shows micrographs of ceramic sherds from the Caraíbas, Fronteira, Lamarão, São Francisco II, Poço Verde, and Justino sites, respectively. In the state of Bahia, plate clusters were observed in ceramics from the Caraíbas site. The Fronteira site presented ceramics with a surface resembling a beehive, which may be related to the presence of spices.

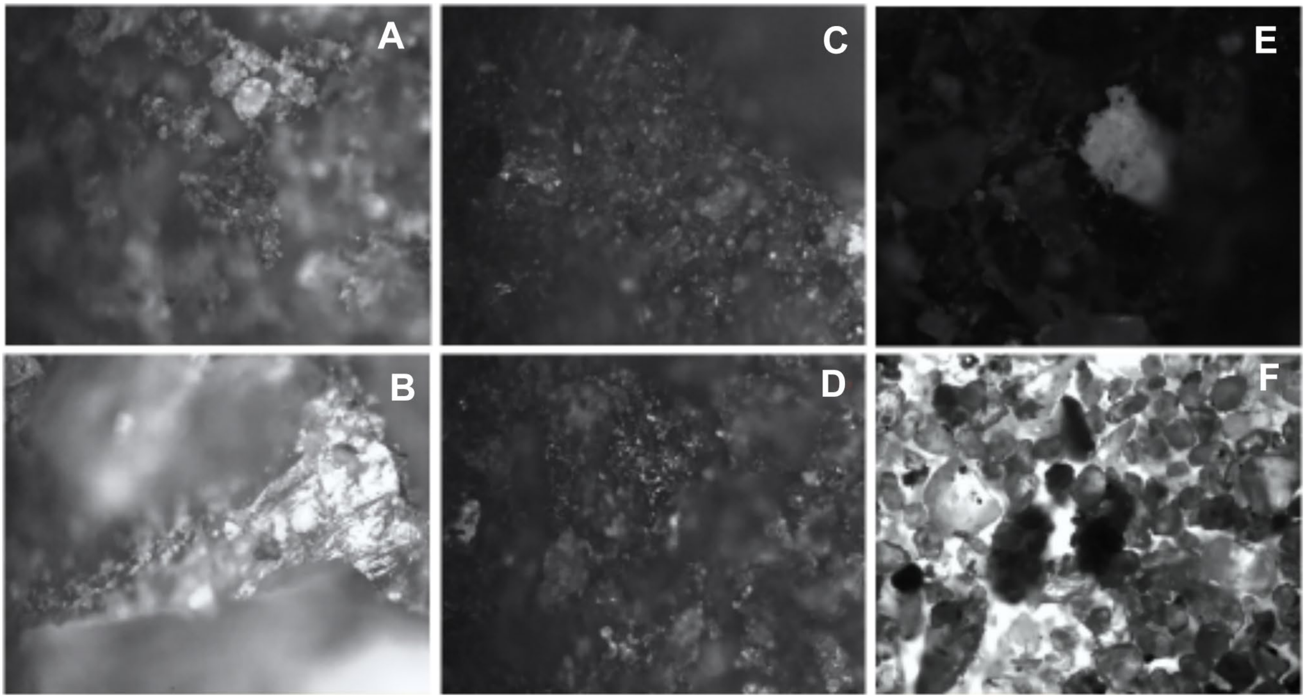

Fig. 3 Photomicrographs of ceramics from archaeological sites in the Xingó region: **A** Caribbean, **B** Border, **C** Lamarão, **D** Saint Francis II, **E** Poço Verde, and **F** Justino

The ceramics from the Lamarão and São Francisco II sites, in the Alagoas region, presented a less porous surface, with more density and small filamentary structures. It was possible at the former site to observe the presence of fungi in the ceramic fragments; these were represented by small spheres.

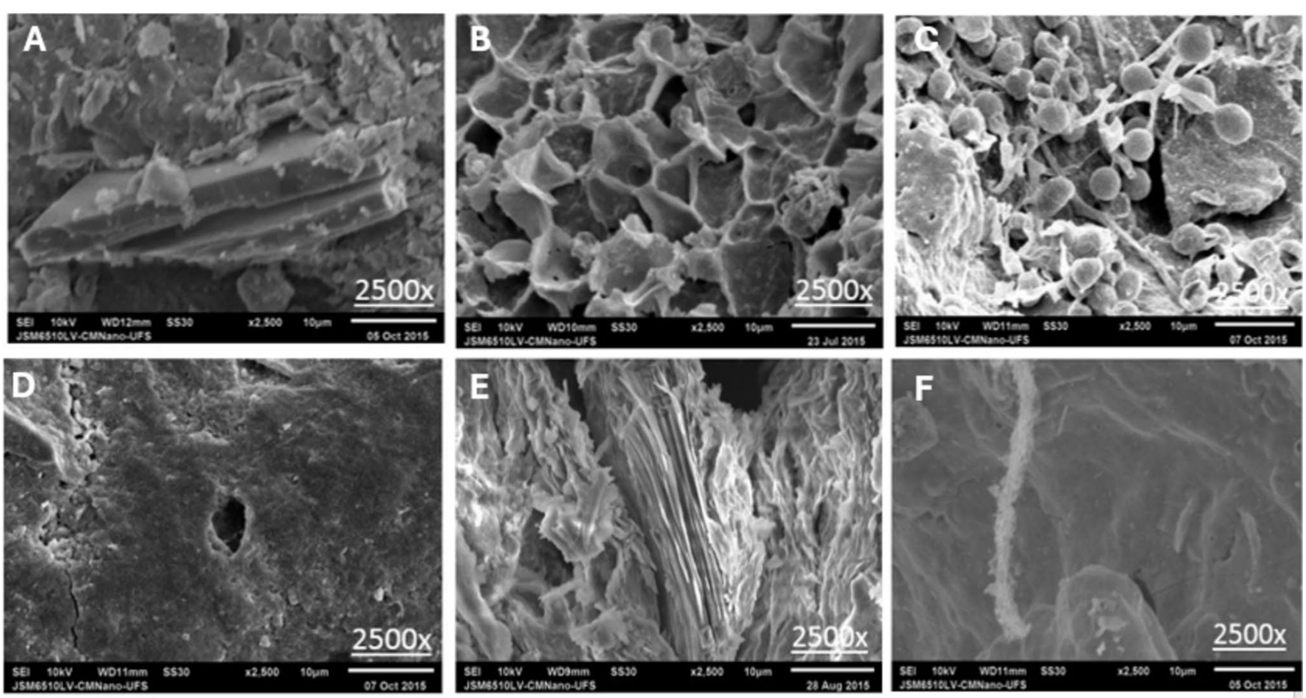

Fig. 4 Scanning electron microscopy images of ceramic sherds from the Xingó region: **A** Caribbean, **B** Border, **C** Lamarão, **D** Saint Francis II, **E** Poço Verde, and **F** Justino

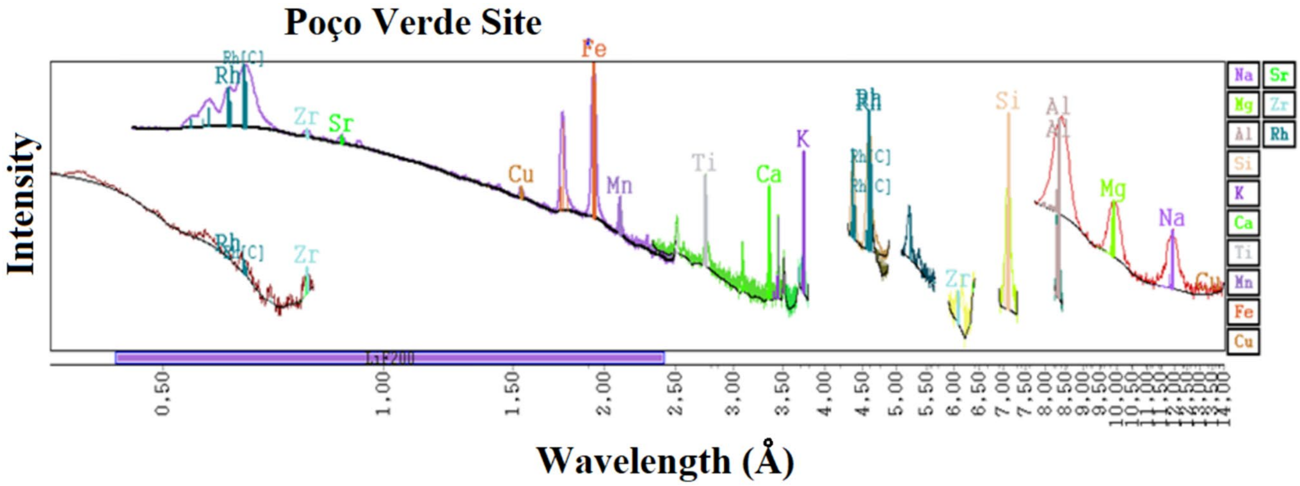

Fig. 5 X-ray fluorescence spectrum of pottery from the Poço Verde site

The ceramic sherd from the Justino site (Sergipe) had a fibrous and filamentous appearance, while the one from the Poço Verde site had a compacted leaf shape. These different features may be related to the presence of spices or antiplastics, such as tree bark; however, since organic spices are rare in the region, it is more likely that they are natural intrusions of plant remains mixed into the clay. On the other hand, if the presence of spices was to be confirmed (thereby indicating that they were intentionally introduced), the sample might open the way to thinking about the exchange of ceramic vessels between different regions, as observed in studies of archaeological artifacts in other sites [34].

Figure 5 presents qualitative data from the XRF analysis of ceramic fragments from the Poço Verde archaeological site; it is possible to visualize the fluorescence lines that identify the chemical elements present in each ceramic. Qualitative data of this type were obtained for ceramic samples from all sites. The quantitative analysis of the elements identified by XRF analysis can be seen in Table 3, which shows the concentration of each chemical element detected at each of the sites.

Combining the quantitative and qualitative results of the XRF measurements, it was possible to observe a majority presence of silicon (Si), aluminum (Al), and oxygen (O) in the samples from all the sites, with similar concentrations. A minority presence of iron (Fe), calcium (Ca), potassium (K), magnesium (Mg), and sodium (Na) was observed. Trace elements (ppm) such as zirconium (Zr), strontium (Sr), copper (Cu), manganese (Mn), titanium (Ti), nickel (Ni), phosphorus (P), and barium (Ba) were also detected.

In the state of Sergipe, the absence of Cu at the Justino site and its presence in the ceramics from the Poço Verde site may indicate that the pieces were made with different clays, obtained from different raw material extraction

Table 3 Concentrations of chemical elements in the pottery from each of the archaeological sites, as identified by X-ray fluorescence analysis

Sites	Concentration (%)							
	Zr	Sr	Cu	Fe	Mn	Ti	Ba	Ca
Caraíbas	0.034	0.061	–	8.684	0.117	0.692	–	2.400
Fronteira	0.021	0.056	–	7.432	0.101	0.744	–	2.740
Lamarão	0.025	0.113	–	4.840	–	0.484	0.410	0.468
S. Francisco II	0.019	0.090	–	8.004	0.098	0.723	0.270	2.330
Poço Verde	0.019	0.024	0.024	8.74	0.099	0.811	–	0.849
Justino	0.033	0.061	–	8.672	0.112	0.676	–	2.360
Sites	**K**	**Ni**	**Si**	**Al**	**P**	**Mg**	**Na**	**O**
Caraíbas	1.43	–	25.830	10.100	0.130	1.810	2.520	46.200
Fronteira	1.500	–	26.240	10.900	0.210	1.640	1.800	46.700
Lamarão	3.480	–	27.670	13.100	–	0.250	1.770	47.400
S. Francisco II	2.440	0.038	25.930	10.100	–	2.090	1.390	46.200
Poço Verde	2.780	–	26.490	11.100	–	1.170	1.280	46.600
Justino	1.400	–	25.970	10,000	0.140	1.800	2.540	46.200

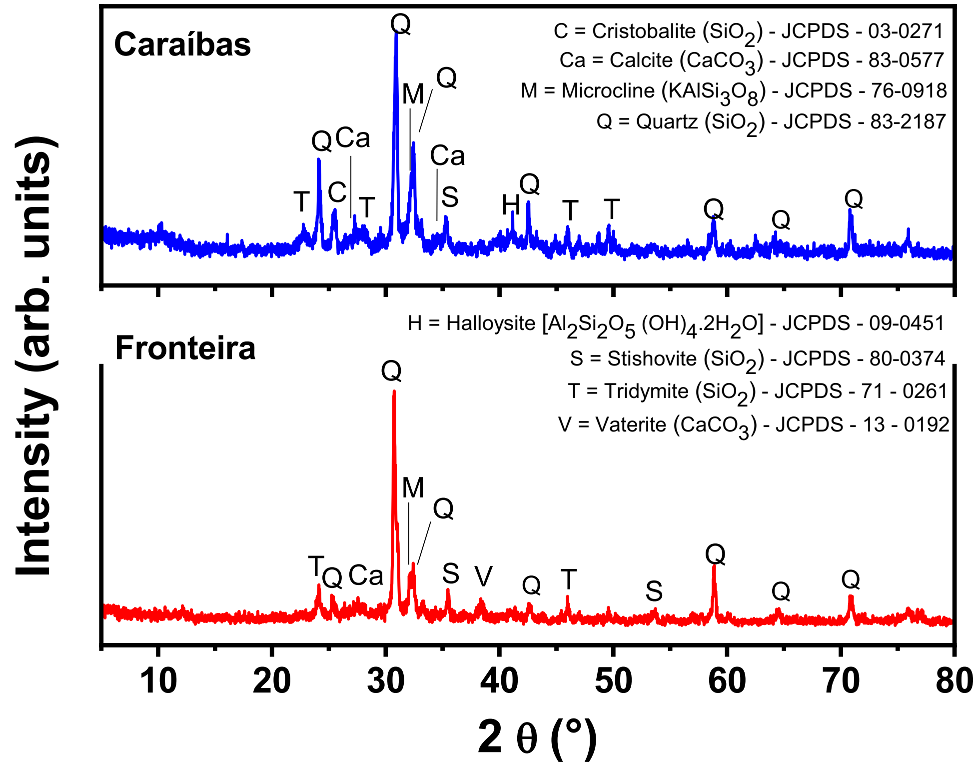

Fig. 6 Diffractograms of ceramic sherds from the sites of Caraíbas and Fronteira (Bahia)

points. Phosphorus was detected only in ceramics from the Justino site (i.e., it was absent in those from the Poço Verde site), confirming the existence of at least two clay collection points. Similarly, in the Alagoas region, the presence of Mn and Ni was detected only in ceramics from the São Francisco II site (i.e., they were absent in those from the Lamarão site). In the Bahia region, the same elements were detected in the ceramics of both sites (Fronteira and Caraíbas). It may

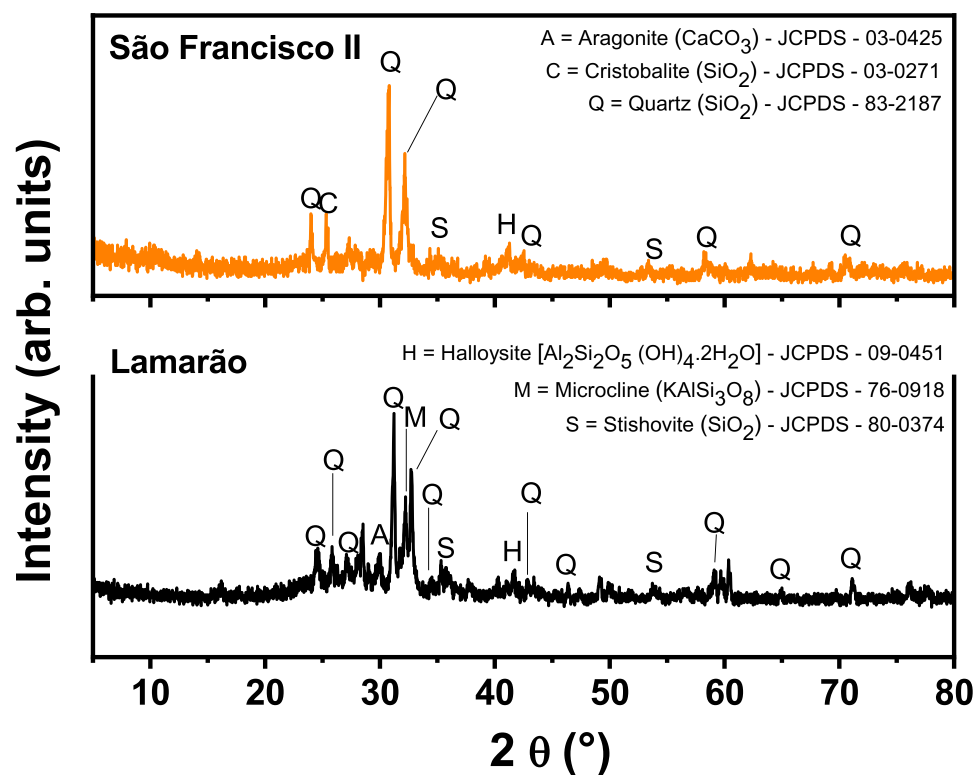

Fig. 7 Diffractograms of ceramic sherds from the sites of São Francisco II and Lamarão (Alagoas)

therefore be possible to assume the existence of a single clay extraction point for the manufacture of ceramic vessels in the municipality of Paulo Afonso (BA). The XRF analysis confirmed the significance of the detection of trace elements in archaeological ceramics in deducing possible extraction points for raw materials.

Figures 6, 7, and 8 show the diffractograms of ceramic sherds found at the sites in the states of Bahia, Alagoas, and Sergipe.

As can be seen, in all samples, there is a predominance of silica (SiO_2) in different structural arrangements, for instance, quartz (which is predominant), cristobalite, stishovite, and tridymite. This indicates that the elements Si and O, found in high concentrations in the XRF measurements, are bonded together to form ordered and well-defined crystalline structures. In a minority of cases, different phases of calcium carbonate ($CaCO_3$) were identified. In the regions of Sergipe and Alagoas, the aragonite phase predominated, while in the Bahia region, calcite and vaterite phases appeared. Except for the ceramics from the Justino and Fronteira sites, halloysite ($Al_2Si2_2O_5(OH)_4$) microcline ($KAlSi_3O_8$) phases were identified in all the samples. These identifications confirm the detection of Al in the XRF measurements.

Because the paste is heated to high temperatures in the production of ceramics, thermal changes can occur during the firing process that cause changes in the structure and bonding of the clay minerals. These changes can be studied using FTIR spectroscopy [35]. For the present study, the information obtained from FRX and XRD measurements was complemented by FTIR measurements, which were used to identify the functional groups present in the structure of the archaeological samples. The FTIR spectra of all the ceramics analyzed are shown in Fig. 9. Table 4 shows the experimental and theoretical values of the infrared absorptions, as well as the possible correlation corresponding to each vibration.

In the ceramic samples, two absorption bands were observed at around 3500 cm^{-1} and 1625 cm^{-1}, corresponding to the normal modes of vibration of the hydroxyl group (–OH) or adsorbed residual water molecules of longitudinal deformation (the "stretching" type) and deformation (the "bending" type), respectively [36]. These bands were present in the FTIR spectra of all samples, but with different relative intensities, possibly due to the desorption of the functional groups that may have been adsorbed on the surface of the particles. In the FTIR weak absorption, bands around 2920 cm^{-1} and 2852 cm^{-1} were identified; these corresponded to the C–H stretching bond. The presence of these bands indicated the presence of organic residues adsorbed on the ceramics (e.g., wood and ground cereal). The presence of organic compounds may indicate that these compounds were present in clay deposits or that artisans added organic matter to increase the plasticity of the ceramics [37, 38]. Absorption bands at 2360 cm^{-1} and 2340 cm^{-1} may be related to the presence of carbon dioxide (C–O) in the atmosphere at the time of measurement [39, 40].

The vibrational modes of the siloxane group (Si–O–Si), whether in the asymmetric stretching mode

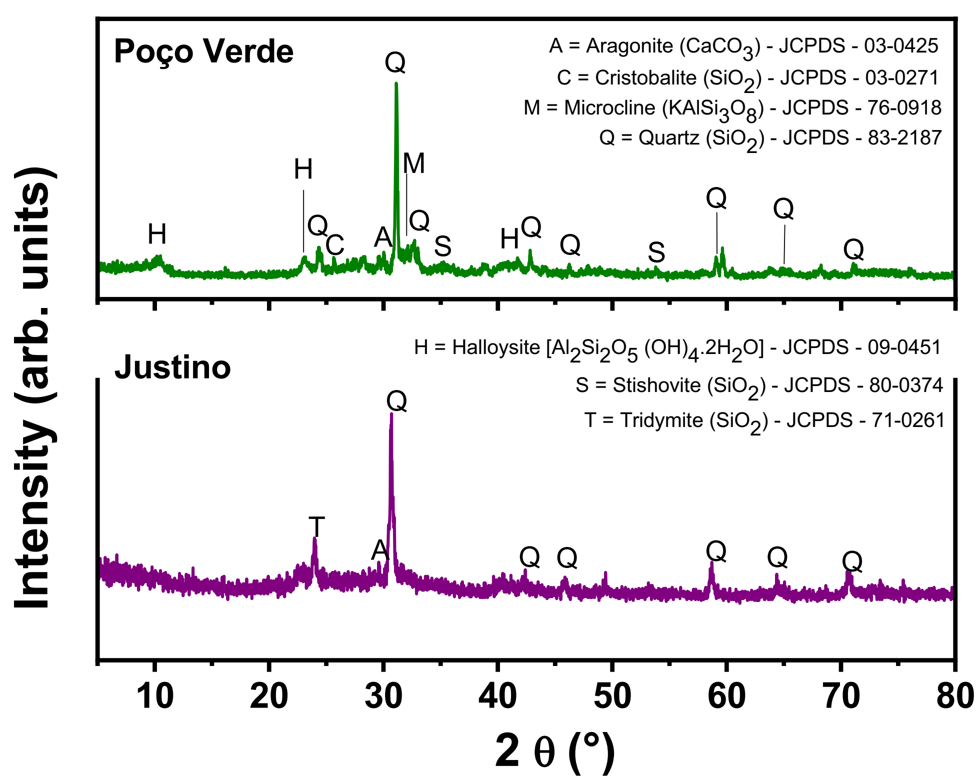

Fig. 8 Diffractograms of ceramic sherds from the archaeological sites of Poço Verde and Justino (Sergipe)

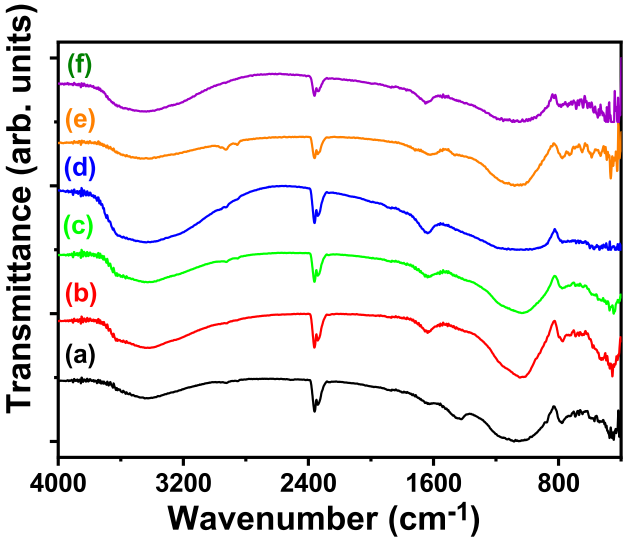

Fig. 9 Fourier-transform infrared spectra of ceramics from the archaeological sites (a) Caraíbas, (b) Fronteira, (c) Lamarão, (d) São Francisco II, (e) Poço Verde, and (f) Justino

(1100 ± 1000 cm^{-1}) or deformation mode (500 ± 400 cm^{-1}), are observed in all ceramics and indicate the presence of silicates in ceramic materials. Quartz is the second most abundant mineral on Earth; along with feldspar, it is often present in ceramics or is added as a flavoring. The absorption band at about 775 cm^{-1} observed in all the FTIR spectra of the samples corresponds to the Si–O bond originating from the quartz structure [37].

The incipient absorption bands near 580 cm^{-1} and 540 cm^{-1} can be associated with the presence of magnetite ($FeO.Fe_2O_3$) and hematite (Fe_2O_3), indicating atmospheric conditions of reduction and oxidation during the firing of ceramics. Some samples showed a weak absorption in the region close to 466 cm^{-1}. This absorption corresponded to the Si–O vibrational mode in the microcline structure ($KAlSi_3O_8$) [35], a result that confirmed what was observed in the diffractograms.

FTIR analysis was used to identify the functional groups present in the ceramics by detecting the vibrational modes of chemical bonds. However, the absence of certain vibrational modes can provide more information about firing temperatures. For example, characteristic absorption bands at 3700 cm^{-1} and 3620 cm^{-1} indicate the presence of hydroxyl groups in the internal structure of a ceramic. These groups are present in ceramics that have been fired at temperatures up to 450 °C. Since typical absorption bands of internally structured hydroxyls were not identified in the Xingó ceramics, it may be concluded that the firing temperature of the ceramics from this area was higher than 450 °C. The same reasoning can be applied if we consider the absorption peak at 915 cm^{-1}, typical of vibrations of the Al(OH) group in octahedral structures, which begin to collapse at a temperature of 500 °C. Although Al was one of the constituents (as detected by FRX and XRD), the Xingó ceramics did not show infrared absorptions at 915 cm^{-1}, indicating that all the samples were heated at temperatures above 500 °C [35, 37, 38].

FTIR analysis of the siloxane groups revealed that the Si–O absorption band can shift to higher frequencies and broaden as the samples are subjected to an increase in firing temperature. In samples heated to 100 °C, the absorption intensity is around 1025 cm^{-1} maximum and moves to the region around 1036 cm^{-1} when the sample is exposed to a temperature of 600 °C. When the ceramic is heated to 650 °C, the FTIR spectrum of a silicate appears as a symmetrical broad band at

Table 4 Experimental infrared absorptions (cm^{-1}) from the archaeological sites (a) Caraíbas, (b) Fronteira, (c) Lamarão, (d) São Francisco II, (e) Poço Verde, and (f) Justino

Wavenumber (cm^{-1}) and relative intensity*							Vibrations
Caraíbas	**Fronteira**	**Lamarão**	**São Francisco II**	**Poço Verde**	**Justino**	**Reference**	
3437 S	3436 S	3426 S	3437 S	3453 S	3447 S	3500	H–O–H stretching water
2926 VW	2921 VW	2925 VW	2923 VW	2929 W	–	2920	C–H stretching
2852 VW	2859 VW	2852 VW	2852 VW	2852 W	–	2852	C–H stretching
2360 VS	2361 VS	2359 VS	2358 VS	2359 VS	2363 VS	2360	C–O
2340 VS	2341 VS	2336 VS	2341 VS	2339 VS	2337 VS	2340	C–O
1638 VW	1641 M	1633 M	1642 M	1624 M	1647 M	1625	H–O–H bending water
1038 VS	1039 VS	1032 VS	1038 VS	1039 VS	1031 VS	1035	Si–O–Si stretching
781 M	774 M	779 M	777 VW	777 VW	791 VW	775	Si–O Quartz
583 VW	579 VW	588 VW	–	589 VW	–	580	Fe–O Magnetite
537 VW	531 VW	547 VW	–	–	–	540	Fe–O Hematite
476 W	–	473 M	–	–	475 VW	480	Si–O–Si bending
460 M	456 M	451 M	–	466 M	–	466	Si–O Microcline

VS very strong, *S* strong, *M* middle, *W* weak, *VW* very weak

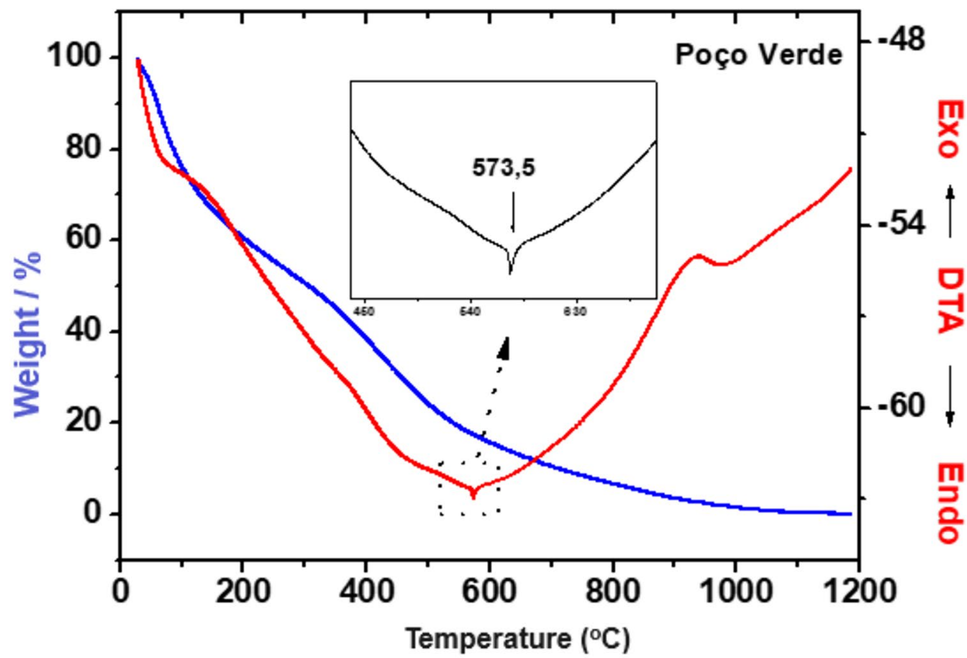

Fig. 10 DTA/TG curves of ceramic sherds from the Poço Verde site (Sergipe)

1035 cm^{-1} for red clays and at 1080 cm^{-1} for white clays. The presence of absorption around 1035 cm^{-1} in the FTIR spectra of all samples indicated the presence of red clay in the ceramic fragments from Xingó; however, the broad band was asymmetric, which may indicate that the ceramics were produced at temperatures below 650 °C. The presence of hematite indicates that the samples were fired in the open air or in a perfectly oxidizing atmosphere at the time of manufacture [35, 37, 38]. In sum, the FTIR analysis provides us with evidence that the Xingó samples were fired at temperatures between 500 and 650 °C under oxidizing atmospheric conditions and that red clay was used.

Figure 10 shows the DTA/TG curves for the Poço Verde ceramic sample. The TG curve shows a mass loss of about 20% in the range from room temperature to 200 °C, which may be related to the evaporation of water molecules from the ceramic surface. In the range between 200 and 400 °C, a further mass loss of about 20% is observed, which may be related to the decomposition of organic compounds present in the material.

The DTA curve reveals the presence of a small endothermic peak at 573.5 °C, which can be better visualized by enlarging the region highlighted in Fig. 8. This peak may be related to the decomposition of halloysite, which occurs at the same temperature. This result is consistent with the identification of the halloysite phase by XRD in ceramic samples from the Poço Verde site. The presence of halloysite crystals may indicate that the firing temperature of these ceramics was below 550 °C. This result accords with the discussion carried out relating to the FTIR measurements, which suggest that firing was carried out in the range of 500–650 °C.

5 Conclusions and Future Research

The multiple archaeometric techniques applied to the Xingó ceramics have clarified some issues relating to the archaeology of the Lower São Francisco River while opening up new questions for future researchers to address. The present study was carried out in the context of a broader understanding of the archaeology of the region [16], including data from understudied sites.

The FTIR analysis suggests that pottery was fired above 500 °C DTA/TG, while the analysis in the Poço Verde site suggests that it was fired below 650 °C. It remains for us to discover whether this has been the maximum firing temperature for the entire region during its long history of pottery production. While it is likely to have been so, Di Prado et al.'s [41] research in the Paraná Basin has pointed to the presence of pottery fired above 900 °C.

Another issue that needs to be better understood arose from our FTIR/MEV analysis. Previous technological studies of the Xingó pottery [14] have indicated the macroscopic presence of minerals in the clays from different sites. While a preliminary experimental study with local clays has indicated that some of these minerals may have been added to the clay by the potters, the FTIR/MEV analysis expands the possibility that these added tempers contained organic matter. In particular, the fibrous element identified in the Justino ceramics may indicate the presence of caraipé (tree bark) in the Xingó region. If confirmed, the presence of this typical Amazonian and Brazilian Cerrado (savannah) temper in Lower São Francisco would provide a framework for understanding precolonial connections between the regions.

Finally, ethnoarchaeological research in other contexts has highlighted major difficulties in understanding the variability of archaeological pottery, including its chemical composition. DeBoer and Lathrap [42] have shown that Shipibo Conibo potters use different recipes (i.e., different clays and different combinations of temper) for each vessel function (e.g., cooking pots, beer mugs, and storage jars). Moreover, even within the same vessel, different clays and tempers can be found for the base, wall, and rim. In future research, we intend to present a methodological proposal to overcome these interpretive handicaps.

The millenary production of ceramics in Lower São Francisco helps toward the understanding of long-term human history. While this craft has persisted since ca. 5000 BP, the choices made by potters have varied across space and time. We have presented a series of archaeometric contributions to facilitate such an understanding, and, following Munita et al. [43], we would argue that interdisciplinary collaboration is fundamental to its pursuit.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing Interests The authors declare no competing interests.

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