Research paper

Pre-historic production of ceramics in the Amazon: Provenience, raw materials, and firing temperatures

Suyanne Flavia Santos Rodrigues, Marcondes Lima da Costa, Herbert Pöllmann, Dirse Clara Kern, Maura Imazio da Silveira, Renato Kipnis

1. Introduction

In archeological studies, ceramic objects represent an important investigative tool, and the analysis of samples can provide important insights into the origin of the raw materials (clays, non-plastic materials) (Dias et al., 2013; Prudente et al., 2006; 2009), possible commercial and cultural interchanges among communities, evidence on technological differences (e.g., modeling, coiling, and throwing), as well as the firing temperatures, based on the mineralogical transformations occurring during the manufacture of the items (Jordanidis et al., 2009; Mohamed et al., 2010; Trindade et al., 2010, 2011). Chemical and mineralogical analyses of samples are used to evaluate these parameters, and have been applied to sherds retrieved from a wide range of archeological sites, especially in Europe (Fermo et al., 2008; Gimenez et al., 2006; Hein et al., 2004; Jordanidis and Garcia-Guinea, 2011; Kramar et al., 2012; Maritan et al., 2013; Montana et al., 2011; Moropoulou et al., 1995; Papadopoulou et al., 2004; Rathossi and Pontikes, 2010; Romani et al., 2000).

In the Amazon, similar studies have been and are being developed, although perspectives on the diversity of raw materials, manufacturing techniques and firing temperatures are still limited (Costa et al., 2004a, b, 2009, 2011, 2012). Studies of anthropogenic soils, especially Amazonian Dark Earth (ADE) are far more numerous (Costa and Kern, 1999; Costa et al., 2013; Glaser et al., 2001; Kern and Kämpf, 1989; Lehmann et al., 2000; Lemos et al., 2011; Lima et al., 2002; Mescouto et al., 2011; Schmidt et al., 2014; Silveira et al., 2011; Smith, 1980; Woods et al., 2009).

The chemical–mineralogical properties of prehistoric ceramics found in the Amazon were investigated with the aim of elucidating the production technology, the raw materials used, and the origin of these materials. For this, sherds were obtained from three archeological sites located in distinct regions of the basin. The mineralogical composition of the samples was determined by X-ray diffraction, optical microscopy, thermal analyses, FT-IR, and SEM-EDS, while the chemical composition was measured using ICP-OES and ICP-MS. The manufacturing process consisted of the coiling technique with the smoothing of surfaces, and the addition of organic and mineral non-plastic materials. The pots were fired at ±600 °C, leading to the formation of an amorphous metakaolinite matrix in which a number of different types of non-plastic materials can be found. These non-plastic materials, together with the phosphates found in the samples, represent the principal differences in the chemical and mineralogical composition of the sherds from different sites. The raw material (clay) used for the production of the ceramic sherds from the Da Mata and Jabuti sites had the same geological origin, and were distinct from those of Monte Dourado 1 in relation to the intensive use of crushed rock. Cariapé was found throughout the region, and the shells reflect the proximity of the Jabuti site to the ocean. The phosphates found in the matrix probably formed during the use of the pots to prepare food, and could not have been part of the raw material, given that they would not have resisted the firing temperature. The evidence indicates that the potters used the materials available locally for the production of ceramics. The use of cariapé at all the sites confirmed that this practice was widespread in the region, representing an important cultural trait of the production of ceramics in the prehistoric Amazon.
Given these shortcomings, the present study investigated the production of archaeological ceramics in the Amazon, with regard to the origin of raw materials (clay and non-plastic materials), the manufacturing processes, and firing temperatures through the chemical and mineralogical characterization of samples from different sites, in order to evaluate the potential technological variation in the productive process in distinct pottery-making populations, providing new insights into the complexity of the prehistoric occupation of the Amazon.

2. Materials and methods

2.1. Materials

For the present study, sherd vessels were obtained from three archaelogical sites in the Brazilian Amazon – Monte Dourado 1, Jabuti and Da Mata (Fig. 1) – based on their geographical distribution and the availability of material for analysis. All the samples were representative of the sides of the pots and were not embossed or painted.

2.1.1. Monte Dourado 1

The Monte Dourado 1 site (central coordinates: UTM 22M 329403/9928604) is located on the right margin of the Jari River, in the district of Monte Dourado, part of the municipality of Almeirim and in the Brazilian state of Pará. The samples from this site (CF-MD1) were collected by Scientia Scientific Consultants Ltd. in May, 2011, and were kindly provided for the present study by this company.

Monte Dourado 1 is a habitation site with Amazonian Dark Earth (ADE) deposits containing high densities of ceramics and smaller quantities of stone tools. This site covers a total area of 235,200 m² (560 m x 420 m), delimited using 401 boreholes. The ADE horizon reaches a depth of 70 cm in some places. The excavations were conducted in artificial layers of 10 cm until no more archaeological remains were encountered (Scientia, 2009). As for the Monte Dourado 1 samples, information on the pottery style is still unavailable.

2.1.2. Da Mata

The Da Mata site (central coordinates: UTM 22M 0550771/9358220) is located on the Atlantic coast of the municipality of Bragança in northeastern Pará. The samples from this site (CF-JAB) were collected by a team of archeologists from the Emilio Goeldi Paraense Museum in Belém coordinated by Dra. Maura Imazio da Silva.

This site is also of the habitation type, and is characterized by a number of patches of ADE, with depths ranging from 60 cm to more than 1 m in places, and large quantities of ceramic material distributed on the surface and lower down. The excavations were conducted in artificial layers of 20 cm until archeological remains were absent. The pottery is of the Mina tradition, described by Simões (1981), and typical of the sambaqui middens of the Amazon region (Silveira et al., 2011).

2.1.3. Jabuti

The Jabuti site (central coordinates: UTM 22M 0550771/9358220) is located on the Atlantic coast of the municipality of Bragança in northeastern Pará. The samples from this site (CF-JAB) were collected by a team of archeologists from the Emilio Goeldi Paraense Museum in Belém coordinated by Dra. Maura Imazio da Silva.

This site is also of the habitation type, and is characterized by a number of patches of ADE, with depths ranging from 60 cm to more than 1 m in places, and large quantities of ceramic material distributed on the surface and lower down. The excavations were conducted in artificial layers of 20 cm until archeological remains were absent. The pottery is of the Mina tradition, described by Simões (1981), and typical of the sambaqui middens of the Amazon region (Silveira et al., 2011).

2.2. Methods

The samples (Table 1) were dried at ambient temperature, and then the attached allochthonous substrate and products of weathering were removed carefully with distilled water. Due to the large amount of material, the sherds from Monte Dourado and Jabuti were subdivided to obtain a sample of 300 g for each site, which was equivalent to the sample collected from the Da Mata site. The samples were classified by thickness, based on the criteria established by Alves (1988), Rye (1981), Braun (1983) and Schiffer et al. (1994), which are normally used for the classification of archeological ceramics. All the sherds analyzed in the present study were either 9 mm thick or less, and were thus classified as thin or very thin, or were at least 12 mm thick, being recorded as medium or thick. The thickness of the samples is an important parameter here, given that the evidence indicates that the thinnest pots were used for cooking.

Following cleaning and the classification of the sherds by their thickness, the sherds were described mesoscopically using a ZEISS-Stemi 2000-C stereomicroscope and photographed with an attached Canon PowerShot G6 camera. During this examination, the coloration of the samples (based on the Munsell color system), their texture, and the non-plastic materials they contained were identified and recorded. Samples were then selected for the mineralogical study using optical and electron microscopy, while the rest of the material...
was ground in an agate mortar for the additional chemical and mineralogical analyses.

The micro-textural characteristics of the ceramic sherdsh were determined using a Carl Zeiss Axiolab 450910 petrographic microscope, with the samples placed on thin slides without coverslips. This procedure was complemented by semi-quantitative chemical analyses coupled by scanning electron microscopy coupled to an energy-dispersive X-ray spectrometry system (SEM-EDS), using a LEO

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth (cm)</th>
<th>Non-plastic</th>
<th>Surface color (Munsell color chart)</th>
<th>Manufacture technique after external aspects</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monte Dourado 1</td>
<td>CF-MD1 9 a</td>
<td>0-10</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
</tr>
<tr>
<td>CF-MD1 12 a</td>
<td>0-10</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>3</td>
</tr>
<tr>
<td>CF-MD1 9 b</td>
<td>10-20</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>19</td>
</tr>
<tr>
<td>CF-MD1 12 b</td>
<td>10-20</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>3</td>
</tr>
<tr>
<td>CF-MD1 9 c</td>
<td>20-30</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>13</td>
</tr>
<tr>
<td>CF-MD1 12 c</td>
<td>20-30</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>3</td>
</tr>
<tr>
<td>CF-MD1 9 d</td>
<td>30-40</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>13</td>
</tr>
<tr>
<td>CF-MD1 12 d</td>
<td>30-40</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>4</td>
</tr>
<tr>
<td>CF-MD1 9 e</td>
<td>40-50</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>16</td>
</tr>
<tr>
<td>CF-MD1 12 e</td>
<td>40-50</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>4</td>
</tr>
<tr>
<td>CF-MD1 9 f</td>
<td>50-60</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>14</td>
</tr>
<tr>
<td>CF-MD1 12 f</td>
<td>50-60</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>4</td>
</tr>
<tr>
<td>CF-MD1 9 g</td>
<td>60-70</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>13</td>
</tr>
<tr>
<td>CF-MD1 12 g</td>
<td>60-70</td>
<td>Mineral* + cariapé</td>
<td>(5YR4/3)</td>
<td>Coil technique/ smooth on the surface</td>
<td>5</td>
</tr>
</tbody>
</table>

| Da Mata ≤ 9 mm | 110 |
| Da Mata ≥ 12 mm | 26 |
| Total | 136 |

| Da Mata ≤ 9 mm | 90 |
| Da Mata ≥ 12 mm | 47 |
| Total | 137 |

Table 1

Description of the sherds analyzed from Monte Dourado 1, Da Mata and Jabuti archeological sites. (*) Most common non-plastic.

1450VP microscope with a voltage of 17.5 kV and a Gresham EDS detector equipped with a Be window and Q500 multi-channel analyzer. The samples were metralyzed with Au and the analyses were run using the IXRF software in the UFPA electronic microscopy laboratory.

The mineral components of the samples were identified by X-ray diffraction (XRD), using the powder method. For this, the samples were ground in an agate mortar and compacted in a sample holder for processing in an XPERT PRO MPD diffractometer with a PW 3040/60 (theta-theta) PANalytical goniometer, copper anode (λCuKα1 = 1.54060), Kβ filter, 40 kV tension generator and 30 mA current generator. The scanning interval was 5–75°, which encompasses the principal peak characteristic of the target minerals. The analyses had a step of 0.0170 (2θ) and a step time of 10.3377 s, and a fixed divergent gap of 0.2393 mm. These analyses were conducted in the UFPA Mineral Characterization Laboratory.

Thermogravimetric and thermodifferential analyses were conducted on subsamples of 0.02 g of the pulverized material, to investigate the thermal behavior of the ceramic sherds. The assays were run at temperatures of up to 1100 °C, with a heating rate of 10 °C/min in an inert atmosphere (N₂), using a PL Thermal Sciences thermo-analyzer simultaneously with an STA 1000/1500 analyzer (Stanton Redcroft Ltd.), in the UFPA mineral characterization laboratory.

The same samples were then analyzed using an FT-IV absorption spectroscopy (FT-IR) to confirm the presence of amorphous and crystalline phases, and organic matter. For this, a compressed pellet of each pulverized sample was prepared from 0.0015 g of the sample and 0.2 g of Potassium bromide (KBr), under a pressure of 1.8 Kbar. The analysis was conducted using a Vertex 70 Bruker spectrometer and the analysis curves TG/DTA (Fig. 3).

3. Results

3.1. Non-plastic materials

The non-plastic materials found in the different ceramic samples included cariapé, shell, and ground rock, depending on the site from which the sample was obtained. Only cariapé was found in the Da Mata samples (Fig. 2b). At Jabuti, most samples contained only shell fragments (Fig. 2c), although those found at a depth of 60 cm contained a combination of shell and cariapé. At Monte Dourado 1, the cariapé was combined with crushed rock (Fig. 2a).

Cariapé is derived from the bark of trees of the species Licania utilis and the genus Moquilea (Linné, 1925), which are widely distributed in the Amazon, and are still used for this purpose by traditional populations (Linné, 1925; Meegs and Evans, 1957). To prepare the temper, the bark is pulverized and calcined to produce amorphous siliceous ash, sometimes in the form of tridymite–cristobalite (Costa et al., 2004b, 2011).

The mineral non-plastic identified in the Monte Dourado 1 samples was metakaolinite. The principal phase of the basic matrix of the ceramic samples was metakaolinite. The background of the XRD patterns are indicative of large amounts of amorphous phases (Fig. 2), which were interpreted as being indicators of the presence of metakaolinite, given that the principal mineral of the raw material used for the production of the pots was kaolinite, and when it is calcined at low temperatures (550–600 °C), it becomes amorphous.

The metakaolinite thus constitutes the fundamental matrix, the principal component of the amorphous to crystalline brown porous mass of the ceramics (Fig. 2). The presence of metakaolinite is also indicated by the aluminosilicate characteristics of the matrix found in the SEM/EDS spot analyses (Fig. 3), as well as the mullite formation when the fragments were burned at 950 °C, as shown in curves TG/DTA (Fig. 3).

3.2. The matrix

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3.2.2. Quartz

Quartz is the second most important phase found in the samples, observed through both the mesoscopic and microscopic analyses, and confirmed by XRD (Fig. 2). The quartz is distributed throughout the metakaolinite matrix, being both a component of the clay raw material and the temper.

3.2.3. Muscovite

This mineral was rarely observed under optical microscopy, but was confirmed as an accessory mineral by XRD in all the samples (Fig. 2). It is present in tiny platelets distributed throughout the metakaolinite matrix, probably as a component of the clay raw material. It is also possible that this mineral was introduced into the ceramics from Monte Dourado 1 as part of the rock temper used at this site.

3.2.4. Iron oxy-hydroxides

Nodules of iron oxide, approximately 500 μm in diameter (Fig. 1), were found in all the samples, and were also present in the brown spots observed in the metakaolinite matrix. These features certainly represent the abundant brown and red spots found in the original clayey raw material.

3.2.5. Anatase

Anatase was identified only by XRD and is probably found in nanocrystals within the matrix of the Jabuti and Da Mata samples (Fig. 2). This mineral is commonly found in the latosols and lateritic formations that are so abundant in the Amazon region. It seems likely that the mottled clays of these lateritic profiles were used as the raw material for the manufacture of the original ceramic pots from which the sherds analyzed in the present study were derived. Anatase is much less common in the region’s sedimentary rocks.

3.2.6. Phosphates

Phosphates, principally of aluminum, were common accessories in the ceramic archeological from Amazonas, but were generally amorphous, and only rarely found in cryptocrystalline forms, such as variscite–strengone and, more rarely, rhodophane (Costa et al., 2004b, 2006, 2011). In the samples analyzed, the aluminum phosphates are accessory and equally amorphous. However, in the Jabuti samples, they were present as microcrystalline candalite–goyazite, observed...
Fig. 2. Mineralogical composition of the sherds from Monte Dourado 1, Da Mata and Jabuti archeological sites by XRD powder analysis and photomicrographs showing different non-plastic materials. Optical microscope, plane polarized light, with 10× lens; Qtz = quartz; Crd = cordierite; Ms = muscovite; Cld = crandallite-goyazite; Ant = anatase; Crs = cristobalite; Ilm = ilmenite; Mc = feldspar; An = plagioclases.
The presence of this mineral was confirmed by an endothermic peak in the thermograms of the samples at 440 °C (Fig. 4), which indicates the dehydroxylation of the mineral (Gilkes and Palmer, 1983) and consequent loss of crystallinity. The SEM/EDS spot analyses revealed that the crandallite–goyazite substituted the shell fragments (Fig. 3). At the other sites, however, the phosphates were found in the pores of the matrix, and in the contact zones between these pores and the temper (Fig. 3). Stoichiometric calculations and SEM/EDS spot analyses of chemicals also allowed the presence of amorphous aluminum phosphates to be inferred in the metakaolinite matrix. This same approach, associated with the FT-IR (Fig. 4b) and the total chemical analyses (Table 2), resulted in the identification of these minerals in the ceramic sherds from Da Mata, albeit in much smaller quantities. These phosphates can be recognized by the anti-symmetric stretching of the P–O, 1035 cm$^{-1}$ (Breitinger et al., 2006) found in the ceramic sherds from all the sites, and equivalent to variscite. Segelerite (CaMgFe(PO$_4$)$_2$(OH)·4(H$_2$O)) was also identified by XRD in the sherds from Monte Dourado 1 (Fig. 2), although the endothermic dehydroxylation peak found at 400 °C (Hochleitner and Fehr, 2010) was not observed in the thermograms (Fig. 4a), presumably as a result of its low concentration, as confirmed by the chemical data. Beyond the stretches referring to P–O, the FT-IR spectra exhibited the stretching of the O–H of the adsorbed water related to the humid content (~3430 cm$^{-1}$) found in the spectra of all the sherds (Fig. 4b). In addition, bands of Si–O and Si–O–Al stretching related to the silicates identified by XRD (Madejová and Komadel, 2001) were found in the sherds from all three sites.

### 4. Discussion

#### 4.1. Raw materials and mineral transformation in firing manufacture of the vessels

Metakaolinite and quartz were the principal components of sherds retrieved from other archeological sites in the Brazilian Amazon (Costa et al., 2004b, 2011) and represent the principal raw materials used for the production of the original vessels. The abundance of these minerals indicates that the raw materials were composed primarily of kaolinite and quartz, and that the firing temperatures did not exceed 600 °C, given that the presence of metakaolinite (Al$_2$Si$_2$O$_7$) indicates that the kaolinite in the raw material was converted into an amorphous phase. The structure of the kaolinite is ruptured during firing at 550 °C, but would have been transformed into mullite at a firing temperature of 950 °C (Evans and White, 1958) as noted in the TG/DTA curves (Fig. 3) which corroborates with the primary use of clays rich in kaolinite.

Kaolinite is the best suited mineral clay for the production of red ceramic, whether archeological or current production, both vessels manufactured as structural material (bricks and tiles) (Kukolev et al., 1972). Clays rich in kaolinite – sedimentary or weathered – are abundant throughout the Amazon region. The quartz associated with this mineral is also abundant, found in fine grains, but does not suffer alterations at the firing temperatures inferred for the samples analyzed in the present study.

The total chemical composition and spot measurements confirm that the basic raw material used for the production of the ceramics...
was an aluminosilicate, while the minor concentrations of K₂O in the Monte Dourado 1 samples (0.6%–1.28%) observed in the Monte Dourado 1 samples confirm the presence of muscovite or potassium feldspars, which would have been added as temper. The levels of CaO (2.69–4.48% by weight) associated with those of Na₂O (0.6%–1.28%) observed in the Monte Dourado 1 samples confirm the presence of plagioclase (Fig. 5a) of the labradorite type (mean CaO/Na₂O ratio = 3.7), identified as temper, whereas in the Da Mata samples, CaO and Na₂O were found at extremely low levels (Na₂O: <0.18%; CaO: <0.34%), confirming the absence of plagioclase. Relatively high levels of MgO were recorded at Monte Dourado 1 and represent cordierite, the only Mg mineral identified by XRD. While the levels of MgO recorded at Jabuti were still substantial (1.28%, on average), they were incompatible with the minerals identified by XRD of the samples from this site.

Similarly, high levels of TiO₂ were only recorded at Monte Dourado 1, and reflect the accessory status of ilmenite in the samples, as identified by XRD. In this case, the ilmenite + labradorite + cordierite + quartz + muscovite) may correspond to fragments of metamorphosed mafic rock which was crushed and added to the basic clay as a non-plastic material. This eliminates the possible use of saprolite (clay with rock
concluded that thin-walled pots were used for cooking food, given the site. 

which were probably amorphous, despite the high levels of Fe2O3 features, although this mineral did not survive the long period of 

found in the analyses (Table 2). No crystalline phase of Fe was identi 

4.2. Firing temperature

The firing temperature of the pots was estimated from the mineralogical transformations of the material. The amorphous metakaolinite domain shows that this temperature was higher than 550 °C, but did not reach 600 °C. This can be deduced from the presence of anatase, which would have been transformed into rutile at higher temperatures (Zhang et al., 2006). When calcined in the laboratory for 2 h at a temperature of 600 °C, the anatase is transformed into rutile.

The hematite may also be an important indicator of firing temperatures, although this mineral did not survive the long period of weathering in the ADE soils, and was reduced to iron hydroxides, which were probably amorphous, despite the high levels of Fe2O3 found in the analyses (Table 2). No crystalline phase of Fe was identified by XRD, except for ilmenite, which is resistant to weathering, and the rare mineral segelerite, found in the samples from Monte Dourado 1.

4.3. Neoformation after the manufacture of the vessels

The relatively high levels of CaO found in the Jabuti samples, independent of the Na2O (<0.18%; Fig. 5b), and combined with the high values of SrO (≤0.16%), in addition to the high levels of P2O5, which respond to the presence of crandallite–goyazite, differentiates this site from the others. At Jabuti, this mineral substitutes pseudomorphically the shell fragments, which would normally be made up of calcite and/or aragonite, which indicates that the crandallite–goyazite was formed after the production of the ceramic pots, possibly during their daily use, and would thus not be a component of the ceramics.

Costa et al. (2006, 2011) related the phosphorus levels to the daily use of the pots for the preparation and storage of food, although Freestone et al. (1994) concluded that the concentrations in the ceramics were derived from the environment in which they were discarded, due to the micro-structure of the material, and were thus not an indicator of the use of the pots. The thinnest sherds (<9 mm) tended to have the highest concentrations of P2O5, however, which supports the conclusion that the enrichment of phosphorus was related primarily to the use of the post for cooking, as proposed by Costa et al. (2006, 2012). Schiffer et al. (1994), Rye (1981), and Braun (1983) all concluded that thin-walled pots were used for cooking food, given that they are better conductors of heat, and are more resistant to thermal shock. The P2O5 content was no more than 11.16% (7.75%, on average) at Jabuti, much lower than the levels recorded at the other two sites. Even so, all the values are higher than those recorded in ceramic vessels retrieved from archeological sites in South Africa (0.007–1.18%) by Legodi and Waal (2007), and in Greece (0.08–0.21%) by Jordanidis et al. (2009) CCR and PAAS (Table 2; Fig. 6a). The lowest levels of P2O5 (1.04%, on average) were recorded in the sherds from Da Mata, although these values are similar to those recorded in studies of samples from other archeological sites in the Amazon region (Costa et al., 2009, 2011).

Like other hydroxylated or hydrated aluminum phosphates, crandallite–goyazite ([(Ca,Sr)Al2(PO4)2(OH)3]·nH2O) is a mineral typical of hydrothermal environments (Schwab et al., 1990), equivalent to that found inside ceramic pots during the cooking of foods, as demonstrated by Costa et al. (2012). If this mineral was present in the raw material, it would not have resisted the inferred firing temperature, and if this temperature had been even higher, e.g., 900–1000 °C, the mineral would have been transformed into a crystalline phase, such as berlinite, and the metakaolinite, into mullite. These findings thus indicate that the aluminum phosphates were probably formed during the use of the pots to cook food, and would thus be important indicators of their use for the preparation of meals.

While the amorphous phosphates of aluminum or microcrystalline minerals such as crandallite–goyazite are derived from the use of the pots for cooking food, the segelerite identified in the sherds from Monte Dourado 1 (Fig. 2) indicates aerobic conditions, typical of flooded environments in which organic matter has accumulated. Under these conditions, the iron oxy-hydroxides in the sherds are partially dissolved by microbial activity, and the iron is reduced, as well as part of the amorphous aluminum phosphates, plagioclases, and the cordierite, which establishes ideal conditions for the precipitation of Ca–Mg–Fe phosphates, such as segelerite. The occurrence mode of the segelerite, partially replacing the aforementioned minerals, reinforces this conclusion.

The swampy conditions in the region of Monte Dourado 1 have persisted to the present day. Phosphates of Fe2+, such as vivianite (Fe3(PO4)2·8H2O) and mitridatite (Ca3Fe4(PO4)4(OH)6·3H2O), have been identified in shreds (Maritan and Mazzoli, 2004), ferruginous lateritic crusts invaded by swamps (Costa and Lemos, 2000; Costa and Sa, 1980; Lemos et al., 2007) or even in swampy ground (Walpersdorf et al., 2013). Like the aluminum phosphates, these iron phosphates suffer thermal collapse (Fig. 4) at temperatures of over 400 °C (Hochleitner and Fehr, 2010). This means that these compounds could not have been part of the raw material, given the firing temperature of the ceramic vessels (550–600 °C).

4.4. Provenience and discrimination of the sherds

The results of the chemical–mineralogical analyses of the sherds (Fig. 6a, b) emphasize the distinct characteristics of each group of samples, which probably reflects the different non-plastic materials (cariapé, shell, and crushed rock) used in the manufacturing process. Crushed metamorphic rocks in the Monte Dourado 1 sherds, and the large quantities of shell substituted by aluminum phosphates in the Jabuti sherds, contribute to the discrimination of the sherds from these sites.

Cariapé was the predominant temper at Da Mata, and the reduced levels of amorphous phosphates are clearly the component that distinguishes this site from the others. Overall, then, the chemical–mineralogical differences among the three sites reflect both the non-plastic materials used during the production process and the possible contamination by phosphates after the production of the pots.

The matrices of the Jabuti and Da Mata sherds were very similar in chemical terms (Table 1; Fig. 7a, b), except of course in the levels of CaO, SrO, MgO, and P2O5, as well as their mineralogical composition, with the exception of the crandallite–goyazite found only at Jabuti. The higher values for SiO2 recorded at Da Mata correspond to the abundance of cariapé, formed basically of SiO2, both amorphous and in the form of tridymite–cristobalite. These similarities in the matrix used at the two sites are further reinforced by the distribution pattern of trace elements (Fig. 7a) and the rare earth elements normalized by the chondrites (Fig. 7b). The negative anomaly of Eu found in the present study is a characteristic of the material equivalent to granitoids and the products of weathering and the resulting aluminosilicate clays deposited in the lakes and alluvial plains found throughout the Amazon, which provided the raw materials for the manufacture of the pots.

The only divergent trace element was Sr, a potential component of shells and foods of marine origin. Calcium carbonates, such as aragonite, the principal component of recent shells, contain strontium (Findlater et al., 2014; Vonhof et al., 1998). The abundance of shell sherds and the coastal location of the Jabuti and Da Mata sites reinforce the relationship with this environment. The raw materials used at these sites were almost certainly derived from local geological deposits which, unlike those at Monte Dourado 1, are dominated by sedimentary rocks of the Barreiras Formation, primarily argillites made up of kaolinite, quartz, and illite/muscovite, as well as alluvial and lacustrine deposits of the coastal plains (Behling and Costa, 2004). On the other hand, the mineralogical assembly identified in the fragments from Monte Dourado 1 site can easily be associated with amphibolites that are part of the Ipitinga Group, the Paleo-Proterozoic geologic unit mapped near the study site (Vasquez et al., 2008).

Fig. 6. a) XRD cluster analyses showing the clear distinction between the three sites; b) chemical diagrams discriminating the three sites based on the chemical composition of their sherds.

Fig. 7. a) Distribution of the contents of the trace elements found in the sherds, normalized by the PAAS; b) distribution of the REE in the sherds normalized by chondrites (Evensen et al., 1978).
5. Conclusions

The sherds analyzed from the three study sites presented distinct non-plant material characteristics, which assign them to different groups. This discrimination was strongly supported by the presence and abundance of aluminum phosphates, in particular crandallite-gooyazite, found primarily in the Jabuti and Da Mata samples. The Monte Dourado 1 site is distinguished from the others due to the use and abundance of aluminum phosphates, in particular crandallite. The chemical and mineralogical similarities and differences found among the sherds indicate the use of local raw materials, without the need for the exchange of raw materials among populations. The use of cariapé in most of the sherds reflects the widespread use of this resource, which may be an important indicator of prehistoric ceramic production in the Amazon region, despite the existence of a few exceptions.

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