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TESE DE DOUTORADO

OS FRAGMENTOS DE CERÂMICA ARQUEOLÓGICA COMO FONTE POTENCIAL DE FERTILIDADE DOS SOLOS TPA

Apresentado por:

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TESE APRESENTADO POR:

SUYANNE FLÁVIA SANTOS RODRIGUES

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“O oleiro não tem direito de fazer do mesmo barro um vaso para fins nobres e outro para uso desonroso? ”

Romanos 9:21

RESUMO

Os solos tipo Terra Preta Arqueológica (TPA) são reconhecidos por sua elevada fertilidade, em forte contraste com os solos pobres da Amazônia. Esta fertilidade parece persistir mesmo após o seu uso intensivo na agricultura. As TPA são geralmente ricas em fragmentos cerâmicos, importantes registros de que estão interligados com ocupação humana na Pré-história. Muitos estudos se concentraram sobre os aspectos estilísticos das vasilhas cerâmicas representativas desses fragmentos, e mais restritamente são motivos de estudos de caracterização químico-mineral, para identificação de matéria prima, procedência, tecnologia, e principalmente a origem do seu conteúdo em P, variado e relativamente elevado. Esses teores de P estão representados por fosfatos de alumínio, em geral, amorfos a variscita-estrengita, e sua origem é creditada ao uso das vasilhas para o preparo de alimentos. Embora já aventado a possibilidade de que estes fragmentos possam responder pela a fertilidade continuada destes solos, estudos experimentais não foram realizados para demonstrar a potencial contribuição destes fragmentos para reconhecida fertilidade das TPA. O presente trabalho demonstra esta possibilidade, e para atingir este fim foram selecionados fragmentos de três sítios arqueológicos com características distintas situados em diferentes porções da Amazônia: Monte Dourado 1 (Almeirim-PA), Jabuti (Bragança-PA) e Da Mata (São José de Ribamar-MA). Inicialmente 325 fragmentos cerâmicos foram descritos mesoscopicamente e submetidos à caracterização mineralógica e química por DRX; microscopia óptica; TG-ATD; IV-FT; MEV-SED; ICP-MS e ICP-OES; adsorção gasosa; medidas dos parâmetros de fertilidade; e ensaios de dessorção de P. Com estes dados objetivou-se identificar matérias primas, processos produtivos, modificações ocorridas durante o uso e após o descarte, e desta forma avaliar as possíveis contribuições destes fragmentos a fertilidade das TPA. A hipótese de contaminação por nutrientes provindos dos alimentos durante o uso das vasilhas para preparação de alimentos foi comprovada através de experimento em laboratório simulando condições de cozimento, onde foi avaliada a incorporação de cálcio e fósforo em panelas cerâmicas similares as arqueológicas. Os resultados mostram que os antigos povos ceramistas utilizaram matérias primas dos arredores de seus sítios. A composição em termos de uma matriz com metacaulinitica e quartzo, por vezes muscovita é comum a todos os fragmentos, indicando matéria prima rica em caulinita e quartzo, fundamental para produção das vasilhas. A metacaulinita sugere que a queima ocorreu em torno de 550°C. Por outro lado, adições de antiplásticos distintos promoveram diferenças químicas e mineralógicas fazendo com que os fragmentos no seu todo divirjam entre si: os do sítio Da Mata se caracterizam pelo emprego exclusivo de cariapé, em Monte Dourado 1 o cariapé com rochas trituradas de mineralogia complexa, e no Jabuti conchas por vezes cariapé. Fosfatos amorfos são comuns a todos os sítios, embora em teores distintos, sendo que fosfatos de alumínio cristalinos tipo crandallita-goyazita foram encontrados apenas no Jabuti e fosfatos de Fe-Mg-Ca, a segelerita, em Monte Dourado 1. Os fosfatos amorfos e a crandallita-goyazita foram interpretados como indicadores de uso das vasilhas representativas dos fragmentos para preparação de alimentos, enquanto a segelerita uma neoformação ocorrida após o sítio ter sido submetido às condições hidromórficas, que persistem até atualidade. Em termos das concentrações de P, nos fragmentos do sítio Da Mata estão as menores, em média, 1,04% de P_2O_5 que assemelham-se a maioria dos fragmentos já investigados, enquanto os do Jabuti são os mais elevados (em média, 7,75%) já conhecidos, e nos do Monte Dourado 1 são, em média, 2,23% . É provável que os altos teores de P, Ca e Sr sejam provenientes da dieta alimentar a base de mariscos, como demonstra a riqueza em conchas nos fragmentos. Os teores elevados de Ca em Monte Dourado 1 refletem a presença de labradorita no antiplástico. A fertilidade potencial dos fragmentos cerâmicos é nitidamente superior a dos solos TPA quando analisados sem os fragmentos. Portanto é plausível se supor que os fragmentos podem ser fonte dos macronutrientes e micronutrientes. Isto foi comprovado através dos ensaios que comprovara a dessorção de P, a qual ocorre de forma lenta, um aspecto muito importante para reforçar a persistência da fertilidade. Essa dessorção é mais bem descrita pelo modelo de Freundlich que sugere interações entre os íons adsorvidos. O experimento que simulou condições de cozimento mostrou que o Ca e o P podem ser adsorvidos tanto nas paredes quanto nas tampas das panelas cerâmicas, porém concentrações mais elevadas são evidenciadas nas paredes. Embora o Ca tenha sido adsorvido não foi identificada uma fase seja ela amorfa ou cristalina contendo este elemento, provavelmente porque o tempo não foi suficiente. Porém quanto ao P, a adsorção ocorreu, e já a partir de 600 h formou-se variscita, um fosfato de alumínio, nas paredes das panelas. Portanto os fosfatos de alumínio podem se formar ainda nas vasilhas cerâmicas durante o preparo de alimento por cozimento, assim, sua presença nas das vasilhas cerâmicas se constitui, em um importante indicador de uso das mesmas para o cozimento de alimentos e seus fragmentos nos solos são fonte potencial importante de fertilidade.

Palavras-chave: Cerâmica Arqueológica. Matérias Primas. Fosfatos de Alumínio. Fertilidade. TPA. Amazônia.

ABSTRACT

Soils of the Amazon Dark Earth (ADE) type are known for their high fertility, which contrasts with the typically poor soils found throughout most of the Amazon. The fertility of these soils appears to persist even after their intensive use for agriculture. The ADE are usually rich in sherds, important evidence linking them to the occupation of the region by prehistoric populations. Many studies have focused on the stylistic characteristics of the vessels represented by these sherds, although less attention has been paid to the chemical and mineralogical features of this material, which are important for the identification of the raw material use to produce the artifacts, provenience, technology, and in particular the origin of their relatively high P content. These high levels of P are derived from aluminum phosphates, which are generally amorphous to variscite-strengite, and have been linked to the use of the pots for the preparation of food. While the possible role of the sherds in the maintenance of the fertility of ADE has been widely discussed, no experimental data have been presented to confirm this connection. This study presents systematic evidence that the sherds contribute to the fertility of the soils. For this, sherds were obtained from three archeological sites with distinct characteristics located in different parts of the Amazon: Monte Dourado 1 (Almeirim, Pará), Jabuti (Bragança, Pará), and Da Mata (São José de Ribamar, Maranhão). Initially, 325 sherds were first described mesoscopically and then their chemical and mineralogical composition was determined by XRD, optical microscopy, TGA/DTA, FT-IR, SEM-EDS, ICP-MS and ICP-OES. Different parameters of fertility were then measured, followed by gaseous adsorption tests, and finally, P desorption assays. These data were used to identify the raw materials used in the fabrication of the vessels, details of the productive process, modifications occurring during the use of the utensils and after being discarded, with the aim of evaluating the potential contribution of these sherds to the fertility of the ADE soils. The hypothesis of contamination by nutrients from foods during the use of the vessels for the preparation of meals was confirmed by a laboratory experiment simulating cooking conditions using ceramic pots similar to the archeological artifacts, and measuring the incorporation of Ca and P during the cooking process. The results indicate that the ancient ceramicist peoples used raw materials available in the area surrounding their habitation sites. The composition of the sherds, all of which are made from a matrix of metakaolinite and quartz, and occasionally muscovite, indicating raw materials rich in kaolinite and quartz, which are fundamental to the production of ceramic artifacts. The presence of metakaolinite indicates that the pots were fired at approximately 550°C. However, the addition of different types of antiplastic contributed to chemical and mineralogical variation among sites in the overall composition of the sherds. At Da Mata, only cariapé was used, while at Monte Dourado 1, the cariapé was mixed with crushed rocks with a complex mineralogical content, and at Jabuti, shells were used in addition to cariapé. Amorphous phosphates are common to all the sites, albeit at distinct levels, with crystalline aluminum phosphates of the crandallite-goyazite type being found only at Jabuti, and Fe-Mg-Ca phosphates, segelerite, being exclusive to Monte Dourado 1. The amorphous phosphates and crandallite-goyazite were considered to be indicators of the use of the original pots (from which the sherds were derived) for the preparation of food, whereas the segelerite was interpreted as a neoformation following exposure of the fragments to the hydromorphic conditions that persist to the present day. The lowest phosphorus concentrations-1.04% of P_2O_5 on average- were recorded at Da Mata, and were similar to the majority of sherds studied up until now, whereas the highest concentrations (a mean of 7.75%) were recorded at Jabuti, the highest values yet reported. At Monte Dourado 1, the mean concentration was 2.23%. It seems likely that the high levels of P, Ca, and Sr are related to a diet rich in shellfish, as reflected in the diversity of shells fragments found in the sherds. The high levels of calcium recorded at Monte Dourado 1 reflect the presence of labradorite in the temper. The potential fertility of the sherds is clearly greater than that of the ADE soil when analyzed without the ceramics. It thus seems reasonable to assume that the sherds are the source of the macro- and micronutrients found in the soil. This was confirmed through desorption assays, which showed that P was desorbed at a slow rate, a characteristic which may be especially important for the persistence of fertility. This process is best described by the Freundlich model, which indicates the occurrence of interactions among the adsorbed ions. The experiment that simulated cooking conditions indicated that the Ca and P may be adsorbed into both the sides and lids of the ceramic pots, albeit with higher concentrations being accumulated in the sides. While calcium was adsorbed, no phase of this element was identified, either amorphous or crystalline, probably because the duration of the experiment was too short. By contrast, the chemical adsorption of the P did occur, and after 600 h of cooking, variscite, an aluminum phosphate, formed in the sides of the pots. Aluminum phosphates may thus form in the ceramic vessels during the cooking of food. These results indicate that the presence of aluminum phosphates in the matrix of the ceramic vessels represents a reliable indicator of their use as cooking vessels, and that the sherds of these utensils in the soil constitute a potentially important source of fertility.

Key words: Sherds; Raw Materials; Aluminum Phosphates; Fertility; ADE; Amazon.

LISTA DE ILUSTRAÇÕES

FIGURAS

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

Contribution of the fertility potential of archaeological sherds to the long-term fertility of Amazonian Dark Earth

Phosphorus in archeological ceramics as evidence of the use of the pots for cooking food

TABELAS

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

Contribution of the fertility potential of archaeological sherds to the long-term fertility of Amazonian Dark Earth

Phosphorus in archeological ceramics as evidence of the use of the pots for cooking food

SUMÁRIO

1 INTRODUÇÃO

Os solos tipo Terra Preta Arqueológica (TPA) vem sendo motivo de diversos estudos em virtude de sua alta fertilidade (Smith 1980; Kern & Kämpf 1989; Kern & Costa 1997; Kämpf & Kern 2005; Glaser & Birk 2012; Schmidt *et al.* 2014), que contrasta com a baixa fertilidade dos Latossolos e Argissolos normalmente encontrados na Amazônia (Rodrigues, 1996; Sanches *et al.* 1982). A ocorrência deste solo foi reconhecida já em 1874, por Charles F. Hartt, um geólogo canadense, que o descreveu nas regiões próximas a Santarém e ao rio Tapajós. Este geólogo o denominou simplesmente como “black soils”. Em 1944, o alemão Friedrich Katzer descreveu características físicas das Terras Pretas na região de Santarém (Myers *et al.* 2003). Alguns anos depois, Sombroek (1966) descreveu propriedades químicas de solos tipo Terras Mulatas nos arredores de Santarém. Desde então, foram desenvolvidos inúmeros trabalhos que descrevem a TPA (Kern & Kämpf 1989), atualmente também conhecida como Arqueo-antrossolos (Kämpf & Kern 2005), Terra Preta de Índio ou simplesmente Terra Preta.

Estudos fundamentados em evidências arqueológicas e pedológicas apontam que a TPA se formara em decorrência da ocupação humana (Sombroek 1966; Smith 1980; Hilbert & Hilbert 1980; Simões & Corrêa 1987; Kern & Kämpf 1989), como resultado do descarte de resíduos orgânicos de naturezas diversas e suas mineralizações, os quais implicaram na modificação das propriedades do solo natural (Kern *et al.* 2009). Esta origem antrópica é amplamente aceita e defendida por Sombroek (1966), Hilbert & Hilbert (1980); Smith (1980); Kern & Kämpf (1989); Neves *et al.* (2003);.Glaser *et al*. (2004); Glaser (2007); Woods & Denevan (2009). Estudos cronológicos indicam que a formação de TPA teria ocorrido no Alto Xingu entre 60 e 1640 AD (Heckenberger *et al.* 2003). Por outro lado, na Amazônia Central, isto teria ocorrido entre 2500 e de 500 a BP (Neves *et al.* 2003).

Em geral, a TPA é caracterizada pelo horizonte A antrópico com espessura média de 30 a 60 cm, podendo atingir até 2 m, enquanto que os solos naturais da Amazônia sob florestas não perturbadas se situam normalmente entre 10 e 15 cm, o que representa a própria profundidade. A coloração escura, já indicada pela própria denominação, é consequência de grandes estoques de matéria orgânica húmica estável (Glaser *et al.* 2001; Glaser & Birk, 2012), variando entre preto e bruno acinzentado muito escuro (N2/; 2,5YR2/0; 5YR2,5/1; 7,5YR 2/0; 10YR 2/0 a 3/4) (Kämpf & Kern, 2005).

As TPA apresentam em média, 507 g kg^{-1} de P disponível, 9,4 cmolc kg^{-1} de Ca + Mg e pH de 5,6, enquanto que Latossolos e Argissolos apresentam apenas 1,7 g kg^{-1} para o P disponível, 1,4 cmolc kg^{-1} para Ca + Mg e pH de 4,5 (Kämpf & Kern 2005). As TPA também apresentam valores comparativamente elevados de Zn, Mn, de CTC e de saturação por bases (Pabst 1991; Kern *et al.* 2003; Sombroek *et al.* 2002; Lehmann *et al.* 2003); alta diversidade microbiológica e sua textura varia de arenosa a argilosa (Kern 1996; Kern & Costa 1997; Lima *et al.* 2002; Kern *et al.* 2003; Kämpf & Kern 2005). Aparentemente, esta fertilidade não se exaure facilmente, mesmo nas condições tropicais a que estão expostos ao longo do tempo, e quando utilizadas por longos períodos para fins de agricultura de subsistência ou de pequena escala (Kern *et al.* 2009).

Associados a TPA estão fragmentos cerâmicos (FC), e líticos (mais restritamente) que juntos constituem o principal legado da cultura material da Amazônia pré-histórica. Estudos químico-minerais destes FC podem contribuir para esclarecer a procedência de sua matéria-prima (argilas, temperos), possíveis intercâmbios culturais e comerciais entre comunidades antigas, oferecer subsídios para avaliar diferenças na técnica de manufatura, e avaliar a temperatura de queima através das transformações mineralógicas ocorridas durante o processo de confecção (Iordanidis *et al.* 2009; Mohamed *et al.* 2010). Esta é uma abordagem muito comum em estudos sobre FC provenientes de diversos sítios, principalmente europeus (Moropoulou *et al.* 1995; Romani *et al.* 2000, Hein *et al.* 2004; Papadopoulou *et al.* 2004; Gimenez *et al.* 2006; Fermo *et al.* 2008; Rathossi & Pontikes, 2010 Iordanidis & Garcia-Guinea 2011; Montana *et al.* 2011, Kramar *et al.* 2012; Maritan *et al.* 2013).

Na Amazônia estudos semelhantes foram e estão sendo realizados (Tabela 1), mas ainda não foram suficientes para precisar a diversidade da matéria prima, da manufatura e temperatura de queima (Costa *et al.* 2004a, 2004b; 2009, 2011, 2012). As propriedades químicas e mineralógicas da TPA ainda parecem ser mais investigadas frente à dos seus FC, principalmente sob o aspecto de fertilidade (Smith 1980; Kern & Kampf, 1989; Costa & Kern 1999; Glaser *et al.* 2001; Lima *et al.* 2002; Lehmann et al, 2003; Woods *et al.* 2009; Silveira *et al.* 2011; Lemos *et al.* 2011; Mescouto *et al.* 2011; Costa *et al.* 2013; Schmidt *et al.* 2014), cujo a origem de sua resiliência ainda é discutida.

Glaser *et al.* (2001) e Glaser & Birk (2012) creditam a fertilidade da TPA a acumulação de carbono proveniente da combustão incompleta de matéria orgânica (C_{pyr} ou *black carbon*) que é maior que a dos solos adjacentes. Esta hipótese explica a capacidade de troca catiônica destes solos, mas o C_{pyr} não poderia ser o responsável pela reposição dos nutrientes, e portanto de sua resiliência, uma vez que sua composição química não lhe confere esta possibilidade. Por outro lado, os FC podem ser uma possível fonte de nutrientes conforme já sugerido por Costa (2010), por conta de sua composição químico-mineralógica equivalente a fragmentos de rochas dispersos no solo, uma lembrança aos saprolitos de solos geogênicos, em que a sua decomposição bioquímica estaria liberando os seus componentes químicos, como P, K, Ca, Mg, Mn, Zn, Cu, entre outros. Esta hipótese é suportada por estudos mineralógicos que mostram que estes FC são constituídos por quartzo, metacaulinita, por vezes hematita, goethita e anatásio, localmente mica, feldspatos e clorita, além de cauixi, cariapé, conchas, cinzas e carvão (Costa *et al.* 2009). Estudos químicos também corroboram com esta hipótese, onde o P é um dos nutrientes chaves e que se encontra como mineral acessório, amorfo ou criptocristalino (Costa *et al.* 2006, 2009), nestes FC.

Os teores de P_2O_5 , em geral, variam entre 0,7 e 3% (Costa *et al.* 2006, 2009). Estes teores elevados também são encontrados em FC de sítio TPA na floresta amazônica Colombiana, aonde chegam a 2,90% P_2O_5 segundo Costa *et al.* (2011). Porém, Costa (2011) encontrou até 4,35% P_2O_5 ao analisar FC de Juruti (Pará), Silva (2010) determinou até 4,68 % P_2O_5 ao analisar FC do mesmo sítio, já Rodrigues (2010) encontrou até 11,16% P_2O_5 em FC de Bragança, estes últimos representam os teores mais elevados determinados em FC provenientes de TPA. Estes valores são superiores aos encontrados em vasilhames cerâmicos de sítios arqueológicos da Grécia (0,08 a 0,21% P_2O_5) (Iordanidis *et al.* 2009) e da Itália (0,12 a 1,01% P_2O_5) (Belfiori *et al.* 2010), por exemplo. Assim como nestes FC, na cerâmica de TPA o fósforo geralmente se encontra como material amorfo, ou seja, normalmente não são identificadas fases minerais de fósforo. No entanto, Maritan & Mazzoli (2004) e Maritan *et al.* (2009) identificaram vivianita ($Fe_3(PO_4)_2.8H_2O$) e mitridatita ($Ca_3Fe_4(PO_4)_4(OH)_6.3H_2O$) interpretados como fosfatos neoformados após o descarte destes FC no solo.

Por outro lado, em FC de TPA provenientes de Cachoeira-Porteira (Pará), Costa *et al.* (2004b) evidenciaram a presença dos fosfatos variscita-estrengita ($(Fe,Al)PO_4.2H_2O$), bem como Costa *et al.* (2009, 2012) e Rodrigues (2010) identificaram o fosfato crandallita-goyazita ($(Ca,Sr)Al_3(PO_4)2(OH)_5.H_2O$) em FC de Bragança (Pará). Nestes casos, o fosfato foi interpretado como oriundo do uso cotidiano das vasilhas, ou seja, quando eram empregados para preparar alimentos (Costa *et al.* 2004a, 2004b; 2006; 2009, 2011; Rodrigues, 2010). Duma (1972), Cackette *et al.* (1987) também defendem que o fósforo é um indicador de uso; Bollong *et al.* (1993) admitem esta possibilidade. Em contrapartida, Freestone *et al.* (1994) e Freestone *et al.* (1985) defendem que elevadas concentrações de P na cerâmica são oriundas do ambiente onde foram descartadas devido sua microestrutura, e portanto não seriam um indicador de uso. Esta é a hipótese classicamente utilizada para explicar a presença deste elemento em FC. Dunnel & Hunt (1990) afirmam que apenas concentrações de fósforo não são suficientes para indicar uso.

Porém, valores determinados por Legodi & Waal (2007) em torno de 1,18% P_2O_5, e por Polvorinos del Rio *et al.* (2005), em torno de 3%, em FC de peças utilitárias, se aproximam dos encontrados por Costa *et al.* (2004 a, 2006, 2009, 2011), corroboram com relação entre o enriquecimento de fósforo e o uso primordial para cozimento de alimentos.

Outra origem do fósforo é creditada à presença de apatita (oriunda de ossos) na matriz cerâmica, e neste caso é caracterizada como um mineral primário, como descrito por Ionescu *et al.* (2011), e por Maritan *et al.* (2009) por exemplo. E por fim, o fósforo é associado a processos de vitrificação como descrito por Morra *et al.* (2012). Porém, nenhuma destas duas últimas possibilidades é pertinente para os FC de TPA, visto que se trata de cerâmica sem vitrificação e a apatita é rara nestes FC (Costa *et al.* 2009).

Além da presença de fósforo já foram evidenciados altos teores de outros nutrientes em FC que estão intimamente ligados a sua composição mineralógica e aos antiplásticos adicionados a matriz argilosa, a exemplo os altos conteúdos de Ca quando empregadas conchas na confecção, como naqueles estudados por Rodrigues (2010) que alcançam 2,12% CaO (análise de FC pulverizado); ou mesmo, naqueles estudados por Iordanidis & Garcia-Guinea (2011) provenientes do norte da Grécia que não provém de TPA, e alcançam até 14,92% CaO (análises pontuais).

No entanto nenhum trabalho tentou demonstrar experimentalmente qual a real potencialidade dos fragmentos contribuírem gradualmente para fertilidade desses solos, e nem mesmo a origem dos elevados teores de P nestes FC.

Tabela 1: Estudos arqueométricos desenvolvidos com cerâmicas arqueológicas provenientes da Amazônia.

Autor	Área de estudo	Abordagem
Nicoli *et al.* (2001); Latini *et al.* (2001)	Acre	Apenas dados químicos
Silva (2010); Kern & Costa (1997); Coelho *et al.* (1996); Costa & Kern (1994)	Caxiuanã (Portel, PA)	Mineralogia e química
Costa *et al.* (2011); Silva (2010)	Quebrada Tacana	Mineralogia, química e textura
Costa *et al.* (2004a; 2004b; 2001; 1993; 1991); Pinto *et al.* (1992)	Cachoeira-Porteira (Oriximiná, PA)	Mineralogia e química
Silva (2010); Parente *et al.* (2009); Kern *et al.* (2013)	Barcarena	Mineralogia e química
Silva (2012); Rodrigues *et al.* (2012)	Da Mata (MA)	Mineralogia e química
Silva (2013)	Salobo (PA)	Mineralogia e química
Toyota (2009), Nunes *et al.* (2012)	Ilha do Marajó (PA)	Ênfase na composição Química
Silva *et al.* (2004)	Xingu (PA)	Ênfase na composição Química
Costa (2011); Silva (2010); Kern *et al.* (2013)	Juruti (Pará)	Mineralogia e química
Kern *et al.* (2013)	Ourilândia do Norte, Canaã dos Carajás, Marabá (PA)	Mineralogia e química
Rodrigues (2010); Silveira *et al.*(2011) Costa *et al.* (2012, 2009); Kern *et al.* (2013)	Bragança (PA)	Mineralogia e química
Rebelato (2007);	Hatahara (AM)	Associação densidade de cerâmica com química do solo
Cano *et al.* (2014)	São Paulo II (AM)	Dados cronológico e temperatura de queima.
Nunes *et al.* (2013)	Hatahara (AM)	Dados químicos
Hanzenfratz *et al.* (2011)	Lago Grande e Osvaldo (AM)	Dados químicos

2 OBJETIVOS DO ESTUDO

2.1 GERAL

O presente trabalho tem por objetivo identificar matérias primas, processos produtivos, modificações ocorridas durante o uso e após o descarte, e desta forma junto a experimentos avaliar as possíveis contribuições destes fragmentos a fertilidade das TPA.

2.2 ESPECÍFICOS

Investigar o processo de produção cerâmica na Amazônia no que diz respeito à proveniência das matérias primas (argila e antiplásticos), manufatura e temperaturas de queima por meio de caracterização química e mineralógica com a finalidade de avaliar as potenciais diferenças tecnológicas utilizadas por diferentes populações ceramistas da pré-história na Amazônia.

Demonstrar experimentalmente a real capacidade destes fragmentos de contribuir com a fertilidade dos solos TPA, mensurando a sua capacidade de dessorção, empregando para isto o fósforo, um dos nutrientes chaves e que se encontra como mineral acessório, amorfo ou criptocristalino, nestes fragmentos de TPA.

Obter vasilhas cerâmicas similares às arqueológicas e submetê-las às condições que simulem cozimento para avaliar a incorporação de fósforo e do cálcio nestes materiais, e assim comprovar experimentalmente a origem do fósforo e do cálcio a partir do cozimento de alimentos em vasilhas (panelas) de cerâmicas equivalentes àquelas encontradas nos perfis de solos TPA. Desta forma será possível avaliar a utilização destes elementos como indicador de uso pretérito para cozimento de alimentos.

3 Área de Estudo

Para o desenvolvimento deste trabalho foram selecionados três sítios arqueológicos com base em sua representação espacial e a disponibilidade de material cerâmico.

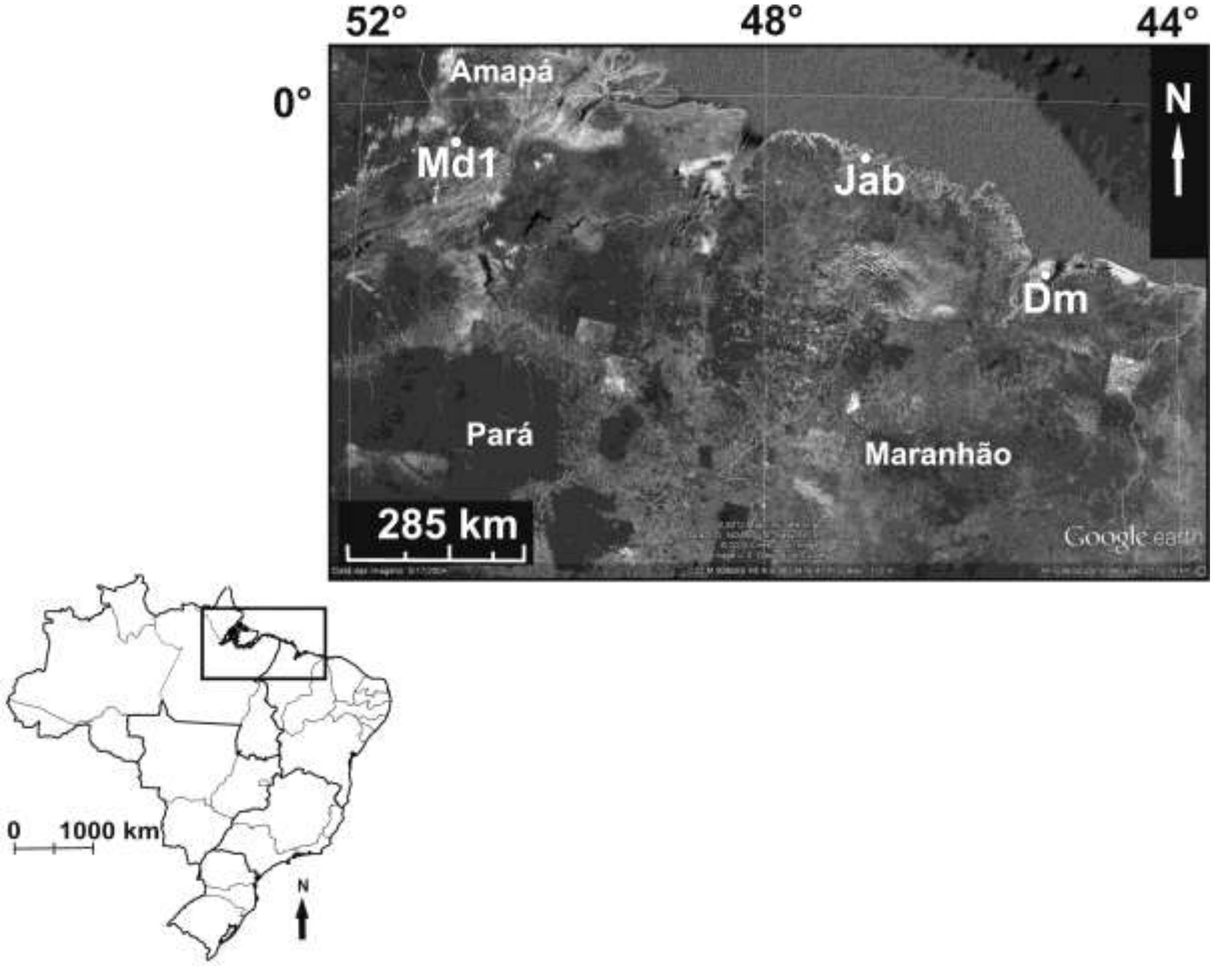

Figura 1: Localização dos sítios Monte Dourado 1(Md1), Jabuti (Jab) e Da Mata (Dm) selecionados para realização deste estudo.

3.1 SITIO MONTE DOURADO 1

O sítio Monte Dourado 1 está localizado no distrito de Monte Dourado pertencente ao município de Almeirim situado à margem direita do rio Jari no extremo norte do Estado do Pará (Tabela 2), distante cerca de 450 Km da capital, Belém. Este é um sítio habitação a céu aberto com alta densidade de material cerâmico e líticos em menor quantidade (Scientia 2011).

As amostras utilizadas neste trabalho provenientes desse sítio foram coletadas pela empresa Scientia Consultoria Científica Ltda. durante o resgate do mesmo. O sítio foi identificado e registrado na etapa de levantamento arqueológico realizado em maio/2011, no âmbito do Projeto de Arqueologia Preventiva nas áreas de intervenção da Usina Hidroelétrica (UHE) de Santo Antônio do Jari, AP/PA (IPHAN, Portaria15 de 05 de maio de 2011-Processo nº 01450.007673/2011-16).

O Monte Dourado 1 está assentado na porção sudeste da área destinada ao canteiro de obras que servirá à construção da UHE Santo Antônio do Jari (Distrito Industrial de Monte Dourado), que corresponde a uma área de interflúvio tabular com relevo onde o declive oscila entre o plano e o suave ondulado. O sítio está implantado sobre a alta vertente, no extremo sudeste de um platô, quando atingem cerca de 300 m acima do nível do mar (Scientia 2011).

Tabela 2: Coordenadas UTM de delimitação do Sítio Monde Dourado 1 (Scientia 2011).

Monte Dourado 1	Coordenada (UTM 22M) Datum SAD 69
Ponto Central	329.280/9.928.520
Limite Norte	329.260/9.928.820
Limite Sul	329.460/9.928.360
Limite Leste	329.580/9.928.540
Limite Oeste	329.220/9.928.580

3.2 SÍTIO JABUTI

O sítio Jabuti está localizado no município de Bragança situado à margem esquerda do rio Caeté no nordeste do estado do Pará, distante cerca de 210 Km da capital, Belém.

As amostras utilizadas neste trabalho provenientes desse sítio foram coletadas junto à equipe do Museu Paraense Emilio Goeldi (MPEG), coordenada pela Dra. Maura Imazio da Silveira, no âmbito do Projeto Estudos Arqueológicos na Costa do Pará sob a chancela do Programa de Estudos Costeiros MPEG (PEC/MPEG). O sítio está situado na “Reserva Extrativista Marinha Caeté–Taperuçu” (coordenadas UTM 22M 0550771 / 9358220) e foi registrado no IPHAN através da ficha de Cadastro Nacional de Sítios Arqueológicos (CNSA-PA - SA – 75-Número de catálogo: 2802) (Silveira 2008).

A paisagem desta região é constituída por campos salinos, mangues e áreas de floresta situadas nas ilhas de terra firme. A vegetação é constituída principalmente de gramíneas e espécies florestais em diferentes estágios de sucessão, que recobrem terrenos de terras firmes e várzeas, sendo a vegetação do sítio composta de florestas (secundárias) contíguas de mangue onde está presente uma grande intensidade de palmeiras, principalmente das espécies inajá (*Maximiliano regia*) e babaçu (*Orbygnia oleífera*). A floresta primitiva, ainda remanescente em pequenos tratos isolados, corresponde ao tipo geral das Florestas Tropicais Úmidas, subtipo Floresta Densa (Piccinin 2009).

Segundo Silveira *et al.* (2011) o Jabuti trata-se de um sítio tipo habitação, onde foi registrada presença de diversas manchas de TPA com profundidade variando de 60 cm a mais de 1m, e grande quantidade de material cerâmico que remetem a Tradição Mina descrita por Simões (1981), distribuído ao longo da superfície e em profundidade.

3.3 SÍTIO DA MATA

O sítio Da Mata está localizado na área rural do município de São José de Ribamar situado no extremo leste da Ilha de São Luís, as margens da Baía de São José no Estado do Maranhão, a 32 Km da capital, São Luís.

As amostras utilizadas neste trabalho provenientes deste sítio, assim como aquelas do Sítio Monte Dourado 1 foram coletadas pela empresa Scientia Consultoria Científica Ltda., porém aqui, durante o resgate dos sítios arqueológicos encontrados nas praças de torres da Linha de Transmissão de 230 KV que interliga as Subestações São Luís II e São Luís III (Maranhão), em implantação pela Eletronorte. Esta linha de transmissão possui aproximadamente 36 Km de extensão passando pelos municípios de São Luís, São José de Ribamar e Paço do Lumiar, e ao longo desta extensão foram localizados 7 sítios arqueológicos, dos quais 4 foram resgatados por se encontrarem exatamente nas praças das torres, um deles o Sítio Da Mata (coordenadas UTM 22M 595850/9715416). Este é um sítio cemitério/habitação, porém em algumas porções estão presentes também materiais históricos nos primeiros 10 cm de profundidade. O material está mais concentrado na porção mais alta do sítio e aqueles arqueológicos se concentram onde o horizonte A do solo é mais escuro (Scientia 2009).

Nesta região a vegetação é representada por capoeira alta, com predominância de palmeiras de babaçu e tucumã, além de alguns focos de árvores frutíferas. O sítio está alocado em relevo ligeiramente ondulado e baixo, apresentando feições colinares típicos de ambiente laterítico. Distante 30 m do sítio existe uma fonte de água cristalina denominado de riacho Jeniparana, usado como área de laser e de onde também é comercializada água como mineral por uma empresa local. Existe ainda uma área de mangue distante 800 m do sítio, de onde é possível ter acesso ao mar quando a maré está alta (Scientia 2009).

4 MATERIAIS E MÉTODOS

4.1 MATERIAIS

Para o presente estudo foram coletados FC nos três sítios indicados, os quais correspondem a paredes sem decoração em virtude de representarem quase a totalidade dos fragmentos coletados nos três sítios selecionados.

No sítio Monte Dourado 1, a área total de 235.200 m² (560m x 420m) foi delimitada por 401 tradagens. Destas, 218 apresentaram material arqueológico. Além das tradagens foi realizada uma trincheira, 2 sondagens $1m^2$ e 6 superfícies ampliadas (SA), no qual o material coletado na sondagem 16 (S16) da SA1 (coordenadas UTM 22M 329403/ 9928604) foi gentilmente cedido para realização deste trabalho. Nesta sondagem o horizonte TPA apresenta 70 cm de profundidade (Scientia 2011). A coletada das amostras foi realizada por níveis artificiais a cada 10 cm até não serem mais percebidos materiais arqueológicos, o que gerou 7 conjuntos de fragmentos, correspondendo um a cada nível artificial escavado, conforme apresentado no artigo 1. Neste sítio a maior concentração de material cerâmico estava no nível de 30-40 cm.

Por outro lado, o sítio Da Mata foi delimitado por 132 tradagens, das quais 68 apresentaram material arqueológico concentrado principalmente nos níveis 10-20 cm. Além das tradagens, foram escavadas 3 superfícies ampliadas (SA), cujo parte das amostras coletadas na SA 2 foi gentilmente cedida para elaboração deste trabalho. Da mesma forma, que o realizado no sítio Monte Dourado 1 a coleta foi estabelecida a cada 10 cm de profundidade até não serem mais percebidos materiais arqueológicos, o que gerou 5 conjuntos de fragmentos correspondendo um a cada nível escavado. Nesta área do sítio o horizonte TPA apresenta 30 cm de profundidade (Scientia 2009).

Já no sítio Jabuti foram verificadas duas áreas onde já existiam 2 perfis abertos, denominados Sondagem 1 e Sondagem 2. Também foi selecionada uma área de 100 m x 100 m, na qual foram abertas picadas em malha com espaçamento regular de 20 m. Nesta malha, as tradagens foram efetuadas com espaçamento 20 m e 10 m, o que possibilitou a identificação de 6 manchas TPA com tamanhos e profundidades variadas (Silveira *et al.* 2011). Os fragmentos aqui estudados foram coletados na Sondagem 1 onde o horizonte TPA apresenta 90 cm de profundidade. A coleta foi conduzida por níveis artificiais, inicialmente de

0-10 cm e posteriormente a cada 20 cm até não serem mais percebidos vestígios arqueológicos (Silveira *et al.* 2011), o que gerou 9 conjuntos de fragmentos correspondendo um a cada nível escavado, assim como ocorreu nos demais sítios. Estes conjuntos estão descritos no artigo 1.

4.2 PREPARAÇÃO DAS AMOSTRAS

As amostras após coletadas foram submetidas à secagem em ambiente de sala de trabalho refrigerada (25ºC e umidade relativa do ar inferior ao ambiente externo). O material de entorno (solo circundante) foi removido cuidadosamente por meio de breve lavagem com água destilada.

Nos sítios Monte Dourado 1 e Jabuti, os FC referentes a cada nível escavado foram quarteados até a obtenção de 300 g de FC devido a grande disponibilidade de material, o mesmo não foi necessário para o material do sítio Da Mata.

Para avaliação da influência da espessura dos FC em suas características químico-minerais, apresentada no artigo 1, os FC foram classificados segundo o proposto por Alves (1988) quanto a sua espessura (Tabela 3), uma vez que segundo Schiffer *et al.* (1994), Rye (1981), Braun (1983) vasilhas com paredes finas eram utilizadas para cozimento. Todos os fragmentos investigados apresentaram espessura igual ou inferior a 9 mm, ou espessuras igual ou superior a 12 mm.

Para todos os procedimentos que requereram pulverização, esta foi realizada em gral de ágata.

Tabela 3: Classificação da espessura dos FC segundo Alves (1988).

Espessura (mm)	Classificação
≤ 6	Muito fina
7- 9	Fina
10 – 14	Média
15 – 20	Grossa
≥20	Muito Grossa

4.3 DESCRIÇÃO MACROSCÓPICA

As amostras foram descritas com auxilio de estereomicroscópio binocular ZEISS-Stemi 2000-C e fotografadas com câmera Canon PowerShot G6 acoplada. Foram enfatizados fatores como coloração (utilizou-se Carta de Munsell), aspecto da pasta, e identificação dos antiplásticos adicionados à pasta durante o processo de confecção. Estes procedimentos foram realizados na Sala de Microscopia- Laboratório de Gemologia do Instituto de Geociências (IG)- Universidade Federal do Pará (UFPA).

4.4 CARACTERIZAÇÃO MINERALÓGICA E QUÍMICA

As caracterizações mineralógicas dos FC foram efetuadas por meio de difração de raios x segundo o método do pó. Para tal as amostras previamente pulverizadas foram compactadas em porta-amostra apropriado. Utilizou-se difratômetro XPERT PRO MPD equipado com goniômetro PW 3040/60 (theta-theta) PANalitical, ânodo de cobre ($\lambda CuK\alpha 1$ = 1,54060), filtro $K\beta$, gerador de tensão com 40 kV e gerador de corrente com 30mA. O intervalo de varredura foi de 5º a 75º, em função de aparecerem, nesse intervalo, os principais picos de caracterização de fases minerais. As análises foram realizadas com passo de 0,0170 (2θ) e tempo de passo de 10,3377 s. Utilizou fenda divergente fixa de 0,2393 mm. Para as interpretações dos difratogramas obtidos, utilizou-se o software XPERT HIGHSCORE.

Os FC foram submetidos à análise química total (elementos maiores, menores e traços) por meio de espectrometria de massa com plasma indutivamente acoplado (Inductively Coupled Plasma Mass Spectrometry-ICP-MS) e espectrometria de emissão ótica com plasma indutivamente acoplado (Inductively Coupled Plasma Emission Spectroscopy-ICP-OES). Estas análises foram realizadas no laboratório comercial AcmeLabs segundo o grupo de análise 4A&4B do referido laboratório. Foram utilizados ICP-MS Perkin Elmer Elan 9000 e ICP-OES Varian. A abertura das amostras foi realizada por meio de fusão do material previamente pulverizado empregando-se como agente fundente o tetraborato de lítio (Anachemia Science) e, posterior diluição em ácido nítrico (Merck).

Complementarmente, foram avaliados perda ao fogo (P.F.) por meio de análise gravimétrica, na qual se avaliou a diferença de massa após a calcinação a 1000 °C. A Tabela 4 apresenta os parâmetros químicos analisados conforme o descrito acima e seus respectivos limites de detecção.

Tabela 4: Parâmetros químicos (PQ) determinados e seus respectivos limites de detecção (LD).

PQ		LD	PQ		LD	PQ		LD
1	SiO_2	0,01 %	21	Cs	0,1mg.L$^-$	41	Y	0,1mg.L$^-$
2	Al_2O_3	0,01 %	22	Cu	0,1 mg.L$^-$	42	Zn	1mg.L$^-$
3	Fe_2O_3	0,04 %	23	Ga	0,5mg.L$^-$	43	Zr	0,1mg.L$^-$
4	CaO	0,01 %	24	Hf	0,1mg.L$^-$	44	La	0,1mg.L$^-$
5	MgO	0,01 %	25	Hg	0,1mg.L$^-$	45	Ce	0,1mg.L$^-$
6	Na_2O	0,01 %	26	Mo	0,1mg.L$^-$	46	Pr	0,02 mg.L$^-$
7	K_2O	0,01 %	27	Nb	0,1mg.L$^-$	47	Nd	0,3 mg.L$^-$
8	MnO	0,01%	28	Ni	0,1mg.L$^-$	48	Sm	0,05 mg.L$^-$
9	TiO2	0,01%	29	Pb	0,1mg.L$^-$	49	Eu	0,02 mg.L$^-$
10	P_2O_5	0,01%	30	Rb	0,1mg.L$^-$	50	Gd	0,05 mg.L$^-$
11	Cr_2O_3	0,002%	31	Sb	0,1mg.L$^-$	51	Tb	0,01 mg.L$^-$
12	P.F.	0,1%	32	Se	0,5mg.L$^-$	52	Dy	0,05 mg.L$^-$
13	Au	0,5 µg.L$^-$	33	Sn	1mg.L$^-$	53	Ho	0,02 mg.L$^-$
14	Ag	0,1mg.L$^-$	34	Sr	0,5mg.L$^-$	54	Er	0,03 mg.L$^-$
15	As	1mg.L$^-$	35	Ta	0,1mg.L$^-$	55	Tm	0,01 mg.L$^-$
16	Ba	1mg.L$^-$	36	Th	0,2mg.L$^-$	56	Yb	0,05 mg.L$^-$
17	Be	1mg.L$^-$	37	Tl	0,1mg.L$^-$	57	Lu	0,01mg.L$^-$
18	Bi	0,1mg.L$^-$	38	U	0,1mg.L$^-$			
19	Cd	0,1mg.L$^-$	39	V	8 mg.L$^-$			
20	Co	0,2 mg.L$^-$	40	W	0,5mg.L$^-$			

Essas determinações foram complementadas com as técnicas de:

Microscopia óptica (MOp): para qual foram preparadas lâminas delgadas com auxílio de serratriz manual Hillquist e placa aquecedora Fanem modelo 186, resina Haraldite da série 750 e endurecedor da série HY951. O desbaste do material foi realizado em politriz com carburunco da série 300, 600 e 1000. As lâminas foram preparadas no Laboratório de Laminação do IG-UFPA, e descritas na Sala de Microscopia- Laboratório de Gemologia (IG-UFPA) onde se utilizou microscópio Carl Zeiss Axiolab Pol 450910 e lentes de aumento de 10, 20, 50 e 100 vezes.

Microscopia eletrônica de varredura com sistema de espectrometria de energia dispersiva de raios-x acoplado (MEV-SED): os FC analisados por esta técnica foram previamente metalizados com Au. Estas análises foram realizadas no Laboratório de Microscopia Eletrônica de Varredura do IG-UFPA, na Martin-Luther-Universität Halle-Wittenberg (Uni-Halle, Alemanha) e Zentrum für Werkstoffanalytik in Lauf (Alemanha).

Análises termogravimétricas (TG) e termodiferencial (DTA): foram obtidas simultaneamente as curvas TG e DTA, utilizou-se 0,020 g de FC (previamente pulverizado) que foram aquecidos até 1100°C sob atmosfera inerte (N_2), taxa de aquecimento de 10°C/min. Estas análises foram realizadas no Laboratório de Caracterização Mineral do IG-UFPA e na Uni-Halle (Alemanha).

Espectroscopia de absorção no infravermelho (IV-FT): para este fim preparou-se inicialmente pastilha prensada de cada amostra pulverizada, utilizando-se 0,0015g de amostra e 0,2 g de brometo de potássio (KBr), sob pressão de 1,8 Kbar. Para esta análise empregou-se espectrômetro Vertex 70 Bruker com registros da faixa espectral de 400 a 4000 cm^{-1}, com medições a cada $4cm^{-1}$, no Laboratório de Mineralogia, Geoquímica e Aplicações do IG-UFPA.

Análise de Adsorção Gasosa (AAG): As análises foram realizadas por adsorção de N_2 a 77 K, na qual 0,2 g de FC previamente pulverizados foram submetidos à pré-tratamento a 120 °C. Para obtenção da área superficial específica foi empregado metodologia proposta por Brunaer-Emmett-Teller (BET). Estas análises foram realizadas na Uni-Halle.

4.5 ANÁLISES DE FERTILIDADE

Os FC previamente pulverizados foram também enviados a Universidade Federal de Viçosa- Departamento de Solos para serem determinados os parâmetros de fertilidade bem como as concentrações dos micronutrientes Fe, Mn, Cu e Zn, conforme a metodologia descrita na tabela 5.

Tabela 5: Parâmetros de fertilidade e micronutrientes (Fe, Mn, Cu e Zn) e métodos empregados para sua determinação.

	Extração	Quantificação
pH	1 : 2.5 (amostra:água)	Potenciométrico (Peech 1965)
P disponível	Mehlich 1	Coloromimetria (Murphy & Rilley1962)
Na trocável	Mehlich 1	Absorção atômica (Hesse 1971)
K trocável	Mehlich 1	Absorção atômica (Hesse 1971)
Fe, Zn, Mn, Cu disponível	Mehlich 1	Absorção atômica (Hesse 1971)
Ca, Mg trocável	KCl 1 mol L^{-1}	Absorção atômica (Hesse 1971)
Al trocável	KCl 1 mol L^{-1}	Titulação com NaOH 0,025 mol L^{-1} (McLean 1965)
H+Al (acidez potencial)	CH_3COO_2Ca 0,5 mol L^{-1}, pH 7	Titulação com NaOH 0,025 mol L^{-1} (McLean 1965)
Matéria orgânica (MO)		Carbono orgânico x 1,724 (Walkley & Black 1934)

4.6 EXPERIMENTO DE DESSORÇÃO DE FÓSFORO

Para este experimento foram selecionadas 2 amostras de cada sítio, uma coletada no horizonte A e outra no AB. Foram avaliados a influência do tamanho do fragmento em dois níveis: ≤ 2 cm e 2 a 4 cm. Desta forma, foram utilizadas 4 amostras de cada sítio, totalizando 12 amostras no experimento. Cada amostra foi submetida a contato com solução de pH constante 4,5±0,1 durante 30, 60, 90, 120, 150 dias. Após o tempo de contato foram determinadas as concentrações de P_2O_5 nas soluções por meio de espectrofotometria na região do visível, método colorimétrico. Empregou-se a metodologia Hach 8048 e espectrofotômetro Hach DR 5000 no Laboratório de Mineralogia Geoquímica e Aplicações do IG-UFPA.

A quantidade de fósforo dessorvido por grama de cerâmica (qe) foi calculado através da Equação (1):

$$qe = [(Ce-Ci)V]/(Mc.1000) \qquad (1)$$

Onde:

qe: quantidade fósforo dessorvido, no equilíbrio, por grama de cerâmica (mg g^{-});

Ci: concentração inicial da solução (mg L^{-});

Ce: concentração de fósforo na solução, no equilíbrio;

V: volume da solução usada no experimento (mL);
Mc: massa de cerâmica utilizada (mg).

Para o estudo do equilíbrio de dessorção os valores obtidos experimentalmente foram aplicados aos modelos matemáticos de Langmuir (1918) (Eq.2) e Freundlich (1906) (Eq.3) os mais utilizados para descrever sistema sólido-líquido. Foram calculados os valores das respectivas constantes e dos coeficientes de correlação. Os dados foram ajustados por regressão não linear através do software Oringin 7.

$$qe = (Qmax.Ce) / (K_L+Ce) \qquad (2)$$

Onde:
qe: quantidade de fósforo, no equilíbrio, por grama de cerâmica (mg g^-);
Ce: concentração de fósforo na solução, no equilíbrio (mg L^-).
Qmax: máxima capacidade de dessorção (mg.g^-);
K_L: constante de equilíbrio (adimensional).

$$qe = K_F.Ce^{1/n} \qquad (3)$$

Onde:
qe: quantidade de fósforo, no equilíbrio, por grama de cerâmica (mg g^-);
Ce: concentração de fósforo na solução, no equilíbrio (mg L^-).

As constantes K_F e n são indicativas da extensão da dessorção e do grau de heterogeneidade da superfície, respectivamente.

A partir dos valores calculados de Qmax e K_L foi calculado o parâmetro de equilíbrio R_L (Eq.4), que indica se a dessorção é favorável ou desfavorável.

$$R_L= [1/(1+K_L.Qmax)] \qquad (4)$$

4.7 EXPERIMENTO DE SIMULAÇÃO DE COZIMENTO EM PANELAS CERÂMICAS: FORMAÇÃO DE FOSFATOS.

Para este experimento foram confeccionadas 6 panelas cerâmicas utilizando-se a técnica acordelada, em um centro ceramista tradicional da cidade de Juruti (Pará) pela artesã Maria da Motta Coimbra. A argila utilizada na confecção das panelas foi coletada no Lago do Piranha (coordenadas UTM 21M 598464/9755450), a jazida de uso comunitário dos artesões da região de Juruti. Utilizou-se como antiplástico cariapé (cinzas da parte mais externa de troncos de árvores do gênero *Moquilea* e *Licania utilis* (Linné 1925), de amplo emprego em fragmentos cerâmico de diversos sítios com TPA (Costa *et al.* 2009) e utilizado até o presente pelas populações tradicionais na Amazônia (Meggers & Evans 1957).

As panelas formatadas foram secas ao ar por 48 h e posteriormente, calcinadas em uma depressão escavada no terreno coberta com lenha por 2 h. Esta etapa de campo foi realizada em novembro de 2010 e contou com a colaboração da Dra. Jucilene Amorim Costa, e com apoio logístico da Scientia Consultoria. Amostras da argila e o cariapé foram caracterizadas por DRX, ICP-OES e MEV-SED conforme ocorreu com os FC.

Em laboratório, as panelas foram submetidas ao contato com soluções de P_2O_5 0,03 % e CaO 0,03 % sob temperatura de ebulição. A cada 200 h uma panela foi retirada do experimento, para serem avaliadas suas alterações químicas e/ou mineralógicas através das técnicas de DRX, ICP-OES e MEV-SED, conforme descrito anteriormente. As análises químicas por ICP-OES foram efetuadas nas paredes e tampas das panelas, enquanto que as análises pontuais por MEV-SED contemplaram também suas bases. O tempo total do experimento foi de 1200 h.

5. RESULTADOS E DISCUSSÕES

Os resultados e discussões, além de novas informações sobre materiais e métodos, se encontram na forma de 3 artigos**:**

1. Pre-historic production of ceramics in the Amazon: Provenience, raw materials, and firing temperatures, submetido a Applied Clay Science;

2. Contribution of the fertility potential of archaeological sherds to the long-term fertility of Amazonian Dark Earth, submetido ao Journal Archaeological Science;

3. Phosphorus in archeological ceramics as evidence of the use of the pots for cooking food, submetido ao Journal Archaeological Science.

5.1 PRE-HISTORIC PRODUCTION OF CERAMICS IN THE AMAZON: PROVENIENCE, RAW MATERIALS, AND FIRING TEMPERATURES

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

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Abstract

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 antiplastics. The pots were fired at ±600°C, leading to the formation of an amorphous metakaolinite matrix in which a number of different types of antiplastic can be found. These antiplastics, 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.

Keywords: sherds; antiplastic; crushed rocks; shells; cariapé; Amazon region.

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, antiplastics), 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 (Iordanidis et al., 2009; Mohamed et al., 2010). 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 (Moropoulou *et al.*, 1995; Romani *et al.*, 2000, Hein *et al.*, 2004; Papadopoulou *et al*., 2004; Gimenez *et al.*, 2006; Fermo *et al*., 2008; Rathossi and Pontikes, 2010; Iordanidis and Garcia-Guinea, 2011; Montana et al., 2011, Kramar et al., 2012, Maritan et al., 2013).

In the Amazon, similar studies have been and are being developed, although perspectives on the diversity of raw materials, manufacturing techniques, firing temperatures are still limited (Costa et al., 2004a, Costa et al., 2004b; Costa et al., 2009, Costa et al, 2011, Costa et al., 2012). Studies of anthropogenic soils, especially Amazonian Dark Earth (ADE) are far more numerous (Smith, 1980; Kern and Kampf, 1989; Costa and Kern, 1999; Glaser et al., 2001; Lima et al., 2002; Lehmann et al, 2003; Woods et al., 2009; Silveira et al., 2011; Lemos et al., 2011; Mescouto et al., 2011; Costa et al., 2013; Schmidt et al., 2014).

Given these shortcomings, the present study investigated the production of archeological ceramics in the Amazon, with regard to the origin of raw materials (clay and antiplastics), the manufacturing processes, and firing temperatures through the chemical and mineralogical characterization of samples from different sites. This permitted the identification of variations in the productive process in distinct pottery-making populations, providing new insights into the complexity of the prehistoric occupation of the Amazon.

Materials and Methods

Materials

For the present study, sherds vessels were obtained from three archeological sites in the Brazilian Amazon – Monte Dourado 1, Jabuti and Da Mata – 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.

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, 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 archeological remains were encountered (Scientia, 2011). The results of the analysis of the style of pottery found at this site have not yet been made available.

Da Mata

The Da Mata site (central coordinates: UTM 22M 595850/9715416) is located in the municipality of São José do Ribamar, in the eastern extreme of São Luís Island, in São José Bay, in the Brazilian state of Maranhão. The samples from this site (CF-DM) were also collected by Scientia Scientific Consultants Ltd. in 2009, under the supervision of Dra. Dirse Clara Kern, who kindly provided the material for the present study.

Da Mata is a cemetery and habitation site, which was delimited using 132 boreholes, of which, 68 produced archeological material. The ADE horizon extended from the surface to a depth of 30 cm. The excavations were conducted in artificial layers of 10 cm until no further archeological remains were encountered (Scientia, 2009). As for the Monte Dourado 1 samples, information on the pottery style is still unavailable.

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 Silveira. 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).

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 shards 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 antiplastics 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 sherds 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 complemented by scanning electron microscopy coupled to an energy-dispersive X-ray spectrometry system (SEM-EDS), using a LEO 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 metalized 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 ($\lambda CuK\alpha 1$ = 1.54060), $K\beta$ filter, 40 kV tension generator and 30 mA current generator. The scanning interval was 5–75º, which encompasses the principal peaks 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 (N_2), 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 spectroscope (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 with a spectral range of 400–4000 cm^{-1}, with measurements taken at every 4 cm^{-1}, in the UFPA Mineralogy, Geochemistry and Applications Laboratory.

The chemical composition representative of the total sample (major, minor, and trace elements) was obtained by Inductively Coupled Plasma Mass Spectrometry (ICP-MS Perkin Elmer Elan 9000) and Inductively Coupled Plasma Emission Spectroscopy (ICP-OES Varian) by AcmeLabs. For this, the pulverized samples were prepared by fusion with lithium tetraborate (Anachemia Science) followed by dilution in nitric acid (Merck). The Loss on

Ignition (LOI) was determined by gravimetry, which consists of the measurement of the mass following calcination at 1000°C, procedure also conducted by AcmeLabs.

Results

The antiplastics 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 (Figure 1a). At Jabuti, most samples contained only shell fragments (Figure 1b), 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 (Figure 1c).

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; Meggers and Evans, 1957). To prepare the antiplastic, the bark is pulverized and calcined to produce amorphous siliceous ash, sometimes in the form of tridimite-cristobalite, SiO_2 (Costa, et al., 2004b, 2011).

The mineral antiplastic identified in the Monte Dourado 1 samples was composed primarily of fragments of ground rock containing quartz (SiO_2), ilmenite ($FeTiO_3$), plagioclases ($(Na_{1-x}, Ca_x)Al_{1+x}Si_{3-x}O_8$), cordierite ($(Mg,Fe)_2Al_4\ Si_5O_{18}.nH_2O$), and cristobalite ($SiO_2$), identified by XRD. It is important to note here that the cristobalite may be related to the cariapé, given that amorphous silica may crystalize into cristobalite during firing (Costa, et al., 2004b, 2011).

Grains and fragments of quartz were found in all the samples (Figure 1) and may have been added intentionally as a antiplastic, but would also have been a principal component of the raw material, which hampers the identification of what material was added to the clay.

The quartz grains vary considerably in size and shape, although they are generally sub-angular and distributed evenly within the clay matrix. The grains were coarser in the samples from Monte Dourado 1.

Table 1: Description of the sherds analyzed in the present study. (*) Most common antiplastic.

Samples	Depth (cm)	Antiplastic	Surface colour (Munsell colour chart)	Manufature technis after external aspects	n
			Monte Dourado 1		
CF-MD1 9 a	0-10	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	22
CF-MD1 12 a	0-10	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	3
CF-MD1 9 b	10-20	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	19
CF-MD1 9b	10-20	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	3
CF-MD1 12c	20-30	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	13
CF-MD1 12 c	20-30	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	3
CF-MD1 9 d	30-40	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	13
CF-MD1 12 d	30-40	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	4
CF-MD1 9 e	40-50	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface es	16
CF-MD1 12 e	40-50	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	4
CF-MD1 9 f	50-60	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	14
CF-MD1 12 f	50-60	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	4
CF-MD1 9 g	60-70	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	13
CF-MD1 12 g	60-70	Cariapé	(5YR4/3)	coil tecnique / smooth on the surface	5
				M. Dourado ≤ 9 mm	110
				M.Dourado ≥ 12 mm	26
				Total	136
			Da Mata		
CF-DM 9 a	0-10	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	14
CF -DM 12 a	0-10	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	8
CF -DM 9 b	10-20	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	28
CF -DM 12 b	10-20	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	10
CF -DM 9 c	20-30	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	18
CF -DM 12 c	20-30	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	8
CF -DM 9 d	30-40	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	14
CF -DM 12 d	30-40	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	12

continuação

CF -DM 9 e	40-50	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	16
CF -DM 12 e	40-50	mineral* + cariapé	(5YR5/4)	coil tecnique / smooth on the surface	9
				Da Mata ≤ 9 mm	90
				Da Mata ≥ 12 mm	47
				Total	137
			Jabuti		
CF-JAB a	0-10	shell*+ cariapé	(5YR5/2)	n.i	5
CF-JAB bc	10-30	shell*+ cariapé	(5YR5/2)	n.i	4
CF-JAB de	30-50	Shell	(5YR5/2)	n.i	4
CF-JAB fg	50-70	Shell	(5YR5/2)	n.i	11
CF-JAB h	70-90	Shell	(5YR5/2)	n.i	4
CF-JAB i	90-110	Shell	(5YR5/2)	n.i	5
CF-JAB j	110-130	Shell	(5YR5/2)	n.i	5
CF-JAB l	130-150	Shell	(5YR5/2)	n.i	7
CF-JAB m	150-70	Shell	(5YR5/2)	n.i	7
				Total	52

Figure1: Photomicrogaphs of sherds analyzed in the present study showing different antiplastics: (a) Cariapé (Da Mata); (b) shell (Jabuti); (c) mineral (Monte Dourado 1). Optical microscope, // with 10 x lens.

The matrix

Metakaolinite

The principal phase of the basic matrix of the ceramic samples was metakaolinite. The backgrounds of the XRD spectra had many shoulders and elevations, which indicates the presence of a large number of amorphous phases (Figure 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 (Figure 1). The presence of components of metakaolinite is indicated by the aluminosilicate characteristics of the matrix found in the SEM/EDS spot analyses (Figure 3), as well as 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 (Figure 4b). In addition, bands of Si-O and Si-O-Al stretching related to the other silicates identified by XRD (Madejová and Komadel, 2001) were found in the sherds from all three sites.

Quartz

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

Muscovite

This mineral was rarely observed under optical microscopy, but was confirmed as an accessory mineral by XRD in all the samples (Figure 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 antiplastic used at this site.

Iron oxy-hydroxides

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

Anatase

Anatase was identified only by XRD and is probably found in nanocrystals within the matrix of the Jabuti and Da Mata samples (Figure 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.

Phosphates

Phosphates, principally of aluminum, were common accessories in the samples, but were generally amorphous, and only rarely found in cryptocrystalline forms, such as variscite-strengite and, more rarely, rhabdophane (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 crandallite-goyazite, observed in large quantities by XRD (Figure 2). The presence of this mineral was confirmed by an endothermic peak in the thermograms of the samples at 440°C (Figure 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 (Figure 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 antiplastic (Figure 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 (Figure 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 ($CaMgFe(PO_4)_2(OH).4(H_2O)$ was also identified by XRD in the sherds from Monte Dourado 1 (Figure 2), although the endothermic dehydroxylation peak found at 400°C (Hochleitner and Fehr, 2010) was not observed in the thermograms (Figure 4a), presumably as a result of its low concentration, as confirmed by the chemical data.

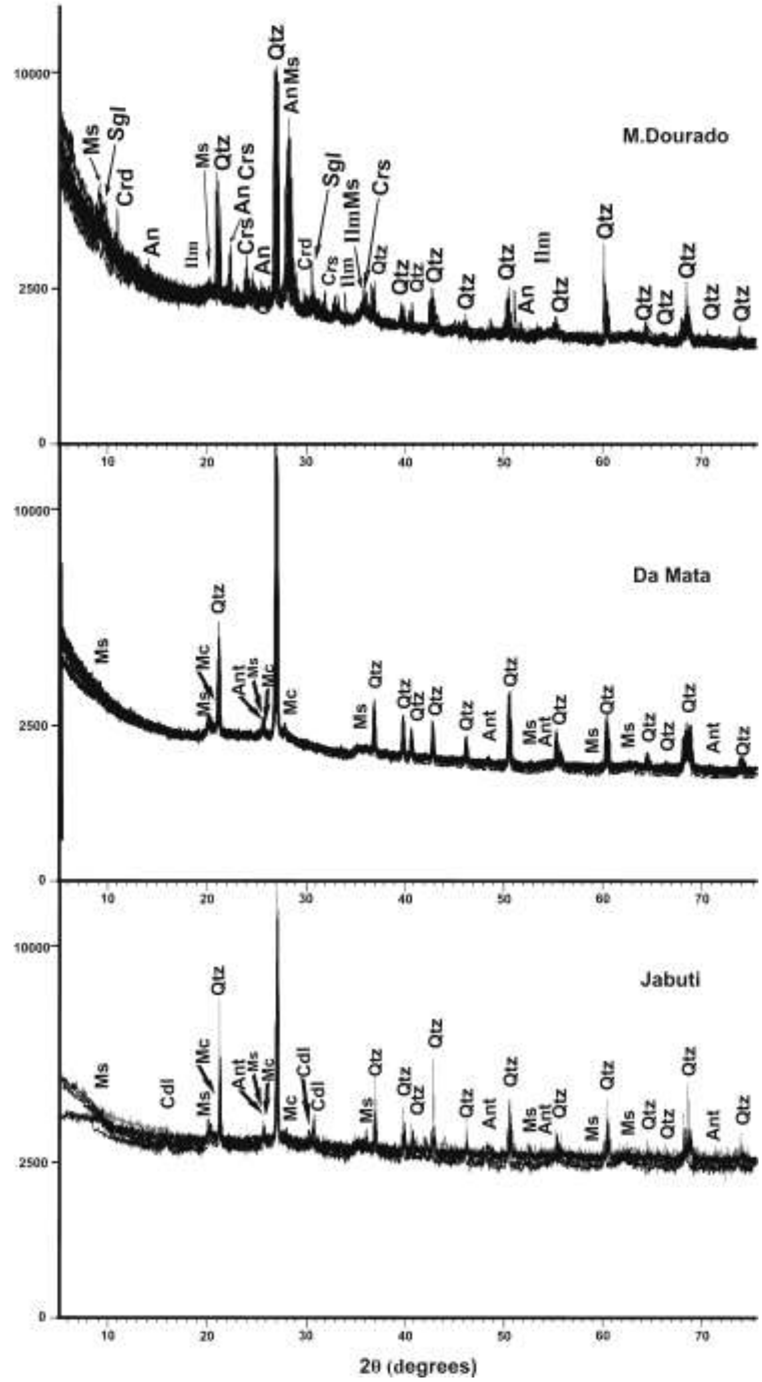
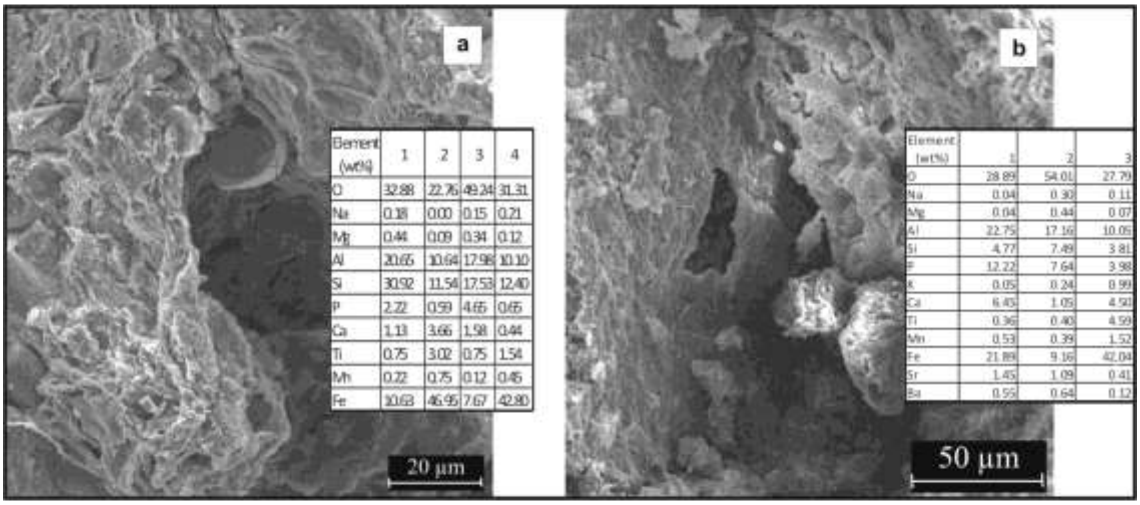


Figure 2: Mineralogical composition of the sherds by XRD powder analysis. Qtz = quartz; Crd = cordierita; Ms = muscovite; Cld = crandallite-goyazite; Ant = anatase; Crs = cristobalite; Ilm = ilminite; Mc = feldspar; An = plagioclases;



Element (wt%)	1	2	3	4
O	32.88	22.76	49.24	31.31
Na	0.18	0.00	0.15	0.21
Mg	0.44	0.09	0.34	0.12
Al	20.65	10.64	17.98	10.10
Si	30.92	11.54	17.53	12.40
P	2.22	0.59	4.65	0.65
Ca	1.13	3.66	1,58	0.44
Ti	0.75	3.02	0.75	1.54
Mn	0.22	0.75	0.12	0.45
Fe	10.63	46.95	7.67	42.80

Element (wt%)	1	2	3
O	28.89	54.01	27.79
Na	0.04	0.30	0.11
Mg	0.04	0.44	0.07
Al	22.75	17.16	10.05
Si	4.77	7.49	3.81
P	12.22	7.64	3.98
K	0.05	0.24	0.99
Ca	6.45	1.05	4.50
Ti	0.36	0.40	4.59
Mn	0.53	0.39	1.52
Fe	21.89	9.16	42.04
Sr	1.45	1.09	0.41
Ba	0.55	0.64	0.12

Figure 3: Scanning electromicrographs and chemical spot analyses conducted by SEM/EDS. Samples from (a) Jabuti and (b) Monte Dourado 1.

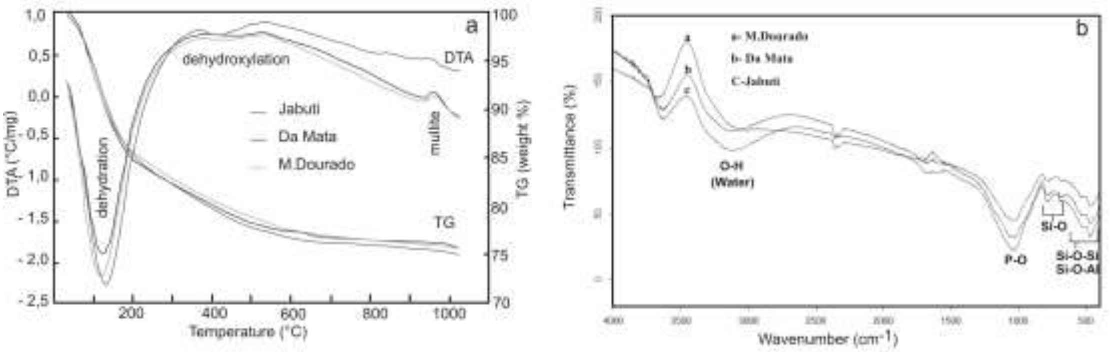


Figure 4: a) Representative thermal analysis curves (TG/DTA) for the sherds analyzed in the present study. b) FT-IR of the sherds showing the P-O bands.

Table 2: Chemical composition (major, minor elements and Loss on Ignition –LOI) of the sherds analyzed in the present study.

Samples	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	SrO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI	Total	n
	wt%													
	Monte Dourado 1													
CF-MD1 9a	49.32	17.08	11.87	1.35	2.75	0.02	0.91	0.36	5.40	2.44	0.13	8.10	99.71	22
CF-MD1 12b	44.37	16.60	19.09	2.12	3.14	0.02	0.83	0.25	7.32	1.40	0.25	4.20	99.57	3
CF-MD1 9b	47.86	15.95	13.49	2.02	3.46	0.02	1.10	0.35	5.68	2.04	0.16	7.60	99.71	19
CF-MD1 12b	46.83	16.29	15.07	2.20	3.69	0.02	1.08	0.52	4.68	1.49	0.17	7.70	99.72	3
CF-MD1 9c	48.75	17.32	10.02	1.69	2.96	0.02	0.74	0.33	4.90	2.56	0.12	10.30	99.69	13
CF-MD1 12c	51.29	13.96	13.66	2.31	3.73	0.02	1.13	0.32	4.09	1.17	0.15	7.90	99.71	3
CF-MD1 9d	47.74	15.73	13.19	1.96	3.24	0.02	0.78	0.24	5.16	1.94	0.15	9.60	99.73	13
CF-MD1 12d	42.20	15.26	15.76	1.64	2.83	0.01	0.61	0.08	6.03	2.17	0.16	12.90	99.64	4
CF-MD1 9e	47.56	15.68	12.44	1.73	3.18	0.02	0.89	0.27	5.61	2.44	0.14	9.70	99.64	16
CF-MD1 12e	40.39	18.69	14.45	2.90	4.49	0.02	1.15	0.24	4.90	2.86	0.16	9.40	99.63	4
CF-MD1 9f	45.64	15.43	12.69	2.21	3.93	0.02	0.93	0.27	5.87	2.50	0.15	10.0	99.62	14
CF-MD1 12f	49.31	16.14	11.17	1.94	3.80	0.02	1.09	0.29	4.57	2.55	0.13	8.70	99.69	4
CF-MD1 9g	44.78	17.03	11.81	1.43	2.97	0.02	0.76	0.29	4.46	3.69	0.12	12.40	99.74	13
CF-MD1 12g	47.52	17.49	11.58	2.25	4.43	0.02	1.28	0.29	2.90	1.93	0.14	9.90	99.71	5
[1]CF-MD1 ≤9 mm	**47.38**	**16.32**	**12.22**	**1.77**	**3.21**	**0.02**	**0.87**	**0.30**	**5.30**	**2.52**	**0.14**	**9.67**	**99.69**	**110**
[2]CF-MD1 ≥ 12 mm	**45.99**	**16.35**	**14.40**	**2.19**	**3.73**	**0.02**	**1.02**	**0.28**	**4.93**	**1.94**	**0.17**	**8.67**	**99.67**	**26**
	Da Mata													
CF-DM 9a	55.48	18.67	3.39	0.41	0.22	0.01	0.11	0.62	1.22	1.19	0.02	18.50	99.83	14
CF-DM 12a	58.29	19.33	2.78	0.39	0.25	0.01	0.12	0.63	1.43	1.00	0.02	15.60	99.84	8
CF-DM 9b	56.43	17.88	3.43	0.38	0.27	0.01	0.12	0.53	1.19	1.06	0.02	18.60	99.91	28
CF-DM 12b	53.20	19.49	3.61	0.38	0.26	0.01	0.16	0.81	1.32	0.92	0.03	19.60	99.78	10
CF-DM 9c	52.92	20.26	3.14	0.63	0.25	0.01	0.10	0.93	1.23	0.90	0.03	19.50	99.89	18
CF -DM 12c	51.92	21.19	2.41	0.39	0.28	0.01	0.17	0.56	1.44	1.20	0.06	20.20	99.82	8
CF-DM 9d	54.76	19.11	4.23	0.51	0.25	0.01	0.12	0.68	1.22	0.98	0.03	18.00	99.89	14
CF -DM 12d	49.23	2244	2.52	0.35	0.24	0.01	0.09	0.43	1.45	1.31	0.02	21.80	99.88	12
CF-DM 9e	60.16	15.81	4.86	0.65	0.34	0.01	0.15	0.80	0.95	0.78	0.08	15.30	99.88	16
CF-DM 12e	53.69	20.13	2.79	0.35	0.21	0.01	0.12	0.66	1.41	1.09	0.01	19.40	99.86	9
[1]CF -DM ≤9mm	**55.95**	**18.35**	**3.81**	**0.52**	**0.27**	0.01	**0.12**	**0.71**	**1.16**	**0.98**	**0.04**	**17.98**	**99.88**	**90**
[2] CF -DM≥ 12mm	**53.27**	**20.52**	**2.82**	**0.37**	**0.25**	0.01	**0.13**	**0.62**	**1.41**	**1.10**	**0.03**	**19.32**	**99.84**	**47**

continuação

Samples	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	SrO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI	Total	n
	wt%													
	Jabuti													
CF-JAB a	51.41	17.21	5.58	0.81	0.45	0.01	0.18	0.74	1.08	4.38	0.01	17.90	99.75	5
CF-JAB bc	54.31	17.13	5.91	0.53	0.62	0.02	0.19	0.90	1.08	6.40	0.01	12.70	99.78	4
CF-JAB de	39.62	20.11	4.59	0.37	0.97	0.04	0.10	0.52	1.10	7.64	0.03	24.70	99.75	4
CF-JAB fg	45.85	17.81	4.73	0.65	1.37	0.16	0.16	0.80	1.17	6.53	0.03	20.50	99.60	11
CF-JAB h	35.65	21.11	4.52	0.59	1.49	0.16	0.16	0.75	1.19	9.26	0.03	24.90	99.65	4
CF-JAB i	31.09	22.07	5.09	0.33	1.80	0.20	0.14	0.59	1.11	11.16	0.03	26.20	99.61	5
CF-JAB j	37.34	21.19	4.70	0.62	1.44	0.19	0.18	0.72	1.13	7.86	0.03	24.40	99.61	5
CF-JAB l	39.12	18.97	5.88	0.79	2.12	0.41	0.15	0.79	1.09	8.82	0.02	21.60	99.35	7
CF-JAB m	39.93	19.76	6.30	0.57	1.28	0.14	0.18	0.82	1.25	7.73	0.02	21.80	99.64	7
[3]CF Jabuti	**41.59**	**19.48**	**5.26**	**0.58**	**1.28**	**0.15**	**0.16**	**0.74**	**1.13**	**7.75**	**0.02**	**21.63**	**99.75**	**52**
[3]CF Da Mata	**54.61**	**19.43**	**3.32**	**0.44**	**0.26**	**53.6**	**0.13**	**0.67**	**1.29**	**1.04**	**0.03**	**18.65**	**99.86**	**137**
[3]CF M. Dourado	**46.68**	**16.33**	**13.31**	**1.98**	**3.47**	**196.7**	**0.95**	**0.29**	**5.11**	**2.23**	**0.15**	**9.17**	**99.68**	**136**
[4]C.Porteira	65.55	16.37	5.79	0.63	0.43	n.d	0.69	0.9	0.86	2.37	0.01	n.d.	-	-
[5]Manduquinha.	71.35	8.60	4.54	0.26	0.19	n.d	0.98	0.59	0.4	1.31	0.01	11.63	99.86	-
[6]Q Tacana	56.53	17.36	3.43	0.42	0.04	n.d	0.06	1.27	1.01	1.34	0.01	18.40	99.87	-
[7]CCR	64.90	14.60	4.40	4.12	2.24	374.6	3.46	3.45	0.52	0.15	0.07	n.d	-	-
[8]PAAS	62.80	18.90	6.50	1.30	2.20	237.1	1.20	3.70	1.00	0.16	0.11	n.d	-	-

(1) Média dos CF do sítio com espessura inferior a 9 mm;(2) média dos CF do sítio com espessura superior a 12 mm; (3) média de todos amostras do sítio; (4) Average of CF from Cachoeira-Porteira (Costa *et al.* 2004a);(5) Average of CF from Manduquinha (Coelho *et al.*. 1996); (6) Average of CF from Quebrada Tacana(Costa *et al.*. 2011); (7) Continental crustal rock (Wedepohl. 1995); (8) Argilas australianas pós- arqueanas (Taylor and McLennan. 1985); n.d.: não determinado; n: número de CF que compõe a amostra

Discussion

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 ($Al_2Si_2O_7$) 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 (Figure 3), but would have been transformed into mullite at a firing temperature of 950°C (Evans and White, 1958). No mullite was found in the present analyses.

Kaolinite is the clay mineral best suited for the production of ceramic vessels, and is still used in the present day for the manufacturing of bricks and roof 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 K_2O in the Monte Dourado 1 samples (< 0.3wt%) reflect the discreet presence of muscovite. In the Da Mata and Jabuti samples, the slightly higher concentrations of K_2O (0.4–0.8%) indicate the presence of muscovite or potassium feldspars, which would have been added as antiplastic.

The levels of CaO (2.69–4.49% by weight) associated with those of Na_2O (0.6–1.28%) observed in the Monte Dourado 1 samples confirm the presence of plagioclases (Figure 5a) of the labradorite type (mean CaO/Na_2O ratio = 3.7), identified as antiplastic, whereas in the Da Mata samples, CaO and Na_2O were found at extremely low levels (Na_2O: < 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 TiO_2 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 (amphibolite) which was crushed and added to the basic clay as a antiplastic. Amphibolites are part of the Ipitinga Group, a Paleo-Proterozoic geologic unit mapped near the study site (Vasquez et al., 2008). This eliminates the possible use of saprolite (clay with rock particles) derived from these rocks as a raw material, given that the plagioclases and cordierite are unable to resist typical tropical weathering. On the other, the relatively high levels of CaO found in the Jabuti samples, independent of the Na_2O (< 0.18%: Figura 5 b), and combined with the high values of SrO (≤ 0.16%), in addition to the high levels of P_2O_5, which respond to the presence of crandallite-goyazite, differentiate 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.

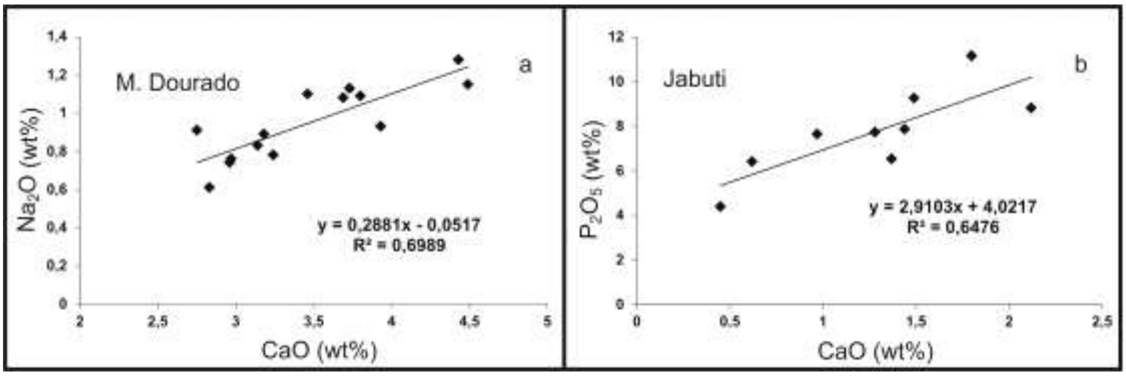


Figure 5 – a- Dispersion diagram showing the positive correlation between the CaO and Na_2O supporting the domain of the plagioclase labradorite in the samples from the Monte Dourado 1 site. b- Dispersion diagram showing a marked positive correlation between the CaO and P_2O_5 supporting the crandallite-goyazite domain in the Jabuti samples.

The results of the chemical-mineralogical analyses of the sherds (Figure 6 a, b) emphasize the distinct characteristics of each group of samples, which probably reflects the different antiplastics (cariapé, shell, and crushed rock) used in the manufacturing process. Rare crushed rocks, such as the mineralized amphibolites in the ilmenite in the Monte Dourado 1 sherds represent a major, anomalous divide, while the large quantities of shell substituted by aluminum phosphates in the Jabuti sherds, together with the relatively high levels of MgO, contribute to the discrimination of the sherds from this site.

Cariapé was the predominant antiplastic 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 antiplastics used during the production process and the possible contamination by phosphates after the production of the pots. 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 P_2O_5, 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 pot were used for cooking food, given that they are better conductors of heat, and are more resistant to thermal shock.

The P_2O_5 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 Iordanidis et al. (2009) CCR and PAAS (Table 2; Figure 6a). The lowest levels of P_2O_5 (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).

The matrices of the Jabuti and Da Mata sherds were very similar in chemical terms (Table 1; Figure 7 a, b), except of course in the levels of CaO, SrO, MgO, and P_2O_5, as well as their mineralogical composition, with the exception of the crandallite-goyazite found only at Jabuti. The higher values for SiO_2 recorded at Da Mata correspond to the abundance of cariapé, formed basically of SiO_2, both amorphous and in the form of tridimite-cristobalite. These similarities in the matrix used at the two sites is further reinforced by the distribution pattern of trace elements (Figure 7 a) and the rare earth elements normalized by the chondrites (Figure 7 b). 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 (Vonhof et al., 1998; Findlater et al., 2014). 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 argilites made up of kaolinite, quartz, and illite/muscovite, as well as alluvial and lacustrine deposits of the coastal plains (Behling and Costa, 2004).

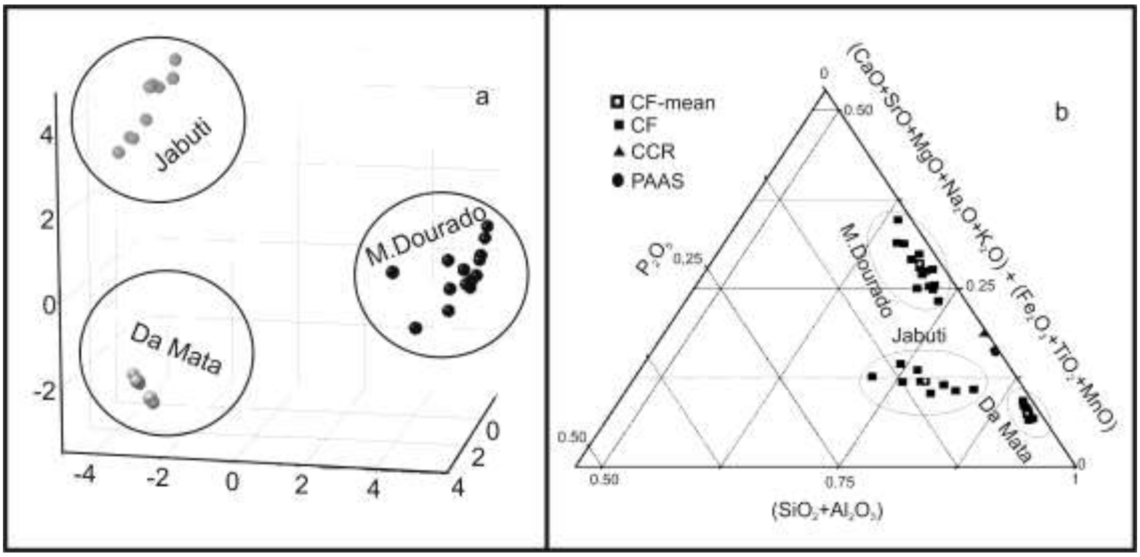


Figure 6 - a) XRD cluster analyses showing the clear distinction between the three sites; b) Chemical diagrams discriminating the three sites based on the chemical composition of their sherds.

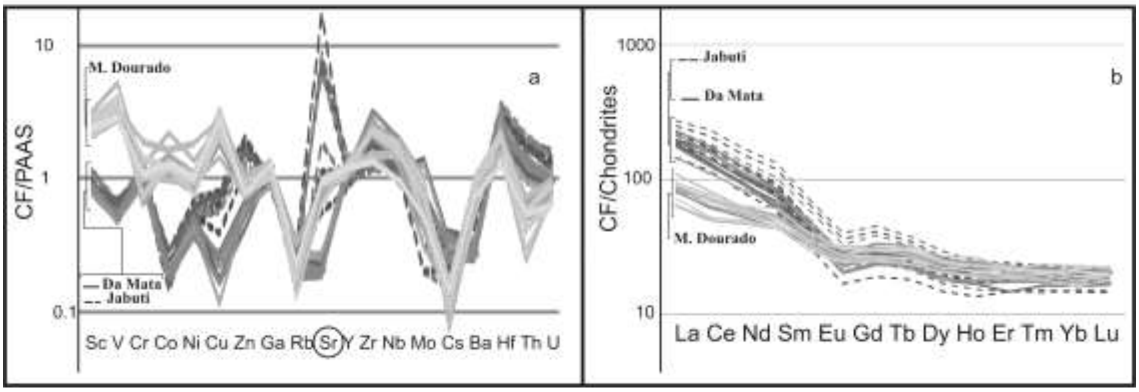


Figure 7- a) Distribution of the contents of the trace elements found in the sherds, normalized by the PAAS; b) Distribution of the REE in the sherds normalized by chondrites (Evensen et al., 1978).

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 hours at a temperature of 600°C, the anatase is transformed into rutile. Like other hydroxylated or hydrated aluminum phosphates, crandallite-goyazite ($(Ca, Sr)Al_3(PO_4)_2(OH)_5$) 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 were 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 mulite.

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. 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 Fe_2O_3 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.

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 seglerite identified in the sherds from Monte Dourado 1 (Figure 2) indicates aerobic conditions, typical of flooded environments in which organic matter has accumulated. Under these conditions, the iron oxy-hydroxides in the sherds is 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 Fe^{2+}, such as vivianite ($Fe_3(PO_4)_2.8H_2O$) and mitridatite ($Ca_3Fe_4(PO_4)_4(OH)_6.3H_2O$), have been identified in sherds (Maritan and Mazzoli, 2004), ferruginous lateritic crusts invaded by swamps (Costa and Sá, 1980; Costa and Lemos, 2000, Lemos et al., 2007) or even in swampy ground (Walpersdorf et al., 2013). Like the aluminum phosphates, these iron phosphates suffer thermal collapse (Figure 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).

Conclusions

The sherds analyzed from the three study sites presented distinct antiplastic characteristics, which assigns them to different groups. This discrimination was strongly supported by the presence and abundance of aluminum phosphates, in particular crandallite-goyazite, found primarily in the Jabuti and Da Mata samples. The Monte Dourado 1 site is distinguished from the others due to the use of metamorphosed mafic rocks (amphibolites) mineralized into ilmenite, found in the area surrounding the study site. The presence of quartz may not necessarily be related to the use of antiplastic, given that it is also a component of the clayey raw material.

Metakaolinite is the fundamental constituent of all the sherds, although the composition of the samples from Jabuti and Da Mata were the most similar. From a chemical viewpoint, the greatest differences were found in the levels of CaO, MgO, SrO, and P_2O_5, which reflect the neoformation of the phosphates and, in part, the shell antiplastic. The levels of SiO_2, Al_2O_3, Fe_2O_3, and TiO_2 suggest the presence of argilites from the Barreiras Formation – the coastal region's dominant geological unit – as the raw material used for the ceramic matrix. The distribution of trace and rare earth elements reinforces these similarities. By contrast, it is possible that the raw material for the ceramics produced at Monte Dourado 1 were clays derived from metamorphosed mafic rocks.

The firing temperature used in the production of the ceramic vessels was above 550°C at all three sites, given the lack of kaolinite, although the presence of anatase in the Jabuti and Da Mata samples indicates that temperatures did not exceed 600°C.

The aluminum phosphates found in the sherds indicate that the original pots were used to cook food, while the presence of segelerite in some samples suggests that the archeological site from which they were obtained was a hydromorphic (swampy) environment during some time in its history. 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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5.2 CONTRIBUTION OF THE FERTILITY POTENTIAL OF ARCHAEOLOGICAL SHERDS TO THE LONG-TERM FERTILITY OF AMAZONIAN DARK EARTH

Contribution of the fertility potential of archaeological sherds to the long-term fertility of Amazonian Dark Earth

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Abstract

Sherds found in Amazonian Dark Earth (ADE) at three different pre-historic settlements in the Amazon were analyzed to investigate their importance in maintaining the well-known fertility of ADE. Indeed, ADE appear to remain fertile even after many cropping cycles under tropical conditions where soils are heavily leached. Phosphorus (P) is a key nutrient which is found on dispersed sherds of ADE in amorphous or cryptocrystalline form, and the P desorption capacity of these sherds was investigated. The mineral composition of sherds was first characterized by x-ray diffraction (XRD), and porosity was determined through gas adsorption. Amounts of plant-available macro- and micronutrients, pH, and organic matter (OM) contents were determined and the fertility level of each was calculated according to an established method. Lastly the sherds were used in P desorption assays, where the influence of the size of sherds (≤2 cm or 2-4 cm) as well as the horizon from which they were collected (A or Ab) was assessed. Sherds obtained at Monte Dourado 1 and Jabuti are highly fertile, more so than ADE, which demonstrates their strong ability to contribute to the resilience of ADE. Such ability was also found, albeit weaker, in sherds from Da Mata. Nutrient availability is intimately linked to weathering in the different phases of the sherds, thus nutrients were not adsorbed from surrounding soil. Phosphorus availability is most notable in the sherds, and is directly related to ceramic porosity. The desorption of P into the soil is favoured and linear, however it occurs slowly which is key for ensuring long-term effects. The rate of P desorption is closely linked to the harshest soil conditions to which sherds were exposed to upon being discarded. The ability of sherds to contribute to the long-term fertility of ADE was demonstrated experimentally, specifically with respect to P availability.

Keywords: nutrients, sherds, Amazonian Dark Earth, fertility, phosphorus

Introduction

In general, soils of the Amazon are known to be of low fertility, and are represented by Latosol and Argisol which combined constitute 75% of soils in the region (Rodrigues, 1996; Sanches et al., 1982). However, dark-colored soils are also found in the Amazon which are known as Amazonian Dark Earth (ADE), archaeo-anthrosols (Kämpf and Kern, 2005) or Black soil of the Indians (*Terra Preta de Índio*). The properties of these soils are entirely different, and they exhibit high fertility (Smith, 1980; Kern and Kämpf, 1989; Kern and Costa, 1997; Kämpf and Kern, 2005; Glaser et al., 2012; Schmidt et al., 2014;) (Table 1). ADE are found throughout the Amazon including in Brazil, Bolivia, Colombia, Ecuador and Venezuela, and individual sites range in size from a few hectares to hundreds of hectares (Kern et al., 2003, 2009).

Recent research based on archaeological and pedological data indicate that ADE were formed under human occupation (Sombroek, 1966; Smith, 1980; Hilbert and Hilbert, 1980; Simões and Corrêa, 1987; Kern and Kämpf, 1989; Roosevelt, 1992). The accumulation of organic matter residues of various types and the mineralization of these residues resulted in soil formation processes whose anthropic origin is unquestionable and is proposed by Sombroek (1966); Hilbert and Hilbert (1980); Smith (1980); Kern and Kämpf (1989); Neves et al. (2003); Glaser et al. (2004); Glaser (2007); and Woods and Denevan (2009). Radiocarbon ages of ADE show that they were formed between 60 and 1,640 AD in the upper

Xingu region (Heckenberger et al., 1999), and between 2,500 and 500 yr BP in central Amazonia (Neves et al., 2003).

In general, ADE is characterized by an intense dark color (black to very dark greyish brown, N2/; 2,5YR2/0; 5YR2,5/1; 7,5YR 2/0; 10YR 2/0 to 3/4) which derives from large stocks of stable humic organic matter in the anthropic A horizon (Glaser et al, 2001; Glaser and Birk, 2012). The average depth of the A horizon is between 30 and 60 cm, but it can reach 2 m) (Kämpf and Kern, 2005). In background Amazonian soils under undisturbed forest, the depth of the A horizon is usually between 10 and 15 cm. On average, the content of available P, Ca + Mg and pH are respectively 507 g kg^{-1}, 9.4 cmolc kg^{-1} and 5.6, while these values in Latosols and Argisols are 1.7 g kg^{-1}, 1.4 cmolc kg^{-1} and 4.5, respectively (Kämpf and Kern, 2005). ADE also contain relatively high levels of zinc, manganese, cation exchange capacity (CEC) and base saturation (Pabst, 1991; Kern et al, 2003; Sombroek et al., 2002; Lehmann et al., 2003). Their texture varies from sandy to clayey, and they support elevated microbial diversity (Kern, 1996; Kern and Costa, 1997; Lima et al, 2002; Kern et al, 2003; Kämpf and Kern, 2005). The main anthropic remains constitute sherds from containers used on a daily basis, which are usually abundant as opposed to lithic sherds which are rarer. Even when used over extended periods for subsistence or small-scale agriculture, the fertility of ADE apparently does not significantly decline (Kern *et al.*, 2009).

The fertility of ADE has been attributed to the accumulation of carbon originating from the incomplete combustion of organic matter (C_{pyr} or black carbon), which is greater than in adjacent soils (Glaser *et al*, 2001; Glaser and Birk, 2012). This hypothesis explains the high CEC of ADE, but C_{pyr} cannot be responsible for supplying nutrients in the soil given its chemical composition. However, sherds could potentially represent a source of nutrients as suggested by Costa (2010), since their chemical and mineralogical composition is equivalent to that of rock fragments dispersed through the soil. For example, as saprolites in geogenic soils decompose through biochemical processes, they release chemical components such as P, K, Ca, Mg, Mn, Zn, and Cu, among others.

The contribution of sherds to the fertility of ADE has not been demonstrated experimentally. Sherds represent the remains of containers which were discarded in middens after being used for food processing and preparation, as well as other uses including ritual and decorative. The chemical and mineralogical composition of these sherds indicates they are somewhat similar to sedimentary and metamorphic rocks since they are mainly composed of quartz, metakaolin, occasionally hematite, goethite and anatase, and also mica, feldspars and chlorite as well as a number of other antiplastics depending on the specific location (Costa et al., 2009). The usual binders *cariapé (Licania utilis or Licania turriuva*), *cauixi* (*Tubella reticulata or Parnula betesil*), crushed rock, shells, ashes and charcoal contribute to the high contents of silicon dioxide and highly soluble carbonates, except for the crushed rock and quartz. Amorphous phases are also generally present, including aluminum phosphates with a P_2O_5 content usually varying between 0.7 and 3 wt% (Costa et al., 2004a; Costa *et al*., 2009; Costa *et al*., 2011). Such values are greater than those found in ceramic containers from archaeological sites in Greece (0.08 to 0.21 wt% P_2O_5) (Iordanidis *et al*., 2009) and Italy (0.12 to 1.01 wt% P_2O_5) (Belfiori *et al*., 2010), for example. The highest P contents were found in sherds from an ADE site near the town of Bragança (Pará State, Brazil), with up to 9.75 wt% P_2O_5 (Costa et al, 2012).

Crystalline phosphates are rare, and when they occur they are micro- to cryptocrystalline and represented by variscite-strengite ($(Fe,Al)PO_4.2H_2O$) (Costa *et al*., 2004b), and to a lesser extent crandallite-goyazite ($(Ca,Sr)Al_3(PO_4)2(OH)_5$.) (Costa et al., 2009; 2012). Mineralogical studies suggest that the source of P is related to the use of containers for cooking food (Costa *et al.*, 2004a; 2004b; 2009; 2011; 2012). However, Freestone *et al.* (1994) proposed that elevated P concentrations result from adsorption from the soil in which the containers were discarded, due do their microporosity. The presence of P in sherds represents a source of nutrients, and not sequestration from the soil matrix. Apart from P, sherds can serve as a source of Ca, given their Ca content reaches 2.85 wt% CaO (Costa et al., 2012). Similarly, sherds from northern Greece studied by Iordanidis and Garcia-Guinea (2011), which are unrelated to ADE, contain up to 14.92 wt% CaO as measured by punctual analysis. Relatively elevated contents of Mg and K are also found as clay including illite and muscovite, as well as microcline.

Table 1: Fertility parameters of ADE compared to typical Amazonian soils

	ADE- AM[1]	ADE-PA[2]	Latosol[2]	Gleysol[2]	Argisol[2]
pH	5.68	5.20	4.70	4.30	3.90
$P_{available}$ [mg dm^{-3}]	69.15	90.00	5.00	4.10	13.00
K [mg dm^{-3}]	0.17	0.13	0.05	0.08	0.06
Ca [cmol$_c$ dm^{-3}]	7.07	4.80	0.20	0.90	0.10
Mg [cmol$_c$ dm^{-3}]	1.31	1.60	0.20	0.90	0.10
Al [cmol$_c$ dm^{-3}]	0.20	0.10	1.50	1.20	2.20
H+Al [cmol$_c$ dm^{-3}]	n.d	2.81	1.49	8.09	7.92
Sum of bases (S) [wt%]	8.55	6.06	0.45	1.88	0.26
CEC [wt%]	8.75	12.33	2.05	2.98	2.76
Base saturation (V) [wt%]	95.20	67.86	26.04	17.89	6.60
Al saturation (m) [wt%]	4.80	0.80	71.19	39.30	77.76

1- Falcão et al., 2009- mean values from 10 ADE sites located in Amazonas State; 2- Costa, 2011- mean values from 5 ADE sites located in Pará State.

As discussed by Costa (2010), when rocks are exposed at the land’s surface they undergo weathering which results in soil formation over geological time, and sherds are also exposed to the same weathering environment upon being discarded. Weathering is more intense under tropical conditions such as prevail in the Amazon, and sherds gradually release chemical components of the minerals that constitute them including Ca, Mg, K and P in addition to trace elements, which represent macro- and micronutrients in the soil. The objective of this work was to demonstrate experimentally that sherds contribute to the fertility of ADE, by measuring the P desorption capacity of sherds. Phosphorus was chosen because it is a key nutrient which is found as an associated mineral in sherds from ADE in either amorphous or cryptocrystalline forms.

Materials

Sherds from three archaeological sites located in the Brazilian Amazon were selected for this study based on the high ceramic content of these sites and their diverse chemico-mineral composition: Monte Dourado 1 (Pará State), Da Mata (Maranhão State) and Jabuti (Pará State). The first two sites underwent archaeological rescue by Scientia Consultoria Cientifica (Scientia scientific advice) whom kindly provided sherds for this study, while the third site was under study by the Museu Paraense Emilio Goeldi (Paraense Museum Emilio Goeldi) which included the participation of the authors whom collected the samples. Samples were collected from dig levels 1 m^2 in size and at each 10 cm depth increment, while taking into consideration the A and B horizons of the soil. At Jabuti sampling took place at 20 cm depth increments. Sherds collected from a given depth increment were pooled, and a 300b g representative subsample was taken. Samples were air dried and described mesoscopically. Samples were subsequently ground in an agate mortal, except for those used in the desorption analysis.

Methods

Mineralogical analyses

The mineralogical composition of sherds was determined by x-ray diffraction, powder method. The diffractometer used was an XPERT PRO MPD equipped with a PANalitical PW 3040/60 (theta-theta) goniometer, a copper anode ($\lambda CuK\alpha 1 = 1.54060$), a $K\beta$ filter, a 40 kV tension generator and a 30mA current generator. Analyses were completed at the Laboratory of Caracterização Mineral (Mineral Characterization) of the Universidade Federal do Pará (Federal University of Pará).

Chemical analyses

Chemical and physico-chemical analyses (Table 2) were carried out at the soils laboratory of Universidade Federal de Viçosa (Federal University of Viçosa).

Table 2: Methods used for the chemical and physico-chemical analysis of sherds.

	Extraction	Quantification
pH	1 : 2.5 (sample:water)	Potenciometer (Peech, 1965)
Available P	Mehlich 1	Colororimetry (Murphy and Rilley,1962)
Exchangeable Na	Mehlich 1	Atomic absorption (Hesse, 1971)
Exchangeable K	Mehlich 1	Atomic absorption (Hesse, 1971)
Exchangeable Fe, Zn, Mn, Cu	Mehlich 1	Atomic absorption (Hesse, 1971)
Exchangeable Ca, Mg	KCl 1 mol L^{-1}	Atomic absorption (Hesse, 1971)
Exchangeable Al	KCl 1 mol L^{-1}	Titration with NaOH 0.025 mol L^{-1} (McLean, 1965).
H+Al (potential acidity)	CH_3COO_2Ca 0.5 mol L^{-1} pH 7	Titration with NaOH 0.025 mol L^{-1} (McLean, 1965).
Organic matter (OM)		Organic carbon x 1.724 (Walkley-Black,1934)

Determination of porosity

In order to assess the desorption potential of sherds, their specific surface area was determined by N_2 adsorption at 77 K. A QUATACHROME model NOVA 1200 gas adsorption analyzer was used following the methodology proposed by Brunaer-Emmett-Teller (BET). Samples were pre-treated to 120° C. This analysis was carried out at University of Halle (Germany).

Phosphorus desorption experiment

Two samples from each of the three sites were used in this experiment, one from the A horizon and one from the AB horizon. Samples were then sorted into two groups based on size: ≤ 2 cm and 2 - 4 cm. This yielded 4 samples per site and a total of 12 samples. Each sample was placed in a solution of constant pH 4.5±0.1 during 30, 60, 90, 120, and 150 days. After each time period the concentration of P_2O_5 in the solution was assessed by spectophotometry in the visible range using a colorimetric method. The Hach 8048 method was used, with a Hach DR 5000 spectrophotometer. Analyses were completed at the Laboratory of Grupo de Mineralogia e Geoquímica Aplicada (Mineralogy and Geochemical Applied Group) of the Universidade Federal do Pará (Federal University of Pará)- Museu de Geociências (Geoscience Museum).

The amount of desorbed P per gram of ceramic (qe) was calculated using Equation 1:

$$qe = [(Ce-Ci)V]/(Mc*1000) \qquad \text{(Eq. 1)}$$

Where:

qe: amount of desorbed P, at equilibrium, per gram of ceramic (mg g^{-1});

Ci: initial P concentration of the solution (mg L^{-1});

Ce: P concentration of the solution, at equilibrium;

V: volume of solution used in the experiment (mL);

Mc: mass of ceramic used (mg).

To examine desorption equilibria, the experimental data was fitted to Langmuir (1918) (Eq. 2) and Freundlich (1906) (Eq. 3) mathematical models which are most frequently used to describe solid-liquid systems. The values of each constant and correlation coefficients were calculated. Data was adjusted for non-linear regression using the software package Origin 7.

$$qe = (Qmax\ Ce) / (K_L+Ce) \qquad \text{(Eq.2)}$$

Where:

qe: amount of P, at equilibrium, per gram of ceramic (mg g^{-1});

Ce: P concentration in solution, at equilibrium (mg L^{-1});

Qmax: maximum desorption capacity (mg g^{-1});

K_L: equilibrium constant (adimensional).

$$qe = K_F\, Ce^{1/n} \qquad \text{(Eq.3)}$$

Where:

qe: amount of P, at equilibrium, per gram of ceramic (mg g^{-1});

Ce: P concentration in solution, at equilibrium (mg L^{-1});

Constants K_F and n relate to the extent of desorption and the level of heterogeneity of the surface, respectively.

Based on the calculated values for Qmax and K_L, equilibrium parameter R_L was calculated (Eq. 4). This parameter indicates whether desorption is favoured or unfavoured.

$$R_L= [1/(1+K_L\ Qmax)] \qquad \text{(Eq.4)}$$

Results

The main phases of all sherds are quartz and metakaolinite. The presence of amorphous metakaolinite is suggested by the elevation of the background in diffractograms. This phase is generated by the breakdown of the kaolin structure during firing. Kaolin is the main mineral in the basic feedstock for making ceramic. The sherds can be distinguished by the presence of other minerals such as phosphates of the crandallite-goyazite type which are frequent at Jabuti, while Al phosphates are amorphous and less abundant at other sites. Also, sherds from Monte Dourado 1 contain minerals which are not found elsewhere, including cordierite, plagioclases, muscovite, ilmenite and segelerite (Table 3). Such results agree with those obtained by Rodrigues et al. (2012) who studied sherds from the same locations, as well as those from Costa et al. (2009, 2012) who studied sherds from Jabuti.

Table 3: Mineralogical composition of sherds determined by XRD, their anitplasctics identified by XRD and stereomicroscopy, and specific surface areas.

ADE Site	Mineralogy	Antiplastic	Specific surface area (m^2 g^{-1})
Monte Dourado 1	metakaolinite, quartz, plagioclase, ilmenite, cordierite, muscovite, cristobalite and seguelerite	Crushed rock and cariapé	62.91
Da Mata	metakaolinite, quartz, muscovite and anatase	Cariapé	19.19
Jabuti	metakaolinite, quartz, cradallite-goyazita, muscovite and anatase	Shell	94.38

The pH values vary between 5.63 and 6.97 (Fig. 1a), and are greater in sherds from Monte Dourado 1. This is due to the abundance of plagioclases, cordierite and micas, which indicate fragments of unaltered rocks in addition to a low OM content (Fig 1b). The pH values of the other two sites are similar, but are lower at Jabuti and this most likely indicates different forms of OM which favoured an increase in exchangeable Al in these sherds.

The OM content at Da Mata and Jabuti is clearly greater than at Monte Dourado 1 (Fig. 1b), presumably owing to the greater use of organic antiplastics at the former sites. Values for sum of bases (S), base saturation (V) and CEC (Fig. 1) show a much greater potential fertility in sherds from Monte Dourado 1 and Jabuti, and are greater than values for ADE (Fig. 1). These values are lower at Da Mata, and this is unexpected given the OM content of sherds from this site (Fig. 1b). Aluminum saturation (m) and Na saturation index (NaSI) values are clearly greater at Da Mata, which shows that sherds from this site have a low potential fertility. Even though they are rich in OM, their fertility is only slightly greater than that of typical tropical soils.

Macro- and micronutrient (Ca, Mg, K, P, Fe, Mn, Cu and Zn) contents of sherds are equivalent to or greater than contents in ADE, except for Mn levels which are clearly lower in sherds (Fig. 2). Again, sites Monte Dourado 1 and Jabuti contain higher levels of these nutrients.

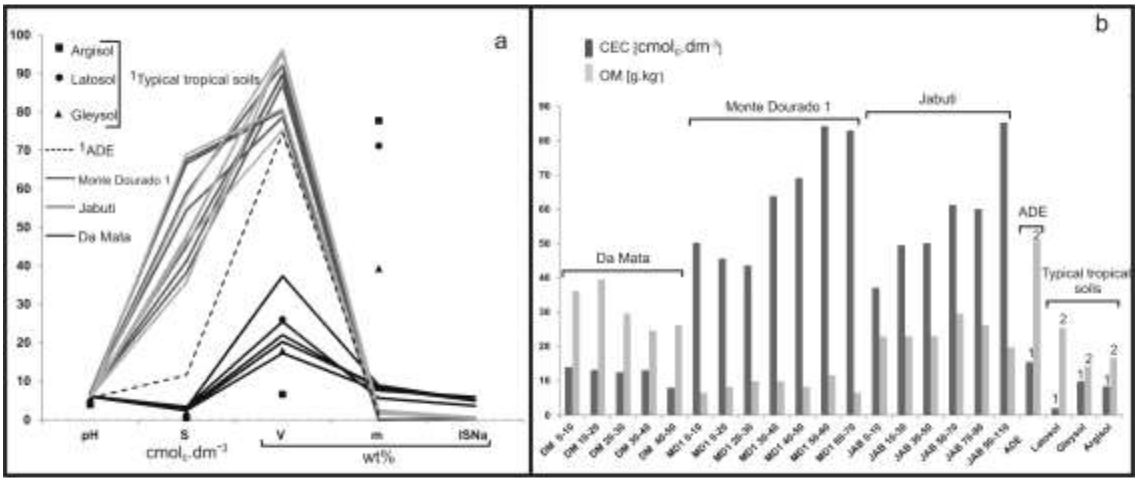

Figure 1: Fertility parameters (a), cation exchange capacity (CEC) and total organic matter (OM) (b) in sherds compared to the average values found in ADE and in the A horizons of typical Amazonian soils 1- Costa (2011), 2- Lima et al. (2002).

Results from the desorption experiment clearly show that the sherds have the ability to release P, and that this ability is greater in sherds from Jabuti. The desorption ability is best illustrated by the Freudlich model (Fig. 3), even though good correlation coefficients were also obtained with the Langmuir model. It must be noted that among sherds collected at a given site, the smallest (≤ 2 cm) invariably have a greater ability to release P over time when compared to larger sherds (2 to 4 cm) (Fig. 4). This was expected given that the greater contact surface favours chemical weathering reactions, and thus weathering would be more advanced in smaller sherds. Similarly, sherds from the A horizon release more P than sherds from horizon AB, which is due to the fact that weathering is more intense in the A horizon.

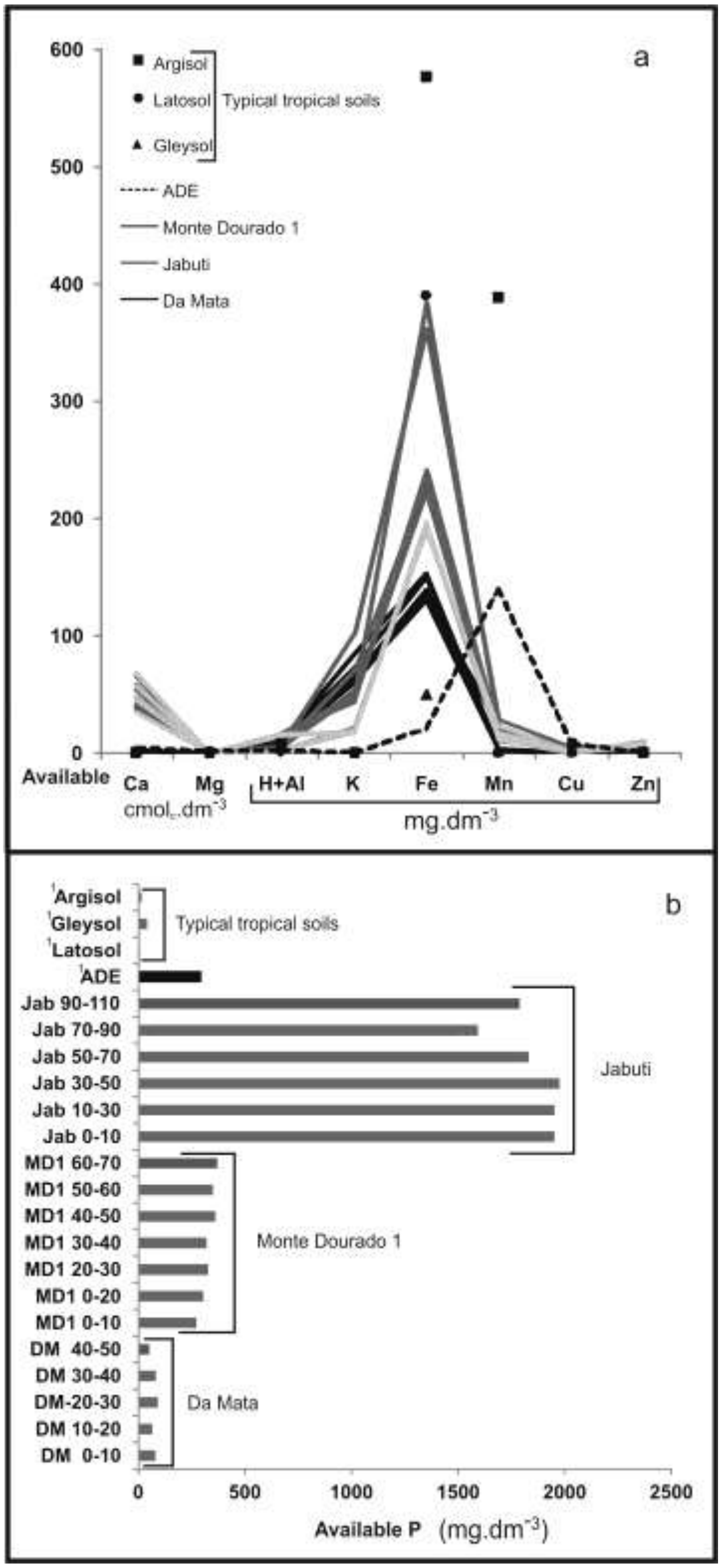

Figure 2: Concentrations of exchangeable nutrients, potential acidity (a) and available P (b) in sherds compared to the average values obtained for ADE and at five different sites, and in the A horizons of typical soils found in the Amazon 1- Costa (2011).

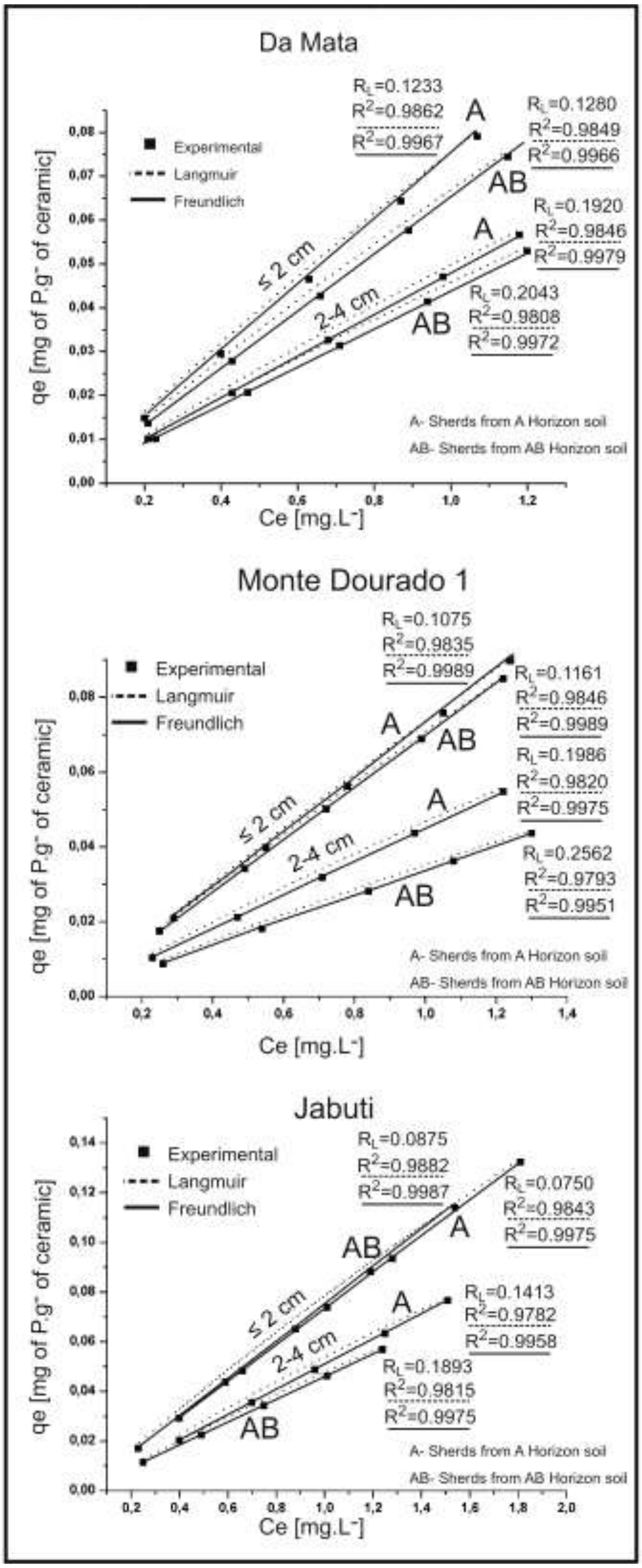

Figure 3: Phosphorus desorption isotherms and their respective coefficients when fitted to Langmuir and Freundlich models.

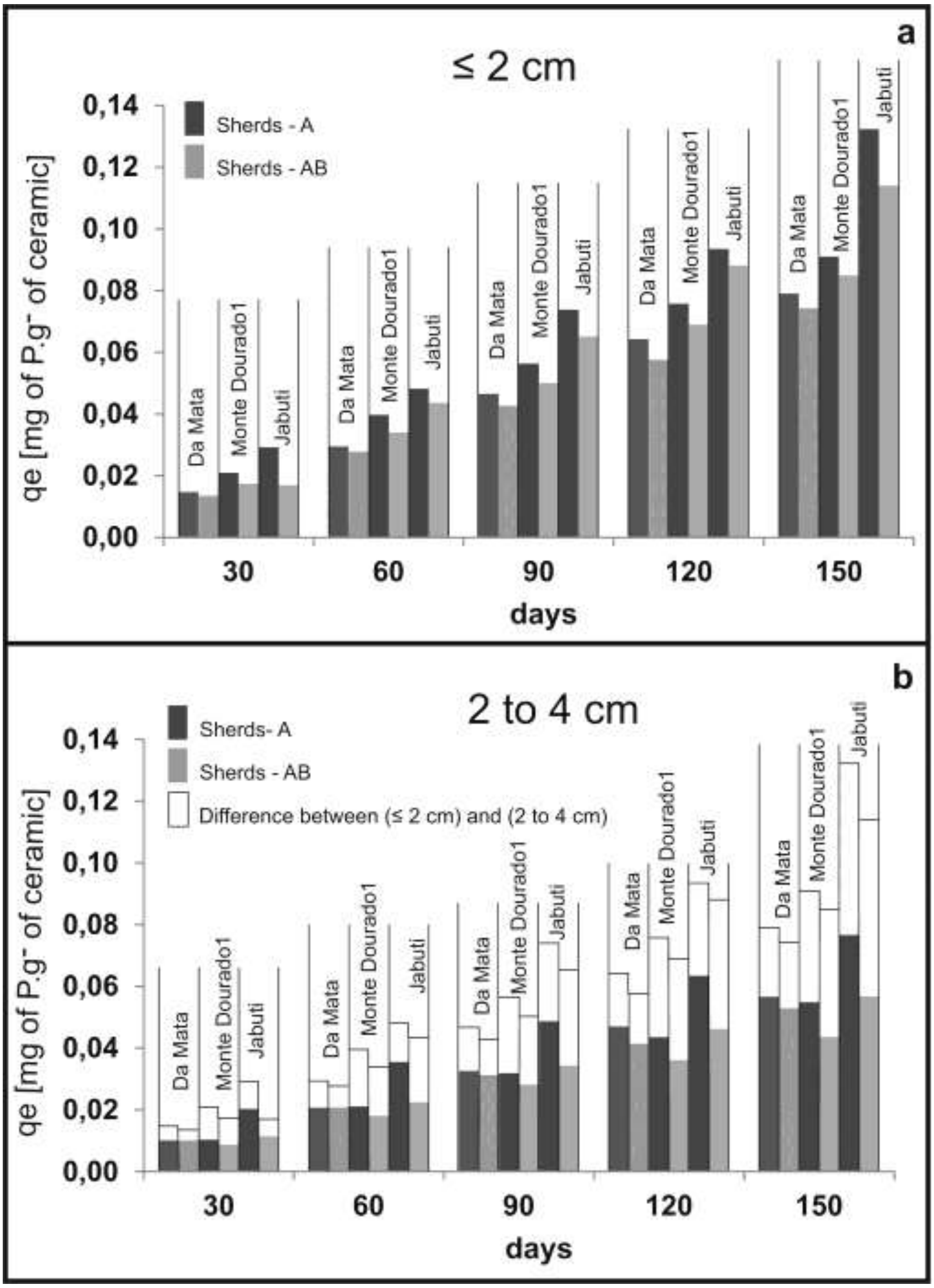

Figure 4: Phosphorus desorption over time and according to sherd size and soil horizon.

Discussion

The availability of nutrients which are essential for plant growth and which were studied here was greater in sherds than in typical Amazonian soils, and was also generally greater than in ADE. When these values are compared to parameters typically used to evaluate soils (Alvarez et al., 1999), Ca availability is high at Monte Dourado 1 and Jabuti (on average 52.24 and 49.98 $\text{cmol}_c\ \text{dm}^{-3}$), respectively. Such values are considered very good for plant growth. Despite Ca availability at Da Mata being considerably lower (on average 2.12 $\text{cmol}_c\ \text{dm}^{-3}$), it is still considered average. However, Ca availability at Da Mata is lower than that obtained for ADE (Costa, 2011; Falcão et al., 2009; Lima et al., 2002). Such large variability between sites illustrates the importance of sherd mineralogy. Plagioclase and cordierite are highly susceptible to weathering (Goldich, 1938; Anand and Gilkes, 1984) and are found abundantly at Monte Dourado 1. These minerals release Ca and Mg, respectively. At Jabuti, these nutrients as well as P and micronutrients derive from crandallite-goyazite, a Ca and strontium phosphate, as well as from potential shells remains consisting of calcium carbonate. Magnesium contents are average in sherds from Da Mata and Monte Dourado 1. At Jabuti sherd Mg contents are low (Alvarez et al., 1999). They are inferior to those found in ADE, and equivalent to amounts found in typical Amazonian soils. Elevated Mg contents could not be expected at this site given the mineralogical composition of sherds. Rodrigues et al. (2012) found greatest total Mg oxide contents in sherds from Monte Dourado 1, on average 1.98 wt%, which indicates a greater availability of Mg from these sherds.

While K availability in sherds from all locations is greater than that of ADE (Costa, 2011; Falcão et al., 2009), K availability is categorized as average in sherds from Da Mata and Monte Dourado 1, and low in sherds from Jabuti. Such low contents are related to low levels or the absence of K-bearing minerals (microcline, muscovite and illite). Also, muscovite is more resistant to weathering than are feldspars and its presence would not significantly contribute to K availability.

This work clearly showed that nutrient availability in the studied sherds was not related to depth within the soil profile, contrarily to ADE where nutrient availability rises sharply from AB to A (Falcão et al., 2009; Kern and Costa, 1997; Kämpf and Kern, 2005; Lima et al., 2002) (Fig. 5). The fact that nutrient availability in sherds is practically constant indicates it is an inherent characteristic of the fragments, and thus that nutrients found in them cannot have been adsorbed from soil as suggested by Freestone *et al.* (1994) in the case of P. Indeed, the stratification of P availability in ADE is even more marked than in other nutrients. The slight difference seen in sherds from the A horizon arises from the fact that these are more weathered, as previously discussed. The greater nutrient contents of ADE in the A horizon is attributed to the fact that contents of soil OM, which retains nutrients, are also greater in this horizon.

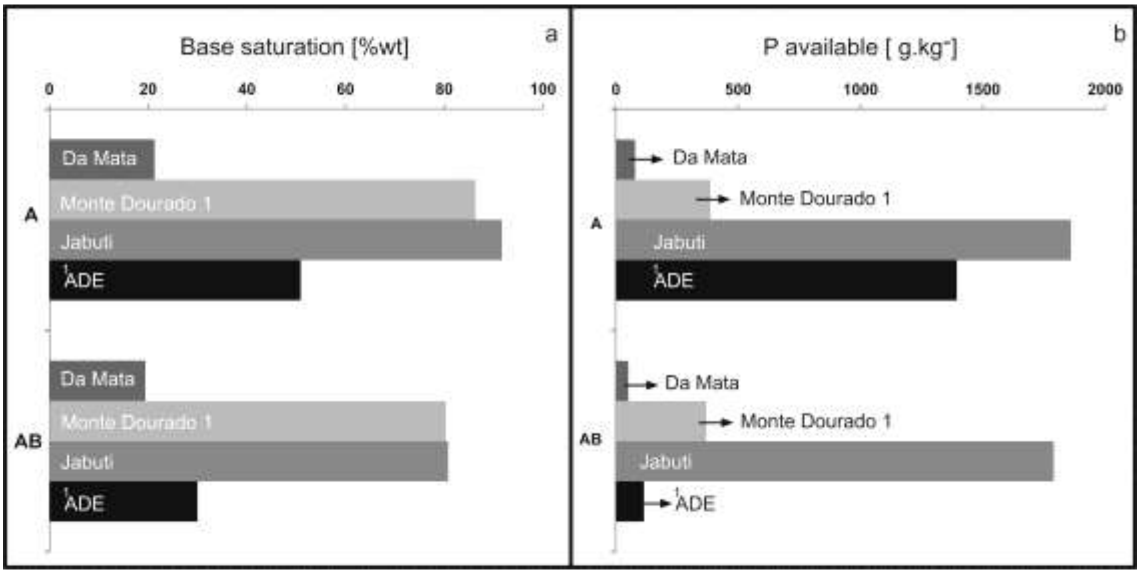

Figure 5: Variation in nutrient availability in sherds and in ADE, according to soil horizon. 1-Lima et al., (2002).

The concentrations of these nutrients, and including Na contents, are used to calculate the sum of bases (S). Average S values were 34.18, 23.94 and 60.5 mg dm^{-3} at Da Mata, Monte Dourado 1 and Jabuti, respectively. Base saturation is an important parameter to evaluate sherd fertility, and based on the classification by Alvarez et al. (1999) these S values are considered as very good which indicates that sherds may contribute to the sustained fertility of ADE.

Another highly relevant parameter is CEC, which in the studied fragments was 12.17, 62.86, 57.30 cmol$_c$ dm^{-3} at Da Mata, Monte Dourado 1 and Jabuti, respectively. Such values classify as good for plant growth at Da Mata, and very good at the other sites. In sherds from Monte Dourado 1 and Jabuti CEC values are greater than typical Amazonian soils and ADE. In sherds, CEC is not related to total OM content as it si in ADE (Glaser, 2007). Organic matter content in sherds is below 7 g kg^{-1}, and this value is considered to be very low (Alvarez et al., 1999). Indeed, even organic antiplastics must be charred to eliminate OM. This is illustrated by the lack of a relationship between OM and CEC (Fig. 1b).

Exchangeable bases contributed more significantly to sherd CEC than did Al, as demonstrated by the values for V of 24.47, 85.44 and 89.87 wt% at Da Mata, Monte Dourado 1 and Jabuti, respectively. The latter two sites classify as very good according to Alvarez et al. (1999), and even exceed values found in ADE. However, V values at Da Mata classify as low. According to the classification given by Embrapa (1999), these data indicate that sherds from Monte Dourado 1 and Jabuti are eutrophic, while sherds from Da Mata are dystrophic. This demonstrates the high fertility potential of sherds from Monte Dourado 1 and Jabuti, and their real contribution to the sustained fertility of ADE. Indeed, the fertility of ADE at Da Mata was also lower than at other sites, as observed by Silva (2012).

Aluminum saturation is very low in all sherds, even those from Da Mata (on average 7.80 w%). This shows that even though sherds are composed mainly of metakaolinite ($Al_2Si_2O_7$) and other aluminosilicates, weathering occurs slowly and released Al must be immediately leached and/or fixed in organomineral complexes. Aluminum saturation values in shreds are similar to those found in ADE, which are less acidic than typical Amazonian soils. Apart from Al, Na can also cause problems for plant growth. However, NaSI values in all sherds are below 8 wt%, and thus the Na contribution of sherds to soil is small and not problematic (Raij, 1991).

The pH of sherds (6.08, 6.83 and 5.79 at Da Mata, Monte Dourado 1 and Jabuti, respectively) was similar to that of ADE, on average 5.2-6.4 (Falcão et al, 2009). Sherd pH was also equivalent to that of rocks, thus sherds do not contribute to lowering the pH of ADE. Such pH values indicate the presence of calcium and magnesium and limit the availability of Al and excessive P fixation as Al phosphate (Raij, 1991), which typically occurs in tropical soils. The greater pH value of sherds at Monte Dourado 1 reflects the availability of Ca and Mg, as presented above, and reduces the amount of exchangeable Al to zero. At Jabuti and Da Mata exchangeable Al contents are greater, 0.96 and 0.24 $cmol_c\ dm^{-3}$ on average, respectively, and nutrient availability is lower.

Of all macro- and micronutrients studied in the sherds, P is the nutrient which is found in greatest amounts in sherds relative to ADE and typical Amazonian soils. As already mentioned, total P is another distinguishing characteristic of sherds. Phosphorus was incorporated into the ceramic pots during food cooking (Costa et al., 2011, 2012), and this seems to have been favoured by the porosity of the ceramic given there is a positive correlation between specific surface area and available P concentration (Table 3). This porosity derives mainly from the chemical and mineral composition of the ceramic which is dominated by amorphous metakaolinite and aluminosilicates, and also from firing at low temperatures of approximately 550°C (Costa et al., 2011, Costa et al., 2012; Rodrigues et al., 2012). In hydrothermally altered soils and environments, phosphorus solutions rapidly interact with aluminosilicate clays and this leads to the formation of amorphous or crystalline Al phosphates (Hudcová, 1970; Kittrick and Jackson, 1954; Rajan, 1976). Among these minerals, crandallite-goyazite was found to be abundant in sherds from Jabuti, another example is variscite-estrengite (Costa et al., 2004b, 2009). At Monte Dourado 1, P is relatively abundant but it does not form a crystalline phase and is present exclusively as amorphous Al phosphates. The latter are more susceptible to weathering and this explains the greater P availability at this site. The segelerite which was observed was clearly formed after disposal of the pots. Total P in sherds from Da Mata was much less abundant (1.04 % wt on average), and present as amorphous Al phosphate (Rodrigues et al., 2012). Lower total P contents explain lower P availability in sherds and ADE at this site, as observed by Silva (2012).

The shapes of P desorption isotherms show that P release followed very similar patterns in all sherds under study, indicating that the released P originates from similar phases, i.e. Al phosphates. All isotherms are of type C, which suggests very porous surfaces with regions of varying P solubility (Giles et al., 1960). Correlation coefficients show that experimental data fit both models, thus either model can be used to predict equilibrium parameters. However, for all sherds the Freundlich model fit slightly better, and this suggests heterogeneous ceramic surfaces (Wu *et al.,* 2009).

Values for R_L in the Lagmuir model show that desorption is unfavoured, according to the classification by Hall et al (1966). They also demonstrate that sherds from Jabuti contribute more P than sherds from other locations, as was also indicated by amounts of available P. Finally, R_L data shows that P desorption is very slow which implies its permanence, until fragments are completely dissolved. At all three sites, sherds measuring ≤ 2 cm released approximately twice as much P than sherds measuring 2 – 4 cm. Thus, P desorption was inversely proportional to sherd size especially in the A horizon. The disintegration of sherds following weathering increases nutrient availability, which supports the idea that fertility is permanent while sherds remain.

Conclusions

Sherds release nutrients into soil, after having been discarded. These nutrients represent constituents of the minerals contained in the sherds, either from the feedstock or secondary minerals which originated during firing or pot use for cooking, in the case of phosphates. These nutrients were not adsorbed from soil. Sherds from Monte Dourado 1 and Jabuti are highly fertile and correspond to eutrophic soils, and thus can enrich ADE. Such an ability is lesser in sherds from Da Mata, which have a less favourable mineralogical composition consisting mainly of metakaolinite and little phosphate.

The availability of P is high, and directly related to the high porosity of sherds as indicated by the specific surface area. The release of P into soil is favoured and linear, but occurs slowly which is fundamental in ensuring long-term contributions. Phosphorus release is greater among smaller sherds and sherds from the A horizon, where weathering is more intense.

Sherds found in ADE, upon weathering, have a high capacity to release nutrients into the soil and thus to represent the source of its fertility and resilience.

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5.3 PHOSPHORUS IN ARCHEOLOGICAL CERAMICS AS EVIDENCE OF THE USE OF THE POTS FOR COOKING FOOD

Phosphorus in archeological ceramics as evidence of the use of the pots for cooking food

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Abstract

The presence of phosphorus in samples of soil, sediments and water is traditionally considered to be an important indicator of human activity, either archeological or contemporary. Traditionally, the presence of phosphorus in archeological ceramics is attributed to adsorption from the soil subsequent to the discarding of the utensil or the presence of the element in the raw material, although a few authors support the hypothesis of the contamination of the pots by food during cooking. Given these conflicting views, the present study investigated experimentally the incorporation of phosphorus (and also calcium) into ceramic pots through trials that simulated cooking conditions, in order to verify the potential of the elements as archeological evidence. The material was analyzed using XRD, total chemical analyses, and SEM/SED. The results indicated clearly that both elements were incorporated through the cooking process. The chemical affinity of phosphorus with aluminum makes this element a potentially important archaeological record of function. Crystalline phases of the variscite type are formed after 600 h of cooking, and depend on the amount of time the pot is in contact with the experimental solution. By contrast, the incorporation of calcium is readily reversible, and the cooking time necessary for the formation of phases is much greater than the working lifespan of a ceramic pot. This means that calcium cannot be used as archeological evidence of cooking.

Keywords: sherds, phosphorus, calcium, cooking, archeological remains.

Introduction

Traditionally, the presence of phosphorus in samples of water, sediments, and soil has been considered to be an important indicator of human activity in both archeological and contemporary material. Anomalous concentrations of this element may be derived from natural or anthropogenic sources (Mackenzie et al., 2002; Mcquartters-Gollop et al., 2007). In archeological soils, phosphorus is considered to be a sensitive and persistent indicator of prehistoric human activity, providing important clues with regard to the type and intensity of occupation (Holliday and Gartner, 2007). Studies of this type have been conducted in many different regions of the world, including Europe, Asia, Africa, and the Americas (Holliday and Gartner, 2007).

In the Amazon, phosphorus is especially useful in studies of Amazonian Dark Earth (ADE), providing important insights into patterns of occupation (Costa et al., 2013; Costa and Kern, 1999; Kern and Kämpf, 1989; Schmidt et al., 2014), frequently in association with sherds, which represent an important archeological vestige with the potential for providing detailed insights into the human occupation of the region. However, studies of the presence of phosphorus in archeological ceramics are relatively scarce, given that the presence of this element is traditionally attributed to its adsorption from the soil in which the sherds were discarded (Freestone et al., 1985, 1994; Duntell and Hunt, 1990; Maritan and Manzolli, 2004;

Maritan et al., 2009), or derived from apatite, normally in the form of bone fragments, when this mineral is found in the ceramic matrix, as described by Ionescu et al. (2011), in which case, it is identified as a primary mineral, that is, derived from the raw material. None of these studies have considered phosphorus as archeological evidence in its own right. This approach normally depends on the extraction and analysis of the organic molecules, in order to establish the function of the vessels represented by the ceramic sherds, principally when they were used for cooking or storing foods (Dudd and Evershed, 1999; Dudd et al., 1998.; Evershed et al., 1995.; Evershed, 2008; Giogi et al, 2010; Goldenberg et al., 2014; Oudemans et al 2007; Saul et al., 2012).

In contrast with this viewpoint, Costa et al., (2004a, 2004b, 2006, 2009, 2011, 2012) have attributed the presence of relatively high levels of phosphorus in ceramic sherds from ADE sites to the daily use of the original vessels for cooking food. In this case, the phosphorus becomes an important form of archeological evidence, indicating the function of the vessels represented by the sherds. Duma (1972) and Cackette et al. (1987) have also linked the presence of phosphorus to contact with organic compounds derived from foodstuffs, and attribute the presence of this element as evidence of the use of the vessels for cooking or storing food. This interpretation was also supported by Bollong et al. (1993).

Costa et al. (2004a, 2009, 2011) recorded P_2O_5 levels of between 1 wt% and 3 wt%, reaching a maximum of 9.75 wt% (Costa et al., 2012). These values are very high when compared with ceramic vessels from North Africa and the Far East, with levels of approximately 0.2% P_2O_5 (Duma, 1972; Bollong et al., 1993), Greece – 0.08–0.21 wt% P_2O_5 (Iordanidis et al., 2009), and Italy – 0.12–1.01 wt% P_2O_5 (Belfiori et al., 2010). While the phosphorus was found in high concentrations in the sherds studied by Costa et al., the mineral phases containing the element are rare, and when present, they are represented primarily by variscite-strengite, and more rarely, rhabdophane (Costa et al., 2009) and crandallite-goyazite (Costa et al., 2012). In general, even when it is not identified by XRD, stoichiometric calculations based on the results of the chemical analyses permit the confirmation of an association with aluminum phosphates of the variscite type (Costa et al., 2009, 2011). Apatite is not usually identified in these studies, except for isolated microfragments of bone. Legodi and Waal (2007) recorded approximately 1.18% P_2O_5 in ceramic sherds of utensil items, a level close to the values recorded by Costa et al. (2004 a, 2006, 2009, 2011), which reinforces the potential relationship between phosphorus enrichment and the past use of the items for cooking food.

The sherds studied by Costa et al. (2004a, 2004b, 2006, 2009, 2011, 2012) were derived from vessels made from clay rich in kaolinite and quartz, with the incorporation of mineral or organic antiplastic, and fired at low temperatures, of approximately 550°C. Under these conditions, the kaolinite becomes amorphous, forming a metakaolinite ceramic matrix, thus remaining predominantly aluminosilicate, with relatively high levels of P_2O_5, neoformed phases containing this compound, infiltrating the pores or the reaction edge between the matrix and the antiplastic. Significant concentrations of CaO, MgO, and occasionally, K_2O, were also found, although these compounds constitute the chemical composition of minerals used to make the ceramics, in the form of fragments of rocks (feldspars, amphiboles, quartz, micas) and shells (calcite, aragonite) incorporated into the ceramic mix as antiplastics. For example, up to 2.85wt% of CaO in the form of calcite and/or aragonite derived from shell fragments (Costa et al., 2012) or up to 3.47 wt% in the form of plagioclases (Rodrigues et al., 2012). Concentrations of CaO of 5.44 wt% have been recorded in ceramic sherds from archeological sites without ADE (Fermo et al., 2008). In this case, the presence of this compound does not appear to represent an archeological record of the past use of the vessels.

Despite this discussion, there is still no experimental evidence to support the cookery hypothesis. Given this, the present study involved the production of ceramic pots following archeological techniques and materials, which were exposed to conditions that simulate the cooking process, in order to evaluate the incorporation of phosphorus and calcium into the ceramics. The results of the experiment provide systematic evidence of the role of cooking in the accumulation of these elements in the ceramic material, equivalent to that found in the ADE soil profiles, and reinforce the potential for the application of these elements as indicators of the use of the ceramic vessels for the preparation of food.

Materials and Methods

Production of the pottery and the experimental simulation of cooking conditions

For the experiment described here, six ceramic pots were made using the coiling technique, which was employed in the production of the majority of the vessels found in association with ADE soils. The pots were made by the artisan Maria da Motta Coimbra at a traditional pottery center in the town of Juruti, in the Brazilian state of Pará.

The basic raw material clay was collected from Piranha Lake (21M 598464/9755450), the communal deposit used by the artisanal potters of the Juruti region. The antiplastic was the local product known as cariapé, made from the ashes of the bark of *Moquilea* and *Licania* trees, which is widely used in the ceramics found at ADE sites (Costa et al., 2009), and continues to be employed in pottery making by traditional Amazonian populations (Meggers and Evans, 1957).

Once the pots were made, they were dried in the open air for 48 hours, and then placed in a pit in the ground and covered with firewood, which was set alight and burned for 2 hours, simulating as closely as possible the prehistoric pottery-making technique. Simultaneously, the chemical and mineralogical composition of the raw material and the pots (before and after firing) was determined, as described below.

In the laboratory, the pots were boiled continuously while containing a solution containing 0.03 wt% P_2O_5 and 0.03 wt% CaO. After 200 h (and every subsequent 200 h), one of the pots was removed from the experiment for the determination of its chemical and mineralogical composition. These analyses focused on the walls and lids of the pots, following the procedures described below.

Chemical and mineralogical analysis

The samples of clay, cariapé antiplastic, and the pots (before and after the experimental trials) were pulverized in an agate mortar. The mineralogical composition was determined by X-ray diffraction, using the powder method, in an XPERT PRO MPD diffractometer equipped with a PANalitical PW 3040/60 (theta-theta) goniometer, and copper anode ($\lambda CuK\alpha 1 = 1.54060$). The analyses were run in the Mineral Characterization Laboratory at the Federal University of Pará (UFPA).

The chemical analyses of the same materials were conducted by ICP-OES (Varian) at Acme-Labs, having been previously fused with lithium tetraborate (Anachemia Science) and then dissolved in nitric acid (Merck). Loss on Ignition (LOI) was determined by a gravimetric analysis following calcination at 1000°C. The raw materials and the pots (before and after the experimental trials) were also examined by SEM/EDS at the Zentrum für Werkstoffanalytik, Lauf, Germany, and in the UFPA Electronic Microscopy Laboratory, in Belém, Brazil.

Results

Description of the raw materials

The clay used to make the pots is composed of kaolinite, muscovite, and quartz (Figure 1), in other words, basically aluminosilicate, as well as iron presumably derived from amorphous oxides and hydroxides, given the lack of evidence of crystalline phases. The concentrations of potassium and magnesium are supported by the presence of muscovite (Table 1).

The levels of calcium and phosphorus found in the material are below mean crustal and PAAS levels, which indicates emphatically that neither of these elements was present in the raw material. However, the cariapé is made up of cristobalite and an amorphous phase (Figure 1). Chemically, it is basically siliceous (Table 1), poor in P and Ca, as shown in the archeological ceramic sherds (Costa et al., 2004a, 2009, 2011). Under SEM, it is similar to the material used in the archeological fragments. The LOI level of this material is also low, given that the organic material was eliminated by calcination prior to its use as a antiplastic. In the clay, this parameter is slightly higher than the theoretical level for kaolinite, indicating the presence of organic material.

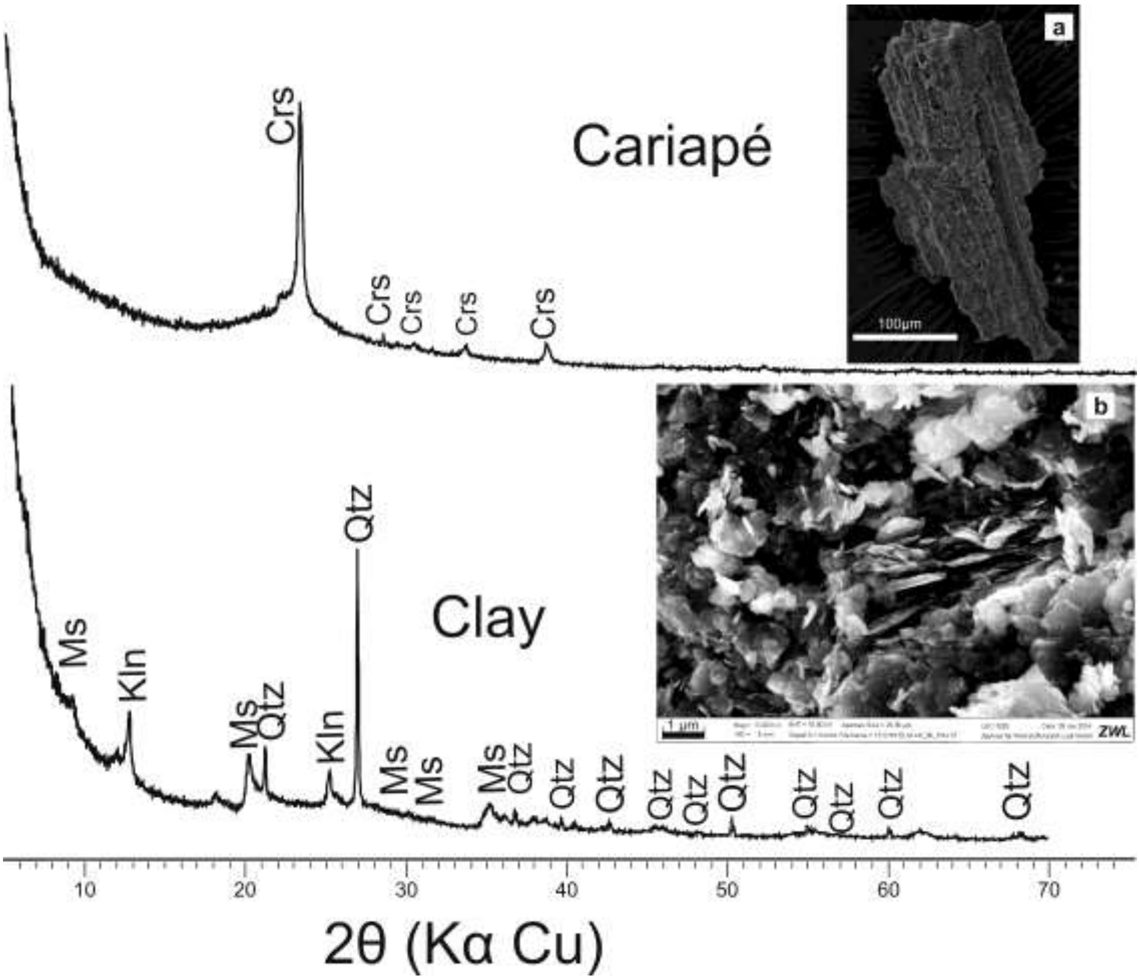


Figure 1: Raw materials used for the production of the ceramic pots used in the experiment. Kln = kaolinite; Qtz = quartz; Ms = muscovite; Crs = cristobalite.

Superficial transformations of the pots and their composition

The calcined pots used in the experimented are composed of an amorphous phase, metakaolinite, quartz, and muscovite (Figure 2). The two latter minerals are derived from the raw material, as demonstrated above, while the metakaolinite was formed during firing, indicating that this process reached 550°C (Evans and White, 1958) as in the archeological ceramics (Costa et al., 2004, 2009, 2011). Superficial alterations to the pots were observed throughout the experiment, reflecting the increasing reactivity of the clay matrix during the course of the trials (Figure 3).

The total chemical composition of the pots after the experiment (Table 1) indicates the incorporation of calcium and phosphorus, although this involved distinct processes for the two elements, as shown in the curve profiles (Figure 4). While both elements are found in the walls and lids of the pots, the highest concentrations were found in the walls. Chemical analyses by EDS coupled to the SEM indicate that even higher concentrations of both phosphorus and calcium are found in the internal surface of the pot bottoms (Figure 5), although the tendency is more pronounced for calcium. After 1200 h of boiling, there is a clear negative correlation between phosphorus and silica (spot analyses), and a positive correlation with aluminum, although, in this portion of the pots, the P/Al ratio is high, indicating that aluminum phosphates are not responsible for the whole of the phosphorus content detected, that is, there may also be phosphorus adsorbed in the pores of the ceramics, without the formation of a phase.

Table 1: Total chemical composition (wt%) of the ceramic pots following the experiment and their raw materials, compared with that of archeological ceramics retrieved from sites in the Amazon.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI	Total
						[wt%]						
Pan 1-wall	66.09	11.75	4.16	0.70	2.33	0.55	1.51	0.66	1.94	0.02	10.20	99.91
Pan 1-lid	61.48	15.08	4.70	0.90	1.37	0.55	1.82	0.75	0.16	0.02	13.00	99.83
Pan 2-wall	63.34	11.18	3.93	0.63	2.56	0.50	1.36	0.64	2.57	0.02	13.10	99.83
Pan 2-lid	65.15	13.05	4.72	0.67	0.99	0.60	1.66	0.80	0.30	0.02	11.90	99.86
Pan 3-wall	58.68	10.43	4.11	0.53	3.05	0.46	1.23	0.58	2.75	0.02	18.10	99.94
Pan 3-lid	66.02	12.31	4.32	0.58	0.94	0.61	1.65	0.77	0.87	0.01	11.80	99.88
Pan 4-wall	48.22	16.39	2.34	0.62	3.88	0.13	1.40	0.52	4.51	0.01	21.90	99.92
Pan 4-lid	66.12	14.57	5.00	0.87	0.93	0.62	1.88	0.82	0.48	0.02	8.60	99.91
Pan 5-wall	52.66	18.94	2.65	0.61	1.88	0.12	1.37	0.56	5.76	0.01	15.40	99.96
Pan 5-lid	63.59	14.26	4.59	0.60	1.31	0.50	1.65	0.76	0.90	0.01	11.70	99.87
Pan 6-wall	50.59	17.09	2.19	0.51	2.68	0.11	1.31	0.54	6.00	0.01	18.90	99.93
Pan 6-lid	66.67	13.12	4.82	0.57	0.72	0.54	1.57	0.78	0.58	0.02	10.50	99.89
Cariapé	96.08	0.05	1.21	0.22	0.59	0.21	0.36	0.01	0.05	0.01	1.20	99.99
Clay	51.71	24.60	3.60	1.00	0.07	0.17	2.21	0.79	0.07	0.01	15.60	99.83
[1]CCR	64.90	14.60	4.40	2.24	4.12	3.46	3.45	0.52	0.15	0.07	n.d.	-
[2]PAAS	62.80	18.90	6.50	2.20	1.30	1.20	3.70	1.00	0.16	0.11	n.d.	-
[3]Manduquinha	71.35	8.60	4.54	0.26	0.19	0.98	0.59	0.40	1.31	0.01	11.63	99.86
[4]C.Porteira	65.55	16.37	5.79	0.63	0.43	0.69	0.90	0.86	2.37	0.01	n.d.	-
[5]Juriti	60.76	16.90	3.76	0.61	0.27	0.20	1.70	0.67	3.58	0.01	11.40	99.86
[6]Tacana	56.53	17.36	3.43	0.42	0.04	0.06	1.27	1.01	1.34	0.01	18.40	99.87
[7]Jabuti	36.90	16.50	10.50	0.95	2.49	0.26	0.82	0.99	8.87	0.20	21.50	99.98

1- Continental crustal rock (Wedepohl, 1995); 2- Argilas australianas pós- arqueanas (Taylor and McLennan. 1985); 3-(Coelho et al., 1996); 4 (Costa et al., 2004a); 5 (Silva, 2010); 6 (Costa et al., 2011); 7 (Costa et al, 2012); n.d.: not determinaded.

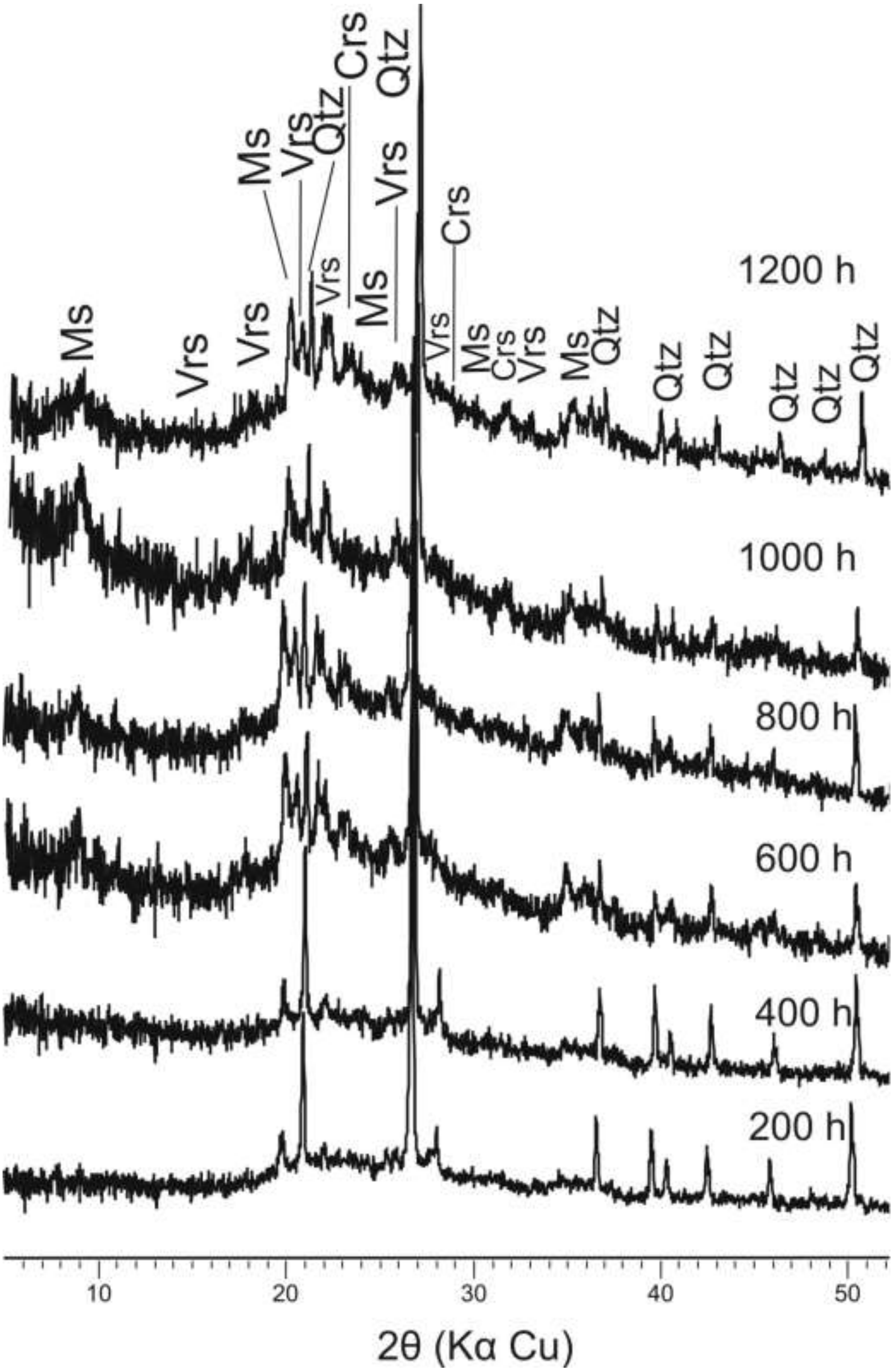


Figure 2: Mineral composition of the pots during the course of the experiment, based on XRD. Qtz-quartz, Vsr-variscite, Ms-muscovite;

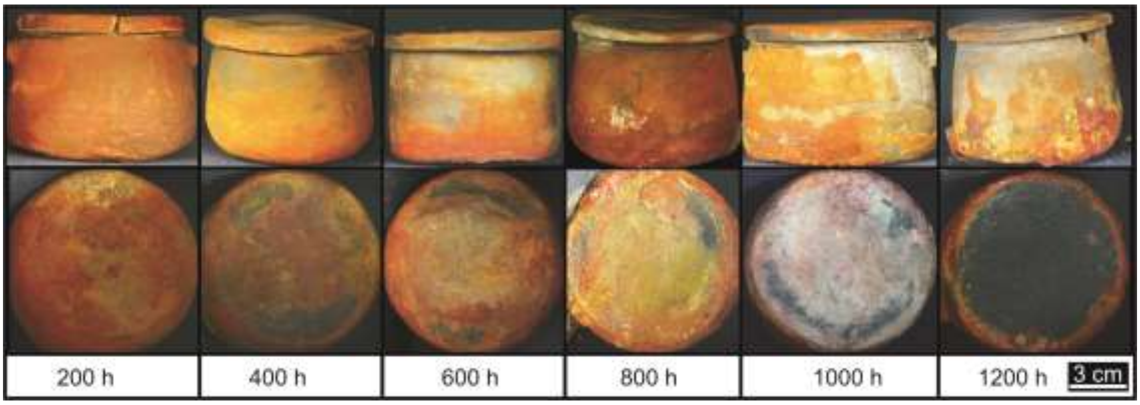


Figure 3: Superficial alterations at the top and bottom of the pots during the course of the experiment.

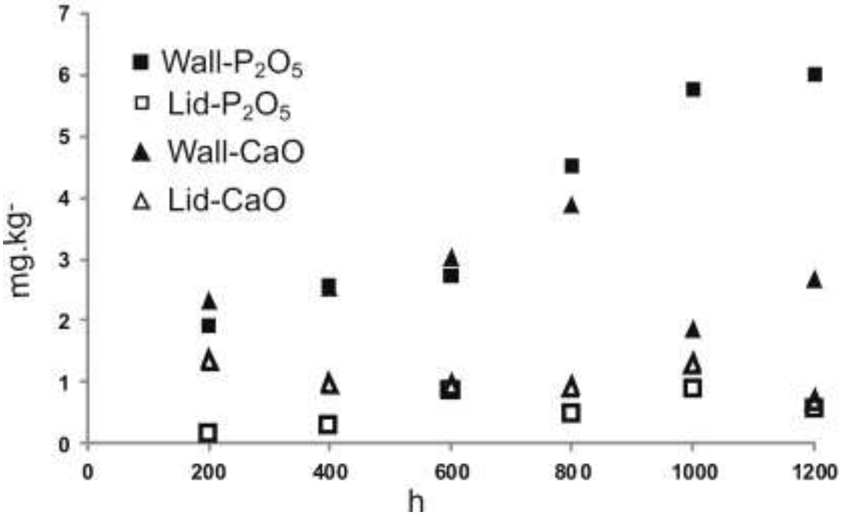
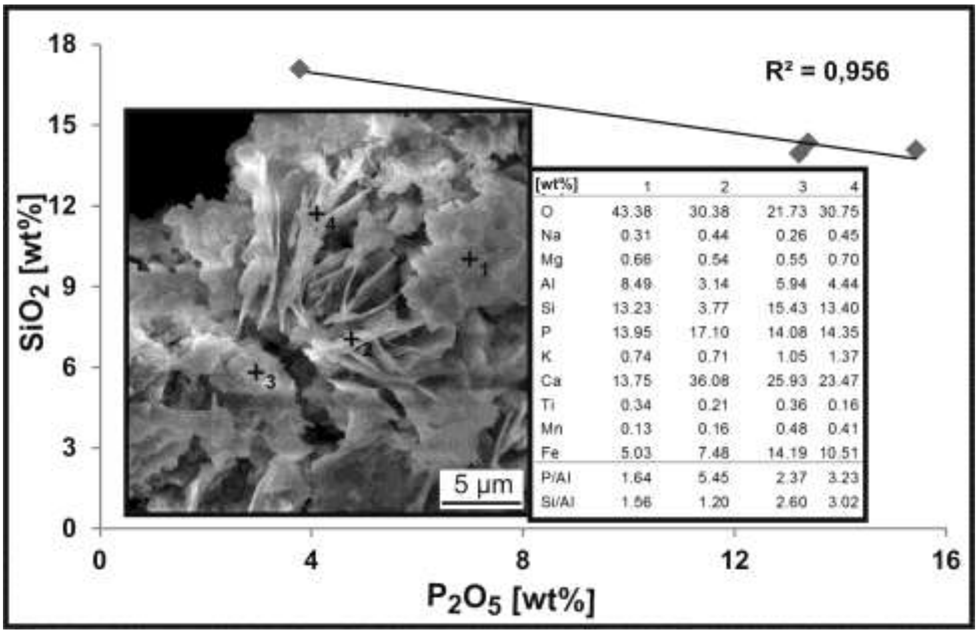


Figure 4: Incorporation of phosphorus (P_2O_5) and calcium (CaO) into the walls and lids of the pots during the course of the experiment.



[wt%]	1	2	3	4
O	43.38	30.38	21.73	30.75
Na	0.31	0.44	0.26	0.45
Mg	0.66	0.54	0.55	0.70
Al	8.49	3.14	5.94	4.44
Si	13.23	3.77	15.43	13.40
P	13.95	17.10	14.08	14.35
K	0.74	0.71	1.05	1.37
Ca	13.75	36.08	25.93	23.47
Ti	0.34	0.21	0.36	0.16
Mn	0.13	0.16	0.48	0.41
Fe	5.03	7.48	14.19	10.51
P/Al	1.64	5.45	2.37	3.23
Si/Al	1.56	1.20	2.60	3.02

Figure 5: Scanning electron microscope image showing the mineral and chemical transformations of the internal surface of the bottom of the pot following 1200 h of trials, and the correlation obtained between P_2O_5 and SiO_2.

Spot analyses of chemical composition also confirmed the tendency for the enrichment of phosphorus and calcium in the internal surfaces of the pots and their lids. These data indicate clearly that the concentrations of both elements increase towards the surface of the material, although the precipitation of these elements in the pores also increases with the time of contact with the solution (Figure 6 and Table 2). The behavior of both elements is more diffuse in the lids, however (Figure 7 and Table 3). The curves obtained from the total chemical analyses reflect the same diffuse behavior in the lids as a whole (Figure 4).

No crystalline phases containing calcium were detected during the experiment (Figure 2), although the development of peaks reflecting the presence of variscite in the pot walls was observed throughout the experiment. This mineral was characterized by XRD only after 600 h of cooking, and was not apparent in the 400 h sample (Figure 2), even though the concentrations of P_2O_5 were already high in the 200 h sample (Table 1), and the lids presented the same concentrations throughout the experiment. Chemical spot analyses confirm the presence of amorphous aluminum phosphate at 200 h, based on the correlation between the phosphorus and the aluminum, and the P/Al ratio found at some points, which is close to the theoretical ratio for variscite (Figure 8). Agglomerations of variscite can be observed clearly by SEM/SED at 1200 h (Figure 9 and Table 4). It is important to note that the texture of the pots tested in the present study is also highly similar to that of the archeological sherds, with the porous surfaces being clearly visible by SEM (Figures 5, 6, and 7).

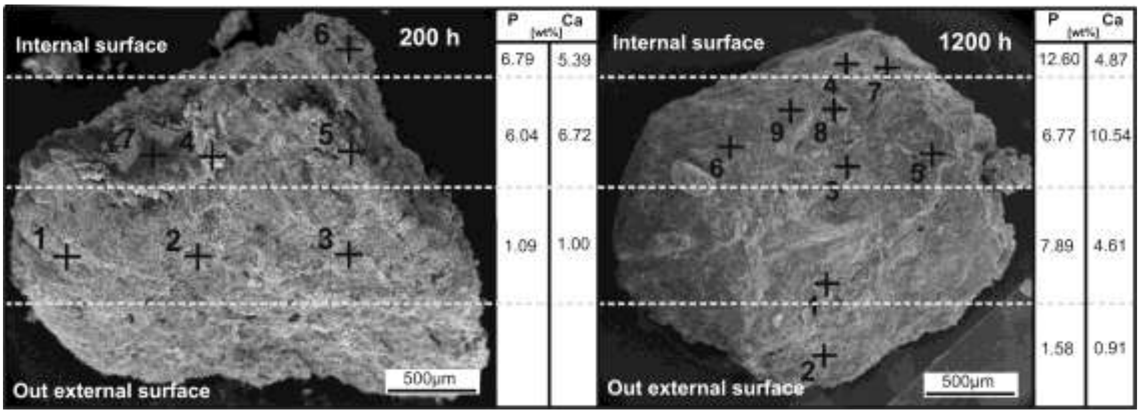


Figure 6: Micrographs of the walls of the pots obtained by SEM, indicating the locations of the chemical spot analyses by EDS, which found the highest concentrations P_2O_5 (wt%) and CaO (wt%) closest to the internal surfaces of the pots.

Table 2: Chemical analyses by EDS of the walls of the pots at the points indicated in Figure 6.

		O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
							[wt%]					
200 h	1	24.39	0.36	0.65	65.86	1.68	1.52	0.13	0.80	0.45	1.95	2.22
	2	31.30	0.17	0.27	50.77	10.11	1.19	0.60	1.51	0.68	0.89	2.50
	3	24.30	0.21	0.09	53.24	9.25	0.55	0.26	0.69	3.35	4.27	3.78
	4	46.20	0.53	0.19	6.44	27.07	7.89	1.54	4.94	0.51	0.11	4.58
	5	32.62	0.25	1.03	7.58	37.62	4.82	1.95	9.77	1.00	0.24	3.11
	6	49.33	0.74	0.32	7.95	26.79	6.79	1.34	5.39	0.38	0.04	0.95
	7	36.24	0.12	0.17	8.39	30.93	5.41	0.93	5.45	0.23	0.40	11.73
1200 h	1	55.15	0.92	1.60	13.41	10.72	7.89	0.89	4.61	1.53	0.97	2.32
	2	25.67	1.11	0.81	65.35	2.30	1.58	0.00	0.91	0.47	1.07	0.72
	3	57.65	0.53	0.33	7.71	9.30	6.47	1.78	13.65	0.26	0.23	2.10
	4	54.84	0.22	0.13	13.23	10.21	16.02	0.26	4.22	0.15	0.07	0.65
	5	51.29	0.63	0.46	11.11	17.75	6.29	1.73	8.31	0.12	0.31	2.01
	6	51.78	0.38	0.11	7.87	19.46	7.93	1.09	9.39	0.39	0.29	1.33
	7	56.73	0.36	1.80	9.72	14.65	9.18	0.70	5.52	0.16	0.22	0.98
	8	62.80	0.72	1.55	7.63	13.64	5.36	0.65	5.27	0.25	0.25	1.89
	9	38.11	0.22	0.51	9.47	23.73	7.31	2.01	13.88	0.33	0.73	3.70

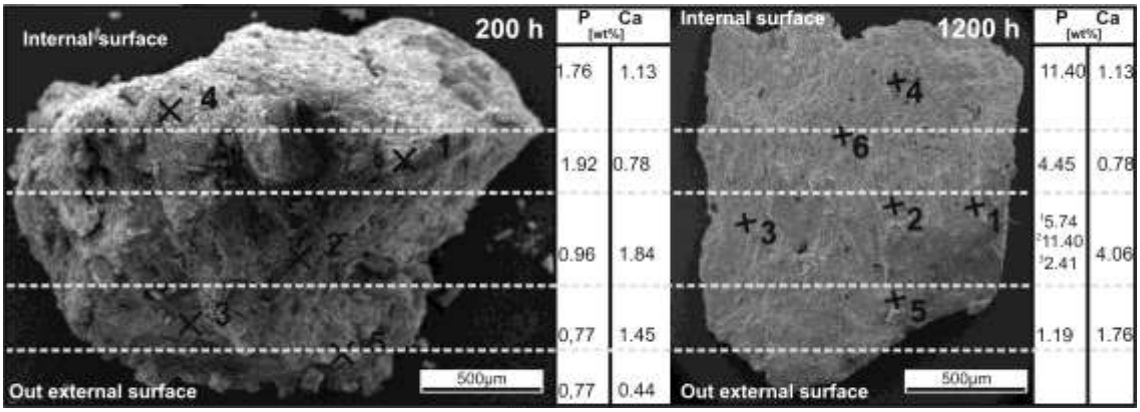
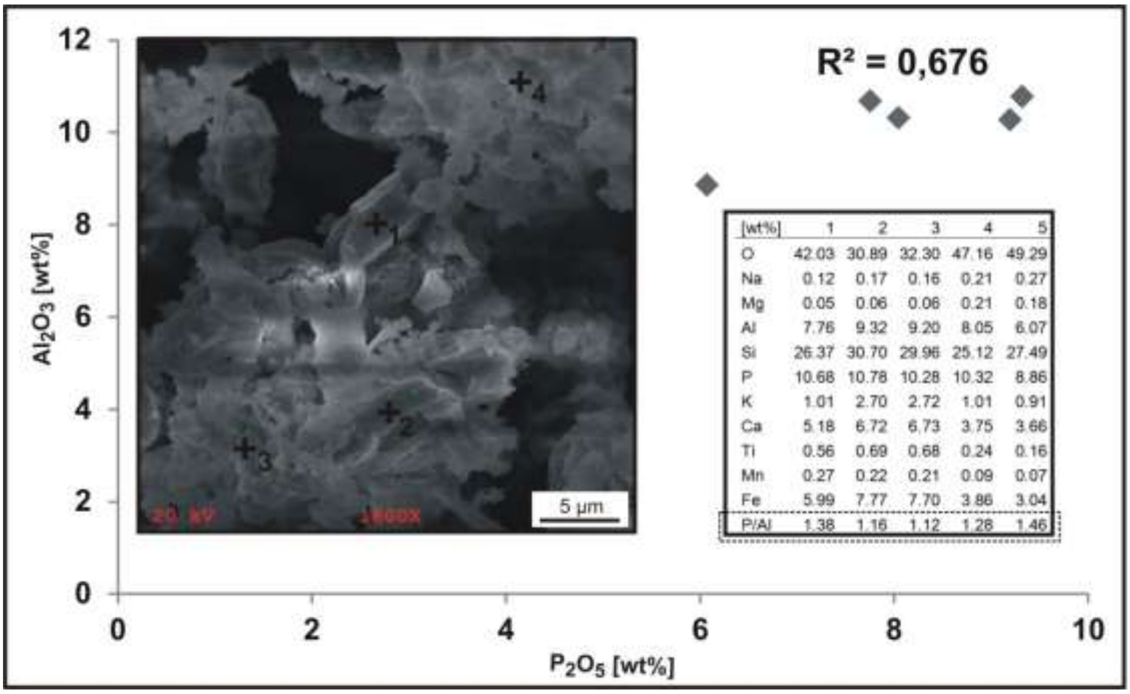


Figure 7: Micrographs of the pot lids obtained by SEM, indicating the locations of the chemical spot analyses by EDS, which recorded a more diffuse arrangement in the concentrations of P_2O_5 (wt%) and CaO (wt%) relative to the internal surfaces of the ceramics.

Table 3: Chemical analysis of the pot lids by EDS at the points indicated in Figure 7.

		O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
							[wt%]					
200 h	1	46.54	0.31	0.76	7.52	37.28	1.92	1.81	0.78	0.28	0.09	2.70
	2	43.55	0.13	0.36	6.92	35.08	0.96	1.46	1.84	2.43	0.27	7.01
	3	43.53	0.62	0.47	11.27	30.92	0.77	2.35	1.45	0.71	0.10	7.82
	4	44.59	0.15	0.53	7.61	38.57	1.76	1.23	1.13	0.51	0.16	3.77
	5	49.60	0.22	0.23	3.89	43.25	0.77	0.32	0.44	0.17	0.04	1.08
1200 h	1	59.93	0.33	1.41	9.47	17.11	5.74	0.57	4.58	0.13	0.10	0.62
	2	59.89	0.23	0.31	13.89	9.14	11.40	0.33	4.25	0.17	0.07	0.32
	3	59.69	0.31	2.21	8.30	21.93	2.41	0.90	3.35	0.20	0.10	0.59
	4	55.15	0.18	0.51	10.94	17.95	10.18	0.53	3.74	0.09	0.12	0.63
	5	61.92	0.33	0.43	2.60	30.46	1.19	0.35	1.76	0.09	0.04	0.82
	6	53.04	0.29	2.55	7.95	12.04	4.45	1.32	8.03	0.59	0.76	8.97



[wt%]	1	2	3	4	5
O	42.03	30.89	32.30	47.16	49.29
Na	0.12	0.17	0.16	0.21	0.27
Mg	0.05	0.06	0.06	0.21	0.18
Al	7.76	9.32	9.20	8.05	6.07
Si	26.37	30.70	29.96	25.12	27.49
P	10.68	10.78	10.28	10.32	8.86
K	1.01	2.70	2.72	1.01	0.91
Ca	5.18	6.72	6.73	3.75	3.66
Ti	0.56	0.69	0.68	0.24	0.16
Mn	0.27	0.22	0.21	0.09	0.07
Fe	5.99	7.77	7.70	3.86	3.04
P/Al	1.38	1.16	1.12	1.28	1.46

Figure 8: Pot wall after 200 h of boiling (detail of point 4 in Figure 6), showing the presence of amorphous aluminum phosphate comparable to variscite, and the correlation obtained between P_2O_5 and Al_2O_3.

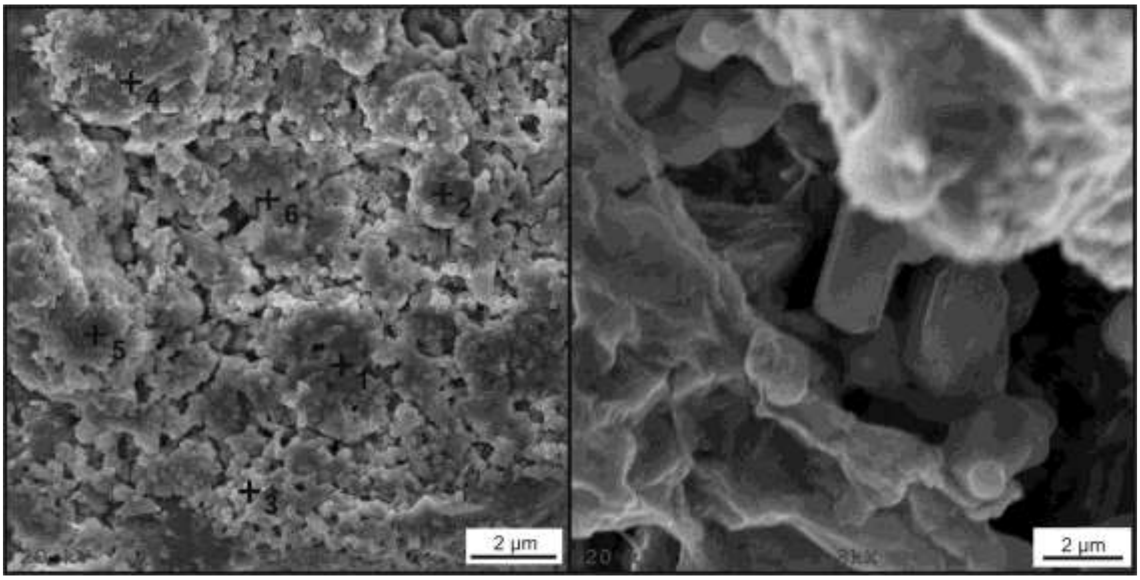


Figure 9: Scanning electron photomicrographs. Detail of point 4 in Figure 6 at 1200 h, probably showing crystals of variscite.

Table 4: Chemical composition analyzed by SEM/EDS at the points indicated in Figure 9 confirming the formation of variscite at 1200 h.

wt%	1	2	3	4	5	6	Variscite theoretical
O	54.07	61.86	59.66	56.10	48.30	60.75	62.35
Na	0.23	0.20	0.26	0.15	0.20	0.22	-
Mg	0.07	0.15	0.03	0.06	0.26	0.01	-
Al	12.41	16.92	15.20	19.67	15.41	15.34	17.53
Si	13.81	1.42	4.59	0.39	10.80	3.68	-
P	15.04	16.93	16.41	21.07	18.24	16.13	20.12
K	0.18	0.08	0.19	0.12	0.24	0.15	-
Ca	3.76	2.02	3.17	1.89	5.55	3.34	-
Ti	0.09	0.05	0.11	0.05	0.11	0.07	-
Mn	0.10	0.07	0.05	0.14	0.22	0.07	-
Fe	0.26	0.30	0.35	0.35	0.69	0.26	-
P/Al	1.21	1.00	1.08	1.07	1.18	1.05	1.15

Discussion

A number of authors have referred to the primary presence of phosphorus in the raw materials used to make pottery (Bollong et al., 1993; Maritam et al., 2009, Ionescu et al., 2011). However, the results of the present study indicate that neither this element nor calcium was present in the raw materials, which supports their interpretation as archeological evidence. The chemical-mineral similarities among the pots produced here and archeological sherds reinforce this conclusion.

The lower concentrations of calcium and phosphorus found in the walls of the pots in comparison with their lids appears to be related to the fact that this part of the pot was in contact only with the vapor of the solution during cooking trials. Both Dunn (1972) and Cackette et al. (1987) also recorded different concentrations of phosphorus in different portions of the archeological vessels, further reinforcing the conclusion that they were derived from the use of the pots for cooking. These studies also recorded decreasing concentrations as the distance from the bottom of the pot increased. In the present study, the highest concentrations of phosphorus were also detected in the internal surface of the pot bottoms. This confirms the approximation of the experimental conditions to those of the prehistoric populations, in particular with regard to the materials and techniques used to make the pots. The similarities in the chemical and mineralogical composition of the experimental pots and the archeological artifacts are strikingly clear.

While phosphorus concentrations are high during the first two stages of the experiment, i.e., 1.94 wt% at 200 h and 2.57 wt% at 400 h, no evidence was found of the formation of variscite. This indicates that time is an additional factor for the formation of the crystalline phases that contain phosphorus through cooking. During these two first stages, however, precursor phases comparable to variscite are present, as indicated by the P/Al ratio, and the correlation between these elements (0.678) obtained in the chemical spot analyses.

Archeological sherds from ADEs with P_2O_5 levels of 3% or less also lack the crystalline phases, although the chemical data align them with amorphous aluminum phosphates of the variscite type (Costa et al, 2006, 2009; 2011). Polvorinos del Rio et al. (2005) also recorded levels of approximately 3% P_2O_5 in domestic pots used for cooking and, as in the present study, no mineral phases were found. Legodi and Waal (2007) recorded a similar situation, with P_2O_5 levels of around 1.18%. This indicates that the archeological vessels were used for approximately 400 hours of cooking.

After 600 h, however, the superficial alterations of the pots become more intense (Figure 5), principally in the bottom of the pots, which may indicate that 400 h represents the approximate working lifespan of these utensils. By 1000 h and then 1200 h, the pot bottoms were increasingly altered, and would become detached when the pots were retrieved (Figure 5). The hypothesis that the prehistoric ceramicists discarded their pots after 400 h is further reinforced by the fact that archeological sherds generally present values of around 3% P_2O_5. The lids consistently presented lower levels, however, with no more than 0.9 wt%, even after 1200 h. This would explain why phosphatic phases are rarely encountered in archeological sherds – it would be necessary to use the pots for much longer periods of time, although the vessels would probably be unable to survive intact.

The formation of aluminum phosphates from kaolinite has been described by a number of authors (Kittrick and Jackson, 1954; Hudcová, 1970; Rajan, 1976), who concluded that the formation of the phosphates depends on the decomposition rate of the kaolinite. In the case of the ceramic pots, the kaolinite was calcined, leading to a collapse in its structure, which almost certainly facilitated the reaction, and reduced the time necessary for the formation of the phosphates. The negative correlation between the phosphorus and the silica, and the superficial alterations suffered by the pots reinforce this hypothesis.

The experimental curve obtained for the presence of phosphorus in the pot walls is similar to a sigmoidal isotherm (Figure 4) in the classification of Giles et al. (1960), indicating low initial levels of adsorption, which increase as the number of adsorbed molecules increases. This means that there was an association among the adsorptive molecules, that is, cooperative adsorption (Giles et al., 1960), which may be associated with the high P/Al ratios indicated by the spot analyses of the clay matrix, as well as the non-uniform distribution of the phosphorus.

The experimental data on the distribution of calcium in both parts of the pots are diffuse, and may reflect adsorption by electrostatic attraction of the cation by the negative charges present on the heterogeneous surface of the metakaolinite matrix (Angove et al., 1998, Heidemann et al., 2005). In this case, a much longer time of contact with the experimental solution would be required for the formation of phases containing calcium. However, there is no correlation between the calcium and the other elements analyzed, which might have corroborated this hypothesis (Figure 10).

This type of adsorption, which is readily reversible (Angove et al., 1998, Heidemann et al., 2005), may account for the lack of calcium phases – crystalline or amorphous – reported in previous studies (Costa et al, 2004, 2009, 2006, 2011). The amount of contact time necessary for the formation of the phases that would fix the calcium in the material – and constitute an important archeological record – would greatly exceed the working lifespan of a ceramic pot. Even so, Costa et al. (2012) highlighted the formation of crandallite-goyazite in archeological ceramics, although in these specific cases, the formation of the mineral was facilitated by the presence of shell fragments used as antiplastic, which were substituted completely by crandallite-goyazite during cooking. In other words, the shell acted as a catalyzer, and the sherds containing this material returned the highest levels of phosphates – 8.75 wt%, on average – yet described.

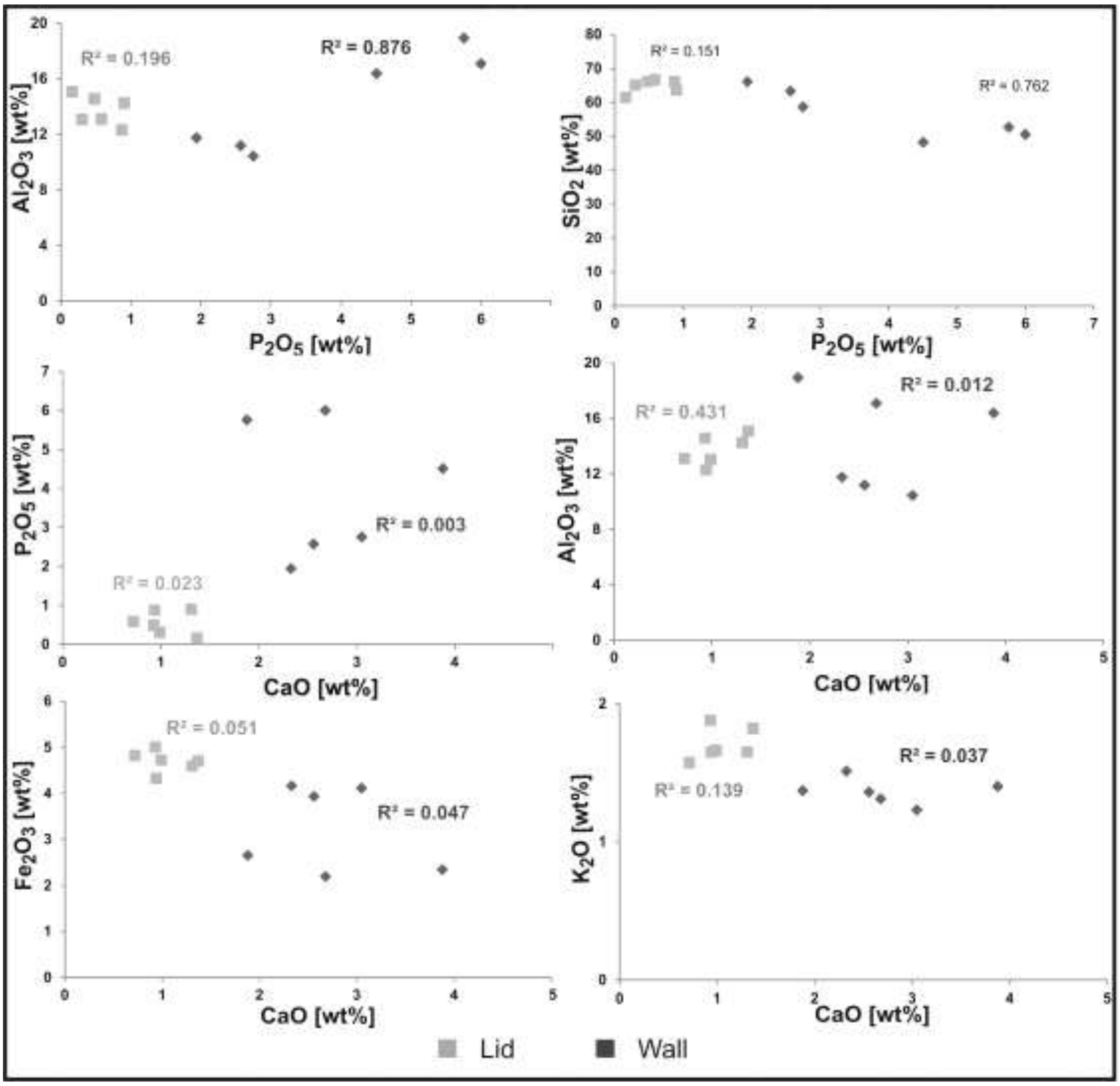


Figure 10: Correlations between the concentrations (wt%) of CaO and Al_2O_3, Fe_2O_3, P_2O_5 and K_2O, as well as P_2O_5 and Al_2O_3, obtained from the results of the total chemical analyses.

Conclusions

The ceramic pots produced in the present study were exactly equivalent to the archeological vessels represented by the sherds in terms of the chemical and mineralogical composition, and texture, validating their usefulness for inferences on the function and use of the archeological samples. No evidence was found of the primary presence of phosphorus or calcium, as indicated in the literature, at least for phosphorus (Bollong et al., 1993; Maritam et al., 2009, Ionescu et al., 2011).

The pots were able to incorporate calcium and phosphorus into their walls and, to a lesser extent, their lids. Direct contact with the phosphorus solution and the total time of immersion were essential parameters for the formation of amorphous aluminum phosphates and those of the variscite type. The chemical affinity between the phosphorus and the aluminum allows for the fixation of the phosphorus in the pot walls, and represents potentially important archeological evidence. The phosphorus thus constitutes an important indicator of the use of the vessels (or the sherds that represent them) for cooking food. However, phases containing calcium were not detected, presumably because the time required for the formation of these phases would greatly exceed the working lifespan of the ceramic pots, which means that this element may not last for long periods of time, and unlike phosphorus, does not constitute potentially meaningful archeological evidence.

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6. CONCLUSÕES

Os FC aqui estudados foram confeccionados com matérias primas oriundas das proximidades de seus sítios. A todos é comum a temperatura de queima em torno de 550°C, e a matriz rica em metacaulinita e quartzo.

As matérias primas argilosas empregadas na confecção dos FC dos sítios Da Mata e Jabuti guardam grande semelhança entre si, o que está relacionado ao emprego de sedimentos da Formação Barreiras que constituem as rochas aflorantes em ambas as regiões. Por outro lado, estes FC são distinguidos pelas diferenças químico-minerais ocasionadas pelo uso de diferentes antiplásticos adicionados a matriz argilosa, cariapé em Da Mata, e o predomínio de conchas em Jabuti. Já os FC de Monte Dourado 1 apresentam assembleia mineralógica mais complexa representada por rochas máficas metamorfizadas (anfibolitos) mineralizadas em ilmenita. Isto é fruto do emprego de rochas trituradas combinadas a cariapé como antiplástico. A presença de quartzo, detectada em todos FC, não significa necessariamente antiplástico, pois ele é também componente da matéria prima argilosa. Estas diferenças são intensificadas pela presença de fosfatos, mais abundantes em Jabuti com a presença de crandallita-goyazita, em Monte Dourado 1 onde a segelerita foi detectada, e mais restritamente em Da Mata onde apenas fosfatos de alumínio amorfos estão presentes. A presença destes fosfatos, exceto segelerita, é creditada ao uso continuados das vasilhas cerâmicas ao cozimento de alimentos. A segelerita também é um fosfato neoformado, mas a mineralização está relacionada ao ambiente de descarte dos FC.

Dentre os FC de um mesmo sítio não houve mudança na matéria prima ou na temperatura de queima empregada. A única diferença detecta está no sítio Jabuti, onde o cariapé combinado às conchas está apenas no nível mais superficial. Também não foram observadas diferenças quando considerados os diferentes intervalos de espessuras selecionados.

Após o descarte no solo, os experimentos mostram que os FC tem elevada capacidade de liberar nutrientes ao serem intemperizados, e, por conseguinte são responsáveis pela resiliência dos solos TPA. Este processo, é mais efetivo entre os FC menores (≤ 2 cm) e no horizonte A, portanto onde as intempéries são mais agressivas.

No entanto, a capacidade de liberar nutrientes é distinta entre os sítios estudados, e reflete claramente as diferentes matérias primas empregadas em suas confecções, bem como a incorporação de P durante o uso.

Os FC dos sítios Jabuti e Monte Dourado 1 são mais férteis e correspondem a solos eutróficos, superando até mesmo a alta fertilidade da TPA, diferentemente daqueles do Da Mata que apresentam menor capacidade. Já a disponibilidade do P é muito elevada, e está diretamente relacionada à alta porosidade dos FC. A liberação deste nutriente é favorável e linear, porém ocorre lentamente, um aspecto fundamental para contribuição em longo prazo.

Por fim, ao serem simuladas condições de cozimento em panelas cerâmicas comparáveis as arqueológicas, tornou-se indiscutível a capacidade destas panelas de incorporar cálcio e fósforo em suas paredes e em menor proporção em suas tampas. O tempo e o contato direto com a solução que contém o fósforo são parâmetros essenciais para formação de fosfatos de alumínio amorfos e tipo variscita. No entanto, a formação de fases que contenham Ca é superior à vida útil de uma panela cerâmica, o que não permite seu uso como indicador de função para cozimento de alimentos.

Portanto os fosfatos de alumínio podem se formar nas vasilhas cerâmicas durante o preparo de alimentos por cozimento, assim, sua presença nas vasilhas cerâmicas se constitui, em um importante indicador de uso das mesmas para o cozimento de alimentos e seus fragmentos nos solos são fonte potencial importante de fertilidade.

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APÊNDICES

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CLAY6480: Notice of manuscript number

Applied Clay Sciences <clay-eo@elsevier.com> 30 de agosto de 2014 01:01
Para: suyanneflavia@hotmail.com, suyanneflavia@gmail.com

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Applied Clay Science

Apêndice 1: Comprovante de submissão do artigo Pre-historic production of ceramics in the Amazon: Provenience, raw materials, and firing teperatures, submetido a Applied Clay Science.

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Suyanne Flavia Santos Rodrigues <suyanneflavia@gmail.com>

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Authors: Suyanne Flávia Santos Rodrigues, MSc.; Marcondes L Costa, post-Phd; Herbert Pöllmann, post-Phd
Article Type: Full Length Article

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Apêndice 2: Comprovante de submissão do artigo Contribution of the fertility potencial of archaeological sherds to the long-term fertility of Amazonian Dark Earth, submetido ao Journal of Archaeological Science.

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Article Type: Full Length Article

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Apêndice 3: Comprovante de submissão do artigo Phosphorus in archaeological ceramics as evidence of the use of the pots for cooking food, submetido ao Journal of Archaeological Science.

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INSTITUTO DE GEOCIÊNCIAS
PROGRAMA DE PÓS-GRADUAÇÃO EM GEOLOGIA E GEOQUÍMICA

PROGRAMA DE PÓS-GRADUAÇÃO EM GEOLOGIA E GEOQUÍMICA
TESE APROVADA COM DISTINÇÃO

PARECER

Sobre a Defesa Pública da Tese de Doutorado de
SUYANNE FLÁVIA SANTOS RODRIGUES

A banca examinadora da Tese de Doutorado de **SUYANNE FLÁVIA SANTOS RODRIGUES,** orientanda do Prof. Marcondes Lima da Costa (UFPA), e composta pelos professores doutores Eduardo Góes Neves (USP), Kelly das Graças Fernandes Dantas (UFPA), Vanda Porpino Lemos (UFPA), e Roberto de Freitas Neves (UFPA), após apresentação da sua tese, intitulada: **"OS FRAGMENTOS DE CERÂMICA ARQUEOLÓGICA COMO FONTE POTENCIAL DE FERTILIDADE DOS SOLOS TPA"** emite o seguinte parecer:

A candidata apresentou um documento composto por três artigos submetidos a periódicos de impacto internacional que atende às exigências básicas para uma tese de doutorado. Realizou sua apresentação de forma clara, organizada e segura no tempo hábil. Na arguição mostrou domínio da temática abordada e respondeu às perguntas formuladas pela banca.

Considerando que a candidata concluiu em tempo hábil, com submissão de três artigos em revistas internacionais e o seu excelente desempenho na apresentação e durante a arguição, a banca examinadora decidiu por unanimidade aprovar a tese de doutorado com distinção.

Belém, 26 de setembro de 2014.

Prof. Marcondes Lima da Costa (UFPA)

Eduardo

Prof. Eduardo Góes Neves (USP)

Kelly G. Fernandes Dantas

Prof.ª Kelly das Graças F. Dantas (UFPA)

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