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ORIGEM BIOMOLECULAR DE RESÍDUOS ORGÂNICOS EM FRAGMENTOS DE CERÂMICAS ARQUEOLÓGICAS DA AMAZÔNIA E SUA RELAÇÃO COM O FÓSFORO CONTIDO

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Como requisito parcial à obtenção do Grau de Doutor em Ciências na Área de GEOQUÍMICA E PETROLOGIA

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RESUMO

A elevada e perene fertilidade dos solos Terra Preta Arqueológica (TPA) na Amazônia, é alvo de investigações desde seu reconhecimento e divulgação e gera interesse até os dias atuais. Interligados a estes solos estão fragmentos de antigos objetos cerâmicos correspondentes a registros da cultura material de sociedades pretéritas, e que aí se encontram fruto do descarte e consequente incorporação aos processos de formação de solos tropicais. Investigações químicas, mineralógicas e de fertilidade apontaram os fragmentos como potenciais colaboradores à resiliente fertilidade dos solos TPA. E mais, recentemente comprovou-se que o fósforo, se apresenta como uma assinatura geoquímica dos fragmentos cerâmicos contidos em sítios com TPA e também os responsáveis pela assinatura química em fósforo desses solos. Essas pesquisas também demonstraram que o fósforo se incorpora aos vasos cerâmicos não vitrificados através do contato da matriz argilosa calcinada com soluções aquosas ricas em nutrientes, como no ato de cozinhar de alimentos. O uso ou função primária de um objeto arqueológico vem sendo determinada há pelo menos meio século na Europa e Ásia a níveis moleculares por meio de extração com solventes e emprego de espectrômetro de massas acoplado à cromatógrafos. Ainda não explorado em fragmentos da Amazônia e admitindo-se que fósforo e matéria orgânica sejam provenientes da mesma fonte, produtos processados durante a vida útil nos antigos utilitários domésticos, o presente trabalho visa caracterizar os possíveis compostos orgânicos preservados confrontando estes dados à classificação técnico-morfológicas dos fragmentos e às informações químico-mineralógicas, especialmente aos conteúdos de fósforo. Para tal, fragmentos cerâmicos de quatro sítios arqueológicos situados próximos a calha do grande rio Amazonas, portanto na direção leste-oeste na região amazônica foram selecionados: Quebrada Tacana (Letícia-Colômbia) a oeste, Juruti (Juruti - PA), Boa Vista (Porto Trombetas - PA) e Raimundo (Caxiuanã - PA) a leste. Inicialmente, os fragmentos foram descritos mesoscopicamente e selecionados para análises de fertilidade, ensaios de dessorção, DRX, MEV-SED, IV-FT, microscopia óptica e GC-MS. Com a obtenção destes dados objetivou-se avaliar a capacidade de fragmentos arqueológicos inseridos no contexto amazônico em preservar compostos orgânicos relacionados à atividades pretéritas de populações antigas confrontando-os à morfologia, composição química, mineralógica e fertilidade aventando sobre o ciclo da peça cerâmica representada por seus fragmentos e sua potencial contribuição à fertilidade dos solos TPA. Os fragmentos cerâmicos demonstraram caráter fértil em nutrientes e micronutrientes, cujas fontes são provenientes da matéria-prima, à exceção do fósforo, nutriente de maior destaque em termos de concentração e com capacidade dessortiva. A temperatura de queima estimada foi divergente em relação aos sítios, baseada nas identificações de caulinita e metacaulinita por IV. Nos sítios Quebrada Tacana e Juruti os fragmentos demonstraram temperatura superior a 600 ºC e inferior a 800 ºC, ao passo que os fragmentos do sítio Boa Vista não ultrapassaram 600 ºC. Os extratos de todos os fragmentos foram dominados por séries de ácidos *n*-alcanóicos de cadeia curta e média (C_{12}-C_{20}), outro componente dominante foi o $C_{18:1}$ (ácido oleico), e em apenas um fragmento pertencente ao sítio Quebrada Tacana foram os sesquiterpenos. O padrão de distribuição entre todos os fragmentos mostrou que o mais abundante foi o $C_{16:0}$, seguido por $C_{18:0}$ e $C_{18:1}$ e pequenas quantidades de *n*-alcanos e *n*-alcanóis de cadeias curtas. A predominância de ácidos graxos livres indica que os lipídios são altamente degradados, uma característica típica de resíduos orgânicos antigos. O extrato lipídico da amostra QT-07 (sítio Quebrada Tacana) composto totalmente por sesquiterpenos, evidencia a presença de resina de plantas. De igual maneira o registro ainda que pouco expressivo de séries de *n*-alcanos e *n*-alcanóis cuja média não ultrapassa 1,3% também são indicativos de contribuição vegetal, para este caso determinados em fragmentos do sítio Raimundo. Os dados mineralógicos asseguram que os lipídios preservados nos fragmentos cerâmicos guardam informações sobre atividades pretéritas, desde que a temperatura de queima indicada é superior a 550 ºC, suficiente para eliminar compostos oxigenados oriundos da matéria-prima, argila e antiplásticos. A presença de biomarcadores diagnósticos de organismos aquáticos foi identificado em apenas dois fragmentos do sítio Quebrada Tacana, o 4,8,12-trimetildecanóico (TMTD) e ademais a identificação de ácidos de cadeias ímpares, $C_{15:0}$ e $C_{17:0}$ juntamente com seus respectivos ácidos ramificados $C_{15:1}$ e $C_{17:1}$ constituem fortes indícios de contribuição de origem animal. Portanto eles podem sugerir que esses fragmentos representem utensílios empregados na preparação prolongada de alimentos, e, conseguintemente por terem tido contato com fontes primárias de nutrientes, no estágio de uso do ciclo cerâmico (adsorção de nutrientes), o estágio de descarte (estágio atual) representaria uma fonte potencial de nutrientes propiciada pela própria degradação principalmente aos fragmentos mais expostos, da superfície e sub-superfície.

Palavras-chave: Fertilidade. Lipídios. Resina. Cromatografia gasosa. Cerâmica. TPA.

ABSTRACT

The high and perennial fertility of the Archaeological Dark Earth (ADE) soils in Amazon has been the subject of research since its recognition and dissemination and generates interest to the present day. Interconnected to these soils are potsherds of old ceramic objects corresponding to records of the material culture of ancient societies, and that are there fruit of the discard and consequent incorporation to the processes of formation of tropical soils. Chemical, mineral, and fertility investigations have identified the potsherds as potential collaborators in the resilient fertility of ADE soils. Moreover, phosphorus has recently been shown to be a geochemical signature of the potsherds contained in sites with ADE and also responsible for the chemical signature in phosphorus of these soils. These researches have also shown that phosphorus is incorporated into unglazed ceramic vessels through the contact of the fired clay matrix with nutrient-rich aqueous solutions, such as in the cooking of food. The use vessel or primary function has been determined for at least half a century in Europe and Asia at molecular levels by means of solvent extraction and the use of a mass spectrometer coupled to the chromatograph. Still not explored in potsherds of the Amazon and assuming that phosphorus and organic matter come from the same source, products processed during the lifetime of use in the vessels, the present work aims to characterize the possible organic compounds preserved confronting these data to the typological characteristics of the potsherds and to the chemical-mineralogical information, especially to the contents of phosphorus. For this, potsherds of four archaeological sites located near the channel of the great Amazon river, therefore in the east-west direction in the Amazon region were selected: Quebrada Tacana (Letícia-Colômbia) to the west, Juruti (Juruti - PA), Boa Vista (Porto Trombetas - PA) e Raimundo (Caxiuanã - PA) to the eastern. Initially, the potsherds were described mesoscopically and selected for fertility analyzes, desorption assays, XRD, SEM-EDS, FT-IR, optical microscopy and GC-MS. The aim of this study was to evaluate the ability of potsherds inserted in the Amazonian context to preserve organic compounds directly linked with vessel use in antiquity, by comparing them with morphology, chemical composition, mineralogical and fertility, on the lifetime of use of the vessel represented by their potsherds and their potential contribution to soil fertility TPA. Potsherds have been shown to be fertile in nutrients and micronutrients, whose sources are derived from the raw material, with the exception of phosphorus, a nutrient of greater prominence in terms of concentration and with desorption capacity. The estimated firing temperature was different from the sites, based on the identification of kaolinite and metakaolinite by IR. In the

Quebrada Tacana and Juruti sites, the potsherds showed a temperature above 600 ºC and below 800 ºC, while the potsherds of the Boa Vista site did not exceed 600 ºC. Extracts from all fragments were dominated by short and medium chain (C_{12}-C_{20}) n-alkanoic acid series, another dominant component was $C_{18:1}$ (oleic acid), and in only one fragment belonging to the Quebrada Tacana site were the sesquiterpenes. The distribution pattern among all the potsherds showed that the most abundant was $C_{16:0}$, followed by $C_{18:0}$ and $C_{18:1}$ and small amounts of n-alkanes and n-alkanols of short chains. The predominance of free fatty acids indicates that lipids are highly degraded, a typical feature of earlier organic residue. The lipid extract of the QT-07 sample (Quebrada Tacana site) composed entirely of sesquiterpenes, evidences the presence of plant resin. In the same way, even if insignificant register of n-alkanes and n-alkanols whose average does not exceed 1.3% are also indicative of plant contribution, for this case determined in potsherds of the Raimundo site. Mineralogical data ensure that the lipids preserved in the potsherds contain information on past activities, provided that the indicated firing temperature is above 550 °C, sufficient to remove oxygenated compounds from the raw material, clay and non-plastics. The presence of diagnostic biomarkers of aquatic organisms was identified in only two potsherds of the Quebrada Tacana site, 4,8,12-trimethyldecanoic (TMTD) and in addition the identification of odd-chain acids, $C_{15:0}$ and $C_{17:0}$ together with their respective $C_{15:1}$ and $C_{17:1}$ branched acids are strong indications of animal contribution. Therefore, they may suggest that these potsherds represent vessels used in the prolonged preparation of foods, and consequently because they have had contact with primary sources of nutrients, in the stage of use of the ceramic cycle (nutrient adsorption), the discard stage (current stage) would represent a potential source of nutrients caused by the degradation itself, mainly to the most exposed potsherds of the surface and sub-surface.

Keywords: Fertility. Lipids. Resin. Gas Chromatography. Ceramic. ADE.

LISTA DE ILUSTRAÇÕES

FIGURAS

LISTA DE TABELAS

SUMÁRIO

1 **INTRODUÇÃO**

Recentemente reconhecido como Antrossolos pelo sistema de classificação WRB (IUSS Working Group WRB, 2014), os solos tipo Terra Preta Arqueológica (TPA) fora denominado pioneiramente pelo geólogo Charles F. Hartt como “black soils” em 1874. Dentre suas características discriminantes aos demais solos da região amazônica, a constatação da elevada fertilidade das TPA impulsionaram os estudos a seu respeito provocando considerável interesse tanto da comunidade científica como dos povos locais.

Inicialmente, o processo de formação destes solos foi o foco em muitas pesquisas, em que algumas hipóteses tentaram explicar o comportamento anômalo da TPA no que diz respeito aos seus elevados conteúdos de K, Ca, Mg, Z, Mn, P, $C_{orgânico}$ e igualmente os valores altos de CTC, pH e saturação por bases. No entanto a discussão mais controversa concentra-se sobre os processos de sua formação, qual seja como resultado da influência antrópica sobre o solo a partir da incorporação de resíduos orgânicos descartados de maneira indiscriminada nos ambientes próximos e mesmo dentro das habitações (Kern 1996), intencional ou não, como se fosse um manejo premeditado. Dada a interação entre solo e resíduos descartados, ocorreria modificação das características morfológicas, físicas, químicas, e mineralógicas e de fertilidade dando origem ao que se conhece como solos TPA (Kern *et al.* 2009).

Como parcela do material destinado ao descarte, tem-se o contributo de origem inorgânica tradicionalmente investigado por arqueólogos como elemento comprobatório da ação antrópica pretérita, os fragmentos de vasilhas cerâmicas em destaque frente aos líticos menos expressivos. Ainda que se tratasse de um legado pretérito, investigações químicas e mineralógicas em fragmentos de cerâmica em solos TPA somente veio a ocorrer nas últimas três décadas.

O emprego de análises químicas e mineralógicas desses fragmentos deu suporte às interpretações de diferentes etapas do processo de manufatura, bem como circulação, uso, descarte e processos pós deposicionais, e dessa forma permitiu construir uma cronologia de ocupação e pós-ocupação de sítios arqueológicos e inferir sobre as funções primárias do objeto cerâmico (Costa *et al.* 2004a, 2004b, 2009, 2011, 2012).

Conquanto exista uma quantidade razoável de informações e dados pedoarqueológicos que apontem a formação das TPA a partir de uma origem antrópica, sua resiliente fertilidade ainda é debatida (Schmidt *et al.* 2014). Glaser *et al.* 2000, Lehman *et al.* 2003, Lehman & Rondon (2006), Jorio *et al.* 2012, Pagano *et al.* 2016 responsabilizam o *black carbon* como perpetuador da fertilidade das TPA. Estima-se que o *black carbon*, C_{pyr} ou bio-char corresponda a 35% da composição da matéria orgânica do solo (MOS). Formado pelo aquecimento da biomassa em ambientes livres ou com pouco oxigênio, as concentrações de C em sua estrutura aromática variam de 70 a 80% e se apresentam em dimensões nanométricas. Comprovadamente sabe-se que possui elevada capacidade de troca catiônica (CTC) dada sua própria estrutura que pela dissociação de íons H^+ de ácidos carboxílicos e grupos fenóis geram cargas negativas com a capacidade de reter macro e micronutrientes, porém necessitam da fonte de nutrientes, para serem responsáveis pela resiliente fertilidade, conforme demonstrara Rodrigues (2014) que ressalta que o C_{pyr} apesar de apresentar elevada CTC, não apresenta composição química que responda pela regeneração de nutrientes aos solos TPA (Costa *et al.* 2010). Por outro lado, Valente e Costa (2017) demonstraram experimentalmente que os fragmentos cerâmicos ao se decomporem paulatinamente durante sua incorporação no perfil de solo tornam lábeis seus constituintes químicos representados por hematita/maghemita/goethita, feldspatos, micas/illitas, clorita, anatásio, por vezes talco e calcita/aragonita provenientes da matéria-prima empregada na confecção, argila e antiplásticos. Enquanto K, Ca, Mg, Mn, Zn e Cu são provenientes da decomposição dos feldspatos, micas/illitas, e em casos isolados, cloritas, calcita (conchas como antiplástico) e talco, o P em grande parte representado por fase amorfa provém de um evento posterior à confecção da peça cerâmica, ou seja, não há correlação dos teores de P com a matéria-prima empregada como já demonstrado por Costa *et al.* 2003, 2004ab, 2009; Rodrigues et al. 2015. Os teores de P, na ordem de 1 até 11%, seriam consequência da manipulação de vasilhames cerâmicos no preparo de alimentos, principalmente cocção. Esta hipótese foi confirmada por Rodrigues *et al.* 2015 e Rodrigues & Costa 2016 ao estimar a temperatura de queima do material cerâmico a partir das transformações mineralógicas e simular condições de cozimento em réplicas de vasilhames cerâmicos.

Com estes experimentos, os autores comprovaram que a fase fosfática presente exclusivamente nestes fragmentos, não suportaria a temperatura de queima empregada na confecção dos cerâmicos, excluindo-se dessa forma sua origem a partir da matéria-prima. Demonstraram ainda que o P é um forte indicador de uso que vasilhas cerâmicas foram empregadas como panelas, no cozimento de alimentos ricos em proteínas animal, pois, é facilmente incorporado à matriz porosa tanto nas paredes quanto nas tampas, em uma reação espontânea entre ele os aluminossilicatos como metacaulinita e caulinita, podendo formar fase mineral em apenas uma semana de uso, num processo que Costa *et al.* 2004a denominaram de hidrotermal.

A necessidade em se estabelecer o uso ou a função primária de um objeto arqueológico principalmente quando este pode fornecer respostas às questões alimentares de uma população pré-existente tem sido traduzida com maior precisão normalmente a níveis moleculares, utilizando detector de espectrometria de massas (EM) acoplado às técnicas cromatográficas, CLAE (cromatografia líquida de alta eficiência) e CG (cromatografia gasosa) (Oudemans & Boon 1991, Evershed et al. 1999, Kimpe *et al.* 2004), em que a cromatografia tem o papel fundamental na seletividade dos constituintes de uma mistura complexa e o detector fornece informação estrutural (Chiaradia *et al.* 2008).

A recuperação de resíduos orgânicos dos poros não vitrificados de objetos cerâmicos arqueológicos vem sendo investigada há quase meio século em sítios do continente europeu, (Oudemans & Boon 1991, Guerrero y Viscaíno 1995, Evershed et al. 1997, Dudd *et al.* 1999, Evershed *et al.* 1999, Copley *et al.* 2000, Craig *et al.* 2009), desde que se constatou que a microestrutura porosa da cerâmica é favorável à preservação de resíduos orgânicos (Evershed *et al.* 1990, Evershed *et al.* 1997, Evershed *et al.* 1999, Craig *et al.* 2004, Koirala & Rosentreter, 2009).

Inicialmente, esta investigação concentrou-se em ácidos graxos e seus derivados por sua natureza química e praticidade analítica (Guerrero y Viscaíno 1995, Evershed *et al.* 1999, Craig *et al.* 2009). Os ácidos graxos apresentam em sua estrutura um grupo carboxila, a maioria de cadeia alifática que ocorre naturalmente em óleos e gorduras. São unidades fundamentais dos acilgliceróis (AG) e fosfolipídios e juntos compõem à classe dos lipídios. Os lipídios de caráter hidrofóbico apresentam solubilidade em solventes orgânicos e correspondem à maior parte dos componentes presentes no tecido adiposo, além de representarem um dos principais constituintes estruturais de células vivas para muitos organismos (Guerrero y Viscaíno, 1995, Nawar 1996, Koirala & Rosentreter, 2009).

Por isso, quando absorvidos e detectados em vasilhames cerâmicos, remontam à diferentes produtos que foram processados ou estocados durante o uso no tempo pretérito (Evershed *et al.* 1999, Hansel *et al.* 2004). Os produtos de degradação dos lipídios representados por moléculas de ácidos graxos, álcoois, terpenos, esteróis podem ser remanescentes de óleos, resinas, ceras vegetais, vinhos, cera de abelha e gorduras de animais (Evershed *et al.* 1990, Oudemans & Boon 1991, Evershed *et al.* 1997, Regert *et al.* 1998, Evershed *et al.* 1999, Hansel *et al.* 2004, Colombini *et al.* 2005, Craig *et al.* 2013, Pecci *et al.* 2013) que podem ser identificadas em associação aos mais variados artefatos arqueológicos.

Entre as biomoléculas frequentemente observadas, estão as relacionadas às gorduras degradadas de animais terrestres (Evershed *et al.* 1997, Regert *et al.* 1998, Dudd *et al.* 1999, Mottram *et al.* 1999). Estas se sobressaem por serem menos susceptíveis às reações de oxirredução e/ou solubilidade em água que moléculas de ácidos graxos insaturados. Regert *et al.* (1998) comprovaram que componentes insaturados se oxidam durante o uso e no ambiente em que são descartados, o que restringe sua detecção nas frações lipídicas de extratos de objetos cerâmicos em que a identificação por vezes é revelada através de seus produtos de polimerização.

Ácidos dicarboxílicos e cetonas de cadeia longa são exemplos de produtos de oxidação (Evershed *et al.* 1995, Raven *et al.* 1997, Regert *et al.* 1998), e pertencem à fração insolúvel de resíduos orgânicos (Oudemans 2006), ou seja, não é possível determiná-los por CG-MS através da extração com solventes orgânicos. Alternativamente, utiliza-se a pirólise de ponto de Curie acoplado (CuPyMs e CuPyGCMS) como ferramenta analítica na obtenção de informações sobre esta fração que tem sua relevância pois a presença de cetonas era creditada somente à fonte de origem vegetal.

Desta maneira, a caracterização de gorduras animais é menos crítica. Com elevada proporção de ácidos graxos saturados (Dewick 2009), sua classificação é obtida por comparação entre a distribuição de ácidos *n*-alcanóicos (principalmente $C_{16:0}$, $C_{18:0}$), ácidos *n*-alquenóicos monoinsaturados ($C_{18:1}$) e AG, mono, di ou tri (MAG, DAG ou

TAG) dos extratos dos fragmentos cerâmicos ao perfil lipídico de amostras de referência modernas (Dudd *et al.* 1999, Evershed *et al.* 1999, Mottram *et al.* 1999).

Entretanto, ainda que eficiente esta metodologia tem limitações, pois, permite inferir sobre as categorias de óleos ou gorduras (Evershed *et al.* 2002). Uma vez que, associados ao uso e descarte dos vasilhames estão processos degradativos, como mencionado anteriormente, a composição lipídica pode alterar-se (Evershed *et al.* 1995, Raven *et al.* 1997, Regert *et al.* 1998, Dudd *et al.* 1999, Baeten *et al.* 2013), e conquanto haja um elevado grau de preservação proporcionado pela própria microestrutura cerâmica (Evershed *et al.* 2002, Evershed *et al.* 1997, Baeten *et al.* 2013), os lipídios estão propensos a um processo contínuo de decomposição (Evershed *et al.* 2002).

Notavelmente, com o avanço da instrumentação micro-analítica, ocorreu uma enorme expansão na detecção de moléculas orgânicas de origem arqueológica resultando em interpretações mais acuradas (Oudemans 2006, Dudd *et al.* 1999). Evershed *et al.* (1994) revolucionaram com a implementação da cromatografia gasosa acoplada à espectrometria de massa de razão isotópica de carbono (GC-C-IRMS) aplicada a materiais arqueológicos.

Como as medidas de $\delta^{13}C$ são direcionadas aos ácidos mais abundantes, $C_{16:0}$ e $C_{18:0}$, o emprego da técnica GC-C-IRMS permite classificar fontes da matéria orgânica preservada de modo mais específico (Dudd *et al.* 1999). Para o caso de fontes animais é possível distinguir entre animais terrestres, ruminantes e não-ruminantes, aves e os de origem aquática, bem como produtos derivados de animais terrestres, como leite, por exemplo, representando um grande avanço às questões paleodietéticas (Evershed *et al.* 1997, Dudd *et al.* 1999, Oras *et al.* 2017).

Para os casos de fontes vegetais, evidências estruturais e isotópicas ($\delta^{13}C$) ajudam a ratificar o processamento de produtos vegetais já apontadas por CG-MS com o diferencial de evidenciar através de valores comparativos de ^{13}C dissimilaridades entre extratos de fragmentos e amostras contemporâneas, sugerindo desta forma a existência de uma fonte alternativa de um dado composto. Evershed *et al.* (1990) ao identificarem cetonas de cadeias longas, nonacosan-15-ona e hentricontan-16-ona em fragmentos da Europa, datados entre a era do Bronze (*ca.* 4000 anos BP) e a Medieval (*ca.* 1000 anos BP) relacionou-as ao processamento de folhas de Brassica oleracea (couve) e Alliumporrum (alho-poró) respectivamente, embora seus resultados não sejam totalmente equivocados, resultados de ^{13}C mostraram-se 10‰ mais enriquecidos nos extratos de que em amostras contemporâneas, conduzindo a crer em uma fonte adicional para estes compostos, estes dados são consistentes com os resultados de Evershed *et al.* (1995) e Raven *et al.* (1997) supracitados que discutem sobre a polimerização de ácidos graxos insaturados.

Na Europa, a relevância da identificação de produtos relacionados às gorduras animais e óleos não é somente revelador da natureza utilitária de recipientes cerâmicos, mas também remete a fatos importantes de culturas antigas como a introdução da agricultura e domesticação de determinadas espécies de animais e cultivo de cereais (Evershed *et al.* 2002, Evershed *et al.* 1997).

Evershed *et al.* (1997), Mottram *et al.* (1999), Copley *et al.* (2005) por meio da técnica GC-C-IRMS evidenciaram com clareza que produtos animais de diferentes classes, ruminantes e não-ruminantes, foram processados em vasos no período Neolítico, e ainda, que fossem processados em vasos com morfologias distintas. Copley *et al.* (2000) detectaram ácidos carboxílicos saturados de cadeia curta, $C_{12:0}$ a $C_{18:0}$, em vasos de Qsar Ibrim no Egito, e muito embora a abundância de $C_{12:0}$ apontasse para uma fonte de origem vegetal, os valores de $\delta^{13}C$ foram essenciais para evidenciar a exploração específica de frutos de palmeiras, tâmara (*Phoenix dactilifera* L.*)* e palmito (*Hyphaena thebaica* L.), no período de *ca* 1000 BC to AD 1800, período correspondente à fase de ocupação do sítio.

Posteriormente, Copley *et al.* (2005a) demonstraram que a dieta alimentar no período correspondente à Idade do Bronze, no sul da Grã-Bretanha, não era baseada somente no consumo de animais de maneira direta, mas também em seus produtos secundários, esta evidência foi constatada desde que a presença de resíduos de leite e até seus derivados foram detectados em quatro sítios da região. A exploração de produtos secundários de ruminantes foi confirmada também por Spangenberg *et al.* (2006) na Suíça, Europa Central, no Neolítico e por Kherbouche *et al.* (2016) no norte da África que somaram a este resultado a detecção de combinações variáveis de resíduos característicos de plantas C_3 e C_4.

Outra importante fonte protéica evidenciada em diversos estudos, principalmente em sítios localizados em áreas costeiras, são as aquáticas, em diferentes níveis tróficos. Perfis típicos de óleos degradados de contribuição aquática são significativos em fragmentos cerâmicos de sítios localizados na costa catarinense, sul do Brasil (Hansel *et al*. 2004), no sítio Qsar Ibrim, Egito (Copley *et al*. 2005b), em Hamwic, Reino Unido, próximo ao mar do Norte (Baeten *et al*. 2013), nos sítios Nida e Šventoji, na costa da Lituânia, próximo ao mar Báltico (Heron *et al*. 2015), na costa central da Patagônia, Argentina (Otero *et al*. 2014) e até na cerâmica mais investigada e antiga que se tem conhecimento no mundo, a japonesa Jōmon (Craig *et al*. 2013).

De maneira geral, os lipídios recuperados de fontes aquáticas que as distinguem das fontes animais terrestres são frequentemente demonstrados como produtos da degradação de ácidos graxos poli(insaturados), ou como ácidos dihidróxi (Copley *et al*. 2005b, Hansel *et al*. 2011), ou como ω(o-alquilfenil) (Hansel *et al*. 2004, Copley *et al*. 2005b, Baeten *et al*. 2013, Craig *et al*. 2013) e ácidos fitânicos combinados com TMTD (ácido 4,8,12-trimetiltridecanóico) (Heron *et al*. 2015), representativos de óleos de origem aquática.

Os fragmentos cerâmicos que provêm de TPA já acumulam alguns estudos com ênfase em dados arqueométricos, porém, dados relacionados à matéria orgânica amorfa preservada em sua estrutura parecem ainda não ter sido explorado. Diante de sua natureza mineralógica e química e a comprovação de que os fragmentos estão relacionados ao processamento de alimentos, através do P como indicador de uso, este trabalho se propôs a investigar a relação entre a matéria orgânica amorfa e P.

2 **OBJETIVOS**

2.1 GERAL

Identificar a natureza e importância dos compostos orgânicos possivelmente associados aos fragmentos cerâmicos arqueológicos de sítios tipo TPA, demonstrando a função dos vasos cerâmicos atualmente fragmentados no preparo de alimentos e avaliar a correlação com o comprovado indicador inorgânico de uso, o fósforo, a fim de contribuir para o entendimento da resiliência dos solos TPA, ricos nestes fragmentos.

2.2 ESPECÍFICOS

Caracterização da composição química, mineralógica, fertilidade e dessorção de nutrientes dos fragmentos cerâmicos com o propósito de determinar a matéria-prima, argila, antiplástico, resina e produtos de alteração pós-descarte

Classificar a origem de óleos e gorduras, ou seja, evidenciar em caráter preliminar, distintas contribuições de ordem vegetal ou animal.

Avaliar a distribuição lipídica de acordo com: a posição dos fragmentos no vasilhame (borda, parede, base, etc.); com o tipo de vasilhame (prato, tigela, etc.), para os casos em que foi possível reconstituir graficamente a sua forma; e ainda intra e intersítio, a fim de demonstrar variabilidade na escolha e/ou disponibilidade dos produtos processados de acordo com cada região.

3 **ÁREAS DE ESTUDO**

3.1 LOCALIZAÇÃO GEOGRÁFICA

Para a execução deste estudo foram selecionados 4 (quatro) sítios arqueológicos com TPA localizados na região amazônica. São eles: Quebrada Tacana, Juruti, Boa Vista e Raimundo.

3.1.1 **Sítio Quebrada Tacana**

O sítio Quebrada Tacana (coordenadas centrais 4°07'6.8"S e 69°55'16.4"O) localiza-se no Trapézio colombiano ao norte da cidade de Letícia (Figura 1). É um sítio tipo TPA identificado nesta região em 1978 durante o desenvolvimento de trabalho de campo do Prof. Pedro Botero da Unidade de Solos do CIAF. A partir destas informações os pesquisadores Gaspar Morcote Ríos e Tomas León Sicard, ambos da Universidade Nacional da Colômbia-Sede Bogotá, através do Projeto "Suelos Negros Amazónicos un Sistema de Cultivo pré histórico: Una Alternativa Agrícola Actual" estudaram estes solos entre outros com o objetivo de recuperar e identificar restos botânicos (fitólitos, pólen, sementes arqueológicas), iniciado ainda em 2006. Atualmente a área do sítio está localizada naquela habitada por tribos indígenas autodenominadas Muruy ou Muruimuinane, que coabitaram logo à sua chegada com índios Ticuna, e que agora habitam nas margens do médio rio Amazonas. O sítio Quebrada Tacana ocupa 2 ha de área, e o horizonte A, antrópico, varia de 10 a 25 cm de profundidade. Durante o trabalho de campo desenvolvido pelos Professores Gaspar Morcote e Tomas Sicard, foram recuperados 6 sementes arqueológicas carbonizadas e centenas de fragmentos cerâmicos que foram lavados, marcados, classificados e registrados (Morcote & Sicard 2007).

3.1.2 **Sítio Juruti**

O sítio Juruti está representado por duas ocorrências de TPA: Terra Preta 1 (TP1) (coordenadas centrais 2°10'01.68"S/56°05'57.58"O) e Terra Preta 2 (TP2), (coordenadas centrais 2°10'36.86"S/56°06'17.05"O) situados no município de Juruti, na margem direita do rio Amazonas, região do Baixo Amazonas, (Figura 1). No município de Juruti já foram catalogados 52 sítios pela empresa Scientia Consultoria Científica Ltda. As ocorrências TP1 e TP2 configuram-se como TPA, juntos abrangem uma área de 60 ha, apresentam Horizonte A de textura relativamente arenosa, cor preta a marrom acinzentado muito escuro (10YR3/2) e presença de carvão, cinzas, fragmentos cerâmicos em abundância e de ossos com tamanho menor ou igual a 1mm. A composição química dos solos é representada por SiO_2, Al_2O_3, Fe_2O_3 e TiO_2 que somados à PF ultrapassam um pouco de mais de 98% dos constituintes em muitas amostras de solo (Costa *et al*. 2013).

3.1.3 **Sítio Boa Vista**

O sítio Boa Vista (coordenadas centrais 1°27'41.18"S e 56°23'58.61") localiza-se na região do Baixo Amazonas a aproximadamente 1 km da vila de Porto Trombetas (município de Oriximiná, estado do Pará) (Figura 1). Ele está representado por duas ocorrências de solos tipo TPA denominadas Boa Vista e Água Fria somando uma área de 13,5 ha incluindo o intervalo entre as duas manchas. O horizonte A, tipo TPA alcança aproximadamente 60 cm de profundidade e contêm fragmentos cerâmicos, implementos, adornos, núcleos e lascas líticas, fragmentos ósseos, sementes calcinadas e carvão, além de seixos rochosos. As primeiras referências a sítios datam dos séculos XVI e XVII quando da exploração do rio Amazonas por viajantes europeus que em parte documentaram o que viram e viveram na forma de crônicas. A partir de 1985 as pesquisas arqueológicas ocorrem sob a perspectiva de Arqueologia de Contrato por solicitação da empresa Mineração Rio do Norte (MRN) para exploração de bauxita, o que continua até a atualidade. Portanto, existe uma gama de informações históricas acerca da região. Em 2001, sob coordenação da pesquisadora Vera Guapindaia o Museu Paraense Emilio Goeldi (MPEG) conveniado à (MRN) e Fundação de Amparo e Desenvolvimento da Pesquisa (FADESP) autorizado pelo Instituto do Patrimônio Histórico e Artístico Nacional (IPHAN), dão continuidade às pesquisas arqueológicas de contrato que dentre os objetivos desta empreitada estava à delimitação e escavação do sítio Boa Vista. Em sua tese de doutorado, Guapindaia (2008) analisou mais de 38.000 fragmentos cerâmicos quanto aos seus aspectos técnicos, morfológicos e estilísticos do sítio Boa Vista, visando definir tipologias cerâmicas (Guapindaia 2008; Guapindaia & Fonseca Junior 2013).

3.1.4 **Sítio Raimundo**

Este sítio (coordenadas centrais 01°45’36.00”S e 51º26’34.3”O) encontra-se dentro da Floresta Nacional de Caxiuanã (FLONA-Caxiuanã), às margens do igarapé Curuá, nos municípios de Portel e Melgaço, entre a ilha do Marajó e o rio Xingu, sob (Figura 1). A FLONA é administrada pelo IBAMA e sua base dista cerca 400 km em linha reta de Belém, capital do Pará. Abrange uma área de 330.000 ha em que 10% foi destinada às instalações da Estação Científica Ferreira Pena (ECFPn), criada pelo Museu Paraense Emílio Goeldi (MPEG). A FLONA é foco de pesquisas multidisciplinares e interinstitucionais em longo prazo, principalmente no que concerne ao seu conteúdo arqueológico, mais especificamente os solos TPA. Já foram registrados 29 sítios arqueológicos distribuídos às margens da baía de Caxiuanã (Carmo *et al*. 2007; Lemos *et al*. 2009; Gurjão *et al*. 2010). O sítio Raimundo ocupa 1,26 ha e apresenta formato elipsóide no sentido norte-sul e está localizado a menos de 200m da margem esquerda do igarapé Curuá, é um sítio com TPA, cujo horizonte A e antropogênico se estende até 21 cm de profundidade. Este contém fragmentos cerâmicos e raízes, apresenta cor preta (10Y R2/1), textura média/argilosa e mineralogia dominada por quartzo, caulinita e goethita e/ou hematita (Carmo 2008). Carmo (2008) investigou seus aspectos mineralógicos, químicos, textural e de fertilidade, enquanto Costa (2011) utilizou várias técnicas para caracterizar e quantificar as formas de fósforo orgânico presentes no solo.

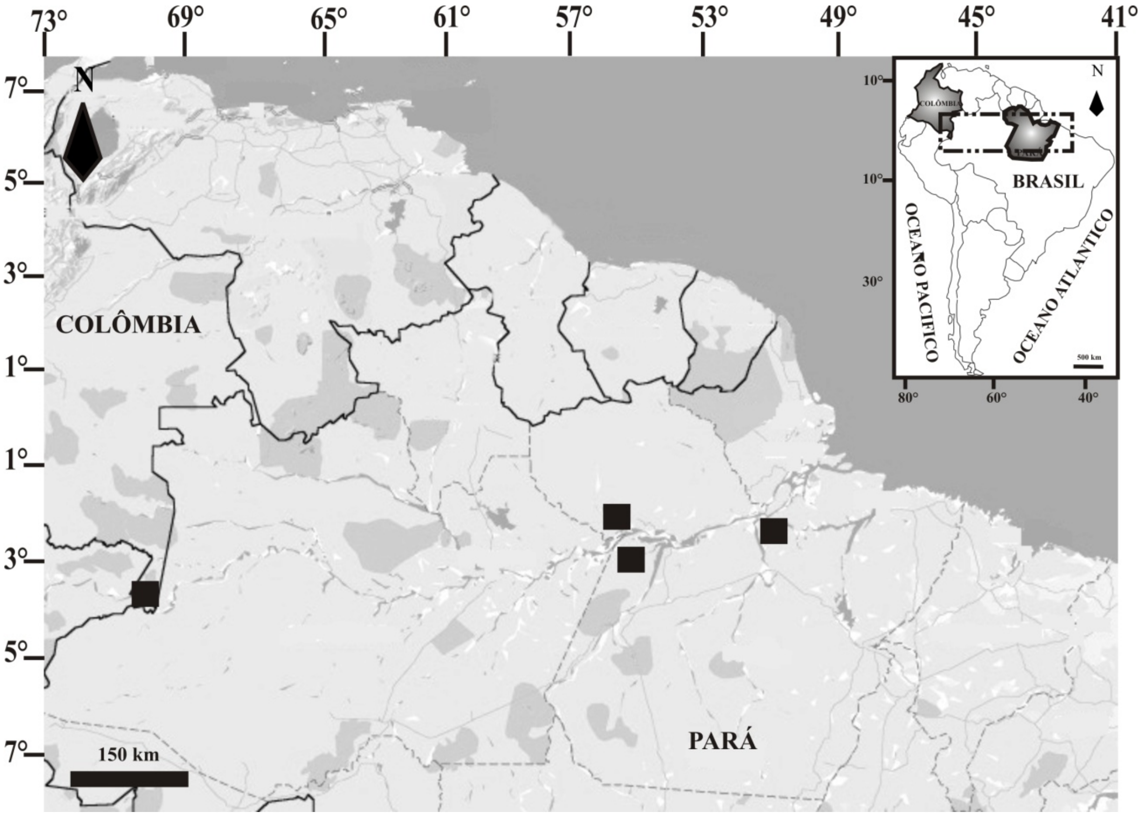

Figura 1 – Mapa de localização dos sítios investigados.

4 **MATERIAIS E MÉTODOS**

4.1 AMOSTRAGEM

4.1.1 **Sítio Quebrada Tacana**

As amostras empregadas na presente investigação foram coletadas por Morcote, como parte de suas pesquisas. Para tal ele realizou escavações no sentido norte-sul através de 11 transectos eqüidistantes 20 metros, formando uma grade (Figura 2). (Morcote & Sicard 2007). Na Tabela 1 seguem as informações dos 23FC do referido sítio.

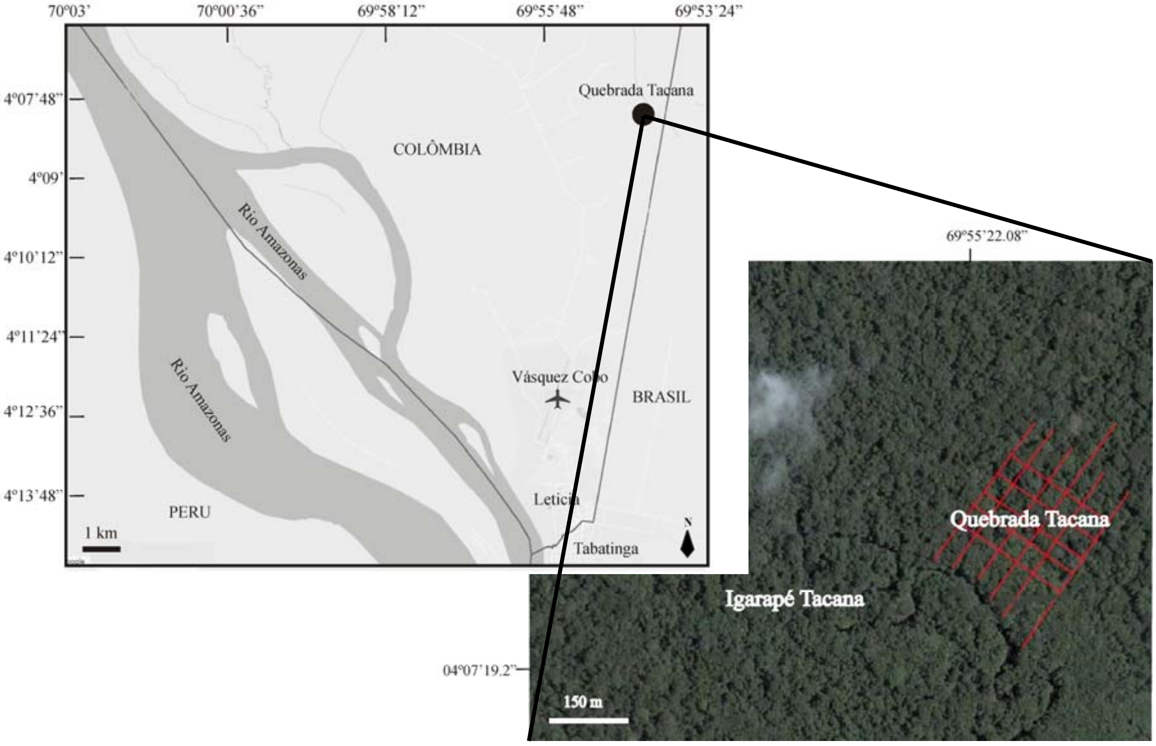

Figura 2 – Prospecções arqueológicas através de transectos, km 10 e 11.
Fonte: (Modificado de Morcote & Sicard 2007).

Tabela 1 – Relação das amostras de fragmentos cerâmicos com a profundidade do perfil de solo TPA.

Código da amostra	Profundidade (cm)	Quadra	Posição e Fragmento
QT-03	15-20	A	Base
QT-04	15-20	C	Borda a base
QT-05	15-20	A	Borda
QT-06	15-20	E	Borda
QT-07	15-20	A	Borda
QT-08	20-25	D	Borda
QT-09	20-25	B	Borda
QT-11	20-25	B	Borda
QT-12	20-25	B	Base e corpo
QT-13	25-30	E	Base
QT-15	25-30	A	Borda
QT-17	25-30	F	Borda
QT-18	30-35	C	Corpo
QT-19	30-35	C	Base e corpo
QT-20	30-35	B	Borda
QT-21	30-35	B	Borda
QT-22	30-35	A	Base e corpo
QT-23	35-40	A	Borda
QT-24	35-40	A	Borda
QT-25	35-40	D	Borda
QT-26	35-40	D	Borda
QT-27	35-40	D	Corpo próximo a base
QT-28	40-45	C	Base

Fonte: Da autora

4.1.2 **Sítio Juruti**

As amostras investigadas neste sítio foram coletadas em intervalos de 10 cm nas sondagens de 50x50 cm de malha regular de 60x120 cm empresa Scientia Consultoria Científica Ltda em 2006 (Figura 3, Tabela 2). Como estas amostras já foram plenamente investigadas por Costa, 2011 quantos aos aspectos mineralógicos e químicos na presente tese elas serão utilizadas apenas para análise de compostos orgânicos, em decorrência de seus expressivos conteúdos de P_2O_5.

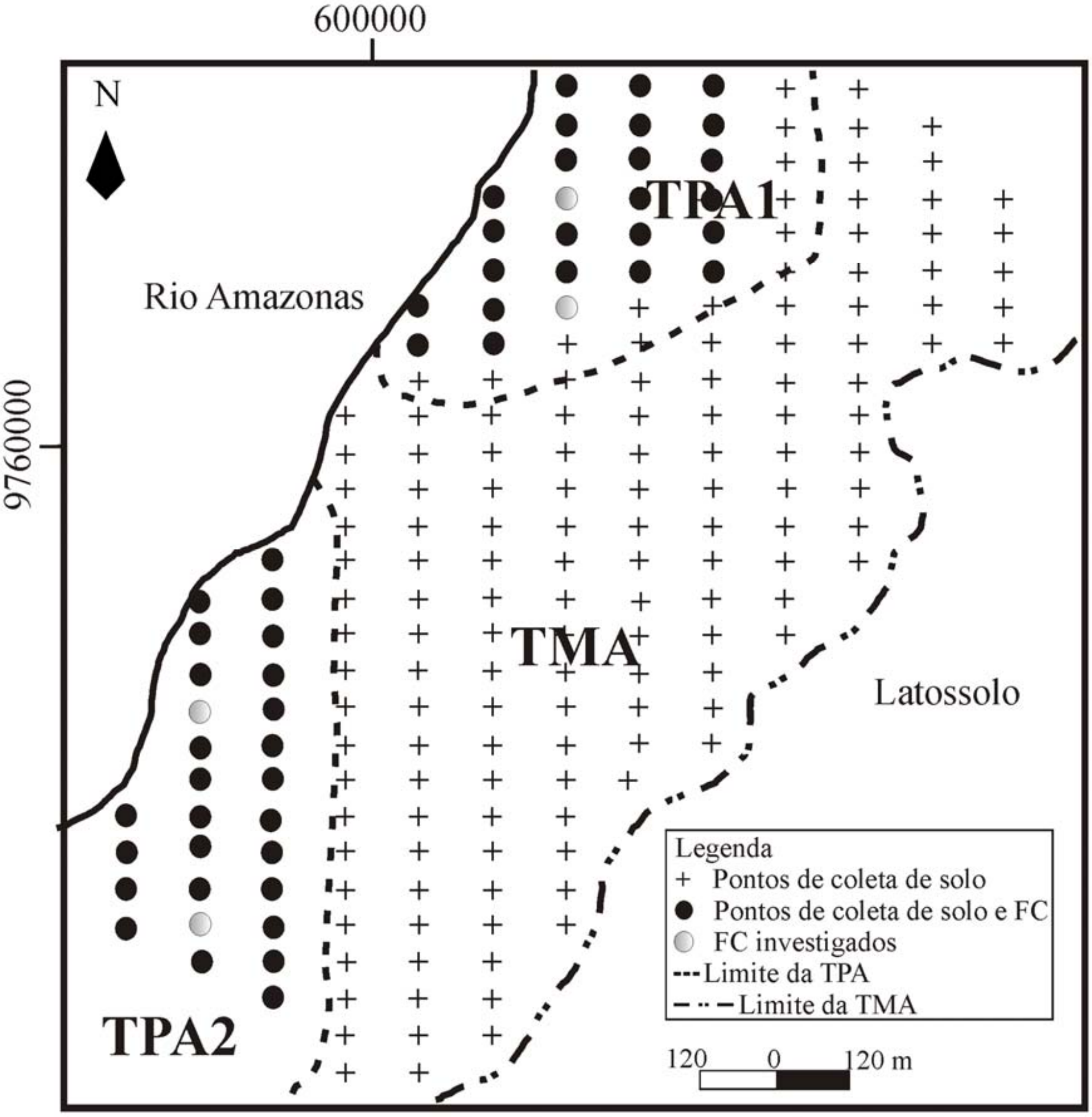

Figura 3 – Localização dos pontos de coleta dos fragmentos cerâmicos do sítio Juruti (modificado de Costa 2011).

Tabela 2 – Relação das amostras dos fragmentos cerâmicos do sítio Juruti.

Código do FC	Profundidade (cm)	Tipo de fragmento
JU1-TP1	50-60	Não diagnóstico
JU2-TP1	10-20	Não diagnóstico
JU1-TP2	40-50	Não diagnóstico
JU2-TP2	10-20	Não diagnóstico

Fonte: Da autora

4.1.3 Sítio Boa Vista

O material arqueológico proveniente do sítio Boa Vista foi cedido pela Profª. Vera Lúcia Calandrini Guapindaia. Este sítio teve suas prospecções iniciadas em 2002 com unidades de 1x1 m, totalizando cerca de 8 escavações e 2 sondagens, realizadas em camadas naturais, controladas por níveis de 5 cm, perfazendo uma área de 77 m² descontínua (Figura 4). Vale ressaltar que o material arqueológico deste sítio, segundo informações extraídas de Guapindaia (2008), é oriundo tanto de tradagens, sondagens, escavações, coletas de superfície como também de doações de moradores locais. A Tabela 3 exibe algumas características das amostras.

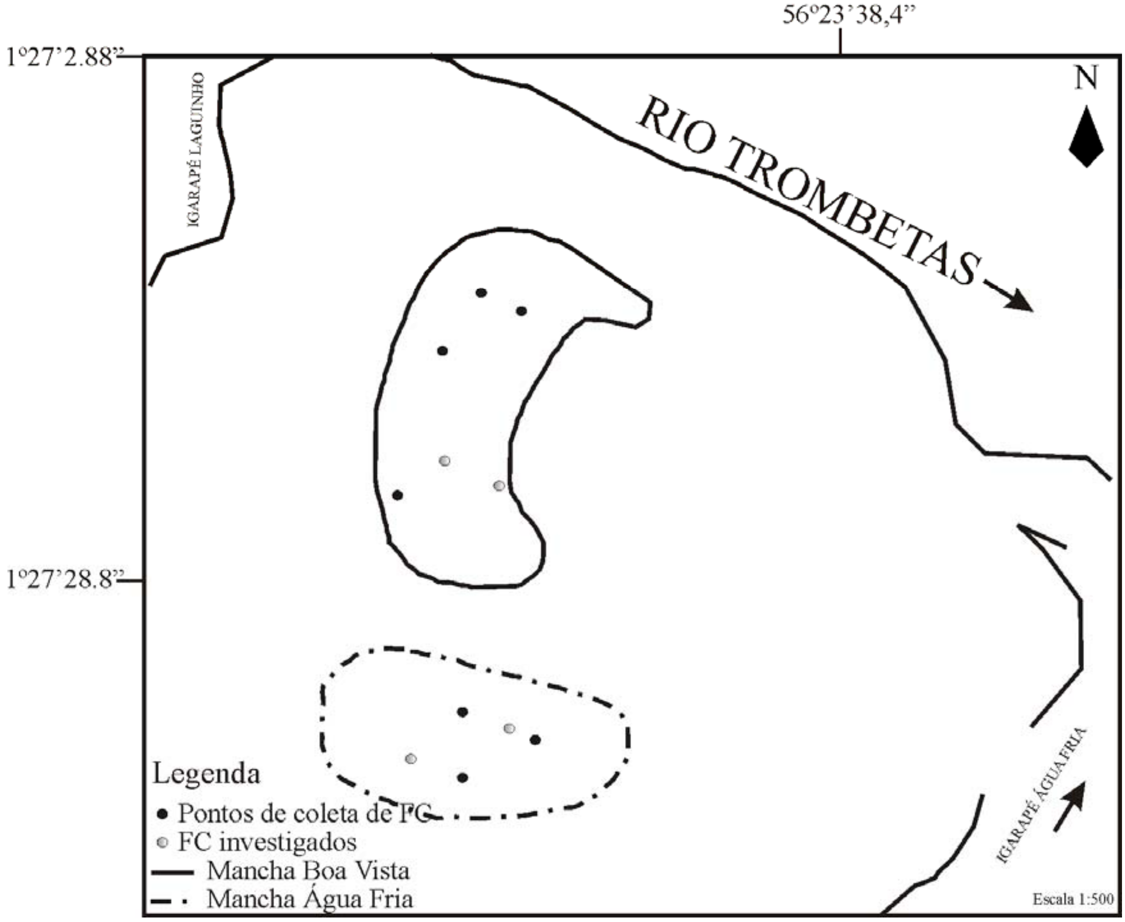

Figura 4 - Localização dos pontos de coleta dos fragmentos cerâmicos do sítio Boa Vista evidenciando as manchas Boa Vista e Água Fria (modificado de Guapindaia 2008).

Tabela 3 – Relação das amostras de fragmentos cerâmicos do sítio Boa Vista com a profundidade do solo TPA.

Código do FC	Profundidade (cm)	Tipo de fragmento	Quantidade de FC
CPT1	5	Borda	1
CPT2	106	Base	2
CPT3	19	Corpo	1
CPT4	39	Corpo	1
CPT5	58	Aplique	1
CPT6	10	Borda	1
CPT7	108	Corpo	1
CPT8	96	Base	2

Fonte: Da autora

4.1.4 **Sítio Raimundo**

As amostras deste sítio investigada nesta tese foram coletadas por Marciléia Silva do Carmo durante o desenvolvimento de seu trabalho de doutorado finalizado em 2008 sob orientação do Prof. Dr. Marcondes Lima da Costa e da pesquisadora Drª. Dirse Clara Kern. A distribuição das amostras coletadas neste sítio está indicada na Figura 5, que mostra um padrão radial, para tentar cobrir a variação de cor dos solos, que eram mais escuros na zona central e gradualmente convergiam para latossolos amarelos em direção às bordas (Figura 5) (Carmo 2008). As 188 amostras, aqui investigadas, restringem-se ao Horizonte A (0-21 cm) distribuídos conforme Tabela 4.

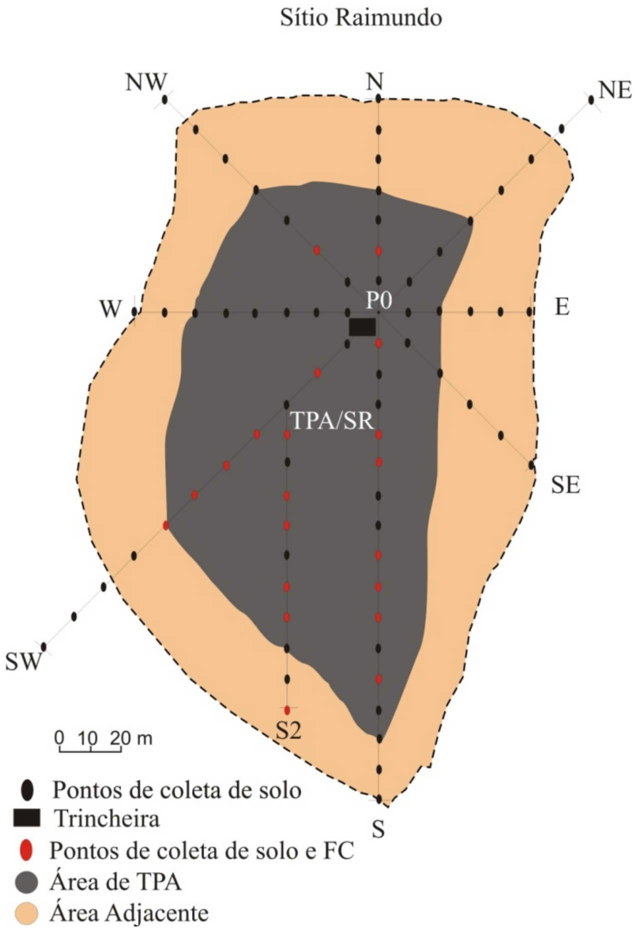

Figura 5 - Localização dos pontos de coleta dos fragmentos cerâmicos do sítio Raimundo, Caxiuanã-PA (Modificado de Carmo 2008).

Tabela 4 - Distribuição dos fragmentos cerâmicos coletados no sítio Raimundo.

Código da amostra	**Transversal**	**Profundidade (cm)**	**Quantidade de FC**
T1-8	P_0S-10	superfície	1
T1-9	P_0S-40	superfície	1
T1-10	P_0S-50	superfície	2
T1-11	P_0S-80	superfície	6
T1-12	P_0S-80	superfície	3
T1-13	P_0S-90	superfície	7
T1-14	P_0S- 90- 100	superfície	1
T1-15	P_0S-100	0-20	13
T1-16	P_0S-100-110	superfície	1
T1-17	P_0SW-20	superfície	7
T1-18	P_0SW-5	superfície	21
T1-19	P_0SW-40	superfície	1
T1-20	P_0SW-40	superfície	5
T1-21	P_0SW-50	superfície	2
T1-22	P_0SW-50-60	superfície	1
T1-23	P_0SW-70	superfície	2
T1-24	P_0S2-10	superfície	2
T1-25	P_0S2-30	superfície	3
T1-26	P_0S2-40	0-20	1
T1-27	P_0S2-60	superfície	2
T1-28	P_0S2-70	superfície	13
T1-30	P_0S2-100	0-20	1
T1-31	P_0N-20	superfície	6
T1-32	P_0N-20	0-20	8
T1-33	P_0O-20	superfície	6
T1-34	P_0O-30-40	superfície	1
T1-35	P_0NW-20	superfície	4
T1-36	P_0E**L**-10	superfície	6
T1-37	P_0SW-30-40	superfície	9
T1-38	a	superfície	1
T1-39	b	superfície	2
T1-40	c	superfície	2
T1-41	d	superfície	10
T1-42	P_0S-120	superfície	11
T1-43	e	superfície	5
T1-44	f	superfície	9

a, e, f: Terreno de D. Firmina (próximo ao rio Caxiuanã); b e d: IBAMA (entrada da praia); c: sem referência. Fonte: Da autora

4.2 DESCRIÇÃO MACROSCÓPICA

Os fragmentos cerâmicos foram descritos a olho desarmado e com auxílio de lupa binocular (ZEISS-Stemi 2000-C, Alemanha) fotografadas com câmera (Canon PowerShot G6 7.1 megapixels, Japão) acoplada a lupa. Determinaram-se características como cor por comparação as cores da *Munsell Soil Color Charts* (Munsell Color Company, 2000), tamanho dos fragmentos mensurados com auxílio de paquímetro e identificação de aditivos e resina incorporados à pasta durante a confecção, entre outros. Estas etapas foram realizadas no Laboratório de Gemologia do Instituto de Geociências – UFPA.

Uma parcela desses fragmentos foi então pulverizada em gral de ágata para serem submetidos às análises por DRX, fertilidade, ensaios de dessorção, FT-IR, e extração dos compostos orgânicos.

Para extração por solvente retirou-se as superfícies periféricas (externa e interna) por um sistema abrasivo a fim de evitar contaminação, seja pelo contato com as mãos ou condições inapropriadas de armazenamento, desta forma, considera-se apenas os resíduos absorvidos. Este procedimento foi indicado por Heron *et al*. (2010).

4.3 CARACTERIZAÇÃO MINERALÓGICA E QUÍMICA

4.3.1 **Difração de Raios-X (DRX)**

Esta técnica foi empregada para a identificação dos minerais e outras fases cristalinas. Empregou-se difratômetro modelo X'PERT PRO MPD (PW 3040/60) da PANalytical, com goniômetro PW3050/60 (θ/θ) e tubo de raios-x cerâmico e anodo de Cu ($K_{\alpha 1}$ = 1,54060 Å). As amostras previamente pulverizadas em gral de ágata foram compactadas em porta-amostra. As condições instrumentais utilizadas foram: varredura de 5 a 75° em 2θ; voltagem de 40kV e corrente de 40mA; passo angular 0,02° e tempo de contagem 10s. As fases mineralógicas foram identificadas sob auxílio do software X'Pert HighScore versão 2.1b com base nos bancos de dados do ICDD (*International Center for Diffraction Data*). As análises por DRX foram conduzidas tanto em amostra total, como também em frações subdividas em superfícies externas e núcleo.

Estas análises foram realizadas no Laboratório de Caracterização Mineral (LCM-IG-UFPA) do Instituto de Geociências da UFPA.

4.3.2 **Microscopia Óptica (MO)**

Esta técnica foi empregada com o objetivo de aprofundar a identificação mineralógica, de fases orgânicas (como os antiplásticos carvão, cariapé, cauixi) e aspectos texturais de todo conjunto do material cerâmico, visando principalmente distinguir fases primárias e neoformadas. Para este fim foram confeccionadas lâminas delgadas polidas na Oficina de Laminação (LAM) do Instituto de Geociências da UFPA. O preparo se iniciou a partir de uma fina seção da amostra obtida por serratriz manual de marca Hillquist para formação de tablete posteriormente seco em placa aquecedora de marca Fanem, modelo 186. Após esse procedimento, os tabletes ficaram em repouso por 24 horas em solução de resina de Haraldite (Araldite) da série GY257, álcool e endurecedor da série HY951. Os tabletes foram fixados em placa de vidro e submetidos a sucessivos desbastes em politriz com carburunco da série 300, 600 e 1000 até alcance da espessura desejada finalizado com um corte na amostra.

As identificações dos minerais e antiplásticos foram realizadas sob auxílio de microscópio ótico de marca Zeiss Axiolab e objetivas de 10 e 20x no Laboratório de Mineralogia-Gemologia do Museu de Geociências da UFPA.

4.3.3 Microscopia Eletrônica de Varredura com Sistema de Energia Dispersivo (MEV-SED)

Esta técnica foi utilizada com o objetivo de se identificar fases minerais não detectadas por DRX ou microscopia ótica ou reforçar aqueles métodos, de baixa ordem cristalina, auxiliar na caracterização dos antiplásticos. As imagens foram obtidas por meio de microscópio eletrônico de varredura (Hitachi, modelo TM3000, Japão) utilizando-se detector de elétrons secundários a voltagem de 15 kV, no Laboratório de Raios X e MEV (LaMiGA-IG-UFPA). As caracterizações semiquantitativas realizaram-se através de detector SED3000, acoplado ao MEV, utilizando software Swift ED. A preparação das amostras não exige metalização, mas requer controle da umidade que pode ser alcançada em estufa com temperatura em torno de 30°C.

4.3.4 **Espectroscopia de Absorção no Infravermelho (IV)**

A espectroscopia de absorção no infravermelho foi aplicada tanto em amostras naturais para verificação da composição inorgânica, um complemento às principais técnicas, DRX e microscopia óptica e eletrônica, bem como nos extratos obtidos por extração com $CHCl_3$:MeOH (2:1) dos resíduos absorvidos.

Para investigação inorgânica, cada fragmento foi fracionado de acordo com as delimitações de cores observadas em sua seção transversal, a cor é uma propriedade física importante na descrição cerâmica, pois, pode fornecer informações relativas à queima como tempo, temperatura e atmosfera, por isso, a partir dos resultados obtidos de cada seção do fragmento pretendem-se discutir sobre condições de queima bem como avaliar possíveis fases minerais formadas por alteração durante o descarte. Os fragmentos após pulverização foram prensados a fim de se obter uma pastilha. A pastilha consiste da mistura de amostra (total e porções fracionadas) e brometo de potássio (KBr, Merck) em uma proporção 1:100 homogeneizada em gral de ágata e obtida a partir de prensagem 8 Kbar em prensa de marca Specac 8.

Para a caracterização das fases orgânicas relacionadas à matéria orgânica amorfa, as análises foram realizadas nos extratos utilizando um porta amostra apropriado para amostras líquidas (Liquid cell, Figura 6), injetando-os por meio de micropipeta e/ou seringa, e, ainda, gotejando-se a fração líquida em pastilhas de KBr, preparadas conforme descrição anterior, as quais foram colocadas em estufa por 5 min a 40ºC para evaporação de solvente.

As análises foram realizadas em equipamento Bruker, modelo Vertex 70, com operação controlada via software Opus 7, registros de faixa espectral de 4000 a 400 cm^{-1} no modo de transmissão. As identificações das bandas de absorção referentes aos estiramentos das ligações registradas nos espectros foram avaliadas por comparação com dados da literatura. Estas análises foram realizadas no LaMiGA (IG-UFPA).

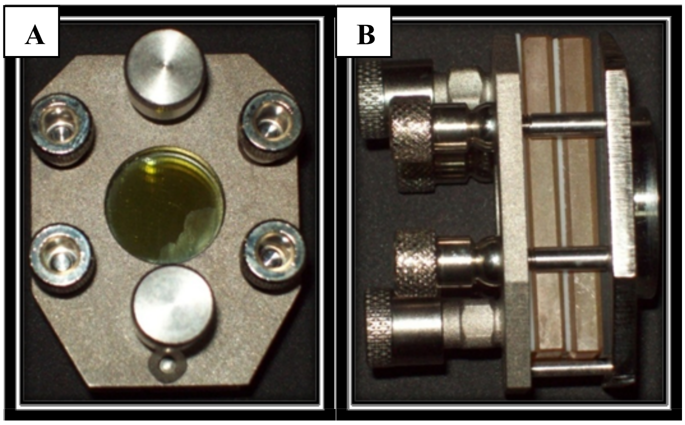

Figura 6 - Porta amostra utilizado para análise dos extratos orgânicos (Liquid cell), A: Vista frontal, B: Vista lateral.

4.3.5 **Fracionamento químico do fósforo**

As metodologias de fracionamento são fundamentadas na solubilidade química das espécies de interesse. Existem numerosos procedimentos de extração seqüencial ou seletiva que englobam 4 a 5 fases sucessivas de tratamentos químicos, envolvendo solubilização preliminar em água, seguida por ácidos e/ou bases fortes diluídas. Em geral, todas as metodologias apresentam vantagens e desvantagens, no entanto nenhuma é universal. Como não existem métodos exclusivos ao fracionamento de fósforo em fragmentos cerâmicos, utilizaram-se procedimentos clássicos de especiação para solos. Portanto, as metodologias aplicadas a este estudo, foram selecionadas avaliando-se as limitações metodológicas que abrangem desde a carência de amostras até as condições existentes no laboratório, o que ocasionou adaptações nos métodos originais.

Todos os procedimentos referentes a este item foram executados no Laboratório de Análises Químicas do Instituto de Geociências da Universidade Federal do Pará.

As vidrarias utilizadas nas etapas descritas a seguir foram imersas em solução de HNO_3(10% v/v) por 24h e sequencialmente enxaguados com água corrente e água destilada, para posterior secagem em estufa a 160°C.

4.3.5.1 Fracionamento do fósforo inorgânico (Pi)

Para o fracionamento do Pi utilizou-se o método proposto originalmente por Chang and Jackson (1957) modificado por Kuo (1996). O método permite quantificar o

Pi nas frações: fósforo ligado ao alumínio (Pi-Al), fósforo ligado ao ferro (Pi-Fe), fósforo ligado ao cálcio (Pi-Ca) e fósforo fracamente ligado ou solúvel (Pi-H_2O) (Figura 5).

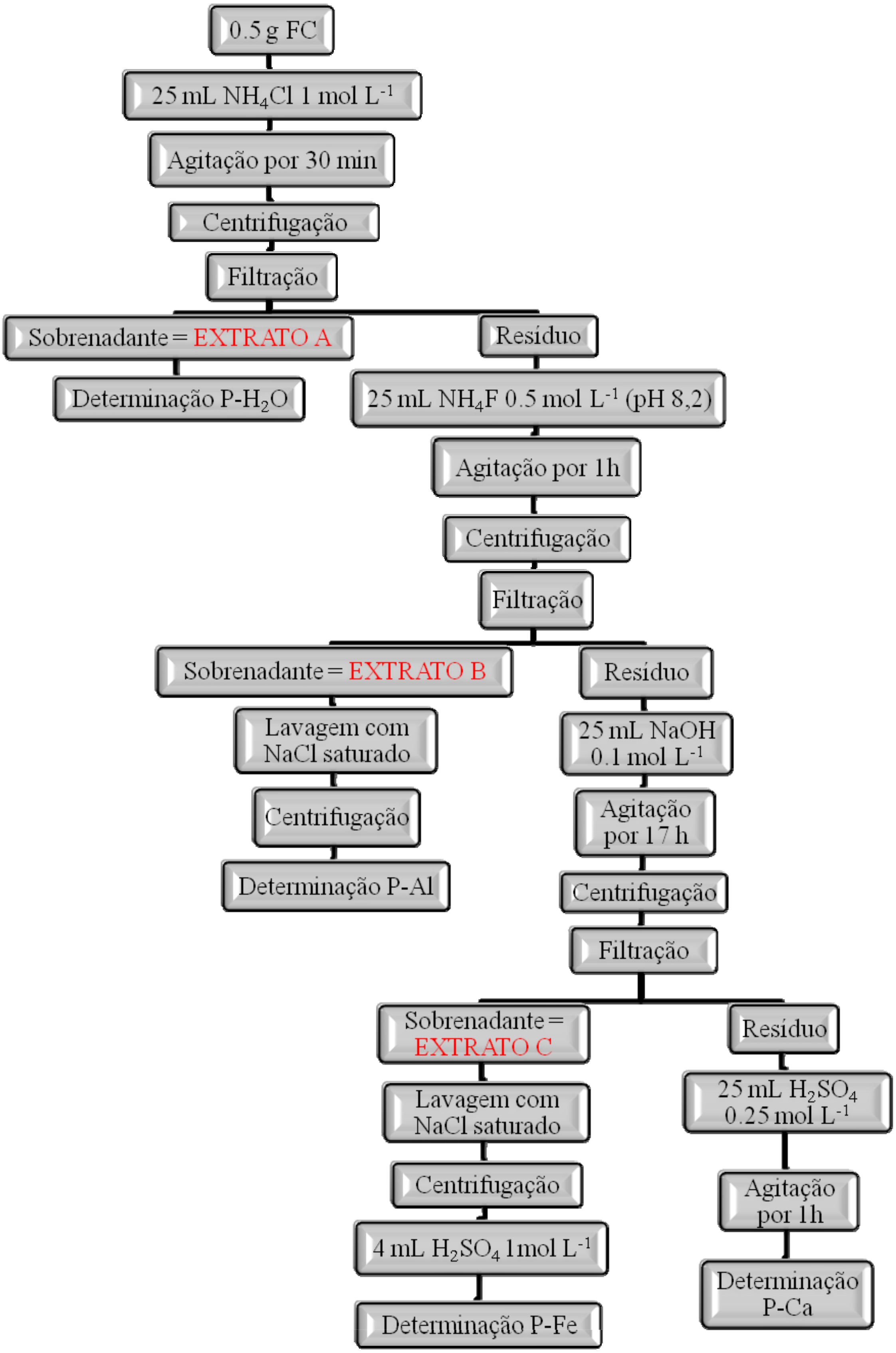

Figura 7 - Esquema de fracionamento do fósforo inorgânico (Pi) proposto por Chang and Jackson (1957) modificado por Kuo (1996).

4.3.6 **Análises de fertilidade**

As análises de fertilidade foram conduzidas utilizando-se solução de Mehlich 1 (HCl 0,05 mol/m^3 + H_2SO_4) para extração de cátions trocáveis (K^{+1}, Ca^{+2} e Mg^{+2}), micronutrientes (Zn, Mn e Cu) e P disponível. Alíquotas (2,5 a 4 g) de fragmentos cerâmicos pulverizados foram transferidos para erlenmeyer de 125 mL, em que a solução de Mehlich 1 foi adicionada a uma razão de 1:10 (g:mL). Os erlenmeyer sofreram agitação por 5 min em agitador horizontal, e permaneceram em repouso por uma noite. O sobrenadante foi filtrado e as concentrações de P disponível foram determinadas utilizando o método azul de molibdênio, enquanto os cátions e micronutrientes por absorção atômica. As análises foram conduzidas nos laboratórios do Instituto de Geociências-UFPA.

4.3.7 **Experimento**

Fragmentos não-pulverizados e 10 mL de solução de ácido cítrico foram adicionados em frascos de polietileno sem tampa. A razão líquido-sólido variou entre 1,5 e 7. A suspensão foi agitada por 5 minutos a 120 rpm. Os intervalos para as determinações dos nutrientes e micronutrientes foram de 1, 30, 180 e 360 dias. A cada determinação, retirava-se 5 mL de sobrenadante que em seguida era adicionado em volume idêntico a mesma concentração de ácido cítrico a fim de manter o volume da suspensão constante. Os nutrientes e micronutrientes foram determinados por colorimetria ou absorção atômica. Os experimentos foram conduzidos a temperatura ambiente no Laboratório de Análises Químicas-IG-UFPA.

4.3.8 **Extração dos lipídios**

A extração da matéria orgânica solúvel foi executada utilizando a infraestrutura do LEPRON (Laboratório de Extração de Produtos Naturais) do curso de Engenharia Química da UFPA sob a liderança do Prof. Dr. José Guilherme Maia cujo foco concentrou-se em uma fração particular do extrato, os ésteres metilados de ácidos graxos (EMAG, ou FAME, fatty acid metil ester).

Todas as vidrarias utilizadas para este processo laboratorial foram levadas a uma solução aquosa com detergente diluído em nível de fervura e depois enxaguadas com água em água destilada em abundância. Após, permaneceram imersos por alguns minutos em uma solução hidroalcoóxida de potássio (KOH 10% em solução de $C_2H_6O:H_2O$ na proporção 9:1) e secas em estufa a 160ºC (Tabela 5).

Tabela 5 - Relação dos solventes, padrões e reagentes utilizados.

Solventes, padrões e reagentes	Fabricante	Pureza
KOH	Nuclear	85%
NaOH	Merck	99,0%
Etanol	Qhemis	99,5%
FAME (com 38 componentes)	Sigma-Aldrich	
BF_3. MeOH	Sigma-Aldrich	
n-Hexano	Tedia	HPLC
Metanol	Sigma-Aldrich	HPLC
Clorofórmio	Tedia	HPLC
n-alcanos (C_8-C_{20})	Sigma-Aldrich	HPLC
n-alcanos (C_{21}-C_{40})	Sigma-Aldrich	HPLC

Na tentativa de se evitar ou mesmo minimizar traços de contaminação do solo, embora este tipo de contaminação seja comprovadamente insignificante de acordo com Heron *et al*. (2010), cada fragmento selecionado para esta análise foi particionado em três porções: uma porção mais externa (aquela que possivelmente teve mais contato com a chama, e após o descarte contato direto com o solo), a porção mais interna (que pode ter tido contato direto com alimentos, no caso em que o fragmento pudesse ter sido parte de um utilitário e também com o solo após o descarte) e uma porção intermediária (Figura 8), para onde os lipídios migram, que foi a porção reservada para esta análise, por ser mais isenta à contaminações.

Para cada conjunto de amostras preparadas, amostras de branco eram submetidas ao mesmo processo e conduzidas às análises.

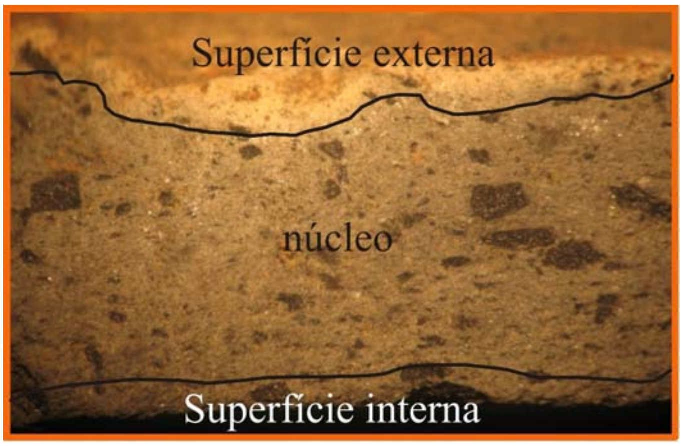

Figura 8 - Delimitação das porções particionadas para extração de compostos orgânicos.

4.3.8.1 Extração dos lipídios totais

Adotou-se métodos convencionais de extração utilizados em materiais cerâmicos arqueológicos que nada mais são do que métodos desenvolvidos para extração de óleos e gorduras em alimentos ligeiramente modificados, conforme descrito por Lantos *et al.* (2015).

Massas entre 1-2 g de amostras previamente pulverizadas sofreram extração com $CHCl_3$:MeOH (2:1, v/v, 10 ml) em banho ultrassom (Branson, modelo 1200, freqüência de operação 40 kHz) por 15 minutos, por duas vezes. A primeira extração foi realizada somente com metanol e a segunda com a mistura dos solventes nas proporções indicadas. Os extratos foram então centrifugados a 3000 rpm/10 minutos em centrífuga (CENTRIBIO) para separação do material sólido. O sobrenadante foi transferido para vials de 2mL e o solvente foi evaporado a temperatura ambiente sob proteção da luz. Após secura, o vial foi pesado e o extrato resuspenso com *n*-hexano. Uma alíquota do extrato foi saponificada.

4.3.8.2 Derivatizações

O extrato foi saponificado com 5 mL de NaOH 0,5M em uma solução etanólica (9:1, v/v), a 70°C por 1 hora em banho maria (Dubnoff Microprocessado, Quimis). Após resfriar a temperatura ambiente, a fração neutra foi extraída com 1,5 mL de *n*-hexano e a fração aquosa acidificada a pH 3 com HCl 3M seguida por extração com 1,5 ml *n*-hexano. A fase orgânica foi evaporada a temperatura ambiente no escuro e 0,5 mL de BF_3.MeOH (trifluoreto de boro em metanol, 1,3M) foi adicionado e aquecido a 60 ºC por 8 minutos. Os ésteres metílicos de ácidos graxos (FAME) foram extraídos com 2 x 0.75 ml de *n*-hexano, seguindo a evaporação de solvente e resuspensão em 50µL de *n*-hexano seqüencialmente conduzida para análise.

4.4 CROMATOGRAFIA GASOSA E CROMATOGRAFIA GASOSA ACOPLADA À ESPECTROMETRIA DE MASSAS (CG/CG-EM)

Estes métodos foram empregados para determinar a matéria orgânica amorfa preservada nos fragmentos sob a fração de metil éster de ácidos graxos. O equipamento empregado consistiu do sistema GCMS-QP2010 Plus (Shimadzu Corporation, Tokyo, Japan), equipado com coluna capilar de sílica fundida Rxi-5ms (Restek Corporation, Bellefonte, PA) de 30m x 0,25 mm (diâmetro) x 0,25 µm (espessura da película), revestida com 5% de difenildimetilpolisiloxano, com auto injetor AOC-20i. As condições de análise foram: temperatura do injetor de 250 °C; programação de temperatura do forno 100 °C (5 min), gradiente de 4°C/min até 260 °C (20 min); gás de arraste He ajustado a uma velocidade linear de 32 cm s^{-1}a 100 ºC, injeção splitless de 1 µL da amostra. Os espectros de massas foram adquiridos com ionização por impacto de elétrons de 70 eV, temperatura da fonte de íon e linha de transferência de 220 e 250 ºC, respectivamente. Os espectros de massa foram obtidos por varredura automática, á 0,3 segundos, com fragmentos de massas na faixa de 39-400 m/z. O índice de retenção foi calculado para todos os componentes, utilizando uma série homóloga de n-alcanos C8-C40 (Sigma-Aldrich), de acordo com a equação linear de Van den Dool e Kratz (1963). Os compostos foram identificados por comparação dos espectros de massas (massa molecular e o padrão de fragmentação) com a biblioteca de software CGMS solution que inclui uma base de dados das bibliotecas Willey, NIST, ADAMS e FFNSC 2, e pelo padrão de 38 componentes da Supelco. As informações semiquantitativas foram obtidas pela normalização da área do pico.

Cada fração foi submetida à quantificação em um CG Shimadzu QP 2010 com detector de ionização de chama (DIC), nas mesmas condições do CG/EM, exceto que o hidrogênio foi utilizado como gás de arraste.

As análises por CG-EM foram executadas no Laboratório Adolpho Ducke do Museu Paraense Emílio Goeldi e interpretadas pela Profa. Eloisa Helena de Aguiar Andrade, co-orientadora desta tese.

5 RESULTADOS E DISCUSSÕES

Os resultados, discussões e conclusões específicas estão apresentadas sob a forma de artigos. O primeiro, já publicado, aborda a fertilidade potencial de fragmentos cerâmicos representados pela constituição química e mineralógica dos próprios fragmentos. Demonstra a importância dos fragmentos para a manutenção da fertilidade do solo TPA, principalmente em relação aos fosfatos. O segundo ressalta os diferentes gradientes de queima a que foram expostos os vasilhames cerâmicos o que reflete diretamente as variações da principal fase mineral presente, a caulinita, ora apresentada como fase primária ora como fase neoformada, estas variações auxiliam no esclarecimento sobre a queima, condições e temperatura, fator de grande relevância na discussão sobre fosfatos e sobre matéria orgânica preservada. O terceiro trata a importância do fósforo como indicador da presença de substâncias orgânicas amorfas em fragmentos arqueológicos e consequentemente a relação destes fragmentos enquanto utilitário com produtos processados como alimentos ou resinas, pelas sociedades pretéritas.

5.1 FERTILITY AND DESORPTION CAPACITY OF ANTHROSOLS (ARCHAEOLOGICAL DARK EARTH – ADE) IN THE AMAZON: THE ROLE OF THE CERAMIC FRAGMENTS (SHERDS)

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Research paper

Fertility and desorption capacity of Anthrosols (Archaeological Dark Earth - ADE) in the Amazon: The role of the ceramic fragments (sherds)

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ABSTRACT

Numerous patches of black soil can be found throughout the Amazon basin, primarily along the margins of rivers. This type of soil is known as Archaeological Dark Earth (ADE) and is formed as a result of prehistoric human occupation and classified as Anthrosols. The chemical characteristics of ADE are distinct from those of the region's predominant soils, making them popular with local subsistence farmers. The patches of ADE are characterized by an abundance of ceramic fragments (sherds) (CF) both on the surface of the patches and within their inner depths. Considering that these sherds are generally composed of quartz, metakaolinite, feldspars, non-plastic materials, often with high levels of aluminum phosphates, the present study focused on their potential contribution to maintenance to the fertility of ADE soils, under the conditions of tropical weathering. With this aim, the mineralogical composition of the sherds was obtained using X-ray diffraction with the support of SEM-EDS readings. In addition, some parameters of fertility were measured as well as phosphates dissolution in the presence of citric acid as a function of time. The nutrients and micronutrients were determined by atomic absorption spectrometry and the molybdenum blue method. The results showed that the fragments analyzed were composed of quartz, feldspars, metakaolinite, micas/illites, and anatase, but differ in the presence/absence of chlorites, talc, cristobalite, and calcites. This study characterized the sherds as highly fertile and provides experimental confirmation that the sherds release phosphor under conditions approximating the natural weathering environment, which indicates that they are an important potential source of nutrients.

1. Introduction

Ceramic fragments (sherds) in general abundant in the horizons of soils of the Archaeological Dark Earth (ADE) are the principal evidence that these soils are related to the prehistoric and pre-colonial occupation of the Amazon basin by Amerindians (Birk et al., 2011; Costa et al., 2004b, 2011a; Glaser and Birk, 2012; Grossman et al., 2010; Novotny et al., 2009) and were classified as Arqueo-Anthrosols (Kämpf and Kern, 2005). The ADE soils were formed following the dumping of ceramic utensils, which either arrived as fragments, or were broken on site. The sherds represent parts of domestic utensils produced in clay with subsequent calcinations, and used primarily for the processing, cooking, and storing of food (Allegretta et al., 2014; Bernedo and Latini, 2013; Machado, 2006). Until recently, studies of these sherds concentrated on their technical and morphological aspects, with the principal aim of identifying technological traits through which the manufacturing culture could be interpreted.

Mineralogical and geochemical studies have provided increasingly important contributions to the field of archaeology and these studies have been successfully applied for investigation of the sherds found in the ADE soils (Cano et al., 2014; Costa et al., 2004b, 2011a,b; Nunes et al., 2013). The data available on the mineralogy and chemical composition of these sherds reveal a predominance of SiO_2 and Al_2O_3, besides the low contents of Fe_2O_3 and TiO_2 which are consistent with high concentrations of metakaolinite and quartz, and hematite/goethite and anatase, as accessory minerals; additionally low variable contents of K, Mg and Ca, among others, may represent feldspars, micas, feldspars, etc. (Costa et al., 2004b, 2011a,b). In general the most prominent characteristic of these sherds from ADE sites is the presence of P_2O_5 at levels of between 0.5% and 12% (Costa et al., 2004b, 2011a,b). However, this P_2O_5 signature is not homogeneous, and only the sherds from the coast of the Brazilian state of Pará examined by (Costa et al., 2004b, 2011a,b) presented micro- and crypto-crystals of crandallite-goyazite, whereas all other samples phosphor should be X-ray diffraction (XRD)-amorphous aluminum phosphates, and, more rarely, variscite, variscite-strengite and crandallite (Costa et al., 2004b, 2011a,b; Rodrigues et al., 2015).

The ADE soils are renowned for its relatively high fertility, which contrasts considerably with the typically poor soils found throughout

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0169-1317/

most of the Amazon basin. This makes ADE an important resource for local agriculture, which is normally of the subsistence type in this region. The nutrient charge of these soils apparently remains unaffected, even after continuous cultivation, which demands an uninterrupted source of nutrients to replace those eliminated by continuous crops and the organisms growing on the soil and erosion/leaching. The identification of this source of nutrients is obviously of the highest priority since it will contribute to understand how we can improve the poor fertility of the Amazon soils. From the geological and pedological viewpoint, the rocks that are the principal source of these nutrients are absent from the A horizons of ADE soils; the ceramic fragments (CF) are the only material that can compared to rock or weathering rocks which are generally present in large quantities in the ADE soil profiles. Since these CF could play an important role in the chemistry and mineralogy of these soils the present study will experimentally demonstrate the potential capacity of the CF to release some of the essential nutrient for the plants, like phosphorus.

2. Materials and methods

2.1. Materials

The sherds analyzed (44 samples) in the present study were obtained from four distinct archaeological sites in the Amazon: Barcarena (1° 33′ 56″ S/48° 44′ 28″ O), Raimundo at Caxiuanã (1° 45′ 36″ S/51° 26′ 34.3″ O), Juruti (Terra Preta 1: 2° 10′ 1.68″ S/56° 5′ 57.58″ O and Terra Preta 2: 2° 10′ 36.86″ S/56° 6′ 17.05″ O), in Brazil, and Quebrada Tacana at Letícia (4° 7′ 9.1″ S/69° 55′ 16.1″ O), in Colombia (Fig. 1). The sherds correspond to the horizon (0–60 cm) of an ADE. Some characteristics of the sherds are listed in Table 1.

2.2. Methods

2.2.1. Mineralogical analysis

The mineralogical composition of the sherds was determined using a PANalytical X'PERT PROMPD (PW 3040/60) X-ray diffractometer (XRD) with a PW3050/60 (θ/θ) goniometer, ceramic X-ray tube, and a cobalt anode ($\lambda CoK\alpha 1 = 1.79026$ Å), except for the sherds from the Raimundo site, for which a copper anode ($\lambda CuK\alpha 1 = 1.54060$ Å) was used. The instrumental conditions used were: scan of 5–75° at 2θ, voltage of 40 kV and current of 40 mA, pass of 0.0170 at 2θ, and 10.3377 s per pass. These analyses were conducted in the UFPA Mineral Characterization Laboratory. The mineralogical studies were also supported by scanning electron microscopy (SEM), using a LEO VP 1450 microscope, with an energy-dispersive X-ray spectrometry system (SED) for chemical microanalyses in the UFPA MEV Laboratory. The images and chemical analyses obtained here contributed to the finalization of the identification of the minerals by XRD, as well as improving the identification of amorphous phases, such as the phosphates. The samples were metalized with Au at a pressure of 3×10^{-1} bar and current of 25 mA.

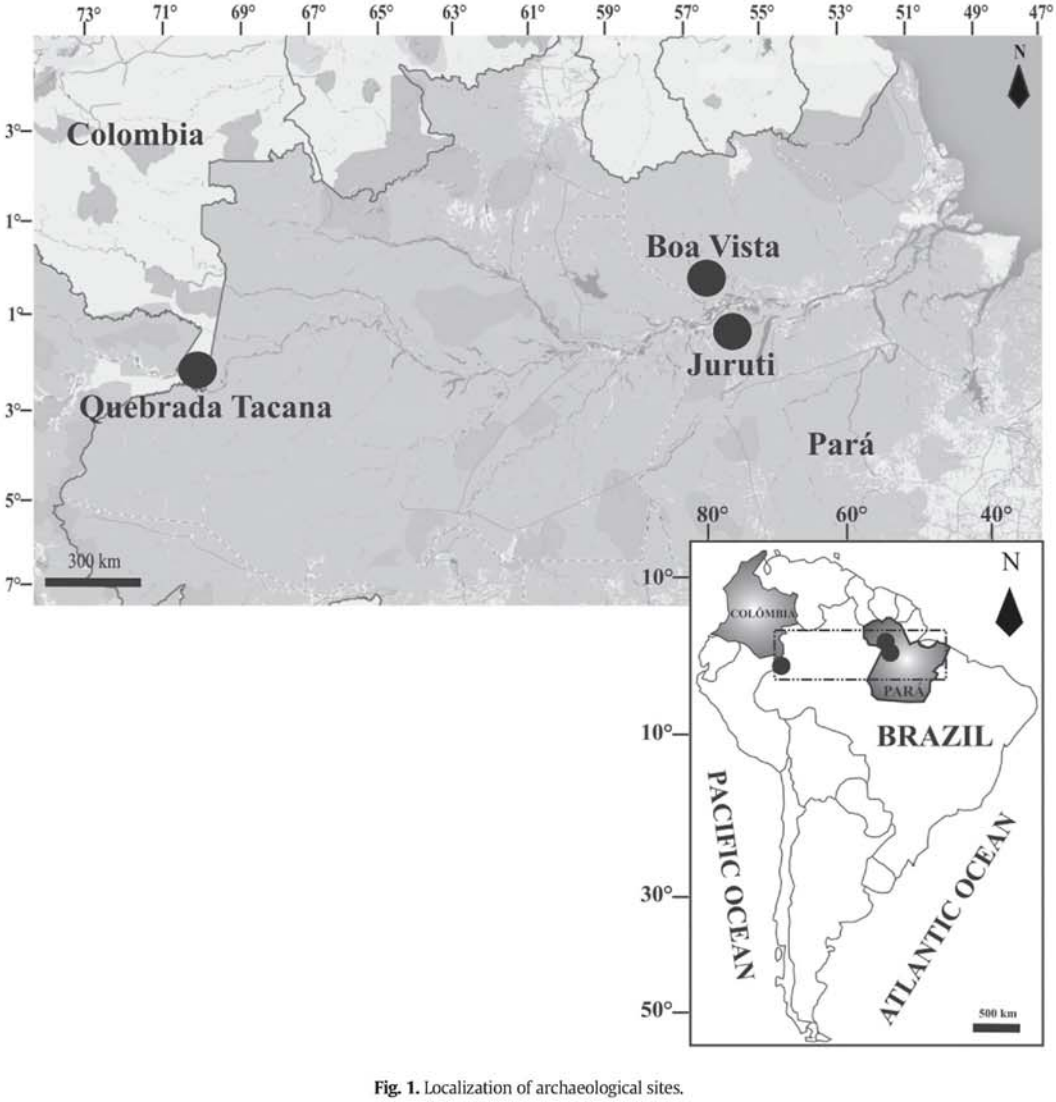

Fig. 1. Localization of archaeological sites.

Table 1
Contents of P, Ca and Mg of the sherds used in the experimental was obtained by Inductively Coupled Plasma Mass Spectrometry (ICP OES Varian by AcmeLabs).

Samples	Depth (cm)	P (%)	Ca (%)	Mg (%)
Raimundo				
T1-15	0–20	0.8	0.55	0.59
T1-40/2	Surface	0.92	0.23	0.3
Q. Tacana				
QT-18	30–35	2.39	0.06	0.36
QT-22	30–35	1.25	0.02	0.29
Barcarena				
BA08-02B	Surface	0.06	0.07	0.57
BA08-03A	10–20	0.04	0.06	0.54
Juruti				
JU1-TP1	50–60	4.68	0.15	0.56
JU2-TP1	10–20	3.38	0.27	0.85

2.2.2. Chemical analysis

The previous analysis of fertility was very important to have an indication of the real potential of sherds in releasing nutrients. The Mehlich-1 solution (0.05 mol/m^3 HCl + 0.125 mol/m^3 H_2SO_4) was used for the extraction of exchangeable cations (K^{+1}, Ca^{+2}, Mg^{+2}), micronutrients (Zn, Mn and Cu), and available P. Aliquots (2.5–4.0 g) of the sherds, which had been pulverized in agate mortar to 25 μm, were transferred to 125 mL Erlenmeyers, to which the Mehlich-1 solution was added at a ratio of 1:10 (g:mL). The Erlenmeyers were agitated for 5 min on a horizontal agitator, and then left to rest overnight. The supernatant was filtered and the concentrations of available P were determined using the molybdenum blue method, while exchangeable cations and micronutrients concentrations were determined by atomic absorption spectrometry (AAS 3300, Perkin Elmer). These analyses were conducted in the UFPA Chemistry Analysis e Atomic Absorption Laboratories, respectively.

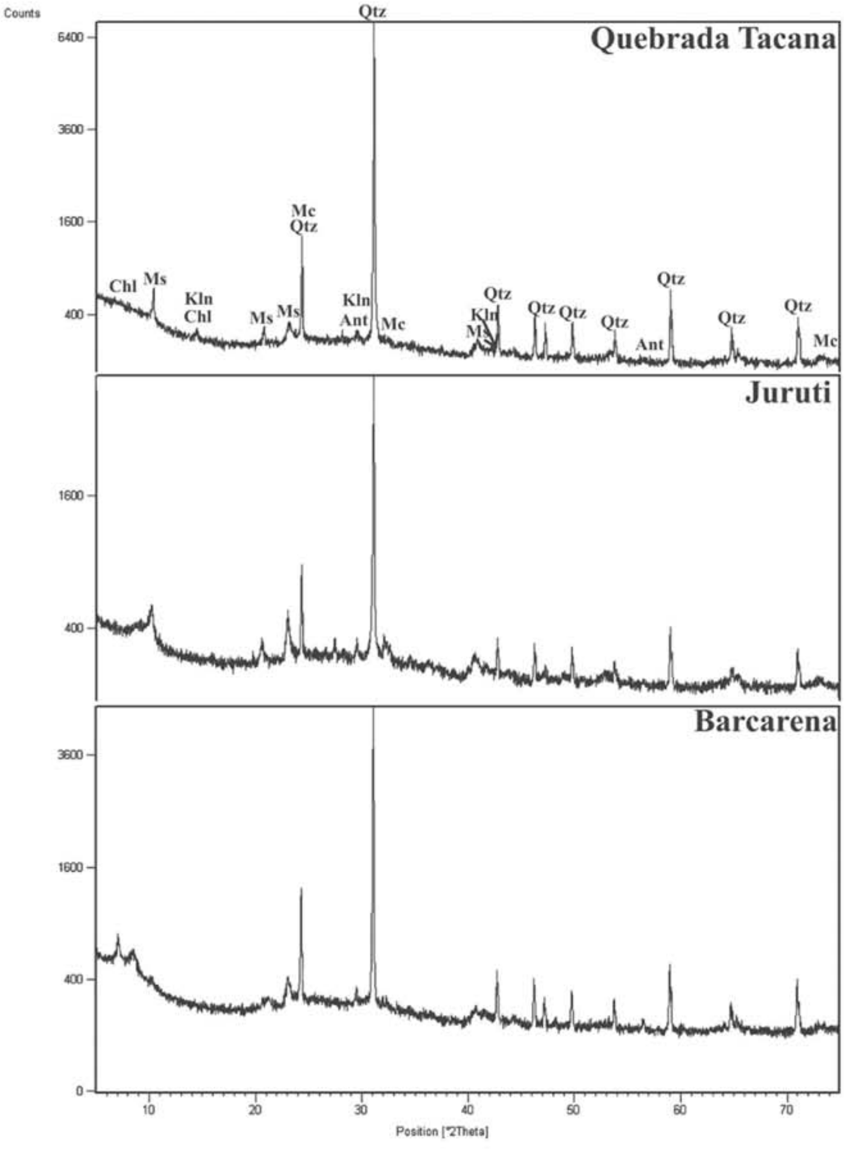

Fig. 2. Minerals identified in the ceramic fragments from Quebrada Tacana, Juruti, and Barcarena using X-ray diffraction with a cobalt anode (λCoKα1 = 1.79026 Å): anatase - Ant; chlorite - Chl; kaolinite – Kln (traces); microcline – Mc; muscovite - Ms; quartz - Qtz.

2.2.3. Experimental set up

Sherds and 10 mL of a given concentration of citric acid solution were added to an open-mouth plastic bottle. Liquid-to-solid ratio varied between 1.5 and 7. The suspension was stirred at speed of 120 rpm for 5 min. After 1 day, 5 mL of supernatant was sampled for determination of P, Ca and Mg, followed by addition of an identical volume of the same concentration of citric acid solution to maintain the suspension volume constant. Soluble P were determined by colorimetric (molybdenum blue method), while Ca and Mg were determined by atomic absorption spectrometry. Experiments were conducted at room temperature in the UFPA Chemistry Analysis.

2.2.4. Adjustment of the isotherm models

Of the numerous theoretical and semi-empirical equations developed for the interpretation or prediction of isotherms, those of Langmuir and Freundlich are among the most frequently-used. The desorption constants were calculated through the construction of isotherms, and the experimental data were adjusted using these mathematical models. The criterion adopted for the selection of the best adjustment was the coefficient of determination (r^2), where the best adjustment is represented by the value closest to 1.

The linear expression of Langmuir's isotherm is given by the equation:

$$Ce/Qe = 1/QmK_L + 1/K_L \tag{1}$$

where: K_L is Langmuir's constant, which expresses the theoretical adsorption capacity of the monolayer, Qm is a constant related to the energy of sorption (mg/L), Ce is the concentration of the sorbate at equilibrium, and Qe is the quantity of ions desorbed per gram of sorbent (mg/g).

Freundlich's expression is provided by the equation:

$$\log Qe = \log K_F + 1/n \log Ce \tag{2}$$

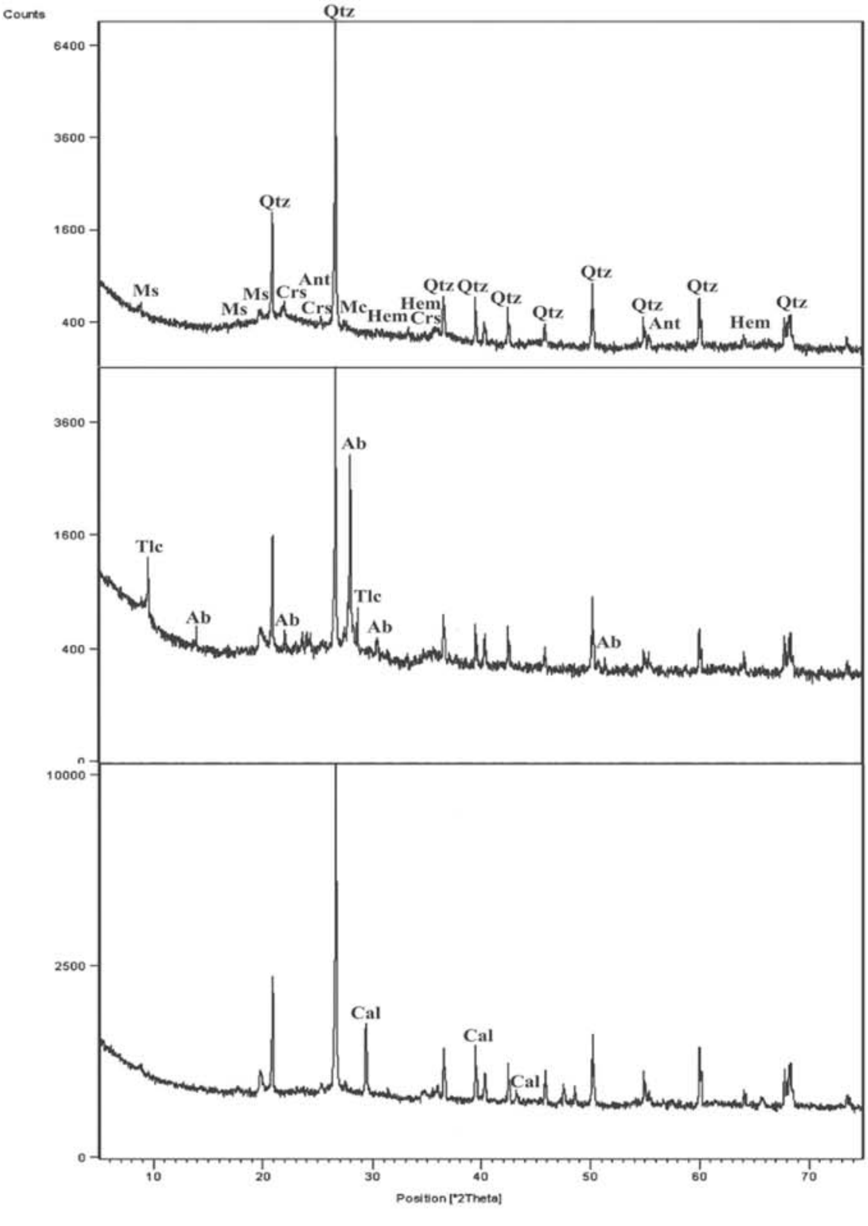

Fig. 3. Minerals identified in the ceramic fragments from Raimundo site using X-ray diffraction with a copper anode ($\lambda CuK\alpha 1 = 1.54060$ Å): albite - Ab; anatase - Ant; calcite – Cal; cristobalite – Crs; chlorite - Chl; hematite - Hem; microcline – Mc; muscovite - Ms; talc – Tlc; quartz – Qtz.

where: Qe is the mass of the solute associated with the solid phase (mg/g), Ce is the concentration of the solute at equilibrium in the solution (mg/L), K_F is Freundlich's constant of sorption (mg/g), and n is an empirical (dimensionless) parameter.

3. Results and discussion

3.1. Mineralogical composition of the sherds

The sherds are composed essentially of quartz and metakaolinite. Metakaolinite is indicated clearly by the elevated background in the XRD and can be proven by the presence of the 4.44 Å reflection (Fig. 2). It is a common component of sherds from archaeological sites in the Amazon region (Costa et al., 2009, 2010; Rodrigues et al., 2015). Muscovite, anatase and feldspars (albite, orthoclase and/or microcline) are also present, depending on the origin of the sherds, that is, the geological characteristics of the source of the raw material. Most of these minerals which were possibly present in the raw material used to produce the ceramic pieces (Costa et al., 2004b; Rodrigues et al., 2015), were either present in sediments or were the weathering products of the granitic rocks or their volcanic equivalents, or their metamorphic products (Costa et al., 2004b; Godfrey-Smith et al., 2005; Plymate et al., 2001; Rogers et al., 1998; Stefanova 2004). The sherds from Barcarena and Quebrada Tacana also contained chlorite and kaolinite (Fig. 2). Chlorites are normally products of hydrothermalism or low grade metamorphism, but can occur in some sedimentary rocks as a result of diagenesis or geothermal processes (Jenkins and Chernosky, 1986; Kirsimäe et al., 2004; Moore and Reynolds, 1997; Scapin. 2003; Suárez et al., 2009; Zanazzi et al., 2009; Zane et al., 1998; Zimák, 1999). These minerals contain variety essential nutrients, therefore, are able to release them to soil solution and consequently to plants.

Cristobalite was only identified in the sherds from Quebrada Tacana and Raimundo (Figs. 2 and 3), and is related to the presence of cauixi and calcinated cariapé, used as aggregate (Costa et al., 2009, 2010). Hematite and/or goethite of a low crystalline order were also found in the samples (Figs. 2 and 3). Talc and calcite were much rarer, and were only detected in the samples from Raimundo (Fig. 3). The calcite was found in the sherds containing fragments of shells, which were probably added to the ceramic mass as coarse temper.

3.2. Potential fertility of the sherds

According to a soil fertility classification in soils established by Alvarez et al. (1999) for soils in Minas Gerais (southeast of Brazil), the sherds investigated may be seen in fact as fertile material. Exchangeable K^+ showed the highest concentration in Juruti sherds (1.6 cmol_c/kg), which were much higher than the very high fertility mean value (Tables 2 and 3). Conversely, K^+ showed the lowest content in Barcarena sherds, 0.7 cmol_c/kg. The values of K^+ are attributed to the gradual dissolution of minerals such as K-feldspars, micas, and even illite, identified by XRD, which are found in widely varying concentrations in the different sherds slightly weathered. These minerals are relatively unstable and will decompose gradually as a function of the natural weathering process typical of the Amazon tropical zone. Likewise, they also represent a source of Mg and micronutrients, over a medium time scale (Martins and Costa, 2009).

The maximum Ca^{2+} content was registered in Raimundo sherds, at almost 30 cmol_c/kg. This Ca^{2+} content may be provide by partially dissolution of the calcite detected Raimundo sherds (Silva, 2010), which constitute the shell fragments has been added as coarse temper (Costa et al., 2011b; Rodrigues et al., 2015). The highest Mg^{2+} concentration was observed in Raimundo and Quebrada Tacana sherds, these values close to mean value for high soil fertility (Tables 2 and 3). The Mg mineral identified by XRD in the sherds were chlorite, illite and talc. The highest value for Sum of Bases (SB) displayed from Raimundo sherds, which was which was related to the high Ca content (Tables 2 and 3).

Table 2
Levels of exchangeable macro and micronutrients, and available P recorded in the sherds from Raimundo, Quebrada Tacana, Juruti and Barcarena sites.

Samples	K (cmol_c/kg)	Ca (cmol_c/kg)	Mg (cmol_c/kg)	SB (cmol_c/kg)	Zn (mg/kg)	Mn (mg/kg)	P (mg/kg)
Raimundo (7)							
T1-13	1.0	0.4	0.2	3.0	1.1	10	4
T1-15	1.2	2.5	<0.02	5.0	2.4	9	7
T1-18/8	0.9	10	<0.02	12.0	4.2	56	9
T1-37	1.2	2	1.2	6.0	0.9	56	8
T1-41/1	0.4	27	0.6	29.0	<0.05	6	1
T1-41/2	0.9	4	0.5	6.0	1.3	26	3
T1-41/4	1.1	1	0.3	3.0	2.4	11	28
Q. Tacana (11)							
QT-02	1.1	1.3	0.4	4	4.4	3	17
QT-03	0.6	0.5	0.4	2	13.5	11	100
QT-05	1.0	0.6	0.4	3	6.5	8	42
QT-06	0.7	<0.3	na	1	na	3	30
QT-14	0.5	0.2	1.4	3	9.5	9	77
QT-15	0.7	4.5	0.2	6	9.7	7	56
QT-18	0.4	0.5	0.2	1	5.1	8	156
QT-19	0.5	na	na	1	7.9	na	1045
QT-22	0.3	0.3	0.1	1	4.5	12	56
QT-25	0.7	0.6	0.2	2	7.5	17	44
QT-27	0.7	na	na	1	5.7	na	12
Juruti (4)							
JU1-TP1	1.6	1.0	0.6	5	7	10	1293
JU2-TP1	1.2	2.2	0.6	5	13	52	2550
JU1-TP2	0.3	na	na	1	17	5.6	657
JU2-TP2	1.1	2.6	0.4	5	15	20	956
Barcarena (5)							
BA08-01	0.3	0.9	0.2	2	3	5	2
BA08-2A	0.4	na	na	1	7	na	5
BA08-2B	0.7	0.3	0.4	2	5	na	2
BA08-3A	0.6	na	na	1	na	na	3
BA08-3B	0.6	0.2	0.4	2	6	na	4

na: not analyzed; (7): number of sample; SB: sum of bases.

Table 3
Categories for the interpretation of the fertility of soils in terms of their content of K, Ca, Mg, Zn, Mn, P and SB compared with the mean levels recorded in the sherds obtained from Raimundo, Quebrada Tacana, Juruti, and Barcarena sites.

	K^{a} (cmol$_c$/kg)	Ca^{a} (cmol$_c$/kg)	Mg^{a} (cmol$_c$/kg)	SB^{a} (cmol$_c$/kg)	Zn^{b} (mg/kg)	Mn^{b} (mg/kg)	P^{a} (mg/kg)
Classification							
Very low	<0.04	≤0.4	≤0.15	<0.60	≤0.4	≤2.0	≤4.0
Low	0.05–0.13	0.4–1.2	0.16–0.45	0.61–1.80	0.5–0.9	3.0–5.0	4.1–8.0
Medium	0.14–0.18	1.21–2.4	0.46–0.90	1.80–3.60	1.0–1.5	6.0–8.0	8.1–12.0
High	0.19–0.31	2.41–4.0	0.91–1.50	3.61–6.0	1.6–2.2	9.0–12.0	12.1–18.0
Very high	>0.31	>4.0	>1.51	>6.0	>2.2	>12.0	>18.0
Sites							
Raimundo (7)	1.0 ± 0.3	70	0.6 ± 0.4	90	2 ± 1.2	24.8 ± 22.1	9
Q. Tacana (11)	0.6 ± 0.2	10	4	2.3 ± 1.6	7.4 ± 2.8	8.7 ± 4.4	149
Juruti (4)	1.0 ± 0.5	2 ± 0.8	0.5 ± 0.1	4 ± 2	13 ± 4.3	27.3 ± 21.9	1364 ± 832
Barcarena (5)	0.52 ± 0.2	0.5 ± 0.4	0.3 ± 0.1	1.6 ± 0.5	5.2 ± 1.7	5	3.2 ± 1.3

(7): number of sample; SB: sum of bases.

[a] Chaves et al. (1998).

[b] Abreu et al. (2007).

The Zn is micronutrient most concentrated, their values were almost invariably for very high fertility classification (Tables 2 and 3). Other potential micronutrient is Mn as well as Zn most likely derived from the decomposition of micas and illites besides chlorites.

The Mehlich-1 method recovered high relatively amounts of available P, especially, Quebrada Tacana and Juruti sherds, which were greater compared to the very high classification soil fertility (Tables 2 and 3). However, the sherds from Barcarena presented extremely low levels of phosphorus, while the Raimundo sherds have median levels of this nutrient (Table 2). Exchangeable K, Ca, Mg, Zn, Mn and available P contents of the sherds, referred to as the potential reserved nutrients were not similar for all samples intra-site or inter-site. As mentioned previously, the mineralogical properties and consequently nutrient stocks of sherds depend on geological origin of raw material (clay), variety non-plastic materials used, firing temperature. Regarding to availability P, it is incorporated into pots for cooking food. This has been studied by Rodrigues et al. (2015), who reported that P was contributed by the minerals generally amorphous, such as variscite-strengite. This data indicate that the sherds contained potentially reserved nutrients and easily releases nutrients, which are considered readily available to be absorbed by plants, indicated its potential as a source of nutrients. Overall, then, the values recorded for the levels of nutrients and micronutrients in the sherds analyzed here are comparable with those obtained for a number of different ADE soils, and are considerably higher, in some cases, for K and P (Fig. 4).

3.3. Desorption assays

The desorption assays of the nutrients were conducted in order to assess the capacity of the CF to liberate their chemical components, given that, when subject to double-acid extraction, they behave as a source of nutrients. The experiments revealed that the ceramic fragments desorbed the nutrients Ca, Mg, and P, at least, with a greater potential for the liberation of P (except for the samples from Barcarena, they carry very low phosphor contents, <1 mg/kg). As demonstrated previously, minerals that contribute to the constitution of the CF – muscovite, illite, K-feldspars, talc, chlorites, and even calcite – are by biochemical weathering the potential sources of nutrients such as K, Ca and Mg, given that they are the only minerals identified in this analysis that contain these elements. As they can be quickly weathered by the typical tropical climatic conditions of the Amazon region, these materials decompose, forming clay minerals and gradually liberate or partially fix these nutrients and other micronutrients in the preexistent or neoformed clay minerals, or even in the organic matter of the ADE soils. The high cation exchange capacity of 2:1 clay minerals and organic matter is well known in the soil (Costa et al., 2004a; Hepper et al., 2006; Li et al., 2011; Önal, 2007; Plante et al., 2011; Plaza et al., 2013; Wang et al., 2011). On the other hand, the amorphous to cryptocrystalline aluminum phosphates are the unique phosphorus phase and this way the principal potential sources of this nutrient.

The isotherms were produced based on the experimental q data (mg/g) as a function of Ce (mg/L) and of the recalculated desorption

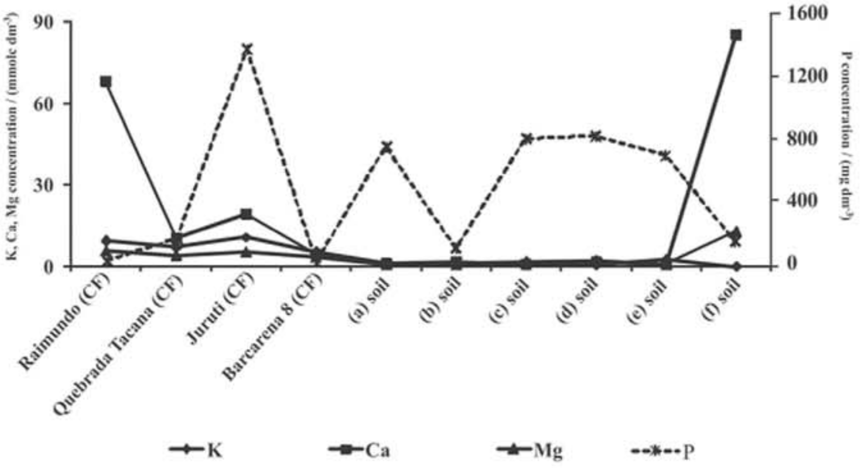

Fig. 4. Comparison of the mean levels of exchangeable cations and available P released in the sherds analyzed in the present study with ADE-type soils from the Amazon region: (a) São João Batista Community (Silva et al., 2011); (b) Lauro Sodré (Silva et al., 2011); (c) Pilão (Silva et al., 2011); (d) Lago do Limão (Silva et al., 2011); (e) Ena (Silva et al., 2011); (f) Ilha de Terra (Lemos et al., 2011).

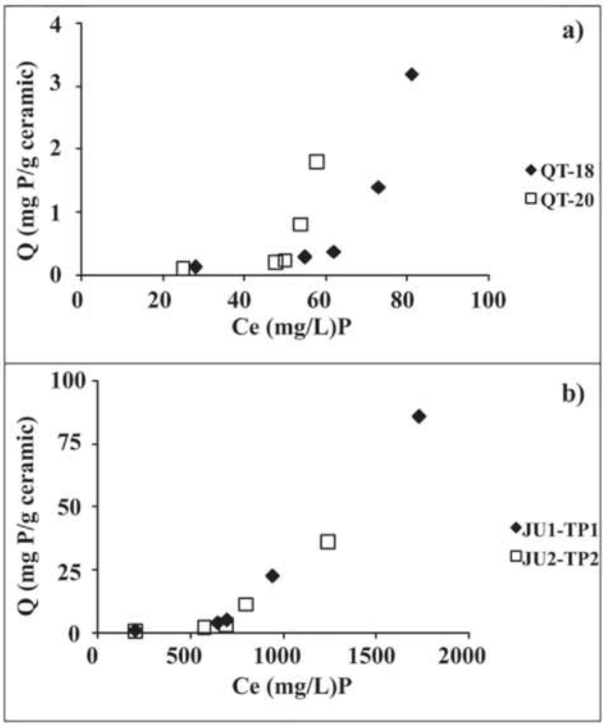

Fig. 5. Desorption isotherms for the phosphorus in the CF: a) Quebrada Tacana; b) Juruti.

capacity derived from the linearized Langmuir and Freundlich equations. The experimental curves for phosphorus are shown in Fig. 5. The correlation coefficients (r^2) obtained from the linearized Langmuir and Freundlich equations (Table 4) indicate that the two models provide a satisfactory description of the desorption behavior of the phosphorus in the CF from Quebrada Tacana and Juruti.

The isotherms obtained for the CF are consistent with type III in the BET (Brunauer, Emmett, and Teller) classification system. This type of isotherm is related to the very weak interactions found in systems containing macro- and mesopores. The isotherms obtained here were consistent with type S, subgroup I of (Giles et al., 1970) modified by (Falone and Vieira, 2004), which can be visualized from the sigmoid form of the curves, and confirmed by the values of $n > 1$ for Freundlich's parameter (Table 3). This type of curve is characterized by initially low levels of desorption, reflecting the fragility of the sorbent-sorbate, with desorption being favored progressively as the number of desorbed molecules increases. In addition to classifying the curve, this parameter implies that a direct relationship exists with the sorption sites, which, in the case of these sherds, suggests the presence of sites with elevated energy levels.

The desorption coefficients (Kf) presented by the isotherms varied from 0.26 to 1.33. According to (Falone and Vieira, 2004), these values indicate low levels of desorption in the fragments analyzed.

The desorption assays demonstrated that Ca and Mg are at equilibrium in the solution, although, based on the results obtained for Mehlich 1, these elements are generally present at relatively low concentrations, except for Ca in the Raimundo CF. As these ions are in very low concentration, no mathematical adjustment was made to reveal the capacity for desorption of these cations by the CFs.

Table 4
Adjustment parameters obtained for the Langmuir and Freundlich models.

Sites	Sample	Langmuir model			Freundlich model		
		K_L	b	r^2	K_F	n	r^2
Quebrada Tacana	QT-18	−90.65	0.003	0.8	0.26	3.55	0.7
	QT-22	−73	0.002	0.6	1.33	4.4	0.6
Juruti	JU1-TP1	−1814	0.005	0.8	0.38	2.22	0.9
	JU2-TP1	−1352	0.003	0.8	0.4	2.49	0.8

4. Conclusions

The Juruti and Quebrada Tacana CF (which are the richest in phosphates), behave as highly fertile material, with high levels of $P_{avaliable}$. At Raimundo, detach the high levels of $Ca_{exchangeable}$ which derived from calcitic shells and increased its SB values but the CF are phosphor poor.

The desorption assays pointed primarily to the liberation of phosphor, in particular from the Quebrada Tacana and Juruti CF. The pH range adopted in the experiment favored the solubilization of the iron phosphates, which was reflected in the very low desorption coefficient (Kf) values. The desorption of the aluminum phosphates occurred on a smaller scale.

Overall, then, the CF marked capacity for the desorption of P, (Ca, and Mg), which is consistent with their chemical-mineralogical composition, certainly favored by the CF weathering since they are part of the profile of ADE soils. Clearly, then, the ceramic fragments may contribute considerably to the fertility of the ADE soils.

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MINERALOGICAL EVALUATION OF ARCHEOLOGICAL DARK EARTH SHERDS AND THEIR ORGANIC EXTRACTS USING INFRARED SPECTROSCOPY AND HIERARCHICAL CLUSTER ANALYSIS

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Abstract

The effects on ceramic products of firing conditions, firing temperatures are assessed here through mineralogical composition by the FT-IR technique. The FT-IR spectra were recorded in the mid IR region 4000 to 400 cm^{-1}. The archaeological pottery sherds were collected from ADE sites in Amazon basin. Samples scraped from either the margins and core of the pottery sherds were analyzed in transmission mode as a powder in KBr pellets or after extraction with $CHCl_3$:MeOH. The results indicate that the pottery sherds were made different temperatures for the sites, in the range of 600-800 ºC from Juruti and Quebrada Tacana pottery sherds whereas Boa Vista at 500-600 ºC. Following extraction, the analyses indicated that the pottery sherds from Quebrada Tacana contained carboxylic acids, confirming that oils or fats were processed in the utilitarian vessels from which the pottery sherds were derived.

Key words: FT-IR, firing temperature, sherds, ADE, mineralogy.

1. Introduction

Sherds or ceramic fragments represent the most abundant type of cultural artifact found in archeological sites. As part of the everyday life of ancient communities, chemical and mineralogical analyses can provide fundamental insights into the process used to produce the pieces, their use and eventual disposable, and even the society that fabricated the vessels. At Archeological Dark Earth (ADE) sites, which are widespread in the Amazon basin, this type of investigation has focused primarily on the raw material, providing data on aspects such as their composition and sources.

Phosphates are the most characteristic chemical-mineralogical feature of Amazonian sherds, being found in varying concentrations and, except in a few isolated cases, they tend to be characterized as amorphous phases under X-ray diffraction. Costa et al. (2003, 2004ab, 2009) have associated this phosphorus content to the foods processed in the utilitarian vessels. This conclusion was reinforced by the studies of Rodrigues *et al*. (2015) and Rodrigues & Costa (2016), who tested the effects of cooking in replica vessels.

The determination of products processed in archaeological vessels, mainly with dietetic foods is usually elucidated by the extraction of the absorbed and preserved amorphous organic matter in the ceramic and its respective sherds. This approach has yet to be applied to sherds obtained from archeological in the Amazon region. Given the importance of amorphous phosphates as indicators of the use of ceramic vessels, and the successful identification of organic material in archeological relics, in particular in Europe (Oudemans & Boon 1991, Guerrero & Viscaíno 1995, Evershed et al. 1997, Dudd et al. 1999, Evershed et al. 1999, Copley et al. 2000, Craig et al. 2009), the present study applied Fourier transformation infrared spectroscopy (FT-IR) to the identification of the phosphatic phases not revealed by other techniques, such as X-Ray

Diffraction (XRD), and to characterize after solvent extraction bands related to preserved organic residues.

In addition to the identification of the target phases, the present study also applied a Hierarchical Cluster Analysis (HCA) to evaluate the similarities among the sherds, both within and between sites. Each fragment was fractioned based on the colors delimited in its transversal section. Color is an important physical property for the description of ceramics, given that it can provide important information on the time, temperature, and air content of the firing process. In this case, the results obtained for each section of the fragment were used to discuss the firing conditions, as well as the possible mineral phases formed by alterations occurring during the disposal of the item. The organic phases related to the amorphous organic matter were also characterized after extraction, according to the limitations of the technique.

2. Materials and methods

2.1. Materials

In the present study, the analyses were conducted on three sites of sherds collected from the archeological sites at QuebradaTacana, Juruti and Boa Vista. These sites range from the Brazilian–Colombian border in the western Amazon basin to eastern Amazonia.

2.1.1. Quebrada Tacana

This ADE site in located in the Colombian trapezium north of the city of Letícia (04°07’09.1”S, 69°55’16.1” W), close to the Brazilian border, in western Amazonia. This site covers an area of 2 hectares, and the horizon of occupation (containing ADE and sherds) varies in depth from 5 cm to 40 cm, with a sandy-loamy texture, black in color (10 YR3/2), with a high density of sherds and botanical remains, i.e., phytoliths, charcoal, and seeds (Morcote & Sicard 2007, Costa et al. 2011).

2.1.2. Juruti

This site encompasses two nearby ADE deposits, denominated TP1 (02°10’01.68” S, 56°05’57.58” W) and TP2 (02°10’36.86”S, 56°06’17.05” W), covering a total area of 60 ha in the municipality of Juruti on the right margin of the lower Amazon River. The A horizon has a relatively sandy texture, the coloration of which ranging from black (2.5YR2.5/1) to very dark grayish brown (10YR3/2), with charcoal, ash, and abundant sherds (Costa et al. 2013).

2.1.3. Boa Vista

This site Boa Vista is 1 km from the settlement of Porto Trombetas, in the municipality of Oriximiná in Pará state, Brazil, in the lower Amazon basin (central coordinates: 01°27’41.18”S, 56°23’58.61” W). This site also encompasses two separate ADE deposits, denominated Boa Vista and Água Fria, with a total area of 13.5 ha. The A horizon, which corresponds to the ADE, is a layer almost 60 cm thick rich in sherds, tools, adornments, lithic, bone fragments, calcined seeds, and charcoal, besides diverse rocks in the form of pebbles (Guapindaia 2008).

2.2. Methods

2.2.1. Macroscopic Description

The study samples (Table 1) were dried at room temperature and when necessary, the exogenous material (attached soil) was removed carefully with distilled water. The samples were described macroscopically through visual inspection, and then using a binocular stereomicroscope with a magnification of up to 5 x (ZEISS-Stemi 2000-C, Germany) and photographed with a coupled Canon PowerShot G6 camera (7.1 megapixels, Japan).

Characteristics, such as the general external appearance (composition of the non-plastic, conservation, pigments, marks, and decoration), color, and dimensions, were recorded in detail. The colors were evaluated in the cross section of each fragment, and classified based on the Munsell Soil Color Charts (Munsell Color Company, 2000). In some cases, it was possible to distinguish as many as three different colors, which may provide important insights into the firing conditions. The dimensions of each fragment were also measured using a caliper. These data were collected in the Mineralogy-Gemology Laboratory of the Geosciences Institute of the Federal University of Pará (UFPA).

Each sherd was then divided into three portions: (i) external (margin), which probably had most contact with flames (either during the firing or use of the vessel, when used for cooking), (ii) core, in this study, this portion was closer to the internal portion, and presumably did not have direct contact with flames in any phase (firing or cooking), nor with the ground after being discarded, and (iii) internal (margin), which may have had direct contact with food, when the fragment was part of a utilitarian vessel.

Table 1. General characteristics of the samples analyzed from the QuebradaTacana, Juruti, and Boa Vista sites.*Crushed rock

Sample	**Depth (cm)**	**Temper**	**Color (Munsell Color)**		**Thickness (mm)**	**Vessel section**
			Margin	**Core**		
Quebrada Tacana						
QT-04	15-20	Mineral + charcoal + cariapé	10YR 7/6	10YR5/3	9	Body/base
QT-11	20-25	Mineral + charcoal + cariapé	10YR 8/2	5Y 5/1	4–9	Rim
QT-15	25-30	Mineral + charcoal	5YR 7/4	Gley1	6	Rim
QT-18	30-35	Mineral + charcoal + cariapé	10YR7/4	2.5Y5/1	9	Body
QT-19	30-35	Mineral + charcoal + cariapé	10YR7/4	2.5Y5/1	9	Body/base
QT-20	30-35	Mineral + charcoal + cariapé	10YR7/6	5Y6/1	5	Rim
QT-21	30-35	Mineral + charcoal + cariapé	10YR8/3	2.5Y7/1	3	Rim
QT-22	30-35	Mineral + charcoal + cariapé	10YR8/4	5Y4/1	9	Body/base
QT-23	35-40	Mineral + cariapé	10YR8/6	2.5Y7/4	3	Rim
QT-24	35-40	Mineral + charcoal + cariapé	10YR8/4	5Y4/1	4–6	Rim
QT-26	35-40	Mineral + cariapé	10YR6/4	5Y6/2	6	Rim
Juruti						
JU2-TP1	10-20	Mineral + cauixi	7.5YR7/6	5Y6/3	10	Not identified
JU2-TP2	10-20	Mineral + cauixi	10YR7/3	5Y2.5/1	10	Not identified
Boa Vista						
CPT1	5	Mineral	10YR4/1	10YR6/4	0.5–12	Rim
CPT2	106	Mineral + cauixi	7.5 YR7/4	7.5YR7/4	4–9	Base
CPT3	19	Mineral	5YR5/6	2.5Y4/1	4	Body
CPT4	39	Mineral	10YR5/3	7YR6/6	4	Body
CPT5	58	Mineral + charcoal + cauixi	5YR6/8	10YR 5/1	-	Adornment
CPT6	10	Mineral	5Y 6/1	7.5YR 5/6	3–5	Rim
CPT7	108	Mineral + cauixi + Cr*	5YR 6/4		3	Body
CPT8	96	Mineral + cauixi + Cr*	2.5 YR	2.5 Y 6/1	9–12	Base

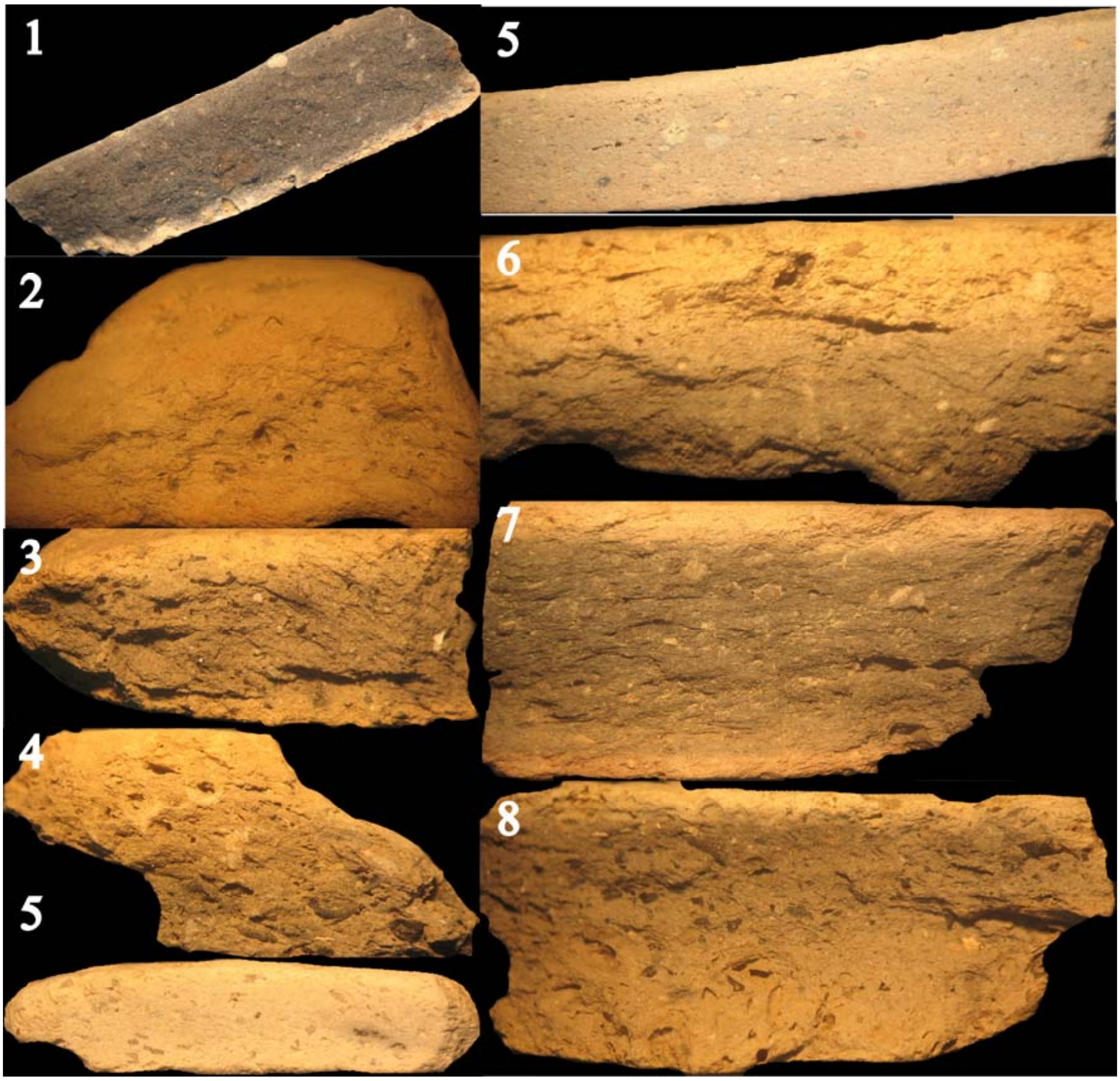

Figure 1. Cross sections of the fragments analyzed and the types of firing identified.1, 3, 8 and 9– oxidant firing, with reduced black core and marked margin (sandwich structure); 2, 5 and 6– oxidant firing, uniformly oxidant; 4 and 7 – external portion light oxidant/internal portion dark.

2.2.2. Extraction of Lipids

Lipids were extracted from the sherds using the conventional methods developed for the extraction of oils and fats from food with minor modifications. For this, pulverized 1–2 g samples of the sherds were prepared for extraction with approximately 3 mL of methanol in an ultrasound bath (Branson 1200, with an operational frequency of 40 kHz) for 15 minutes, with the procedure being repeated after adding chloroform at a ratio of 2:1 ($CHCl_3$:MeOH, 10 ml). The extracts were then centrifuged at 3000 rpm for 10 minutes in a Centribio centrifuge for the decantation of the solid material. The supernatant was dried, and re-suspended in *n*-hexane for the derivation of an aliquot.

2.2.3. Derivatization

The fatty acid methyl esters (FAME) were separated with 0.5 mL of BF_3.MeOH (Boron trifluoride-methanol, 1.3M) at 60ºC for 8 minutes. After cooling at room temperature, the mixture was extracted using *n*-hexane (2 x 0.75 mL) and the evaporated solvent.

2.2.4. Fourier transformation infrared spectroscopy and pre-processing of the data

To characterize the inorganic phases, the pulverized sherds were first pressed to produce a pellet. To obtain the pellets, each sample was mixed with potassium bromide (KBr, Merck, 99% FT-IR purity) at a ratio of 1:100, homogenized in an agate mortar and then pressed at 8 Kbar in a Specac 8 press. The spectra were acquired in a Bruker Vertex 70 spectrometer, with an L-alanine detector dosed with triglycinsulfate at room temperature (RT-DLaTGS). The system was operated by Opus 7 software in the 4000–400 cm^{-1} spectral region in the transmission mode, with a spectral resolution of 4cm^{-1} and mirror movement velocity of 10 kHz. The absorption bands representing the stretching of the bands recorded in the spectra were identified visually and compared with the data available in the literature.

The FAMEs were identified using an accessory appropriate for the analysis of liquid samples (liquid cell angular, A145, Bruker Optics Inc.), which consists of ZnSe windows and Teflon and neoprene spacers. The supports for the crystals and spacers have two vertical holes corresponding to the entrance and exit of the sample, which is injected using a micropipette or syringe. Following each analysis, the crystals were cleaned with a soft cloth soaked in*n*-hexane P.A.As a reference, pure KBr pellets were prepared, as described above, and the extracts from each sample were dispersed, dried in a stove for 5 minutes at 40ºC to eliminate the solvent (Lettieri 2015). These analyses were conducted in the UFPA Mineralogy, Geochemistry and Applications Laboratory (LaMiGA).

The data were processed in the Opus 7 software (Bruker Optics Inc.) for the correction of the baseline and the calculation of the second derivative of the 1200–800 cm^{-1} region, which includes the stretching bands of the different phosphate, P–O(H), and silicate groups (Luengo et al. 2006). Silicates are normally present in the raw material. The data for the 1500–400 cm^{-1} region, which concentrated most of the bands observed in the sherds, were also processed, together with the 4000–3000 cm^{-1} region, given that the different intensities, shape and positions of the bands related to the absorption of water may provide important insights into the composition of the samples. Phosphates represent a digital fingerprint of the ADE sherds of the Amazon region, and are only detected as a mineral phase by XRD, which requires the use of the FT-IR technique. These compounds are important because of their intimate relationship with the use of the ceramic vessels for the preparation of food, primarily in cooking (Costa et al. 2003, 2004ab, 2009, Rodrigues and Costa 2016).

The FT-IR system was not purged of free-CO_2, which resulted in the appearance of CO_2 absorption bands in the spectrum as a doublet in the region of approximately 2340 cm^{-1}, together with marked peaks in the 3400 cm^{-1} region, which is related to the absorbed water, despite the fact that the pulverized portions of the sherds were dried out prior to analysis, and a background spectrum was acquired prior to each analysis, and was subtracted automatically by the software from the sample spectrum.

3. Results and Discussion

3.1. Variability intra sites

3.1.1. Quebrada Tacana

Traces of kaolinite were found in the external portion (probably closer to the flames) in four sherds, as indicated by ~3600 cm^{-1} (see Figure 2), through the stretching of the symmetric O–H vibration (Ghosh 1976, Madejová 2003). This may indicate an incomplete dehydroxylation of the kaolinite during the firing, indicating a firing temperature lower than550°C. However, the presence of two broad bands in the 3700–3600 cm^{-1} (vibrations of structural hydroxyls) and 1100–1000 cm^{-1} (Si–O) regions, substituting the 3 or 4 peaks characteristic of the kaolinite in the core of the fragment (which was probably less exposed to the flames), indicates the complete collapse of the clay mineral. In this case, the presence of kaolinite only in the external portion probably represents a neo-formed phase resulting from the progressive rehydroxilation of its metastable phase through the chemical recombination with the water in the environment (Hall et al. 2013) after the disposal of the sherds. During its time in the soil, the fragment will have suffered weathering or pedogenesis, which would have occurred from the most external portion of the fragment inwards, which excludes the possibility that the vessels from which the sherds were derived were fired at temperatures lower than 550 ºC.

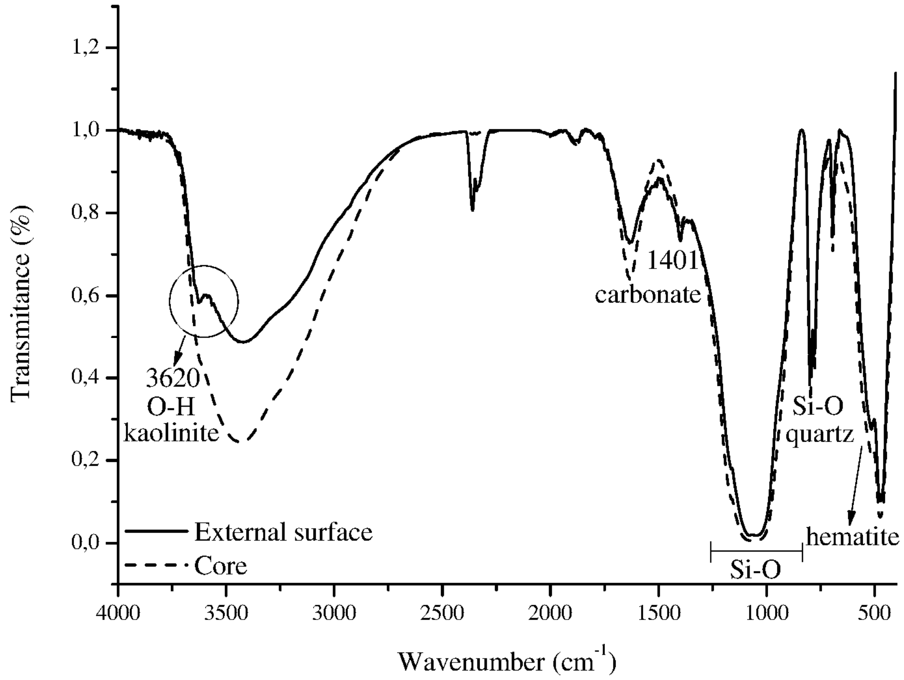

Figure 2. Total spectrum of FC QT-04 acquired in the transmission mode. Note the two broad bands in the 3700–3600 and 1100–1000 cm^{-1} region, which are characteristic of metakaolinite, and the presence of a shoulder at 3600 cm^{-1} in the external portion of the fragment, representing the remains of kaolinite.

The stretching of the Si–O band was also observed in the 778 and 797 cm^{-1}doublet, which refers to the quartz, and ~540 cm^{-1}, the hematite. Differentiated bands were observed in all the sherds from this site, in particular on the shoulder at ~1400cm^{-1}, which is generally attributed to the presence of carbonates (Ghosh 1978, De Benedetto et al. 2002, Stuart 2004, Ferreira et al. 2013, Singh & Sharma 2016, Medeghini et al. 2016). Trace bands were also detected at 2920 and 2850 cm^{-1} (Figure 3), which indicates the presence of organic substances (Lettieri 2015). These bands appear in almost all the sherds and are recorded as negative occurrences in some cases.

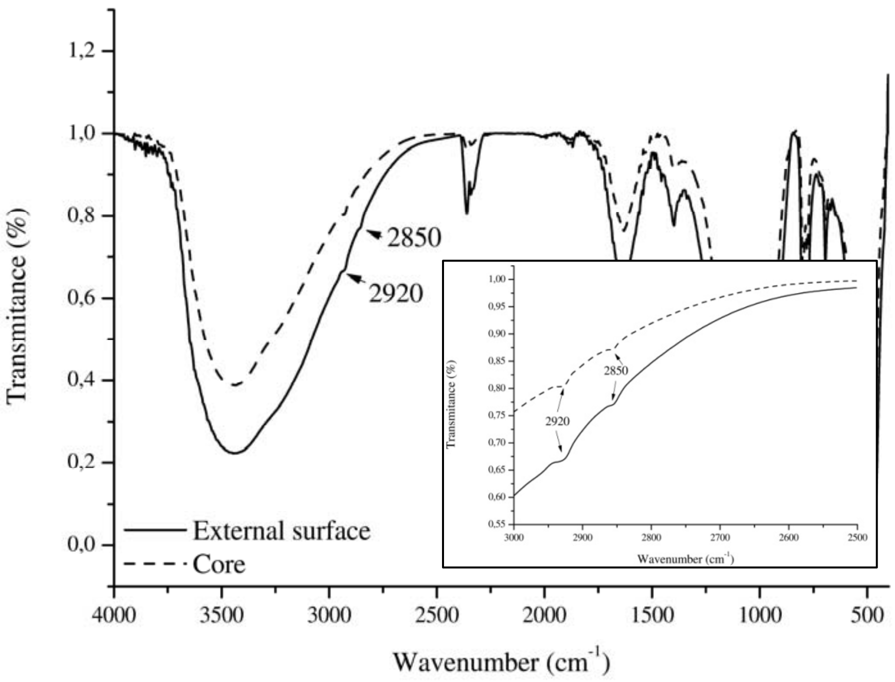

Figure 3. Records of organic substances, in the 2920 and 2850 cm^{-1} bands, obtained in the transmission mode.

The results of the HCA (Figure 4) plotted for the spectrum in the 4000-3000 cm^{-1}range, which corresponds to the O–H stretching of the adsorbed water, at 3400, and the structural O–H at 3700-3600 cm^{-1}, which resulted in the formation of two groups, mixing different portions of the sherds. The first group includes the samples with more intense bands in the external portion of the sherd, which presumably had direct contact with the flames. In addition, most of the sherds were classified as rim pieces, which would have limited their direct contact with aqueous solutions, as during cooking, although this is the part of the fragment that has most contact with the soil after disposal, given the manner in which the sherds come to rest in the soil profile, which indicates a less advanced stage in the rehydroxilation process, which may eventually result in the novel formation of kaolinite, as discussed above. This second group includes sherds with more intense bands in the nucleus, and includes sherds classified mainly as base or body parts, portions of the vessel which will have had more contact with aqueous solutions. Using the FT-IR technique, Lettieri (2015) demonstrated that the bands that refer to the adsorption of water expand toward the internal portion (core) of the sherd and related this finding to the processing of foods, during which specific parts of the vessel, such as its base and body, have greater contact with aqueous solutions, leading to an increase in the intensity of the bands related to the adsorbed water.

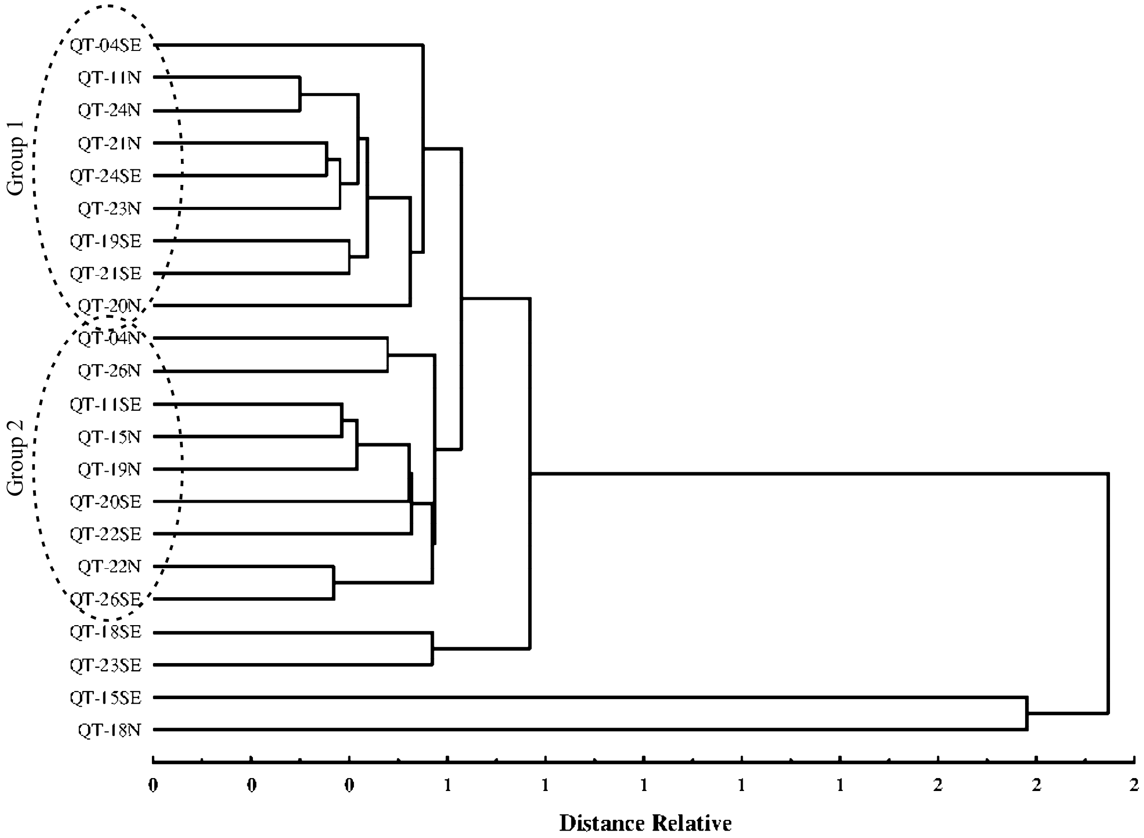

Figure 4. HCA of the ceramic fragments from Quebrada Tacana in the 4000-3000 cm^{-1} spectral region, the region corresponding the O–H stretching of the adsorbed water and the structure of the kaolinite.

3.1.2. Juruti

Very little qualitative variation was found in the sherds from the Juruti site, in the bands recorded for the external and core portions of the samples, except for the presence of kaolinite, recorded at 3630 cm^{-1}, characteristic of O–H stretching, which was recorded only in the external portion of fragment JU2-TP1 (Figure 5) (Ghosh 1976, Madejová 2003). This configuration is similar to that found in the QuebradaTacana sherds, which indicates that the kaolinite is also present in a neo-formed phase, derived from the metakaolinite present in the material, which indicates that the firing temperature used was also above 550 ºC. The other spectral regions recorded were found in all the sherds from this site. The results show bands corresponding to the adsorptive water, in the 3400 (O–H) and 1650 cm^{-1} (H–O–H) spectral regions (Figure 6).

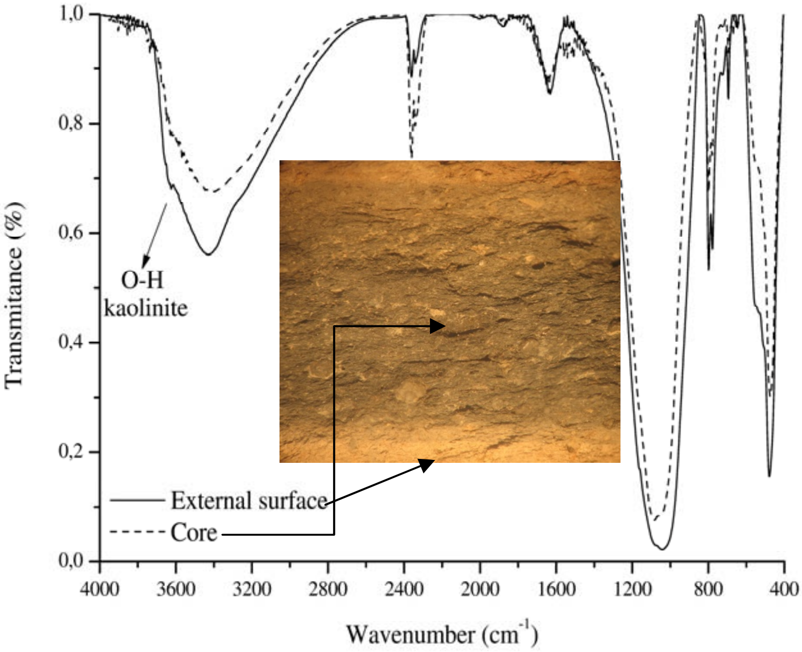

Figure 5. Total spectrum of the FC JU2-TP1 sample acquired by the transmission mode, highlighting the kaolinite recorded at 3600 cm^{-1} (structural O–H).

Vibrations of 470 cm^{-1} related to the Si-O-Si, a vestige of the clay minerals, predominantly kaolinite or metakaolinite, are present, while bands of around 3600 cm^{-1} from the O-H stretching of the kaolinite and 915 cm^{-1}, of the Al(OH) vibrations of the structure of the octahedron leaf were not recorded in the other sherds, which indicates the complete dehydroxylation of the kaolinite (Velraj et al. 2009, Annamalai et al. 2014), which indicates that the firing temperature was higher than 600 ºC, but lower than 800 ºC. A broad band in the 1100–1000 cm^{-1} region of these sherds also indicates firing at temperatures above 550 ºC and the structural degradation of the clay (Stuart 2004, Ravisankar et al. 2011, Ravisankar et al. 2014). This band appears in different positions within the sherds, being centered on either 1044 cm^{-1}or 1089 cm^{-1}, irrespective of the sherds or of the portion analyzed, that is, either external or core. This region coincides with that of the phosphates (Stuart 2004), which reach 4.5% of the content of the sherds at this site (P_2O_5). Even though the mineral phase was not revealed by XRD, the data collected using other techniques, such as SEM-EDS, total chemical analyses and even fertility analyses in previous studies, together with the physical characteristics of the sherds, indicate clearly that the vessels were used for the preparation of food.

It is also possible to discern a 778 and 797 cm^{-1} doublet of the stretching of the Si–O band, of quartz and hematite, at 540 cm^{-1}, and the Fe–O stretching (De Benedetto et al. 2002, Venkatachalapathy & Manoharan 2001, Velraj et al. 2009). The principal variations found in these sherds were in the relative intensity of the bands. JU2-TP2 sherd, from deposit TP2, behaved in the exact opposite way to the sherds from deposit TP1, in terms of the intensity of the bands recorded in the different portions. In this case, the band intensities corresponding to the adsorbed water were more intense in the core portion than the external portion (Figure 6). As observed by Lettieri (2015), the bands corresponding to the adsorbed water increased towards the interior of the sherds, where the duration of the contact with aqueous substance during the use of the vessel was much longer. In general, this region is interpreted as evidence of the adsorption of humidity during the preparation of the pellets prior to analysis, although, as shown by Velraj et al. (2009, 2015), even after refiring at different temperatures, this band persists at up to 800 ºC.

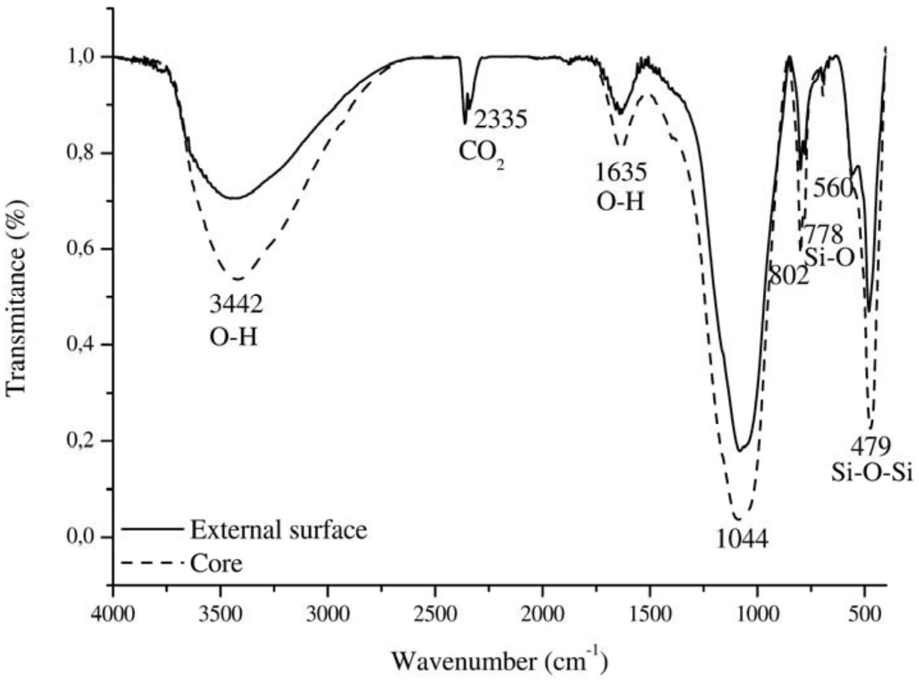

Figure 6. Total spectrum of the JU2-TP2 sherd obtained in transmission mode showing the principal bands.

Another important, albeit subtle difference in the sherds from this site was observed in the 800–600 cm^{-1} region (Ghosh 1978, Akyuz et al. 2008, Seetha & Velraj 2014) (Figure 7).This region is characteristic of alkaline feldspars, and these bands are highlighted in the sherds from deposit TP1, with two distinct peaks at 724 and 649 cm^{-1}. Feldspars have been recorded in sherds from the Amazon region, where they have been reported as a mineral component of the raw material, included intentionally in the clay mass with the objective of improved the plasticity of the material (Costa et al., 2004ab). In this case, the absence or the lack of detection of the feldspars from deposit TP2 indicate that, while the two deposits are close to one another geographically, the clays were not obtained from the same source.

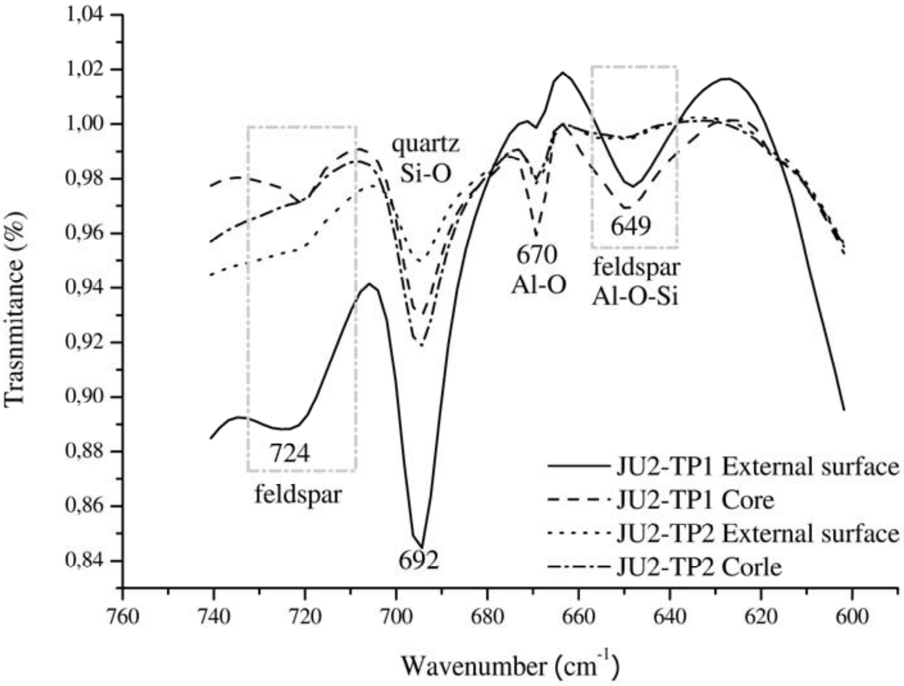

Figure 7. Detail of the spectra of samples JU2-TP1 and JU2-TP2 in the 800–600 cm^{-1} region, highlighting the vibrations that correspond to the feldspars.

3.1.3. Boa Vista

The kaolinite stretching bands were more common in the sherds from this site. This compound is marked by the detection of stretching bands at 3630 cm^{-1}, which are characteristic of O-H stretching, in the external portions, although in two sherds from this site, this band was also detected in the core of the sherds. The kaolinite in these samples must be derived from the raw material used, indicating that the firing temperature was insufficient to provoke the collapse of the structure of this clay mineral, given that Al(OH) vibrations were also recorded in the structure of the octahedron leaf at 915 cm^{-1} (Figure 8). These findings indicate that the sherds underwent gradients of firing, which differentiated the more margin portions of the ceramic vessels from those at their core. This is reflected in the differentiated behavior of the kaolinite in the context of the firing of the different portions, with the external portion, which presumably had more contact with the flames, presenting traces of this clay mineral in the 3700 and 3630 cm^{-1} bands, both at low intensity, with a tendency for the formation of a single, broad band characteristic of its metastable phase, metakaolinite. This indicates that the structure of the kaolinite did not collapse completely. However, the core portion, which was less exposed to heat, maintained not only the bands mentioned above, but also those related to the Al(OH) vibrations of the structure of the octahedron leaf at 915 cm^{-1} (Figure 8). The transition of kaolinite ($Al_2Si_2O_5(OH)_4$) to metakaolinite ($Al_2Si_2O_7.2H_2O$) occurs at temperatures of around 600 °C (Annamalai et al. 2014, Ricci et al. 2016), indicating that the firing temperature used to produce the ceramics at this site did not exceed this temperature.

It was also possible to identify the 778 and 797 cm^{-1}doublet that refers to the stretching of the Si–O bond of quartz, and 580 and 540 cm^{-1} bands, attributed to magnetite and hematite, respectively. The combined presence of magnetite and hematite was confirmed in only one fragment, and indicates the incomplete transformation of magnetite into hematite, reflecting the unstable firing conditions, which may have been related to an atmosphere that was not completely oxidant, which may occur in open-air firing.

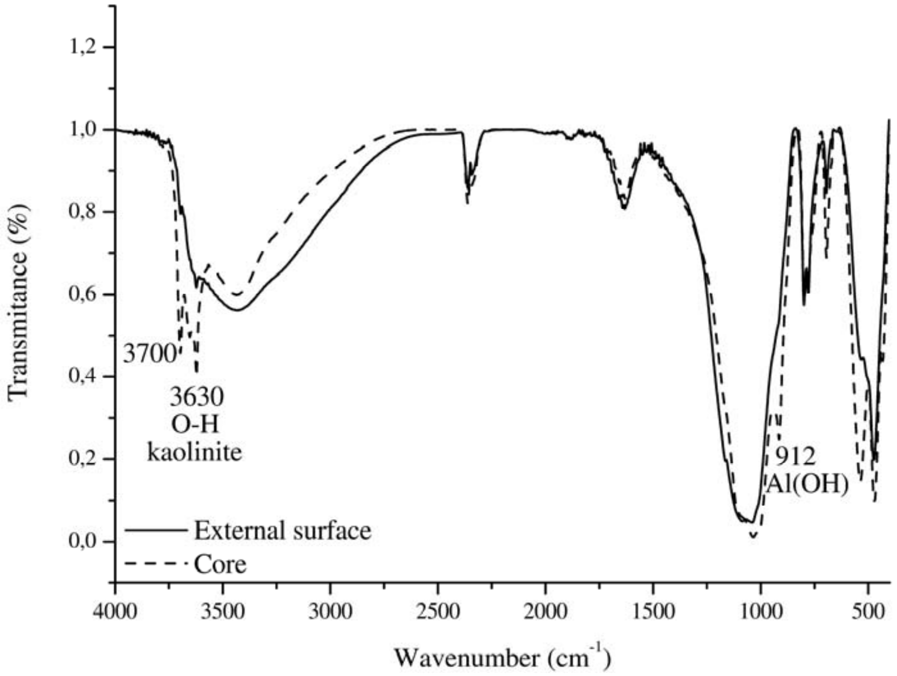

Figure 8. Total spectrum of the FC CPT7 acquired in the transmission mode, showing the bands that represent the kaolinite in the middle portion of the fragment and the external portion during the formation of the metakaolinite, indicated by the two broad bands in the 4000–3000 and 1100–1000 cm^{-1} regions.

3.1.4. Organic fraction

Organic substances were only found in the sherds from QuebradaTacana, which does not necessarily mean that these substances were not preserved at the other sites, given that the concentrations are typically very low, and are often below the sensitivity threshold of the technique. In the spectrum obtained here, the band representing the C–H stretching, at approximately 2964 cm^{-1}, was highlighted after extraction (Figure 9). This band was recorded in the samples prior to extraction, although it was almost imperceptible (Figure 3). The extraction confirmed the presence of organic substances in the sherds. Following the mineralogical investigation described above, which indicated firing temperatures of between 650 ºC and 800 ºC, it seems unlikely the possibility of the raw material origin, because organic material, does not resist temperatures above 400 ºC, nor would it have originated post-burial, given that the fraction identified here was hydrophobic, which would restrict its mobility from the ground to the interior of the sherds, as well as the fact that great care was taken to analyze only the core portion of the sherd, which would guarantee that the sample analyzed had no contact with the ground. The sum of the evidence thus indicates that the presence of these substances in the sherds prior to their burial, that is, from the use of the vessels.

In addition to the band recorded at 2964 cm^{-1}, signals were also detected at 1197 cm^{-1}, corresponding to the C–O stretching of esters (Ascough et al. 2011), and in the 1270–1250 cm^{-1} region, where the strength of the band indicated the presence of a significant carboxylic acid (COOH) content, which contributes to the formation of fatty acids. This is the only site at which evidence was found of the use of charcoal and cariapé as non-plastic, that is, materials of plant origin, extracted from tree bark. The presence of these components may have influenced the results, although the absence or bands in the 1420–1430 cm^{-1} region, which are characteristic of cellulose (Ascough et al. 2011), were not recorded in the spectra either before or after extraction. This finding, together with the questions on firing temperatures, discussed above, excludes these non-plastics as the potential source of the organic substances detected in the sherds. One additional finding that supports this conclusion is the absence of these bands in the sample analyzed from the other sites, as well as the analytical blanks.

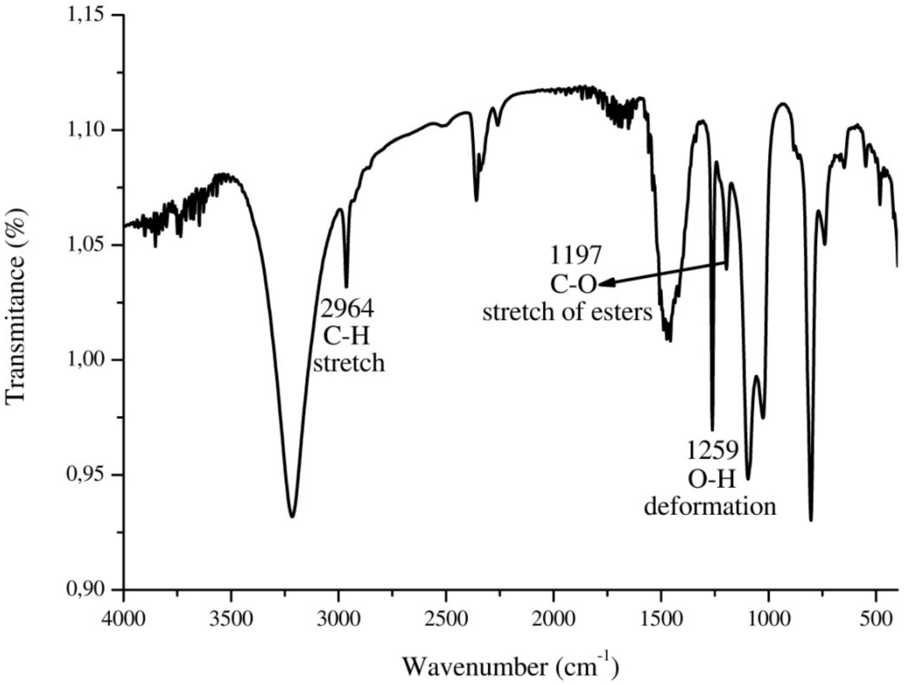

Figure 9. Total spectrum of the Quebrada Tacana sherd after extraction, showing the clear stretching of the C–H, C–O, and O–H bands.

4. Conclusions

The FT–IR technique clearly has enormous potential for the mineralogical characterization of the sherds. Important aspects of the mineralogical variation of the samples were revealed, in particular in the distinct portions of the sherds from the different sites, as well as the identification of primary and neoformed phases. The kaolinite detected in the sherds from Juruti and Quebrada Tacana represents a secondary phase, and an estimated firing temperature of 600–800 ºC, whereas in Boa Vista, it is related to the raw material, and indicates firing temperatures of 500–600 ºC. Phosphates, while present in the sherds, could not be better defined by the analytical technique, given that their characteristic region overlaps with that of silicates, such as kaolinite, metakaolinite, quartz and feldspars, which were also present in the sherds, although the intensity and breadth of the bands are consistent with the contribution of phosphates. Following extraction, the analyses indicated that the sherds from

QuebradaTacana contained carboxylic acids, confirming that oils or fats were processed in the utilitarian vessels from which the sherds were derived.

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5.3 PHOSPHORUS IN THE IDENTIFICATION OF LIPID RESIDUES IN ARCHAEOLOGICAL CERAMICS (ARCHAEOLOGICAL DARK EARTH-ADE)

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Abstract

Report the organic residue analysis of ceramic vessels from ADE sites, in the Amazon. Gas chromatography mass spectrometry (GC-MS) analysis of a small number of sherds from Quebrada Tacana site produced results that are also consistent with processing of aquatic products. In addition, identification of odd-chain acids together with their respective branched acids is strong indicators of animal contribution. Phosphorus, lipids and depth in the soil profile showed a good correlation. Sherds that were collected on or near the soil surface expressed the lowest phosphorus contents and lipids were not detected. Therefore, they may suggest that these potsherds represent vessels used in the prolonged preparation of foods.

Keywords: Residue analysis, Lipids, Resins, Gas chromatography, Mass spectrometry, Phosphorus

Introduction

Lipid residue analyses in archaeological objects can provide a new dimension to traditional archaeological investigations. In the Amazon, one of the greatest archaeological legacies is represented by numerous occurrences of Archaeological Dark Earth (ADE), classified as Anthrosols by [1]. The ceramic represent the type of material culture most abundant as attested by the frequent occurrence of sherds or ceramic fragments in the ADE soils that are renowned for its high and perennial fertility.

[2, 3, 4, 5, 6]blame the black carbon as perpetuating the fertility of the ADE. The structure of black carbon alone explains its cation exchange capacity (CEC), however, with almost 80% of C in its composition cannot account for the supply of nutrients to the soil. Unlike the black carbon, ceramic fragments, abundant in surface and depth in the soil profiles of the archaeological sites with ADE, represent a nutrient source due to their chemical and mineralogical composition and recognized desorption potential [7].

Across macro and micronutrients, only P escapes to the constitution of the raw material, but generally is present in the fragments. P is a geochemical signature in the sherds of ADE sites and becomes an important archaeological evidence of the use of vessels for cooking food [8], [9], [10]. Therefore, its incorporation into the unglazed pores ceramics occurs through the contact of the clay matrix with primary sources of nutrients, possibly processed foods in past household utensils, mainly with high protein content [8].

The connection of an archaeological object to its primary function has been established for at least half a century throughout Eurasia through the extraction and determination of molecular assemblages [11, 12, 13, 14, 15, 16, 17]. The use of this methodology as well as allowing a greater approximation of the actual ceramic function, has contributed to the reconstruction of cultural and economic practices of ancient societies, especially with the advancement of micro-analytical instrumentation as the direct dating in the lipids extracted from ceramics that allowed associate the arrival of the ceramic to Neolithic periodic in Eurasia [18,19].

The ceramics fragments recovered from ADE sites, submitted to the analysis techniques traditionally directed to soil and rock matrices, from the perspective of obtaining information about the raw material from which it originates arouse interest in its organic content. Not yet explored in ceramics fragments of the Amazon, it provides with more acquiescence data pertinent to the nature of the processed product, sometimes related to the diet of a population, which may strengthen phosphorus as archaeological evidence of cooking food.

This work investigates the presence and/or absence of lipid residues and integrates this information with specific vessels typologies as well as specific parts of the vessel and in the case of non-diagnostic fragments, which represent a large majority, this comparison will be due to the physical characteristics of the fragments themselves, such as color, thickness, concavity, etc. Through a preliminary initiation of organic geochemical analyses in ceramics of ADE sites, it is still intended to assume phosphorus as a potential indicator of the presence of organic compounds preserved in these fragments, assuming that both come from the same source. For this, fragments with variable phosphorus contents were used and compared them with the results of the organic fraction in terms of distribution and concentration.

The archaeological sites

The archaeological ceramics sherds examined in this study belong to four archaeological sites from Amazon basin in the range western to eastern:

The QuebradaTacana site in located in the Colombian trapezium north of the city of Letícia (04°07’09.1”S, 69°55’16.1” W).This site covers an area with 2 ha and variable anthropic horizon, 10 to 25 cm depth and presents high density of ceramic fragments and botanical remains (phytoliths, charcoal and seeds) [20, 21].

The Juruti site, located on land of the municipality of the same name, coordinates 2 ° 10'01.68 "S / 56 ° 05'57.58" W and 2 ° 10'36.86 "S / 56 ° 06'17.05" W, on the margins of the Amazon river. The anthropic horizon reaches a depth of 60 cm and presents coal, ashes, ceramics fragments in abundance and millimeters bones;

The Boa Vista site is located 1 km from the village of Porto Trombetas (municipality of Oriximiná, PA state), in the Lower Amazon, and its central coordinates are 1 ° 27'41.18 "S and 56°23'58.61 "W. This site also involves two distinct occurrences of ADE called Boa Vista and Agua Fria, totaling 13.5 ha of area. The A horizon corresponding ADE, with nearly 60 cm thick is rich in ceramics fragments, implements, ornaments, cores and lithics flakes, bones fragments, seeds calcined and coal, and several rocks in the form of pebbles [22].

The Raimundo site is located in the Caxiuanã National Forest Reserve, in the Portel and Melgaço municipalities, under coordinates 01°45'36.00 "S and 51º26'34.3" W. This site is about 400 km straight from the capital Belém (Pará-Brazil) and is a region with more than two dozen of ADE distributed on the margins of the Caxiuanã Bay [23, 24, 25]. Dimensioned in 1.26 ha, it presents an ellipsoid shape and A Horizon of up to 21 cm with a large occurrence of ceramic fragments and roots.

Materials and methods

Standard ceramics*(Analytical Blank)*

Standards ceramics were made using a mixture of local clay (Juruti-Pará) and non-plastic (Cariapé, *Moquilea* and *Licaniautilis*). The standards samples were calcined for 48 hours in the open air. This material was donated by PhD Suyanne Rodrigues who characterized both clay and cariapé during the development of her doctoral work.

Archaeological fragments

Ceramics fragments were investigated of the four indicated sites, which present great variation in their technical-morphological characteristics.

The QuebradaTacana sherds were collected in 15-45 cm soil depth, the fragments with the lowest thickness vary between 5 and 9 mm, and only one fragment categorized as base has a thickness of 16 mm. The non-plastic identified were mineral, charcoal and cariapé occurring in isolation or associated manner. They represent individually different categories, rim, base, wall and were reconstituted graphically by the researcher MSc. Gaspar Morcote Ríos, who ceded the samples for this work (Table 1).

The Juruti sherds investigated in this study are undecorated. They were collected in the 10-60 cm soil profile, with a thickness ranging from 5 to 10 mm. The predominant non-plastic is the cauixi associated with the mineral and were classified as non-diagnostic fragments.

The Boa Vista site contains fragments collected between 5 and 108 cm depth, with thickness ranging from 0.5 to 12 mm. The non-plastics present were mineral, cauixi, charcoal and crushed rock, only the mineral occurs in an isolated manner and charcoal was observed in only one fragment. Represent rim, base, wall and adornment. The plastic is decoration predominant (Table 1).

Those of the Raimundo site, the majority coming from the topsoil horizon, are the most heterogeneous, with a thickness ranging from 4 to 20 mm. In these fragments as non-plastics are minerals, coal, cariapé, cauixi, shells, chamotte and crushed rock, found alone or even together in a same fragment. The fragments collected at this site represent both the rim and the wall (mainly), but for the vast majority, it was not possible to diagnose the position in the respective pottery vessel, much less its graphical reconstitution. The present decoration is plastic, however restricted. In some fragments, it was still possible to find traces of use (Table 1).

Table 1. General characteristics of the analyzed fragments of the Quebrada Tacana, Juruti, Boa Vista and Raimundo sites.

			CF Color (After Munsell Chart Color)			
Samples	**Soil Depth (cm)**	**Tempers**	**Surface**	**Middle**	**Thickness (mm)**	**Vessel part**
QUEBRADA TACANA						
QT-04	15-20	Mineral + charcoal + cariapé	10YR 7/6	10YR5/3	9	Body/base
QT-06	15-20	Mineral + charcoal + cariapé	10YR 6/4	10YR 6/4	9	Rim
QT-07	15-20	Mineral + charcoal + cariapé	10YR 6/4	10YR 6/4	5 to 7	Rim
QT-08	20-25	Mineral + charcoal + cariapé	10YR 8/2	10YR 8/2	5	Rim
QT-09	20-25	Carvão	2.5YR 6/8	5Y 4/1	6 to 7	Rim
QT-11	20-25	Mineral + charcoal + cariapé	10YR 8/2	5Y 5/1	4 to 9	Rim
QT-12	20-25	Cariapé	10YR 6/3	Gley1 7/1	7 to 11	Body/base
QT-13	25-20	Carvão	10YR7/8	10YR 5/3	9	Base
QT-15	25-30	Mineral + charcoal	5YR 7/4	Gley1	6	Rim
QT-18	30-35	Mineral + charcoal + cariapé	10YR7/4	2.5Y5/1	9	Body
QT-20	30-35	Mineral + charcoal + cariapé	10YR7/6	5Y6/1	5	Rim
QT-21	30-35	Mineral + charcoal + cariapé	10YR8/3	2.5Y7/1	3	Rim
QT-22	30-35	Mineral + charcoal + cariapé	10YR8/4	5Y4/1	9	Body/base
QT-23	35-40	Mineral + cariapé	10YR8/6	2.5Y7/4	3	Rim
QT-24	35-40	Mineral + charcoal + cariapé	10YR8/4	5Y4/1	4 to 6	Rim
QT-26	35-40	Mineral + cariapé	10YR6/4	5Y6/2	6	Rim
JURUTI						
JU2-TP1	10-20	Mineral + cauixi	7.5YR7/6	5Y6/3	10	Unknown
JU1-TP1	40-50	Mineral + cauixi	7.5YR7/6	5Y 5/2	8 to 10	Unknown
JU2-TP2	10-20	Mineral + cauixi	10YR7/3	5Y2.5/1	10	Unknown
BOA VISTA						
CPT1	5	Mineral	10YR4/1	10YR6/4	0,5 to 12	Rim
CPT2	106	Mineral + cauixi	7.5 YR7/4	7.5YR7/4	4 to 9	Base
CPT3	19	Mineral	5YR5/6	2.5Y4/1	4	Body
CPT4	39	Mineral	10YR5/3	7YR6/6	4	Body
CPT5	58	Mineral + carvão + cauixi	5YR6/8	10YR 5/1		Adornment
CPT6	10	Mineral	5Y 6/1	7.5YR 5/6	3 to 5	Rim
CPT7	108	Mineral + cauixi + Cr*	5YR 6/4		3	Body
CPT8	96	Mineral + cauixi + Cr*	2.5 YR 6/8	2.5 Y 6/1	9 to 12	Base
RAIMUNDO						
NF1	surface	Mineral	7YR6/6	5Y5/1	10	Unknown
NF2	surface	Mineral + charcoal	7YR6/6	5Y5/1	10	Body
NF4	surface	Charcoal	10YR6/6	5Y4/1	16	Unknown
NF5	surface	Mineral	5YR6/8	5YR6/8	7	Body
NF6	surface	Mineral	7.5YR7/6	5Y5/1	6	Rim
NF7	surface	Mineral + charcoal	5YR7/6	5Y4/1	7	Body
NF8	surface	Mineral + cauixi	7.5YR7/6	5Y5/1	7	Rim
NF9	surface	Mineral + charcoal	5YR6/6	5Y5/1	6	Rim
NF10	surface	Mineral + cauixi	10YR6/3	5YR6/8	10	Rim
NF11	surface	Charcoal + cariapé	7.5YR7/6	5Y6/1	4	Unknown

NF15	surface	Mineral	7.5YR7/6	5Y5/1	14	Unknown
NF16	surface	Mineral + charcoal	5YR7/6	5Y3/1	7	Rim
NF17	surface	Mineral + charcoal	5YR7/8	5Y5/1	10	Unknown
NF18	surface	Mineral	2.5Y6/6	2.5Y5/2	8	Rim
NF19	surface	Mineral + charcoal	7.5YR7/6	5Y3/1	10	Unknown
NF20	surface	Charcoal + cariapé	10YR6/3	5Y5/1	20	Unknown
NF21	surface	Mineral + charcoal	7.5YR6/6	10YR6/6	5	Body
NF22	surface	Mineral + Cr*	7YR7/8	2.5Y4/1	3	Body
NF23	surface	Mineral+ charcoal +Cr*	7.5YR6/8	7.5YR5/6	7	Body
NF24	surface	Mineral + cariapé	5YR6/8	5Y3/1	8	Body
NF25	surface	Charcoal + Cr* + cariapé	5YR6/6	5Y5/1	8	Body
NF26	surface	Mineral+ charcoal +Cr*			0.5 to 1.4	Body
NF27	surface	Charcoal + cariapé			7	Body
NF28	surface	Mineral + Cr* + cauixi				Body
NF29	surface	Mineral + Cr*	7.5YR6/6	5YR6/8	15	Base

Extraction of lipids

The analytical procedure was described elsewhere (Valente & Costa, unpublished yet).

All glassware used for this laboratory process was taken to an aqueous solution with detergent diluted at boiling level and then rinsed with water and plenty of distilled water. Afterwards, they were immersed for a few minutes in a potassium hydroalcoholic solution (10% KOH in a C_2H_6O: H_2O solution in a 9:1 ratio).They were dried in an oven at 160ºC. All glassware and tools were sonicated in solvent and nitrile gloves were used in both sample preparation and extraction. All reagents used were of analytical grade or HPLC. For each set of prepared samples, analytical blanks were submitted to the same process and conducted the analyzes to identify possible contaminations from non-archaeological sources.

Masses between 1-2 g of sprayed previously samples in agate mortar and pestle it suffered lipid extraction with $CHCl_3$:MeOH (2:1, v/v, 10 ml) in an ultrasound bath (2 x 15 min). The first extraction was performed only with methanol and the second with the mixture of solvents in the proportions indicated. The extracts were then centrifuged for 10 min at 3000 rpm for separation of the solid material.The supernatant was transferred into vials and the extract was concentrated at ambient temperature under protection of light. The extract was saponified with 5 mL of 0.5M NaOH in an ethanolic solution (9:1, v/v) at 70 ° C for 1 hour. After cooling to ambient temperature, the neutral fraction was extracted with 1.5 mL of *n*-hexane and the aqueous fraction acidified to pH

3 with 3M HCl followed by extraction with 1.5 mL *n*-hexane.The organic phase was evaporated at ambient temperature under protection of light and 0.5 mL of BF_3.MeOH (boron trifluoride in methanol, 1.3M) was added and heated for 8 minutes. This fraction, containing the fatty acid methyl esters (FAME), was extracted twice with 0.75 mL, with *n*-hexane, followed by the extract concentration, which was conducted for analysis after resuspension with 50 µL of *n*-hexane. This stage was developed with the infrastructure of the LEPRON (Natural Products Extraction Laboratory) of the Chemical Engineering course of UFPA, under the leadership of Prof. José Guilherme Maia.

GC/GC-MS

GC/GC-MS analyzes were performed on a GCMS-QP2010 Plus system (Shimadzu Corporation, Tokyo, Japan), equipped with a capillary column fused silica Rxi-5ms (Restek Corporation, Bellefonte, PA) of 30m x 0.25 mm (diameter) x 0.25 µm (film thickness), coated with 5% diphenyldimethylpolysiloxane, with auto injectorAOC-20i. The conditions of analysis were: injector temperature of 250 °C; furnace temperature programming 100 ^{o}C (5 min), gradient from 4^{o}C/min to 260 ^{o}C (20 min); drag gas He adjusted at a linear velocity of 32 cm s^{-1} at 100 °C, splitless injection of 1 µL of the sample. The mass spectra were obtained with electron impact ionization of 70 eV, ion source temperature and transfer line of 220 and 250 ºC, respectively. Mass spectra were obtained by automatic scanning, at 0.3 seconds, with mass fragments in the range of 39-400 m/z. The retention index was calculated for all components using a homologous series of C_8-C_{40} n-alkanes (Sigma-Aldrich), according to the linear equation of [26].Compounds were identified by comparing mass spectra (molecular mass and fragmentation pattern) with the GCMS solution software library including a database of the Willey, NIST, ADAMS and FFNSC 2 libraries, and by the standard 38 components of the Supelco. Semiquantitatives informations were obtained by normalizing the peak area.

Each fraction was subjected to quantification in a GC Shimadzu QP 2010 with flame ionization detector, under the same GC/EM conditions, except for the drag gas used, which was hydrogen. These GC-EM analyzes were performed at the Laboratory of Adolpho Ducke of the Museu Paraense Emílio Goeldi and interpreted by Prof. Eloisa Helena de Aguiar Andrade, co-author of this work.

Results and discussions

Organic residues: general composition

Lipid preservation varied considerably across the sherds investigated, between sites and intra sites. In addition to environmental conditions, lipid preservation may also depend on different vessels uses, the nature of the clayey matrix. Fragments extracts showed aliphatic lipids, (un)saturated fatty acids of medium to long chain including $C_{12:0}$, $C_{14:0}$, $C_{15:0}$,$C_{16:0}$, $C_{17:0}$, $C_{18:0}$, $C_{18:1}$, $C_{19:0}$, $C_{20:0}$, $C_{21:0}$, $C_{22:0}$, $C_{23:0}$ e $C_{24:0}$. This distribution suggests that the pottery vessels represented by the fragments investigated were associated with food processing. The predominance of free fatty acids indicates that lipids are highly degraded, a typical feature of ancient organics residues.

In the absence of biomarkers, the interpretation is based on the presence of alkanes and abundances of fatty acids. One of the criteria used is the ratio of fatty acids that decompose into similar ratios. Although this criterion does not allow for a very specific distinction between the residues, it enables discrimination in broader classes such as terrestrial and aquatic animals and vegetables.

Palmitic acid ($C_{16:0}$) is the most pronounced in half of the samples. Palmitic acid is followed by stearic ($C_{18:0}$) in almost half of the samples and by oleic ($C_{18:1}$ (9c)) in only five. For the fragments of the QuebradaTacana site the sum of the mean of the two mean compounds is about 40% of the total lipid composition, except for a fragment that reaches a much higher value 80%. Those of Juruti presented behavior similar to QuebradaTacana.

Oleic acid was the most abundant in only one fragment of the QuebradaTacana (QT-24) site, followed by palmitic. This fragment, categorized as rim (Figure 1), must have belonged according to the graphic reconstruction to a pottery vessel with a smaller rim diameter than its central region, equivalent to pots (*dolium*), a very common pottery vessel between European sites [27]. The graphical reconstruction of the pottery vessel added to the predominance of oleic acid indicates storing and processing vegetables products in this vessel.

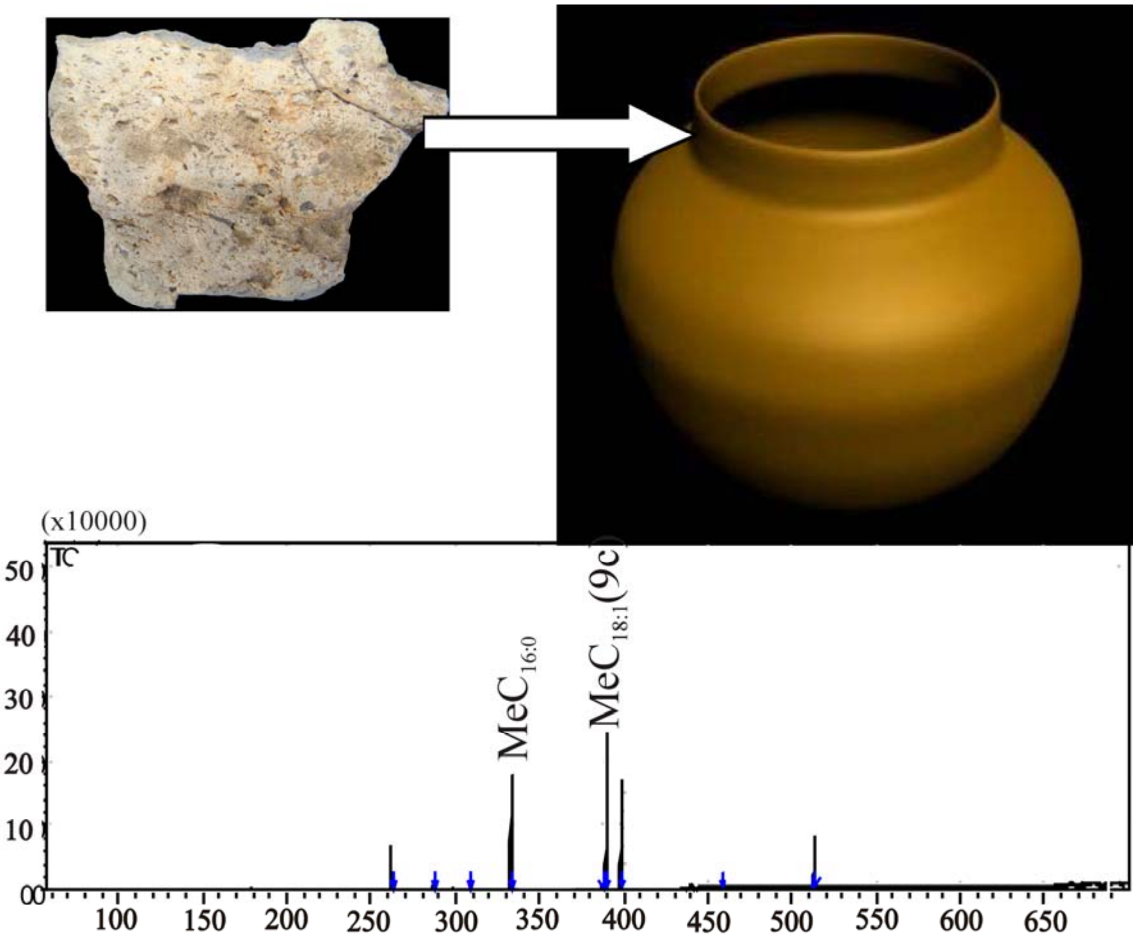

Figure 1. Rim fragment (QT-23 sample) of the Quebrada Tacana site reconstituted graphically with its corresponding chromatrogram highlighting the predominance of oleic acid.

Palmitic and stearic acids are observed in both animal and vegetable sources. The high abundance of one rather than other suggests the nature of the contribution. When stearic acid is superior to palmitic acid, an animal contribution is suggested, since stearic acid is superior in many terrestrial animal sources, while in vegetables, fruits and aquatic organisms contain in small proportions [27, 28]. Stearic acid was the most abundant in only three fragments of the Raimundo site. The morphological characterization was limited due to the fact that they were very small (between 2.6 and 4 cm, greater side), but according to the classification proposed by [29] considering the thickness, these fragments are thin (thickness <9 mm), which increases the probability of that they have belonged to pottery vessels utilized for cooking.

The ratio of $C_{18:0}$/$C_{16:0}$ (stearic/palmitic) peak area points to a contribution of lipids of animal origin to the sherds from QuebradaTacana and Juruti site ($C_{18:0}$/ $C_{16:0} \geq$

0.5), while for the fragments of the Raimundo site half have plant oil contribution (Table 2).

Table 2. Results and interpretation of residue analysis.

Sites (n)	S/P*	FONTE	Aquatic biomarkers[1] (n)
Quebrada Tacana (6)	0.9	animal	2
Juruti (2)	0.9	animal	-
Raimundo (8)	1.1	animal	-
Raimundo (8)	0.3	vegetal	-

(n): number of sherds with lipids
*: means values

[1] Partial aquatic biomarkers isoprenoid fatty acid

It is noticeable that odd chain fatty acids ($C_{15:0}$ and $C_{17:0}$) and the relative abundance of $C_{18:0}$ (stearic acid) hint at animal-related fat [30, 31]. This behavior was demonstrated by sherds of the QuebradaTacana and Juruti sites, which also presented their respective branched chain fatty acids ($C_{15:1}$ and $C_{17:1}$), consistent with S/P ratios interpretations (Table 2), which indicated the same origin for fragments of these sites[30, 32].

Biomarkers: aquatic sources

Aquatic resources are characterized by the abundance of long chain unsaturated fatty acids, however unsaturated chains are more prone to oxidation which compromises the role of these compounds as suitable markers. In contrast, isoprenoid fatty acids, especially 4,8,12-trimethyldecanoic (4,8,12-TMTD), 3,7,11,15 tetramethylhexadecanoic (phytanic) and 2,6,10,14-tetramethylpentadecanoic acid (pristane), they are result from phytol degradation in aquatic environments and also present in aquatic organism tissues, either marine or freshwater [33, 34, 35, 36].

Two sherds of the QuebradaTacana site contained traces of the isoprenoid 4,8,12-TMTD (Figure 2). This particular isoprenoid is found at very high concentrations in organisms of aquatic origin, and is typically not found in terrestrial plants or animals [19, 36], therefore, it is described as a unique compound of aquatic organisms, unlike the phytanic and pristane acids which can be identified in tissues of ruminant animals, formed in the rumen of the animal through bacterial oxidation and hydrogenation of phytol, which in turn is a constituent of chlorophyll [19].It is therefore possible that these two sherds belonged to a pottery vessel used for the processing aquatic products, *e.g.*fish. Although this site and no other investigated here are close to the sea, they are all close to flowing lakes and rivers, like the Amazon river and its great tributaries, as well as the majority of ADE sites in the Amazon, which sustains the presence of water sources.

In addition to 4,8,12-TMTD acid, another criterion that supports this origin is the predominance of palmitic acid ($C_{16:0}$) in these samples, which tends to be more abundant in aquatic and vegetable sources, the identification of less specific biomarkers as monounsaturated acids, $C_{17:1}$ (heptadecenoico), was also observed in the same extracts [37, 38, 31].The co-occurrence of $C_{17:1}$ (heptadecenoico), $C_{19:1}$ (nonadecenoico) (unidentified in these fragments) with isoprenoid fatty acids was suggested by [38] as new biomarkers for aquatic food sources.

The fragments that presented these biomarkers of aquatic origin were categorized as rim of small bowls whose edge diameter was larger than the base, which constitutes a pottery cooking.

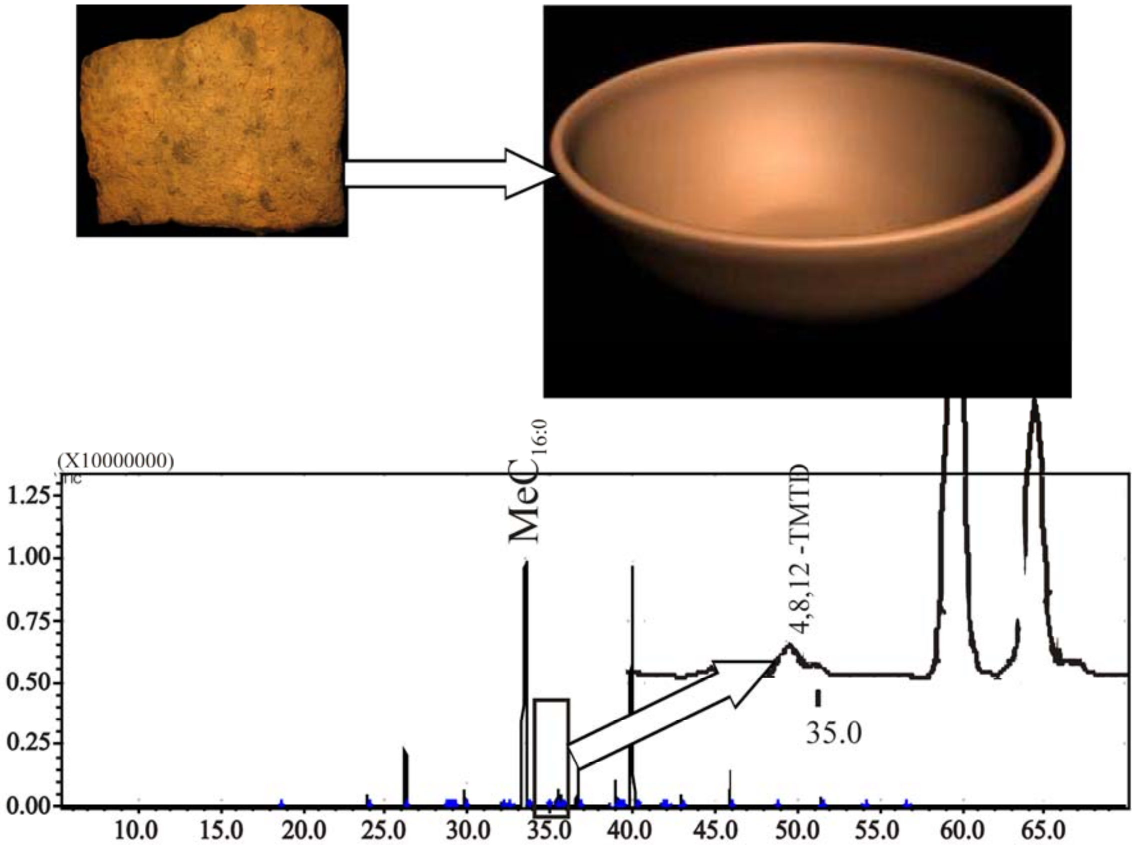

Figure 2. Aquatic biomarker traces on pottery vessel rim fragment of the Quebrada Tacana site.

Resins

The discovery of resinous materials in archeological contexts provides valuable information on the variety of products explored in the daily life of ancient societies. In their report [20] identified resin in fragments of the Quebrada Tacana site and during the macroscopic description of these fragments in the present work was observed a very thin film with resinous luster, superposing the surface in a discontinuous way, as if had worn in some areas, in addition to darkened spots with resinous luster (Figure 3).This possible resin appears only one sherd, whose extract was dominated by sesquiterpenes (Figure 3). Sesquiterpenes are C_{15} chain terpenoids derived from isoprene (C_5) units [39, 40]. They can be derived from resin, wood or wood extracts [41].

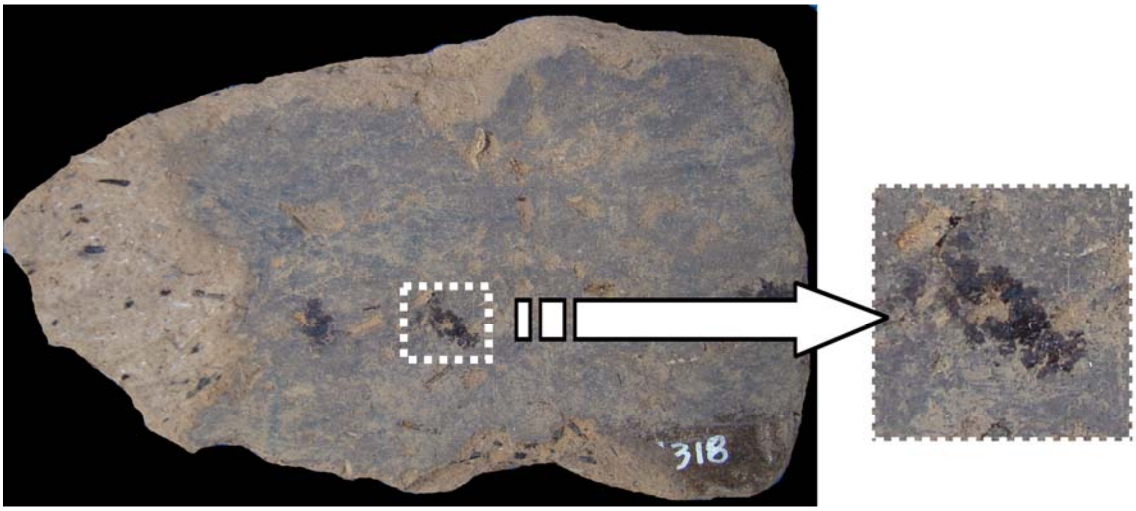

Figure 3. Ceramic fragment with black resin remnants on the inner surface.

Relation P x Lipids

In order of decreasing P content, the fragments of the Juruti site are the ones with the highest content followed by QuebradaTacana and Raimundo sites. The mean concentrations of P_2O_5 are 3.6; 1.3 and 0.4% and the maximums for each site are 4.7; 2.9 and 0.9% respectively. The presence of phosphorus in archaeological site fragments with ADE is related to the cooking of foods in the past ceramic pots[8, 9, 42, 10] as well as the origin of lipids dates back to different products processed or stocked in these pottery vessels.

The fragments of the Juruti site presented compatible lipid distribution with residues of processed products, however the presence of biomarkers was not observed. With the highest phosphorus content, it was expected to identify indications of animal products processing, especially fish, it was given also the location of the site, on the margins of the Amazon River with its large floodplain lakes. One factor that may have contributed to this lack of evidence may be related to the position of the fragment in the soil profile near the top, susceptible of much greater alteration by the weathering and therefore, much more marked decomposition of its mineral constituents, especially those more susceptible, such as phosphates.

The fragments that showed the best preservation of the lipids were those from the Quebrada Tacana site, especially those from AB horizon of the soil profile. No lipids were identified on fragments of the A horizon at the surface except for the QT-07 sample, which indicated evidence only of resin-related sesquiterpenes. The P_2O_5

contents in the ceramic fragments behave along the soil profile increasing from A to AB horizons, and decrease at the end of the profile. The maximum contents of P_2O_5 are concentrated in AB horizon, probably because they are less susceptible to weathering as discussed above. Preserved residues were detected in fragments located at 25 cm from the soil profile. The identification of biomarkers and even less specific ones were detected at trace levels only in corresponding fragments between 30-35 cm depth (AB horizon), which demonstrates a preservation relationship not only with the profile but also with phosphorus.

The fragments of the Raimundo site, with the lowest levels of phosphorus between the sites investigated, presented a characteristic lipid distribution of processed products, however, without the registration of biomarkers. The methyl stearate/methyl palmitate ratios indicate to the processing of products of plant origin for about half of the fragments investigated, which in addition to the collection location of most of the fragments, the surface may justify the low phosphorus content and no evidence of biomarkers.

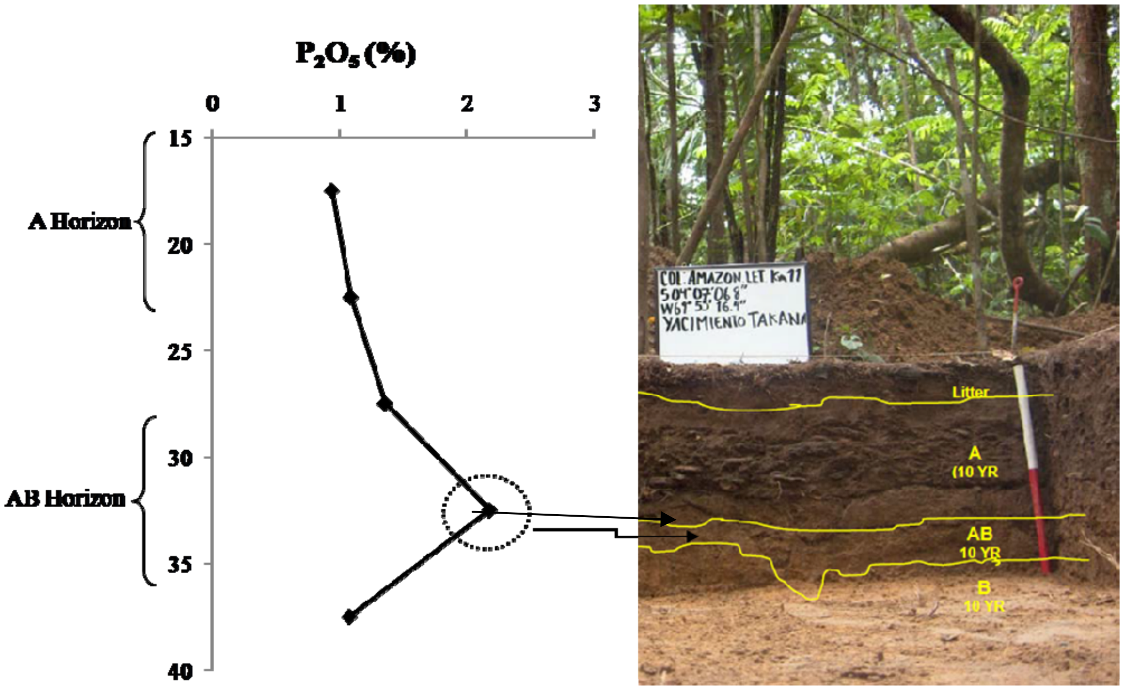

Figure 4. Distribution of total P_2O_5 (%) in the fragments of the Quebrada Tacana site through the ADE soil profile.

CONCLUSIONS

The results showed that the preservation of lipids in archeological ceramic fragments of the Amazon region imposed on severe conditions of hot and humid tropical weathering is possible. Although the absence of specific compounds makes it impossible to classify more specific among groups of processed products, phosphorus content, inorganic indicators of food cooking, seems to be a good prerequisite for the selection of samples for lipid extraction. The relation between phosphorus, lipids and depth to which they were collected in the soil profile showed a good correlation, in which the fragments that expressed the lowest phosphorus contents were those that were collected on or near the soil surface and still or no lipids were detected, as in the case of the fragments of the Quebrada Tacana site, no biomarkers were identified, as for the fragments of the Raimundo and Juruti sites. In contrast, fragments that were less susceptible to weathering, such as those collected in AB Horizon, had higher phosphorus content, demonstrating that it is being consumed at lower rates when compared to those located in the anthropic Horizon itself, therefore, would be more preserved, as well as specific biomolecules of processed products, as occurred for these fragments.

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6 CONCLUSÕES

Os fragmentos cerâmicos dos sítios investigados apesar de demonstrar emprego unilateral da matéria-prima empregada, argila (caulinita ou metacaulinita) e quartzo, apresentam certas dissimilaridades em sua composição química e mineralógica, além de antiplásticos. Estas variações por sua vez, são responsáveis diretas no caráter fértil do material cerâmico**.** Em que, fragmentos do sítio Raimundo por conter conchas empregadas como antiplástico à matriz argilosa, destacam-se com elevados conteúdos de $Ca_{\text{trocável}}$ e consequentemente a SB. O único nutriente sem ligação com a matéria-prima, o fósforo, faz-se presente como fase amorfa, com forte relação com o uso do fragmento pertencente a um utilitário cerâmico, apresenta-se com altos níveis de P disponível e ainda dessorção favorável. Além dos dados mineralógicos observados por DRX, a técnica de FT-IR aplicada a diferentes porções nos fragmentos, evidenciou claramente fases primárias e neoformada bem como estimativa de temperatura de queima. Em fragmentos de Juruti e Quebrada Tacana ficou estimada acima de 600 º C, porém sem ultrapassar 800 ºC, baseado no comportamento da principal argila empregada, a caulinita, ao passo que em Boa Vista a faixa foi menor, entre 500-600 ºC. Os fosfatos por estarem em fase amorfa não puderam ser caracterizados por DRX, e a técnica de FT-IR não foi totalmente efetiva pelo fato da região característica dos fosfatos coincidir com a dos silicatos, como caulinita, metacaulinita, quartzo e feldspatos, ainda que diferenças nas intensidades e larguras das bandas sugiram uma contribuição adicional. Compostos orgânicos investigados tanto por IV quanto por CG-CG/MS indicaram a preservação da matéria orgânica. Séries de ácidos *n*-alcanóicos de cadeia curta e média (C_{12}-C_{20}) foram comuns entre os fragmentos dos sítios investigados. As variações ocorreram por conta do padrão de distribuição entre os ácidos graxos, presença de ácidos graxos ímpares de cadeia linear e ramificados, resinas (com ocorrência isolada) e biomarcadores aquáticos. O ácido palmítico foi o mais abundante em muitos fragmentos seguido esteárico ($C_{18:0}$) e oléico ($C_{18:1}$). Padrão típico de lipídios degradados. Sesquiterpenos, representativos de resinas vegetais, foram detectados em somente um fragmento pertencente ao sítio Quebrada. Outro indicativo de contribuição vegetal são as séries de *n*-alcanos e *n*-alcanóis cuja média não ultrapassa 1,3%, presença observada em fragmentos do sítio Raimundo. O processamento de produtos de origem aquática foi evidenciado em fragmentos do sítio Quebrada Tacana através de biomarcadores diagnósticos, estes mesmos fragmentos demosntram os maiores conteúdos de fósforo entre as amostras coletadas e analisadas neste sítio, o que já denotava forte relação com o processamento de proteínas. Ainda que os demais fragmentos apresentem teor médio de 1% (fósforo), este critério de modo individual parece não ser suficiente como pré requisito de indicação de biomoléculas representativas de produtos processados preteritamente, porém, o comportamento dos teores de fósforo ao longo do perfil de TPA, exibe claramente que maiores conteúdos de fósforo destacam-se em fragmentos coletados no Horizonte AB, menos susceptíveis ao intemperismo. De igual maneira biomarcadores foram preservados nos mesmos fragmentos o que corrobora para a preservação nos horizontes menos superficiais, o que poderia também a vir justificar a não identificação em fragmentos que foram coletados nos níveis mais superficiais, a exemplo os pertencentes ao sítio Raimundo.

Portanto, os fragmentos investigados devem representar utensílios empregados na preparação, estoque e armazenamento de produtos consumidos por sociedades antigas. A não observação de biomarcadores ou mesmo padrão de distribuição de ácidos graxos não denota necessariamente que vasilhames ao qual pertenceram os fragmentos não tenham sido empregados em atividades cotidianas, pois, o intenso clima quente e úmido da Amazônia diferentemente do europeu não deve ser favorável a preservação de moléculas tão antigas, mas ainda sim o registro é possível.

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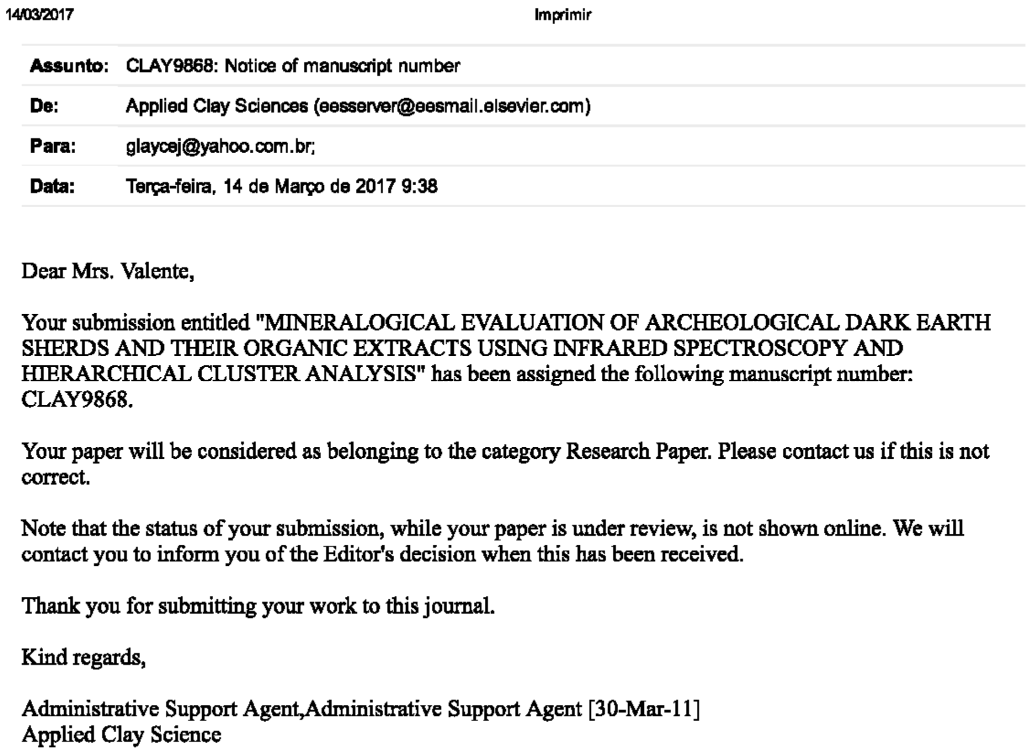
APÊNDICES

APÊNCIDE A – COMPROVANTE DE SUBMISSÃO DO ARTIGO “MINERALOGICAL EVALUATION OF ARCHAEOLOGICAL DARK EARTH SHERDS AND THEIR ORGANIC EXTRACTS USING INFRARED SPECTROSCOPY AND HIERARQUICAL CLUSTER ANALYSIS”



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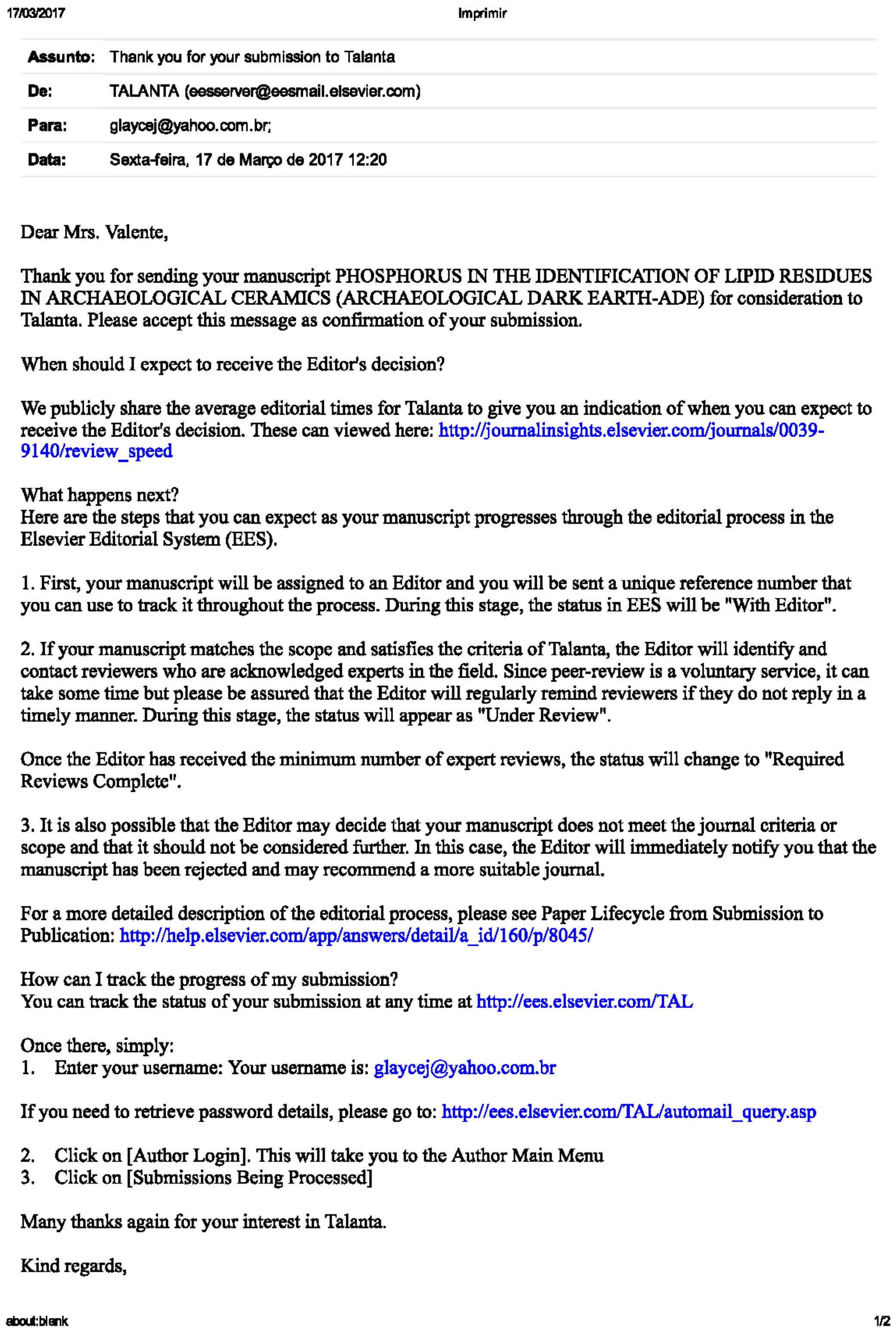

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PARECER

Sobre a Defesa Pública da Tese de Doutorado de
GLAYCE JHOLY SOUZA DA SILVA VALENTE

A banca examinadora da Tese de Doutorado de **GLAYCE JHOLY SOUZA DA SILVA VALENTE**, sob orientação do Prof. Dr. Marcondes Lima da Costa (UFPA), constituída pelos professores doutores Dirse Clara Kern (MPEG), Kelly das Graças Fernandes Dantas (UFPA), Thais Alessandra Bastos Caminha Sanjad (UFPA) e Carlos Emmerson Ferreira da Costa (UFPA), após apresentação da tese intitulada **"ORIGEM BIOMOLECULAR DE RESÍDUOS ORGÂNICOS EM FRAGMENTOS DE CERÂMICAS ARQUEOLÓGICAS DA AMAZÔNIA E SUA RELAÇÃO COM O FÓSFORO CONTIDO"** emite o seguinte parecer:

A candidata realizou sua apresentação de forma clara, organizada e segura no tempo hábil de trinta e oito minutos. Na arguição mostrou domínio da temática abordada e respondeu às perguntas formuladas pela banca. O trabalho escrito, com relevante contribuição interdisciplinar, foi apresentado na forma de três artigos, sendo um já publicado e os outros dois submetidos a periódicos de impacto internacional, que atendem às exigências básicas para uma tese de doutorado.

Dessa forma, a banca examinadora decide, por unanimidade, aprovar a tese de doutorado de Glayce Jholy Souza da Silva Valente.

Belém, 04 de abril de 2017.

Prof. Dr. Marcondes Lima da Costa (Orientador – UFPA)

Prof.ª Dr.ª Dirse Clara Kern (MPEG)

Kelly G. Fernandes Dantas

Prof.ª Dr.ª Kelly das Graças Fernandes Dantas (UFPA)

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