

The ceramic artifacts in archaeological black earth (terra preta) from lower Amazon region, Brazil: Mineralogy.

Marcondes Lima da COSTA¹ (*), Dirse Clara KERN², Alice Helena Eleotério PINTO¹, Jorge Raimundo da Trindade SOUZA³

ABSTRACT

Several archaeological black earth (ABE) sites occur in the Amazon region. They contain fragments of ceramic artifacts, which are very important for the archaeological purpose. In order to improve the archaeological study in the region we carried out a detailed mineralogical and chemical study of the fragments of ceramic artifacts found in the two ABE sites of Cachoeira-Porteira, in the Lower Amazon Region. Their ceramics comprise the following tempers: cauxi, cariapé, sand, sand +feldspars, crushed ceramic and so on and are composed of quartz, clay equivalent material (mainly burned kaolinite), feldspars, hematite, goethite, maghemite, phosphates, anatase, and minerals of Mn and Ba. Cauxi and cariapé, siliceous organic compounds, were found too. The mineralogical composition and the morphology of their grains indicate a saprolite (clayey material rich on quartz) derived from fine-grained felsic igneous rocks or sedimentary rocks as source material for ceramic artifacts, where silica-rich components such cauxi, cariapé and/or sand (feldspar and rock fragments) were intentionally added to them. The high content of (Al,Fe)-phosphates, amorphous to low crystalline, must be product of the contact between the clayey matrix of pottery wall and the hot aqueous solution formed during the daily cooking of animal foods (main source of phosphor). The phosphate crystallization took place during the discharge of the potteries put together with waste of organic material from animal and vegetal origin, and leaving to the formation of the ABE-soil profile.

KEY WORDS

Terra Preta, Black Earth, Archaeological ceramic fragment, Lower Amazon, Phosphates, Mineralogy.

Artefatos cerâmicos em sítios arqueológicos com terra preta na região do baixo Amazonas, Brasil: Mineralogia.

RESUMO

Sítios arqueológicos com Terra Preta, denominados de Terra Preta de Índio ou ainda Terra Preta Arqueológica (TPA) são muito frequentes na Amazônia. As TPA geralmente contém fragmentos de vasos cerâmicos, por vezes abundantes, além de líticos, que são materiais de grande importância para os estudos arqueológicos. Para consubstanciar esses estudos, realizou-se pesquisas mineralógicas e químicas em fragmentos cerâmicos provenientes de dois sítios arqueológicos da região de Cachoeira-Porteira, Estado do Pará. Os fragmentos foram classificados segundo seus principais temperos em: cauxi, cariapé, areia+feldspatos e caco de vaso cerâmico. Mineralogicamente são compostos de quartzo, minerais de argila calcinados (especialmente caulinita), feldspatos (albita e microclínio), hematita, goethita, maghemita, variscita-estrelada, fosfatos amorfos, anatásio, e raramente apatita, rhabdopbana e óxidos de Mn e Ba. Cauxi e cariapé são componentes orgânicos silicosos e amorfos a DRX. A composição mineralógica e a morfologia dos seus grãos indicam saprolito (material argiloso rico em quartzo) derivado de rochas ígneas félsicas de granulação fina ou rochas sedimentares ricas em sílica, foram intencionalmente adicionados. O elevado conteúdo de fosfatos de Al-Fe, amorfos ou como de baixa cristalinidade, originou-se a partir do contato entre a matriz argilosa da parede do vaso cerâmico com a solução aquosa quente durante o cozimento diário de alimentos de origem animal (principal fonte de fósforo). A cristalização dos fosfatos deve ter prosseguida mesmo depois que os vasos foram descartados, e juntos com os restos de matéria orgânica vegetal e animal incorporaram-se aos solos residuais. Participaram desta forma na formação dos solos tipo TPA.

PALAVRAS-CHAVE

Terra Preta, Fragmentos de cerâmica arqueológica, Baixo Amazonas, Fosfatos, Mineralogia.

¹ Geosciences Center/UFPa, 66075-110 Belém-PA, Brazil – Fax: (091) 3183 1609/211 1428, Phone/Fax: (091) 3183 1428 / 249 5028, E-mail: mlc@ufpa.br or kaxinawa@uol.com.br

² Museu Paraense Emílio Goeldi/MPEG, Belém-PA, Brazil.

³ Chemistry Department/UFPa, 66075-110 Belém-PA, Brazil

INTRODUCTION

Black earth soils, called by natives Indian black earth (Terra Preta de Índio in Portuguese) or classified by archaeologists as archaeological black earth (ABE) are very common found in the landscape of the Amazon region. The ABEs have been identified since 1879 and since there are being studied by naturalists, archaeologists and pedologists (Smith, 1879; Ranzani *et al.*, 1962; Sombroek, 1966; Balec, 1989; Kern & Kämpf, 1989, 1990). Several researchers have been carried out in order to study the pedological features of these soils as well as attempts to description and morphological classification of their ceramic artifacts as important tools for understanding the peopling of the Amazon region (Ranzani *et al.*, *op. cit.*; Falesi, 1974; Simões, 1982; Eden *et al.*, 1984). A pedological study of these soils considering the determination and distribution of label contents of P, Ca, Mg, K, Na, Mn, Zn and Fe in the soil profiles was carried out by Kern (1988), Kern & Kämpf (1989 and 1990), Kern *et al.* (1997) in archaeological sites near to Cachoeira-Porteira village, along the Trombetas River, in the Lower Amazon region. The authors in the National Forest Reserve of CAXIUANÁ (< biblio >) are investigating similar material. The results obtained until now show that the black earths may be a pedological, chemical and mineralogical modification of preexisting soils by pre-historic human (Indian) activities and settling in the later past time. On the contrary of the black earth which are being in detail investigated no consideration has been made about the mineralogy, texture, and chemistry of the archaeological ceramic artifacts found in great quantity in these soils. The application of the mineralogical and geochemical techniques, known as archaeometry (Mommson, 1986) to study archaeological lithic and ceramic artifacts and as fingerprints aid in understanding modern pottery sourcing have been successfully employed elsewhere by several authors (Noll, 1978; Letsch & Noll, 1983; Freestone & Middleton, 1987; Redmount, 1996; Strazicich, 1998; Costa *et al.*, 1991; Costa & Kern, 1996).

Since the 1970's the archaeometric studies have been used to characterize the physical and chemical conditions of the preparation, modification and alteration of the ceramic artifacts, their raw material, its chemical and mineralogical composition and of course the provenance of the raw materials (Zaun, 1982; Freestone & Middleton, *op. cit.*).

In the way that the ABEs from Cachoeira-Porteira at Trombetas river region are rich on archaeological ceramic artifacts and that its black soils have been well investigated by Kern (1988) and Kern & Kämpf (1989) of *Museu Paraense Emílio Goeldi (MPEG)* in Belém (Pará, Brazil), as well as the archaeological characterization of its ceramic materials, we decide to develop a mineralogical study of the fragments of ceramic artifact found inside the ABEs from Cachoeira-Porteira. This paper presents these data and discuss their source, utility and alteration during their daily use and importance for archaeology and geology.

PHYSIOGRAPHIC AND ARCHAEOLOGICAL ASPECTS

The Trombetas river and its tributaries are well known to be rich in archaeological sites along their margins (Ranzani *et al.*, 1962; Kern, 1988) (Fig. 1). It is left margin tributary of the Amazon river, located in the Lower Amazon region (Fig. 1). Near to the village Cachoeira-Porteira (Oriximiná Municipality, Pará State) occurs several sites ABE, as well as in the confluence of Trombetas, Mapuera and Cachorro rivers (Fig. 1). The sites are located 21 m above the river water level in the dry season.

The actual climate of the region is rainy equatorial and dominated by dense tropical forest (the *Hyläea Amazonica*) including bamboo (*Guadua* sp.) and secondary forest (*capoeira*).

The drainage system is dense, the valleys are overflowed, normally have a rocky bottom and under this condition present water falls and/or rapids. River dikes and channels give origin to several lakes and islands of different forms and sizes.

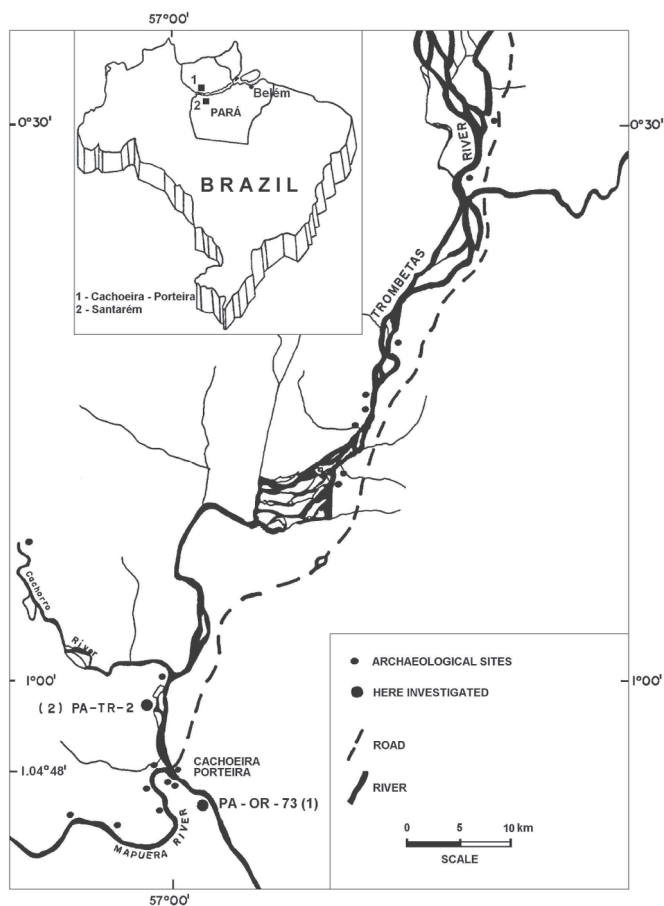


Figure 1 - Location map of the archaeological black earth (ABE) sites by Cachoeira-Porteira in the Lower Amazon region.

The soils are composed mainly by yellow to red *Latosols*, yellowish brown *Podzols* and *Structured Red Earth (Terra Roxa Estruturada)*. The alluvial soils are found in the flood plains. The ABE classified as anthropogenic soils (Ranzani *et al.*, 1962, Kern, 1988) are well distributed in the region, and marked by several small sub-circular areas of 1 to 8 ha located near each other and developed preferentially over the yellow *Latosols* and *Petroplintbosal* (Kern, 1988: Kern & Kämpf, 1989).

The fragments of ceramic artifacts present tempers made of cauxi, cariapé, sand, and fragments of rocks and feldspars (Hilbert, 1955). The tempers after Meggers & Evans (1970) are exotic material intentionally put in the ceramics during their confection. The cauxi (*Tubella reticulata* and *Parnula betesil*), for example, is fresh water spongy that cumulates on trunks of trees, boats, and so on. The artifact with cauxi temper carry the *Konduri* style culture (Nimuendaju, 1948), which are typical of ABEs from Trombetas and Jamundá rivers. They are ceramics for daily use. The *Konduri* lived from 900 years BP until the first contact with Europeans in 16 and 17 century when they extinguished. The cauxi temper has its origin in the Lower Amazon region, where cauxi occurs. The tradition of cauxi temper was modified lately by the introduction of a cariapé temper, a tree outer skin (Hilbert, 1955), representing a *Bignoniaceae*, *Moquilea*, *Licania utilis*, and *Turiuva*. Before the cariapé get in the ceramics as raw material it need to be burned. Although the cariapé ceramics are less homogeneous than the those ones with cauxi, they have the advantages to avoid stomach diseases normally promoted by cauxi artifacts when the food are prepared inside of them (Hilbert, *op. cit.*).

GEOLOGICAL SETTING

The region around the village Cachoeira-Porteira comprises paleozoic to mesozoic sedimentary rocks (sandstones and claystones) of Lower Amazon basin laying the proterozoic volcanic acid rocks of Iricoumé Formation and Mapuera Granite (Fig. 2). Dikes of basic rocks crosscut the paleozoic formations. Laterite profiles derived from these formations also occur in the area and have been afterward partly transformed into *Latosols*, widespread in the region. Clays, sands and pebbles found commonly on the riverbanks and lakes as well as the *Latosols* are the youngest (Holocene in age) geological manifestations on the region.

The two archaeological sites studied here (Figs. 1 and 2) are just located over the *Latosols* derived from sedimentary rocks, close to volcanic and plutonic rocks.

MATERIALS AND METHODS

Sampling

The ceramic fragments of ABEs studied here were collected by MPEG (Museu Paraense Emilio Goeldi) in 1988, with

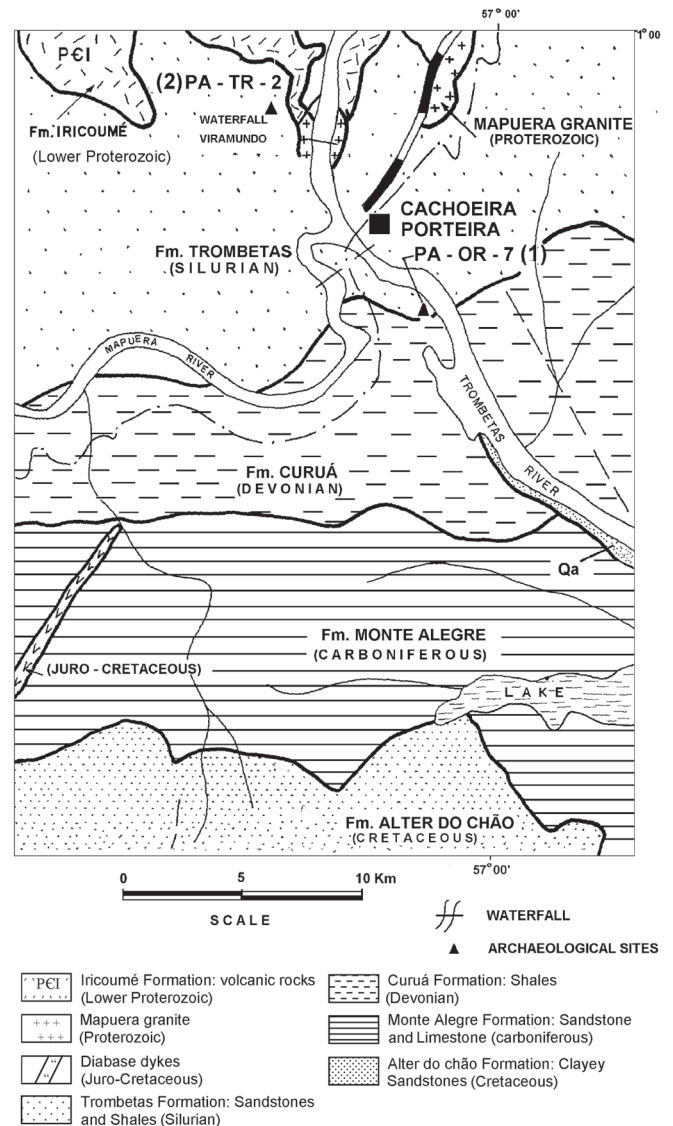


Figure 2 - A simplified geological map of the region near to Cachoeira-Porteira, Lower Amazon region.

participation of co-author Dirse Clara Kern before the lake of the then projected hydroelectric power might flood the area. For the present work 51 samples of ceramics were taken from the sites 1 (PA-OR-73) and 2 (PA-TR-2). The sampling was performed along standard trenches following the soil horizons A_p , A_1 , A_2 and A_3 . Samples of the raw cauxi and cariapé were also taken from the adjoining area and considered here.

Petrographical Analysis

From the 51 collected samples we selected 15 representing the different tempers for thin sections and study by optical microscope. The petrographical description followed the general procedures used for rock analyses.

Mineralogical Determinations

The 51 samples were submitted to XRD (Philips diffractometry, PQ-1050, with copper anode) in order to determine the mineralogy. Then 10 samples have been submitted to infrared spectrometry (Perkin-Elmer FT-IR spectrophotometer, model 1960X) and thermal and thermogravimetric analyses (Du Pont Instruments model STA 1000/1500 and 910 DSC). Four samples, each one from each temper, have been analyzed by scanning electron microscope (SEM) with EDS (STEREOCAN 200) at Brazilian Company for Metallurgy and Mining, Brazil.

The quantification of the main minerals were possible keeping the whole chemical composition and the mineral chemistry.

RESULTS AND DISCUSSION

Pedoarchaeological Data

The fragments of ceramic artifacts are almost restrict to the A-horizons (A_p , A_1 , A_2 and A_3) (Fig. 3 a and b). The sand *plus* feldspars ceramics domain in Site 1 and are followed by cauxi and lately by cariapé ceramics. Their distribution in the profile does not change significantly although the sand *plus* feldspars slightly decreases and cauxi increases slowly to A_3 horizon. In the Site 2 however the sand tempers are more abundant than those with cauxi are.

The majority of the fragments of ceramic artifacts (97.7% in frequency) presents only incomplete oxidation caused by firing and shows inner grayish black and outer reddish color. The ceramic fragments represent potteries without any decoration and may be correlated to Santarém Culture or *Konduri* Complex. They are parts of put, bowl and dish of daily use (Fig. 3c). The ceramics with cauxi temper are much more homogeneous than the others with cariapé, those with sand (quartz) are more heterogeneous, hard, showing bad finishing, variable color, thickness around 5mm, fine incisions and no painting.

Textural Features

Ceramics with cariapé temper (Figs. 4a and 5a,b). They are composed mainly by quartz grains and fragments of cariapé of different size and forms which are distributed in a cryptocrystalline clay matrix. The cariapé fragments have a elongate platy forms and display a slight orientation in the clayey matrix. The quartz grains present fair outlines and are cryptocrystalline to polycrystalline and show undulating extinction. They may be also strong fractured. The matrix has yellowish brown color, is micro to cryptocrystalline up to amorphous and is made mainly of clay minerals.

Ceramics with cauxi temper (Figs. 4b and 5c, d, e). These ceramics are typified by their high content of cauxi spicules in a cryptocrystalline clay matrix where quartz grains can also occur. The cauxi spicules may occur as isolated needles or form aggregates, and sometimes display a slight

orientation. The quartz grains and the matrix behave similar to ceramic with cariapé temper.

Ceramics with sand temper (Fig. 4c). The domain of quartz grains in the same cryptocrystalline clayey matrix described above characterizes the ceramics. The quartz grains are abundant, have also fair outline and corrosion gulfs indicative of reaction borders. Undulating extinction and features of recrystallization are also frequent.

Ceramics with sand plus feldspar temper (Fig. 4d). The general aspect is similar to the sand temper and can be distinguished throughout the abundance of feldspar grains and polycrystalline quartz. Rock fragments occur as well as iron oxides in forms of grains and fracture infillings.

Ceramics with older crushed ceramics (Fig. 4e and 5f). They are made up of fragments of all types of the other ceramic tempers, dispersed in a cryptocrystalline clay matrix. This kind of texture indicates reutilization of older ceramic artifacts.

Minerals Identified

The minerals identified by XRD in the investigated ceramic fragments are (Table 1): quartz, thermal-modified clay mineral (partly burned kaolinite probably), albite, microcline, hematite, maghemite, goethite, anatase and aluminum-iron phosphates (variscite-strengite).

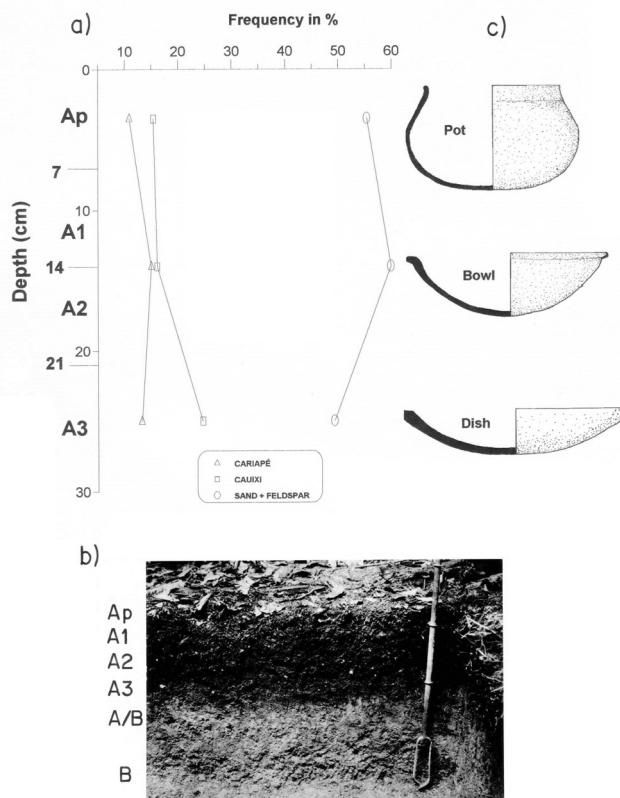


Figure 3 - a) The ABE soil profile and the frequency distribution of its ceramic tempers; b) textural aspects; c) types of daily used ceramics.

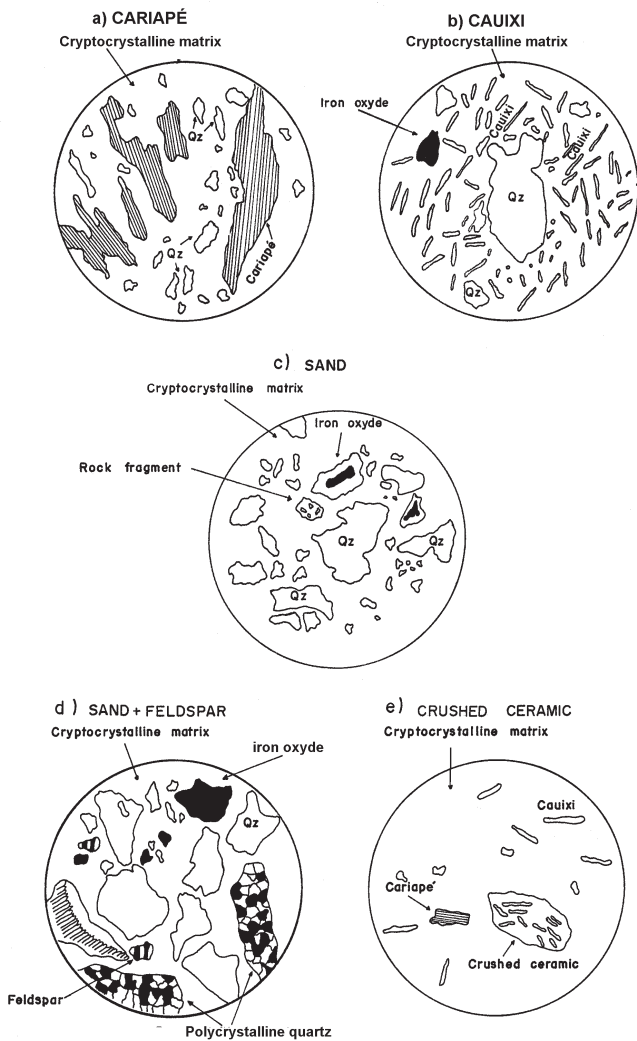


Figure 4 - Textural aspects of the ceramics under light polarized microscope after each temper.

Quartz, thermal-modified clay mineral and albite are the principal minerals. However microcline, goethite, hematite, maghemite and phosphate are still significant (3 to 11 wt.%). As silica-rich substances also occur cauxi and cariapé which are amorphous to XRD. Cariapé that originally is amorphous, when burned may contain some XRD reflections of tridymite and/or cristobalite. The high background of XRD patterns suggest the presence of amorphous to low crystalline compounds, which may be represented by partly burned clay minerals (which should be derived mainly from kaolinite), cauxi and cariapé (Fig. 6).

The ceramics with cauxi, cariapé, sand, and cariapé *plus* sand are richer on quartz (43 to 53 wt.%) while sand *plus* feldspar temper contains as expected much more albite and microcline and less quartz, burned clay minerals, and phosphates than the others (Table 1) do. The iron minerals (hematite, goethite and maghemite) are abundant mainly in the cariapé and sand *plus*

feldspars tempers where hematite is always the most frequent. The contents of anatase therefore do not display any significant change among the different tempers. Hematite and maghemite might be formed from goethite of ceramic raw material during its firing, as product of heating.

The mineralogical composition (quartz, clay minerals and feldspars) does not present any special changing after the tempers. Slightly changing may be only observed in the *sand plus feldspar* ceramic temper (Fig. 7).

Description of the Minerals and Mineral Chemistry

Quartz and Amorphous Silica (Cauxi and Cariapé)
Quartz together amorphous silica (cauxi and cariapé) are the most abundant component of ceramics. Infrared spectra

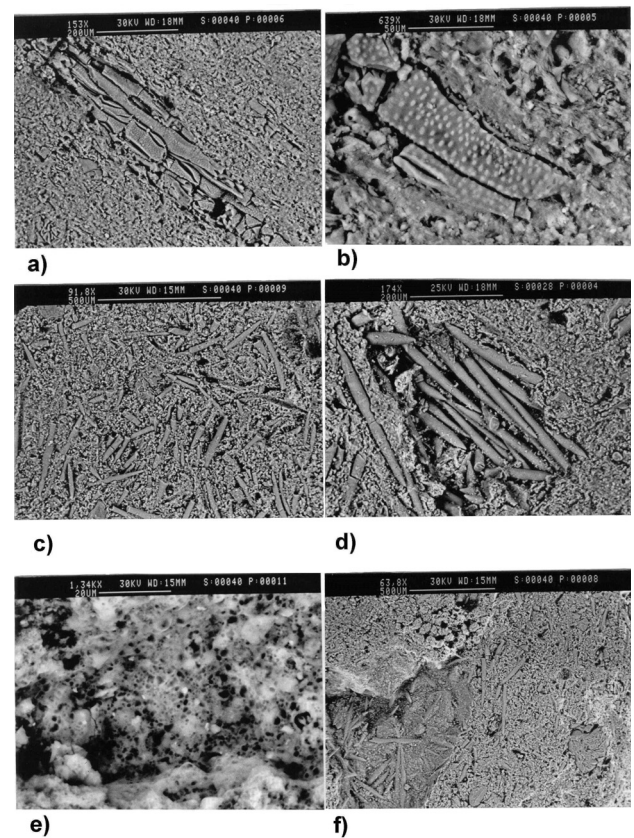


Figure 5 - The textural aspects of the fragments of ceramic artifacts under scanning electron microscope: a) Ceramic with cariapé temper showing the cariapé structure in the clayey matrix; b) Details of cariapé showing white spots composed of SiO_2 ; c) Ceramic with cauxi temper rich on cauxi spicules displayed in the clayey matrix; d) Details of an aggregate of cauxi spicules; e) A crosscut of a cauxi spicule showing its typical inner channel; f) Ceramic with older crushed ceramic (cauxi temper) on bottom left side.

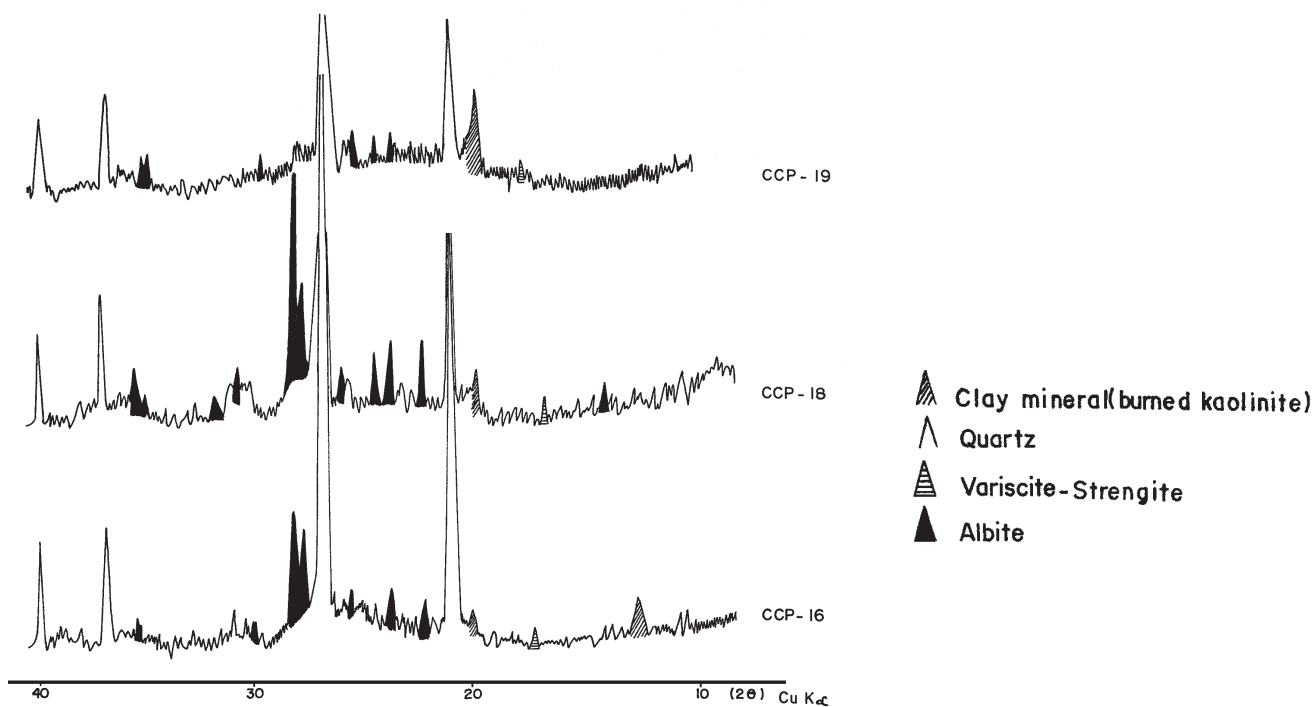


Figure 6 - XRD patterns of ceramic artifacts after the tempers.

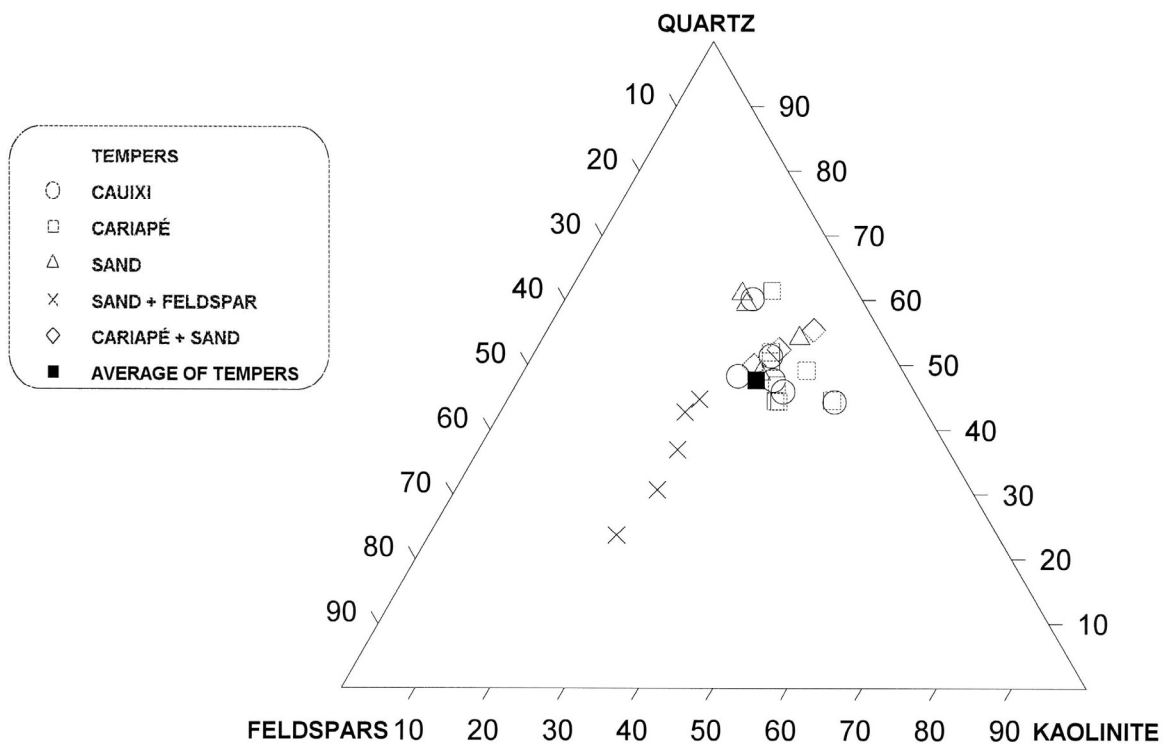


Figure 7 - The mineralogical composition on the diagram quartz-feldspars-kaolinite.

Table 1 - Mineralogical composition (Wt.%) of the archaeological ceramics after their tempers.

	QUARTZ	ALBITE	MICROCLINE	KAOLINITE	MAGHEMITE	HEMATITE	GOETHITE	VARISCITE	ANATASE	TOTAL
CAUIXI										
01	46.2	12.0	9.5	28.0	-	5.0	-	1.0	0.8	102.5
19	35.2	9.4	7.7	33.3	-	4.5	-	6.7	0.9	97.7
19 *	37.3	2.6	7.1	37.2	2.3	-	3.4	6.9	0.9	97.6
23	42.4	11.1	5.0	30.6	-	5.1	-	4.2	0.9	99.3
32	40.1	7.9	7.4	32.0	-	4.4	-	5.5	1.0	98.3
35	53.3	7.3	5.6	22.5	-	4.3	-	5.7	0.7	99.4
AVERAGE	42.4	8.4	7.1	30.6	2.3	4.3	3.4	5.0	0.9	
CARIAPÉ										
04	39.0	12.6	2.3	29.2	-	8.4	-	6.7	1.0	99.2
04 *	35.3	6.5	2.8	34.7	4.2	-	7.1	7.3	1.0	98.9
08	36.5	12.0	3.9	29.7	-	8.9	-	6.8	1.0	98.8
14	38.1	11.7	4.7	31.5	-	9.1	-	7.2	1.0	103.3
25	43.6	10.5	4.1	28.1	-	7.6	-	5.5	0.8	100.2
40	43.8	11.1	2.7	26.9	-	7.5	-	6.3	0.9	99.2
41	51.6	8.8	0.8	22.8	-	6.4	-	7.0	0.7	98.1
49	41.4	8.2	2.7	32.0	-	9.5	-	4.5	1.0	99.3
AVERAGE	41.2	10.2	3.0	29.4	4.2	8.2	7.1	6.4	0.9	
SAND										
05	52.8	10.6	3.5	22.2	-	5.3	-	4.6	0.8	99.8
12	54.7	10.2	3.8	21.1	-	5.1	-	4.9	0.7	100.5
16	43.5	9.7	7.6	28.7	-	4.1	-	4.0	0.9	98.5
22	48.4	7.6	2.5	30.9	-	3.2	-	6.8	1.0	100.4
AVERAGE	49.8	9.5	4.3	25.7	-	4.4	-	5.1	0.8	
SAND + FELDSPAR										
02	31.5	22.6	8.4	22.9	-	8.5	-	5.6	0.8	100.3
18	27.3	26.3	11.2	24.1	-	7.7	-	2.5	0.8	99.9
24	40.7	16.1	10.7	23.5	-	5.3	-	2.5	0.7	99.5
24 *	38.4	19.1	10.0	22.3	4.2	-	3.6	2.7	0.7	101.0
28	21.2	36.4	9.3	22.5	-	6.3	-	4.7	0.8	101.2
AVERAGE	31.8	24.1	9.9	23.1	4.2	7.0	3.6	3.6	0.8	
CARIAPÉ + SAND										
07	43.2	12.6	4.2	26.5	-	6.5	-	5.6	0.9	99.5
15	44.7	9.7	2.8	27.6	-	7.6	-	6.2	0.9	99.5
15 *	46.0	4.6	2.7	29.9	3.5	-	5.8	6.2	0.8	99.5
AVERAGE	44.6	10.7	3.3	27.8	3.5	7.0	5.8	6.0	0.8	
AVERAGE ALL TEMPERS										
	41.4	12.2	5.5	27.7	3.5	6.4	5.0	5.3	0.9	

* chemical analyses by XRF at Geosol-Laboratories. (-) not calculated

(Fig. 8) show the wide absorption bands of the OH/H₂O and Si-O of cauxi and cariapé. They overlap the bands of the clay minerals. Cariapé contains more OH than cauxi and has probably a cellulose framework. SEM/EDS analyses of both materials confirm the domain of Si (Fig. 9). Whole chemical analyses for cauxi and cariapé (Table 2) show that they are mainly composed of SiO₂ and L.O.I. where cauxi is richer on SiO₂ than cariapé.

Clay Mineral This is the second most abundant mineral phase in the ABE-ceramics. XRD patterns of all samples in general do not show the typical reflection (001) at 7.1Å of kaolinite well developed (Fig.6). On the other side the reflection (hkl) at 4.4 Å is still observed. The IR-spectra by comparison with Wada (1989) and

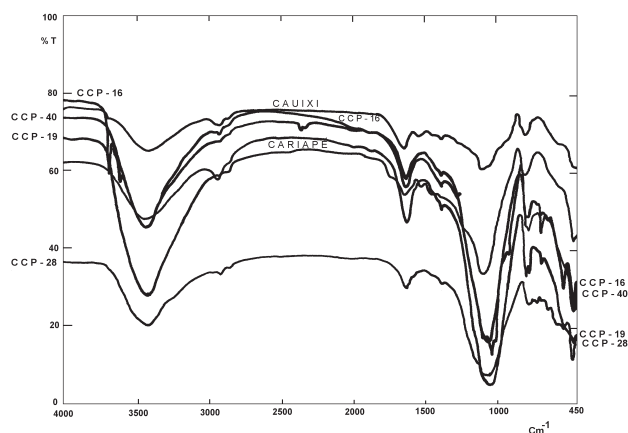


Figure 8 - Infrared spectra of ceramic artifacts after the tempers, and of cauxi and cariapé.

Dixon (1989) also indicate the presence of pre-existing kaolinite group and/or minerals of allophane group. These data and considering that kaolinite is the most common mineral of clay sediments and weathering products from Amazon (Costa, 1997; Costa & Moraes, 1998) we consider the burned clay material as derived from kaolinite principally and thermally modified during the firing of the ceramic artifacts. The archaeological data presented in the previous items show that the ceramic artifacts were clearly submitted to firing and in such way the clay minerals must have experimented structural modification, where the modification degree gives an idea about the temperature of firing. By 500 to 600°C the clay minerals, such kaolinite or allophane becomes quasi-amorphous or amorphous (Dixon, *op. cit.*; Wada, 1989). This might have been the highest temperature reached by these ceramics, when one takes in account the XRD patterns. This is the temperature observed during the heating of present *caboclo* pottery of the Amazon region, after our observation in the field and after Prof. Dr. J.R. Freitas (verbal communication) in primitive oven. On the other side the temperature may reach until 1100°C in

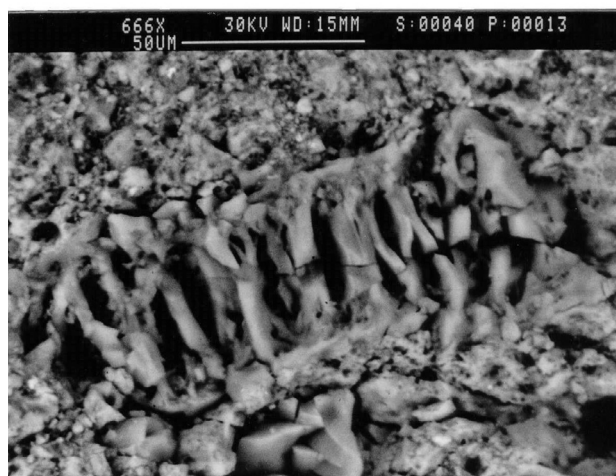
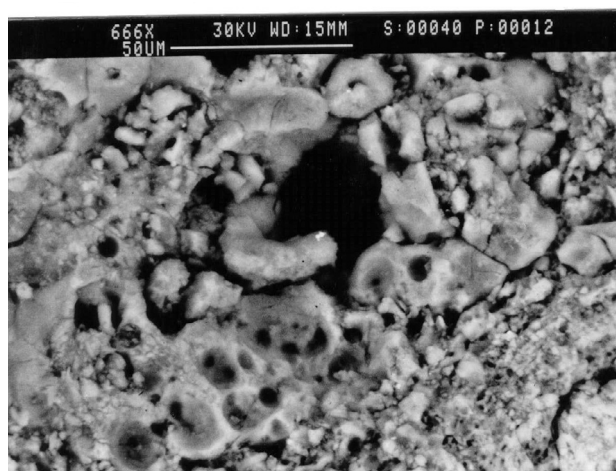
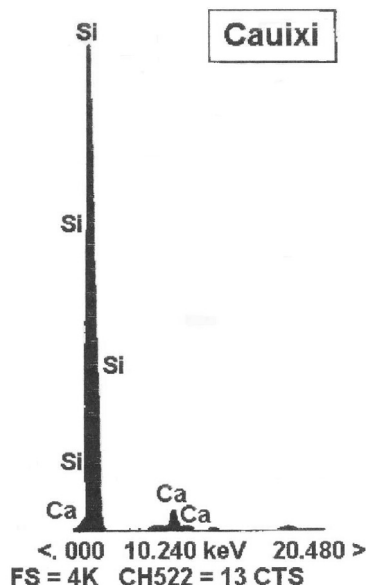


Figure 9 - SEM/EDS analysis of cauxi and SEM-photomicrographs of cauxi and cariapé, where the analyses were realized.

Table 2 - Chemical composition of cauxi and cariapé

Wt. %	CAUXI	CARIAPÉ
SiO ₂	82.90	56.40
Al ₂ O ₃	0.38	< 0.10
Fe ₂ O ₃	0.60	< 0.10
FeO	na	na
CaO	< 0.05	0.34
MgO	< 0.10	0.11
Na ₂ O	< 0.10	< 0.11
K ₂ O	0.01	0.06
TiO ₂	< 0.05	< 0.05
P ₂ O ₅	0.10	0.05
MnO	< 0.10	< 0.10
F	< 0.003	< 0.01
L.O.I	16.02	42.93
TOTAL	100.01	99.89
S	0.21	0.12
CO ₂	4.04	15.51

na: not analyzed

the furnace for firing bricks and roofing tiles. The primitive processes used to elaborate them may explain the variable cristallinity of the common clay mineral, caused by temperature instability during the burning, as expected in such primitive process observed inside of the primitive Indians and Amazon *caboclos*. SEM/EDS analyses show that this material, that constitutes the dominant matrix of all investigated samples (Fig. 5a,c,e), is composed mainly by Si and Al followed by Fe and Ti (Fig. 10a). Ca and K may be also present and are related to feldspars. The slight DRX-data still indicating the presence of kaolinite suggest the neof ormation of this phase during the pedogenesis of black earth, the common product of the actual weathering in the Amazon region.

Phosphates and Minerals of Ba and Mn Some XRD patterns show reflections which can be indexed to variscite, Al(PO₄).2H₂O, a common mineral found in weathering profiles (Costa, 1982) and in hydrothermal veins. It was not observed under the optical microscope probably due to its cryptocrystalline forms, which are frequent in these environments. SEM/EDS at different points in the clayey matrix have demonstrated that some small and well distributed crystallites are made of P, Al and Fe (Fig. 10 b, c). These data together with XRD (Fig. 6) ones, suggest that the solid solution variscite-strengite, (Al,Fe)(PO₄).2H₂O, may be the main phosphate mineral. Redmount (1996) reported (Al-Fe)-phosphates in Egyptian ceramics too.

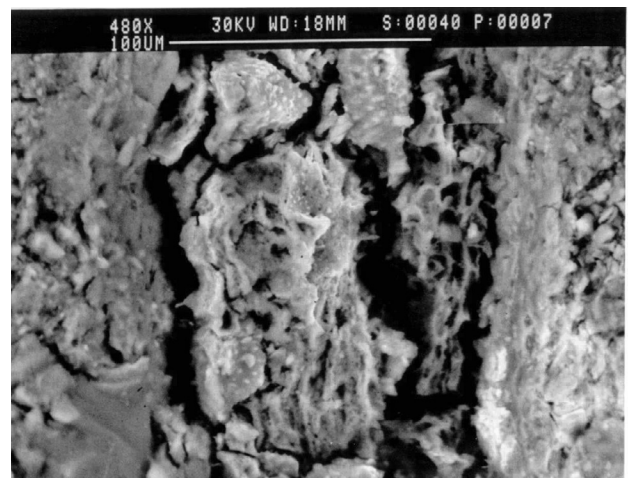
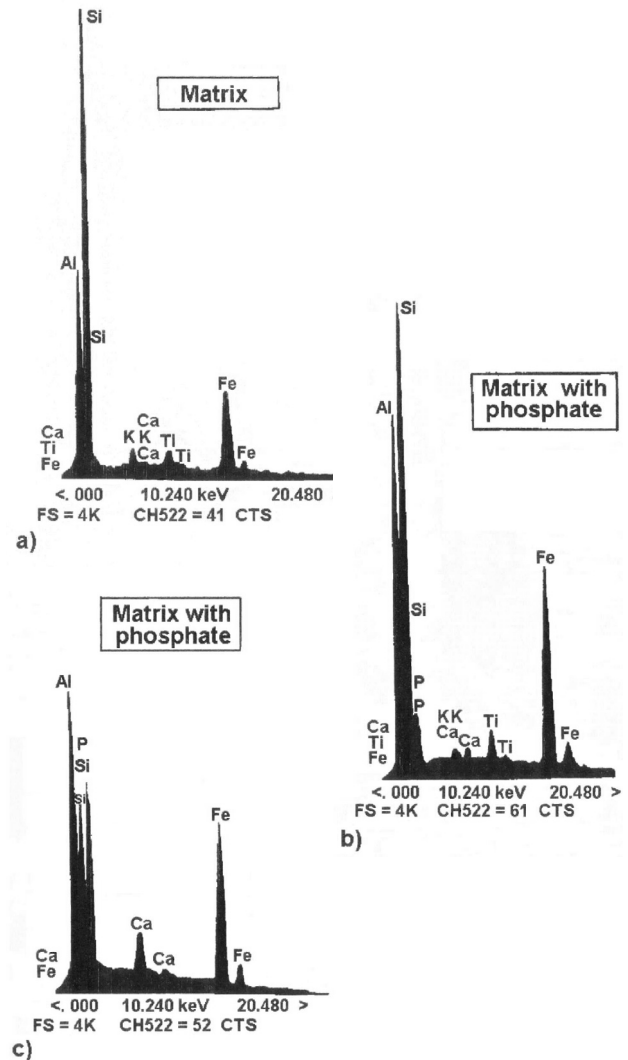


Figure 10 - SEM/EDS analyses of the clayey matrix showing the high proportion of P and Fe: a) only clayey matrix; b and c) The clayey matrix with phosphate.

SEM/EDS analyses and SEM photomicrographs allowed to identify within the cauxi spicules and in the clayey matrix a new growing mineral aggregates (Fig. 11a) which has at the outer border a high Ba content. On the other side the inner part is rich on Mn, Fe, Ba, Al and P (Fig. 11b) probably as Mn-hydroxide (e.g. romanechite) and aluminum-phosphate (variscite-strengite). All these minerals have developed in the clayey matrix.

Although seldom it was also detected by SEM/EDS analyses (Fig. 12a) very small aggregates of Ce-phosphates in the clayey matrix, correlated to rabdophanite, $CePO_4 \cdot H_2O$.

Phosphates and Ba and Mn minerals are found replacing the former clayey matrix and cariapé framework as pseudomorphous substitution (Fig. 10c, 11a and b, and 12a).

A small and rare bone fragment made of apatite has been also found in the matrix (Fig. 12b). Possibly it may represent an incorporation of bone waste during the ceramic preparation.

Feldspars They are the third most abundant minerals of ABE ceramics and are represented by low albite and microcline after XRD patterns and optical microscopy. They occur as isolated grain or as rock-fragments. Unweathered feldspar grains with uneven outline and cutting edge floating in the matrix may suggest that they have been introduced intentionally into clayey matrix

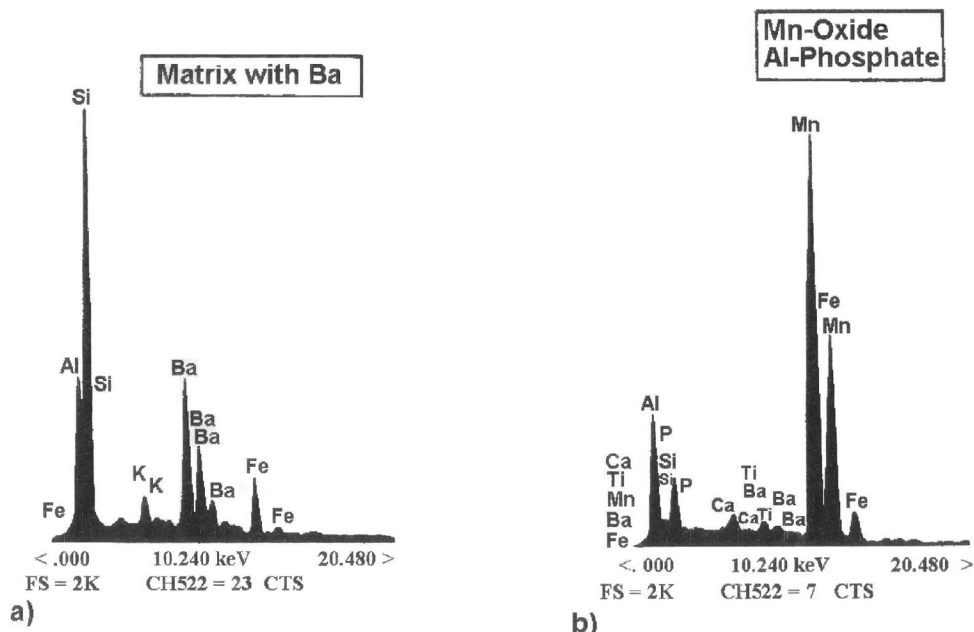
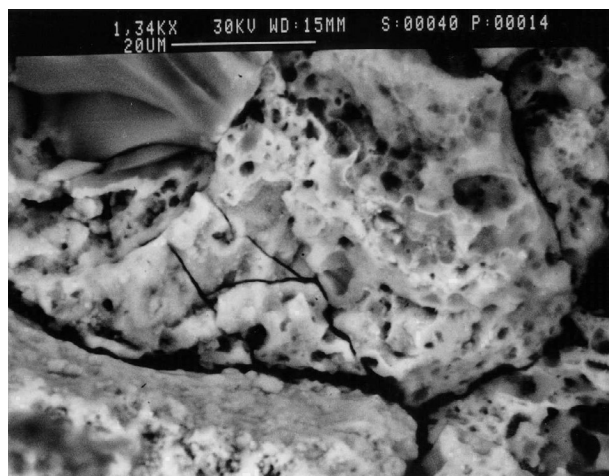
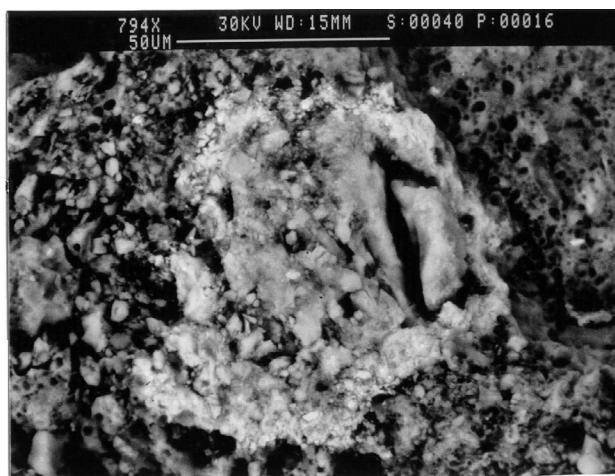


Figure 11 - SEM/EDS analyses of Ba and Mn mineral as well as phosphate developed in the clayey matrix: a) Ba in the outer zone (hell gray); b) Mn and P in the inner zone (gray).

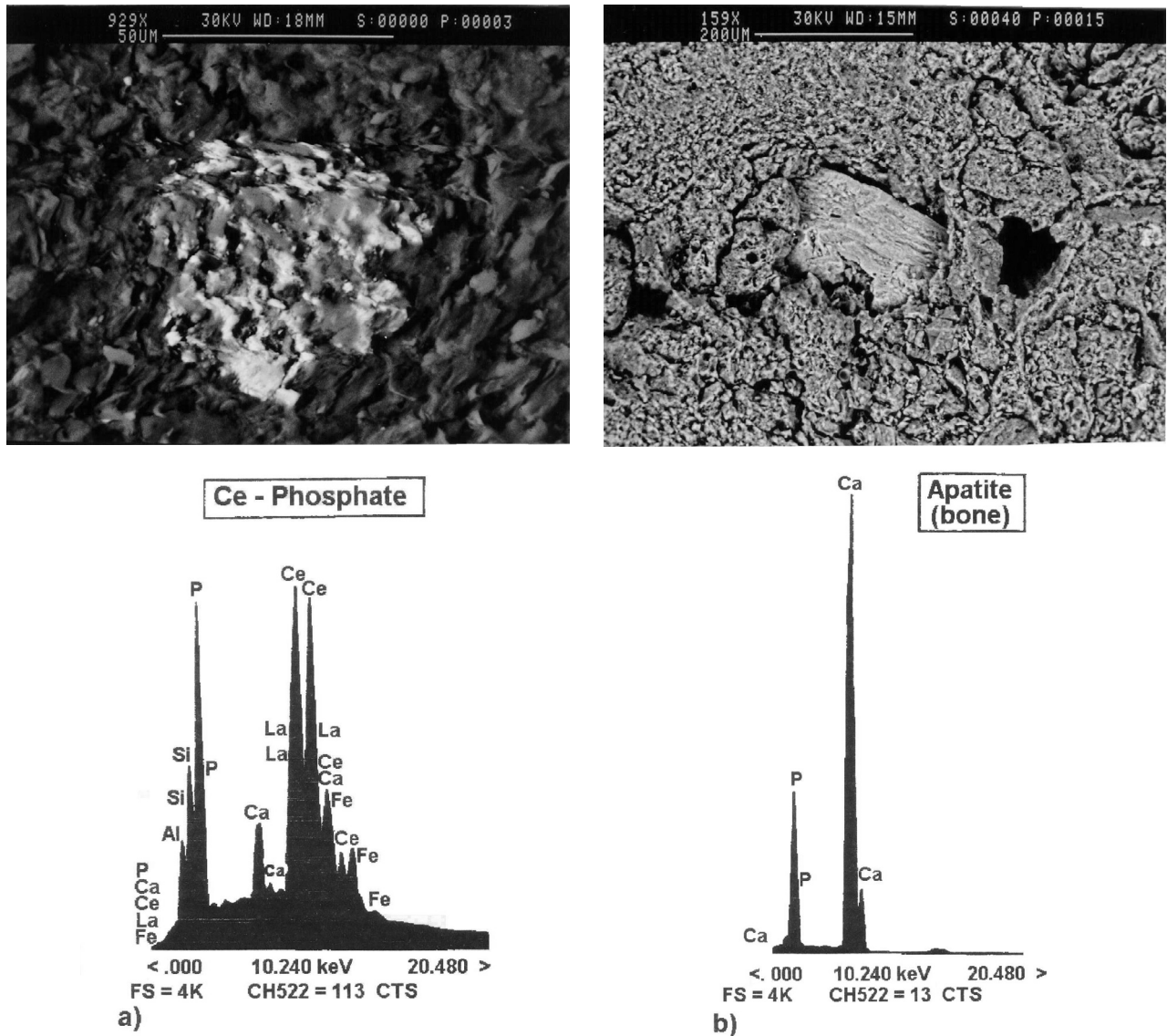


Figure 12 - SEM/EDS analyses of: a) Ce-phosphate (rhabdophane) in the clayey matrix; b) Bone fragment (apatite) inside of the clayey matrix.

in the same way as cauxi and cariapé did in order to improve the raw material.

Iron Oxy-hydroxides Minerals All ABE fragments of ceramic artifacts contain iron oxy-hydroxides minerals as hematite, goethite and maghemite after XRD patterns. They are found as visible grains, mottling and microcrystalline aggregates. The presence of maghemite, although in little amount, explains the magnetism of some ceramic fragments. The burning of the iron-mottled clayey material (as clayey saprolite), the probable raw material of ceramic artifacts, may have produced maghemite partly. Maghemite was detected in lithic artifacts in other archaeological sites (Roosevelt *et al.*, 1996) as well as in fired surficial Amazon soils (Costa,

1991). The presence of some goethite in the studied fragment of ceramics may represent the hydration of hematite and maghemite during the formation of the black earth as part of the pedogenesis, which led to the formation of the ABE.

Anatase Almost all XRD patterns display the principal reflection of anatase at 3.5\AA , a common accessory mineral in weathered rocks and lateritic soils. SEM/EDS analyses for the clayey matrix showed sometimes small Ti aggregates (Fig. 14a and b) pseudomorphous after the clayey matrix. The SEM/EDS analyses (Figs. 10 and 11) of the clayey material show fair homogeneous distribution of low content of Ti in the matrix as very small crystals.

CONCLUSIONS

The fragments of ABE-ceramic artifacts come from earthenware's (potteries) of daily use of *Konduri* culture. The ceramics are simple, showing partial oxidation and slight painting. Regarding the temper they comprise ceramics with cauxi, cariapé, sand, sand *plus* feldspars, and crushed ceramics or mixing among them.

The ceramics are made of cryptocrystalline clay-derived (burned clayey material) matrix, in which grains or fragments of quartz, feldspars and crystalline rocks as well as cauxi spicules and cariapé platelets are well distributed. Spicules of cauxi and platelets of cariapé display a slight orientation reflecting the elaboration process as described by Hilbert (1955) in ceramics of other archaeological sites. The fragments of quartz, feldspars and crystalline rocks have quite different size and forms and show a fair outline. Quartz may be monocrystalline to polycrystalline, stretched and with undulating extinction. Their grains can show reaction gulfs (partial dissolution) and lacking of roundness as well as the feldspars and rock fragments. All these features allow to conclude that most of mineral grains were taken from fresh crystalline rocks and intentionally crushed and introduced into clay material as well as cauxi and cariapé.

The above described minerals and organic substances led to identify the following materials as raw materials for the ceramics:

- 1) clay material derived from weathering (saprolite/mottling zone) of fine crystalline and less frequent sedimentary rocks (indicated by clay-derived minerals and iron oxy-hydroxides, anatase and quartz);
- 2) fresh crystalline rocks crushed (feldspars, quartz and rock fragments);
- 3) organic materials (cauxi and burned cariapé).

The mineralogical similarity between the different ceramic tempers mainly for the most abundant ones permit

to conclude that the basic raw materials used to their preparation were nearly the same. The domain of clayey materials (closely derived from kaolinite) and quartz suggest a saprolite (clayey mottled zone) derived from fine-grained acid rocks, for example rhyolites and/or fine-grained granites/granodiorites or even clayey sedimentary rocks to ask as a main source of raw material.

The abundance of fresh feldspars, rocks fragments and roundless quartz indicate that coarse igneous rocks, e.g. granites, granodiorites, and even rhyolites and quartz of veins were used as temper, after crushing. It's possible that pre-historic Indians extracted the fresh rocks from the same place where they took the clayey saprolite.

To improve the plasticity of the raw material they introduce organic material like cauxi and cariapé, crushed quartz, or even old ceramic (waste) crushed, in an old process of recycling.

Until present days cauxi is found in many lakes and rivers near to archaeological sites of Amazon region as well as cariapé in the forest do (Fig.13). Fresh and weathered rhyolites, granites and granodiorites occur near to the sites 1 and 2 (Fig. 2).

The (Al,Fe)-phosphates (5.3 Wt. % in average) in the ceramics of the ABE of Cachoeira-Porteira do not show to be of primary origin, from the clayey saprolite or clay sediments. In the ceramic fragments they are found exclusively in the clay-matrix. Freestone & Middleton (1987) reported phosphates within the clay matrix in some Far East ceramics too. There the clay source and local soils contain less than 0.5 wt. % P_2O_5 . The local soils of Cahoeira-Porteira show less than 0.036 wt. % P_2O_5 (Kern, 1988). In the modern ceramics, calcium phosphates are added to act as flux and to vitrify the final ceramic product. However, the ancient ceramics with high P_2O_5 content are not vitrified, so in this case, P_2O_5 was not used for this purpose (Freestone & Middleton, *op.cit.*). Freestone & Middleton *op.cit.* conclude that P_2O_5 content (identified as very fine-grained Ca-phosphate but not apatite) is a result of

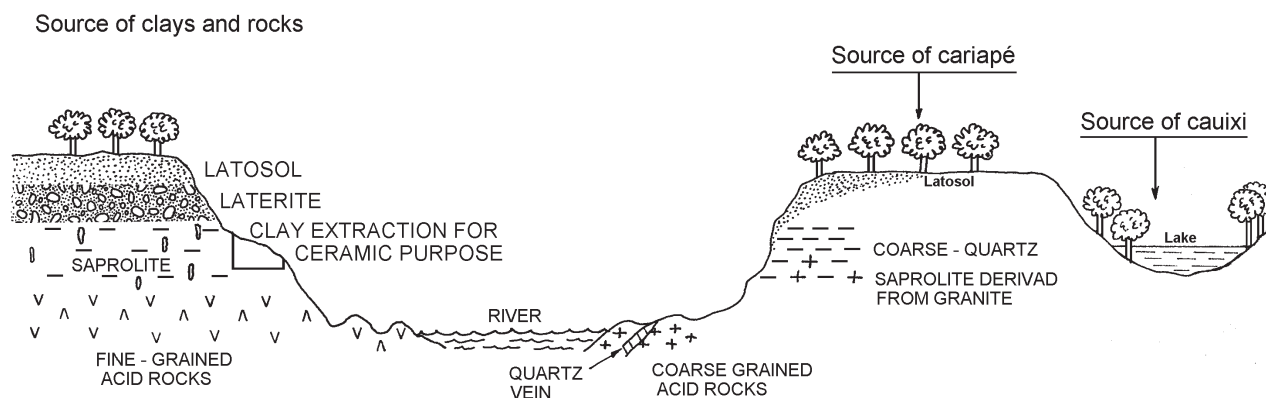


Figure 13 - Geological cross-section showing the possible sources of the raw materials for manufacture the ABE ceramics at Cachoeira-Porteira.

environment contamination. The most important source of phosphor contamination occurs during the cooking of food, mainly meals and fishes, some roots, the principal diet of the ancient Indians of Amazon. The cooking behaves as hydrothermal process, where the chemical nutrients go partially into solution and may react with the aluminous silicate (former clay minerals) of the ceramic potteries. (Al,Fe)-phosphates (variscite-strengite, crandallite group, wavellite, and so on) form preferentially in this condition in the groundmass (Kittrick & Jackson, 1955; Hsu, 1968; Kafkafi *et al.*, 1967; Yariv & Cross, 1979 and Costa, 1982); the cooking of food in the potteries also leaves to partial rehydration of clay-derived minerals (neof ormation of some kaolinite), recrystallization of anatase and formation of other Ti-minerals, Ba-Mn-oxides, rhabdophanite. Clay-derived minerals, hematite and maghemite formed during the firing of the ceramics; tridymite and cristobalite formed during the pre-ceramic burning of cariapé and cauxi; bone waste and others were incorporated during pottery confection.

The young age of the culture itself (900 to 400 years BP) and low temperature (cooking temperature) can explain the low cristallinity and too fine-grained nature of these neoformed phosphates. It is possible that the reaction (and contamination) may continue after the discarding of the ceramics as wastes and during their incorporation into anthropogenic soil profile developed at the time of the settlement and after the abandonment of it.

The pedogenesis afterward the discharge of the ceramic artifacts left to the formation of the black earth soils, during the actual tropical weathering phase. This led to superficial deferrification (destruction of hematite and maghemite) of the ceramic fragments and to form goethite and kaolinite as well.

ACKNOWLEDGMENTS

We would like to thank the full assistance of the *Companhia Brasileira de Metalurgia e Mineração - CBMM* during the conduction of the SEM/EDS analyses in its laboratory, specially the contribution of Dr. Bruno Riffel and Dr. Abrahão Issa Filho. This research was financially supported by Brazilian National Program for Development of the Sciences and Technology (PADCT/FINEP) as well as by Brazilian National Council for Sciences and Technology (CNPq). We are grateful to Anselmo José Monteiro dos Santos, who in life made the first drawings of this paper and to Elias Leão Moraes for his contribution during the elaboration of the computer drawings. The authors would like to thank the two anonymous reviewers for their very important suggestions for manuscript corrections.

LITERATURE CITED

Balec, W. 1989 Cultura na Vegetação da Amazônia Brasileira. *Bol. Mus. Para. Emilio Goeldi*, Coleção Eduardo Galvão. p. 95 - 109.

- Costa, M.L. 1982 *Petrologisch-geochemische Untersuchungen zur Genese der Bauxite und Phosphat-Laterite der Region Gurupi (Ost-Amazonien)*. Ph.D. Thesis. Erlangen-Nuernberg University. Germany., 189 p.
- Costa, M.L. 1991 Aspectos geológicos dos lateritos da Amazônia. *Revista Brasileira de Geociências.*, 21 (2):146 160.
- Costa, M.L. 1997 Lateritisation as a major process of ore deposit formation in the Amazon region. *Exploration Mining Geology*, 6(1): 79-104.
- Costa, M. L.; Kern, D. C.; Pinto, A. H. E.; Souza, J. R. T., 2002, The ceramic artifacts in archaeological black earth from Lower Amazon Region, Brazil: Chemistry and Geochemical Evolution. *Acta Amazonica* (submitted).
- Costa, M.L.; Kern, D.C.; Souza, J.R.T.; Pinto, A.H.E. 1991 A mineralogia e a geoquímica na cerâmica arqueológica de Oriximiná, PA. In: *Proceedings of the 3rd Brazilian Geochemical Congress*, São Paulo, SBGq, 1: 1-3.
- Costa, M.L.; Kern, D.C. 1996 The mineralogy of archaeological ceramics from pre-Indian black earth sites in Amazon region. In: *International Congress on Applied Mineralogy*, 5, Varsóvia, Polónia., 6/1996.
- Costa, M.L.; Kern, D.C. 1999 Geochemical signatures of tropical soils with archaeological black earth in the Amazon. *Journal of Geochemical Exploration*, 66(1/2), 369-385.
- Costa, M.L.; Moraes, E.L. 1998 Mineralogy, geochemistry and genesis of kaolins from the Amazon region. *Mineralium Deposita*, 33 (3):283-297.
- Dixon, J.B., 1989 Kaolin and serpentine group minerals. In: J.B. Dixon & S.B. Weed - *Minerals in soil environments*. Soil Sciences Society of America, 2nd. Ed., Madison, p. 467-525.
- Eden, M. J.; Bray, W.; Herrera, L.; Meevan, C. 1984 Terra Preta Soils and their archaeological context in the Caquetá Basin of Southeast Colombia. *American Antiquity*, 49(1)125-140.
- Falesi, I. 1974 Soils of Brazilian Amazon. In: Ch. Wagley. (ed). *Man in the Amazon*. Gainesville, p. 201-29.
- Freestone, F. C.; Middleton, A. P. 1987 Mineralogical applications of the analytical SEM in archaeology. *Mineralogical Magazine*, 51:21-31.
- Hilbert, P.P. 1955 A cerâmica arqueológica da região de Oriximiná. Belém, Instituto de Antropologia e Etnologia does Pará. p.76.
- Hsu, P. 1968 Interaction between aluminum and phosphate in aqueous solution. *Adv. Chem.*, 73: 115-127.
- Kafkafi, U.; Posner, A. M.; Quirk, J. P. 1967 Desorption of phosphate from kaolinite. *Soil Sciences Society of America*, 31:348-353.
- Kern, D.C. 1988 *Caracterização pedológica de solos com terra arqueológica na região de Oriximiná-PA*. Porto Alegre. MSc Thesis. Soils Department, Universidade Federal do Rio Grande do Sul. 231p.
- Kern, D.C. 1996 *Geoquímica e pedogeoquímica em Sítios Arqueológicos com Terra Preta na Floresta Nacional de Caxiuanã (Portel-PA)*. Doctor Thesis, Centro de Geociências. Universidade Federal do Pará. 124 p.

- Kern D. C.; Kämpf N. 1989 O Efeito de Antigos Assentamentos Indígenas na Formação de Solos com Terra Preta Arqueológica na Região de Oriximiná-Pa. *Revista Brasileira de Ciências do Solo*, Campinas, 13:219-25.
- Kern, D. C.; Kämpf, N., 1990 Características Físicas e Morfológicas dos Solos com TPA e sua importância para os estudos Arqueológicos. Santa Cruz do Sul - RS. *Newsletter CEPA*, 17(20): 277-85.
- Kern, D.C.; Costa, M.L.; Frazão, L.J.F., 1997 Caracterização geoquímica de solos antrópicos na região de Caxiuanã, Pará. In: *ABEQUA, 1997. Livro de resumos*, Curitiba, p. 281-284.
- Kern, D.; Costa, M.L. 1997 Os Solos Antrópicos. In: P. L.B. Lisboa (Org.) - *Caxiuanã*. MCT/CNPq, Museu Paraense Emílio Goeldi-MPEG, Belém-PA, p. 105-119.
- Kern, D.C.; Costa, M. L.; Frazão, F. J. L., 1999. Geoquímica de Sítio Arqueológico com Terra Preta no Centro da Cidade de Quatipuru-PA. *VI Simp. Geol. Amazônia Manaus/AM.*, 408-411.
- Kittrick, J. A.; Jackson, M. L. 1955 Rate of phosphate react ion with soil minerals and electron microscope. Observations on the reaction mechanism. *Soil Sciences Society of America*, 19: 292-295.
- Krauskopf, K.B. 1982 *Introduction to geochemistry*. McGraw-Hill, Auckland, p. 617.
- Letsch, J.; Noll, W. 1983 Mineralogie und Technik der frühen Keramiken Thessaliens. *Neues Jahrbuch Mineralogie Abhandlung*, 147(2):109-146.
- Meggers, B. J.; Evans, C. 1970 Como interpretar a linguagem da cerâmica. In: *Manual para arqueólogos*. Smithsonian Institution. Washington, p. 111.
- Melatti, J.C. 1972 *Índios do Brasil. Etnologia Brasileira*. 2a ed. Brasília. p.236.
- Mommsen, H. 1986 *Archaeometrie: Neuere naturwissenschaftliche Methoden und Erfolge in der Archaeologie*. B.G. Teubner Stuttgart, p. 304.
- Nimuendaju, C. 1948 Os Tapajós. *Museu Paraense Emílio Goeldi Newsletter*, 10:93-106.
- Noll, W., 1978 Mineralogie und Technik der bemalten Keramiken Altägyptens. *Neues Jahrbuch, Mineralogie-Abhandlung*, 133(3): 227-290.
- Ranzani, G.; Kinjo, T.; Freire, O. 1962 Ocorrência de "Plaggen Epipedon" no Brasil. *Boletim Técnico-Científico da Escola Superior de Agricultura. "Luiz de Queiroz"* 5:1-11.
- Redmount, C.A. 1996 Major and trace element analysis of modern Egyptian pottery. *Journal of Archaeological Science*, 23: 741-762.
- Roosevelt, A. C.; Costa, M. L.; Lopes Machado, C.; Michab, M.; Mercier, N.; Valladas, H.; Feathers, J.; Barnett, W.; Imazio da Silveira, M.; Herderson, A.; Silva, J.; Chernoff, B.; Reese, D.S.; Holman, J.A.; Toth, N.; Schick, K. 1996 Paleo-Indian Cave Dwellers in the Amazon the Peopling of the Americas. *Science*. 272: 373-384.
- Scholz, H. 1980 Mineralstoffe und Spurenelemente - nötig fuer unserer Gesundheit. *Paracelsus Verlag*, p. 192.
- Simões, M.F. 1982 A Pré-História da Bacia Amazônica: Uma tentativa de reconstituição. In: *Cultura Indígena, textos e catálogo*. Semana do Índio, Museu Goeldi, Belém, p:5-21.
- Sjoberg, A. 1976 Phosphate Analysis of Anthropoc Soil. *Journal of Field Archaeology*, 3:448-454.
- Smith, H.H. 1879 *The amazons and the coast*. Charles Scribner's sons, New York, 644p.
- Smith, N.J.H. 1980 Anthrosols and Human Carrying Capacity in Amazonia, In: *Annals of the Association of American Geographers*, 70(4):553-66.
- Sombroek, W. 1966 *Amazon soils: A Reconnaissance of the Soils of the Brazilian Amazon Region*. Wageningen, Center for Agricultural Publications and Documentation. 292 p.
- Strazicich, N.M. 1998 Clay sources, pottery production, and regional economy in Chalchihuites, Mexico, A. D. 200-900. *Latin American Antiquity*, 9(3): 259-274.
- Yariv, S.; Cross, H. 1979 *Geochemistry of colloid systems*. Springer-Verlag, Berlin, 450 p.
- Zaun, P. E. 1982 Über der Bodenlagerung auf antike Keramik. Mineralneu- und -rueckbildungen als moegliche Grundlagen fuer neue Datierungshilfen. Ein Beitrag zur archaeometrischen Forschung. *Neues Jahrbuch fuer Mineralogie, Monatsheft*, 3: 106-118.
- Wada, K. 1989 Allophane and imogolite. In: J.B. Dixon & S.B. Weed - *Minerals in soil environments*. Soil Sciences Society of America, Madison, 2nd. Ed., p. 1051-1087.

**RECEBIDO EM 05/07/2002
ACEITO EM 23/03/2004**