Capítulo 19

ORIGIN OF THE PHOSPHATES IN THE CERAMIC ARTIFACTS FROM ARCHAEOLOGICAL DARK EARTH IN THE LOWER AMAZON REGION

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Introduction

There are several archaeological sites in the Amazon region mostly represented by archaeological dark earth (ADE). During the last decades they have been object of archaeological, archeogeochemical and pedogeochemical researches in function of the vestiges left by their ancestors, as the ceramic and the own black to dark soils, that are of invaluable values for understanding the life style of the pre-historic occupation of the Amazon region (Smith 1879, Balée 1986, Kern & Kämpf 1989, 1990).

The ADE soils carry out a high quantity of ceramic fragments, spread in surface and extending until the horizon AB. The ceramic fragments certainly are resultants of the discards of ceramic utensils made by communities of the time and used as utensils in preparing foods and also in its storage. Besides these materials, they are also found lithic artifacts and several fragments of bones, shells, etc, which can get information that are useful in identificatify habits of the prehistoric communities (Ranzani et al. 1962, Falesi 1974, Eden et al. 1984).

The ceramic are certainly parts of pottery made by the population, which occupied the presenr ADE area and used raw material coming from the neighboring areas. The making technology and the finish are parameters to measure the evolutionary degree of population (Lisboa 2002).

Ceramic artifact of high quality are produced since several thousand years in China, Old Greece, Roman Empire, and in many other, including the people of the Andean highlands, the Amazon pre-historic population just produced artifacts in red ceramic. Only the Marajoara and Tapajonica cultures, achieved larger success in developing ceramic with fort artistic appeal. These are so young that could survive to partly to the bad weather of the humid tropical climate of the last millennia (Costa et al. 2004 a, b).

One of the main answers of this climate to the abandoned establishments went to its transformation in dark earth, a rich soil in organic matter and with high fertility (Kern et al. 2003).

The analytical methods and techniques of the geology, mineralogy and geochemistry which are been applied with success in the study of ceramic of archaeological ranches and historical buildings, is nowadays known as archaeometry (Noll 1978, Zaun 1982, Letsch & Noll 1983, Momsen 1986, Freestone & Middleton 1987, Costa et al. 1991, Waters 1992, Redmount 1996, Strazicich 1998, Rapp 2002) and several papers have been published about cultural inheritance. The study of archaeological ceramic in Amazonian is part of this context and the first results these studies here presented are contributed to understand the origin and the composition of the material used in its making as well as in the making techniques, and, consequently the life form and the habits of the people that produced them.

The Phosphor in Archaeological Ceramic

In the chemical-mineralogical investigations accomplished in the archaeological ceramic fragments of ADE sites of Amazon region the presence of relatively elevated contents of phosphor (1 to 2% of P_2O_5, on the average) is frequent. Phosphor concentrations above 0.2% have been commonly found in archaeological ceramic vases, as being an use indicator (Duma 1972, Freestone et al. 1994), after P_2O_5, CaO and FeO. U patter content distribution along traverse through the pottery wall, that is to say, enrichment inside and on the outside, what would indicate phosphor absorption starting from the adjoining soils.

Freestone et al. 1994 also stand out that the phosphor concentrations are not restricted to vases used in the cooking, nor for ornamental, as for example, the Romans. Several authors believe that phosphor comes into ceramic fragments after its deposition in the waste place, the phosphor presence should be post-depositional (Dunnel & Hunt 1990).

Bollong et al. 1993 observed that the vases found in the ground surface display lower phosphor contents than those buried, suggesting that the phosphor would have been leached out of the vase surface during the tropical weathering. In the specific case of the fragments of archaeological ceramic of ADE sites of Amazonian, the contents of P_2O_5 that on the average are between 1 and 2%, could arrive at 5%, it was not observed until the actual investigation a dependence with the soil horizons, and/or enrichment of up to 5% in P_2O_5 starting from soils with less that 0.1% of phosphor. The large quantity of ceramic fragments rich in phosphor in the ADE, and the very low phosphor content in the soil are practically not enough, to explain a mass balance.

Before this it has been looking for through continuous investigations enlarging the universe of sites and ceramic types, with the objective of discovering the possible source of the phosphor starting from the nature of its use. The present work presents a discussion about this possibility that will be confronted shortly with the experimental works.

While in the ceramic vases of the Far East the phosphor has been reported as apatite in very fine grains (Freestone & Middleton 1987) or still as rare Ca phosphate, Redmount 1996 mentions Al and Fe phosphates in Egyptian ceramic. In the ceramic fragments investigated at ADE sites most it has not been allowing to identify a type of phosphate, however, variscite-strengite, $(Al, Fe)(PO_4).2(H_2O)$ has been confirmed by countless analyses of SEM/EDS. Recently XRD analyses allowed identify crandallite, $CaAl_3(PO_4)_2(OH)_5$, which are under sub micrometer crystals according to the analyses of SEM/EDS. Beyond of those, although very rare, it was found rhabphane, $CePO_4.H_2O$ and apatite, the last one as part of bone fragments. Everything indicates that the phosphor in this ADE ceramic largely meets as phosphate of aluminum still amorphous.

The Characteristics of the Ceramic

The archaeological ceramic, in function of its physical and mineralogical constitution, they have been resisting to the weathering conditions of the tropical climate, certainly still aided by the small space time of exposition. The short time period of exposition can be indicated by, still found fragments of these ceramic with drawings and paintings very well preserved in the sites, be buried or not.

Besides the raw material made of clay the pre-historic ceramists added the so called tempers: cariapé, cauixi, ceramic remains and sands (Hilbert 1955). The cauixi (*Tubella reticulata* and *Parnula betesil*) (Figure 1), for example, is fresh water spongy that accumulates in logs of trees, ships, and in the bottom sediments of lakes and rivers. The cauixi is SiO_2 rich amorphous organic material. That addictive was generally used in the making of ceramic vases found at the several archaeological sites of Amazonian. The cauixi tradition was modified by the introduction of the cariapé temper (Figure 1), a peel of well-known tree as cariapé (Bignoniaceae, *Moquilea* sp., *Licania utilis* and *Turiuva* sp.(?) (Hilbert 1955) (Nowadays it's a Chrysobalanaceae, *Moquilea* sp., *Licania utilis*) that is also constituted of amorphous SiO_2. Before being added into the ceramic the cariapé needed to be roasted, for remotion of the no-siliceous organic components (cellulose) that harm the durability of the ceramic. The cariapé comes out as elongate fragments or small pallets, with fibrous structure, which is sharply visible in the images of SEM (Figure 2).

The sand temper represents the addition of this material to the clay mass. The sand fraction is, represented by fragments of quartz, and/or feldspars or still of rocks (Figure 3).

The ceramic remains represent the re-use of the discard ceramic, that were triturated and added the clay mass. They can, still be found with cariapé and cauixi (Figure 4).

Figure 1

An image get by optical microscope through a thin section of ceramic fragment showing the tempers *cariapé* and spicules of *cauixi* in a cryptocristalline clay matrix.

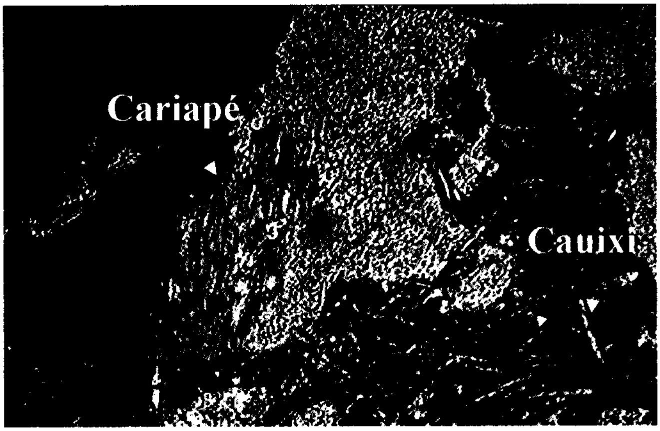
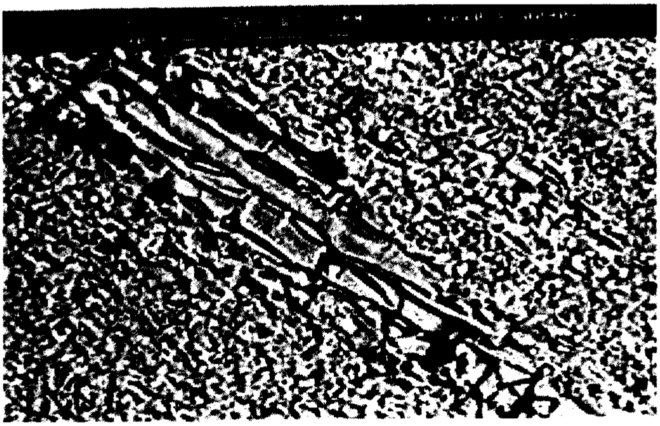


Figure 2

An image obtained by SEM/EDS showing the morphological aspect of the temper cariapé formed bya fibrous structure include in clay matrix and found in the ceramic fragment from Cachoeira-Porteira (Costa et al. 2004b).



Mineralogical Composition of the Ceramic

There are still few investigations about the mineralogi, textural aspects and chemical composition of ceramic artifacts found in the archaeological sites of Amazonioan and its geochemical importance. They stand out the works of Costa et al. 1991, 1993, 2001, 2003, 2004a and 2004b and Pinto et al. 1992 that studied researched the ceramic of Cachoeira-Porteira (Oriximiná,

Figure 3

An image get by optical microscope (// nicols) in thin section of ceramic fragments showing the sands temper, mainly quartz grains inside in a cryptocristalline clay matrix

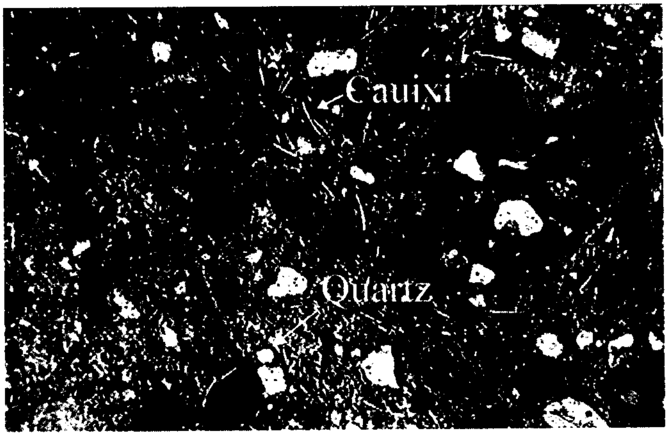
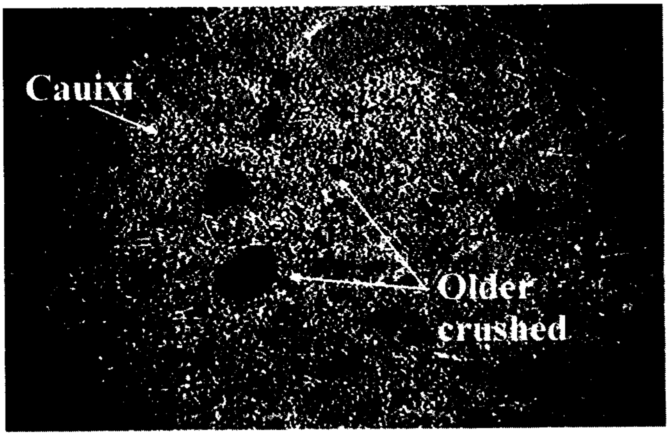


Figure 4

An image get by optical microscope (// nicol) of fragment of ceramic showing reused of the rest of older ceramic fragments (dark color) in clay criptocystalline matrix.



Pará), Costa & Kern 1994, Kern & Costa 2001, Coelho et al. 1996 that approach the archaeological and riparian ceramic of Caxiuanã partially, Latini et al. 2001 and Nicoli et al. 2001 that just obtained data chemical of the ceramic of Acre and Lima et al. 2002 for ceramic near to Manaus and border Amazonas-Colombia also emphasized the chemical-mineralogical aspects. The ceramic fragments here approached, coming from Cachoeira-Porteira and Caxiuanã (Figure 5) in Lower Amazon region and from Northeast of Pará close to Atlantic cost line. They are constituted mainly of quartz, partially crystalline clay minerals after to be burned (calcined kaolinite), illite, feldspars (albite and perhaps microcline), muscovite, anatase, besides maghemite (ã-Fe_2O_3) or hematite (á-Fe_2O_3) and per times amphibole (Table 1). The Albite is found frequently as accessory of the ceramic fragments and its abundance can be related to the sand temper.

Figure 5

Location map of the archaeological dark earth (ADE) sites Cachoeira-Porteira, Caxiuanã and Quatipuru in the Amazon region

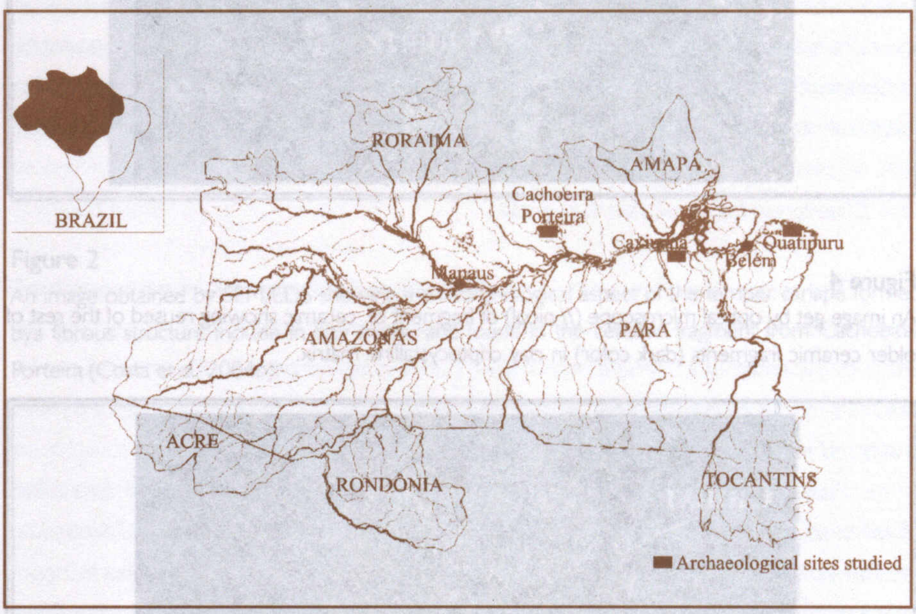


Table 1

Average mineralogical composition (% Wt) of the ceramic fragments from Cachoeira-Porteira (Oriximiná) and Manduquinha (Caxiuanã)

ADE sites	quartz + (cauixi + cariapé)	kaolinite	albite	illite	iron oxides (maghemite + hematite)	phosphates (variscite)	anatase
*Cachoeira-Porteira	41.4	27.7	12.2	-	9.9	5.3	0.9
Manduquinha	57.2	10.4	8.3	6.5	4.5	2.9	0.4

*Costa et al. (2004b).

Figure 6

Images and semiquantitative chemical analysis of the clay matrix obtained by SEM/EDS showing the presence, besides Al and Si (clay minerals), high proportion of P, Ca and Fe (variscite-strengite and/or crandallite) (a) [illegible] and (b) [illegible]

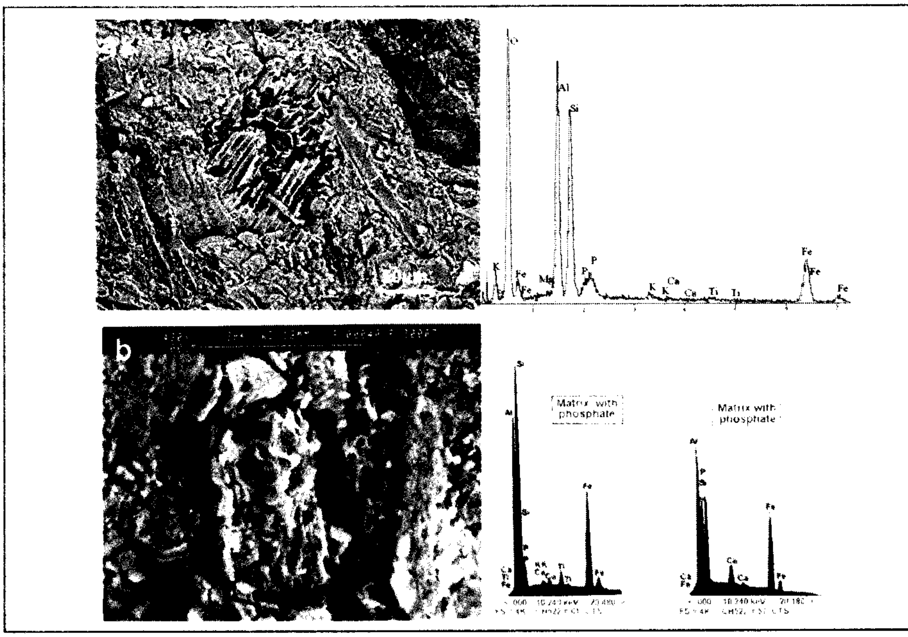
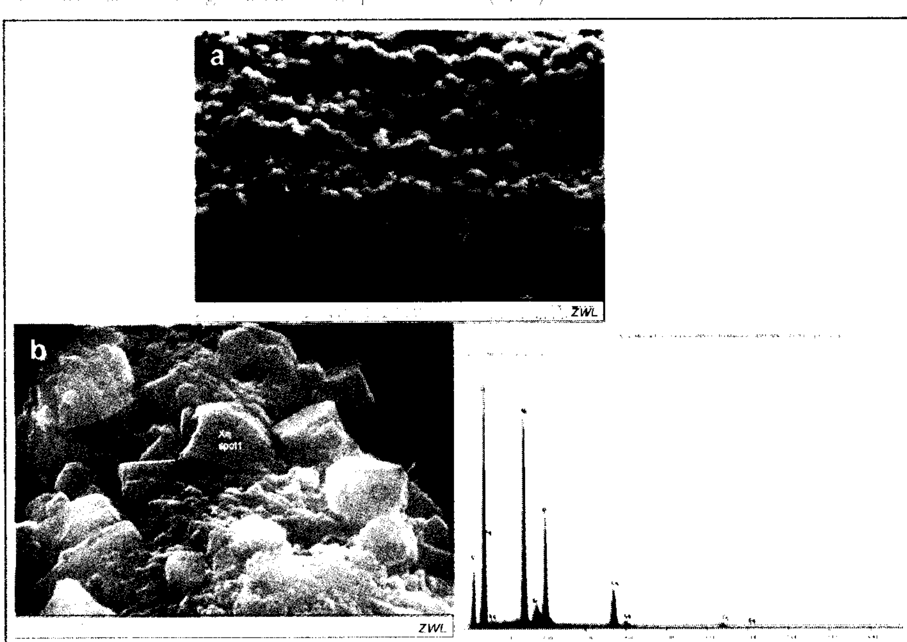


Figure 7

Image and semiquantitative chemical analysis obtained by SEM/EDS of ceramic fragments from northeast Pará showing crandallite (a) spheroids and (b) crystals



The phosphates represent one or more important mineral phases in the studied ceramic. Rarely are they identified by XRD or by optical microscope. However the whole chemical analyses in general show relatively elevated contents of P_2O_5, the average for the ADE site varying from 1 to 2%, but reaching 3.30% locally. The semi quantitative microanalyses accomplished in SEM/EDS allowed to identify in the matrix the presence of cryptocrystalline material generally constituted by phosphor, aluminum and some times iron, indicating aluminum phosphate of the type variscite-strengite, $(Al, Fe)(PO_4).2(H_2O)$, in Caxiuanã and Cachoeira-Porteira (Figure 6), while in the Northeast of Pará so much XRD as SEM/EDS shows the clear domain of crandallite, $CaAl_3(PO_4)_2(OH)_5$ (Figure 7). It is observed that there is a certain preference of the phosphor for the contact zone matrix cariapé (Figure 8).

Chemical Composition

The ceramic fragments of Cachoeira-Porteira, Caxiuanã and Northeast Pará are constituted mainly by SiO_2 and Al_2O_3 (Table 2). The high contents of SiO_2 answer for the high contents of quartz, besides cauixi and cariapé, and when associated to the values of

Figure 8

Mineralogical composition of the ceramic fragments in the diagrams kaolinite-variscite-illite and hematite-anatase-variscite and its relationship with the tempers cauixi, cariapé and sands

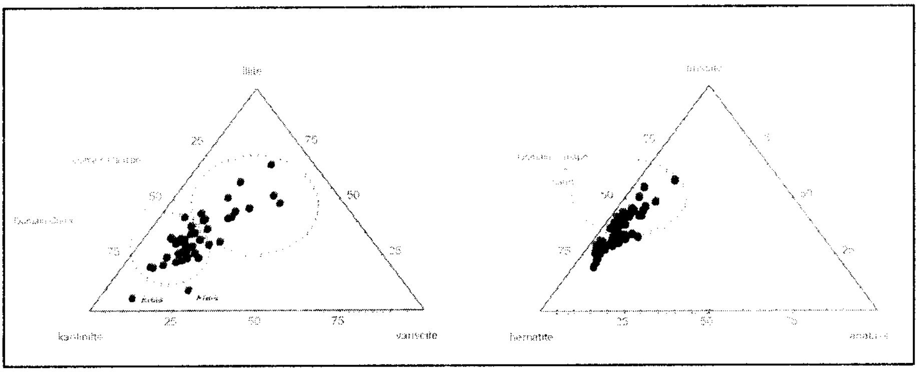


Table 2

Average chemical composition (% Wt) of the archaeological ceramics

ADE sites	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	Na_2O	K_2O	TiO_2	MgO	CaO	LOI
*Cachoeira-Porteira	65.55	16.37	5.79	2.37	0.69	0.90	0.86	0.63	0.43	7.54
Manduquinha	71.35	8.60	4.54	1.31	0.98	0.59	0.40	0.26	0.19	11.63

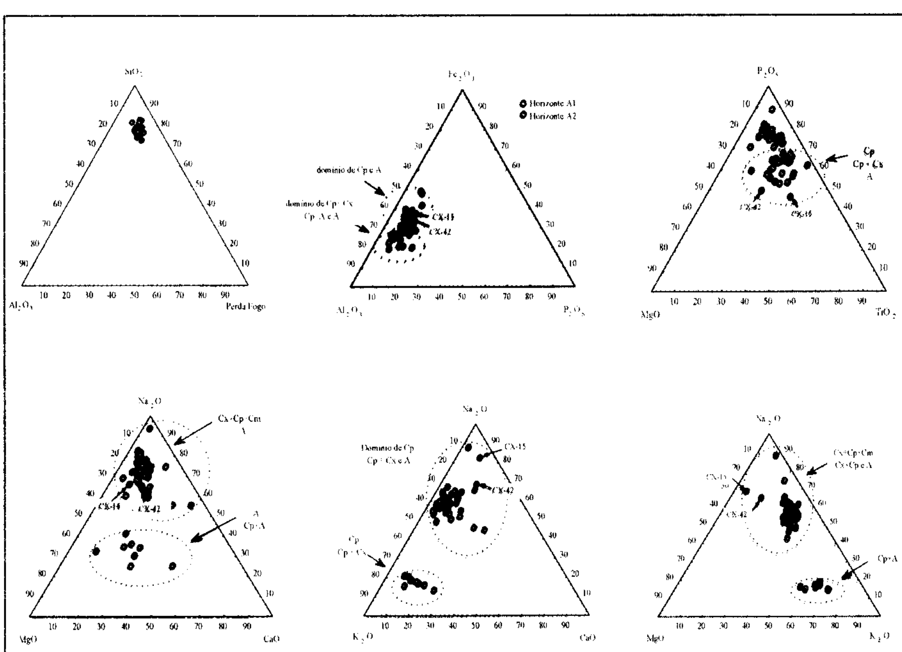
* Costa et al. (2004a)

Al_2O_3 they represent the burned clay minerals (mostly kaolinite) and illite, the feldspars and micas. The still relatively elevated values of Na_2O and K_2O confirm the expressive presence of albite, and illite + muscovite, respectively. The Loss of Ignition (LOI) is relatively high and reflect the presence of clay partially burned, and, therefore slightly dehydrated (it burns incomplete as already demonstrated by the partial oxidation of ceramic). The contents of P_2O_5 detach the presence of phosphate, that in the absence or in the relatively low content of CaO, as it is the case of Cachoeira-Porteira and Caxiuanã, is interpreted as aluminum phosphates like variscite-strengite or crandallite, as referred above.

There is no correlacion between the chemical composition of the ceramic fragments and soil horizons (A or B of the ADE), (Figure 9), even for phosphor, what contradicts the premise of Freestone et al. 1994 that the source of the phosphor comes from the adjoin soils. From the point of view of the contents of the main components SiO_2, Al_2O_3 and LOI (Figure 9a), that constitute the dominant mineral and organic phases, there are no significant differences among types of ceramic classified according to the tempers. This means that the basic raw material used for the making of the ceramic artifacts was fine material, of clay grain size, rich in quartz and clay minerals, mainly kaolinite, possibly of claystones or saprolites derived from aluminosilicate rocks.

Figure 9

Diagrams showing the chemical composition of the ceramic fragments after the different tempers (A = sand, Cp = cariapé, Cx = cauixi, Cm = crushed older ceramics).



The diagram Al_2O_3-Fe_2O_3-P_2O_5 (Figure 9b) although it shows a larger spreading on the chemical composition, it doesn't discriminate the tempers and leaves clear that the phosphor contents oscillate relatively very few. The contents of iron oxihydroxides minerals and aluminum silicates (burned kaolinite, feldspars) show antagonistic tendency, that is to say negative correlation.

In the diagram MgO-P_2O_5-TiO_2 (Figure 9c) a larger spreading of the chemical composition is observed, with slight tendency to discriminate the fragments with domain of the temper cariapé. For its time the diagrams elaborated starting from the earthy alkaline and alkaline metals (Na_2O, K_2O, CaO and MgO) they discriminate two chemical fields clearly: 1) of the highest contents of Na_2O (Figure 9 d, f), which correspond to most of the samples of fragments; and 2) of the highest contents of K_2O (Figure 9 f, e) or K_2O-MgO (CaO), portraying the mineralogy made of albite and illite+muscovite, respectively.

The Phosphates

Although phosphate minerals constitute a mineral class rich in mineral species, little of those are abundant in the Earth Crust. These mineral can be formed in many environmental conditions and can be found in several types of rocks, like igneous from ultramafic the felsic composition, metamorphic rocks in general and also in the sedimentary ones, chemical or detritic. They also occur in the pegmatitic and hydrothermal veins and can still be found in great abundance in the lateritic rocks and soils.

The most abundant phosphate is apatite. In the hydrothermal and pegmatitic environments, besides apatite, occur the phosphates of Mn, Fe, Fe-Mn, Al, Al-Fe, Ca-Sr-Al. For its time in the laterites and tropical soils aluminum phosphates, Al-Fe and Al-Ca-Sr they are the main representatives. That is to say, the aluminum and aluminum-iron phosphates are specially formed in environment of low temperature, as the hydrothermal veins and the soils, mainly the lateric ones (Costa 1997, Kittrick & Jackson 1955, Kafkafi et al. 1967, Hsu 1968). In the soils and lateritic profiles the most common phosphates are crandallite-goyazite, variscite-strengite, wardite, senegalite and wavellite.

An interesting fact is that the phosphates minerals until now identified in the archaeological ceramic fragments of the Amazon are variscite, variscite-strengite and crandallite, as shown previously, that is to say, the same minerals found in hydrothermal environment, soils and lateritic materials. Therefore, it seems there to be an intimate relationship of the ceramic fragments with one of these environments or with everyone. To understand these relationships it will be made a description of the process of making of the ceramic.

Process of Making

The first step is identify an appropriate clayey raw material near to people community (near future ADE). To improve the clay raw material it's necessary already to add an or more types of tempers described previously, as cauixi, cariapé, sands or same remains of ceramic, or mixture of them. The mixture was obtained by hands and the feet movements and the pottery established manually, being used the traditional techniques, transmitted of generation in generation, and that arrived at our days. In the production of the pottery pieces the well-known method was used by the caboclos as candlewicks ("acordelados"). The candlewicks were put upon, amended one in the other ones and, then, planed with a "cuia" piece. The polish process ("caliça"), used to make waterproof the pieces and to give them brilliant finish, it was done with inajá, a palm (*Attalea maripa*) seed, found frequently in the area.

For decoration effect, they used commonly the incision and excision techniques, characteristics of the Marajoara ceramic. Exploring floral reasons, the ceramists used the engobe-liquid clay of different colorations, applied on the humid piece with a point of kneaded grass, that sometimes did of paintbrush. Soon after it is exposed in the sun to evaporate, and it is later on burned. With the utensil still hot it is promoted its impermeable with the resin taicica or jutaicica. Being depended on the use of the utensil makes a finishing with drawings or incisions (Kern 1996).

Generally the burning is made at night, to avoid the effects of the heat and of the winds, and far away from the strange people's eyes, because that, they believed the ceramists, it could harm the final result. During the burning, the pieces were placed down of mouth, on a layer of stones and burned slowly, to open sky, firing with chip and peels of trees (Kern 1996).

Use and Discard of the Ceramic

The made ceramic vases were mainly for the daily use to prepare foods and also to store them, as transport and guard of water, among others. Special vases were prepared as urns, many still found with human bones. The great accumulations of ceramic fragments found at the archaeological sites represent vases of daily use, discarded close to de home when they were useless. The own way of occurrence of these fragments indicates this procedure, which can still be observed in the current days.

Origin of Phosphates in the Ceramic

An outstanding and persistent aspect of the chemical composition of the fragments of archaeological ceramic of Amazonian, as shown previously, are relatively the high contents of P_2O_5, already identified by Costa et al. 1991, 1993, 2001, Costa & Kern 1999, Latini et al. 2001, Nicoli et al. 2001 and more recently by Lima et al. 2002, Costa et al. 2004a, 2004b.

The values of P_2O_5 found at the Manduquinha site (Caxiuanã) range from 0.71 to 2.1%, slightly lower the those determined by Costa et al. 1993 in the area of Cachoeira-Porteira (Lower Amazons region). In the of Quatipuru site and Bragança coastal area (Northeast of Pará) the phosphor contents oscillate from 0.47 to 3.30% in weight. These values would correspond of 2 to 6% of a phosphate mineral equivalent to aluminum phosphates, which were already detected by XRD in some samples. They are of the variscite-strengite and crandallite group, that is to say, aluminum phosphates.

While Duma 1972 and partly Bollong et al. 1993 admitted that the phosphor had an origin after the use for the ceramic, Freestone & Middletone 1985, Dunnel & Hunt 1990, Freestone et al. 1994, among other, consider that the presence of phosphor in the ceramic vases is fruit of the environment in that it was discarded, for adsorption of the phosphor of the bearing material, for example, the soil.

This hypothesis under the general geochemical point of view is perfectly realizable, as indicated by studies of chemical kinetics, involving the clay minerals, the available aluminum and the phosphor of the soil, forming aluminum phosphates (Hsu 1968, Kittrick 1955, Wada 1989). However they can not explain the formation of high phosphor contents in the ceramic starting from soils poor in this element, and that even so, relative to the neighboring soils, without dark earth, they still continue relatively rich in phosphor.

The ceramic fragments investigated here come from Caxiuanã, Cachoeira-Porteira and Northeast Pará do not display any relationship between the soils and the phosphor content in the ceramic. The phosphor content in the ADE, where it is relatively enriched, it ranges among 0,05 and 0.28% of P_2O_5, while in the neighboring latosols they are below 0.036% P_2O_5, always more concentrated in the first 20 cm from the surface. After this picture and considering that the great majority of the studied fragments represents vases of daily use, the results presented here show that the phosphor found as part of the ceramic fragments of ADE seems preferably to be related to its use, the results presented here ed for Duma 1972, although in ceramic different from those of Amazonian.

The ceramic fragments studied here don't present any vitrification also , what is usually done with phosphates. Therefore, this process doesn't contribute to the origin of the phosphor. Trace elements like Zn, Mn, Cu, and (Sr, Ba), (Ca), (Mg) they get rich to the A horizon of the ADE soils relatively to B horizon and to adjacent Latosol. These values are those found in the ceramic. That is to say, while phosphor would get rich abruptly in relation to the adjacent soils the others, except Ba, they don't make it. This seems also to contradict the pure alone phosphor adsorption for the ceramic starting from the soils.

The diet of the old people of Amazon region based on cassava (*Manihot esculenta*), several root, fruits of several palm trees, as well as foods of animal nature, most vertebrates, that besides proteins and fats, contain a lot of phosphorus, mainly in the bony fabric. Besides the diet foods contain Ca, Ba, Mg, Mn, Ba, Zn, Pb, and so on.

These foods when stored, but mainly when cooked by long time and repeatedly in the ceramic vases, they were dissolved partly in the hot water, forming a typical hydrothermal solution, that was in contact with the heated up wall of the vase, which would not have been burned at very high temperature, still staying with high porosity and formed of amorphous material or of low crystallinity, mainly the previous clay minerals. In this situation the fine-grained and low crystalline aluminosilicate of pottery walls react with the phosphor rich solution get forming the aluminum phosphate minerals.

These reactions are plenty known in the sciences of the soils and in the processes of minerals formation found inside of hydrothermal bodies (Kittrick et al. 1955, Hsu 1968, Kafkafi et al. 1967, Yariv et al. 1979). The kinetics of phosphate formation increases with the hydrothermal conditions, and the cooking of food can be marked as an hydrothermal environment. This way it is ended that the largest phosphor source for the formation of the amorphous phosphates or microcrystalline ones of the archaeological ceramic of Amazonian is represented by the foods, mainly during cooking of foods inside of the potteries. Another possibility would be the urns mortuaries, in that the temperature would be the surface environment, and no hydrothermal condition.

The main chemical reactions waited in the formation of the phosphate in the studied ceramic, where H_3PO_4, Ca^{2+}, among other, coming from the partial decomposition of the foods during the cooking, are:

$$\underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_{4\,(s)}} + 2H_3PO_{4(aq)} + 3H_2O \rightarrow \underset{\text{(variscite)}}{2AlPO_4.2H_2O_{(s)}} + 2Si(OH)_{4(aq)}$$

$$\underset{\text{(kaolinite)}}{3Al_2Si_2O_5(OH)_{4\,(s)}} + 4H_3PO_{4(aq)} + 5H_2O + 2Ca^{2+} \rightarrow \underset{\text{(crandallite)}}{2CaAl_3(PO_4)_2(OH)_{5(s)}} + 6Si(OH)_{4(aq)}.$$

Acknowledgments

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