The ceramic artifacts in archaeological black earth (terra preta) from Lower Amazon region, Brazil: chemistry and geochemical evolution.

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ABSTRACT

This paper carried out a chemical investigation of archaeological ceramic artifacts found in archaeological sites with Black Earth (ABE) in the Lower Amazon Region at Cachoeira-Porteira, State of Pará, Brazil. The ceramic artifacts, mostly of daily use, belong to *Konduri* culture (from 900 to 400 years BP). They are constituted of SiO_2, Al_2O_3, Fe_2O_3, Na_2O and P_2O_5; SiO_2 and Al_2O_3 together add up to 80 % and indicate influence of acid rocks, transformed into clay minerals basically kaolinite. The relative high contents of P_2O_5 (2.37 % in average) come out as (Al,Fe)-phosphate, an uncommon fact in primitive red ceramics, but found in some roman and egyptian archaeological sites. The contents of the trace elements are similar or below the Earth's crust average. This chemical composition (except P_2O_5) detaches saprolite material derived acid igneous rocks or sedimentary ones as the main raw material of the ceramics. The contents of K, Na and Ca represent the feldspars and rock fragments possibly introduced into saprolitic groundmass, indicated by mineralogical studies. The presence of cauixi and cariapé as well as quartz sand was confirmed by optical microscope, SEM analyses and by the high silica contents of ceramic fragments. Phosphorus was possibly incorporated into groundmass during cooking of foods, and ABE soil profile formation developed on yellow *Latosols*. The raw materials and its tempers (cauixi, or cariapé, feldspar, crushed rocks, old ceramic artifacts and quartz fragments) are found close to the sites and therefore and certainly came from them.

KEY WORDS

Terra preta, Black earth, Lower Amazon, Soil, Chemistry, Phosphorus, Geochemical Evolution

Artefatos cerâmicos em sítios arqueológicos com terra preta na região do baixo Amazonas, Brasil: composição química e evolução geoquímica.

RESUMO

Neste trabalho realizou-se a caracterização química de fragmentos de artefatos cerâmicos encontrados em sítios arqueológicos com terra preta no Baixo Amazonas (Cachoeira-Porteira, Pará, Brasil), representativos da cultura Konduri *(de 900 a 400 anos AP). Esses fragmentos são constituídos de SiO_2, Al_2O_3, Fe_2O_3, Na_2O e P_2O_5, sendo que SiO_2 e Al_2O_3 juntos, perfazem mais de 80 % em peso. Os teores de P_2O_5 são relativamente elevados (2,37 % em média) sob a forma de (Al,Fe)-fosfatos, incomuns em cerâmicas vermelhas primitivas, mas encontrados em algumas cerâmicas arqueológicas egípcias e romanas. As concentrações dos elementos traços são comparáveis ou mesmo inferiores ao nível crustal, embora a composição total seja próxima a mesma. A composição química (exceto P_2O_5) em conjunto com os dados mineralógicos e texturais indicam material saprolítico derivado de rochas ígneas félsicas ou rochas sedimentares como matéria-prima das cerâmicas. Os teores de K, Ca e Na mostram que os feldspatos e fragmentos de rochas foram adicionados ao material argiloso, como sugerido pela mineralogia. Os altos teores de sílica respondem pela presença de cauixi, cariapé e/ou areias quartzosas. Fósforo deve ter sido incorporado à matriz argilosa da cerâmica, quando do cozimento de alimentos nos vasos cerâmicos, e ainda, em parte, durante a formação do perfil de solo tipo ABE sobre* Latossolos Amarelos. *A matéria prima e os temperos (cauixi, cariapé, rochas trituradas e fragmentos de vasos cerâmicos descartados) encontram-se disponíveis próximos aos sítios até a atualidade, e portanto foram a área fonte dos mesmos para a confecção dos artefatos cerâmicos..*

PALAVRAS-CHAVE

Terra preta, Baixo Amazonas, Solos, Composição química, Fósforo, Evolução geoquímica.

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INTRODUCTION

After Costa *et al.,* (2004) the black earth soils, called by *natives Indian black earth* (Terra Preta de Índio in Portuguese) or by archaeologists as *archaeological black each (ABE)* are very commonly found in the landscape of the Amazon region and described by naturalists, archaeologists and pedologists (Smith, 1879; Ranzani *et al.,* 1962; Sombroek, 1966; Balee, 1986; Kern & Kampf, 1989, 1990). Pedological studies and morphological description and classification of their ceramics artifacts as important tools for understanding the peopling of the Amazon region were carried out (Ranzani *et al.*, 1962; Falesi, 1974; Simoes, 1982; Eden *et al.*, 1984; Kern (1988), Kern & Kampf (1989 E 1990), Kern *et al.,* (1997). Multi-element geochemistry was conducted at Caxiuana bay by Kern (1996), Kern & Costa, (1997) and Costa & Kern (1999). Although very abundant in the ABE sites, the fragments of ceramics artifacts have not yet been investigated. The first attempt was realized by Costa *et al.*, (2004), who studied the mineralogy of the fragments of ceramic artifacts from Cachoeira-Porteira. The present work carried out a chemical characterization of these materials, which represent the *Konduri* style culture (Nimuendaju, 1948), in order to complete the previous investigation of Costa *et al.*, (2004) and to contribute to understand the pre-historic peopling of the Amazon region. The results obtained until now show that the black earth may be a pedological, chemical and mineralogical modification of preexisting soils by pre-historic human (Indian) activities and settling in the later past time. Mineralogical and geochemical techniques have been successfully applied in the last decades to study archaeological artifacts in order to improve the interpretation of the archaeological data (Noll, 1978; Zaun, 1982; Letsch & Noll, 1983; Momsen, 1986, Freestone & Middleton, 1987; Redmont, 1996; Strazicich, 1999; Costa *et al.* 1991; Costa & Kern, 1996).

Along the Trombetas river and its tributaries, there are several archaeological sites (Ranzani *et al.,* 1962; Kern, 1988). Close to the village Cachoeira-Porteira (Oriximiná Municipality, state Pará), the investigated area on the Trombetas river, occu sever site of ABE (Fig.1).

The actual climate is rainy equatorial, with tropical forest. The drainage system is dense, the valleys are overflowed, and normally have a rocky bottom, and under these conditions water falls and/or rapids are present.

The soils are composed mainly by yellow to red *Latosols*, yellowish brown *Podzols* and *Structured Red Earth (Terra Roxa Estruturada)*. The ABE are classified as anthropogenic soils (Ranzani *et al.*, 1962, Kern, 1988; Kern, 1996), developed primordially over the llow *Latosols* and *Petroplinthosol* (Kern, 1988: Kern & Kaempf, 1989).

Paleozoic to Mesozoic sedimentary rocks (sandstones and claystones) of Lower Amazon basin covering the proterozoic volcanic acid rocks of Iricoumé Formation and the Mapuera Granite constitute the main geological units of the region and are crosscut by basic dikes. Laterite profiles caped by *Latosol*s are also common, as well as holocene clays, sands and pebbles on the riverbanks and lakes (Costa *et al*., 2004).

MATERIALS AND METHODS

Sampling

The fragments of ceramic artifacts of ABEs with distinct tempers investigated here were collected by MPEG (Museu Paraense Emilio Goeldi) in 1988, with the participation of co-author Dirse Clara Kern in antecipation of the lake projected for hydroelectric power of Cachoeira-Porteira. For the present work 51 samples of ceramic fragments covering all the types of tempers were taken from the sites 1 (PA-OR-73) and 2 (PA-TR-2) (Fig.1). After Meggers & Evans (1970) tempers are exotic material intentionally put in the ceramics during their confection. The identified tempers are mainly ceramic fragments with cariapé; ceramics with cauxi; ceramics with sand; ceramics with sand plus feldspar; and ceramics with older crushed ceramics. The sampling was performed along standard trenches along the soil horizons A_p, A_1, A_2 and A_3, the horizons that carry ceramic fragments. The mineralogical study of these materials was carried out by Costa *et al* (2004).
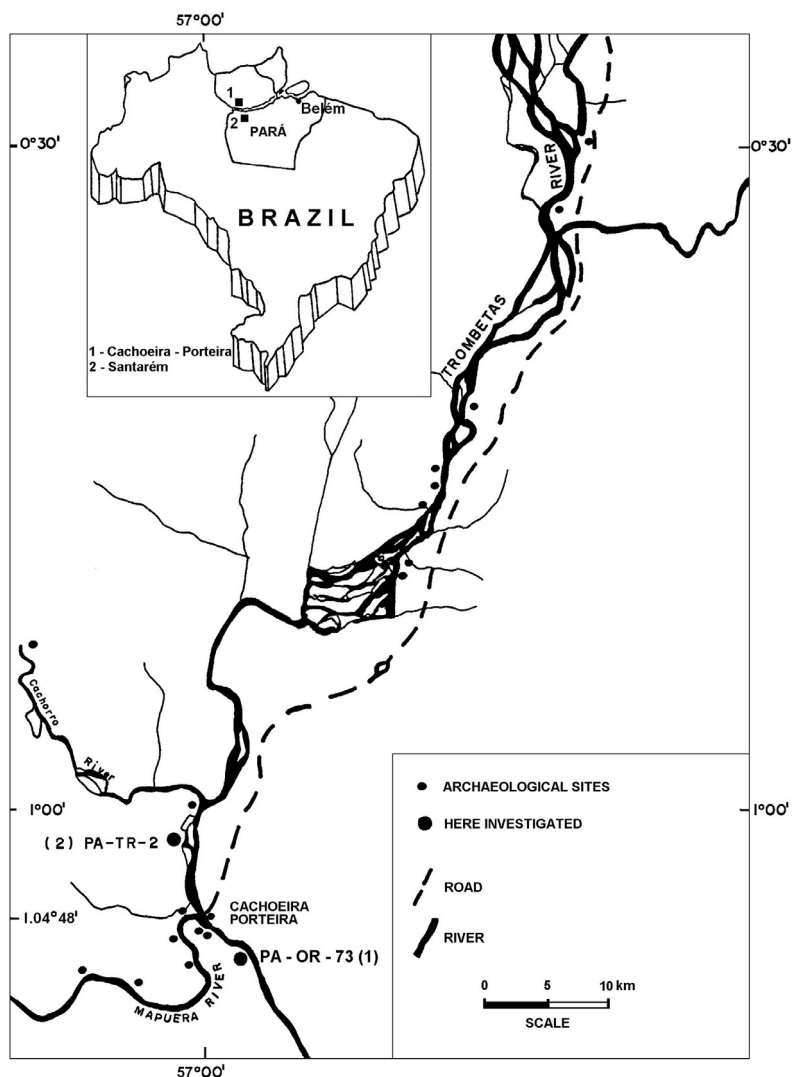
Chemical Analyses

Whole chemical analyses of 22 samples of ceramic fragments with distinct tempers were performed by XRF spectrometry, atomic absorption spectrometry and wet chemical methods in the Centro de Geociências from Universidade Federal do Pará-UFPa. XRF, OES (optical emission spectrograph), and ICP-AES were also performed in four selected samples for major and trace elements at Lakefield-Geosol (Belo Horizonte, Brazil). These four samples were also investigated by Scanning Electron Microscope with Energy Dispersive System at the laboratory facilities of the *Companhia Brasileira de Metalurgia e Mineração – CBMM*, in São Paulo, in order to get images and chemical analyses.

RESULTS AND DISCUSSION

Chemical Composition

To help understanding the chemical treatment and discussion of chemical analyses it should be very important to summarize the physical composition of the ceramic fragments after each temper described by Costa *et al.* (2004). Quartz and burned clay-derived mineral (originally interpreted to be kaolinite) are the more abundant minerals. Feldspars (albite and microcline) are frequent in ceramic

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Figure 1 – Location map of two sites of archaeological black earth (ABE) investigated at Cachoeira-Porteira, Lower Amazon region (after COSTA *et al.,* 2004).

fragments with sand and feldspar tempers. Illite, hematite, maghemite, goethite, and anatase are found in low quantities for all ceramic fragment tempers. Although in less quantities (3 to 11 wt.%) amorphous and microcrystalline aluminum phosphates are found all over the ceramic fragments. Cauxi and cariapé are the organic tempers found in several ceramic fragments, and after their presence are the ceramic fragments classified into cauixi or cariapé temper.

The results of the chemical analyses (Table 1) show small variation among the average of the different tempers. This is clearly demonstrated by diagrams SiO_2- Al_2O_3 - K_2O (Fig. 2) and Fe_2O_3 - P_2O_5 – TiO_2 (Fig. 3), where most samples fall close together, the ceramic fragments with sand+feldspar temper being less similar.

SiO_2 values vary from 63.5 to 70.8 wt. % (the average of each

ceramic temper), and those from Al_2O_3 from 14.7 to 17.4 wt %, and together comprise more than 80 wt.% of whole ceramic chemical composition. Fe_2O_3 is the third most abundant element and reaches 5.79 Wt. % on average. The alkali elements (as K_2O, Na_2O, CaO and MgO) constitute together less than 3 wt. %. On the other side come out the relative high contents of P_2O_5, 2.37 wt. % in average. The H_2O+ values reach 7.54 wt. % on average, which is still high for burned ceramic material (mainly clay material). The Al_2O_3 and H_2O+ contents explain the great abundance of clay-derived minerals.. The relative high contents of H_2O+ confirm the abundance of partial dehydroxylation of clay-material derived from kaolinite as main mineral of the ceramics and the neoformation of kaolinite (Costa *et al.*, 2004). It means that the fragments reabsorved water along its discarded and incorporation into ABE-soil formation. The extremely high SiO_2 contents correspond, besides clay-derived material and the abundance of quartz, as sand grains and rock fragments, to the presence of cauixi (*Tubella reticulata and Parnula betesil*), and cariapé (*Bignomiacea, Moquilea, Licania utilis, and Turiuva;* Hilbert, 1955). Cauixi and cariapé are the SiO_2-bearing organic materials (Costa *et al.*, 1991, 2004). The iron contents represent hematite and goethite, and some maghemite, minerals also identified in the studied ceramic fragments. K_2O, Na_2O and CaO built the feldspars (microcline and albite) and together with MgO indicate the presence of illite in the raw material. The predominance of SiO_2, Al_2O_3 and H_2O+ plus Fe_2O_3 (together they make up more than 93 Wt. % of whole sample) confirm clay-derived minerals, quartz and some iron oxyhydroxides as the main minerals of ceramic fragments . The chemical and mineralogical data, as well as textural aspects, leave one to conclude that the main raw material for ceramic elaboration comes from fine-grained clay-quartz rich material (for example saprolites, claystones, shales, and so on). The P_2O_5 contents however are relatively high for clay material normally used for ceramic purpose. They compose basically the amorphous to criptocrystalline (Al,Fe)-phosphate. The H_2O+ contents are still high (5.6 to 8.9 Wt %) showing the rehydration of the ceramic vessel after theeir discharging and the formation of the soil with black earth, the formation of ABE, and as consequence the neoformation of kaolinite and goethite after Costa *et al.* (2004).

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Table 1 - Whole chemical analyses of ABE-ceramics after their tempers (Wt.%).

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	BaO	P_2O_5	MnO	ZnO	H_2O^+	H_2O^-	CO_2
CAUIXI																
01	73.19	0.79	15.84	4.47	-	1.28	0.41	-	1.61	-	0.47	939.4	242.2	1.84	0.69	-
19	61.78	0.91	18.84	4.06	-	0.79	0.32	-	1.31	-	3.02	331.3	314.8	10.78	3.99	-
19 *	60.80	0.87	18.30	6.40	0.73	0.39	0.21	0.19	1.20	0.89	3.10	-	-	9.89	-	0.30
23	67.05	0.90	16.85	4.63	-	0.58	0.38	-	0.84	-	1.89	252.1	237.3	8.26	3.95	-
32	64.97	1.02	17.53	3.94	-	0.58	0.42	-	1.26	-	2.46	315.1	205.3	9.13	3.85	-
35	72.12	0.69	13.39	3.89	-	0.59	0.25	-	0.95	-	2.57	156.9	217.2	6.91	3.46	-
AVERAGE	66.65	0.86	16.79	4.57	0.73	0.70	0.33	0.19	1.20	0.89	2.25	339.0	243.4	7.80	3.17	0.30
CARIAPÉ																
04	62.26	0.98	16.96	7.59	-	0.76	0.43	-	0.39	-	3.03	205.6	341.3	9.53	4.24	-
04 *	57.18	0.96	18.30	6.40	1.30	0.57	0.53	0.46	0.47	0.14	3.30	-	-	9.81	-	0.40
08	60.61	1.02	17.34	7.99	-	0.81	0.41	-	0.66	-	3.05	168.4	276.3	9.07	3.19	-
14	60.75	1.02	18.25	8.18	-	0.75	0.40	-	0.79	-	3.26	140.7	267.4	8.06	3.12	-
25	66.11	0.84	15.99	6.86	-	0.47	0.36	-	0.69	-	2.49	205.1	205.6	7.70	4.00	-
40	65.18	0.95	15.60	6.77	-	0.71	0.38	-	0.45	-	2.82	157.1	147.1	8.62	3.57	-
41	68.27	0.74	13.39	5.77	-	0.30	0.30	-	0.13	-	3.15	202.8	50.1	9.00	2.91	-
49	63.26	1.02	16.42	8.52	-	0.30	0.28	-	0.45	-	2.03	93.8	133.6	9.47	3.08	-
AVERAGE	62.95	0.94	16.53	7.26	1.30	0.58	0.39	0.46	0.50	0.14	2.52	153.3	203.0	8.91	3.44	0.40
SAND																
05	72.22	0.81	13.26	4.81	-	0.59	0.36	-	0.59	-	2.09	203.6	216.8	6.65	3.30	-
12	72.53	0.75	12.88	4.60	-	0.72	0.35	-	0.64	-	2.19	124.1	254.0	4.69	2.88	-
16	68.15	0.86	16.23	3.67	-	0.31	0.33	-	1.29	-	1.81	217.1	135.9	7.88	2.35	-
22	69.29	0.98	16.59	2.88	-	0.16	0.26	-	0.43	-	3.08	266.7	159.7	7.39	3.45	-
AVERAGE	70.79	0.85	14.74	3.99	-	0.44	0.32	-	0.74	-	2.29	203.1	191.6	6.65	2.99	-
SAND + FELDSPAR																
02	62.19	0.83	17.43	7.66	-	0.70	0.77	-	1.42	-	2.52	172.0	241.9	6.49	3.11	-
18	61.80	0.78	17.94	6.93	-	1.30	0.84	-	1.91	-	1.14	502.7	243.1	6.32	3.49	-

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cont. table 1

	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	FeO	MgO	CaO	Na$_2$O	K$_2$O	BaO	P$_2$O$_5$	MnO	ZnO	H$_2$O$^+$	H2O$^-$	CO$_2$
SAND + FELDSPAR																
24	69.01	0.71	15.66	4.74	-	0.80	0.55	-	1.81	-	1.14	202.5	348.8	4.86	2.74	-
24 *	67.90	0.66	15.60	3.20	1.30	0.47	0.44	1.70	1.70	0.14	1.20	-	-	4.99	-	0.20
28	61.24	0.84	20.28	5.70	-	0.63	1.24	-	1.58	-	2.12	201.8	164.3	5.29	2.42	-
AVERAGE	64.43	0.76	17.38	5.65	1.30	0.78	0.77	1.70	1.68	0.14	1.62	269.7	249.5	5.59	2.94	0.20
CARIAPÉ + SAND																
07	66.37	0.89	15.87	8.85	-	0.81	0.43	-	0.72	-	2.53	313.4	262.8	7.12	3.30	-
15	65.59	0.86	15.62	6.82	-	0.63	0.33	-	0.48	-	2.80	219.8	236.5	8.33	3.50	-
15 *	64.60	0.79	15.40	5.20	1.10	0.41	0.21	0.42	0.45	0.76	3.30	-	-	8.07	-	0.30
AVERAGE	65.52	0.85	15.63	6.29	1.10	0.62	0.32	0.42	0.55	0.76	2.88	266.6	249.6	7.84	3.40	0.30
AVERAGE ALL TEMPERS																
	65.55	0.86	16.37	5.79	1.11	0.63	0.43	0.69	0.90	0.48	2.37	254.2	184.7	7.54	3.21	0.30
EARTH'S CRUST	55.20	1.60	15.30	2.80	5.80	5.20	8.80	2.90	2.90	0.05	0.30	2000				

Identification of the main raw material after chemical composition

The diagram SiO$_2$-Al$_2$O$_3$-10(K$_2$O) (Fig.2) show that ceramics have a single field composition, nearest to the field of granitic saprolite and then to shale and the Earth's crust average. On the other hand the average of each ceramic fragment temper studied here are aligned in a single field parallel to the P$_2$O$_5$-Fe$_2$O$_3$-edge of the diagram Fe$_2$O$_3$-TiO$_2$-P$_2$O$_5$ (Fig. 3), far from the Earth's crust composition, saprolite derived from granite and shale. This deviation is caused by the anomalous contents of P$_2$O$_5$ and indicates that P$_2$O$_5$ was not a part of the original material but was probably incorporated after the elaboration of the ceramic vessels, certainly during the their daily use and/or afterward the discard of them.

The contents of trace elements are similarly distributed inside of different ceramic tempers in the same way as the major elements. It means that the ceramic vessels independent of ceramic tempers were made of quite similar raw materials. If these elements are compared to their average in the Earth's Crust they show the following pattern: a) elements with contents clearly above the Earth's crust level: Zn, Ba, Pb, Zr, Y, Mo, Sc and Sn e; b) contents similarly to the Earth's crust average : Cu, B, La, Ce, Nd and Eu; c) contents below the Earth's crust average : Cl, Co, Ga, V, Y, Mn, Sm, Gd, Dy, Ho, Er, Yb and Lu).

The organic foreign materials, cauixi and cariapé, display a very low content of trace elements, specially cariapé (Table 2). Only Ba reaches 152 ppm in cariapé, although in the ceramic it can reach up to 0.89 wt. % of BaO. This BaO values is too high even for feldspar-bearing rocks. Locally Ba, sometimes Mn, are strong concentrated in the matrix as showed previously by SEM/EDS analyses. They form their own mineral, interpreted to be Mn-oxyhydroxides(Costa *et al*., 2004). Barium, phosphorus and even Pb seem to be the anomalous elements found in the ceramic fragments of Cachoeira-Porteira. The anomalous values of Ba were frequently found in the ceramic fragments with cauixi and cariapé+sand temper.

In general the contents of trace elements found in the ceramic fragments of Cachoeira-Porteira, can be well correlated to saprolites derived either from granites/rhyolites or to granodiorites/dacites. They can be slightly correlated to the Earth's Crust average as well. The higher contents of Zr, Sc and Sn might have been promoted by weathering processes forming the saprolite, confirmed by the decreasing of Cl, Co, Cu, V, Mn and heavy rare earth elements (Sm, Gd, Dy, Ho, Er, Yb and Lu) as demonstrated before. The contents of the rare earth elements (REE) fall in the domain of the Earth's crust abundance and granitic rocks and its weathered products.

The distribution curves of REE normalized to chondrites (Fig. 4) are quite similar to each other and display a negative Eu-anomaly and depletion toward HREE. This pattern falls close to granite-derived saprolite and is only partially comparable with the Earth's crust and granite average. Cauxi and cariapé present a distinct pattern with

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very low concentration of REE and therefore do not contribute to relative high concentration of REE found in the ceramic fragments.

Unlikely the saprolite formation can not promote the strong increasing of the contents of elements like Ba, Zn and Pb (expecting a weathering of acid igneous rocks or common clay sedimentary rocks). These elements similarly to phosphorus, La, Ce, Nd and Mn as earlier described, they (mainly Ba and Pb) were probably introduced after ceramic elaboration.

The major and trace elements indicate that the main raw materials used for the elaboration of the ceramic artifacts have a composition close do saprolite derived from acid rocks (fine-grained granite/rhyolite) or shales and claystones. However, elements like P, Ba and Pb (Zn) and their minerals present as foreign components of the raw materials. They may have been possibly incorporated only after the elaboration of the ceramic vessels, probably during cooking and other daily uses.

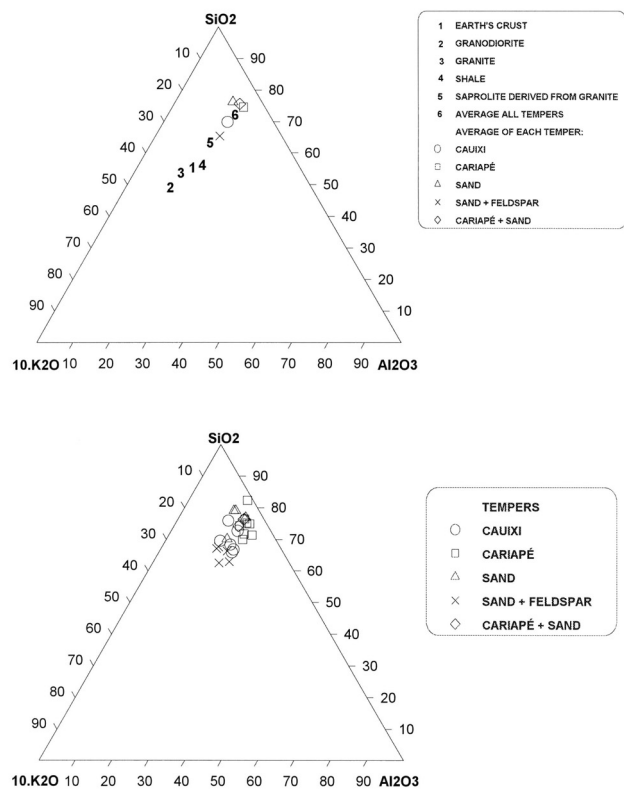## THE ORIGIN OF CERAMIC RAW MATERIAL AND THEIR TRANSFORMATION DURING USE AND DISCARD (AS ABE COMPONENT)

The raw material of the ABE-ceramics

Petrographical and chemical studies have been used by Redmount (1996) and Strazicich (1998) to identify the raw material and the source of ceramics from Egypt and Mexico, respectively. The chemical composition data obtained here and the textural and the mineralogical presented by Costa *et al.*, (2004) allow us to propose the following materials as raw materials for the ceramics of Cachoeira-Porteira:

1) **Clay materials** (mainly kaolinite) from the saprolite horizons or mottled zone of weathered fine-grained acid rocks, for example rhyolites and/or fine-grained granites or even clayey sedimentary rocks (shale). The high contents of Al_2O_3 and SiO_2 are compatible to kaolinite-rich saprolite or mottled zone derived from that kind of rocks;

2) **Slightly coarse crushed igneous rocks**, e.g. granites, granodiorites, rhyolites and quartz of veins; they explain the presence of unweathered feldspars and roundless quartz grains (Costa *et al.*, , 2004) and the relatively high content of K, Na and Ca for the inferred saprolite. The addition of quartz grains , cauixi and cariapé has only promoted a slight unbalancing in SiO_2 relatively to Al_2O_3 turned the composition a little far from Earth's Crust level (Fig. 2). In contrast, the feldspar grains
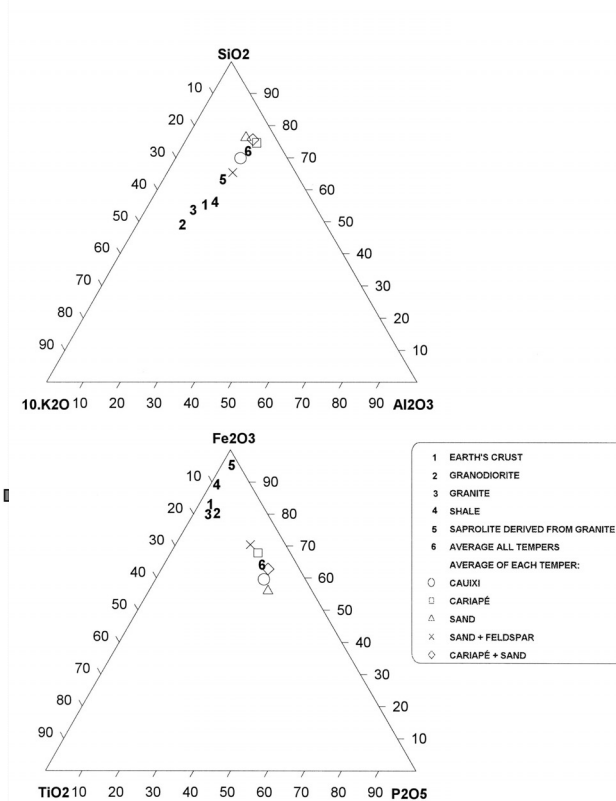

Figure 2 - Chemical composition of the ceramics on the diagram SiO_2-$10K_2O$-Al_2O_3 compared to the composition of Earth's crust abundance, granite, granodiorite, shale and granitic saprolite

Figure 3 - Chemical composition of the ceramics on the diagram Fe_2O_3-TiO_2-P_2O_5.

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Table 2 - Trace element contents (in ppm) of ABE-ceramics after their tempers, and of cauixi and cariapé.

SAMPLES	Cl	Co	Cu	Be	B	Zr	Ga	Mo	V	Sc	Y	Sn	Pb	Zn	Sr
CERAMICS															
CCP - 04	56	9	72	<2	<10	380	<5	152	17	50	<5	45	182	130	
CCP - 15	4	8	46	<2	<10	375	<5	116	17	48	<5	45	132	86	
CCP - 19	48	8	40	<2	<10	375	<5	152	16	68	<5	60	128	42	
CCP - 24	29	10	36	<2	<10	580	<5	180	13	42	<5	40	132	400	
AVERAGE	34	9	49	<2	<10	428	<5	150	16	52	<5	48	144	165	
CAUIXI			21	-	19	27	<5	5	120	<5	12	-	22	<200	-
CARIAPÉ			10	-	19	<10	<5	<5	63	<5	<10	-	<10	<200	-
EARTH'S CRUST *	130	22	50	3	10	165	18	1.5	110	20	35	2.5	12.5	70	375

SAMPLES	Ba	Cr	Mn	Ni	La	Ce	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu
CERAMICS															
CCP - 04					45.40	95.52	37.07	5.415	1.070	3.736	2.867	0.575	1.563	1.613	0.25
CCP - 15					39.52	83.26	29.96	5.055	0.924	3.583	3.191	0.655	1.842	1.920	0.25
CCP - 19					32.13	69.20	26.96	4.814	0.859	3.338	3.035	0.624	1.774	1.868	0.24
CCP - 24					23.82	51.72	22.54	3.947	0.097	2.729	2.334	0.488	1.426	1.411	0.20
AVERAGE					35.22	74.84	29.13	4.810	0.940	3.350	2.857	0.585	1.651	1.710	0.24
CAUIXI	44	18	58	19	5.945	11.20	3.77	0.380	0.108	0.325	0.292	0.050	0.130	0.172	0.03
CARIAPÉ	152	22	25	17	9.854	18.55	3.28	0.600	0.067	0.310	0.235	0.042	0.110	0.128	0.02
EARTH'S CRUST *	500	100	1,000	75	35	70	30	7	1.2	7	6	1.5	3.5	3.5	0.6

obviously kept some Na_2O, CaO, and K_2O inside the clayey matrix, which can be observed in the chemical analyses of these ceramics (Table 1);

3) **Cauixi and/or cariapé**. They cannot be found naturally in saprolite or mottled zone. Cauixi can be observed in some young lake sediments and water column e.g. Caxiuanã bay in Eastern Amazon; cauixi are found as cm-long aggregates fixed in the trees on the margin of rivers and lakes with clear or black water, as well as dsitributed on the surface of bottom sediments of lakes and some black water rivers. Cariapé is a tree skin found in the neighboring forest. Both materials rich on SiO_2 are common in the Amazon region and in the area studied here.

4) **Older discarded ceramics**. They possibly represent discarded ceramic vessels, that were intentionally fine crushed for reuse. The fine fragments obtained can be well characterized under optical microscope;

The texture of ceramics shows that the clay-derived matrix was the basic raw material into which crushed rocks and/or crushed minerals (feldspars and quartz), quartz sand, cauixi and/or cariapé and/or older ceramics were intentionally added. After the archaeologists the last four main components (crushed rocks, and minerals; quartz sand; cauixi und cariapé; and old ceramics) intentionally added are denominated tempers (Meggers & Evans, 1970) and used to classify the archaeological ceramic fragments.

On the other hand there is no evidence of phosphorus- and barium-lead-bearing raw material .

The Source Area of Raw Material

Weathered and unweathered rhyolites, granitic and granodioritic rocks occur quite near to the sites 1 and 2 (COSTA *et al*., 2004). Cauixi is found to the present day in many lakes and rivers near archaeological sites and in many places of the Amazon region. Cariapé can be found in the surrounding rain forest (Fig. 5) as well. The region is also rich in archaeological sites with ABE and potteries, that can be recycled.

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Origin of Phosphorus and Phosphates and Other Elements like Mn and Ba.

Phosphorus is one of the few chemical elements, which are completely anomalous in the investigated ABE-ceramic artifacts. The contents of P_2O_5 range from 1.7 to 2.8 wt. % (average of each tempers) and are represented basically by variscite-strengite and amorphous phosphates; apatite and rhabdophane are rare. Freestone & Middleton (1987) reported contents of P_2O_5 in similar range within the clay matrix in some Far East ceramics. There the clay source and local soils contain less than 0.5 wt. %. The local soils of Cahoeira-Porteira also show low P_2O_5 values, less than 0.036 wt. % (Kern, 1988). In the modern ceramic artifacts, 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, 1987). Freestone & Middleton conclude that P_2O_5 content is a result of environmental contamination. The mineral, a calcium phosphate but not apatite, is very fine-grained. In Cachoeira-Porteira, the ceramic is not vitrified and the phosphorus contents in the ceramic fragments do not correlate with CaO, under relatively low contents. Phosphorus forms (Al-Fe)-phosphates alone.

The ceramic fragments represent potteries of daily use, for cooking and stocking foods. The diets of the ancient Indians were similar to that of todays, basically of animal and vegetal origin. This diet includes meals make up of bones, liver, crumb, bowels, etc. as well as many different types of roots such as manioc, potatoes, yam, fruits of palm trees, different chestnuts (Brazil nut, and so on). Most of these foods may contain a high content of P_2O_5 as well as Mn, Ba, Mg, Zn, (Pb) (Scholz, 1980). The meals with bones and fishes, as well as nuts, were certainly the most important source of phosphorus. During long and repeatedly cooking and stocking of food there was transference of food components into ceramic vessels, that were even porous. During the cooking with much boiling water, which corresponds to a true high temperature water solution (hydrothermal solution), rich in the above mentioned elements released from the foods (Fig.6), like phosphorus, they go into the solution (broth or soup), and react with the clay-derived groundmass, disordered or amorphous. Disordered or amorphous clay or even crystalline clay minerals and iron oxyhydroxides react with phosphorus forming aluminous and iron phosphates such as variscite-strengite, crandallite group, wavellite, and so on (Kittrick *et al*., 1955; HSU, 1968; Kafkafi *et al.,* 1967; Yariv *et al*., 1979 and Costa, 1982) . In the archaeological ceramic fragments of Cachoeira-Porteira on average 94% of the phosphorus is absorbed (Table 3) in the mineral structure, confirming the presence of the phosphate phases. The kinetic of the phosphates formation increases under hydrothermal condition, and the cooking of food may be assigned as hydrothermal environment. The reactions for phosphate formation can be written as follows.
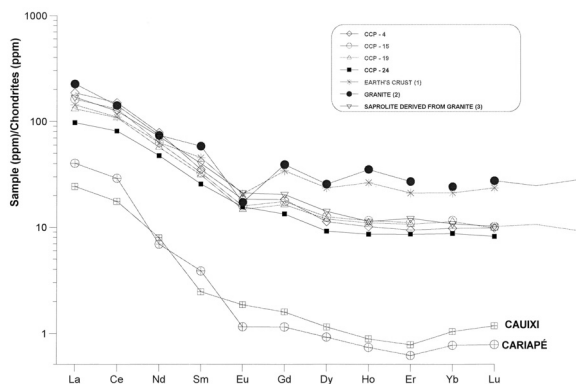
Figure 4 - REE concentrations normalized to chondrites and compared to Earth' crust abundance, granite, granitic saprolite, and cauixi and cariapé. (1)(2) KRAUSKOPF (1982); (3) DUDDY (1980). Chondrite REE were normalized after abundances of chondrites in WAKITA *et al.* (1971).

Source of clays and rocks
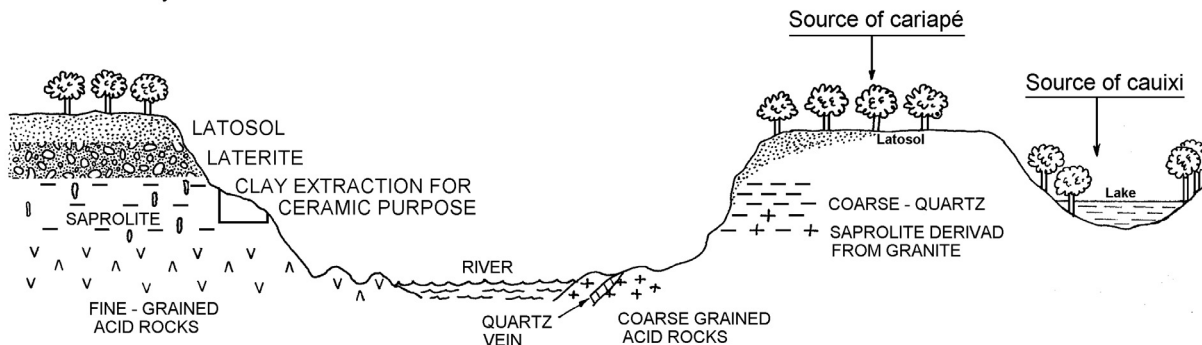
Figure 5 – Simplified geological cross-section showing the different sources of raw materials of archaeological potteries from Cachoeira-Porteira. After COSTA *et al.,* (2002).

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Table 3 - Disposable and total phosphorus in ABE-ceramics.

SAMPLES	DISPOSABLE PHOSPHORUS (ppm)	TOTAL PHOSPHORUS(ppm)	% OF DISPOSABLE PHOSPHORUS TO TOTAL PHOSPHORUS
CCP-25	398	10,776	3.7
CCP-26	580	17,241	3.4
CCP-27	2100	18,996	11.1
CCP-28	842	7,698	10.9
CCP-29	351	15,733	2.2
CCP-30	323	10,490	2.2
CCP-31	189	14,655	1.3
CCP-32	814	9,602	8.5
CCP-33	291	7,602	3.8
CCP-34	255	9,267	2.7
CCP-35	1753	10,146	17.3
CCP-36	765	5,819	13.1
CCP-37	400	13,793	2.9
CCP-38	281	9,063	3.1
CCP-39	374	6,897	5.4
CCP-40	514	11,638	4.4
AVERAGE	639	11,212	6.0

$Al_2Si_2O_5(OH)_{4(s)} + 2H_3PO_{4(aq)} + 3H_2O \Leftrightarrow 2AlPO_4.2H_2O + 2Si(OH)_{4(aq)}$ or $SiO_2.H_2O_{(s)\ (1)}$ Kaolinite (clay) in boiling water variscite opal (ceramic body) water (broth or soup) (end-use of ceramics) $Fe_2O_3 + 2\ H_3PO_{4(aq)} + H_2O \Leftrightarrow 2FePO_4.2H_2O_{(s)\ (2)}$ hematite strengite.

H_3PO_4 comes possibly from the desagregation and decomposition of organic material mainly bones and fishes during cooking, besides vegetal diet. The anomalous concentrations of Ba, Zn and Pb (also Zr, Sc and Mo) in whole ceramics and of Ba and Mn in some places of clay-derived matrix might have come from animal and vegetal foods and precipitated as (Ba,Mn)-oxyhydroxides, similarly to phosphates. This makes possible the potteries contamination by foods during cooking (Fig.6). This process might be responsible for promoting the formation of phosphates, manganese and barium oxides as mineral equivalents. The short time of the reactions (no older than the culture itself, 900 to 400 years BP) and low temperature (cooking temperature) can explain the low crystallinity and the very fine-grained nature of these neoformed minerals. It is possible that this kind of reactions (and contamination) may continue after the discarding of the ceramics (wastes) and during their incorporation into anthropic soil profile developed at the time of the settlement and after the abandonment of it (Fig.6), the formation of the black earth (ABE). The formation of phosphates, and locally of Ba, Mn and REE minerals equivalents suggest that the pre-historic settlements at Cachoeira-Porteira were occupied by gathering and hunting people who stayed for a long time in the site, and possibly came back to the site several times..

The Geochemical Evolution of ABE-Ceramics

900 to 400 years BP the pre-historic peoples lived in small groups along the margins of Trombetas/Nhamundá rivers and their lakes. For their daily necessities of transport, water keeping and food cooking, they made many ceramic artifacts (potteries). The majority of the artifacts were slightly painted and burned. The raw materials for making the potteries came certainly from neighboring areas close to sites and include clay material from a saprolite or mottled zone derived from rhyolite/granite or from shales. Other materials are cauixi, cariapé and crushed rocks. All these materials are abundant in the area. This is the motive we assumed that the pre-historic peoples collected the raw materials around the area, close to the sites. The ceramic matrix is composed of Si, Al, Fe, Ti and Mg (Fig. 6), which shows its still clayey composition. To improve the plasticity properties of this

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matrix the Indians intentionally added either cauxi, cariapé, quartz sand or crushed rocks and feldspars, that promoted a SiO_2-enrichment, sn important chemical aspect of the tempers. The addition of feldspars, which obviously contributes with K, Na and Ca into raw material improves the firing temperature.

The firing of the potteries occur in open atmosphere (Fig.6), possibly in the same primitive way as the actual Indians and caboclos still do. The firing temperature didn't exceed 600 °C, as demonstrated by partial dehydroxylation of clay material and the formation of maghemite. This phase formed **the ceramic minerals:** dehydroxylation of clay giving rise to burned clay, maghemite and recrystallization of anatase. Maghemite promotes the slightly brown to red color of the potteries.

After much firing potteries were used for daily purposes as cooking and conserving foods. At this phase they get in contact with meals, fishes, roots and so on, in boiling water, become contaminated and form minerals like aluminum phosphates and Ba-Mn oxyhydroxides mineral equivalents (**post-ceramic minerals**), which may contain the elements Mg, Ca, Ba, Zn, Pb, Y, and so on.

Finally the potteries after several uses become old, break down and are discarded together with many other organic (vegetal and animal) material waste. Gradually the biological and chemical-weathering agents which are very active under the humid and tropical climate in the region for the last 10.000 years, attack them. After the people leave the site the rain forest envelopes the area and the weathering becomes more active and develops the soil profiles incorporating the great organic matter coming from pre-historic people waste. Chemical elements such P, Mg, Ca, Mn, Ba, Zn, Pb, etc. are fixed partly and concentrated in the organic humus of ABE soils and possibly is partly absorved in the ceramic fragments, contributing to formation of phosphates and Mn oxyhydroxides in less extension. During this phase the clay-derived materials and hematite/maghemite rehydrated and form kaolinite and goethite, respectively (post-ceramic minerals or pedogenic minerals)(Fig.6). The concentration of ceramic fragments in the A horizons shows that the ABE development is restrict to the top of pre-existing latosols. The high content of organic matter of the A horizons explains its gray color, caused the deferrugination the outer skin of the ceramic fragments, which become yellowish gray.

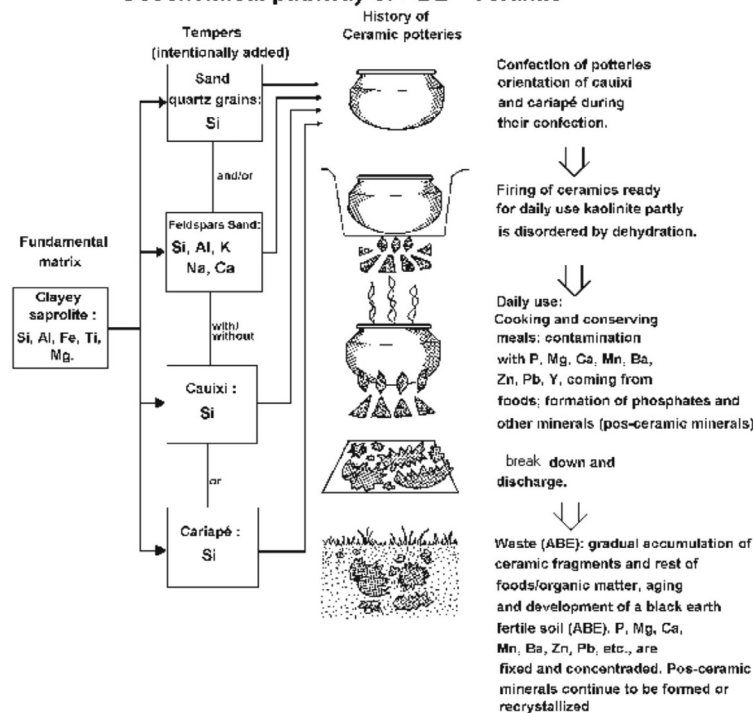**Figure 6 -** The geochemical pathway (evolution) of ceramic fragments (potteries) found

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