


# Study of exchange networks between two Amazon archaeological sites by INAA

Roberto Hazenfratz<sup>1</sup>  · Casimiro S. Munita<sup>1</sup> · Michael D. Glascock<sup>2</sup> · Eduardo G. Neves<sup>3</sup>

Received: 15 September 2015 / Published online: 8 March 2016  
© Akadémiai Kiadó, Budapest, Hungary 2016

**Abstract** This work comprises the utilization of instrumental neutron activation analysis to determine the concentration of 24 chemical elements in pottery shards from two large archaeological sites in central Amazon, Lago Grande and Osvaldo. The multidimensional data set was analyzed by cluster and principal component analysis for defining chemical groups of pottery. The results were correlated to potential exchange networks driven by three mechanisms: trade, exogamic marriage and territorial integration in the region. All of them have important consequences for archaeological research regarding the Amazonian pre-colonial occupation.

**Keywords** Archaeometry · Amazonian pottery · Neutron activation analysis · Amazonian archaeology · Multivariate analysis

## Introduction

One of the main objectives in Archaeology is the study of ancient human groups by their material vestiges. As it is not possible to observe the human behavior of those

societies directly, the analysis of those materials vestiges is essential [1]. In many parts of the world, pottery shards are the most common type of artifact due to their high resistance to most physical–chemical soil conditions. Their macroscopic characteristics as decoration, color, form and function make them useful cultural and chronological indicators in Archaeology [2].

On the other hand, the microscopic characteristics of pottery shards, as their elemental chemical composition, can be used to infer their origin and possible trade routes, location of sources of raw materials for the ceramic production, production methods, among other aspects [3].

Trace elements, like the lanthanides and some transition metals, are important in physical–chemical characterization of archaeological ceramics due to their geochemical properties. They are found typically dispersed in nature, and their concentration profiles depends on the igneous rock formation and contribute to differentiate between ceramic materials made of different clays, which are formed by weathering of the original rocks [4, 5], as expressed in the *provenance postulate* [6]. One of the most employed techniques for elemental characterization of ceramics is neutron activation analysis [7, 8], which is suitable in terms of analytical accuracy and precision for trace elements quantification and needs only  $\approx 100$  mg of sample for adequate analysis. This is important in research designs in which sample destructiveness is a factor to be minimized.

In this interdisciplinary work, instrumental neutron activation analysis (INAA) was applied for quantitative determination of trace and some microelements in ceramic material from Central Amazon, in the confluence region of Negro and Solimões rivers in Brazil. The sites selected for sampling were Lago Grande and Osvaldo, which represent a microcosm of the region that is suitable to test

✉ Roberto Hazenfratz  
roberto@usp.br

<sup>1</sup> Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, University of São Paulo, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, CEP 05508-000 São Paulo, Brazil

<sup>2</sup> Archaeometry Laboratory, University of Missouri Research Reactor, 1513 Research Park Drive, Columbia, MO 65211, USA

<sup>3</sup> Museu de Arqueologia e Etnologia, Universidade de São Paulo, Av. Prof. Almeida Prado, 1466, Cidade Universitária, CEP 05508-900 São Paulo, SP, Brazil

archaeological hypotheses. The material analyzed was excavated under the context of Central Amazon Project (PAC), coordinated by Prof. Eduardo Góes Neves, from the University of São Paulo, in cooperation with the Federal University of Amazon.

## Archaeological framework

By the end of the fifteenth century, the Amazon basin was densely occupied by different indigenous people. The first European travelers in the region wrote about the existence of large settlements, occupied by thousands of peoples and interconnected by roads in extensive commercial networks and regional political federations [9]. That picture contrasts with the current ethnographic situation, characterized by sparse occupations with low demographic density, in which the activities are organized by age and genre structures.

The perspective of the environmental determinism is that the Amazonian pre-colonial occupations were similar to the current ethnographic picture. In this way, the existence of complex human organizations would not be possible in the tropical forest, due to natural limitations that would stimulate an intense mobility of its inhabitants [10, 11]. Under this perspective, the high degree of material vestiges in the archaeological record would be the result of multiple reoccupations.

One of the alternative perspectives arguments in favor of large settlements in the pre-colonial period, called *cacicados*, which would be based in a hierarchic organization with a center of power of regional reach. In this way, this critical view tries to diminish the role of environmental difficulties as a limiting factor for the emergence of complex societies, which contrasts with the current ethnographic picture. The decrease and dispersion of populations would be linked to the European colonization, which brought sickness, war and slavery to those people [11, 12].

Ceramics have been classified in groups (phases) in Central Amazon since 1968, by German archaeologist Peter Hilbert [13], establishing a chronology for the cultural groups that lived in that place prior to the European contact. The refined chronology based on  $^{14}\text{C}$  dating may be found in Table 1.

Those ceramic phases were defined based on the decoration, form of the vessel, and mostly on the kind of temper used in the paste. The two phases discussed in this work, Manacapuru and Paredão, are linked to an early macro-ceramic complex called Incised Rim tradition, that is characterized by the use of *cauixi* (a river sponge) as temper, and has a geographical distribution that extends from de Orinoco Basin up to the Upper Xingú, in Brazil. They also have other shared general characteristics such as

**Table 1** Ceramic chronology for the central Amazon based on  $^{14}\text{C}$  dating

Ceramic Phase	Period (century)
Açutuba	III B.C.–III A.D.
Manacapuru	VI A.D.–X A.D.
Paredão	VIII A.D.–XI A.D.
Guarita	IX A.D.–XVI A.D.

Source [13]

large rims; the presence of plastic decorations (incisions) frequently on the rim surfaces; and presence of red engobe.

The sites Lago Grande and Osvaldo are located in the confluence region of the Negro and Solimões rivers in the Central Amazon, Brazil (Fig. 1). The confluence region is formed by hills and mounts, crossed seasonally by *igarapés* (narrow water channels). The Amazon forest is the original vegetation of the region.

The Lago Grande site has around  $500 \times 400$  m and is located in one of the spits that extends into the Grande Lake. It was chosen for intensive excavation because it presents high archaeological material density associated with dark earth and well-preserved structures, such as defensive trenches in strategic locations. The ceramic material was found up to 1 m deep [15]. Most pottery shards found in Lago Grande are representative of Paredão ceramic phase. However, Manacapuru pottery shards were also found in lower proportion. The latter ceramic phase is related to the same ceramic tradition as Paredão, but dominates the archaeological record of other sites, like Osvaldo.

The Osvaldo site is a spit of  $700 \times 250$  m, limited by the Limão Lake north and by *igarapés* east and west. Archaeological remains were found up to 1 m deep and in association with dark earths. Most of the ceramic material is classified as Manacapuru. Nevertheless, it presents Paredão ceramics in lower proportion. It is believed to present a single component context, characteristic of a unique occupation. It makes Osvaldo important to study settlement patterns and the use of space [13].

Lago Grande and Osvaldo are located around 9 km of each other, which makes them interesting to study potential exchange networks. Previous studies [13–16] identified pottery shards that do not represent the characteristic ceramic phase of each site. Manacapuru ceramics in Lago Grande and Paredão ceramics in Osvaldo could have an external origin, and be a correlate of an exchange network as they were contemporary for some time. That potential network could be part of a broader context related to a regional system of interaction, which have already been observed in other regions of Amazon, but has not been intensively investigated in its central region. Those systems



**Fig. 1** Lago Grande and Oswaldo archaeological sites in the Negro and Solimões rivers confluence region. *Source* Ezilon maps and [14]

would be characterized by common ideology and cultural aspects, extensive exchange networks, exogamic marriages and inter-communitarian alliances.

The study of Lago Grande and Oswaldo is interesting for theories that try to contest the ecological determinism, as those sites are located in regions that are not alongside the watercourse of Negro and Solimões rivers, which would be the best region to get natural resources for life. They contain dark earth in the archaeological record, which may be a correlate that the former inhabitants practiced agriculture and fishing. In this way, they would overcome the natural difficulties imposed by the tropical forest environment by a combination of activities to obtain food and other resources [14]. That dynamic could create the conditions for the emergence of social complexity and sedentary occupations in the region [11, 17, 18].

### Materials and methods

The approach adopted in this work comprises the sampling of ceramic material from Lago Grande and Oswaldo archaeological sites, with unknown origin of raw materials. INAA was carried out for the determination of the elemental concentration profiles. Due to the number of variables generated (24 elements), multivariate pattern recognition and reduction techniques were applied for grouping samples with similar elemental composition, seeking for geochemical and archaeological evidences to justify the definition of such chemical groups.

### Instrumental neutron activation analysis (INAA)

Approximately 200 ceramic fragments were chosen for elemental analysis. The samples from Lago Grande were

excavated in three regions with a high density of archaeological vestiges [15], which many archaeologists believe to be associated to reuse of materials for house elevation or funerary purposes. For this reason, it was considered a convenient area to represent the archaeological record of Lago Grande. Furthermore, all the stratigraphic levels were represented. The samples from Osvaldo represent the stratigraphy from the surface down to the levels associated with the highest density of ceramic materials (concentrated in 0–40 cm) and the presence of dark anthropogenic soils, sampled in a large area of the site.

The lateral external surfaces of pottery shards, without decoration, were removed with a tungsten carbide sharpening rotary file. After this procedure, holes were made on the samples with a tungsten carbide cutter rotary file (diameters of 1.5 and 2.2 mm), attached to a variable speed drill. Around 500 mg of powdered sample were obtained from 3 to 8 holes on the side surface of the ceramic fragment, preventing the drill from crossing over the walls. That powder was then collected, dried for 24 h in an oven at 104 °C and stored in desiccators for posterior weighing [19, 20].

Around 120 mg of each sample were weighed in polyethylene involucres and sealed with sealing iron. Each involucres was wrapped in aluminum foil. Groups of up to 7 ceramic powdered samples and two reference materials were wrapped in another aluminum foil, in order to group them in a parallel fashion to receive approximately the same neutron flux inside the nuclear reactor. The Standard Reference Material NIST–SRM 1633b was used as standard for analysis and IAEA–Soil-7 for the analytical quality control [21]. The samples were irradiated in the swimming pool research reactor IEA – R1 of the Nuclear and Energy Research Institute, in São Paulo, at a thermal neutron flux of  $1.2\text{--}1.6 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  for 8 h, for most of the samples.

The gamma-ray spectrometry was carried out with a hyper pure germanium detector (model GX 2519 from Canberra), with a resolution of 1.90 keV at the 1332.5 keV gamma peak of  $^{60}\text{Co}$ . The spectra were collected by a Canberra S-100 MCA plate with 8192 channels. The software Genie-2000 Gamma Acquisition & Analysis, v. 3.1.a, developed by Canberra, was used to analyze the gamma-ray spectra.

Two measurement series were carried out. The elements As, K, La, Lu, Na, Nd, Sb, Sm, U and Yb were measured after 5–7 days of decay. The elements Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Tb, Th and Zn were measured after 25–30 days of decay.

### Multivariate statistical analysis

All the concentrations were reported in  $\mu\text{g g}^{-1}$  prior to any transformation. It is recommended to rescale the data

before applying multivariate analysis to compensate differences of scale in the elemental concentrations. It contributes to homogenize the weights of the variables in multivariate analysis [22]. It might also improve the condition of normality, assumed in many multivariate techniques. In archaeometric studies, the elemental concentrations are frequently logarithmically transformed based on the assumption that trace elements have a lognormal distribution in many geochemical contexts [23–25], although formal tests should be performed prior to further conclusions about data distribution. In this work, the elemental concentrations were rescaled to base-10 logarithms.

Many multivariate methods are sensitive to outliers and it is convenient to identify and remove them before analysis. The quadratic Mahalanobis distance matrix between each sample coordinates vector and the mean vector was calculated by a routine developed in *Scilab* software. The values were compared with the critical value of Wilks for identification of multivariate outliers [26].

Cluster analysis (CA) for the log-transformed data was carried out as implemented in the *MURRAP* software, according to Eq. (1). In this hierarchical clustering method, the measure of distance between groups to be minimized is the average of the distances of their elements:

$$d[G_1, G_2] = \sum_{j \in G_1} \sum_{k \in G_2} \frac{d_{jk}^2}{g_1 g_2} \quad (1)$$

where  $g_1$  and  $g_2$  are the number of samples in clusters 1 and 2 and  $d_{jk}^2$  is the Squared-mean Euclidean distance (SMED) between the logarithms of concentrations, given by (adapted from [23]):

$$d_{jk}^2 = \frac{1}{\min(p_j, p_k)} \sum_{i=1}^{\min(p_j, p_k)} [\log(C_{ij}) - \log(C_{ik})]^2 \quad (2)$$

where  $p_j$  and  $p_k$  are the number of variables (chemical elements) available for samples  $j$  and  $k$ , and  $C_{ij}$  is the concentration of element  $i$  in the sample  $j$ . The advantage of this metric is that eliminates problems regarding missing values, as it averages over only the elements with concentrations higher than the detection limit for INAA. It prevents from estimation of such values or elimination of samples.

Visual inspection of dendrograms from cluster analysis is a useful method for the identification of preliminary groups, working properly for discrimination of groups of high hypersphericity and multidimensionally well separated. However, it can fail in data sets with high correlation between variables. To minimize this problem, the groups defined in the clustering procedure were refined using the Mahalanobis distances of samples to the group centroids

and associated to F distribution to calculate the pertinence probabilities to each group [23].

The principal component analysis (PCA) was carried out for dimensionality reduction and visualization of the groups defined in CA. This reduction is obtained by the transformation of the original variables in a new set of uncorrelated ones, the principal components, extracted in such way to maximize the system variance explained by the first few components. PCA was carried out with the covariance matrix [27], as the data set was already log-transformed to compensate scale differences.

The softwares used for the statistical treatment were *MURRAP* 8.6, developed at the MURR Archaeometry Laboratory, *R Statistical Package* 2.13.0, and *Scilab* 5.2.2.

## Results and discussion

The analytical quality control of INAA results was carried out by irradiating the reference material IAEA-Soil-7 as an unknown sample within the batches of ceramic powder samples. The details can be found in [28]. Fifteen elements were selected according the analytical quality parameters ( $s < 15\%$  and Bias  $< 10\%$  for approved elements and Bias  $< 25\%$  for warning elements): As, K, La, Lu, Na, Yb, Ce, Co, Cr, Cs, Eu, Fe, Hf, Sc and Th. All those elements presented coefficients of variation lower than 15% and only K presented that value higher than 10% (14.4%). Correction for uranium fission by fast neutrons was not necessary for the data set, as 82% of its concentration in pottery shards were lower than  $5\ \mu\text{g g}^{-1}$ , a value suggested as reference for those corrections [23]. Additionally, interferences due to the plastic involucre were discarded according to INAA results, since all the elements of interest presented concentrations lower than the detection limit. The element Co was removed from multivariate analysis due to evidences of contamination in the sample preparation using a tungsten carbide rotary file [28, 29].

Among the elements selected, only Na, K and Fe were not measured in concentrations in the order of  $\mu\text{g g}^{-1}$  or lower in the ceramic data set. The mean concentrations of the chemical elements measured in this work are presented in Table 2.

By analyzing Table 2, it is possible to observe a general tendency of lower coefficients of variation for the clay sources near Osvaldo site. This is an expected result considering that non-plastic materials (like sand, crushed shards and shells) may be added to the paste in the ceramic production, and even different sources of clay might be selected. In the case of Lago Grande and Osvaldo, archaeological analyses found that the main temper used was *cauxi*, a fresh water sponge [13]. Crushed shards and *cariapé*, a material extracted from trees, may also be found

as secondary sources of non-plastic materials in Paredão and Manacapuru ceramics.

Ratios between concentrations of chemical elements in *cauxi* and pottery shards were calculated combining INAA results. The ratios varied between 3% for sodium and 26% for iron. Iron can be found covering silica spicules mainly as  $\text{Fe}_2\text{O}_3$  of fluvial origin [30].

Approximate estimations of the area fraction of spicules in optical microscopy in relation to the remaining components in the ceramic paste were always below 20%. Assuming proportion in area equal to proportion in volume, a mass density of  $2\ \text{g cm}^{-3}$  for *cauxi* [31] and  $1.3\ \text{g cm}^{-3}$  for the pottery shards, the mass fraction of *cauxi* in the samples was estimated as lower than 30% for the 17 samples observed in the optical microscope. Ignoring any volatility of the chemical elements associated to the biogenic silica during the ancient firing by former inhabitants of Lago Grande and Osvaldo, the maximum dilution in the elemental concentration in pottery would be always lower than 22.2% for iron (the least affected element) and lower than 29.1% for sodium (the most affected element).

From the previous estimations, it would be inferred that all the chemical elements concentrations should present patterns of dilution due to the insertion of temper during ceramic manufacture. Nonetheless, it was observed strong patterns of chemical enrichments for the elements sodium ( $\approx 300\%$ ) and potassium ( $\approx 60\%$ ) in the pottery shards, which was considered as an indication of diagenetic effects.

The criteria to choose the chemical elements selected for analysis among the total 24 elements measured by INAA were the acceptance in the quality control analysis, a minimum value for missing values (10%) and the inexistence of interferences. In this sense, fourteen elements were selected for CA and PCA: As, K, La, Lu, Na, Yb, Ce, Cr, Cs, Eu, Fe, Hf, Sc and Th. Potassium had around 20% missing values, but it was maintained in the analyzes to investigate evidences of enrichment due to diagenetic effects.

Eleven multivariate outliers were found among 177 analyzed samples with no missing values in the elemental concentrations. The reasons for the existence of outliers can be improper analytical determination, but it is not the only possible explanation. No clear patterns were identified for the outliers. Problems in the analytical determination for three of the outliers were identified. The remaining eight samples classified as outliers were tagged with a “Warning” status and maintained in the multivariate analysis as they might represent different chemical groups underrepresented in relation to the dominant ones, diagenetic effects or intentional modification in the ceramic production. In the case where they did not yielded useful information, they were eliminated.

**Table 2** Descriptive parameters for the concentrations of chemical elements in pottery shards from Lago Grande and Osvaldo archaeological sites in Central Amazon

Element	<i>n</i>	Lago Grande		Osvaldo		Osvaldo fired clays	
		Mean	$\sigma$ (%)	Mean	$\sigma$ (%)	Mean	$\sigma$ (%)
As	176	8.2	39.6	5.7	56.9	9.9	24.3
K (mg/g)	142	11.2	45.9	10.0	41.5	6.5	45.8
La	181	42	27	42	25	82	6
Lu (ng/g)	180	481	26	498	21	810	11
Na (mg/g)	181	2.1	71.6	1.8	63.6	0.5	37.4
Yb	181	3.0	25.5	3.1	20.2	5.1	11.1
Ce	177	88	38	82	32	143	15
Co	177	10	59	12	129	3	30
Cr	177	67.7	18.4	63.4	18.5	97.9	19.8
Cs	175	9.3	36.7	8.9	34.7	10.7	27.5
Eu	176	1.3	32.0	1.3	30.6	2.1	8.4
Fe (mg/g)	177	37.9	24.6	34.1	18.2	49.8	18.9
Hf	177	6.8	35.1	7.9	39.9	21.6	13.2
Sc	177	15.6	18.6	15.1	20.5	17.7	12.4
Th	177	14.5	16.6	15.0	20.3	30.7	18.3

Concentrations are in  $\mu\text{g g}^{-1}$  unless indicated

Cluster analysis for the log-transformed data of the fourteen chemical elements selected was performed in order to identify archaeologically meaningful chemical groups. It was defined that the minimum cut in the dendrogram should differentiate the Osvaldo clay samples, as the univariate inspection has already indicated significant differences in the concentrations of the chemical elements (Table 2). Further cuts in lower linkage distances were analyzed looking for archaeological correlations that would justify the definition of more chemical groups. In the absence of such correlations, the minimum cut was maintained.

In a first approach, the data from the two archaeological sites were analyzed together to assess general patterns and to verify a posteriori whether the provenance would be a factor responsible for the separation of chemical groups. This first approach assisted in the identification of diagenetic effects affecting the elements Na, K, Cs, Hf and As. However, no clear evidences of correlation between the chemical groups and archaeological factors as site provenance, ceramic phase, depth or kind of ceramic object were identified.

PCA analysis assisted in the verification of possible diagenetic effects that could be active in a hydrological dynamic region as the Solimões and Negro rivers confluence in Brazil. Sodium was identified as an element intensely altered in the depositional context, dominating the weight coefficients in the first component by an order of magnitude with respect to the majority of the elements. It was assessed that it would lead to a spurious partition of the samples in chemical groups with no archaeological

significance. The absence of calcareous sources of clays in the region and lower concentrations of sodium in the cauxi samples ( $\approx 3\%$  of the concentration in pottery) with respect to the pottery shards led to an alternative geochemical hypothesis for the enrichment of sodium over the depositional time.

There are evidences in the literature that a change in the sodium profile is possible in ceramic materials fired at low temperatures [32–34]. The geochemical hypothesis for the enrichment of sodium in the clay samples would result from the availability of sodium in the confluence region due to the weathering of feldspars to kaolinite of sediments from Andean and sub-Andean regions, linked to the cycles of sediment deposition on the flooding plains of Negro and Solimões rivers [35, 36]. Rainwater could be another important source of sodium in the rivers of the region [37].

In this way, sodium was eliminated from the analyses due to its dominance in PCA and evidences of diagenetic effects that could obscure culturally driven patterns of interest. Similar arguments can be extended for the element potassium, but its enrichment was one order of magnitude lower. Relative dominance of that element in PCA with no clear reasons, associated to geochemical evidences in the literature that a change in its profile is possible in archaeological ceramics [32], also led to the exclusion of that element from the analyzes.

Potential diagenetic effects were also identified for the elements Cs, As and Hf, although in a lower magnitude than the enrichment of sodium and potassium. The evidences for such effects were low correlation coefficients, parameters of dispersion of the variation matrix and

geochemical evidence in the literature [33, 38, 39]. After the exclusion of sodium and potassium, it was verified that hafnium dominated the first and fourth components, responsible for 54 % of the system variance. Cesium and arsenium dominated the second and third component, responsible for 33 % of the system variance. The change in the chemical groups observed after the extraction of those three elements in the PCA might indicate geochemical patterns affected by post-depositional effects that could also obscure archaeological and cultural correlation of INAA results.

After the first approach analyzing all the data combined in the PCA, the chemical elements selected for the exploration of chemical groups of archaeological relevance were La, Lu, Yb, Ce, Cr, Eu, Fe, Sc and Th.

The data from Lago Grande and Osvaldo were analyzed separately in a second approach. Samples that were the last to cluster to the mass of the data, evident outliers in the clustering procedure, were removed in order to increase the resolution of the dendrograms in terms of linkage distance. For the  $\log_{10}$ -transformed data, two chemical groups were identified for each archaeological site. The largest group (A) for Lago Grande contained 68 samples and the smallest one (B) contained 36 samples. The largest group (A) for Osvaldo contained 38 samples and the smallest one (B) contained 17 samples.

Following a first visualization of results, a refinement of the cluster classification was undertaken in order to take the correlation structure of data into account. The reasons to exclude samples were location outside the 95 % confidence region of ellipses, pertinence probability lower than 1 % to any of the groups [4], and samples without analytical traceability associated to outlying values of the reference material IAEA-Soil-7. The projection of the refined

classification of samples on the two first principal components is showed in Fig. 2.

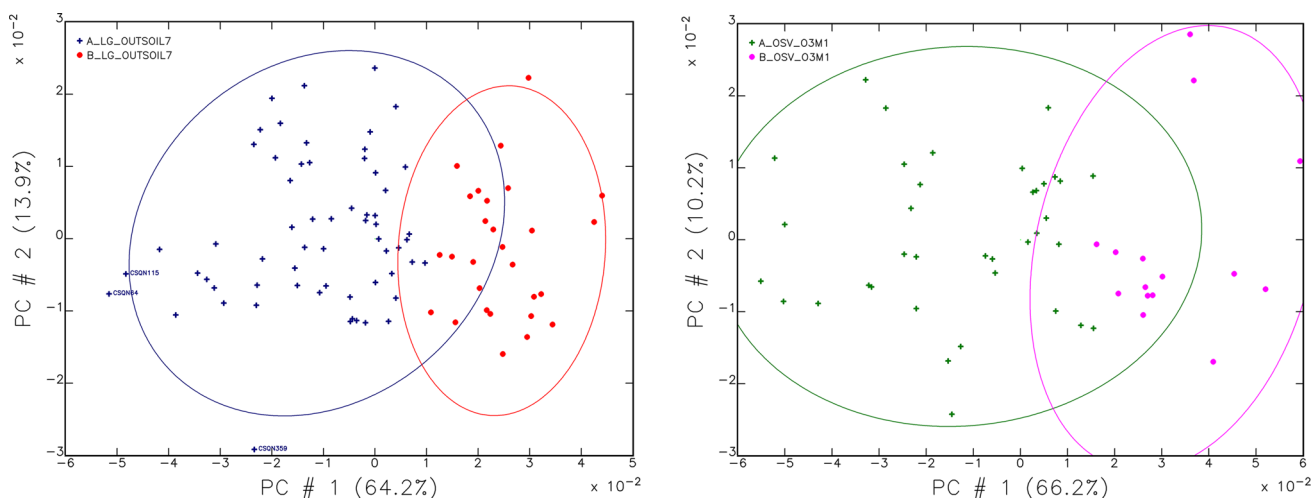
The two groups defined for each site presented a separation according to what is expected from physical–chemical analyzes of pottery from similar geological environment, in intraregional context, with some degree of superposition [32].

Table 3 shows means and standard deviations for the chemical groups defined for Lago Grande and Osvaldo in CA and PCA. Figure 3 shows the projection of data on the two first principal components of the refined data for both sites combined.

In Table 3, it is possible to observe that the concentrations of chemical elements in the group B are higher than in A for both sites. In fact, in Fig. 3 it was observed a significant superposition between groups A, the groups with the lowest elemental concentrations. The same can be stated for groups B, which have the highest elemental concentrations. The similarities in the concentrations and their dispersion for groups A and B in Table 3 is reflected in the superposition of the ellipses of chemical groups observed in Fig. 3.

An indirect validation of the chemical groups defined can be done by the analysis of the coefficients of variation ( $cv$ ). For Lago Grande, the  $cv$  values varied between 11 % and 20 % for group A (exception for iron with  $cv = 22$  %), and between 11 and 15 % for group B (exception for cerium with  $cv = 17$  %). For Osvaldo, the  $cv$  values varied between 11 and 20 % for group A, and varied between 10 and 14 % (exception for cerium with  $cv = 23$  %) for group B.

Harbottle [40] suggested that analytically well-determined groups frequently would present coefficients of variation between 15 and 20 %. Bishop [32] compared



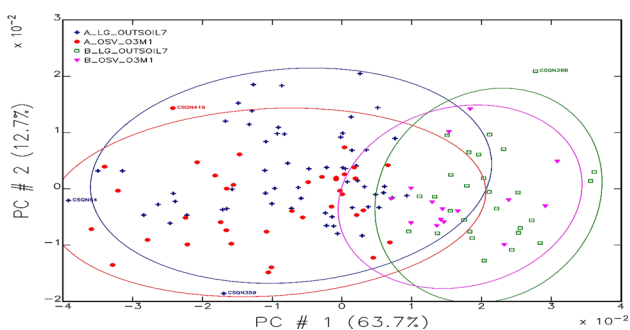
**Fig. 2** PCA scores of elemental concentration data from Lago Grande (*left*) and Osvaldo (*right*) archaeological pottery after the refinement of the classification in cluster analysis. *Ellipses* represent the 95 % confidence region

**Table 3** Mean concentrations of chemical elements in the chemical groups of pottery defined for Lago Grande and Osvaldo archaeological sites

Element	Lago Grande		Osvaldo	
	A ( $n = 61$ )	B ( $n = 28$ )	A ( $n = 37$ )	B ( $n = 15$ )
Sc	$14.8 \pm 1.9$	$18.6 \pm 2.1$	$13.8 \pm 2.0$	$18.7 \pm 2.3$
Cr	$64.3 \pm 8.3$	$79.1 \pm 10.2$	$59.0 \pm 7.4$	$75.3 \pm 9.6$
Fe	$36543 \pm 7991$	$44197 \pm 6505$	$32432 \pm 5723$	$39165 \pm 3728$
La	$38 \pm 5$	$50 \pm 5$	$38 \pm 4$	$47 \pm 7$
Ce	$75 \pm 11$	$104 \pm 17$	$71 \pm 12$	$107 \pm 24$
Eu	$1.1 \pm 0.2$	$1.7 \pm 0.2$	$1.1 \pm 0.2$	$1.5 \pm 0.2$
Yb	$2.7 \pm 0.4$	$3.5 \pm 0.4$	$2.9 \pm 0.4$	$3.3 \pm 0.4$
Lu	$0.45 \pm 0.07$	$0.56 \pm 0.07$	$0.47 \pm 0.07$	$0.55 \pm 0.06$
Th	$13.7 \pm 1.5$	$16.6 \pm 2.0$	$13.8 \pm 2.2$	$17.2 \pm 2.4$

Concentrations are in  $\mu\text{g g}^{-1}$

The parameter  $n$  represents the number of samples in each group



**Fig. 3** PCA scores of elemental concentration data from Lago Grande and Osvaldo archaeological pottery combined after classification refinement. Ellipses represent the 95 % confidence region

many archaeometric studies throughout the world and observed that chemical groups properly determined would present coefficients of variation between 10 and 15 %. The  $cv$  values for groups A of Lago Grande and Osvaldo match the variation suggested by Harbottle, and the  $cv$  values for groups B match the interval suggested by Bishop.

The abundance criterion cannot be applied in this work [22], as the sampling was driven to increase the number of samples regarding the probably exogenous ceramic material at each site.

### Some archaeological implications

Ideally, the chemical groups defined in the previous session would be correlate of only one ceramic paste recipe. However, there are many constraints to this direct approach.

The first factor of complexity is the possibility of combination of different clay sources to produce a ceramic artifact. Chromatic analyzes of Portocarrero [14] and Lima

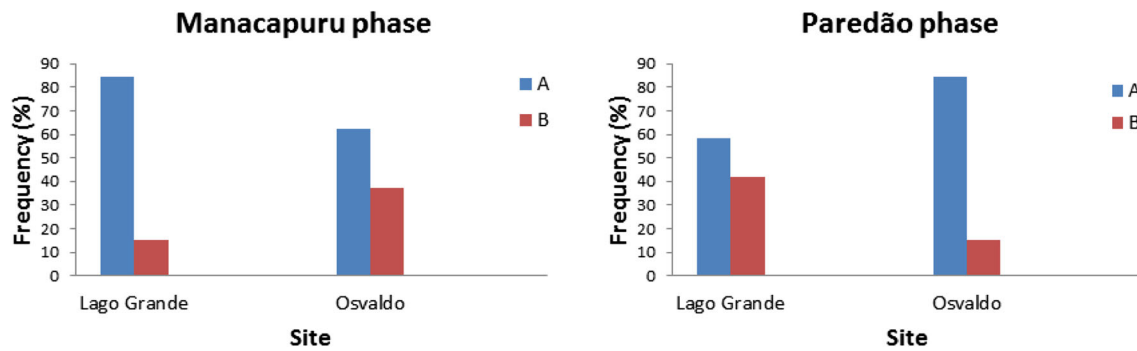
[13] indicated that the probability of combination of clays is high for the ceramic materials studied in this work. This variability may be driven by the different performance criteria required for objects in different uses by people.

Based on the classification of ceramic phases for each pottery shard by the archaeologists, a histogram of their distribution in the chemical groups defined in the multivariate analysis was plotted in Fig. 4.

Some hypotheses can be drawn from Fig. 4. The Manacapuru samples concentrate in the group A for Osvaldo and in a higher degree for Lago Grande. The Paredão samples concentrate in the group A for Lago Grande and in a higher degree for Osvaldo. The concentration of the pottery shards representing both ceramic phases in the groups A, would indicate that the combination of raw materials, or recipes, represented by such groups would be the preferred one by ceramists from both sites.

The fact that the distribution of Manacapuru and Paredão ceramics in the chemical groups were not the same for both sites in Fig. 4 have two potential implications regarding trade assumption. First, it might indicate a change in the selection of raw materials (mainly clay and non-plastics) for the ceramics produced especially for trade between Lago Grande and Osvaldo. A second possibility would be that exogenous ceramics would enter both sites not only by direct trade between Lago Grande and Osvaldo, but also by trade with other Manacapuru and Paredão contemporary sites. The archaeological evidences for such an assumption are the higher time span for Lago Grande occupation when compared to Osvaldo, regional networks identified in other regions of Amazon [16], and the existence of other contemporary sites that have also produced Manacapuru and Paredão ceramics. Furthermore, preliminary comparisons of data from Lago Grande and Osvaldo with Hatahara and Açutuba, other important archaeological





**Fig. 4** Distribution of Paredão and Manacapuru pottery shards in the chemical groups of Lago Grande and Osvaldo archaeological sites

sites in Central Amazon, indicated a partial geochemical superposition among samples of pottery shards analyzed by INAA [28]. This might indicate a larger exchange network.

More generally, three mechanisms may be inferred for exchange networks in Central Amazon: trade, exogamic marriage and territorial integration. Trade would be a means of reinforce social and political integration in the region by commercial relations. On the other hand, ethnographic research identified the practice of exogamic marriages in current times [41]. In this modality, women would carry gifts from their original village, and/or continuing producing ceramics in an “old fashion”, looking for raw materials and means of production practiced prior to the marriage. The identification of hybrid ceramic pieces in Lago Grande would corroborate this mechanism (Lima, 2008). The last mechanism of territorial integration would imply that the ancient inhabitants of Lago Grande, Osvaldo and other contemporary sites used common sources of raw materials. There are evidences in the ethnographic literature for the region that those three mechanisms could have occurred [13, 16]. In this sense, the multivariate geochemical patterns identified in this work would reflect complex and multimodal means of social and cultural interaction in Central Amazon.

The existence of lakes connected by *igarapés* (little water channels) along the Negro and Solimões confluence region, connecting the lakes around which Lago Grande and Osvaldo are located in flooding periods, would facilitate the contact between those peoples. Archaeological research suggests [17] that the existence of exchange networks would be a condition for the existence of long-term occupations, as identified in archaeological record of Lago Grande, and evidences of pre-Columbian forms of agriculture in interfluvial uplands within Amazonia. It contrasts with the short-term occupations documented ethnographically and gives an additional basis for theories that minimize the role of ecological constraints for the emergence of social complexity and sedentary occupations in the region.

## Conclusion

Multivariate statistical analysis of elemental concentration data, obtained by INAA, was carried out with samples of pottery shards from Lago Grande and Osvaldo, two important and representative archaeological sites in Central Amazon. Regarding analytical and geochemical concerns, it is not advisable to use the chemical elements Na, K, Cs, As and Hf for statistical analysis of pottery from the region, if one seeks for archaeologically meaningful groups. A set of evidences of diagenetic effects and potential geochemical mechanisms has been identified and would drive post-depositional alterations in those elements. Furthermore, the methodological approach adopted yielded useful results for the archaeological context considered in this work.

The combination of cluster and principal component analysis was used for the definition of two chemical groups of pottery shards for each site. Their pairwise superposition in the two first principal components indicated geochemical similarities that may be archaeologically interpreted. The results might be correlate of complex and multimodal mechanisms of interaction, like trade, exogamic marriage and territorial integration. In any case, it generated evidences of socio-cultural interactions in Central Amazon, which may have implications for the archaeological theories regarding the pre-colonial Amazonian occupation that try to minimize the role of environmental constraints for the emergence of social complexity in the region.

The definition of more chemical groups was tried for the data set used in this work. However, there were problems of sample size for some groups. Additionally, no obvious archaeological correlations were found for such a higher resolution in the clustering procedure. Sampling expansion of ceramic artifacts from Central Amazon would help to work in a higher geochemical resolution and seek for further archaeological evidences and relations that would be useful to Amazonian Archaeology.

**Acknowledgments** This work was realized with the support from *São Paulo Research Foundation*—FAPESP—Brazil (Process Number: 2010/07659-0), and partially with the support of *Conselho Nacional de Desenvolvimento Científico e Tecnológico*—CNPq—Brazil (Process Number: 134116/2009-7). The *MURRAP* freeware software was made available by the Archaeometry Laboratory at the University of Missouri Research Reactor, managed by Dr. Michael Glascock.

## References

- Pollard M, Heron C (1996) *Archaeological chemistry*. The Royal Society of Chemistry, Cambridge
- Velde B, Druc IC (1999) *Archaeological ceramic materials: origin and utilization*. Springer, Berlin
- Glascock MD, Neff H (2003) Neutron activation analysis and provenance research in archaeology. *Meas Sci Technol* 14:1516–1526
- Glascock MD, Neff H, Vaughn KJ (2004) Instrumental neutron activation analysis and multivariate statistics for pottery provenance. *Hyper Interact* 154:95–105
- Munita CS (2005) Contribuição da análise por ativação com nêutrons a estudos arqueométricos: estudo de caso. *Canindé* 6:159–181
- Weigand PC, Harbottle G, Sayre EV (1977) Turquoise sources and source analysis: Mesoamerica and the Southwestern U.S.A. In: Early TK, Ericson JE (eds) *Exchange systems in prehistory*. Academic Press Inc., New York, pp 15–34
- Dias MI, Prudêncio MI (2007) Neutron activation analysis of archaeological materials: an overview of ITN NAA laboratory. *Port Archaeom* 49(2):383–393
- Tite MS (2008) Ceramic production, provenance and use—a review. *Archaeometry* 50(2):216–231
- Neves EG (2008) Ecology, ceramic chronology and distribution, long-term history, and political change in the Amazonian floodplain. In: Silverman H, Isbell WH (eds) *Handbook of South American archaeology*. Springer, New York, pp 359–379
- Meggers BJ (1996) *Amazonia: man and culture in a Counterfeit Paradise*. Smithsonian Institution Press, Washington, DC
- Machado JS (2006) Dos artefatos às aldeias: os vestígios arqueológicos no entendimento das formas de organização social da Amazônia. *Rev Antropol* 49(2):755p
- Heckenberger MJ, Neves EG (2009) Amazonian archaeology. *Ann Rev Anthropol* 38:251–266
- Lima H (2008) *História das Caretas: A Tradição Borda Incisa na Amazônia Central*. PhD Thesis, Universidade de São Paulo, Brazil
- Portocarrero RC (2006) *A variabilidade espacial no sítio Osvaldo. Estudo de um assentamento da tradição barrancóide na Amazônia central*. PhD dissertation, Universidade de São Paulo, Brazil
- Donatti PB (2003) *A ocupação pré-colonial da área do Lago Grande, Iranduba, AM*. PhD dissertation, Universidade de São Paulo, Brazil
- Mongeló GZ (2011) Processos de interação entre os sítios Lago Grande e Osvaldo (AM) baseados no material cerâmico. *Rev Museu de Arqueol e Etnol* 11:109–114
- Neves EG, Petersen J (2006) Political economy and pre-columbian landscape transformations in central Amazonia. *Time Complex Hist Ecol*, 279–310
- Silva FA (2009) A etnoarqueologia na Amazônia: contribuições e perspectivas. *Bol Mus Para Emílio Goeldi Ciênc hum* 4(1):27–37
- Bishop RL, Canouts V, De Atley SP, Qöyawayma A, Aikins CW (1988) The formation of ceramic analytical groups: hopi pottery production and exchange, A.C. 1300–1600. *J Field Archaeol* 15(3):317–337
- Munita CS, Paiva RP, Alves MA, Oliveira PMS, Momose EF (2003) Provenance study of archaeological ceramics. *J Trace Microprobe Tech* 21:697–706
- Blackman MJ, Bishop RL (2007) The Smithsonian-NIST partnership: the application of instrumental neutron activation analysis to archaeology. *Archaeometry* 49(2):321–341
- Harbottle G (1982) Chemical characterization in Archaeology. In: Ericson JE, Earle TK (eds) *Contexts for pre-historic exchange*. Academic Press, New York, pp 13–51
- Glascock MD (1992) Characterization of archaeological ceramics at MURR by neutron activation analysis and multivariate statistics. In: Neff H (ed) *Chemical characterization of ceramic pastes in archaeology*. Pre-History Press, Madison, pp 11–26
- Beier T, Mommsen H (1994) Modified Mahalanobis filters for grouping pottery by chemical composition. *Archaeometry* 36(2):287–306
- Koch GS, Link RF (2002) *Statistical analysis of geological data*. Courier Dove Publications, New York
- Oliveira PMS, Munita CS (2003) Influência do valor crítico na detecção de valores discrepantes em arqueometria. *Anais do 10º SEAGRO, Lavras, 7–11 julho*
- Baxter MJ (1994) *Exploratory multivariate analysis in archaeology*. Edinburgh University Press, Edinburgh
- Hazenfratz-Marks R. (2014) *Nêutrons, radiação e arqueologia: estudo de caso multianalítico de cerâmicas da tradição borda incisa na Amazônia Central*. PhD Thesis, University of São Paulo, Brazil
- Attas M, Fossey JM, Yaffe L (1984) Corrections for drill-bit contamination in sampling ancient pottery for neutron activation analysis. *Archaeometry* 26(1):104–107
- Keding R, Jensen M, Yue Y (2010) Characterization of the mesoporous amorphous silica in the fresh water sponge *Cauxi*. In: Munir ZA, Ohji T and Hotta Y (eds) *Innovative processing and manufacturing of advanced ceramics and composites*, pp 115–129
- Demaster DJ (2005) The diagenesis of biogenic silica: chemical transformations occurring in the water column, seabed, and crust. In: Mackenzie FT (ed) *Treatise of geochemistry*, vol 7. Elsevier, Amsterdam, pp 87–98
- Bishop RL (2003) Instrumental neutron activation analysis of archaeological ceramics: progress and challenges. In: IAEA-TRS416—nuclear analytical techniques in archaeological investigations, Vienna, chap. 2, pp 35–44
- Schwedt A, Mommsen H, Zacharias N (2004) Post-depositional elemental alterations in pottery: neutron activation analysis of surface and core samples. *Archaeometry* 46(1):85–101
- Buxeda I, Garrigós J, Mommsen H, Tsolakidou A (2002) Alterations of Na-, K-, and Rb- concentrations in Mycenaean pottery and a proposed explanation using X-ray diffraction. *Archaeometry* 44(2):187–198
- Martinelli LA, Victoria RL, Dematte JLI, Richey JE, Devol AH (1993) Chemical and mineralogical composition of Amazon River floodplain sediments, Brazil. *Appl Geochem* 8:391–402
- Vital H, Statterger K (2000) Major and trace elements of stream sediments from the lowermost Amazon River. *Chem Geol* 168:151–168
- Gaillardet J, Dupré B, Allègre CJ, Négrel P (1997) Chemical and physical denudation in the Amazon River Basin. *Chem Geol* 142:141–173
- Gaudette HE, Grim RE, Metzger CF (1996) Illite: a model based on the sorption behavior of Cesium. *Am Mineral* 51(11):1649–1656
- Schwedt A, Mommsen H (2007) On the influence of drying and firing of clay on the formation of trace element concentration profiles within pottery. *Archaeometry* 49(3):495–509

40. Harbottle G (1982) Provenance studies using neutron activation analysis: the role of standardization. In: Olin JS, Franklin AD (eds) *Archaeological ceramics*. Smithsonian Institution Press, Washington, DC, pp 67–77
41. Moraes CP (2006) *Arqueologia na Amazônia central vista de uma perspectiva da região do Lago do Limão*. PhD dissertation, Universidade de São Paulo, Brazil