Preliminary archaeometric study in the Lapa Grande de Taquaraçu archaeological site.

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This paper analyzes the concentrations of Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Nd, Rb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn determined from sixty sediment samples obtained from the Lapa Grande de Taquaraçu archaeological site using INAA. The site is located in the municipality of Jaboticatuba, about 60 km from Belo Horizonte, Minas Gerais state in Brazil. The data set was studied by means of cluster analysis, principal component analysis and discriminant analysis. The study showed three different compositional groups that represent the fluvial environment and the deposition in the shelter. The crystalline phases of each group were studied using XRD.

Introduction

Soil chemistry can help in archaeological research as a prospecting technique to locate sites with few or no visible archaeological features and to find boundaries [Konrad et al. 1983, Cavanagh et al. 1988].

However, physical and chemical properties of sediments found in a shelter can be altered as a result of human activity through the addition of organic and inorganic constituents. The elemental concentrations in sediments and the anthropogenic influence can be revealed by analyzing minor and trace elements. Several researchers identify specific activities using trace elements. Soil phosphorus analysis in organic and inorganic forms such as phosphate (PO_4) levels was the first and remains the best known of chemical indicators of anthropogenic activity [Arrhenius, 1929; Craddock et al. 1986; Holliday and Gartner, 2007]. Additionally, phosphorus levels have been used as a relative indicator of continued use and intensity of occupation [Wells et al. 2000]. In order to achieve this, it is necessary to treat anthropogenic sediments holistically and to analyze more than one attribute of the sediment [Middleton, 2004] since anthropogenic sediment is formed by complex interactions between human and natural factors [Middleton 2004]. In this paper, it would be premature to provide a detailed and exhaustive study of sediments found in the Lapa Grande de Taquaraçu archaeological site used as a shelter because the site still requires several years of field and laboratory study. Instead, the purpose here is to provide a preliminary result using trace elements determined by INAA and XRD that may aid in understanding the human occupation.

Study area

The archeological site of Lapa Grande de Taquaraçu is a rocky Paleo-Indian shelter from the Holocene period, located on the left margin of the Taquaraçu river, city of Jaboticatubas in Minas Gerais state, a little over 60 kilometers from Belo Horizonte. The size of the shelter is approximately 30m in length by 9m in width at its widest point. It faces west and its floor is elevated 7m above the river that runs alongside it (Figure 1). The ^{14}C

datings indicate an occupation hiatus in the Mid-Holocene period between 1100 and 8000 years A.P.

Figure 1.Overview of Lapa Grande de Taquaraçu site

The time of transition from the Pleistocene to the Holocene period was defined by a series of distinct stages marked by different periods of temperature and rainfall rate changes [Dillehay, 2008]. The driest period, characterized by expanding areas of savannas during the Mid-Holocene period, was an important factor that could have seriously affected human occupation [Pessenda, *et* al., 2010], leading to the abandonment of large areas originally occupied by human groups [Araujo, 2005]. Within this context, the Lapa Grande do Taquaraçu site, despite being located in a karst area but not in the main karst area of Lagoa Santa [Oliveira, *et al*., 2012] widely explored by Peter Lund [Guimarães and Holten, 1997], plays an important role in the abandonment of the karst in this region, since it is located near a source of perennial water, which probably remained active during the drought season and became an option for refuge/occupation for the people of that time.

The karst where the Lapa Grande de Taquaraçu shelter is located is part of the Serra de Santa Helena mountain range, which, in turn, along with the Jequitaí, Sete Lagoas, Lagoa do Jacaré, Serra da Saudade and Três Marias formations, are part of the Bambuí group, which is a thick carbonate succession [Dardenne, 1981] of the São Francisco basin, covering an extensive area of the São Francisco Craton, a Neoproterozoic geotectonic unit formed from the Brasiliana orogeny [Alkmin and Martins, 2001].

Carbonate rocks (limestone, marble and dolomite), of which the main mineral is calcite (and/or dolomite), which dissociates in the Ca2+ and/or Mg^{2+} and CO_3^{2-} ions through water action, are among the most favorable for karstification. Rocks made of halite and/or gypsum, despite being highly soluble originate karstic system only in special situations, such as arid and semiarid areas, because they weather so quickly under humid conditions it does not allow the karst to fully develop.

Corrosive rock agents are rainwater, initially acidified with atmospheric CO2, which undergo a large amount of enrichment in carbonic acid when they pass through the soil because the respiration of plant roots and the decomposition of organic matter result in high CO2 content in the soil. Carbonic acid is almost entirely consumed in the first meters of groundwater seepage in the rocky batch, and in the deeper parts, only a small part of this acid remains to dissolve the rock [Teixeira *et al*, 2008].

Experimental

Analytical procedures

The sediments samples were prepared by manually grinding them into an agate mortar and pestle until a thin enough granulometry was obtained. The particle size required had to pass through a 100 mesh sieve. These materials were dried in an oven for 24 h, at 105°C and stored in a desiccator.

INAA

Constituent Elements in Coal Fly Ash (NIST-SRM-1633b) were used as a standard and Trace Elements in Soil (IAEA-Soil 7) was used to check the analysis throughout the analysis. These materials were dried in an oven for 2 h at 105°C and stored in a desiccator until weighing.

About 120 mg of sediments samples, one standard (NIST-SRM1633b) and one IAEA-Soil 7 were weighed in poltethylene bags and wrapped in Al foil. Groups of 10 samples and one reference material were packed in aluminum foil and irradiated in the research reactor´s pool, IAE-R1, at IPEN-CNEN/SP, Brazil, with a thermal neutron flux of about 5 x 10^{12} n cm^{-2} s^{-1} for 8 h.

Two measurements series were carried out using a Ge (hyperpure) detector, model GX 2519 from Canberra, with resolution of 1.9 keV at the 1332.49 keV gamma peak of ^{60}Co and an S-100 MCA from Canberra with 8192 channels. K, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days cooling time and Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Th and Zn after 25-30 days. Gamma ray spectra analysis and the concentrations were carried out using the Genie-2000 Neutron Activation Analysis Processing Procedure from Canberra [ ].

XRD

All diffraction measurements were performed on a RIGAKU diffractometer, Model Miniflex II using a step of 0.05° (θ) with 1 second reading for each step. The measurements were initiated at 5° (θ) and ended at 80° (θ). The difractograms were analyzed using the *Crystallographica Search-Match* program, version 1.11.

Statistical treatment of dataset

Through INAA it is possible to determine several chemical elements and the interpretation of the data is complex, especially when a large number of samples are analyzed. Then, multivariate statistical methods are generally used for data handling and assessment. In multivariate statistical techniques, each element can be considered a point in multidimensional space and the number of dimensions is equivalent to the number of elements measured. Groups of elements with similar composition form a cloud of points surrounding its centroids. In this paper, the dataset was studied using cluster analysis, principal component analysis and discriminant analysis

Sampling

The 4 excavated quadrants named G7, H7, H8, D17 have a well preserved stratigraphy, which makes it possible to detect the existence of an archaeological batch of approximately 80 cm, with a high density of lithic and faunal material, and a few ceramic fragments on the surface. In general, the archaeological batch is gray and powdery in appearance, lying on a flat block of limestone, with some presence of archaeological material, later on an altered section appears, reddish and archaeologically sterile, that was part of the original cave floor.

Figure 2. Top view of a hollowed out quadrant, which shows a clear difference in color in the sediment. The back shows an altered section and the sides show a grayish sediment

Results and discussion

The analytical quality control of the method was tested using the determination of Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn using a dataset of 19 independent determinations of the reference material IAEA Soil 7, Trace Elements in Soil. The homogeneity of the set of results for each element was studied using Dixon´s Q test for statistical treatment of rejection of deviant values at the 95 % confidence level [Rorabacher, 1991]. In the dataset, no outliers were found. The observed results were compared to the certified values. The RSD for most elements (Ce, Co, Eu, Fe, Hf, Na, Rb, Sc, Sm, Th, U, Yb, and Zn) was around 5% or less, i.e. comparable with that found in the literature [Kuleff and Djingova, 1990]. For the elements determined with a precision of 10 % or more (Cs, K, La, Ta) ours results are also in agreement with those found in the literature [Kuleff and Djingova, 1990]. The determination of Zn is not reliable as a consequence of a strong γ-ray interference by ^{46}Sc (1120.3 keV) and ^{182}Ta (1121.41 keV). The interference by the ^{235}U fission in the determination of La, Ce, and Nd was negligible because the U concentration did not exceed 5 ppm and the rare earth elements were not extremely low [Glascock, 1992]. In this work, we considered only elements determined with an RSD better than 10 %. This precision is considered by several authors as suitable for the choice of chemical elements using multivariate statistical methods [Bishop et al. 1990]. Although Rb, Tb, Sm, K, Ta, showed a RSD less than 10 %, it was not included in the dataset due to the natural heterogeneity.

Therefore, elements Ce, Co, Cs, Eu, Fe, Hf, La, Na, Sc, Th, U and Yb were used in the sediments data analyses. None of these elements contained missing values.

In geochemistry, concentration data is often assumed to follow a lognormal distribution after being $\log_{10}$ transformed [Ahrens, 1954].

In addition, the dataset of the sediment was submitted to an outlying test using the Mahalanobis distance [Grubbs, 1950]. Outliers can be a considerable influence on multivariate statistical methods because they may disturb homogeneous groups. For each of *n* samples and *p* variables, the Mahalanobis distance (D_i) was taken from the sample to the centroid, as calculated by the expression [Grubbs, 1950]

$$D_i = \sqrt{(x_i - \bar{x})' S^{-1} (x_i - \bar{x})} \qquad (1)$$

where ´ is the transpose matrix; $S = \sum_{i=1}^{n} (x_i - \bar{x})' (x_i - \bar{x})$ is the variance-covariance sampling matrix and, $(x_i - \bar{x})$ is the vector of difference between the concentrations measured in one group and the concentrations measured in the other group. Each one of these values is compared with the critical value, *cv*, which can be calculated using the lambda Wilks criteria [Penny 1996], calculated as follows:

$$\frac{p(n-1)^2 F_{p,n-p-1;\alpha/n}}{n(n-p-1+pF_{p,n-p-1,\alpha/n})} \qquad (2)$$

where p is the number of variables; n is the number of samples and F, is the F test called “Fisher distribution” (F = s_1^2/s_2^2 where s_1^2 and s_2^2 are the sample variances), with p degrees of freedom at a significance level of α/n, $\alpha = 0.05$.

When the value found by expression (1) is larger than the critical value produced by expression (2), the sample is considered to be an outlier. Thus, the *Mahalanobis* distance values for each sample were calculated and compared to the critical value. In accordance with the *Mahalanobis* distance rule, five sediments sample outliers were found and removed from the data. Due to the small size of this compositional group, it is difficult to know whether it is a real group. We believe that the outlier samples could be related to contamination processes that may have occurred during burial and this notion is strengthened by the fact that lower or higher concentrations of Ce, Na, and Th were found as compared with other samples.

The 55 samples were then analyzed using cluster analysis, principal component analysis and discriminant analysis.

Cluster analysis is usually used as an initial inspection of the results because it is a fast and efficient way of evaluating relationships between the data. The cluster technique of grouping similar objects according to their characteristics and the analysis is based on the similarity/dissimilarity matrix, where the distance between all pairs of samples measured is calculated using one of the many measured distances [Sayre and Dodson, 1975]. In this work, we used the Ward method and the squared Euclidean distance because it exaggerates differences in the data and produces a clearly identifiable cluster dendrogram.

Figure 3 shows the dendrogram of the cluster analysis, which in turn shows the presence of two principal groups, where, apparently, the largest group is divided into two subgroups (I and III).

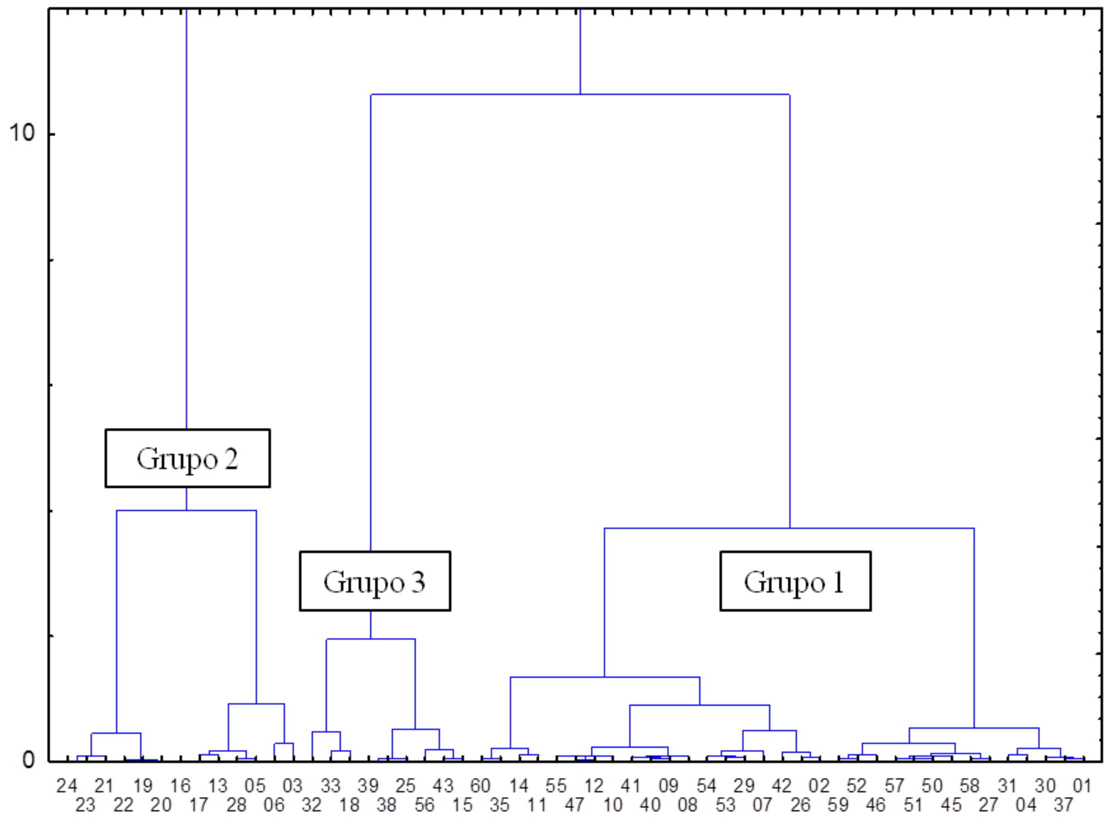

Figura 3. Dendrogram of cluster analysis for the sediment samples

Initially, the data obtained by cluster was worked by assuming the existence of only two groups, where it was supposed that these two groups corresponded to sedimentation of geological and anthropogenic origin. However, after using other statistical methods in the analysis, the presence of a third group became apparent. To confirm the case of the existence of a third group, the results were submitted to principal component analysis, PCA.

PCA involves transforming the data set based on the auto vector to determine the magnitude and direction of maximum variance in the distribution of the data set in hyperspace [Glascock and Neff, 2003]. The first principal component is a linear combination of the original variables and is aimed at maximum variance. The second component is estimated to be aimed at remaining maximum variance (2nd most important), the third component carries the third most important amount of information.

Table 1 shows the results of the variance-covariance matrix for the first three principal components. Also included are the loadings of the principal component for each element. In the first component, the explained variance was 90.27%, in the second, 3,85% and 2,46% in the third. Therefore, the variance explained by these three components was 96.58%, while the first two accounted for 94.12% of the total variance of the database.

Tabela 1. Results of the variance-covariance matrix for the first three principal componentes.

Element	PC 1	PC 2	PC 3
Ce	0,24589	0,10292	-0,2221
Co	0,37202	-0,3868	-0,0667
Cr	0,291011	0,01106	0,28186
Cs	0,31187	0,12484	0,11539
Eu	0,21976	-0,254	-0,3125
Fe	0,33139	0,03643	-0,0291
Hf	0,17734	0,45635	0,15125
La	0,13092	-0,0074	-0,3655
Lu	0,30123	-0,0067	-0,1139
Na	0,16077	-0,5819	0,54366
Sc	0,31815	0,02042	-0,064
Th	0,2468	0,30243	-0,1067
U	0,20697	0,34136	0,49828
Yb	0,30156	-0,053	-0,1618
var. explained (%)	90,27	3,85	2,46

According to Table 1, the elements that showed higher loading on the first component were Ce, Co, Cr, Cs, Eu, Fe, Lu, Th and Yb. Hf and Th in the second component and Na and U in the third component. Uranium is distributed in the three principal components and Cr into two principal components. In a way, all the elements selected for the characterization of sediments using multivariate statistical analysis at the Taquaraçu site are well correlated. Another fact that also merits attention is that the elements with higher loading are the elements of the first transition series (Co, Cr, Fe and Sc) and the rare earth elements (Ce, Eu, La, Yb and Lu), which is consistent with the literature in other studies [MacDonald *et al.*, 2011].

Figure 4 shows the graph of principal component 1 versus principal component 2 in the 55 sediment samples.

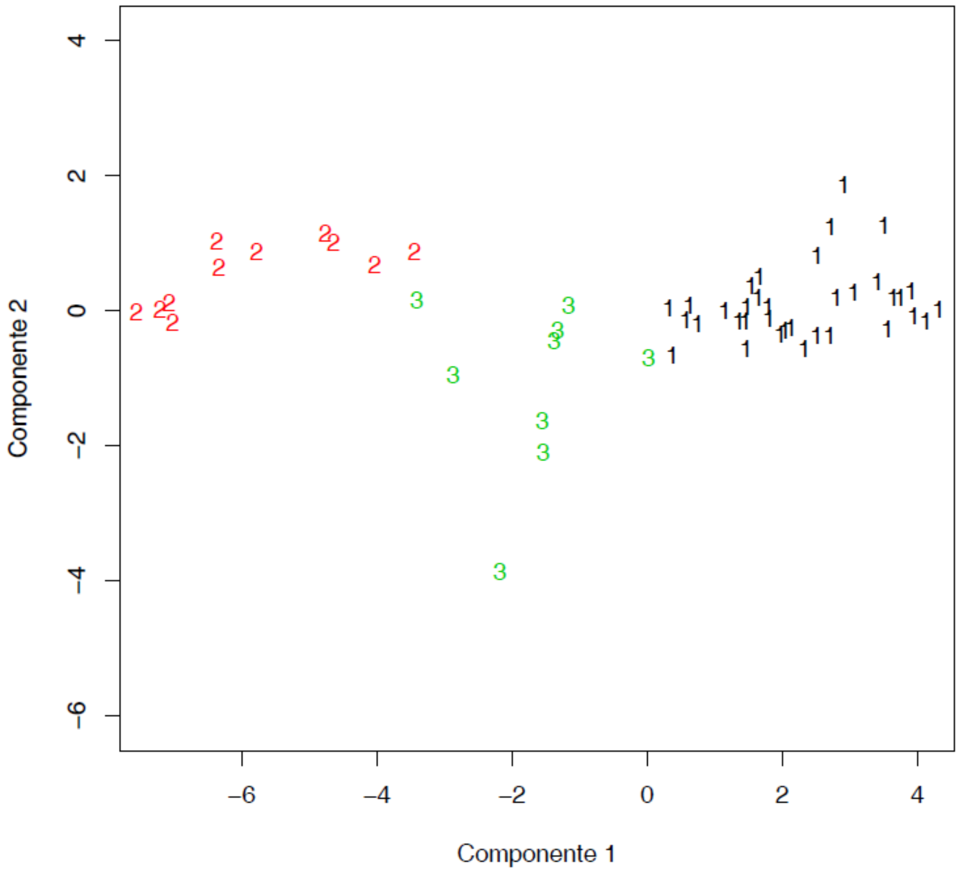

Figure 4. Principal component 1 vs principal componente.

As shown in Figure 4, the results confirm the existence of three sample groups. Group I is formed by 35 samples, Group II by 12 and Group III by eight samples. The scattering of the samples in Group III may be due to the fact that some of the samples have a certain probability of belonging to another group. Bivariate graphs were drawn up to confirm this possibility. Figure 5 shows the Co versus Th and Sc versus Yb biplot. In these figures, the existence of three distinct compositional groups can clearly be seen.

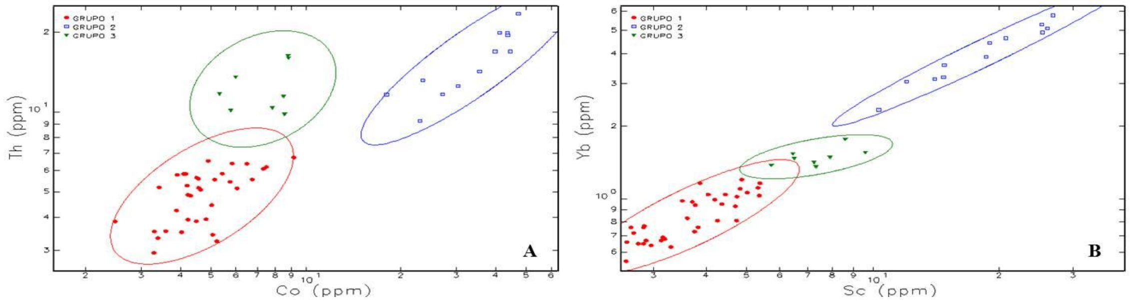

Figure 5. Bivariate plots of Co vs. Th (A) and Sc vs. Yb (B). The ellipses represent a confidence level of 95%.

Although we were able to separate the sediment samples of the Taquaraçu site into three compositional groups differentiated by bivariate graph using the combination of almost all the 14 elements that are included in the database, the best difference between the groups (largest distance) involved the elements Co vs. Th and Sc vs. Yb. Nevertheless, such elements are part of the chemical groups of the periodical table that are most important in archeometric studies from the geochemical standpoint, transition metals (Sc and Co) and inner transition metals (Yb and Th), where Yb is part of the heavy rare earths.

In order to confirm the existence of the three groups, the results were studied using discriminant analysis. Discriminant analysis is another technique used to reduce sample dimensionality. Discriminant analysis differs from PCA in the way that it extracts a new set of variables that maximize the difference of the total variance of the data set [Hair *et al.*, 2005]. The purpose of this technique is to find the functions of the original variables (discriminant function) that explain the differences between the samples.

Figure 6 shows discriminant function 1 vs. discriminant function 2 in which the three different chemical composition groups in the sediment of the Lapa Grande de Taquaraçu archaeological site were identified.

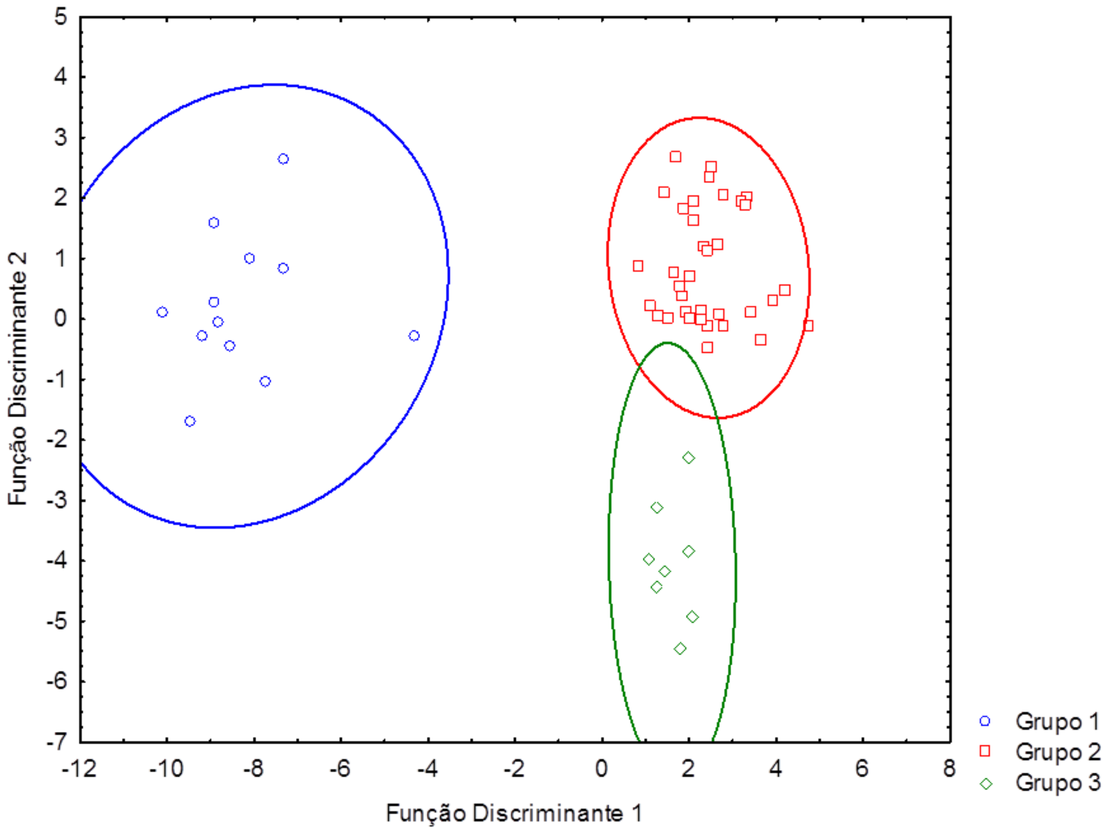

Figura 6. Discriminant function 1 vs discriminant function 2. The ellipses represent a confidence level of 95%.

The INAA method enables several elements [Alex *et al.*, 2012], to be defined simultaneously and the analyst measures a large number, many of which may not be very informative. Therefore, it is necessary to identify the most relevant subset of elements and to remove the variables with the least amount of relevant information, while preserving multivariate data structure and minimizing the loss of essential information. The Procrustes analysis was used for this paper in conjunction with a stopping rule to select the variables that are in some way suitable for discrimination purposes. The concept of Procrustes uses the measured distance, M^2, between two k-dimensional configurations. The value of M^2 is determined for each variable and the resulting value indicates the effect in the configuration and identifies the variable that has the lowest effect when eliminated. The variable is important in explaining the structure of the data, when the sum of residues (M^2) is higher than the critical value (*cv*). More details of the procedure can be found elsewhere [, Krzanowski, 1987, 1996, Munita et al 2013]. Table 2 shows the results of the selection procedure, including the sequence of elimination.

Table 2. Variable selection with stopping rule, n = 55.

	Fe	Lu	Ce	Eu	Cr, Th, U, Co, Yb, Cs, Na, La, Sc e Hf
M^2	1.25	4.97	11.4	21.1	
cv	19.1	18.1	17.2	16.3	

In Table 2, the first element to be eliminated was Fe, where M^2 is 1.25 and the *cv* is 19.1. When the variable is eliminated, the associated configuration is changed to the extent that it becomes unacceptable, which occurs when M^2 becomes greater than the critical value. This value was reached with Eu, whose value of M2 was 21.1 and of critical value, 16.3. The procedure suggests that the Fe, Lu and Ce variables be eliminated, one by one, and the elements Eu, Cr, Th, U, Co, Yb, Cs, Na, La, Sc and Hf should be considered in the database.

In order to confirm this assumption, the results of 55 samples were subjected to a new principal component analysis using the eleven variables selected in the Procrustes analysis. Figure 7 shows the graph of principal component 1 versus principal component 2, which shows the existence of three different compositional groups. When Figures 4 and 7 are compared, it becomes apparent that using the variables selected through Procrustes, the complete data structure is represented perfectly without a loss of information. This result shows that the sediment of the Lapa Grande de Taquaraçu site can be characterized by the analysis of Eu, Cr, Th, U, Co, Yb, Cs, Na, La, Sc and Hf.

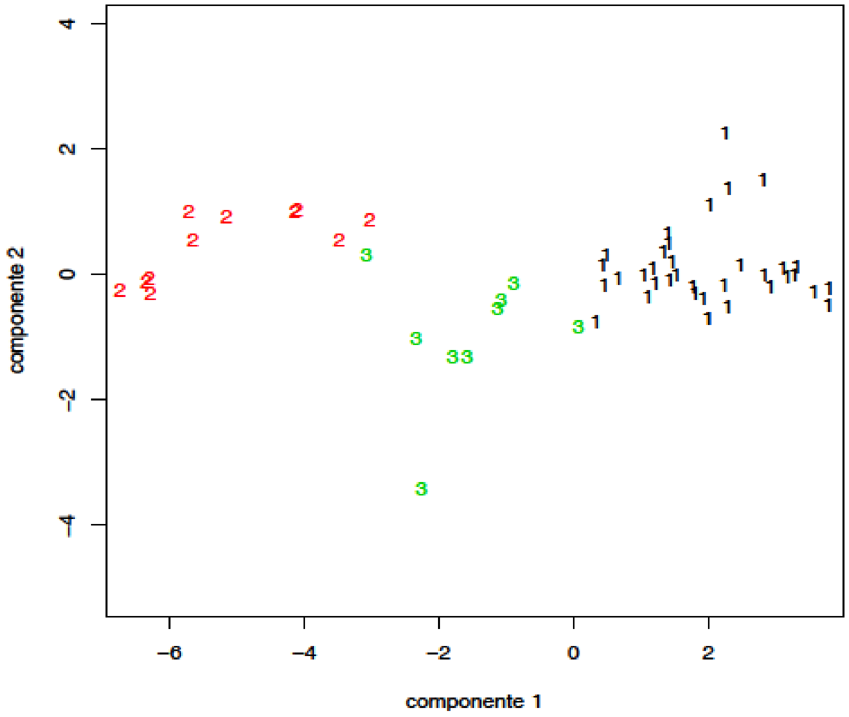

Figure 7. Pricipal componente 1 vs principal component 2 using the variables Eu, Cr, Th, U, Co, Yb, Cs, Na, La, Sc e Hf.

The results of the chemical composition show that the Lapa Grande de Taquaraçu site is formed by three different groups. According to the studies [Araujo *et al*., 2006] the site has an archaeological stratum approximately 1 meter deep. After it appears the sedimentation composed of what would be the original back of the shelter. Table 3 shows the groups, the amount, the excavation quadrant and the depth of the samples.

Group I consists of samples from the excavation of four quadrants, consisting of 13 samples from quadrant G7, one from H7, 15 from H8, three from D17 and three without specification of quadrant and depth. Of the 12 samples that form Group II, eleven are from quadrant G7 and one is from H7. In that which refers to Group III, five samples derived from quadrant H8, one from G7 and two without specification of quadrant and depth. As shown in Table 3, the separation of the sediment samples of Groups I and II occurred mostly according to the depth.

Table 3. Distributionof samples according to the group, quadrant and depth.

Group	Sample number	Quadrant	Depth (cm)
I	13	G7	10 – 90
	1	H7	80
	15	H8	10 - 80
	3	D17	10 – 70
	3	---	---
II	11	G7	90 - 140
	1	H7	80
III	5	H8	20 – 50
	1	G7	50
	2	---	---

The elementary concentration values of the samples as a whole and by group were analyzed to study the behavior of the analyzed elements. The data of the means of the concentrations, separated according to the groups formed, is shown in Table 4.

Table 4. Mean and standard deviation of the elemental concentrations for each group, n = 55 in mg/kg.

Element	Sample	Group I	Group II	Group III
Ce	45,83±29,23	27,7±6,06	92,02±22,61	55,87±13,9
Co	11,76±13,17	4,85±1,37	34,79±10	7,44±1,5
Cr	33,50±26,96	18,26±5,06	77,58±23,83	34,06±9,74
Cs	4,28±3,65	2,2±0,61	10,20±3,33	4,51±1,37
Eu	0,79±0,51	0,51±0,1	1,66±0,36	0,73±0,22
Fe	24116±22152	11651±3200	60658±20221	23838±5230
Hf	3,29±1,74	2,24±0,53	5,01±1,05	5,29±2,25
La	29,86±10,82	23,44±3,67	45,67±9,0	34,02±7,71
Lu	0,26±0,22	0,14±0,03	0,63±0,17	0,26±0,03
Na	1171±638	893±350	2143±501	929±282
Sc	7,63±6,77	3,79±0,9	18,97±5,86	7,41±1,26
Th	8,39±5,26	4,94±1,1	15,75±4,32	12,44±2,61
U	1,60±0,9	1,09±0,38	2,79±0,78	2,01±0,8
Yb	1,66±1,42	0,86±0,2	4,11±1,07	1,50±0,13

The mean of the concentrations of the 55 samples showed a large scatter when treated together, column 2. On the other hand, when the mean of the concentrations of each sample group are taken into consideration (3, 4 and 5), less of a data scatter is observed. Table 4 shows that the concentration is higher for the elements of Group II as compared with the other groups, with the exception of Hf, whose concentration is higher in Group III.

Table 4 also shows that Group I, which supposedly corresponds to the samples of the anthropogenic group, shows a lower concentration of each element. This data goes against the work about studies of anthropogenic sediments because human activities generate a large volume of waste that finds its way into the soil causing an increase in elemental concentration, for example, craft activities, food preparation, among others [Middleton and Price, 1996; Entwistle, 2000; King, 2008].]. Covered sites, or shelters, such as in the case of Lapa Grande de Taquaraçu, are less affected by weathering and these areas are expected to be less eroded and to have increased soil enrichment due to chemical compounds [Barba, 1986; 2007]. However, this was not what was detected at the Lapa Grande de Taquaraçu site, where the group that corresponds to the anthropogenic stratum, shows the lowest concentration of the three compositional groups.

Unless the sediment is otherwise severely leached, disturbed or altered, the residue that incorporates and that modifies the elementary concentration in the sediment can be detected and identified through chemical analysis [Barba, 1990; Barba *et al.*, 1996; Middleton and Price, 1996; Middleton, 2004; Vincke *et al.*, 2011]. Thus, the low levels of elemental concentration in Group I may be explained by a possible flood that may have occurred in the Taquaraçu river that borders the site, located a few meters from its margin.

With the purpose of studying the possible differences in the crystalline structure between the three different compositional groups formed by the sediments of the Taquaraçu site, x-ray diffraction measurements were taken. From a total of 8 samples, three belong to Group I, three to Group II and two to Group III.

The samples in Group I contained calcite as their major constituent. On the other hand, the main constituent of the Group II and III samples was quartz with no, or at least no observed, amount of calcite. Although Ca has not been determined by INAA, it can be inferred that it is present in the samples due to the lithology of the rock on which the Lapa Grande de Taquaraçu site is formed, since it consists of limestone of high chemical purity, which may be influencing the amount of calcite.

Therefore, based on the XRD spectra, we can assume that the Ca is present in the samples that would correspond to the group considered anthropogenic, Group I, in the form of calcite and this crystalline phase is much superior to the quartz one. This greater amount of calcite may be due to the dissolution of limestone, however, fire ash is predominantly composed of calcite, due to decomposition of the calcium oxalate present in timber [Canti, 2003]. At the site of Lapa das Boleiras [Araujo *et al.*, 2008], near the Lapa Grande de Taquaraçu site, the presence of Ca is higher in the ashes, which were recognized as archaeological and this concentration decreases for samples that are not ash, similar to what occurs in the Lapa Grande de Taquaraçu site. Thus, the assumption that the calcite present in Group I may have originated from the burning of wood, and as such, is of anthropic origin, cannot be ignored.

Conclusion

Sixty sediment samples from four quadrants excavated from the rocky shelter of Lapa Grande de Taquaraçu were analyzed. The samples were studied using instrumental neutron activation analysis (INAA) in which the Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Sc, Th, U and Yb concentrations were defined. The results of the elementary analysis were submitted to group, principal and discriminant component analysis. The study showed the existence of three different compositional groups, where the depth of the samples had a significant role in the formation of groups. A subset of variables was also determined from the data matrix using Procrustes analysis. The results showed that only eleven variables (Eu, Cr, Th, U, Co, Yb, Cs, Na, La, Sc and Hf) are suitable for discrimination purposes. Some sediment samples from each group were analyzed by XRD and the results showed that there are differences in the crystalline phases of the samples of each group. The samples in Group I contained calcite as their major constituent, which may be due to the burning of timber. In the other two groups, the main species found was quartz.

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