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Chemical characterization by INAA of Brazilian ceramics and cultural implications

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Archaeological ceramic fragments from Água Limpa site, in São Paulo, Brazil, were analyzed using instrumental neutron activation analysis. Multivariate statistical methods including Pearson correlation coefficient, cluster and principal components analysis were used to interpret the concentration data. Rare earth and alkaline elements were highly correlated. Six principal components explained 74.9% of the total variance and five clusters were found. The sample chemical composition showed that all samples have the same provenance.

Introduction

Ceramic chemical composition characteristics play an important role in the study of ceramic provenance.[1,2] The composition of any ceramic fragment depends on the types and proportions of clay paste and mineral, rock, grog, and organic tempers used in its manufacturing.[1,3] It is well established that pottery can be grouped based on similarities or dissimilarities derived from chemical data.[2,4] Chemical differentiation of groups depends on the occurrence and measurement of discriminating elements within the clay matrix, that is, those elements showing significant concentration differences between production centers. In short, the combined total geochemical signature of the completed pot is the sum of constituents used and modified during the ceramic manufacturing process.[3]

Instrumental neutron activation analysis (INAA), is an excellent technique for analyzing ceramic materials, because it combines great analytical sensitivity with a relatively small sample, allowing the simultaneous determination of several elements in a large range of concentration, without any chemical treatment.[5–8] Moreover, for provenance studies, it is necessary to increase both sensitivity and accuracy to obtain the largest possible number of determinations with an analytical dispersion lower than the dispersion due to the differences of ceramic provenance.

The aim of this research is to characterize by means of inorganic constituents, the Brazilian pre-historical ceramic source from one archaeological site as potential indicators of the indian culture. The data obtained will help archaeological studies that are being made in the region with the objective of making spatial, temporal and cultural reconstruction of this time.

Experimental

Standard, ceramic and check sample preparation

Plain and red painted ceramic fragments from Água Limpa archaeological site, Monte Alto town, São Paulo State were analyzed. Archaeological characteristics of the site and samples were studied by Alves.[9,10]

Powered samples were obtained from ceramic fragments by cleaning an outer surface and drilling to a depth of 2–3 mm using a tungsten carbide rotary file attached to the end of a flexible shaft, variable speed drill. Depending on thickness, 3 or 5 holes were drilled as deep into the core of the sherd as possible without drilling through the walls. Finally, the powered samples were dried in an oven at 105 °C for 24 hours and stored in a desiccator.

Buffalo River Sediment (NIST-SRM-2704) and Coal Fly Ash (ICHTJ-CTA-FFA-1) were used as standards, and Brick Clay (NIST-SRM-679) and Ohio Red Clay were used as check samples in all analysis. These materials were dried in an oven at 105 °C for 24 hours and stored in a desiccator until weighing.

Description of the method

About 100 mg of ceramic samples, Brick Clay, Ohio Red Clay, Buffalo River Sediment and Coal Fly Ash were weighed into polyethylene bags and wrapped in aluminum foil. Groups of 6 ceramic samples and one of each reference material were packed in aluminum foil and irradiated in the swimming pool research reactor IEA-R1m at a thermal neutron flux of about $5 \cdot 10^{12}$ n·cm^{-2}·s^{-1} for 8 hours.

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Two measurement series were carried out using a Ge (hyperpure) detector (model GX 2020 from Canberra, resolution of 1.90 keV at the 1332.49 keV gamma-peak of ^{60}Co), spectra were collected with a Canberra S-100 MCA with 8192 channels. As, Ba, K, La, Lu, Na, Nd, Sm and Yb were measured after 7 days cooling time and Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, Zn and U after 15 days. Gamma-ray spectra analyses were carried out using the Vispect II software, developed by Dr. D. PICCOT, Saclay, France.

Results and discussion

For quality control purposes, Brick Clay and Ohio Red Clay were analyzed with each group of six samples. For both materials the precision for most elements was around 5% (As, Ce, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sb, Sc, Th) and only for Ba, Nd, Sm, Ta, Tb, U, Yb and Zn was around 10%. The interference of ^{235}U fission products in the determination of La and Ce was negligible. For most elements observed values agreed with certified or published ones.

Range, mean and standard deviation of 90 ceramic fragment analysis are presented in Table 1. The elemental concentration data were analyzed by means of Pearson correlation coefficients, cluster and principal components analysis (PCA) in order to obtain information about the ceramic source. Strong positive correlations among rare earth elements (REEs); As and Fe; Na, K and Rb; Cs and Cr; and Sc and Th were observed.

Table 1. Range, mean and standard deviation of elemental concentrations obtained for 90 samples of Água Limpa site (in $\mu g \cdot g^{-1}$) unless indicated

Element	Range	Mean ± SD	Element	Range	Mean ± SD
As	0.2 – 7.2	2.2 ± 1.1	Na	217 – 4068	1843 ± 690
Ba	671 – 2350	1308 ± 341	Nd	37 – 137	60 ± 14
Ce	84.9 – 356	126 ± 34	Rb	3 – 120	71 ± 17
Co	11.2 – 52.4	22.0 ± 7.5	Sb	0.08 – 0.65	0.25 ± 0.06
Cr	82 – 275	159 ± 35	Sc	10.16 – 44.9	16.2 ± 4.0
Cs	0.3 – 3.0	1.8 ± 0.5	Sm	6.33 – 23.76	9.8 ± 2.1
Eu	1.78 – 7.1	2.6 ± 0.7	Ta	1.2 – 16.4	3.7 ± 1.6
Fe, %	1.81 – 9.67	3.4 ± 1.0	Tb	0.67 – 2.6	1.1 ± 0.3
Hf	5.4 – 23.7	8.7 ± 2.1	Th	9.06 – 27.7	12.9 ± 2.5
K, %	0.24 – 2.7	1.8 ± 0.4	U	0.8 – 4.7	1.4 ± 0.5
La	43.6 – 178.9	72.9 ± 16.6	Yb	2.07 – 5.8	3.2 ± 0.6
Lu	0.24 – 0.67	0.38 ± 0.06	Zn	16 – 229	65 ± 30

Table 2. Factor loadings, communalities and associated variance

Element	PC1	PC2	PC3	PC4	PC5	PC6	Communality
As	–0.009	0.008	0.042	0.879	0.041	0.062	0.780
Ba	0.130	0.262	0.107	0.026	0.702	–0.055	0.593
Ce	0.652	–0.031	0.499	–0.252	0.071	0.101	0.754
Cr	0.405	0.156	0.790	–0.127	–0.078	0.092	0.844
Cs	0.223	0.479	0.381	–0.313	0.075	0.475	0.754
Eu	0.912	0.036	0.240	–0.042	0.101	–0.048	0.906
Fe	0.237	0.096	–0.357	0.793	0.054	–0.078	0.831
Hf	–0.044	–0.522	0.389	0.150	–0.276	–0.081	0.531
K	0.042	0.798	–0.003	0.093	0.121	–0.052	0.665
La	0.910	0.116	0.140	–0.045	0.111	–0.093	0.884
Lu	0.772	0.197	0.056	0.107	–0.089	0.063	0.660
Na	0.124	0.691	–0.046	0.380	–0.215	–0.275	0.761
Nd	0.853	–0.013	0.141	0.122	0.054	0.082	0.773
Rb	0.176	0.885	0.121	–0.075	0.130	0.189	0.887
Sb	0.008	–0.066	0.224	0.080	0.015	0.818	0.730
Sc	0.183	–0.580	0.611	0.003	0.101	0.042	0.755
Sm	0.935	0.064	0.207	–0.038	0.018	–0.045	0.925
Tb	0.833	0.009	0.128	0.024	–0.036	0.094	0.721
Th	0.303	–0.045	0.796	–0.124	–0.036	0.170	0.774
U	0.087	0.014	0.423	–0.018	–0.718	–0.080	0.709
Yb	0.818	0.044	–0.059	0.162	–0.063	0.029	0.706
Zn	–0.036	–0.107	0.262	0.107	0.452	–0.481	0.529
Variance, %	27.8	13.3	12.7	8.4	6.5	6.1	

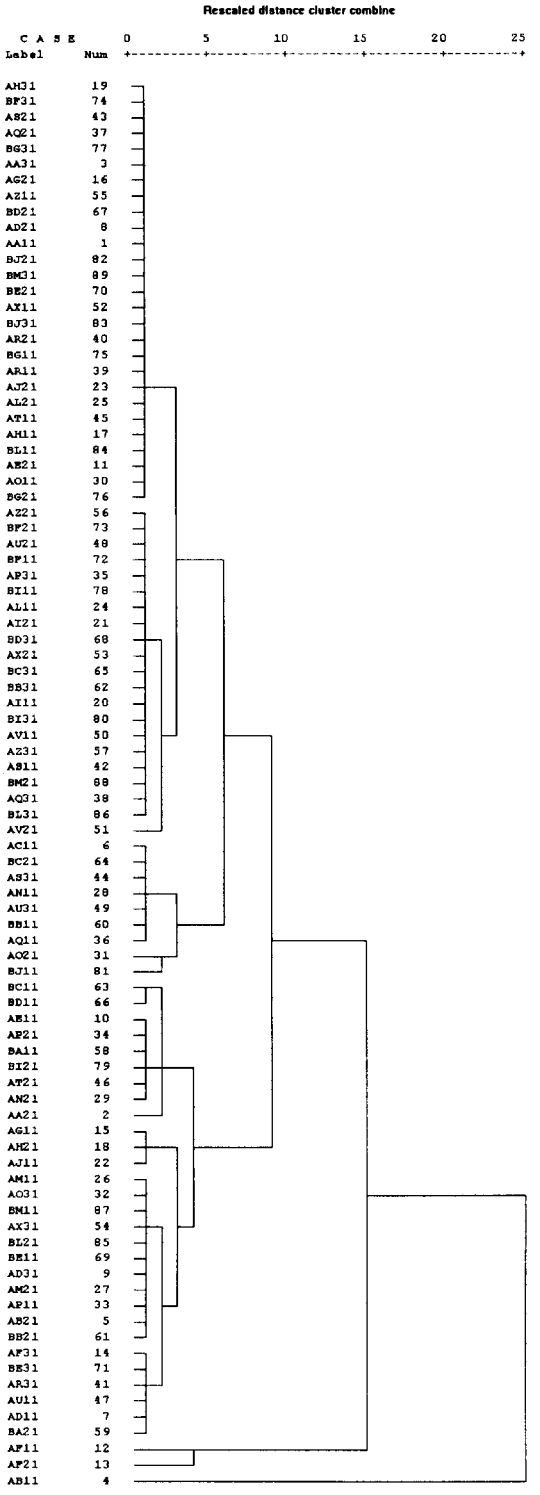

Fig. 1. Dendrogram of 89 samples from Água Limpa site

The Statistical Package for the Social Sciences (SPSS) was used to perform the hierarchical cluster analysis on the whole data-set using all elements, except Co and Ta, whose concentration can be affected by tungsten carbide files.[11] Squared Euclidean distances were used to calculate dissimilarities between samples. The resulting dendrogram shown in Fig. 1 allows the identification of five coherent groupings among the samples.

In the first cluster 58.9% of samples are grouped, whereas 10% of samples are grouped in the second and third cluster and 22% of samples appear in the fourth. A separate grouping appears to be created by samples AF11, AF21 and AB11, because of their elemental composition which shows anomalously high abundances of Ba, Na and Rb or As and Fe with respect to other samples. These samples could belong to ceramics produced with different clays available in the same territory.

Six components were extracted from PCA, being responsible for 74.9% of the variability of the data. The six component loadings are given in Table 2.The first component was responsible for 27.8% of the total variance and had high loadings for REEs. These elements tend to be concentrated in the finer sediments and are absorbed onto clay surfaces.

Only K, Na and Rb were separated in the second component. These elements seem to reflect the underlying variation due to differences in feldspar abundance. In several papers K has been considered as a member of the potassium mica clay group or as part of the nonplastic inclusions.[12] The addition of quartz sand temper can contribute to potassium-bearing minerals such as muscovite, biotite and, of course, potassium feldspar.

Component 1 can be considered to be more closely associated with ceramic matrix, while component 2 seems to be related to the feldspar which frequently occurs in greater abundance as part of the quartz sand temper.[12] This hypothesis should be confirmed by petrographic studies.

The fourth component had high loadings of As and Fe. Iron is a major determinant of paste color. It is important to note that all samples had high concentrations of iron.

It is also important to note that without chemical composition information it would have been very difficult to consider the fine-paste and tempered pottery had been manufactured from the same clay resources. Even among the tempered ceramics, statistical analysis is difficult due to the variation in elemental concentration resulting from differing amounts of temper.

Petrographic information may be a valuable aid in understanding the observed variability within the concentration data. Observations made from the chemical data should be verified by petrographic study of samples. This study will continue with a petrographic examination.

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