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Neutron Activation Analysis of Pre-Columbian Pottery in Venezuela

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Abstract. Pre-Hispanic pottery figurines from north-central Venezuela islands and mainland were analysed by neutron activation analysis (INAA and PGAA) at the Budapest Research to establish their provenience. In order to classify the samples of figurines, characteristic molecular and atomic components were determined. Several mass ratios were calculated for significant classification of the object of two origins. Results shed light on the origin of island figurines and suggest specific areas of their production on the mainland, contributing to better understanding of late pre-Hispanic migration patterns in the southeastern Caribbean region.

Keywords: INAA, PGAA, pre-Hispanic figurines, pottery, provenance study

1. Introduction

Amerindian population navigated seasonally between the Venezuelan north central regions to the Caribbean islands including the Los Roques Archipelago (LR). It is assumed that the bearers of the Valencia style pottery, from the Valencia Lake Basin (VLB), visited the Los Roques islands between A.D.1300 and 1500. In order to establish colonization or demographic expansion of the VLB-settlers, a large set of samples of almost eight hundred pre-Hispanic human pottery figurines are under study. Half of these have been recovered in four sites, systematically

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excavated in the Los Roques Archipelago. The origin of LR-island figurines (similar to that shown in Figure 1), potteries and other artefacts of archaeological importance, has been established on stylistic consideration, suggesting their relation to Valencia Lake Basin culture. To confirm this hypothesis on their origin, physical analysis other than stylistic consideration must be included.

Analyses in the modes of instrumental neutron activation (INAA) [1], prompt gamma neutron (PGAA) [2] and neutron resonance capture (NRCA) [3], have been applied in several field of study including archaeology for its sensitivity (10^{-3} to 10^{-10} grams per gram of sample) and accuracy (usually between two and ten percent of the reported value). These non-destructive, multi-element analytical techniques are useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in large or bulk samples as often encountered in archaeology. Depending on the requirements such as sample size or restriction on how manipulation should be carried out, it is up to the analyst to selects the analytical procedure e.g. INAA, PGAA or NRCA. For these analytical techniques, the basic essentials required to carry out a samples analysis, is a source of neutrons, instrumentation suitable for detecting gamma rays, software for spectrum analysis and a detailed knowledge of the reactions that occur when neutrons interact with target nuclei.

This paper aims to enrich a database of Venezuelan archaeology required to discuss the provenance of the pre-Hispanic pottery figurines using non-destructive neutron activation analysis, INAA and PGAA.

2. Samples origin and instrumentation

A set of samples from Valencia Lake Basin and Los Roques Archipelago was selected, representing different figurine styles (*Standardized*, *Imitative*, and *Heterogeneous)* [4,5]. In Figure 2 we show the site locations and samples origin. The figurine matrix material can be considered as an anthropologically metamorphosed sedimentary rock with clay as the major substance and shell, grit or sand as its minor components, consisting mainly from Al_2O_3, SiO_2 and H_2O with impurities as oxides of Ca, Fe, K, Mg, Na and Ti. However, most of the geochemically important elements, such as H, B, C, N, O, Si, P, S and also Fe are difficult to quantify with INAA because of the absence or very low natural abundance of corresponding isotopes and low (n,γ) nuclear reactions cross-sections. In these cases the PGAA method is more suitable allowing the panoramic analysis of silica-based geological rocks and of ceramics too [6]. Since the pottery sample is a low absorbing material for thermal neutrons the technique provide an average bulk composition.

Neutron activation analysis sensitivities, in its different mode, depend on the concentration of a particular element and radionuclide parameters such as parent isotope abundance, neutron cross-section, half-life, and gamma ray relative intensity. Further favourable characteristics are: negligible matrix effects, excellent selectivity and high sensitivity for about 75 elements.

The measurements were performed at the Budapest Neutron Centre facility where the 10 MW reactor provides several vertical neutron channels a cold neutron beam for sample irradiation. For INAA, short irradiation (5 min) was carried out in a pneumatic rabbit system, while the long irradiation (24 h) were accomplished in a revolving vertical channel. Samples were measured in a high-rate gamma spectrometer equipped with the latest Westphal's Loss-Free Counting (LFC) module with dual spectrum storage option to compensate all kind of pulse losses. For automatic analysis of complex gamma-ray spectra, HYPERMET-PC program package [7] is available. For concentration calculation the KAYZERO software package was used [8]. In the other case i.e. PGAA, cold neutron beam of 3 $10^7 cm^{-2}s^{-1}$ is provided at the irradiation chamber 36 m away from the reactor. Prompt gamma photons are collected by a HPGE-BGO detector with Compton suppressor. Also in this case spectra were analysed with the program HYPERMET-PC modified for the PGAA technique [9] and the concentration calculations are performed by an Excel-based macro. One important aspect of these two techniques is the standardization procedure. The applied method using compound nuclear constants (i. e. so called k0-factors determined experimentally in individual standardization measurements with high accuracy) eliminates the use of standard preparations for each set of measurements, and therefore possible errors related to nuclear data are as low as possible. It is worth mentioning that k0-values [10,11] and related nuclear data are now established for a large set of (n, γ) reactions and the method is now operational in more than 50 laboratories worldwide. (Its performance was recently evaluated in extensive tests by analysing European multielement standard reference materials developed at IRMM (Geel-Belgium).

3. Results and discussion

In Table 1 we show typical results and the relative uncertainty produced analysing prompt gamma spectra of samples irradiated with thermal neutrons. The first row is the sample code and the first column indicates the concentration of major components in weight %, and those of the trace in ppm followed by the uncertainty value. The concentrations of major components are given in oxide forms, as it is usual in geochemistry. Because of the poor sensitivity for oxygen, the values are calculated from the element concentration by oxidation numbers of the given elements.
Data shown in the different figures were collected to complement the already existing values corresponding so far to more than 100 archaeological samples. In figure 3 the LR-values exhibit a larger data scattering than VLB values. This observation may indicate that LR samples contain clay of several mining sites in opposition to the VLB samples that probably correspond to a single mining-clay or to places with similar geological formation. It is interesting to observe that data shown with "**x**-points" fit in the region of values related to VLB. This has a particular significance since these values refer to samples that have been already classified as VLB origin and current analysis confirms the accuracy of that classification. Trace elemental concentration could be considered to characterize better their origin from continental or else clay mining. Under this assumption a three-variant graphic is produced from concentration values of Sc, Gd and Sm these were selected from around the 30 measured elements. Further, a set of results are shown in Figure 5, in which we include data, that corresponds to samples for which already the origin has been established, shown, with "**o**". Similar results are given in Figure 6 and 7 corresponding to collected data [12] and reinterpreted here to evidence the importance of this study. From these two bivariate diagrams we may observe that both samples groups i.e. VLB and LR suggest that they have the same origin even if the tendency line, drawn only for eye guide, show a different slope. However observing the set of figures already mentioned, we might distinguish a dense group of values corresponding to both archaeological sites. Data corresponding to samples of Table 1, follow similar pattern and this could be important in data interpretation and classification of the objects of different excavation. In all these graphics we did not distinguish between data obtained either with INAA or PGAA since we were interested in elemental concentration only, so as to provide an argument for provenance studies.

4. Conclusions

A set of archaeological samples analysed by PGA ha been reported here with data previously acquired with INAA and PGAA techniques. These data complement those required to assess figurine and other pre-Hispanic artefacts provenance; so far some 100 samples from the Valencia Lake Basin and Los Roques archipelago have been analysed. Principal component analysis (PCA) of data reported [2] reveal some significant differences between the objects and to reduce the uncertainty a set of figurine were analysed to establish the origin of pottery figurines and to identify specific areas of production even in the case where they were stylistically different. Insular samples mentioned in Table 1 have a relationship with the continental samples (see Figure 3) and reinforce the previous hypothesis according to which the Los Roques and Lake Valencia figurines have similarity concerning elemental composition of major and trace elements and may suggest close connection of pre-Hispanic societies. However this conclusion is not clearly supported. For example: A345, AM645 and MA1505 insular samples have three trace elemental concentration values that fit well within the continentals VLB100, VLB8 and VLB58574 samples (see Figure 4) but the others are scattered. On the other hand, the MA880 and E82C17A insular sample compositional data show different scattered values from the VLB ones; we have to note that in both cases we observe values that depart e.g. VLB58579 from the expected values. Their importance is related to elemental composition of the bulk clay employed to manufactured figurines: in fact we expect scattered data also from samples of different mining site.

The process of the reconstruction of cultural and chronological regional sequences in north-central Venezuela region is far from being conclusive; however, we may assert that the results obtained in this study reinforce the existing thesis on close relationships which existed in the pre-Hispanic past between the inhabitants of the inland located Valencia Lake Basin and the human groups that exploited on seasonal basis the natural resources on the off shore Caribbean islands.

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Figure 1. A typical set of figurines for provenance study recovered from archaeological site in the Los Roques Archipelago (Venezuela).

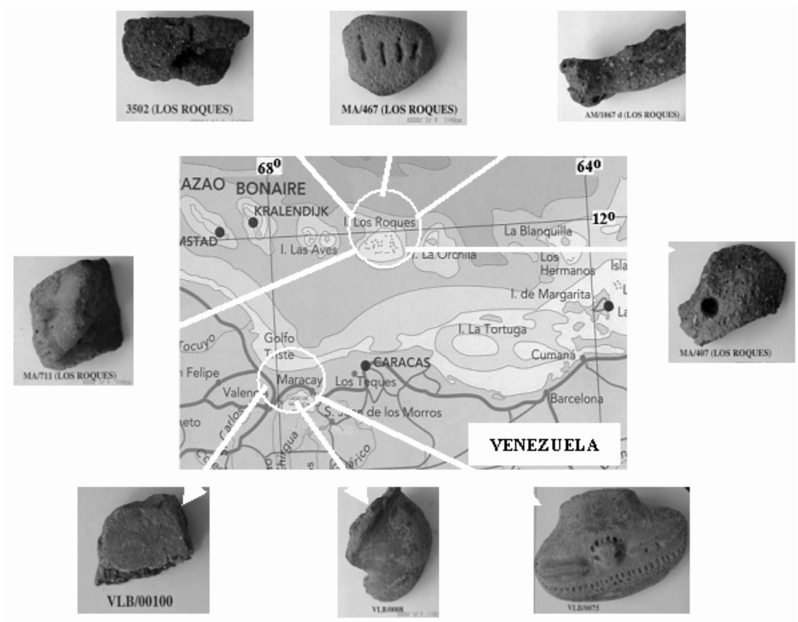

Figure 2. Location of the Valencia Lake Basin and Los Roques island archaeological sites; some pictures of analysed samples are given.

Table 1. Set of data obtained from processed gamma spectra (PGAA) of a group of figurines from Los Roques.

	AM 464		E82 C17A		A 345		MA 1505		MA 427		MA 880	
Molec.	c% ox/ox	*unc %*	c% ox/ox	*unc %*	C% ox/ox	*unc %*	c% ox/ox	*unc %*	c% ox/ox	*Unc %*	c% ox/ox	*unc %*
H2O	1.70	*1.6*	5.92	*1.3*	1.82	*1.5*	1.98	*1.4*	4.19	*1.3*	5.81	*1.3*
Na2O	2.60	*2.9*	2.25	*2.5*	3.12	*1.7*	2.73	*2.8*	3.26	*2.5*	1.59	*3.2*
MgO	1.65	*10.9*	1.78	*12.2*	1.34	*16.2*	1.81	*13.3*	1.27	*13.2*	1.97	*11.3*
Al2O3	15.17	*2.9*	15.96	*2.1*	16.25	*2.8*	15.58	*2.1*	14.86	*2.1*	18.22	*2.1*
SiO2	68.20	*2.4*	63.54	*2.4*	68.44	*2.4*	68.59	*2.5*	67.84	*2.5*	61.28	*2.4*
K2O	3.60	*2.0*	2.98	*2.0*	2.66	*2.2*	2.84	*2.1*	3.09	*2.0*	1.71	*2.2*
CaO	1.61	*3.7*	1.51	*4.0*	1.12	*4.2*	1.49	*3.7*	1.43	*3.7*	1.00	*4.7*
TiO2	0.52	*2.0*	0.55	*2.0*	0.52	*2.1*	0.52	*1.9*	0.42	*2.1*	0.87	*1.9*
MnO	0.07	*3.6*	0.10	*3.1*	0.08	*3.7*	0.04	*3.5*	0.14	*2.4*	0.05	*4.0*
Fe2O3	4.79	*2.0*	5.39	*1.9*	4.50	*2.3*	4.35	*2.1*	3.44	*1.9*	7.33	*1.9*
TRACE	/ppm											
B	19.60	*1.3*	27.40	*1.3*	13.01	*1.3*	30.28	*1.2*	42.21	*1.3*	87.88	*1.3*
Cl	344.93	*5.0*	89.23	*7.0*	489.33	*4.9*	414.42	*4.5*	315.45	*4.4*	929.00	*4.5*
Sc	17.82	*17.5*	0.00		15.63	*19.2*	14.21	*14.6*	0.00		33.08	*7.4*
V	108.71	*10.8*	0.00		73.64	*16.7*	94.20	*11.9*	0.00		259.50	*6.5*
Cr	0.00		0.00		507.80	*11.9*	0.00		0.00		0.00	
Nd	0.00		0.00		40.58	*12.3*	43.53	*10.7*	30.91	*14.8*	26.87	*16.7*
Sm	5.57	*2.0*	5.31	*2.0*	5.72	*2.1*	4.89	*1.9*	4.06	*2.2*	2.61	*2.3*
Gd	7.48	*3.9*	6.72	*4.1*	7.68	*4.1*	5.54	*4.1*	5.23	*3.4*	3.15	*3.6*

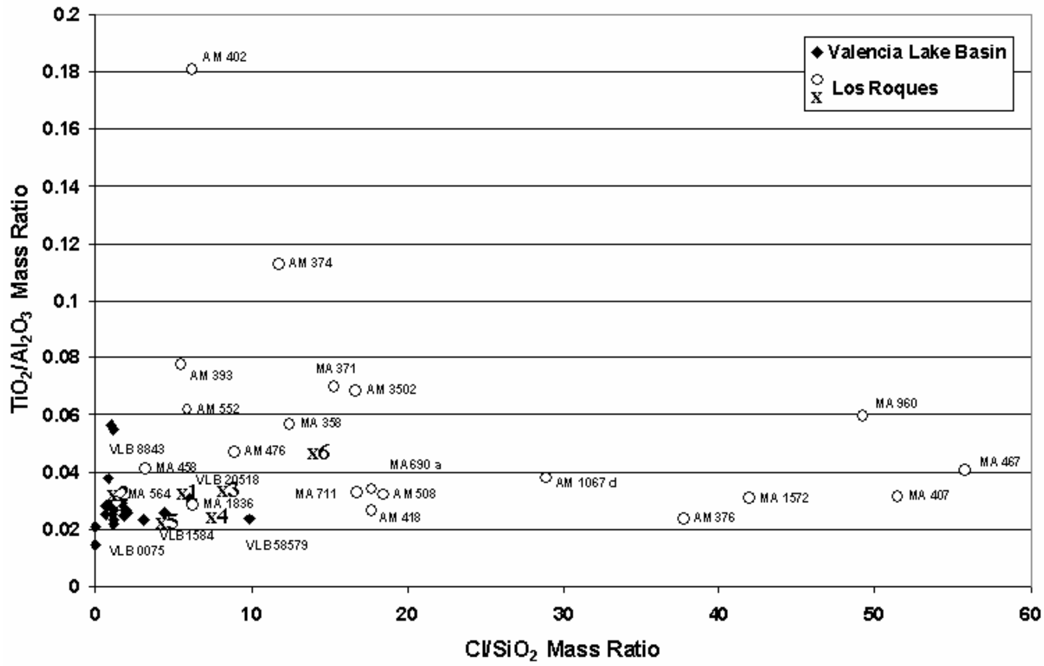

Figure 3.Comparison of results for the groups of archaeological samples. Diamond points indicate Valencia Lake Basin and all others Los Roques samples. X-Points are data collected to confirm the hypothesis on figurine provenance.

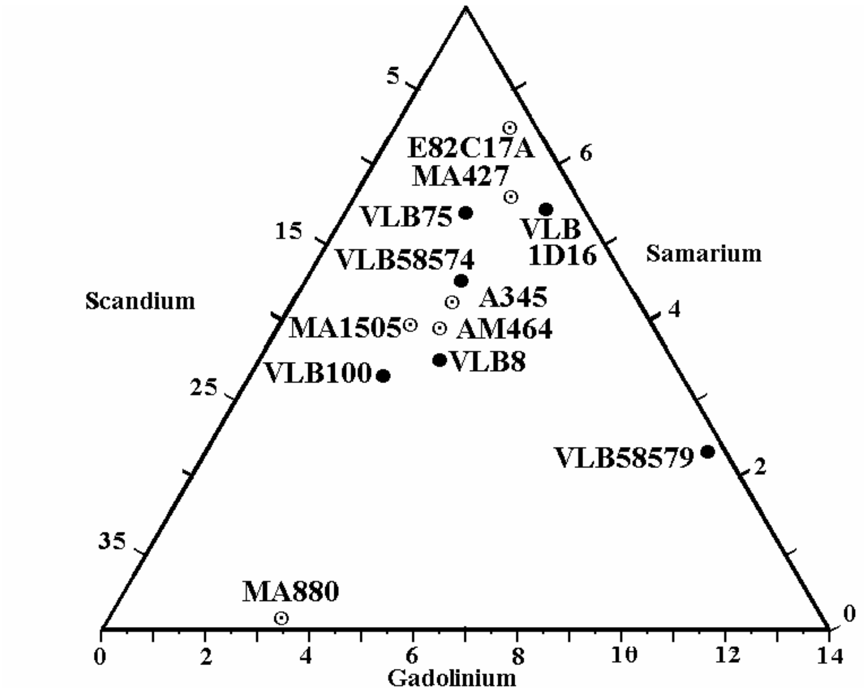

Figure 4. Three parameter representation of elemental concentration. Numbers on the axes indicate concentration in (ppm) and every point corresponds to the codified sample VLB for the Valencia Lake Basin and the others to Los Roques.

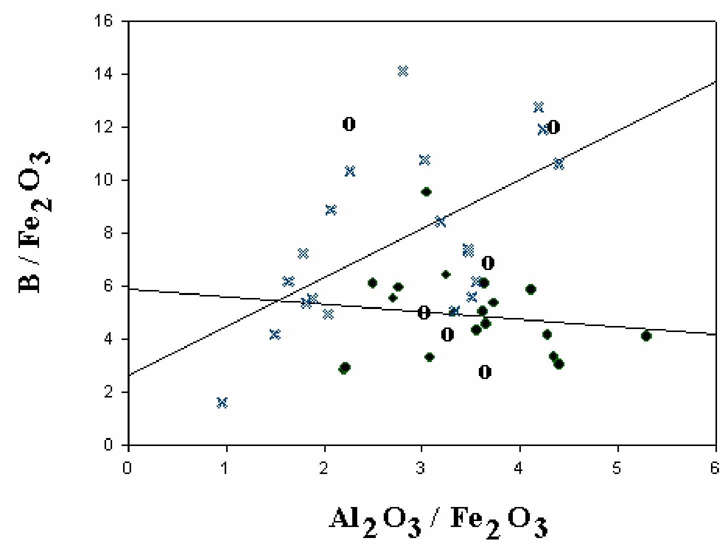

Figure 5. Data comparison of VLB samples (•) and Los Roques (x,o). The tendency line is shown for eye guide only.

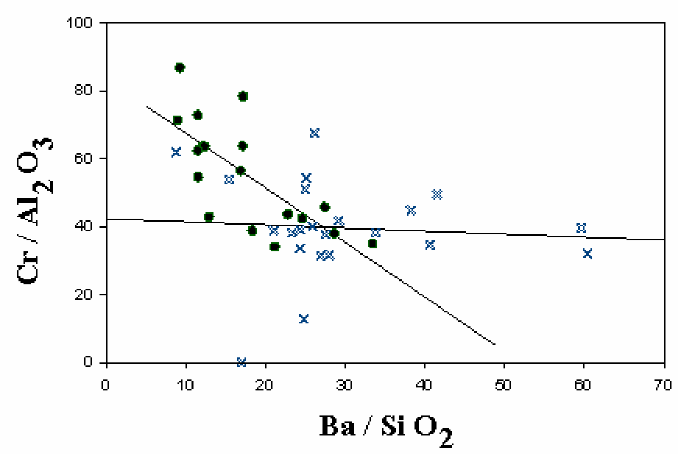

Figure 6. Pottery data for VLB samples (•) and Los Roques (x) which show significant classification of the object of two origins. Bivariate diagrams were constructed (e.g. Al and Si as major elements). The tendency line is shown for eye guide only.

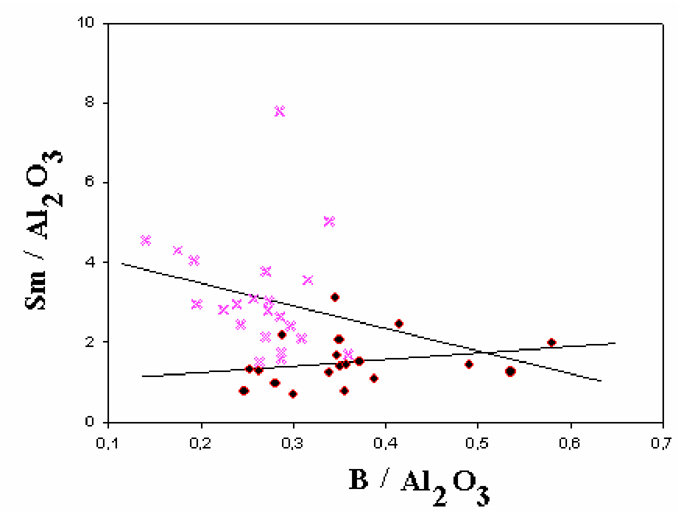

Figure 7. Pottery data for VLB samples (•) and Los Roques (x). Similar to Figure 6, this was constructed from concentration of Al as major and trace elements (Sm and B). The tendency line is shown for eye guide only.