Provenance study of Amerindian pottery figurines with Prompt Gamma Activation Analysis

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Abstract A Prompt Gamma Activation Analysis (PGAA) facility has been in operation at the Budapest Neutron Centre (BNC) since 1996. Nonetheless that PGAA is a relatively new method, its applicability to archeological research has already been established by several studies. Archaeologists of the Simón Bolívar University initiated a research project aimed to perform a provenance study of pre-Hispanic pottery figurines. Forty samples were selected from two archaeological sites excavated in the Los Roques Archipelago. Almost five hundred figurines have been recovered altogether in four sites of the Archipelago. Amerindian groups from the adjacent Venezuela mainland were identified as island sites' occupants, between A.D. 1200 and the European contact period. Forty fragments of figurines were investigated by PGAA, the concentrations of major- and some trace components being determined. Among others, K_2O, Cl and Cr were found to be the most significant indicators of the samples originated from the Lake Valencia Basin (mainland) and from Los Roques Islands. By relating the island figurines to their stylistical and chemical counterparts from the mainland we will provide chronological information on hundreds of mainland figurines.

Key words pre-Hispanic culture • pottery • non-destructive analysis • PGAA

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Introduction

The bearers of the Valencia style pottery (or the Valencioids) from the Lake Valencia Basin (north-central Venezuela mainland), had achieved control of the adjacent areas, including most of the central coast and began to colonize and exploit the oceanic islands to the north, between A.D. 1200 and the European contact period [1]. The abundance, size and functional diversity of the archaeological sites and their geographical spread suggest a demographic expansion of the Valencioid people and possibly an effective integration of the local Amerindian populations within the region. However, the current knowledge of the nature and dynamics of the relationships that existed between culturally different inhabitants of the *Valencioid Sphere of Interaction* is extremely limited. The only recent systematic excavations within the geographical borders of the *Sphere* have been carried out in the Los Roques Archipelago, 140 km off the mainland coast, where the Valencioid sites have been located on six islands [2]. Four sites yielded hundreds of human pottery figurines, some of which have been recovered in primary, ritual contexts [5]. Though the Valencioid artefacts from the mainland portion of the *Sphere* had attained worldwide notoriety as early as 1889 (at the Universal Exposition of Paris), examples of systematic research in this area are still very scant. In fact, the only systematic excavations on the mainland portion of the *Sphere* had been carried out in this area in the 1930s [2].

As a consequence, the public and private collectors all over the world hold hundreds of mainland figurines and other Valencioid artefacts that lack provenance and contextual data.

By performing non-destructive chemical analyses of the figurines we aim to add the new dimension to the connections that have been made during the interpretative process of the social reality and meaning of the Los Roques figurines, and to evaluate the hypotheses that explain the origin of their stylistic differentiation. We expected that the available stylistic and contextual descriptions of the figurines will provide interpretive frame to the patterns observed in the chemical data, helping to build bridges between the potentially relevant data sets. We are confident that the results of this research will contribute to our understanding of the nature of the relationships within the *Valencioid Sphere of Interaction* and especially, between the core area (the Lake Valencia Basin) and the periphery (the coast and the oceanic islands). We expect that we would also shed light on the significance of the figurines that are the "hallmark" of the Valencioid material culture.

Prompt Gamma Activation Analysis (PGAA) is based on the detection of prompt gamma photons, emitted following the capture of thermal or sub-thermal neutrons into the atomic nucleus. This is, in principal, capable to simultaneously identifying all chemical elements, although with very different sensitivities [8]. The method is suitable for qualitative and quantitative analysis of a few grams of solid, liquid and gaseous samples.

Contrary to the conventional Instrumental Neutron Activation Analysis (INAA), all the chemical elements emit prompt-gamma photons; thus PGAA is suitable for detection of every element. Indeed, most of the geochemical important light elements, such as H, B, C, N, O, Si, P, S and also Fe are impossible to detect with usual INAA because of the absence or very low natural abundance of the corresponding isotopes which undergo (n,β) nuclear reactions. Aluminum, as a major component, is also problematic for INAA measurements, because of the very high count rate produced by β^- decay of ^{28}Al [3].

PGAA, in principle, is suitable for quantitative determination of major- and some trace components of silica-based geological rocks and of ceramics, too. One has to take into account that because the sample is transparent to neutrons, an average bulk composition of the investigated volume is obtained. In order to gain the maximum information from the objects, combination of available complementary methods (PGAA, INAA, XRF, etc.) are strongly recommended.

Previous PGAA analyses were carried out over 8 samples indicating significant differences between the Lake Valencia Basin and the Los Roques figurine assemblages [6]. In this research we sampled a wider group of figurines samples in order to recognise their chemical characteristics and to establish relations using the chemical composition parameters.

Experimental

Instrumental

The Prompt Gamma Activation Analysis facility at the Budapest Neutron Centre has been gradually developed since 1996 [4, 10]. The Budapest Research Reactor, which supplies neutrons for irradiation experiments, is a 10 MW, water-cooled, water-moderated research reactor. Neutrons, transported by horizontal evacuated guides are cooled by a liquid H cell down to 20 K. At the end of the 36-m long guide, where the PGAA facility takes place, the thermal equivalent flux of neutrons is 5×10^7 cm^{-2}·s^{-1}. The samples are placed into a fixed position of a sample holder chamber, where the usual beam-size of 2×2 cm^2 can be reduced to a 1×1 cm^2 or smaller spot. The prompt-gamma photons, whose energy range lies between 50 keV and 11 MeV and which are characteristic of a given element, are collected with a complex detector system. The detector apparatus consists of a 5-cm diameter Canberra n-type high purity germanium (HPGe) surrounded by 8 bismuth-germanate (BGO) scintillation detectors, in order to perform Compton-suppression. The relative efficiency of the HPGe detector is 25% and the *FWHM* is 1.8 keV at 1332 keV (measured with a ^{60}Co source). The sample to detector distance was kept at 23.5 cm. A Canberra 8713 ADC and an S100 type 16 k-multichannel analyser with an automatic dead-time correction, collects the spectra. The collected spectra are evaluated by Hypermet PC, a gamma spectrum evaluation program developed at the Institute of Isotopes, Budapest [9].

The element identification during PGAA is based on the precise determination of gamma peak energies and intensities, as it is described by Perry *et al.* [8]. The detected gamma ray intensity A_E is directly proportional to the mass of a given element m, the analytical sensitivity S and the measurement time t.

$$(1) \qquad A_E = m \cdot S \cdot t$$

and

$$(2) \qquad S = \frac{N_A}{M} \cdot \theta \cdot \sigma_0 \cdot I_\gamma \cdot \Phi_0 \cdot \varepsilon\left(E_\gamma\right) \ .$$

The analytical sensitivity S is expressed in units of counts·s^{-1}·g^{-1} in Eq. (2). It is proportional to the neutron capture cross-section σ_0, of the nucleus, the isotopic abundance θ and the gamma yield I_γ, which are nuclear constants, as well as to the neutron flux Φ_0 and the detector efficiency $\varepsilon(E_\gamma)$, which are characteristics of the measuring system. Further symbols in Eq. (2) are: the Avogadro number, N_A, and the atomic mass of a given element, M. The mass ratios, or equivalently the weight-percentage ratios of arbitrary elements X and Y will be independent of the actual amount of the sample and also of the exact neutron flux. It can be calculated from peak area ratios and sensitivity ratios:

$$(3) \qquad \frac{w_X(\%)}{w_Y(\%)} = \frac{m_X}{m_Y} = \frac{A_X}{A_Y} \cdot \frac{S_{\gamma,Y}}{S_{\gamma,X}} \ .$$

The sensitivities for the most intensive prompt-gamma lines of all chemical elements were determined by internal standardisation measurements at the Budapest Research Reactor [11]. When all major elementary components are determined by PGAA, it is not necessary to measure a standard comparator material with the sample, since the concentrations can be determined using Eqs. (3) and (4):

(4) $$\Sigma_{w_i}(\%) = 100.$$

This criterion is usually fulfilled in case of geological samples, except the poorly detectable oxygen. The concentration of oxygen is calculated according to the usual oxidation states of major components.

It can be seen that the principal errors in determining the concentrations include statistical uncertainties of the peak areas and the sensitivities. The latter, which include the σ_0, I_γ, and $\varepsilon(E_\gamma)$ coeffitients, typically have standard deviations less than a few per cents, therefore the total uncertainty is primarily determined by the counting statistics. In case of geological samples, and similarly of ceramics, most of the major components and some traces of high sensitivities can be detected within a precision of a few per cent.

The sensitivities and the equivalent detection limits of PGAA vary over a wide range for different elements. For the elements of interest, one can determine detection limits for PGAA, C_L, from the measured spectra according to the following equation:

(5) $$C_L = \frac{2 \cdot \sigma_B \cdot FWHM}{S \cdot t}$$

where σ_B is the standard deviation of the baseline (background) counts in the spectrum and $FWHM$ is the typical full-width-at-half-maximum value of the significant γ-ray line. Detection limits for the sub-thermal neutron beam were calculated from a spectrum of a typical 3-hour-long measurement of a sample, supposing interference-free peak identification (see Table 2).

The samples

PGAA analysis of 40 samples, most of them being figurine fragments was carried out at the Budapest Research Reactor, 21 of which originated from the Los Roques Archipelago, while 19 came from the Lake Valencia Basin. The samples did not undergo previous restoration or cleaning process, except mechanical removing their soil contamination. They were simply placed into the normal sample position and irradiated in a specific area of 2×2 cm^2. In case of larger objects, the chamber was removed, and the object was placed into the same position relative to the detector system. The data acquisition time has varied between 780 and 47,500 seconds, depending on the sample size, in order to gain sufficiently good statistics for spectrum evaluation. After irradiation, the samples were cooled for a few days, in order to let the residual radioactivity decay. All the objects were checked prior to shipping back to the museums involved.

Table 1 shows the main stylistic characteristics and locations where the samples were collected (see Fig. 1).

Results and discussion

As we expected from previous investigations of geological samples, we were able to determine all the major components, such as H$_2$O, Na$_2$O, MgO, Al$_2$O$_3$, SiO$_2$, K$_2$O, CaO, TiO$_2$, MnO and Fe$_2$O$_3$ with sufficient precision.

In addition, we identified some geologically important trace elements, like B, S, Cl, Sc, V, Cr, Ba, Sm, Eu, and Gd with extremely high sensitivities for B and some rare-earth elements. The detailed concentration data and their precision of two characteristic samples, together with the detection limits are shown in Tables 2a and 2b. In order to classify the objects, characteristic chemical components were sought. Several mass ratios were calculated, and from those, which show significant classification of the object of two origins, bivariate diagrams were constructed.

We were able to classify the samples according to Na$_2$O, K$_2$O, Ti$_2$O, B, Cl and Cr more or less significantly (see Figs. 2 and 3). The geochemical explanation for the importance of these elements, however, is not given here. The best element to differentiate was found to be chlorine. The samples from the Islands show higher Cl content, though the reason for this is unknown. Since the Los Roques artefacts were buried for 600–800 years and the pottery could have been in contact with sea water during the transportation of the artefacts (crossing 140 km of open sea), this observation could be explained by the adsorption of NaCl from sea water. However, contrary to the behaviour of Cl, no such extended Na content can be observed in the same objects. Furthermore, PGAA reveals the bulk compositions of the samples, which means that the inhomogenities on the surface are suppressed.

In addition to the characteristic elemental ratios, Principal Component Analysis (PCA) was applied to the standardised data, in order to seek patterns of differential

Fig. 1. Region of North Central of Venezuela within the Caribbean.

Table 1. Archaeological descriptions of the investigated objects.

Sample no.	Inventory no.	Locality archaeological information	Specimen	Stylistic and/or typological information
1	VLB 00100	Peninsula La Cabrera, Los Tamarindos site, northeastern shore of Lake Valencia	figurine leg	standardised
2	VLB 0075	Peninsula La Cabrera, Los Tamarindos site, northeastern shore of Lake Valencia	figurine head	standardised or imitative
3	3502	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	figurine leg	heterogeneous
4	AM 1067 d	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/C, level 20–40 cm	figurine head fragment	standardised (standing straight legs canoe-shaped crest)
5	VLB 0008	Peninsula La Cabrera, Los Tamarindos site, northeastern shore Lake Valencia	figurine trunk with leg	heterogeneous?
6	MA 467	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	figurine leg	standardised (seated spread legs)
7	MA 407	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	figurine trunk (female with head)	standardised (red top rounded head)
8	MA 711	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/C, level 20–40 cm	figurine trunk fragment with akimbo arm	standardised
9	AM 402	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	human figurine	imitative (seated spread legs with inverted canoe-shaped crest)
10	AM 374	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	figurine trunk with head	heterogeneous (standing without crest three-dimensional anatomical figure)
11	AM 393	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	below waist fragment	heterogeneous
12	MA 960	Krasky Island, Los Roques Archipelago, trench KR/A/A, level 20–40 cm	figurine legs	imitative
13	VLB 1590	Peninsula La Cabrera, Los Tamarindos site, northeastern shore of Lake Valencia	figurine head	heterogeneous
14	VLB 1585	Peninsula La Cabrera, Los Tamarindos site, northeastern shore of Lake Valencia	figurine leg	standardised (seated)
15	MA 1572	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/C, level 20–40 cm	figurine fragment	standardised
16	VLB 1601	Peninsula La Cabrera, Los Tamarindos site, northeastern shore of Lake Valencia	figurine head fragment	standardised
17	MA 690 a	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/C, level 20–40 cm	seated female figurine	standardised (seated spread legs with canoe-shaped crest)
18	VLB 3745	Lake Valencia, eastern shore	figurine head fragment	imitative
19	VLB 1584	Peninsula La Cabrera, Los Tamarindos site, northeastern shore of Lake Valencia	figurine head fragment	standardised
20	VLB 1415	Lake Valencia Basin	figurine head fragment	standardised
21	VLB 8843	CIA site, northeastern shore of Lake Valencia	figurine trunk (male) with head	standardised
22	VLB 8843	CIA site, northeastern shore of Lake Valencia	figurine trunk (male) with head	standardised
23	VLB 20517	Caña de Azucar site, Lake Valencia Basin	figurine leg	standardised
24	MA 1836	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/C, level 0–20 cm	figurine leg fragments	standardised
25	VLB D-33	La Mata site, eastern shore of Lake Valencia	figurine head fragment	standardised
26	VLB 20518	La Mata site, eastern shore of Lake Valencia	figurine head fragment	standardised
27	AM 476	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	figurine trunk	heterogeneous

Table 1. Continued.

Sample no.	Inventory no.	Locality archaeological information	Specimen	Stylistic and/or typological information
28	MA 564	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/A, level 0–20 cm	figurine leg	imitative
29	MA 564	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/A, level 0–20 cm	female figurine	standardised (seated bent-knee, deformed head)
30	VLB 20519	La Mata site, eastern shore of Lake Valencia	figurine head fragment	standardised
31	MA 358	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	figurine head	imitative
32	AM 552	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	figurine legs	standardised
33	VLB D16	Tocorón site, southeastern shore of Lake Valencia	figurine head fragment	standardised
34	VLB 58579	eastern shore, Lake Valencia	figurine head fragment	imitative
35	VLB 58565	eastern shore, Lake Valencia	figurine head fragment	imitative
36	VLB 58574	eastern shore, Lake Valencia	figurine head fragment	imitative
37	AM 376	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 20–40 cm	figurine	standardised (seated bent-knee, red top deformed head)
38	AM 418	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 0–20 cm	figurine	standardised (standing straight legs with plain crest)
39	AM 1508	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/C, level 20–40 cm	figurine head fragment	standardised
40	MA 371	Dos Mosquises Island, Los Roques Archipelago, trench DM/A/B, level 0–20 cm	figurine	heterogeneous (standing without crest three-dimensional anatomical figure)

distribution of the samples within the compositional space. We used a shareware version of Excel-based "XLSTAT" software to perform the PCA calculations. This would allow us to see the data dispersion when the correlation among the elements was a part of the data analysis. As the components are linear combination of all the original composition data, PCA can reveal some significant differences/similarities between the objects – even in the absence of rigorously defined groups. According to PCA of all the measured samples, the pottery samples, which were excavated in the Valencia Lake Basin ($-1 < $ 2nd PC < 6) are significantly different from those, which were excavated in the Los

Roques Islands ($-6 < $ 2nd PC < 2). However, there is an overlapping around the 2nd PC $= 0$ region (see Fig. 4).

Conclusions

In this paper, we introduced the Prompt Gamma Activation Analysis, an absolutely non-destructive analytical method, which is applicable in investigation of pre-Columbian pottery figurines. We were able to determine all the major- and some interesting trace components of the bulk material with satisfying precision. Searching for characteristic
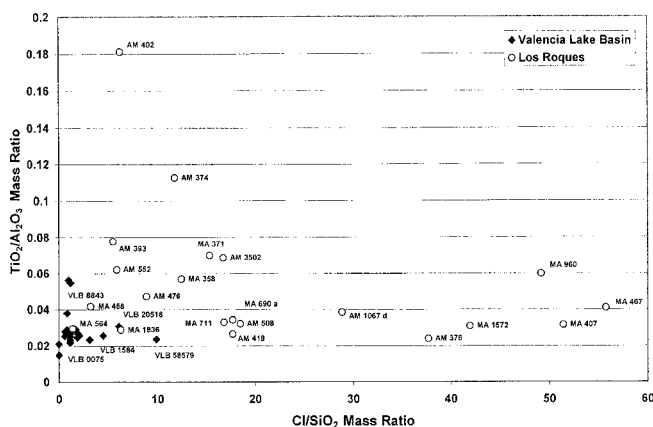

Fig. 2. TiO_2/Al_2O_3 *vs.* Cl/SiO_2 for the objects measured by PGAA.
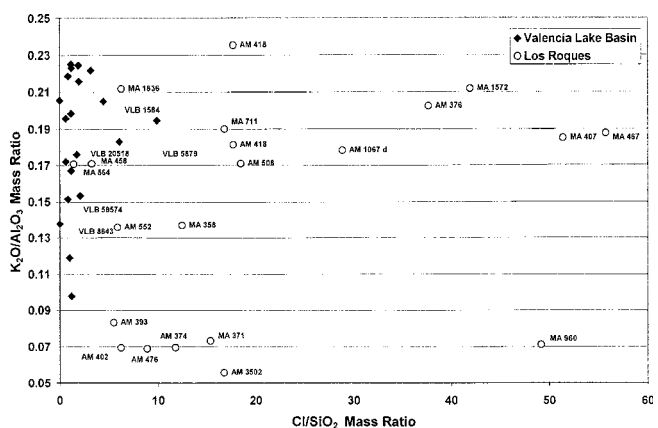

Fig. 3. K_2O/Al_2O_3 *vs.* Cl/SiO_2 for the objects measured by PGAA.

Table 2a. Detection limits and major components of two characteristic samples originated from Valencia Lake Basin and Los Roques, consequently.

w%	H_2O	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Det. lim.	0.004	0.02	0.24	0.12	0.18	0.03	0.16	0.01	0.008	0.02
VLB00100	4.49±0.05	1.03±0.03	1.9±0.2	16.9±0.3	64±1.5	3.65±0.07	1.61±0.06	0.45±0.02	0.048±0.002	5.5±0.1
MA 467	4.79±0.05	3.03±0.05	2.0±0.1	14.2±0.2	66±1.5	2.66±0.05	1.32±0.04	0.58±0.03	0.064±0.001	4.4±0.1

Table 2b. Detection limits and trace components of two characteristic samples originated from Valencia Lake Basin and Los Roques, consequently.

µg/g	B	Cl	Sc	V	Cr	Sm	Gd
Det. lim.	0.06	6	6	16	60	0.02	0.02
VLB00100	52.8±0.5	124±5	22±2	126±11	204±11	5.8±30	6.9±0.3
MA 467	37.5±0.3	3680±120	12±1	72±4	367±20	4.1±0.1	4.6±0.2
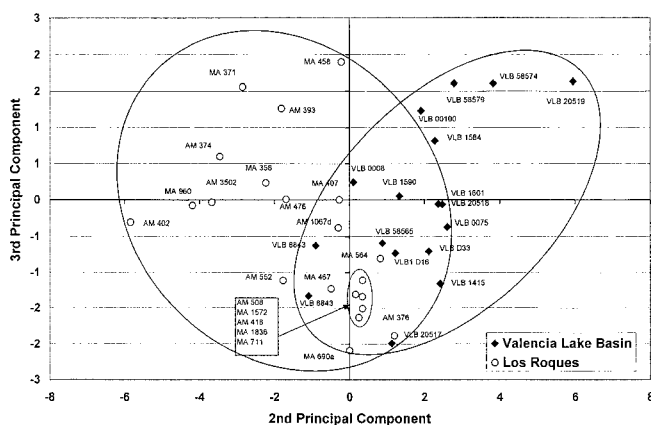
Fig. 4. Principal Component Analysis of the objects measured by PGAA.

elemental ratios, Na_2O, K_2O, Ti_2O, Cr, and Cl were found to reveal significant differences between the samples originated from the Los Roques and Lake Valencia Basin regions, respectively. The increased level of Cl in the Los Roques objects requires further study; it cannot be attributed to the sea water alone. The separation of different origin samples seems to be reinforced by Principal Component Analysis, too.

However, the observed differences between the objects must be supported by other analytical and stylistical studies. In case of the coarse-textured and tempered pottery, the petrographic analysis is advisable [7, 12], but unfortunately this technique requires partial or total destruction of the objects (many of the investigated figurines are museum objects with unique value).

We also suggest further research on the weathering effects, which is essential in case of archaeological pottery, buried for hundreds or thousands of years. It is also necessary to study soil samples taken from the vicinity of the archaeological sites, and compare the chemical composition of the objects and the original clay material. There are several sites in the mainland that we have to sample and, finally, we will certainly see that some site-samples are more related to island specimens, while other may be not related at all. We think that this paper is an important contribution toward an overarching project that needs to be continued.

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