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Nuclear Analytical Techniques in Archaeological Investigations

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FOREWORD

Pre-Hispanic pottery has long been a focal point of archaeological investigations in the New World, particularly in Latin American countries where these studies can form bridges from the ancient population to modern society. Identification of the chemical composition of ceramic materials can help in this connection to identify: (a) ancient production centres, (b) ceramic production modalities and special techniques, (c) trade habits and, hence, the socioeconomic interactions of the past.

Some of the countries of this continent have only recently introduced nuclear analytical facilities that are ready to be applied to relevant applications in various fields. A particularly successful combination of analytical expertise and a field of common interest in the Latin American region was created through the Co-ordinated Research Project (CRP) on Nuclear Analytical Techniques in Archaeological Investigations, organized by the IAEA following the recommendations of an Advisory Group meeting. The first Research Co-ordination Meeting (RCM) of the CRP was held in June 1997 at the Smithsonian Institution in Washington, DC, where the participants were introduced to the concept of the project and the preliminary work plans were outlined. Emphasis was given to a close collaboration between analytical scientists and archaeologists — from the definition of the problem, selection of sampling sites and samples to interpretation of analytical results using multifunctional statistical analysis. Also highlighted was the validation of analytical techniques using several certified reference materials. In April 1999 a second RCM was held in Cuzco, Peru, to present and discuss preliminary results of the individual projects and to refine the methods used.

The final RCM, which was held in Santiago, Chile, from 6–10 November 2000, revealed extensive information obtained by the participating research groups during the CRP, which is described in detail in this report. As the research objectives of each group were very particular, i.e. related to each country's specific situation, the range of results is exceptionally broad. The results demonstrated the great potential of the combination of nuclear analysis and archaeological research.

It is hoped that the research teams maintain their collaboration and that others will learn from them in their respective countries to spread the idea of co-operative research in various fields and to use the expertise they have gained to advance nuclear analytical techniques. It would be most desirable to foster this approach through future activities in the region with more countries involved and, possibly, to apply it to common problems in the region.

The IAEA wishes to thank all the participants in the CRP for their valuable contributions. R.L. Bishop from the Center for Materials Research and Education of the Smithsonian Institution helped a great deal with his emphasis on using the interdisciplinary approach and in encouraging the participants to go beyond mere phenomenological interpretations and to use their imaginations rather than the descriptive approach alone.

The IAEA officers responsible for this CRP were M.A.R. Walsh, A.V.R. Reddy and M. Rossbach of the Division of Physical and Chemical Sciences.

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Part I

OVERVIEW OF THE CO-ORDINATED RESEARCH PROJECT

Chapter 1

TECHNIQUES USED AND RESULTS OBTAINED

1.1. INTRODUCTION

Identification of archaeological artefacts according to morphological or stylistic criteria sometimes cannot be readily achieved between different production sites or origins based on visual inspection alone. Chemical analysis, together with statistical data treatment, is used extensively to supplement archaeological investigations when provenance studies or socioeconomic aspects are concerned [1.1–1.3]. A number of different analytical techniques have been applied with varying degrees of success, but all of them need to have multielement capability and sufficient sensitivity to detect traces of elements in the various matrices. Coins and other metallic artefacts, stones and obsidians, pottery, and wooden tiles and other organic material artefacts, have all been subjected to chemical fingerprinting and provenancing. The real success story of this technique, however, comes from the investigation of ceramics dating from throughout archaeological times. Pottery was important in trade, and the composition of pottery is strongly related to the source of clay and the recipe of the fabrication. This is highly site specific and, although similar in style and appearance, in critical cases it is possible to distinguish among the products of different producers by determining the chemical composition.

On the basis of the recommendations of an Advisory Group meeting, the IAEA initiated a Co-ordinated Research Project (CRP) in Latin America to introduce principles associated with archaeo-chemical ‘fingerprinting’. These principles involved characterization of ceramic materials through the application of nuclear analytical methods. Seven laboratories from six countries participated in teams each composed of an analytical scientist and an archaeologist to investigate national problems of archaeological interest.

Considerable achievements were made during the three year duration of the project. Understanding of each other’s discipline by the scientists involved, as well as by the teams of the different laboratories, was strengthened. Also, perception of the scientific process from the formulation of the problem to the evaluation of large data sets, including appropriate quality assurance, was strongly enhanced. Promotion of the beneficial use of nuclear analytical techniques to solve common problems is one of the important mandates of the IAEA. It has been successfully demonstrated within this project that instrumental neutron activation analysis (INAA) could add valuable information to the interpretation of archaeological problems. There is interest to initiate similar activities in other regions, i.e. Europe and Asia.

The participants were satisfied with the opportunities made available through the CRP to extend their experience to this important field of research, the need for which is increasingly gaining importance in the Latin American region. The guided introduction and formation of interdisciplinary groups from each participating country, coupled with the exchange of experiences among the different groups, strongly enhanced awareness of the capabilities of the method and demonstrated the appropriateness of INAA for archaeological research. As the technique was successfully applied under a wide variety of social and environmental conditions, it opened new perspectives for future research and enhanced recognition of the importance of formulating appropriate research objectives prior to the application of analytical techniques to solve archaeological problems.

1.2. SUMMARY OF RESEARCH RESULTS

The Peruvian team from the Instituto Peruano de Energía Nuclear (IPEN) provided the results of their national project within which about 400 ceramic samples of pre-Columbian origin were analysed. By using multivariate statistical analysis, nine distinct groups of pottery were identified. These groups coincided either with the place of origin or with time as determined by differences in stratigraphic occurrence. Different ceramic styles represent different cultural or geographic zones, and these differences can be better resolved using elemental fingerprinting techniques.

The team from Argentina (from the Comisión Nacional de Energía Atomica (CNEA)) presented their national research project dealing with the comparison of pottery from two distinct areas in the northwest part of Argentina, close to the Andes. More or less the same range of elements was determined, but there was no distinct grouping since different concentrations could be found by statistical means. It was concluded that the raw materials for the preparation of the pottery were very similar chemically, or, due to extensive trading activities, the exchange of ceramics between the groups was too large to identify any particular grouping on the basis of elemental concentrations.

The São Paulo group (IPEN (Br)), the first team from Brazil, presented the results of 24 elements in 149 ceramic samples from three different sites in the state of Minas Gerais. Three distinct and very confined clusters of pottery could be identified using the multivariate data analysis. It was concluded that at each investigated site one single clay deposit was used for production, and that no exchange between adjacent social groups took place 1000–1500 years before.

The Belo Horizonte group from the Centro de Desenvolvimento de Tecnología Nuclear (CDTN), the second team from Brazil, gave a very interesting presentation on pottery samples from the water catchment area along the Rio Negro and from the Amazon area close to the coast. The project involved a study of a double ring shaped village, half of which belonged to the Uru tradition and the other half to the Aratu tradition (1200 A.D.). In all three cases a clear distinction could be made among the pottery types due to their elemental composition, even though the geomorphology of the Amazon basin suggests not very distinct differences between sites and/or the excavation sites were very close to each other (ring shaped village). This finding suggests that in neighbouring places different groups of potters made ceramics using different clay deposits and that distinct differences exist in the origin of pottery in the catchment area of the Rio Negro (exchange through trade did not prevail).

The Chilean team from the Comisión Chilean de Energía Nuclear (CCHEN) presented results of investigations of ceramic artefacts and clay samples from the Maipo region in Chile. Eight different sites were investigated from four subregions from the Andes to the coastal sites. The main goal of the investigation was to find evidence of the regional interaction and organization in the Aconcagua culture during the late intermediate period (900–1450 A.D.) in central Chile. With the exception of As concentrations, no distinct concentration differences could be found to determine patterns within the investigated study area. This was attributed to (a) the extreme geological heterogeneity of the region, (b) the mixing of clays of different origins to produce specific colour effects and (c) the dispersion of the pottery producers. Rather than a specialized pottery manufacture, every family had their own resources, production and recipes resulting in an enormous diversity of chemical compositions.

From Cuba, two national projects were presented: one (from the Centro de Estudios Aplicados al Desarrollo Nuclear (CEADEN) on "Classification of the regional aborigine ceramic production and distribution in the central region of Cuba based on INAA" and the other (from the Instituto Nacional de Investigaciones Nucleares (ININ)) on "Classification of majolica pottery from colonial Havana based on INAA". In the first presentation about 400 samples from archaic sites were analysed, with the result that three distinct groups could be identified in a principal component analysis. In the second presentation colonial pottery from various sources was analysed and some of the samples could be reclassified as originating from Italy (Liguria) rather than from Spain, as had been assumed from the glaze resembling the Sevilla blue type.

Forty-two ceramic sherds from a temple excavated near Mexico City were analysed but only a rough distinction could be made between the Mexico City and Puebla ceramics on the basis of Mn, Hf, Sc, Fe, Co and Cr. It was recommended to use analytical results of sherds of known origin rather than the elemental concentrations of natural clay beds to calibrate the technique in order to identify groups of different origin.

The protocols used by the participants for sampling, sample preparation and analysis, data evaluation, and quality control exercises and results are described in the following sections.

1.3. SAMPLE SELECTION OF ARCHAEOLOGICAL CERAMIC MATERIALS FOR INAA

A sampling strategy is required whenever compositional analysis is done because only a selected number of specimens can undergo specialized and costly procedures. Sampling procedures will definitely depend upon the archaeological problem formulation.

When nuclear activation techniques are to be used, some kind of provenance question is most commonly involved. That means that a regional or supra-regional scale of analysis is the most frequent working level at which to investigate the movement of goods or people, to find evidence of production localities and the distribution of vessels in a spatial dimension, or to distinguish local from non-local vessels. Sampling must be sufficient, in terms of the number of specimens analysed, that stated research objectives have the possibility of being met. Usually this will mean sufficient numbers and inclusiveness of the ceramic categories that are relevant to the objectives.

Ceramic analysis begins with some taxonomic procedure in order to organize all the sherds and vessels from one or many sites, or a whole study area. These procedures are dependent upon the theoretical orientation adopted and the research questions to be addressed but often involve sorting sherds into groups based on surface treatment, decoration, morphology and fabric characteristics in a manner that maximizes intra-group similarities and inter-group differences. These groupings may be related to different issues such as functional, symbolic or cultural traditions. Once the ceramic assemblage has been classified and analysed using diverse variables and traditional archaeological techniques, the groups that are formed are the sampling strata for the selection of the samples that will undergo further analytical scrutiny (see Table 1.1).

It is widely recognized that pottery is a heterogeneous material that reflects the merging of different sources of natural and cultural variation. One of the main concerns for sample design is how to obtain a sample whose intra-group variation will not obscure inter-group differences. Although the number of specimens is a definite variable affecting the possibility of regional distinctions, some consideration of the geological and geochemical characteristics of the region is required. This is especially so since raw materials (clay and temper) need not coincide in the place of procurement.

Raw materials for ceramic manufacture may exhibit marked differences regionally and enable the recognition of microzones that can be equated with 'resource procurement zones' [1.4]. This situation has been used as a generalization under the assumption that intrasource variability is less than that encountered between sources [1.5]. Such a generalization, although not valid in all geographical situations, is a good starting point for the theoretical validity of compositional

TABLE 1.1. SOURCES OF COMPLEMENTARY INFORMATION

Sources of complementary information	Research group						
	CNEA	CCHEN	CDTN	CEADEN	ININ	IPEN (Br)	IPEN (Pe)
Archaeological records	▨	▨	▨	▨	▨	▨	▨
Historic and/or archival documents	▨			▨	▨	▨	▨
Geography and/or geology	▨	▨	▨	▨	▨		▨
Stylistic description	▨	▨	▨	▨	▨	▨	▨
Mineralogical analysis	▨	▨			▨	▨	
Petrographical analysis		▨		▨	▨	▨	▨
Optical low resolution microscopy inspection	▨	▨	▨	▨			
Dating techniques (^{14}C, TL)	▨	▨				▨	▨
SEM[a]				▨	▨	▨	
PIXE[b]					▨		

[a] Scanning electron microscopy.

[b] Particle induced X ray emission.

analyses. Another useful guide is that derived from ethnography, where it has been recognized that potters in traditional societies will not usually walk more than 7 km from their household to obtain the resources for making pots [1.6].

When there is considerable homogeneity over extended areas, however, the places of procurement will be more difficult to distinguish. Apart from sampling vessels or their fragments, prior knowledge of the geological and geochemical characteristics as well as the sampling of natural resources is sometimes helpful, since the ceramic elemental composition ultimately depends upon them.

1.3.1. Sampling of ceramic materials

From a statistical point of view, the number of samples falling into each suspected group should be large enough to ensure a statistically meaningful data set including the failure samples (e.g. outliers, misclassified samples, analytical failures and concentrations below the detection limits). Multivariate analysis requires a large number of samples to be reliable. A rule of thumb was developed for giving guidance on the number of required samples. It is based on the calculation of the number of degrees of freedom per variable in the analysis, $N - (V - 1)/2$; this number should be at least 30 and preferably 60 or greater. These values are seldom met in archaeological case studies of neutron activation analysis applications. A more realistic rule of thumb is “to initially submit 10–15 examples of each major class of interest from each site within a survey area” [1.1]. It is important to be aware that the compositional pattern can be seriously altered as a result of substantially increased sampling of specimens [1.7].

Once the ceramic groups have been determined, the archaeological problem to be solved should be the starting point in any definition of criteria for compositional sampling strategy. Sampling involves decisions at different levels. The first level determines the study area strata, which might be, for example, sites, environmental conditions or ceramic ware characteristics. At this level, the total number of neutron activation analysis samples that will be analysed in a project must be estimated in order to have an appreciation of the magnitude of the work to be done and of whether the quantity of data is coherent enough, and relevant and sufficient to the research problem. The second level determines the samples that will represent each study area stratum. A proportionate or non-proportionate strategy might be selected. It is a common procedure to prefer the most abundant ceramic classes in the sites under study. In spite of this general statement, some researchers include exotic and peculiar rare pieces to solve interaction and/or exchange issues.

There are two main strategies for sampling: random and problem oriented. Both must determine the percentage of the whole to be analysed through neutron activation analysis. In the first, infrequently used, case the whole ceramic universe is subjected to a selection dependent upon random numbers. In the second case, the analyst determines which previously determined groups (sampling strata) will be sampled and selects a proportionate number of sherds from each group to meet the percentage established.

The selected samples must be recorded in a database, which might be the same as that used for the general recording of the materials in the archaeological investigation in order to correlate the elemental data with other ceramic attributes as well as with other archaeological materials, spatial dimensions, chronologies and contexts. Sherds are coded according to provenance (collection unit) and have an individual register number. Photographs and a piece of the sherd analysed are kept with the database for future control tests.

1.3.2. Sampling of clays

The sampling of clays gives additional and supplemental information about the study region.

The basic clay containing sediment that is used for making pottery is frequently mixed with other materials (temper) to achieve better working properties. Because of this mixing, it is not often likely that one will find a match between the compositional profile of a resource extraction location and the pottery manufactured with the corresponding raw materials [1.1]. The relevance of clay analysis is that it provides mineralogical and chemical knowledge from which to interpret the variability of ceramic data [1.1]. Even in quite geologically homogeneous situations, regional trends in chemical composition have been observed that have enabled the assignment of a ceramic compositional profile to a likely zone of origin within the region [1.8].

The clay collection and sampling strategy can be a systematic approach to survey a locale (micro-zone) or region, or there might be occasional testing of some clay sources and tempering materials. Clay beds are not homogeneous. They can have marked differences in weathering of parent materials and great differences in grain size, mainly in the coarse fraction (mineral inclusions). Variations occur horizontally (along the spatial dimension) or stratigraphically (along the progressive events of bed formation). These variations must be considered when collecting the sample to ensure the representativeness of what is later analysed and the extent of its utility for archaeological interpretation. Sampling at different spots along the clay bed is recommended. Another important consideration to bear in mind is that the exact locations exploited in the past might not have been sampled.

The clay material should then be processed for analysis taking care not to contaminate the sample with the hands (sterile gloves) or other agents. The sample can be kneaded and moulded with no additives or it might need the addition of water to reach plasticity. In this last case, distilled deionized water must be used to prevent contamination with present day minerals contained in water. After drying, the test tiles are fired to a pre-determined temperature.

A complete database is kept for the records with the relevant information from clays.

1.3.3. Contamination issues

Nuclear analytical techniques determine the concentration of chemical elements in a sample. These concentrations are dependent upon several factors. Original elemental concentrations of the clay matrix and tempering materials, alteration of these concentrations by the manufacturing procedures of the artisan, alterations during the use of the vessel and those introduced after the vessel (whole or fractured) was buried in the soil. The elemental alterations during manufacture can be considered as an integral and very significant aspect of the cultural imprint of the vessel and, as such, an aspect of the archaeological information derived from the analyses. Use of related variations should be thought about carefully, because they might bias or reinforce the results depending on the archaeological problems being studied. When results that reflect differences in sherds due to their functional uses are not desired, sampling should consider a differentiation among the morpho-functional categories. The possibility of post-depositional contamination should be considered. Ceramic materials are affected mainly on their outer surfaces. The extent of contamination penetration in a ceramic sherd depends largely upon the paste characteristics (porosity, hardness, firing temperature, etc.) and the contaminating agent, so a careful consideration of these situations must be taken into account. In sample preparation, the removal of the outer surfaces with a tungsten carbide burr is directed towards diminishing this eventual contamination.

1.4. DESCRIPTION OF THE ANALYTICAL PROTOCOLS

1.4.1. Neutron activation analysis: Generalities

Neutron activation analysis (NAA) is a well known nuclear analytical technique based on the nuclear reactions that occur in the atomic nucleus due to irradiation with neutrons. The radioactive products (usually gamma emitters) of these reactions are characterized through the radiation they emit, among other features, and quantified through different methods, allowing determination of the element concentrations in the sample.

NAA allows the simultaneous determination of a great number of elements with high accuracy and precision. The technique is sensitive enough to permit the determination of concentrations of the order of ppm or below, although it is also possible to determine the major and minor elements [1.9].

Depending on the neutron source and the energy distribution of the neutrons, different nuclear reactions may occur, with the production of different radioactive isotopes. The most common sources of neutrons for NAA are research reactors, which can have different characteristics. Thermal neutrons, causing capture reactions, are most commonly used although there is also fast NAA with high energy neutrons, usually from an accelerator, and epithermal NAA with epithermal neutrons. Within this CRP, all the participants used thermal neutron flux from nuclear reactors.

Regarding sample treatment after irradiation, two methods can be used: INAA or radiochemical NAA (RNAA). INAA consists in measuring the irradiated samples, after an adequate decay time, without further treatment. When a radiochemical separation is performed on the irradiated sample, the method is called RNAA and it is used when it is necessary to separate one isotope of interest from the rest of the radionuclides, to improve detection limits or to eliminate interferences. For a multi-elemental analysis, INAA is the chosen alternative. Having in mind the large number of samples involved in the project and the need for multielemental determination, INAA was chosen by all the participants.

For quantification of the radioactive products, different methods are used, the most common ones being the relative and k_0 methods. In the relative method, samples and standard materials of known elemental concentrations are irradiated together. After irradiation, they are subject to the same procedures. A comparison of peak areas from unknown samples and a standard material allows the determination of the concentrations in the samples. The k_0 method is a parametric method based on the use of a nuclear compound constant k_0, the ratio of thermal to epithermal neutron fluxes, and the use of only one element as comparator and standard [1.10].

The measurement of gamma ray spectra is performed using high resolution Ge hyperpure detectors. The signal leaving the detector is amplified and the pulses sent to the high speed analog to digital converter (ADC). This digital information goes to a multichannel pulse height analyser module where the spectrum is collected. Different softwares are used for data acquisition, and concentration calculations are made based on these data [1.11].

A general consensus among the participating teams was reached on the meaning of choosing appropriate protocols, in order to ensure an adequate trade-off between maximum precision and a throughput of samples in sufficient numbers to obtain statistically significant data in a reasonable period of time. The required precision, however, has to be high enough that the variation in the data set for a given group caused by the analytical errors be smaller than the natural compositional variation within the group.

1.4.2. Sample preparation techniques

The surface of the ceramic samples (sherds or vessels) was cleaned before taking the analytical aliquots, trying to remove the surface areas exposed to weathering and therefore to avoid the possible post-depositional alterations of the composition of the paste. All the surfaces and sections of the area from which the analytical portion was taken were scraped with a tungsten carbide rotary file, discarding the powder, and in some cases the treated surface was further cleaned with a brush and rinsed with deionized water.

Furthermore, two procedures were employed for sample preparation: (a) crushing with an agate mortar and pestle; (b) removal of powder by drilling or abrasion with tungsten carbide drills or burrs, respectively, at several locations in order to obtain a more representative sample [1.12]. The latter technique, while having the advantage of lessening the damage to the archaeological material, as well as the resulting speed and ease, was found to occasionally produce contamination, increasing the resulting concentrations of W and Co [1.13]. The first technique avoids the risks of contamination and ensures a better homogenization of the obtained sample. After the samples were powdered, they were air dried in ovens at 105–110°C for 24 h and then allowed to cool in desiccators before the analytical portion was weighed out. The final choice of the more convenient procedure is conditioned by the size, hardness and decoration of the sherds. It is also dependent on the possibility to destroy or alter the shape of the provided material.

The size of the analytical portion must be large enough to provide a representative sample. This varies with the ceramic texture: while very fine wares may be accurately represented by a few hundred milligrammes, coarser wares require larger samples. Finally, the size of the analytical (powdered) sample varied with the facility, depending on reactor flux, irradiation time and counting set-up, among other factors. Table 1.2 shows the specific sampling procedures followed by each participating team.

Some of the projects included in their sampling strategies the collection of clays from procurement areas that were of relevance for the intended research objectives. Sometimes the clay samples were grounded, homogenized and dried in the way described above for ceramic samples. When analysing powdered (but non-fired) clays, the resulting concentration values need to be increased by 10–15% in order to correct for the losses of moisture due to firing the pottery [1.14]. In the Chilean research the clay samples were prepared with deionized water, moulded, allowed to dry at air temperature and then fired at 700°C for 20 min in an electric furnace.

1.4.3. Standardization

With the exception of two laboratories (IPEN (Pe) and the CDTN (Br), where Pe and Br denote Peru and Brazil, respectively) where the k_0 technique has been adopted and established for routine analysis for several years, the teams used the

TABLE 1.2. CERAMIC SAMPLE PREPARATIVE PROCEDURES USED

Procedure	Sample size						
	CNEA	CCHEN	CDTN	CEADEN	ININ	IPEN (Br)	IPEN (Pe)
Crushing in agate mortar and pestle	2–3 g	2–3 g			1–3 g		2–3 g
Removal by drilling or abrasion		400 mg	1 g	300 mg		400 mg	
Irradiated/ measured sample	100–150 mg	150–250 mg	300 mg	100–200 mg	100–150 mg	90–120 mg	250 mg

comparative methods with multielement standards. To ensure traceability of the results, the IAEA supplied two certified reference materials: NIST SRM 679 (brick clay) and NIST SRM 1633b (coal fly ash). The first, as well as the Ohio Red Clay, was used as reference samples in all of the analyses, whereas the latter, as well as other SRM materials (IAEA SOIL-7, SOIL-5 and SL-1; NIST SRM-2704 and SRM-6; ICHTJ-CTA-FFA-1), was used as multielemental standard for quantification of the elements in the sample.

1.4.4. Elements to be determined: Choice of reactions and isotopes for quantification

The specificity of each laboratory facility (Table 1.3) conditions the set of analysed elements. Table 1.4 summarizes the analytical reactions and lines commonly accepted by NAA laboratories [1.11] and specifies the elements determined by each laboratory during the performance of this CRP. However, the set of chemical elements used for the evaluation of statistically differentiated populations of ceramic samples, leading to the interpretation of the respective archaeological contexts or the solution of specific questions, varies from one investigation to another. A major issue to take into account during the choice of 'useful' elements is their possible mobility in the environments where the fragments were collected. Some elements, such as the alkalis, are more subject to leaching or concentration processes, and therefore must be examined considering the possibility that the samples might have been exposed to such processes.

There are some groups of elements that are of major importance for the intended application. The elements having a remarkable differentiation during the processes of formation of igneous rocks, such as the rare earth elements (REEs), Cr, Th and Sc, provide information that is valuable for revealing differences in the clay composition. In as far as these elements are concentrated during the weathering processes leading to the formation of the clay beds, their resulting concentrations will impose differences in the clays and the pottery manufactured from these sources. The alkali and earth alkali metals (Na, K, Rb, Cs, Ca, Sr and Ba) are present in the composition of the feldspar materials that constitute the most abundant minerals in the earth's crust. Differences in the Na/K ratio are often an indicator of the proportion in the relative abundance of plagioclase and potassium feldspar. Calcium can often indicate the presence of calcite or another calcium containing compound. Therefore, whenever differences in mineral compositions in the pottery are present, some indication might arise from the inspection of the concentration of the alkali or alkali/earth metals associated with these minerals. Transition metals (Mn, Fe, Co, etc.) are found in higher proportions in oxidized sediments and might reveal the presence of metal oxide inclusions in the ceramic paste. In general, the choice of the elements to be determined varies for each

TABLE 1.3. ANALYTICAL FACILITIES OF THE PARTICIPATING LABORATORIES

Research group	Nuclear research reactor	Flux ($n \cdot cm^{-2} \cdot s^{-1}$)	Set-up	t_{irr}[a]	t_{cool}	t_{meas}
CNEA	RA3, water pool type, water cooler, maximum power 4.5 MW, 20% U enriched fuel	3×10^{13}	I	5 h[b]	6–8 d	1 h
			II		30 d	1.5 h
CCHEN	RECH-1, water pool type, water cooler, maximum power 5 MW, U–Al fuel elements, 45% U enriched fuel	4×10^{12}	I	8 h	6–7 d	1 h
			II		25–30 d	2 h
CDTN	TRIGA-Mark I IPR R1, water pool type, water cooler, maximum power 100 kW, 20% U enriched fuel	6.6×10^{11}	I	5 min	10 min	10 min
			II	4 h	12 h	3 h
			III	20 h	10 d	4 h
CEADEN	Access granted to research facilities of CAE, ININ, IPEN (Pe) and NIST		I	1–5 h	6–8 d	0.5 h
			II		4–6 w	1–1.5 h
ININ	TRIGA-Mark III, pool type, water cooler, maximum power 1 MW, U–Zr–H fuel rods, U enrichment 30–70%	1×10^{13}	I	1 min	1 min	500 s
			II		3 h	1–1.5 h
			III	5 h	1–3 w	1.5–2 h
IPEN (Br)	IEA-R1m, swimming pool type, water cooler, maximum power 2–5 MW, U enrichment 20%	2×10^{12}	I	8 h	7–8 d	90 min
			II		16–17 d	
IPEN (Pe)	RP10, water pool type, water cooler, maximum power 10 MW, U–Al fuel elements, 20% U enriched fuel	1.4×10^{13}	I	5 s	15 m	15 min
			II	40 min	5–7 d	3–5 h
					3–4 w	

[a] t_{irr}, t_{cool}, t_{meas}: irradiation, cooling and measuring times, respectively.

[b] w, week; h, hour; min, minutes; s, seconds.

TABLE 1.4. ISOTOPES AND ENERGIES USED FOR QUANTIFICATION

Element	Reaction	$T_{1/2}$	Energy (keV)	CNEA	CCHEN	CDTN	CEADEN	ININ	IPEN (Br)	IPEN (Pe)
Na	^{23}Na(n,γ)^{24}Na	14.96 h	1368.3		▨	▨	▨	▨	▨	▨
Mg	^{26}Mg(n,γ)^{27}Mg	9.46 min	843.8, 1014.4					▨		
Al	^{27}Al(n,γ)^{28}Al	2.24 min	1778.9			▨				▨
K	^{41}K(n,γ)^{42}K	12.36 h	1524.6		▨	▨	▨	▨	▨	▨
Ca	^{46}Ca(n,γ)^{47}Ca	4.54 d	1297.1		▨			▨		
Sc	^{45}Sc(n,γ)^{46}Sc	83.8 d	889.3, 1120.5	▨	▨	▨	▨	▨	▨	▨
Ti	^{50}Ti(n,γ)^{51}Ti	5.76 min	320.1			▨		▨		▨
V	^{51}V(n,γ)^{52}V	3.75 min	1434.1			▨				▨
Cr	^{50}Cr(n,γ)^{51}Cr	27.7 d	320.1	▨	▨	▨	▨	▨	▨	▨
Mn	^{55}Mn(n,γ)^{56}Mn	2.58 h	846.7, 1810.7			▨		▨		▨
Fe	^{58}Fe(n,γ)^{59}Fe	44.5 d	1099.2, 1291.6	▨	▨	▨	▨	▨	▨	▨
Co	^{59}Co(n,γ)^{60}Co	5.27 a	1173.2, 1332.6	▨	▨	▨	▨	▨	▨	▨
Zn	^{64}Zn(n,γ)^{65}Zn	244 d	1115.6		▨		▨	▨	▨	▨
Ga	^{71}Ga(n,γ)^{72}Ga	14.1 h	834			▨				
As	^{75}As(n,γ)^{76}As	26.3 h	559.1	▨	▨	▨	▨		▨	▨
Rb	^{85}Rb(n,γ)^{86}Rb	18.66 d	1076.6	▨	▨	▨	▨	▨	▨	▨
Sr	^{84}Sr(n,γ)^{85}Sr	64.84 d	514		▨			▨		
Sb	^{121}Sb(n,γ)^{122}Sb	2.72 d	564.2	▨	▨		▨		▨	▨
Sb	^{123}Sb(n,γ)^{124}Sb	60.2 d	1690.98	▨	▨					

TABLE 1.4. (cont.)

Cs	$^{133}Cs(n,\gamma)^{134}Cs$	2.06 a	795.8	▨	▨	▨	▨	▨	▨	▨
Ba	$^{130}Ba(n,\gamma)^{131}Ba$	11.8 d	373.2, 496.3	▨	▨	▨	▨	▨	▨	▨
La	$^{139}La(n,\gamma)^{140}La$	1.68 d	1596.4, 815	▨	▨	▨	▨		▨	▨
Ce	$^{140}Ce(n,\gamma)^{141}Ce$	32.5 d	145.4	▨	▨	▨	▨	▨	▨	▨
Nd	$^{146}Nd(n,\gamma)^{147}Nd$	11.0 d	91.1	▨			▨		▨	
Gd	$^{152}Gd(n,\gamma)^{153}Gd$	241.6 d	103.0	▨						
Sm	$^{152}Sm(n,\gamma)^{153}Sm$	1.9 d	103.2	▨	▨		▨		▨	▨
Eu	$^{151}Eu(n,\gamma)^{152}Eu$	5.25 a	344.3, 778.9, 1408.01	▨	▨		▨	▨	▨	
Tb	$^{159}Tb(n,\gamma)^{169}Tb$	72.3 d	879.3	▨	▨		▨		▨	
Dy	$^{164}Dy(n,\gamma)^{165}Dy$	2.33 h	94.7							▨
Yb	$^{174}Yb(n,\gamma)^{175}Yb$	4.19 d	396.3	▨	▨				▨	
Yb	$^{168}Yb(n,\gamma)^{169}Yb$	72.3 d	197.9, 177.2	▨			▨			▨
Lu	$^{176}Lu(n,\gamma)^{177}Lu$	6.71 d	208.4, 113.0	▨	▨		▨		▨	
Hf	$^{180}Hf(n,\gamma)^{181}Hf$	42.4 d	482.3, 133	▨	▨		▨	▨	▨	▨
Ta	$^{181}Ta(n,\gamma)^{182}Ta$	114.5 d	1221, 100.1	▨	▨	▨	▨		▨	▨
W	$^{186}W(n,\gamma)^{187}W$	23.9 h	479.6, 685.7		▨					▨
Th	$^{232}Th(n,\gamma)^{233}Pa$	27 d	311.9, 300.1	▨	▨		▨	▨	▨	▨
U	$^{238}U(n,\gamma)^{239}Np$	2.35 d	277.6, 106.1	▨	▨		▨		▨	▨

specific problem, depending on the inferences that might be made from the geology of the area studied [1.15].

1.4.5. Other sources or related techniques providing complementary information

It has been clearly demonstrated that a blind approach to the statistical interpretation of the data obtained by NAA may lead to erroneous conclusions. In fact, an adequate comprehension of the sources of chemical variability is possible only through the study of several sources of information (archaeological contexts, historical references, the geography and geology of the procurement material zones, etc.) and the mineralogical analysis of the paste inclusions [1.16, 1.17]. The research conducted by each of the participating teams involved the use of information from several sources, which are summarized in Section 1.4.6.

1.4.6. Quality control activities

Each participating laboratory performed several actions to control the quality of the results obtained, such as analysis of additional standard reference materials (all of the laboratories) and internal control replicates (IPEN (Pe) and ININ for all of the samples; CNEA, 10%; CDTN, 15%) and exchange of several samples among some laboratories for intercomparison analysis (five samples between CNEA, CCHEN, IPEN (Br) and the University of Pavia, Italy), among others. An additional study on the results obtained from the analysis of brick clay and Ohio Red Clay is reported in Ref. [1.18]. Since the laboratory of CEADEN performed the NAA in several nuclear reactor facilities, an internal control sample was included in all of the sample sets analysed in the different facilities. In general, good agreement was observed among the results obtained for most of the elements.

1.4.6.1. Results of the interlaboratory comparison performed

An intercomparison run was arranged to assess the quality of the results of the participating laboratories, making them comparable with other data obtained elsewhere. The exercise included three different materials:

Ohio Red Clay: foreseen for comparison of analytical precision each team performed from five to ten analyses, spread over multiple activation runs.

NIST SRM 679 (brick clay): was chosen to control the accuracy of the results by carrying out the analysis of at least three replicates.

CRP flower pot: a sample of unknown composition (a ‘blind’ sample) was distributed to each of the participants for a minimum of three analyses. The sample consisted of a large flower pot with no decorations, which was acquired by the

TABLE 1.5. RESULTS OF ANALYSIS OF BRICK CLAY (NIST SRM 679)

(concentrations are in µg/g unless otherwise indicated; ND, not determined; asterisks, in per cent)

	Certified information value[a]	Experimental concentration values (average ± std dev.)							
		Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 5	Lab. 6	Lab. 7	Lab. 8
Number of replicates		2	3	4	12	5	27	1	>100
Na*	0.1304 ± 0.019	0.143 ± 0.010	0.134 ± 0.020	0.122 ± 0.041	0.134 ± 0.048	ND	0.123 ± 0.023	ND	0.136 ± 0.030
Mg	7552 ± 44	ND	ND	ND	8200 ± 1200	ND	ND	ND	ND
Al*	11.01 ± 0.17	ND	12.4 ± 0.4	ND	10.52 ± 0.24	ND	ND	ND	ND
K*	2.433 ± 0.0235	2.65 ± 0.50	2.80 ± 0.03	2.07 ± 0.10	2.51 ± 0.31	ND	2.35 ± 0.17	ND	2.30 ± 0.12
Sc	22.5	22.62 ± 0.53	23.00 ± 0.40	22.82 ± 0.56	23.15 ± 0.65	24.1 ± 1.2	22.9 ± 1.3	ND	23.01 ± 0.39
Ti*	0.577 ± 0.02	ND	ND	ND	0.55 ± 0.07	ND	ND	ND	ND
V	170	ND	180 ± 10	ND	159 ± 8	ND	ND	ND	ND
Cr	109.7 ± 2.5	95 ± 6	90 ± 7	108 ± 5	120 ± 7	108 ± 10	104 ± 5	ND	108.0 ± 3.4
Mn	1730	ND	2030 ± 30	ND	1660 ± 39	ND	ND	ND	ND
Fe*	9.05 ± 0.11	8.75 ± 0.34	9.05 ± 0.06	9.00 ± 0.30	9.03 ± 0.26	9.46 ± 0.49	9.18 ± 0.49	ND	9.03 ± 0.27
Co	26	25.85 ± 0.57	24 ± 3	25.7 ± 0.4	25.2 ± 1.5	28.1 ± 1.6	25.2 ± 1.0	ND	26.74 ± 0.52
Zn	150	132 ± 19	ND	ND	157 ± 28	ND	144 ± 26	ND	129 ± 14
As	9.7 ± 0.4	9.15 ± 0.78	9.8 ± 0.9	9.20 ± 0.72	10.07 ± 0.95	16.9 ± 6.8	9.77 ± 0.90	ND	10.00 ± 0.54
Rb	190	192 ± 18	210 ± 20	178.5 ± 1.3	202 ± 21	183 ± 20	184 ± 11	ND	218 ± 17
Sb	1.1 ± 0.1	0.86 ± 0.07	ND	0.93 ± 0.06	1.05 ± 0.11	1.24 ± 0.20	0.92 ± 0.07	ND	0.98 ± 0.16
Cs	9.6	9.65 ± 0.35	10.0 ± 1.0	10.38 ± 0.42	10.84 ± 0.66	10.65 ± 1.25	9.72 ± 0.42	ND	9.66 ± 0.30
Ba	432.0 ± 4.9	415 ± 10	ND	474 ± 73	484 ± 71	429 ± 81	457 ± 54	ND	473 ± 58

TABLE 1.5. (cont.)

La	52 ± 4	51.0 ± 2.8	47 ± 1	51.8 ± 1.7	50.5 ± 1.4	57 ± 10	50 ± 4	ND	56.4 ± 0.9
Ce	105	110.5 ± 1.4	80 ± 3	109 ± 6	118 ± 4	110 ± 9	102 ± 4	ND	102.6 ± 2.5
Nd	44 ± 7	36 ± 5	ND	ND	ND	ND	49 ± 8	ND	47 ± 5
Sm	9.35 ± 0.32	8.45 ± 0.35	9.68 ± 0.34	ND	9.88 ± 0.33	10.05 ± 0.80	8.90 ± 0.84	ND	9.16 ± 0.16
Eu	1.9	1.95 ± 0.07	1.86 ± 0.03	ND	ND	2.03 ± 0.17	1.76 ± 0.09	ND	1.69 ± 0.05
Tb	1.20 ± 0.04	1.40 ± 0.14	1.14 ± 0.05	ND	ND	1.24 ± 0.22	1.21 ± 0.22	ND	1.21 ± 0.17
Dy	7	ND	ND	ND	6.7 ± 0.5	ND	ND	ND	ND
Yb	3.98 ± 0.25	3.55 ± 0.64	ND	3.98 ± 0.24	4.27 ± 0.22	3.86 ± 0.39	4.11 ± 0.55	ND	4.11 ± 0.22
Lu	0.57 ± 0.07	0.47 ± 0.01	ND	0.56 ± 0.04	ND	0.66 ± 0.13	0.53 ± 0.06	ND	0.615 ± 0.043
Hf	4.6	4.60 ± 0.42	ND	4.62 ± 0.13	4.68 ± 0.32	4.82 ± 0.82	4.36 ± 0.23	ND	4.57 ± 0.18
Ta	1.23 ± 0.05	1.70 ± 0.00	1.20 ± 0.10	1.17 ± 0.11	ND	1.24 ± 0.09	1.30 ± 0.22	ND	1.242 ± 0.089
Th	14	7.83 ± 0.11	ND	13.85 ± 0.54	15.05 ± 0.76	14.6 ± 1.1	13.92 ± 0.78	ND	14.34 ± 0.39
U	2.6 ± 0.07 c	1.6 ± 0.0	ND	2.90 ± 0.14	3.49 ± 0.72	3.48 ± 1.48	2.64 ± 0.28	ND	2.41 ± 0.37

[a] Values provided by taking arithmetic means of laboratory results after elimination of outliers according to Dixon's *Q* test.

TABLE 1.6. RESULTS OF THE ANALYSIS OF OHIO RED CLAY

(concentrations are in µg/g unless otherwise indicated; ND, not determined; asterisks, in per cent)

		Experimental concentration values (µg/g) (average ± std. dev.)							
	Certified information value (µg/g)[a]	Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 5	Lab. 6	Lab. 7	Lab. 8
Number of replicates		2	3	4	12	5	27	1	>100
Na*	0.142 ± 0.006	0.138 ± 0.010	0.151 ± 0.003	0.136 ± 0.003	0.147 ± 0.003	ND	0.135 ± 0.01	0.19 ± 0.01	0.144 ± 0.003
Mg	0.7	ND	ND	ND	ND	ND	ND	0.69 ± 0.06	ND
Al*	9.7	ND	9.80 ± 0.1	ND	9.60 ± 0.25	ND	ND	ND	ND
K*	3.45 ± 0.49	2.78 ± 0.67	3.60 ± 0.2	3.18 ± 0.11	3.45 ± 0.11	ND	3.38 ± 0.29	4.40 ± 0.13	3.36 ± 0.14
Sc	18.24 ± 0.31	18.4 ± 1.0	18.0 ± 1.0	18.0 ± 0.6	18.41 ± 0.66	18.60 ± 0.87	18.47 ± 0.91	20 ± 1	17.78 ± 0.29
V	217 ± 16	ND	220 ± 5	ND	200 ± 5	ND	ND	232 ± 28	ND
Cr	88 ± 7	76 ± 6	85 ± 8	86 ± 3	98 ± 6	87 ± 13	90 ± 3	95 ± 5	90 ± 3
Mn	249 ± 3	ND	250 ± 20	ND	246 ± 6	ND	ND	251 ± 10	ND
Fe*	5.24 ± 0.20	5.68 ± 0.31	5.2 ± 0.4	5.14 ± 0.17	5.05 ± 0.18	5.21 ± 0.10	5.24 ± 0.28	7.65 ± 0.25	5.16 ± 0.11
Co	22.0 ± 1.3	23.4 ± 1.8	21 ± 2	22.6 ± 0.7	22.6 ± 0.9	23.44 ± 0.97	22.5 ± 0.8	20.0 ± 0.6	20.6 ± 0.5
Zn	104	70 ± 11	ND	ND	102 ± 25	ND	106 ± 11	ND	ND
As	14.6 ± 0.6	13.57 ± 0.87	15 ± 1	14.41 ± 0.67	15.1 ± 0.7	19.4 ± 5.7	15.4 ± 1.4	14.6 ± 1.3	14.19 ± 0.56
Rb	176 ± 7	179 ± 7	180 ± 20	162 ± 6	182 ± 11	182 ± 9	175 ± 10	170 ± 10	201 ± 12
Sb	1.38 ± 0.19	1.12 ± 0.15	ND	1.29 ± 0.10	1.36 ± 0.15	1.73 ± 0.23	1.31 ± 0.08	1.33 ± 0.25	1.49 ± 0.10
Cs	10.7 ± 0.6	11.6 ± 1.7	11 ± 1	10.20 ± 0.56	10.53 ± 0.63	11.37 ± 0.92	10.19 ± 0.46	10.4 ± 0.7	10.18 ± 0.32
Ba	651 ± 51	719 ± 131	ND	604 ± 34	621 ± 62	614 ± 79	603 ± 59	703 ± 23	690 ± 53
La	52 ± 2	52 ± 5	54 ± 1	52.0 ± 1.7	51 ± 2	56.1 ± 0.9	51 ± 5	50.0 ± 1.2	54.6 ± 1.2

TABLE 1.6. (cont.)

Ce	108 ± 13	119 ± 13	80 ± 2	110 ± 6	124 ± 5	118 ± 5	113 ± 3	114 ± 4	105.8 ± 2.3
Nd	46 ± 3	44 ± 5	ND	ND	50 ± 8	ND	48 ± 8	43 ± 2	45 ± 7
Sm	8.9 ± 0.8	8.2 ± 1.2	ND	9.2 ± 0.3	9.5 ± 1.1	10.3 ± 0.3	8.85 ± 0.98	8.2 ± 0.5	8.28 ± 0.28
Eu	1.70 ± 0.15	1.72 ± 0.12	ND	1.81 ± 0.05	ND	1.87 ± 0.23	1.74 ± 0.10	1.62 ± 0.09	1.456 ± 0.039
Tb	1.3 ± 0.4	1.7 ± 0.4	ND	1.08 ± 0.10	ND	ND	ND	ND	1.11 ± 0.13
Dy	7	ND	ND	ND	7.11 ± 0.46	ND	ND	7.25 ± 1.2	ND
Yb	4.28 ± 0.10	4.22 ± 0.31	ND	4.23 ± 0.13	4.73 ± 0.22	4.35 ± 0.21	4.17 ± 0.43	4.3 ± 0.8	4.43 ± 0.22
Lu	0.62 ± 0.08	0.55 ± 0.08	ND	0.64 ± 0.02	ND	0.75 ± 0.04	0.56 ± 0.07	0.55 ± 0.03	0.663 ± 0.046
Hf	7.28 ± 0.39	7.35 ± 0.97	ND	7.93 ± 0.22	7.34 ± 0.31	7.28 ± 0.73	6.95 ± 0.25	6.7 ± 0.4	7.43 ± 0.26
Ta	1.54 ± 0.36	2.23 ± 0.33	1.3 ± 0.2	1.35 ± 0.08	ND	1.46 ± 0.22	1.17 ± 0.11	1.82 ± 0.25	1.457 ± 0.082
Th	15 ± 1	13.3 ± 3.8	ND	14.10 ± 0.62	15.99 ± 0.59	16.21 ± 0.90	15.32 ± 0.65	ND	15.28 ± 0.33
U	3.01 ± 0.28	3.1 ± 0.9	ND	2.66 ± 0.24	3.4 ± 0.4	3.1 ± 0.5	3.08 ± 0.25	3.1 ± 0.3	2.62 ± 0.44

[a] Values provided taking arithmetic means of laboratory results after elimination of outliers according to Dixon's *Q* test.

TABLE 1.7. RESULTS OF THE ANALYSIS OF THE BLIND SAMPLE (IAEA POT)

(concentrations are in µg/g unless otherwise indicated; ND, not determined; asterisks, in per cent)

	Experimental concentration values (µg/g) (average ± std dev.)							
	Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 5	Lab. 6	Lab. 7	Lab. 8[a]
Replicates	5	3	4	6	5	6	1	>100
Na*	0.556 ± 0.040	0.580 ± 0.010	0.540 ± 0.080	0.558 ± 0.020	ND	0.501 ± 0.020	ND	0.592 ± 0.010
Mg*	ND	ND	ND	1.37 ± 0.09	ND	ND	0.81 ± 0.05	ND
Al*	ND	11.2 ± 0.6	ND	9.63 ± 0.28	ND	ND	ND	ND
K*	2.71 ± 0.30	3.60 ± 0.10	3.27 ± 0.09	3.49 ± 0.08	ND	3.04 ± 0.30	2.00 ± 0.04	3.17 ± 0.09
Ca*	ND	ND	ND	0.81 ± 0.04	ND	ND	ND	ND
Sc	20.1 ± 1.3	18 ± 1	19.8 ± 0.6	18.8 ± 0.3	19.2 ± 0.9	17.6 ± 1.0	11.4 ± 0.5	18.41 ± 0.11
Ti*	ND	ND	ND	0.63 ± 0.03	ND	ND	0.54 ± 0.01	ND
V	ND	ND	ND	139 ± 6	ND	ND	ND	ND
Cr	93 ± 14	80 ± 7	102 ± 3	111 ± 5	96 ± 6	93 ± 5	71 ± 4	95.4 ± 2.4
Mn	ND	470 ± 40	ND	1239 ± 26	ND	ND	1100 ± 100	ND
Fe*	5.51 ± 0.44	5.3 ± 0.1	5.66 ± 0.15	5.33 ± 0.11	5.36 ± 0.30	5.99 ± 0.30	3.63 ± 0.34	5.47 ± 0.05
Co	25.6 ± 2.9[b]	27 ± 7[b]	36 ± 2[b]	20.71 ± 0.23	42 ± 4[b]	35.4 ± 2.3[b]	18 ± 1	22.4 ± 0.5
Zn	85 ± 12	ND	ND	191 ± 10	ND	195 ± 20	75 ± 10	146 ± 7
As	23.5 ± 1.9	33 ± 7	26.8 ± 0.9	28.0 ± 1.2	33.7 ± 4.1	24.1 ± 1.6	14.5 ± 1.2	27.6 ± 0.5
Rb	203 ± 36	170 ± 30	179 ± 10	192 ± 22	161 ± 10	183 ± 8	184 ± 10	193 ± 8
Sb	2.8 ± 0.3	ND	2.9 ± 0.2	3.1 ± 0.1	3.3 ± 0.4	2.81 ± 0.09	ND	2.90 ± 0.14
Cs	14.4 ± 2.6	13 ± 2	13.8 ± 0.6	11.6 ± 0.4	13.5 ± 0.9	12.3 ± 0.5	12.8 ± 1.1	12.5 ± 0.3
Ba	853 ± 64	ND	690 ± 55	652 ± 52	721 ± 74	642 ± 45	754 ± 65	673 ± 56
La	55 ± 4	42 ± 2	59 ± 2	52 ± 2	55 ± 5	46 ± 2	54 ± 5	59.8 ± 0.5
Ce	116 ± 11	ND	121 ± 7	127.3 ± 2.5	109 ± 6	108.6 ± 2.2	89 ± 11	104.0 ± 2.2
Nd	48 ± 3	ND	ND	ND	ND	37.4 ± 1.3	46 ± 3	44 ± 5
Sm	9.24 ± 0.59	ND	9.81 ± 0.29	10.67 ± 0.30	9.9 ± 1.0	7.41 ± 0.89	6.7 ± 0.8	8.72 ± 0.09

TABLE 1.7. (cont.)

Eu	1.98 ± 0.30	ND	2.14 ± 0.10	ND	2.14 ± 0.13	1.84 ± 0.04	1.5 ± 0.1	1.81 ± 0.03
Tb	1.68 ± 0.84	ND	1.13 ± 0.13	1.28 ± 0.29	1.19 ± 0.41	ND	1.6 ± 0.2	1.14 ± 0.11
Dy	ND	ND	ND	7.1 ± 0.2	ND	ND	ND	ND
Yb	3.68 ± 0.37	ND	3.77 ± 0.23	4.07 ± 0.30	3.65 ± 0.40	3.41 ± 0.19	3.5 ± 0.3	3.84 ± 0.32
Lu	0.496 ± 0.060	ND	0.0590 ± 0.040	ND	0.619 ± 0.070	0.490 ± 0.040	ND	0.528 ± 0.030
Hf	8.6 ± 1.6	ND	8.71 ± 0.32	8.67 ± 0.37	7.90 ± 0.38	7.84 ± 0.19	6.9 ± 0.9	8.21 ± 0.16
Ta	1.98 ± 0.22[a]	1.40 ± 0.20	1.57 ± 0.14	1.57 ± 0.10	1.56 ± 0.11	0.994 ± 0.11	2.7 ± 0.5	1.57 ± 0.10
								2.86 ± 0.11
Th	16.6 ± 1.6	ND	17.4 ± 0.9	18.7 ± 0.8	17.2 ± 1.4	16.2 ± 0.8	11.8 ± 1.1	17.2 ± 0.6
U	4.7 ± 0.5	ND	4.96 ± 0.36	4.8 ± 0.7	4.3 ± 1.4	3.98 ± 0.26	2.5 ± 0.5	3.38 ± 0.35

[a] Laboratory 8 presented data taken by two sampling methods: drilling and grounding.

[b] Increased due to contamination from drilling process.

TABLE 1.8. MEAN CONCENTRATION VALUES FOR THE OHIO RED CLAY FROM THIS WORK COMPARED WITH PUBLISHED VALUES [1.13]
(*concentrations are given in µg/g unless otherwise indicated)*

Element	Kuleff and Djingova [1.19]	This work
Na*	0.140 ± 0.007	0.142 ± 0.006
Mg	0.73	0.7
Al*	9.45 ± 0.38	9.7
K*	3.55 ± 0.20	3.45 ± 0.49
Sc	18.95 ± 1.17	18.24 ± 0.31
V	211 ± 26	217 ± 16
Cr	90.7 ± 7.4	88 ± 7
Mn	253 ± 10	249 ± 3
Fe*	5.33 ± 0.2	5.24 ± 0.20
Co	22.0 ± 1.3	22.0 ± 1.3
Zn	104	104
As	14.1 ± 0.9	14.6 ± 0.6
Rb	184 ± 8.5	176 ± 7
Sb	1.39 ± 0.09	1.38 ± 0.19
Cs	10.6 ± 0.7	10.7 ± 0.6
Ba	668 ± 43	651 ± 51
La	50.9 ± 3.1	52 ± 2
Ce	109.7 ± 6.5	108 ± 13
Nd	42.3 ± 2.8	46 ± 3
Sm	8.0 ± 0.6	8.9 ± 0.8
Eu	1.54 ± 0.14	1.70 ± 0.15
Tb	1.06 ± 0.04	1.3 ± 0.4
Dy	7.4 ± 1.4	7
Yb	4.27 ± 0.16	4.28 ± 0.10
Lu	0.64 ± 0.09	0.62 ± 0.08
Hf	7.16 ± 0.54	7.28 ± 0.39
Ta	1.65 ± 0.21	1.54 ± 0.36
Th	15.1 ± 0.8	15 ± 1
U	2.96 ± 0.34	3.01 ± 0.28

Note: *, in per cent; ±, after rejection of outliers.

Smithsonian Institution Conservation and Analytical Laboratory, sponsors of the first RCM at Washington, DC, and broken into fragments that were distributed among the participating teams.

The results obtained are summarized in Tables 1.5–1.7 and are shown graphically in Figs 1.1–1.6. Each result is followed by ± one standard deviation or ± the estimated standard uncertainty reported. The codes are assigned to the different laboratories randomly so that the identities of the laboratories are lost. It can be seen that, except for the case of a few outliers in the determination of some elements, the degree of agreement between the laboratories can be considered as good, being acceptable for the archaeological applications of the technique. This is true at least for the cases where sharing of analytical databases from different laboratories was not required. Also it can be seen, in Table 1.8, that the mean values of the results reported by participant laboratories in this interlaboratory comparison run agree very well with the recently published values of Kuleff and Djingova [1.19].

1.4.7. Statistical evaluation of the data

The classification of ceramic samples into groups is feasible, as they are statistically differentiable by their chemical profile. In the case of ceramic samples, the chemical paste compositional reference units (CPCRUs) are based on the assumption that the composition of the paste of a given ceramic object is determined by the characteristics of the clay and temper materials used for its manufacture. The chemical behaviour of igneous and sedimentary rocks can be used as a reference for multivariate analysis, since the differences between the ratios of abundance of different elements reflect geological changes. Pottery is a multicomponent system. It is usually thought of as being composed of clay minerals (particles less than 0.02 mm) and non-plastic inclusions (temper). The clay–temper dichotomy, therefore, requires some conceptual elaboration to appreciate the sources of chemical variation in compositional analysis.

The application of a multielemental technique such as NAA for the elemental characterization of ceramic samples generates a huge quantity of data, consisting of a matrix of the concentrations evaluated for m elements in N samples (cases). The chemical profile can be used to: (a) form statistically significant individual groups of similar samples, or (b) assign samples of unknown origin to already existing groups. However, it becomes impossible to investigate the possible relationships between elemental concentrations in suspected group of samples by a visual inspection of the data alone, and more advanced methods of data handling and evaluation are needed.

The data sets have to be thoroughly examined to exclude the cases presenting missing or wrong values. Several tests can be performed to find deviations from normality within each of the a priori foreseen groups of cases. After the data have been examined, the main steps in their interpretation are [1.16]: (a) transformation of data, when the uneven concentration ranges of the determined elements may impose different weights in subsequent analysis; (b) data exploration in the search for some kind of structure; (c) reduction of the dimensionality of the data, in order to ease their interpretation, and in the search for some ordination; (d) confirmation of groups, according to some suspected (or revealed) structure; (e) evaluation of group membership probabilities.

Several transformations of ceramic compositional data have been suggested in previous works, but the scaling of the concentration values to log 10 values provides a frequently used way of compensation for the differences in concentration levels (i.e. major elements such as iron and trace elements such as REEs). This choice is based on the observations of log–normal distributions of the compositional data sets [1.20, 1.21].

The existence of correlation between elements should be investigated and appreciated. As an example among the commonly determined elements, the naturally occurring correlation between REEs can be cited, as well as other kinds of correlation such as those between Na, K, Rb, Cs and Ba, as they have similar properties, or between Fe, Co, Mn and Sc. Although there is not a straight chemical cause for strong correlation between Cr and Hf, one is sometimes found. Scatter plots can be used to visualize highly correlated elements or deviations from the expected correlation ratios. Another way of displaying the data is the use of distribution plots to identify possible anomalies in the concentrations. One should not regard highly correlated elements as constituting redundant data. In fact, the pattern of interelemental correlation provides important information that can be incorporated in various statistical procedures for distinguishing among groups of pottery or in attributing an unknown sample to a known group.

When dealing with a large set of data resulting from the analysis of many samples and elements, cluster analysis is the first approach in identifying the existence of statistically meaningful compositional groups. The analysis is based on the calculation of a dissimilarity matrix for all possible pairs of samples using one of various possible distance measurements. These are a way of describing the proximity between samples lying as points in a logarithmic concentration space. Different approaches can be used, such as (a) the normal Euclidean distance, (b) the squared Euclidean distance, (c) the mean squared Euclidean distance and (d) the mean Euclidean distance, among others. The results of cluster analysis are presented as dendograms showing the order in which samples were clustered together and the levels of the intersample distances. A visual inspection of the dendogram can be a useful and simple way of initially identifying groups.

When the compositional results are highly correlated, principal component analysis (PCA), which is a powerful tool for dealing with data, can be used, allowing one to simplify the exploration and the interpretation of the results. Each sample can be thought as a point represented in a space of n dimensions where each dimension is a measured parameter (each determined element). The basic purpose of PCA is to reduce the number of dimensions of a data set of related variables so that a minimum number of factors can explain the maximum variance of the related data. The dimensionality of the data matrix is reduced by extraction of the principal components (eigenvectors of the major product $X'X$, where X is the data matrix). The first extracted component accounts for the largest amount of the total variation of the data and is a linear combination of the original variables. The second component accounts for the maximum amount of the remaining total variation that has not already been accounted for in the first component and has to be orthogonal to it. This procedure continues until the number of components is equal to the number of original variables. The samples can be represented in a principal component space, converting their original position in the concentration space to their principal scores. The coefficients of the eigenvectors used to compute the scores are the principal component loadings and they provide information for the identification of correlated variables. It is often possible to describe 70% or more of the original variance using the first three extracted components, and so with the minimal loss of original information. The extracted components can be further rotated using different methods in order to provide greater agreement between axes and variable correlation, thus easing the interpretation of the causes conditioning the observed differences.

Multivariate analysis requires a large number of samples in order to be reliable. A rule of thumb has been developed for providing guidance on the number of required samples [1.22] for V variables in N cases. It is based on the calculation of the number of degrees of freedom per variable: $N - 1 - (V - 1)/2$, this number having to be at least 30 and preferably 60 or more. Another rule of thumb can be applied to the determination of the number of factors to be retained. The eigenvalues of a correlation matrix are the signal to noise ratios for the associated eigenvector or principal component. Generally factors with eigenvalues higher than 1 are used for interpretation, as they are considered to be more signal than noise.

The confirmation of statistically meaningful groups is usually carried out by using single group or between group evaluative procedures. A single group can be evaluated by inspection of the cohesiveness of the individual means and the standard deviation. On the basis of many studies of ceramic variation from projects carried out around the world, well constituted ceramic groups appear to have univariate spreads of the order of 10–15%, depending on the precision to which the concentrations are determined. What actually constitutes an acceptable limit in a given project, however, is a matter of empirical determination. Rigorous statistical evaluation may proceed by calculation of the Mahalanobis distance of a sample from a group’s multivariate centroid. The likelihood that a sample can diverge from the centroid as far as it does and yet be considered to be a member of the group can be calculated using an F test, which includes the information about group variance.

Canonical discriminant analysis can also be used for group definition when using as input variables the component scores extracted by PCA, since these scores fulfil the requirements of orthogonality and quasi-normal distribution of the input data. The procedure described by Davis [1.23] can be used to evaluate the distances between each individual sample and the centroids of the supposed groups. A set of discriminant functions, based on linear combinations of the predictor variables, which provides the best discrimination between the groups, is generated. The functions are generated from a sample of cases for which group membership is 'known', and are further applied to the other cases, with measurements for the predictor variables but unknown group membership. The prior probabilities of belonging to a given group can be computed. The Mahalanobis distance from sample to each alternative group centroid provides the criterion for evaluating the relative probabilities of membership of the specimen in each of the groups.

The use of statistics is to guide the search for and evaluation of structure in the data. It provides a powerful interpretative tool, but must be used in combination with information meaningful from the archaeological and geological contexts.

1.5. CONCLUSIONS

The interdisciplinary approach is the most productive way of advancing in several scientific fields. It is especially useful in the study of the chemical composition of ceramic samples by NAA, considering the necessary interaction between archaeologists and chemical analysts. During the implementation of this CRP, great benefits were obtained from the interactive and interdisciplinary approach developed, starting from the very redefinition of the projects through the sampling strategies to the statistical analyses and the archaeological interpretation of the data obtained. In our opinion, NAA is useful only if the analyst and archaeologist counterparts are working together throughout the whole project.

In this CRP, seven laboratories from six countries were involved, each working on different archaeological problems. The possibility of co-operation between groups and the exchange of opinions and points of view enhanced the interpretation of each laboratory's results. An intercomparison of analytical results between the participating laboratories was performed following the accepted protocols, this time directed to the ceramic analysis. The exercise involved the analysis of both standard and blind samples. The results obtained revealed standardized precision, accuracy and sensitivity that will allow archaeological data to be pooled from different laboratories in the future. After four years of interaction, the research teams had achieved a better understanding of each other's disciplines, possibilities and constraints.

From the analyst's point of view, there is no doubt that this CRP was extremely useful. It is felt that new working trends were opened in NAA, widening its scope to archaeological perspectives. This had not been the case previously.

From the archaeologist's point of view one of the most positive achievements was contact with a new area of research and the experience gained from working under the guidance of experts, such as R.L. Bishop and L. Van Zelst, as well as working with analysts from other countries. In all of the countries involved, a priori systematic experience in NAA applied to archaeological ceramic did not exist. Therefore, only through this guided learning process was it made possible to acquire the necessary and complementary background (geochemical and statistical) needed to solve the problems arising from data interpretation. None of the countries, on their own, would have been able to achieve such consolidated results without the co-operation made possible under the CRP. The working teams will now be able to share their knowledge and experience with other groups. An extended period of experience in an important field of research for the region has been achieved. These archaeological results will certainly have widespread effects, and this CRP will be considered to have initiated a new line of enquiry that from now on can be expected in archaeological investigations.

An important output of the co-operation is the added experience obtained through the discussion at the third research co-ordination meeting (RCM) held in Santiago, Chile, of the results of the research conducted by the groups. This experience was applied to situations over a wide range of cultural complexity, ranging from very simple societies with non-specialized ceramic production to complex political and economic systems. This broad spectrum of problems shows the versatility of NAA and its suitability for a wide range of social and environmental situations, and surpasses the original expectations. A more realistic perspective on what can be expected from the technique and what problems can be solved has been achieved.

For a long time NAA has been demonstrated to have enough precision, sensitivity, accuracy, resolution power and fitness of purpose to be applied to archaeological investigations. But this CRP has shown that the technique must always be applied within a clearly formulated research problem and context. It should be applied after obtaining a reasonable amount of general archaeological information and after specific ceramic analysis has been performed in order to obtain an understanding of the materials that will be submitted to NAA. An increased awareness of the importance of using extensive archaeological information in the formulation of appropriate research objectives prior to elemental analysis has resulted.

Although not mandatory, there is an increased awareness of the importance of obtaining supplementary information on clays and natural resources to understand the geochemical characteristics of the regions where problems are investigated.

1.6. RECOMMENDATIONS

Logistical problems can be solved given flexibility and if the scheduled activities are accomplished. Ideally the first co-ordination meeting should take place at the very beginning of the project.

It is extremely important to ensure the participation of a geologist with knowledge of the geochemistry of the areas being studied to contribute to both the NAA problem formulation and the interpretation of the variability in the data. A statistician and/or geostatistician would also be very useful for the handling and interpretation of the data.

Benefits should be gained from the standardized laboratory procedures achieved in this CRP. One important outcome of this project might be to continue with new projects, but this time, to gather data from different laboratories to solve a common (regional) research problem. At the same time, this idea would help to consolidate the interdisciplinary working teams in the countries involved and at a regional level.

REFERENCES

[1.1] BISHOP, R.L., RANDS, R.L., HOLLEY, G.R., “Ceramic compositional analysis in archaeological perspective”, Advances in Archaeological Method and Theory, Vol. 5 (SCHIFFER, M.D., Ed.), Academic Press, New York (1982) 275–331.

[1.2] NEFF, H., “Neutron activation analysis for provenance determination in archaeology”, Modern Analytical Methods in Art and Archaeology (CILIBERTO, E., SPOTO, G., Eds), Chemical Analysis, Vol. 55, Wiley, New York (2000) 81–134.

[1.3] PEISACH, M., PINEDA, C.A., JACOBSON, L., LOUBSER, J.H.N., Analytical studies of pottery from Soutpansberg, J. Radioanal. Nucl. Chem. **151** (1991) 229–237.

[1.4] RANDS, R.L., BISHOP, R.L., “Resource procurement zones and patterns of ceramic exchange in the Palenque Region, Mexico”, Models and Methods in Regional Exchange (FRY, R.E., Ed.), SAA Papers, Society for American Archaeology, Washington, DC (1980) 19–46.

[1.5] WEIGAND, P.C., HARBOTTLE, G., SAYRE, E.V., “Turquoise sources and source analysis: Mesoamerica and the Southwestern U.S.A.”, Exchange Systems in Prehistory (EARLE, T.K., ERICSON, J.E., Eds), Academic Press, New York (1977) 15–34.

[1.6] ARNOLD, D.E., Ceramic Theory and Cultural Process, Cambridge University Press, Cambridge (1985).

[1.7] BISHOP, R.L., “Pre-Columbian pottery: Research in the Maya Region”, Archaeometry of Pre-Columbian Sites and Artifacts (SCOTT, D.A., MEYERS, P., Eds), Getty Conservation Institute, Los Angeles, CA (1994) 15–65.

[1.8] NEFF, H., BOVE, F.J., LOU, B.L., PIECHOWSKI, M.F., “Ceramic raw materials survey in the Pacific coastal Guatemala”, Chemical Characterization of Ceramic Pastes in Archaeology (NEFF, H., Ed.), Prehistory Press, Madison, WI (1992) 59–92.

[1.9] ALFASSI, Z.B., Activation Analysis, Vol. 2, CRC Press, Boca Raton, FL (1995) Ch. 11.

[1.10] DE CORTE, F., The k_0 Standardization Method, Habil. thesis, University of Ghent (1987).

[1.11] INTERNATIONAL ATOMIC ENERGY AGENCY, Practical Aspects of Operating a Neutron Activation Analysis Laboratory, IAEA-TECDOC-564, Vienna (1990).

[1.12] BISHOP, R.L., “Ceramic paste compositional chemistry: Initial observations of variation in the Tucson basin”, The Archaeology of San Xavier Bridge Site (AZBB:13-14) Tucson basin, Southern Arizona, Appendix E (RAVESLOOT, J.C., Ed.), Arizona State Museum, University of Arizona, Tucson (1987) 395–408.

[1.13] ATTAS, M., et al., Corrections for drill-bit contamination in sampling ancient pottery for neutron activation analysis, Archaeometry **26** 1 (1984) 104–107.

[1.14] BISHOP, R.L., Smithsonian Center for Materials Research and Education, Washington, DC, personal communication, 1999.

[1.15] RANKAMA, K., SAHAMA, T.G., Geoquímica (AGUILAR, N.A., Ed.), Madrid (1962) 862 pp.

[1.16] BISHOP, R.L., NEFF, H., “Compositional data analysis in archaeology”, Archaeological Chemistry IV (ALLEN, R.O., Ed.), Advances in Chemistry Series, Vol. 220, American Chemistry Society, Washington, DC (1987) 57–86.

[1.17] BISHOP, R.L., “Aspects of ceramic compositional modelling”, Models and Methods in Regional Exchange (FRY, R.E., Ed.), SAA papers No. 1, Society for American Archaeology, Washington, DC (1980) 47–65.

[1.18] MUNITA, C.S., et al., Intercomparison among three activation analysis laboratories in South America, J. Trace Microprobe Techniques (in press).

[1.19] KULEFF, I., DJINGOVA, R., Mean elements determined in Ohio Red Clay, J. Radioanal. Nucl. Chem. **237** 1–2 (1998) 3–6.

[1.20] SAYRE, E.V., Brookhaven Procedures for Statistical Analyses of Multivariate Archaeometric Data, Rep. BNL-21693, Brookhaven Natl Lab., Upton, NY (1975).

[1.21] GLASCOCK, M.D., “Characterization of archaeological ceramics at MURR by neutron activation analysis and multivariate statistics”, Chemical Characterization of Ceramic Paste in Archaeology (NEFF, H., Ed.), Monographs in World Archaeology No. 7, Prehistory Press, Madison, WI (1992) 11–26.

[1.22] HENRY, R.C., Multivariate receptor models — Current practise and future trends, Chemometrics Intelligent Lab. Systems **60** 1–2 (2002) 43–48.

[1.23] DAVIS, J.C., Statistics and Data Analysis in Geology, 2nd edn, Wiley, New York (1986).

Part II

REPORTS BY PARTICIPANTS IN THE CO-ORDINATED RESEARCH PROJECT

Chapter 2

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF ARCHAEOLOGICAL CERAMICS: PROGRESS AND CHALLENGES

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Abstract

Instrumental neutron activation analysis (INAA) has become a widely used technique in the characterization of archaeological ceramics. Early applications, primarily developmental in nature, have been replaced by studies that attempt to place the derived analytical data in a larger archaeological and behavioural context. If archaeology is to increasingly exploit the great potential of INAA to address a broad range of social and cultural issues involving ceramics, greater attention must be paid to the various sources of variation that contribute to the chemical composition of pottery. In addition, as all research takes place within a social context, efforts must be made to increase the communication between archaeologists and other scientists, as this will contribute to the fulfilment of the archaeological research objectives.

2.1. INTRODUCTION

Almost a half century has passed since Sayre and his colleagues began to apply instrumental neutron activation analyses (INAA) to the study of archaeological ceramics [2.1, 2.2]. The advances in instrumentation that have taken place since that time, and the interested involvement of scientists, such as Sayre, Gordus, Perlman, Harbottle and Glascock, have contributed to INAA being the preferred technique for the compositional characterization of archaeological materials. However, these scientists were not alone in their dedication to the methodological development of archaeology. Rands laboured to make ‘archaeological sense’ out of an increasing accumulation of analytical data [2.3, 2.4]. His efforts and the efforts of other archaeologists who worked closely with analytical scientists demonstrated the relevance of data to specific archaeological problems and helped to establish INAA as an integral part of the archaeological tool kit.

2.2. DEVELOPMENTAL PARTNERSHIP

The first archaeological applications of INAA were primarily methodological in nature, with the broadly posed archaeological question: "Could Maya pottery be seen as chemically different from that of the Aztec?" As instrumentation developed, progressing from the use of sodium iodide crystal scintillators to the employment of lithium drifted germanium detectors in the mid-1960s, a relatively vast range of elements could be detected and quantified. Further developments established greater levels of precision. By the early 1970s, INAA began to move from the stage of technique development to one of problem application. Instrumental systems, however, were not the only part of the application that were undergoing change.

During the early period of INAA development, archaeology was largely focused on issues of classification and chronology. Gradually, sufficient fieldwork was carried out to provide the general outlines of the cultural history of most parts of the world. In accomplishing this, however, archaeologists began to realize the staggering complexity of the archaeological record for which an explanation was needed. Similarities of material content, for example, were frequently explained by factors such as diffusion or migration. Here the use of INAA could make a significant difference, for it offered the possibility of identifying pottery that was locally produced and that which was imported. Information regarding contacts between cultures and the direction of cultural contacts became available. Amongst other contributions, INAA helped to free archaeology from having to resort to the generalized concept of diffusion as a primary mechanism of cultural change.

The evolution of nuclear instrumentation in the 1970s was accompanied by a dramatic increase in computational power. Pencils and calculators were replaced by huge mainframe computers, which could carry out the analysis of gamma spectra in a fraction of the time previously required. Computers also made possible a new field of investigation, one concerned with 'numerical taxonomy', first applied to biology but which was soon found to be relevant for other fields. In contrast to traditional taxonomic approaches that used statistics to describe differences among groups already formed, in numerical taxonomy the use was advocated of statistical methods to form groups of biological specimens based upon numerical descriptors. Shortly after publication of Sneath and Sokal's landmark book*, Principles of Numerical Taxonomy* [2.5], in 1973, many of the algorithms proposed for forming groups were being applied to INAA data matrices at Brookhaven National Laboratory. Gradually, the tools were being put in place to permit large scale compositional investigations of archaeological pottery.

As the tools were changing, so too was archaeology's focus and philosophical orientation. Through the 1960s archaeology had also undergone significant changes that called for a greater contextualization of information and the use of explicit, deductively based models. Guided by general systems theory and ecology, culture was considered by many archaeologists to be an integrated entity consisting of many interacting parts, where factors affecting one part, such as economic activity, would have a resulting influence on other parts. Concepts associated with trade and exchange became increasingly important as factors to be considered in studies of evolving socio-political complexity, and INAA applications, capable of differentiating non-locally produced from locally produced pottery, were easily incorporated into large research programmes.

Archaeologists in the 1980s continued the diversification of theoretical approaches that had begun in the 1960s. Discontented with the inability to discover 'general laws', archaeologists began to search for new theoretical models. Analytical studies of material culture proliferated, but few seemed to have a firm problem focus [2.6], and were frequently 'buried' in appendices rather than incorporated into project syntheses. The archaeological 'scientism' of the 1980s was ripe for a critique, and one came from those who espoused the importance of behaviour and ideological meaning over that of the structure and function of systems. Material culture was viewed by some archaeologists as human behaviour that has been somehow transformed. This represented an attempt to conceptualize cultural material within an environment of cultural meaning that could be seen over long time periods. Rather than being generalized to a system level, the individual, as part of a social group, came into focus for the archaeological study of human behaviour as a producer of culture and pottery.

Despite the increasing attention paid to theoretical concepts and problem oriented research, archaeological pottery is most often subjected to classification and description. Part of that description may take the form of a table of elemental constituents of the ceramic paste. The summary of these data by various numerical procedures often achieves a partitioning of the data matrix, but the meaning of these partitions is often not readily apparent. Herein lies one of the greatest limitations in the use of INAA for the study of archaeological pottery for, while the elemental constituents of a ceramic object are expressed with a determinable degree of analytical precision, these data are — rarely or poorly — incorporated into the model of social, political or economic inference. The distinction between the technique itself and its application as part of a contextually driven research methodology serves to draw attention to the objective aspects of the former and the inferential nature of the latter. Unfortunately, unintegrated research falls short of reaching the level of archaeological significance and too often fails to justify the resources expended. Far more can be gained in archaeological research when there is the full participation of both chemists and archaeologists focusing on common objectives.

2.3. CHALLENGES IN THE INTERPRETATION OF INAA DATA FROM CERAMIC SYSTEMS

As a result of the dedication of nuclear and physical chemists and the support of administrators who looked towards the more imaginative applications of nuclear research, the general protocol for the application of INAA to the study of archaeological ceramics has been well established. Instrumental improvements were coupled with the use of appropriate well characterized standard reference materials, permitting the calculation of elemental abundances to a common reference. Thus, a developmental 'plateau' was reached by the 1980s where some 18–20 elemental abundances were quantified with acceptable analytical precision and good sample throughput. Most laboratories today quantify a similar suite of elemental abundances. Differences in that list can be explained with reference to at least three considerations:

(a) A lower number of elemental determinations as a result of lower neutron flux;
(b) A higher number of elemental abundances reflecting multiple irradiations of samples, as found in laboratories that incorporate prompt gamma analysis;
(c) Willingness of some laboratories to quantify and use elemental determinations that have larger analytical errors than are acceptable to others.

Regardless of the specifics, the technical aspects associated with the application of INAA to questions surrounding archaeological pottery have become somewhat routine. However, despite a fairly explosive increase in articles using INAA, significant challenges lie ahead in attempts to glean a maximum of archaeological information from a well quantified data matrix [2.7]. This is the frontier, which is bounded only by our willingness, or reluctance, to understand and archaeologically conceptualize the product that physical and nuclear scientists have given us. Fortunately, there are several examples, including this IAEA Co-ordinated Research Project, to suggest that archaeologists and scientists have come to realize that they are equal partners in this very interdisciplinary effort. As a consequence, the search for archaeological explanation has moved beyond the frontier that seeks to determine local and non-local pottery and into the domains of the human behaviour and symbolic expression of ancient potters. Such aspirations, however, demand that researchers pay close attention to the sources of variation that occur in the compositional analysis of pottery, from the traditional use of raw materials to the 'high tech' procedures that are applied to cultural products.

2.3.1. Variations in natural and cultural systems

Conceptually, we can consider that the total amount of the observed variation V_T^2 in a ceramic group is a composite of the variations arising from those which are found in the characteristics of the raw materials V_N^2, the analytical process V_A^2, the cultural context of ceramic preparation and use V_C^2, the sampling strategy V_S^2 and applicable post-depositional influences V_P^2:

$$V_T^2 = V_N^2 + V_A^2 + V_C^2 + V_S^2 + V_P^2$$

(expanded from Ref. [2.8]). The naturally occurring variation V_N^2 is a function of the mineralogy and geochemistry of the parent material and the influence of the mechanical processes and the chemical process of the weathering cycle that leads to the composition of the deposits of clays and other raw materials that were available for use in pottery. How localized or homogeneous are the clays of the region? Are the clays formed in ponds or do they occur as rectilinear secondary deposits along a given river drainage system? How finely must resources in a given geographical region be distinguished to meet archaeological objectives? Even with extensive analysis of raw materials, it is unlikely that one will be able to determine with a high degree of accuracy the range of variation in raw materials that was available to potters. Nevertheless, the consideration of geological resources and processes may offer insights regarding different elemental associations and expected levels of elemental occurrence.

In contrast to our inability to realistically obtain parameters for the natural environment, the variation that is associated with the analytical procedure V_N^2 can be calculated. This factor involves such concerns as sensitivity, selectivity and interference, precision, counting of statistical errors, weighing of errors, inhomogeneity in reference materials, background subtraction and accuracy. Rather than the various components being considered in isolation, analytical measurement of element variation is expressed in the precision derived from the analysis of standard reference materials. The variation resulting from the analytical procedure is minimized to the extent possible in order for INAA to have maximum resolving power. Since an underlying objective of the application is the differentiation of pottery produced at loci that might be geographically closely located, too much analytical error could substantially lessen the reliability to which compositionally different raw material sources might be distinguished. Through extensive application, however, it appears that the determination of several elemental concentrations with analytical errors of less than 5% is required to address common questions of archaeological ceramic production on an intraregional, as opposed to an interregional, level. Resolution is sharpened as the error drops.

The variation that arises from the choices made by potters (V_C^2) responding to natural, social and cultural constraints is insufficiently considered in many applications of INAA to pottery. The selection and processing of raw materials are conditioned by a wide range of behavioural choices including distance to suitable resources and the need to produce pottery to meet functional or social requirements.

Once acquired, the composition of the raw materials, each with its inherent chemical variation, may be modified from what was originally selected through subtractive processes of winnowing, sieving or levigation. Conversely, the composition can be changed through the addition of materials, for example addition of a tempering material (non-plastics or clays), to modify the base clay's properties.

Ceramic production tends to be fairly conservative in traditional societies, which can result in similar paste recipes lasting for several generations. In contrast, decoration and form may undergo considerable elaboration, decline and extinction rather quickly. The relative continuity and change in ceramic composition through time can increase the reliability of determining whether pottery is locally produced. The continuation of a characteristic chemical profile over more than a single recognized time span, and one that is observed to occur in several of the more frequent types or classes of pottery, lends support to the inference of local production. Moreover, within a given tradition of ceramic production, compositional subgroupings of highly similar items of pottery are possible, which, beyond local production, may reflect aspects of the organization of ceramic production. Such a chemical subset, if found to co-vary with increased homogeneity of form or decorative attributes, might be explained as some sort of ceramic intensification or specialization. In contrast, the lack of strong, discernable, group tendencies in the data might reflect household or occasional production of pottery, where many families had access to openly available or internally highly variable resources. The variation accounted for in V_{C}^2, therefore, reflects the natural, social and cultural context of ceramic production, aspects of which may be inferred from identifiable partitioning of the compositional data matrix.

Related to the above are the sources of variation that enter into consideration through sampling, V_{S}^2. This is not the sampling error that was mentioned under analytical variation. It is the part of the research design that governs what pottery will be submitted for analysis. To what extent does the selected pottery relate to the specific questions raised? Is there a reasonable expectation that one will be able to determine a 'local' compositional pattern? Will a sufficient number of samples be selected that questions regarding the organization of production might be addressed? Regardless of the question, the analysis of an 'insufficient' number of samples will limit the extent to which subgroups are discerned, and by extension limit the behavioural inferences that might be made from the data structure.

The sampling design must reflect the nature of the pottery. Coarsely textured pottery will probably be more variable in composition than finely textured pottery because of the influence of non-plastic minerals or other components of the ceramic's elemental composition. In general, coarser pottery will require a greater number of samples to be analysed to form a well characterized ceramic group. The scale of the compositional investigation also drastically influences sampling design. Research can be conducted at the level of region, subregion or site and, under some conditions, interregionally. The structure within an assembled data set may reflect different scales. While subject to experimental determination, there is, of course, no a priori reason to assume that a single compositional group will serve to realistically represent a site or a region. In spite of the often conservative nature of potters, practices change, raw materials become exhausted and new ones found, while the evolution of society results in different organizational structures and influences on ceramic production. Field and laboratory analyses frequently occur at different times, and the archaeological assemblages might not be readily available as chemical analysis proceeds. Accordingly, it is useful to have available 20–30 samples of each type or class of pottery being considered, from each time unit, from each site at the start of a project. (As used here, the word ‘type’ refers to members of a recognizable paste group with similar formal or decorative characteristics, and not necessarily to type as a formal taxonomic unit of classification.) As chemical and data analysis proceeds, some initial patterns might be observable in the resulting data. A sufficient number of samples must be available to improve the strength of these patterns.

The variation that is related to post-discard and post-depositional change in a ceramic’s chemical composition V_{P}^2 represents a potential concern. The interaction of rainfall or groundwater with pottery may be to leach out certain constituents, especially the alkali elements. In contrast to leaching, a possible mechanism for increased variation may be through enrichment caused by adsorption (e.g. sodium or barium in sea spray). While several leaching studies have been carried out, starting, in fact, with the earliest applications of the technique to the study of archaeological pottery, only alkali elements have been found to undergo extensive leaching or enrichment — as would be expected given their chemical behaviour. Nor does the temperature at which most New World pottery is fired (below 1000°C) appear to pose a problem of loss in elemental concentration (at least as the elements generally determined by INAA are concerned). Thus, while it is reasonable to question what variation in ceramic composition might have been caused by post-depositional conditions, it does not appear to be a highly significant factor for the elements routinely determined.

2.3.2. Data analysis

All of the above sources of variation are important to varying degrees in influencing the quantified determination of elemental constituents in pottery by INAA. Once these data have been obtained, part of the process of bridging between analysis and interpretation proceeds through the use of various statistical methods. While various methods are used, as discussed elsewhere in this report, it is important to be aware of the ‘structure imposing’ as well as the ‘structure revealing’ influence of the statistical approaches. Various clustering algorithms may partition a data matrix into subsets. What is sought, however, is an approach that will reveal patterning — archaeological patterning — in the data [2.9–2.12].

Quantitative chemical analyses for ceramic characterization, by INAA or other techniques, directly provide only one type of data: elemental abundances. The analysed samples lie with varying point densities in a multivariate concentration space. As a step towards simplification, whereby patterning might be more easily visualized, the dimensionality of the data may be reduced, perhaps to a two dimensional cluster result or a bivariate plot. Other statistical procedures may be used to reduce the dimensionality by representing the sample concentration positions in terms of some form of linear combinations of the original measurements. Whatever the procedures used to promote the understanding of the underlying data structure, and to communicate it to others, efforts should be made to portray the structure as simply as possible. For example, it is well established that if one can see that two groups are significantly separated along any reference axis, be it elemental concentration or some other form of representation, the groups will remain separated in the multivariate space. The converse is quite different however. Two groups might not be significantly separated along any single reference axis but they may yet be separable when two or more dimensions of the data are considered.

Similar to the efforts made to understand the sources and influences of variation in the ceramic compositional data, careful attention must be given to the numerical procedures used to seek patterning in the data. The approaches taken to form subsets of the data and to evaluate their significance are of critical importance, for the resultant groups constitute the reference sets against which various models of behavioural interaction are evaluated.

2.4. BRIDGING FROM ANALYSIS TO INTERPRETATION: BEYOND DEMONSTRATION OF CONTACT

Given the fragmentary nature of the archaeological record, the multiple sources of variation observed in ceramic compositions, the limitations imposed by sampling and the informed, yet subjective, application of multivariate statistical procedures, it is somewhat amazing that INAA works as well as it does in addressing archaeological questions. For example, during more than 25 years of research in the Maya lowlands of southern Mexico and northern Central America, there have been repeated demonstrations that INAA data can be used to attribute ceramics to a highly delimited production source area or site. These data, which require a very good degree of analytical precision (e.g. several elements at 2% or better and many at 5% or better), have allowed investigators to place non-provenanced vessels into a spatial perspective. These vessels are noted for their elaborate scenes, glyphic texts and other historical or ritual informational content. On the basis of the frequently demonstrated co-variations between themes, display of line and glyphic context, these data can be interpreted as revealing the products of individual workshops and even the idiosyncratic expression of individual painting styles. In other words, we may be seeing, reflected in the INAA data, aspects of social behaviour that relate to the organization of ceramic production and other aspects of social life [2.13, 2.14].

The success just cited was, of course, made possible by the input of historical art information. By themselves, the analytical data do not indicate where the ceramic was made, how it moved in a social context to arrive at the point of modern recovery, anything about the organization of production or even the meaning of a specimen's compositional similarity to another ceramic vessel. Thus, in all archaeological applications, a fundamental question remains: What do these data mean? Frequently, interpretations are ambiguous. This should be of no great surprise for human beings, the creators of the pottery that we study, are known for their creativity, reflectivity and intent — all of which have non-deterministic characteristics. To make matters worse, these human qualities, reflected in patterns of production, exchange and consumption, are only dimly reflected in the fragmentary archaeological record. Archaeological interpretation requires that one must bridge among different conceptual spheres, where contextual and analytical findings are considered from the standpoint of human interaction — where the archaeological record can be described (explained) in terms of choices that were made in the past. The demonstration that a particular ceramic found at site A was, in fact, manufactured from raw material resources in or around site B is an objective application of the analytical technique but one that is subject to alternative economic, political or symbolic interpretation. For example, an elaborately decorated non-local vessel, rather than having been acquired as a consequence of economic activity, may reflect aspects of a prestige system wherein the object takes on great value merely because it is non-local.

Frequently, interpretations are offered in terms of suggested models of human interaction that provide a structure for synthesis. But accurate interpretations are seldom possible, leaving the meaning of even the rigorously derived analytical data susceptible to alternative explanations. Ultimately, the ability of archaeologists to make more accurate inferences about past behaviour depends on understanding the relationship between the material and the non-material aspects of culture and society as they have changed through time. Communication between investigators, analysts and archaeologists is critical [2.15]. Each must become knowledgeable about the perspectives and concepts of the other so that extraneous variation in the investigation may be avoided. Ongoing feedback between parties is essential for maintaining research objectives and ensuring that technique resolution is adequate for the questions being addressed. This will maximize the resources — human and instrumental — that are given to the archaeological investigation and will contribute to INAA moving beyond the differentiation of locally and non-locally produced pottery, into more contextualized contexts of human behaviour. The bridging from INAA data to the more accurate archaeological explanations of social life represents an ultimate challenge that still lies ahead.

REFERENCES

[2.1] SAYRE, E.V., DODSON, R.W., Neutron activation study of Mediterranean potsherds, Am. J. Archae. **61** (1957) 35–41.

[2.2] SAYRE, E.V., MURRENHOFF, A., WEICK, C.F., The Non-destructive Analysis of Ancient Potsherds through Neutron Activation, Publ. BNL (T-122), Brookhaven Natl Lab., Upton, NY (1958).

[2.3] RANDS, R.L, WEINER, M.G., "Integrative approaches in the compositional characterization of ceramic pastes", Chemical Characterization of Ceramic Pastes in Archaeology (Monographs in World Archaeology), No. 7 (NEFF, H., Ed.), Prehistory Press, Madison, WI (1992) 31–58.

[2.4] RANDS, R.L., BISHOP, R.L., "Resource procurement zones and patterns of ceramic exchange in the Palenque region, Mexico", Models and Methods in Regional exchange, SAA Papers No. 1 (FRY, R.E., Ed.), Society for American Archaeology, Washington, DC (1980) 19–46.

[2.5] SNEATH, P.H.A., SOKAL, R.R., Principles of Numerical Taxonomy, W.H. Freeman, San Francisco, CA (1973).

[2.6] BEAUDRY, M., SHEPARD, A.O., "New World paste-compositional investigations", A Ceramic Legacy (BISHOP, R., LANGE, F.W., Eds), University of Colorado Press, Niwot, CO (1991) 224–256.

[2.7] BISHOP, R.L., RANDS, R.L., HOLLEY, G.R., "Ceramic compositional analysis in archaeological perspective", Advances in Archaeological Method and Theory, Vol. 5 (SCHIFFER, M.D., Ed.), Academic Press, New York (1982) 275–330.

[2.8] HARBOTTLE, G., "Activation analysis in archaeology", Radiochemistry, Vol. 3 (NEWTON, G.W.A., Ed.), The Chemical Society, London (1976) 33–72.

[2.9] BISHOP, R.L., HARBOTTLE, G., SAYRE, E.V., "Chemical and mathematical procedures employed in the Maya fine paste ceramics project", Analyses of Fine Paste Ceramics, Excavations at Seibal, Vol. 15 (SABLOFF, J.A., Ed.), Peabody Museum of Archaeology and Ethnology, Cambridge (1982) 272–282.

[2.10] BISHOP, R.L., NEFF, H., "Compositional data analysis in archaeology", Archaeological Chemistry, Vol. 4 (ALLEN, R.O., Ed.), American Chemical Society, Washington, DC (1989) 57–86.

[2.11] GLASCOCK, M., "Neutron activation analysis", Chemical Characterization of Ceramic Pastes in Archaeology, Monographs in World Archaeology, No. 7 (NEFF, H., Ed.), Prehistory Press, Madison, WI (1992) 11–30.

[2.12] NEFF, H., "Neutron activation analysis for provenance determination in archaeology", Modern Analytical Methods in Art and Archaeology (CILIBERTO, E., SPOTO, G., Eds), Chemical Analysis: A Series of Monographs on Analytical Chemistry and its Applications, Vol. 155 (WINEFORDNER, J., Ed.), Wiley, New York (2000) 81–134.

[2.13] BISHOP, R.L., REENTS, D.J., HARBOTTLE, G., SAYRE, E.V., VAN ZELST, L., "The area group: An example of style and paste compositional co-variation in Maya pottery", Proc. 5th Palenque Round Table, 1983 (FIELDS, V.M., Ed.), Pre-columbian Art Research Institute, San Francisco, CA (1985) 79–84.

[2.14] REENTS, D.J., BISHOP, R.L., "History and ritual events on a Petexbatun Classic Maya polychrome vessel", ibid., pp. 57–63.

[2.15] DE ATLEY, S., BISHOP, R.L., "Toward an integrated interface for archaeology and archaeometry", A Ceramic Legacy (BISHOP, R., LANGE, F.W., Eds), University of Colorado Press, Niwot, CO (1991) 358–380.

Chapter 3

PROVENANCE ARCHAEOLOGICAL STUDIES OF CERAMIC RAW MATERIALS AND ARTEFACTS USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS: THE CASES OF CHASCHUIL AND BOLSÓN DE FIAMBALÁ (CATAMARCA, ARGENTINA)

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Abstract

A study is presented of raw materials and sherds from the southern Puna region of Argentina that were analysed using instrumental neutron activation analysis (INAA). The study region is located at the headwaters of the river Chaschuil and its tributaries. The sampled areas include the upper Chaschuil basin and the lower Bolsón de Fiambalá, especially within the dispersion area of the Batungasta archaeological site. The hypothesis is made that those Puna areas with higher resource concentrations were occupied by both gatherer–hunter and farming societies, to explain the differences in the distribution of archaeological material. Regarding mobility, the hypothesis is made that the Puna region of the Chaschuil basin served as a corridor for the circulation of goods, fuel and information, interconnecting large areas including the facilities at the bottom of the valley, especially at Bolsón de Fiambalá. An evaluation of the analytical and technological studies of the ceramic materials within the working hypotheses is presented here.

3.1. INTRODUCTION

Neutron activation analysis (NAA) is a powerful tool for discussing archaeological problems such as the following: (a) the use of land by past societies, (b) group mobility strategies in the past, (c) comparison of exploited sources of ceramic raw materials with non-exploited sources, (d) manufacturing centres and their range of influence and distribution, (e) the kind of goods transported and exchanged [3.1–3.4].

The objectives of the Chaschuil Archaeological Project (PACh), a research project of the University of Catamarca (Argentina), are among the archaeological problems to which INAA can be applied. PACh is an interdisciplinary regional archaeology project in the Argentine southern Puna and its goals are to explain land use, focusing on the study of both environmental and artefactual variability. In order to accomplish these goals, the project comprises paleo-environmental, ecological, geomorphological, geo-archaeological and taphonomical techniques and provenance studies of the ceramic raw materials used in the manufacture of ceramic artefacts. Together with archaeological data, they provide the basis for models of mobility and exchange among past societies in the southern Puna [3.5–3.8].

The study performed within the CRP is part of the PACh, and the results will allow the discussion and modelling of pre-Hispanic social relationships in the Catamarca southwestern macro-region, especially between Puna and mesothermal valley environments, located at 3500–4200 and 1500 metres above sea level, respectively (Fig. 3.1). This work presents the evaluation of the analytical and technological studies of the ceramic materials within the working hypotheses. Attention is called to the fact that a land reutilization by ceramic–agricultural societies is observed, from early times until the appearance of the Incas. Raw materials from the mesothermal valleys that are considered possible manufacturing areas for ceramic lots were recovered in the Puna area [3.9].

3.2. INVESTIGATION AREA

The study region is located at the headwaters of the Chaschuil river and its tributaries (Cazadero Grande, Las Lozas and San Francisco). It can be defined as a high altitude area, located between 3500 and 4200 m above sea level (ASL) on a south–north gradient, with vegetation types typical of both the Puna and Altoandino districts. Latitude and longitude conform to a semi-desert weather, with gravitation wind and water as the main landscape modelling agents [3.5].

The sampled areas included the upper Chaschuil basin and the lower Bolsón de Fiambalá, specifically within the dispersion area of the Batungasta archaeological site (1500 m ASL). Also, systematic excavations at archaeological sites located in the Puna region were conducted in order to recover stratified ceramic samples, candidates for context dating. It is important to highlight the fact that the Chaschuil and Bolsón de Fiambalá areas are separated by a lineal distance of more than 200 km (Fig. 3.1).

3.3. ENVIRONMENT AND ARCHAEOLOGICAL RECORD

Tectonic forces generating the Andean range stimulated the appearance of other elevations of lower altitude, as well as the formation of elongated depressions such

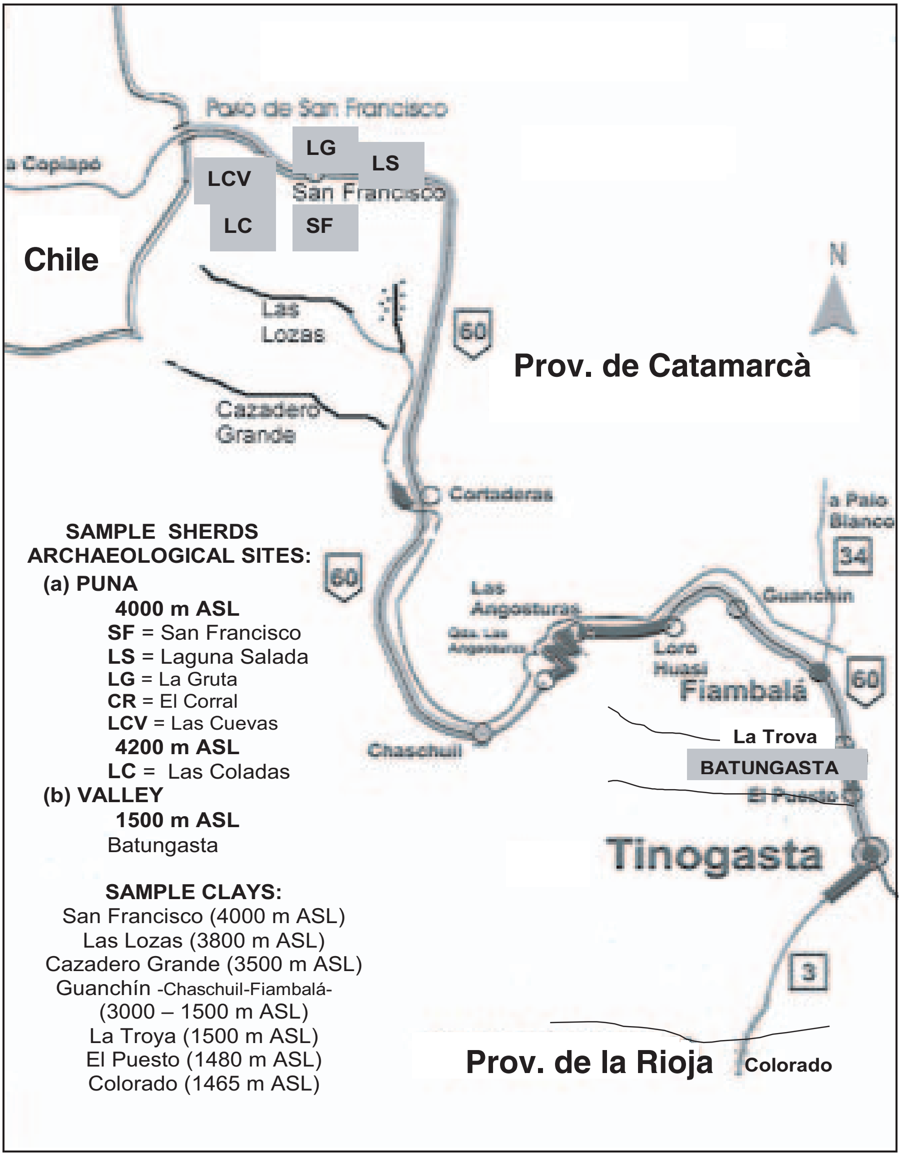

FIG. 3.1. Puna and valley areas. Provenance of sherds. Archaeological sites and sampled clay areas. The distance between the Puna and valley areas is about 100 km.

as the Chaschuil valley. Thus the region presents a combination of abrupt mountainous and flat surfaces corresponding to the cordillera area and the vegas and pampas, respectively. Low altitude areas act as depressions, receptacle-like, locked up by higher altitude spaces. This differentiation expresses itself through the area geology, monogenetic centres (andesites and basalts) and volcanic strata (andesites, basalts, basaltic andesites and piroclastic andesites) occurring in the cordillera area, while depressions are characterized by the presence of modern dendritic accumulations [3.10].

The ecotopographic characteristics of the Puna region condition the use of land and it can be stated that:

(a) The high relative topography of the Puna region limits and conditions the use of space and the communication among zones.
(b) The Puna is a region where resources are heterogeneously distributed. Some areas have concentrated resources while in others they are dispersed, this polarization being highly accentuated.
(c) The topography and the availability of water and firewood were critical factors for the settlement of human populations in the past.

The hypothesis can be stated that if the Puna region has heterogeneously distributed resources then those parts favoured with higher resource concentration were occupied by both gatherer–hunter and farming societies. So differences are expected in the distribution of archaeological materials, these differences being related to the different hunting and productive strategies developed through time, then modelling the differences or similarities in the use of space as an exploitable resource with not only economic but also ceremonial connotations [3.7].

The hypothesis about the mobility in the past is that the Puna region of Chaschuil served as a corridor for the circulation of goods, fuel and information, interconnecting large areas in both the longitudinal and transverse directions, and relating to other facilities located at the bottom of mesothermal valleys, especially at Bolsón de Fiambalá. Thus it should be expected that ceramics recovered in the Puna area were manufactured with raw materials coming from the valley area rather than with existing local ceramic materials for a potential period of 2000 years.

3.4. METHODOLOGY

3.4.1. Archaeological studies

Density, frequency, distribution, shape and decoration studies are adequate for comparison of the artefacts coming from different environments, as they allow modelling of land use, intensity, ways of use and functionality [3.11–3.13]. Distributional archaeology allows this type of discussion as it emphasizes spatial dimension, allowing one to:

(a) Focus the analysis on the study of variability, both artefactual and environmental;
(b) Explore large areas in order to research the archaeological record on a regional scale, in terms of topographic–ecological bases and considering their forming processes;
(c) Discuss the conditions of space occupational stability;
(d) Select excavation sites for the analysis of temporal variation.

The sub-basins present in the study region were considered as analytical units. They have different altitudes that increase upwards following a south–north gradient and east–west direction. They are: (a) Cazadero Grande (CG) (3500–4000 m ASL), (b) Las Lozas (LZ) (3800–4000 m ASL) and (c) San Francisco (SF) with its sub-area Las Coladas, distant 10 km (4000–4250 m ASL). The sub-basins are within approximately 40 km from each other (Fig. 3.1). In addition to this, potential raw material (clay, sand and other mineral inclusions) source locations were sampled both in the Puna (Vega San Francisco, Las Lozas and Cazadero Grande) and in the valleys (the rivers: Guanchín, 1500–3000 m ASL; La Troya, 1500 m ASL; El Puesto, 1480 m ASL; Colorado, 1465 m ASL). The availability, plasticity, workability and textural fractions of sampled deposits were considered [3.5].

Technological analyses of ceramic material from the Chaschuil region and Bolsón de Fiambalá were made, using low magnification techniques (binocular microscope). The analysed samples were:

(a) 474 sherds from superficial archaeological sites from the Chaschuil region (Puna),
(b) 162 sherds from stratified archaeological sites from the Chaschuil region (Puna),
(c) 1263 sherds from superficial archaeological sites from Bolsón de Fiambalá (a mesothermal valley).

On the basis of these studies, a set of samples ($N = 321$), from the Puna ($N = 195$) and from the mesothermal valleys ($N = 126$), was selected for elemental characterization using INAA. Decorated and undecorated sherds were selected, the former ones representing a 2000 year period within the existing periods for the northwestern Argentine region. In addition, 54 samples from clay deposits from the Puna ($N = 9$) and the valleys ($N = 45$) were analysed and X ray diffraction (XRD) was performed on 23 of these samples.

3.4.2. Analytical studies

3.4.2.1. Sample preparation

Samples were prepared using a grinding method. To ensure sample homogeneity, a fragment of about 2 cm^2 (2–3 g) was used, cleaning its whole surface by scrapping with a tungsten carbide rotary file and discarding the powder. Then the piece was ground in an agate mortar and the fine powder obtained was dried in an oven at 105°C for 24 h, allowed to cool in a desiccator and kept in a clean glass flask until its analysis. A drilling method was also tried on the clean sherds. Several perforations were drilled on the sherd transverse section using a tungsten carbide drill, and about 300 mg of powder were collected. The two sample preparation methods were tried on some large enough sherds and the analytical results compared. Contamination of cobalt from the drill was observed and it was found that the drilling method could not be used with small fragments because they broke under contact with the drill. As the set of samples for analysis includes several small fragments, the grinding method was adopted for the preparation of the whole set.

3.4.2.2. Analytical procedures

The samples were prepared and analysed by INAA at the laboratories of the Nuclear Analytical Techniques Group of the Ezeiza Atomic Centre (Argentine Atomic Energy Commission). Masses of about 100 mg of the samples were sealed in high purity quartz ampoules and then put into aluminium capsules, together with reference materials for their irradiation. Irradiation was carried out at the RA-3 reactor (thermal neutron flux, 3×10^{13} cm^{-2}·s^{-1}) of the Ezeiza Atomic Centre for 5 h. Two measurements were performed after approximately seven and thirty day decays, respectively, for the determination of twenty-two elements: As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, La, Lu, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U and Yb. The measurements were done using Ortec HPGe detectors (30% efficiency and 1.8 keV resolution for the 1332.5 keV ^{60}Co peak) coupled to a Canberra Series 85 multichannel analyser and an Ortec 919 multichannel analyser module (using Gamma Vision software for data acquisition). To calculate concentrations, a software developed at the laboratory was used and NIST SRM-1633b coal fly ash was used for quantification.

3.4.2.3. Quality control

About 10% of the samples were analysed in duplicate and the results were in good agreement. The reproducibility of the analytical method was tested, analysing standard reference materials (NIST SRM-2709 San Joaquín soil, NIST SRM-679 brick clay and USGS andesite (AGV)) and control charts were drawn. The results from the analysis of the SRMs San Joaquín soil and brick clay were compared with those from the INAA laboratories of Brazil (IPEN) and Chile, and they showed an agreement within a 95% confidence level for Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Sc, Sm, Th and Yb [3.14]. Five ceramic samples were sent to these two laboratories and another one to Italy (University of Pavia). The relative error for 67% of the elements (Ce, Cr, Cs, Eu, Fe, Hf, K, Lu, Na, Rb, Sc, Sm, Th, U, Yb and Zn) was less than 10% for all five samples. For 25% of the elements (As, Ba, Co, La, Sr and Ta) it was between 10 and 15% for two samples, being less than 10% for the others. Only Sb and Tb had relative errors higher than 15%, for two samples (Sb) and one sample (Tb). These results showed good agreement among the laboratories. The INAA laboratories also took part in the intercomparison run organized within the CRP.

3.5. RESULTS

3.5.1. Technological characteristics of analysed samples

3.5.1.1. Samples from potential raw material sources (clay, sand and other mineral inclusion sources)

Figure 3.1 shows the sites in the Puna region and the mesothermal valley where clay deposits were sampled, from 1465 to 4200 m ASL. Raw material studies showed that:

(a) The nine clay deposits sampled in the Puna (3500–4200 m ASL) correspond to secondary clays, meteorized and/or transported and deposited according to the geomorphological and geological characteristics of the area. These clays are rare but have high plasticity and workability. Textural analysis showed high sandy fractions, without differences among basins. XRD showed 50% good quality clays for ceramic manufacture, low presence of clay fractions (10–25%), high presence of calcite and high to medium presence of feldspar.

(b) Clay deposits from the river Guanchín area (19 deposits) were sampled from 1500 to 3000 m ASL. Clays from higher altitudes have a high sandy fraction and low plasticity. On the contrary, the macroscopic characteristics of low altitude deposits are similar to those from the La Troya river area 25 km away.

(c) At the river La Troya and Quebrada (1500 m ASL), 17 clay deposits were sampled, showing secondary clays, meteorized and transported by fluvial agents in a sedimentary environment. Clays are common, have a low presence of sandy texture fractions, and have excellent properties regarding their plasticity and workability. XRD showed 100% good quality clays for ceramic manufacture, a high presence of clay fractions (17–45% concentration values), a low presence of calcite and feldspar, and a high presence of quartz (24–45%).

(d) The four sampled deposits from the river El Puesto (1480 m ASL) and three from the river Colorado (1465 m ASL) presented macroscopic characteristics similar to those from the La Troya area, at distances of approximately 8 and 50 km, respectively.

3.5.1.2. Puna sherds (3500–4200 m ASL)

The ceramics are mainly found at the 4000 m level and are associated with archaeological sites with two types of architectural feature: complex peripheral rectangular rooms and poorly conserved circular rooms. Both types show evidence of having been reclaimed for a long time, and also, they are located on the banks of vegas associated with rocky formations [3.5–3.8]. Despite strong superficial evidence of the Incas, sherds from earlier cultural periods were recovered from the surface. The analysed sherds (*N* = 195) come from surface collection (*N* = 76) and systematic excavations (*N* = 119) and have been classified within the existing periods for the Argentine northwestern area [3.15] on the basis of their ceramic styles and/or their technological characteristics. In this way, surface sherds define a potential 2000 year palimpsest, as they represent different ceramic–agricultural periods: (a) early (300 B.C.–650 A.D.), (b) middle (650–850 A.D.), (c) late (850–1480 A.D.) and (e) Inca (1480 A.D. until the Hispanic presence). These temporal ranges should not be considered as absolute ones but as period models of macroregional scope. Thermoluminiscence[1] dating of four ceramic samples classified as Ciénaga (two, early period), Aguada (one, middle period) and Inca (one, Inca period) covered a 765 year range for the occupation of the Puna at 4000 m ASL [3.8]. Table 3.1 presents the sample composition related to their site of recovery and chronological period. The mentioned sites are located within a range of approximately 7 km.

Sherds were mostly small, so that it was impossible in most cases to ascribe pot shapes and/or parts. Figure 3.2(a) shows the technological behaviour trend of Puna samples: illustrating the antiplastic portion of the matrix, its mineral composition, size and firing percentage in sherds classified into ceramic–agricultural periods (with the exception of an undetermined group of undecorated ordinary sherds). In general the temper shows the predominant presence of quartz whatever the temper grain size; a predominant presence of calcite, rock fragments and mica can also be observed as a function of temper grain size. The sherds also present other inclusions in a low

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[1] Dating was done at the thermoluminiscence laboratory of the Universidad Católica de Chile. Dating results were: (a) UCTL 1305–1450 A.D., Inca pot; (b) UCTL 1306–1075 A.D., Aguada pot; (c) UCTL 1307–735 A.D. Ciénaga pot; (d) UCTL 1308–685 A.D., Ciénaga pot.

TABLE 3.1. PROVENIENCE OF PUNA SHERDS

Archaeological site	Provenance	Period (northwestern Argentina)					
		Early	Middle	Late	Inca	Undetermined	Total
Laguna Salada (3980 m ASL)	Surface dispersion	12	0	0	2	14	44
	Excavation	11		1		4	
San Francisco (4000 m ASL)	Surface dispersion	7	5	2	14	15	114
	Excavation	0	0	0	67	4	
	Excavation peripheral area (El Corral)	12	0	0	0	1	13
Las Coladas (4200 m ASL)	Surface dispersion	0	0	0	5	0	13
	Excavation	0	0	0	8	0	
Las Grutas Alero 12 (Asociado Laguna Salada)	Excavation	0	0	0	0	6	6
Las Cuevas (Alero) (4030 m ASL)	Excavation	0	0	0	0	5	5
Subtotal by period		42	5	3	96	49	
Total number of Puna sherds							195

percentage (i.e. feldspar, ground sherds and glass). Medium and small antiplastic sizes prevail over coarse and very coarse, these being principally associated with ordinary sherds. For early period pots, reducing atmosphere firing is predominant. Figure 3.2(a) refers to Puna surface samples as they have a wider diversity than those from systematic excavations. Most excavated sherds (*N* = 119) were classified as Inca type (75 of 119) with technological characteristics similar to those from the surface

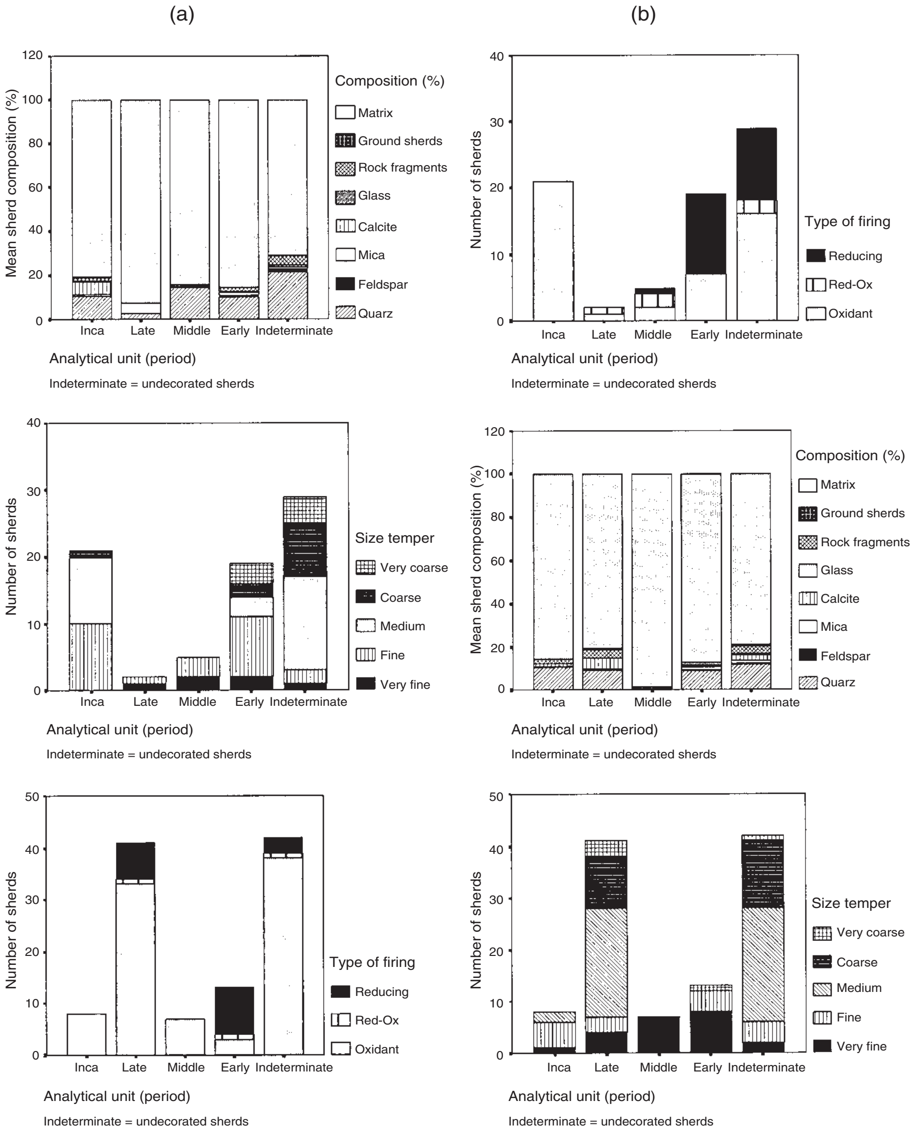

FIG. 3.2. Technological profiles of: (a) Puna sherds (N = 76 of 195), (b) mesothermal valley sherds (N = 113).

(Table 3.1). Those sherds classified as undetermined correspond to undecorated ones, both from surface collection and from excavation.

3.5.1.3. Mesothermal valley sherds (1500 m ASL)

Sherds (*N* = 113) were selected from among those coming from systematic collections at the Batungasta site ceramic dispersion area and from excavation outside adobe enclosures towards the east of the site. The Batungasta archaeological site is located on the right margin of the river La Troya (1500 m ASL). An area equivalent to 9000 m^2 was sampled using radial transects centred on the site. The area was selected on the hypothesis that the Batungasta site played a fundamental role in the past due to its strategic position in Quebrada La Troya as:

(a) The gateway for the economic exploitation of the Andean areas;
(b) A node in a network of goods, fuel and information circulation, pointing to the west and connecting valley areas on both sides of the Andes;
(c) A production and manufacturing site acting as a goods emission centre towards other areas and altitudinal levels (the mesothermal valleys of Abaucán and Chaschuil and their respective Puna and Altoandino domains).

The recovered sherds stemmed from all the ceramic–agricultural periods, with the highest proportion corresponding to the late period. Owing to the conditions of the material it was possible to classify it according to its stylistic and technological characteristics. These characteristics are presented in Fig. 3.2(b) considering the same variables as for Puna sherds (Fig. 3.2(a)) to facilitate comparison. In general, quartz prevails over other antiplastic mineral components, although at a lower proportion if compared with the quartz in Puna sherds and with smaller sizes.

3.5.2. Evaluation of results

The elemental concentrations of the clays and sherds were evaluated by factor analysis using the SPSS 9.0 code after a logarithmic transformation of the data. The results for As, Ba, Gd, Nd, Ta, Tb, Sb and U were not considered due to missing values or high uncertainty values. The clay results were increased by 10% to account for the expected difference in concentrations between fired and non-fired clays, as the clays to be included for data treatment had not been fired [3.16]. The PCA method was used to analyse a covariance matrix and to generate the factors which were subjected to Varimax rotation. By keeping those factors with eigenvalues higher than one, a number of factors were chosen to account for a percentage of the total variance. Factor loadings and the percentage of variance explained are indicated in each figure.

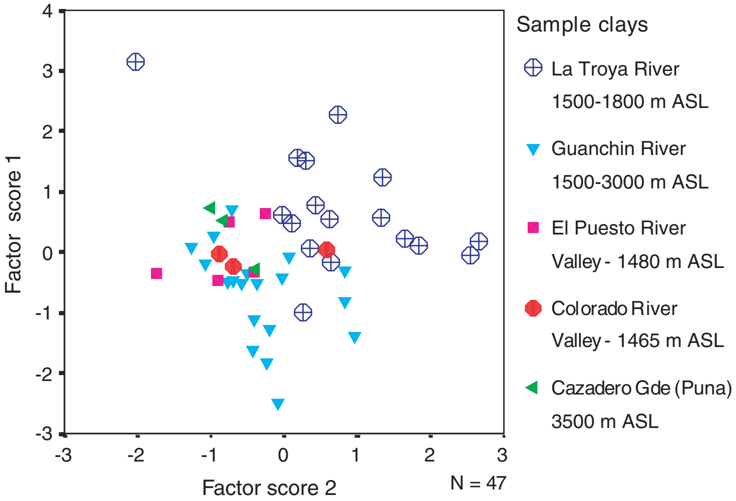

FIG. 3.3. Factor analysis for Puna and valley clays.

TABLE 3.2. ROTATED COMPONENT MATRIX FOR FIG. 3.3

	Rescaled component	
	1	2
lg Ce	0.778	0.502
lg Co	0.768	0.561
lg Cr	0.823	0.457
lg Cs	0.823	0.449
lg Eu	0.769	0.468
lg Fe	0.797	0.519
lg Hf	0.525	–0.066
lg La	0.401	0.754
lg Lu	0.097	0.953
lg Rb	0.311	0.755
lg Sc	0.689	0.655
lg Sm	0.352	0.846
lg Th	0.782	0.549
lg Yb	0.373	0.743
Variance explained (%)	40.49	39.38

Notes: Extraction method, principal component analysis; rotation method, varimax with Kaiser normalization. The rotation converged in three iterations.

3.5.2.1. Evaluation of the elemental composition of clays from the Puna (N = 9) and the mesothermal valleys (N = 44). Total sample size: N = 53

The first statistical treatment (*N* = 53) showed the grouping of clays from the valleys and Cazadero Grande (the Puna at 3500 m ASL) and outliers from San Francisco (the Puna at 4000 m ASL) and Las Lozas (the Puna at 3800 m ASL). After removing these outliers and repeating the factor analysis on the remaining data it was found that one sample from La Troya (1500 m ASL) separated from the group. Figure 3.3 and Table 3.2 show the representation after the application of factor analysis to the clay matrix including Cazadero Grande (the Puna at 3500 m ASL) samples and the remaining valley clays (*N* = 47). Two components were obtained, accounting for 84.7% of the total variance. The first component had high loadings for Co, Cr, Fe, Sc, Eu, Ce and Cs, and the second for rare earths, Th and Rb. A great difference was observed between most of the La Troya samples and the ones from nearby areas. Clays from Cazadero Grande overlapped with those from Guanchín, Colorado and El Puesto, in spite of the different provenance environments.

3.5.2.2. Evaluation of the elemental composition of Puna sherds (surface, N = 76; excavation, N = 119) and clays

Puna sherds come from different archaeological sites, located at 4000 m ASL (Table 3.1). Figure 3.4 and Table 3.3 represent two of the three components obtained

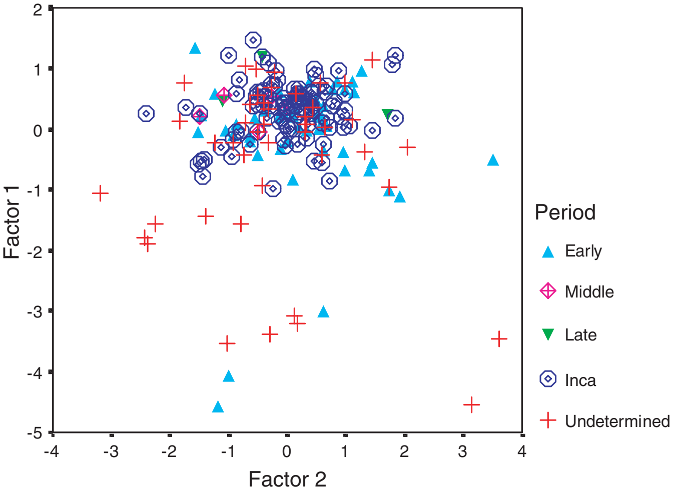

FIG. 3.4. Factor analysis for Puna sherds: extraction method, principal component analysis (PCA); rotation method, varimax with Kaiser normalization. The rotation converged in six iterations.

TABLE 3.3. ROTATED COMPONENT MATRIX FOR FIGS 3.4 AND 3.5

	Rescaled component		
	1	2	3
lg Ce	0.647	0.488	0.198
lg Co	0.867	0.150	0.021
lg Cr	0.829	0.224	0.028
lg Cs	0.214	–0.081	0.958
lg Eu	0.778	0.231	–0.029
lg Fe	0.914	0.140	0.167
lg Hf	0.352	0.192	0.031
lg La	0.592	0.607	0.035
lg Lu	0.184	0.826	–0.057
lg Rb	–0.203	0.504	0.646
lg Sc	0.891	0.197	–0.046
lg Sm	0.564	0.741	0.015
lg Th	0.167	0.769	0.286
lg Yb	0.302	0.683	–0.013
Variance explained (%)	36.59	24.13	10.66

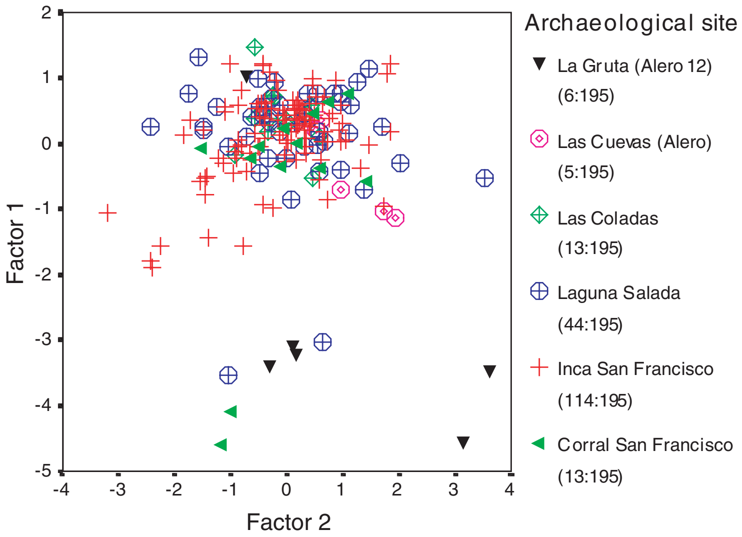

FIG. 3.5. Archaeological sites of the Puna sherds.

for these sherds, which account for 71.38% of the total variance. The first component was defined by Ce, Co, Cr, Eu, Fe and Sc, the second by Th and rare earths, and the third by Cs and Rb. The samples were classified and labelled according to the period to which they belong. The graphic shows a quite compact group with undecorated (ordinary) sherds on the periphery of the group. The nucleus of the grouping represents a cultural palimpsest as it comprises sherds belonging to different cultural periods. Figure 3.5 and Table 3.3 present the same relationship among samples but as a function of the provenance site in the Puna. A similarity in the chemical profiles of the sherds can be observed in spite of the spatial differentiation of the sites (Laguna Salada, San Francisco and Las Coladas) or of their proximity (Las Cuevas, San Francisco and El Corral). Thus it can be inferred that for the manufacture of ceramic artefacts, recovered at the Puna level at 4000 m ASL, the same raw materials were used for a period of about 800 years. The exception is a very small subgroup (7 of 195) of early and undetermined period sherds, recovered at the Las Grutas Alero 12, Laguna Salada and El Corral sites, with a different chemical profile. It is interesting that these cases do not have different technological characteristics, with the exception of a high percentage (50%) of mineral coarse antiplastics and the major presence of mica. Figure 3.6 and Table 3.4 present the relationship between the Puna sherds and clays other than those from San Francisco and Las Lozas (Section 3.5.2.1). Three components were defined that account for 76.7% of the total variance, and the similarity of the chemical profiles of the Puna sherds and (principally) the La Troya

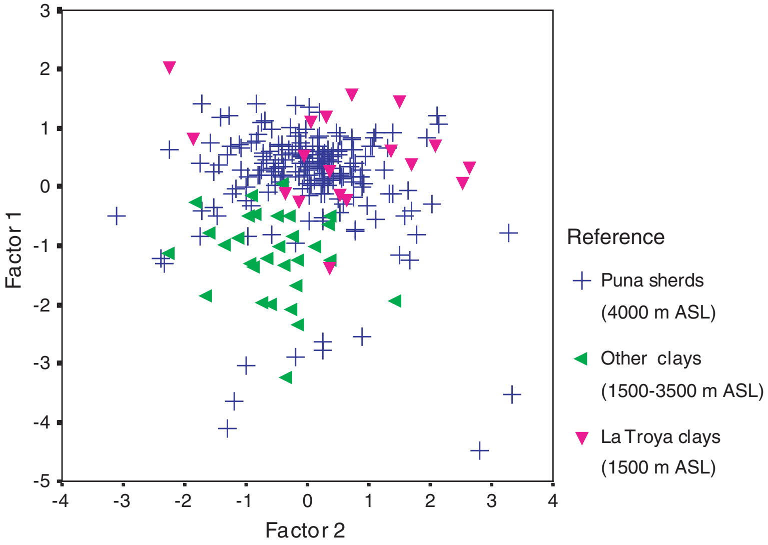

FIG. 3.6. Factor analysis for Puna sherds and clays (N = 242).

TABLE 3.4. ROTATED COMPONENT MATRIX FOR FIG. 3.6

	Rescaled component		
	1	2	3
lg Ce	0.672	0.443	0.368
lg Co	0.845	0.255	0.289
lg Cr	0.824	0.261	0.255
lg Cs	0.376	0.000	0.917
lg Eu	0.773	0.309	0.043
lg Fe	0.880	0.214	0.304
lg Hf	0.370	0.120	–0.022
lg La	0.553	0.619	0.254
lg Lu	0.194	0.859	0.093
lg Rb	–0.008	0.408	0.802
lg Sc	0.844	0.319	0.269
lg Sm	0.523	0.710	0.314
lg Th	0.378	0.571	0.572
lg Yb	0.360	0.688	0.161
Variance explained (%)	36.41	22.70	17.56

clays can be observed. When using factor analysis on a matrix of only Puna sherds (Figs 3.4 and 3.5), thorium appears in the second factor together with the rare earths; after including the clays (Fig. 3.6), the thorium loadings for factors 2 (rare earth) and 3 (Cs, Rb) are comparable.

3.5.2.3. Evaluation of NAA results for valley sherds (surface (N = 109) and excavation (N = 4))

Batungasta ceramic dispersion area sherds, labelled by the period to which they belong, are shown in Fig. 3.7 and Table 3.5 (see also Table 3.6). Three components were obtained, accounting for 68.9% of the total variance. The first two are represented in the graphic. Transition elements have high loadings in the first component, rare earth elements in the second and alkaline elements in the third. The samples are distributed forming a principal and tighter grouping including middle and early sherds and some from the late period, with others from this period (11 of 47),

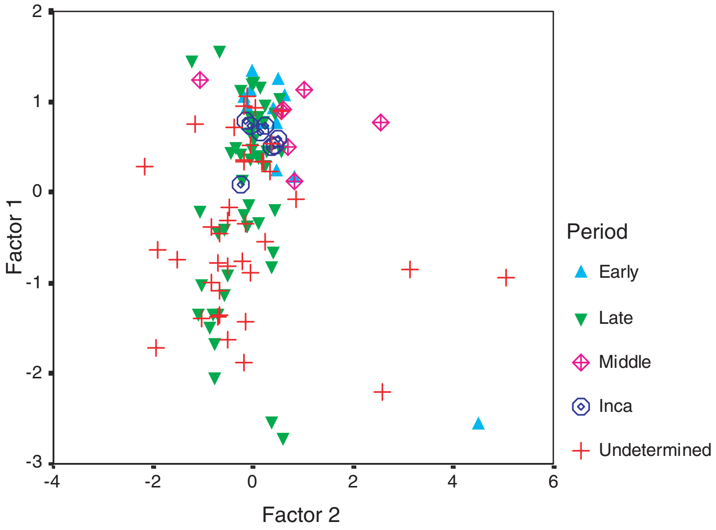

FIG. 3.7. Factor analysis for valley sherds (N = 114).

TABLE 3.5. ROTATED COMPONENT MATRIX FOR FIG. 3.7

	Rescaled component		
	1	2	3
lg Ce	0.605	0.563	0.222
lg Co	0.611	0.672	–0.078
lg Cr	0.881	0.336	0.020
lg Cs	–0.018	0.063	0.896
lg Eu	0.745	0.440	0.127
lg Fe	0.874	0.402	0.088
lg Hf	0.365	0.221	0.023
lg La	0.207	0.791	0.152
lg Lu	0.308	0.689	0.192
lg Rb	0.328	0.303	0.725
lg Sc	0.922	–0.059	0.061
lg Sm	0.353	0.795	0.145
lg Th	–0.004	0.024	0.263
lg Yb	0.105	0.875	0.086
Variance explained (%)	29.99	27.72	11.21

TABLE 3.6. PROVENANCE OF BATUNGASTA VALLEY SHERDS

	Period (northwestern Argentina)					
Provenance	Early	Middle	Late	Inca	Undetermined	Total
Excavation rooms	1	0	0	0	3	4
Periphery E	1	0	0	0	2	3
Periphery NE	8	1	18	2	11	40
Periphery N	1	1	0	0	0	2
Periphery S	7	5	29	6	23	70
Subtotal by period	18	7	47	8	39	
Total number of valley sherds						119

together with undecorated sherds, appearing in looser association with this tight group. This is interesting because of the potential roles of the site in the past, as it allows local ceramic manufacturing to be inferred during the site occupation. It is also interesting that the four sherds from excavations outside the adobe enclosures (Section 3.5.1.3) are also separate from the principal group of samples. Radiocarbon dating of the vegetal material included in the adobe bricks from these places resulted in dating to the Hispanic indigenous period [3.5], but there are no analytical data from the sherds of this period.

3.5.2.4. Evaluation of the relationships between Puna (N = 195) and valley sherds (N = 113) and clays (N = 47). Total samples size: N = 355

Factor analysis results for sherds recovered in the Puna ($N = 195$) and in the valleys ($N = 115$) are shown in Fig. 3.8 and Table 3.7, with three components accounting for 70.4% of the total variance. Transition elements and europium have high loadings in the first component, rare earths and thorium in the second and alkalines in the third. The obtained grouping of samples indicates that sherds recovered at different altitudinal levels and separated by more than 200 km have similar chemical profiles. From the characteristics of the valley (existence of ceramic raw materials, firewood and combustion structures (kilns), located at the periphery of Batungasta), it is inferred that the sherds recovered at the Puna level were manufactured with valley clays within a period of 800 years. This period is represented not only by the ceramic styles but also by the thermoluminescence dates.

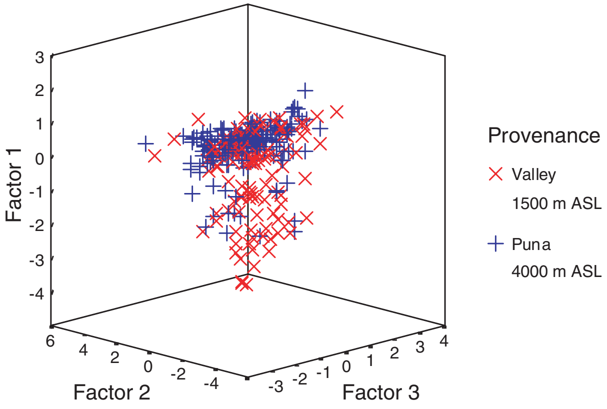

FIG. 3.8. Factor analysis for Puna and valley sherds (N = 308).

TABLE 3.7. ROTATED COMPONENT MATRIX FOR FIG. 3.8

	Rescaled component		
	1	2	3
lg Ce	0.585	0.562	0.220
lg Co	0.776	0.356	0.051
lg Cr	0.909	0.243	0.057
lg Cs	0.035	–0.031	0.970
lg Eu	0.766	0.367	0.068
lg Fe	0.918	0.264	0.148
lg Hf	0.342	0.262	0.040
lg La	0.402	0.784	0.069
lg Lu	0.272	0.802	0.012
lg Rb	0.166	0.397	0.612
lg Sc	0.889	0.103	0.018
lg Sm	0.499	0.785	0.064
lg Th	0.030	0.517	0.255
lg Yb	0.295	0.763	0.040
Variance explained (%)	33.64	26.20	10.52

Notes: Extraction method, PCA; rotation method, varimax with Kaiser normalization.

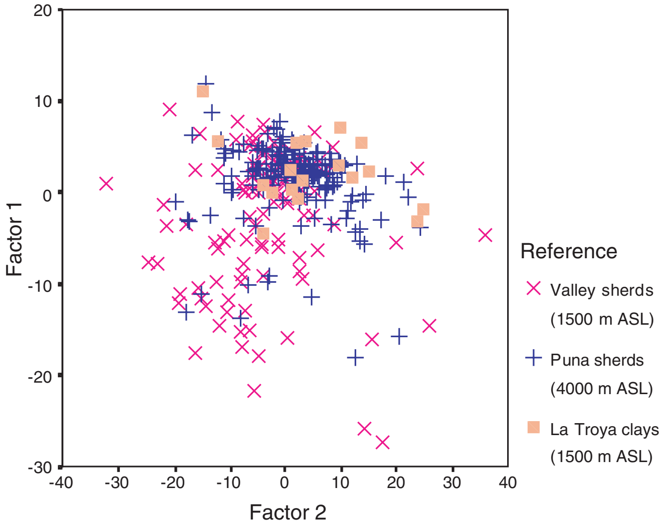

FIG. 3.9. Factor analysis for Puna and valley sherds (N = 308) and La Troya clays (N = 17).

TABLE 3.8. ROTATED COMPONENT MATRIX FOR FIG. 3.9

	Rescaled component		
	1	2	3
lg Ce	0.601	0.541	0.240
lg Co	0.787	0.333	0.063
lg Cr	0.908	0.235	0.077
lg Cs	0.028	–0.070	0.974
lg Eu	0.767	0.367	0.020
lg Fe	0.920	0.256	0.148
lg Hf	0.362	0.223	0.036
lg La	0.392	0.790	0.105
lg Lu	0.260	0.824	–0.014
lg Rb	0.145	0.376	0.617
lg Sc	0.882	0.130	0.010
lg Sm	0.474	0.789	0.121
lg Th	0.056	0.488	0.318
lg Yb	0.323	0.739	0.028
Variance explained (%)	33.62	24.69	11.94

Notes: Extraction method, PCA; rotation method, varimax with Kaiser normalization. The rotation converged in four iterations.

If the already statistically selected clays are incorporated in the sherd matrix, it can be observed that the La Troya clays (*N* = 17) are the most similar to the Puna and Batungasta site periphery sherds (Fig. 3.9 and Table 3.8), although a minor number of the sherd group are from clays from sites other than La Troya (Fig. 3.10 and Table 3.9). Both these figures show the two first components, as these are the principally supporting elements: transition elements for the first and rare earths for the second; alkalines have high loadings in the third component.

3.6. DISCUSSION

(a) Sherds from the Puna and the valleys have similar technological profiles, although they originate from a potential 2000 year period, as a function of the cultural period for northwestern Argentina, since the analysed sherds have chrono-cultural-stylistic characteristics corresponding to the early, middle, late and Inca periods (Figs 3.2(a) and (b)).

(b) The chemical profiles of ceramic raw materials from the Puna and the valleys have significant interregional differences (Fig. 3.3). This agrees with the results of XRD that confirm the valley clays to be of better quality than the Puna ones, although some of the latter, from Cazadero Grande, are suitable for ceramic manufacture and have a chemical profile similar to those from Guanchín.

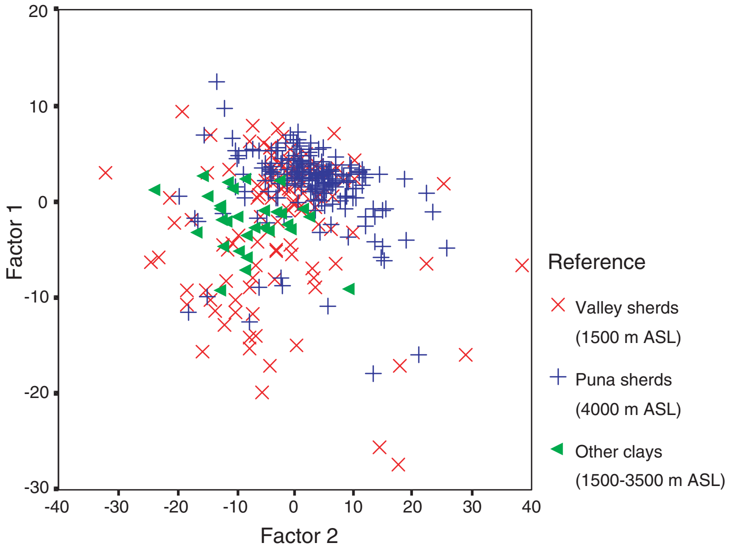

FIG. 3.10. Factor analysis for Puna and valley sherds and other clays (without those from La Troya) (N = 338).

TABLE 3.9. ROTATED COMPONENT MATRIX FOR FIG. 3.10

	Rescaled component		
	1	2	3
lg Ce	0.559	0.518	0.419
lg Co	0.765	0.361	0.234
lg Cr	0.898	0.272	0.103
lg Cs	0.150	–0.022	0.977
lg Eu	0.746	0.381	0.126
lg Fe	0.899	0.283	0.206
lg Hf	0.325	0.256	0.021
lg La	0.392	0.755	0.240
lg Lu	0.257	0.799	0.137
lg Rb	0.193	0.352	0.666
lg Sc	0.870	0.159	0.176
lg Sm	0.489	0.764	0.241
lg Th	0.119	0.448	0.582
lg Yb	0.279	0.758	0.162
Variance explained (%)	32.44	24.86	15.92

Notes: Extraction method, PCA; rotation method, varimax with Kaiser normalization. The rotation converged in five iterations.

(c) La Troya clays are different from the other valley clays. The La Troya clays can be considered as local as they are from the Batungasta installation site and its dispersion area, from where surface sherds were collected.

(d) Puna sherds (*N* = 195) (surface and excavation) have similar profiles, forming a dense group despite their temporal differences, as they represent all the temporal periods of the Argentine northwestern area. According to thermoluminescence dating, the archaeological sites at the 4000 m level were reoccupied for a period of 765 years (Figs 3.4 and 3.5).

(e) The elemental profiles of the Puna sherds (*N* = 195) overlap with those of the valley clays, especially with the ones from La Troya (Fig. 3.6).

(f) Surface sherds from the mesothermal valleys (*N* = 113), from the Batungasta dispersion area, have similar elemental profiles but with larger variabilities than those from the Puna. Sherds on the periphery of the group principally correspond to the late period or cannot be dated. Included in this last group are those undecorated sherds that could be attributed to the late period, owing to their technological characteristics (Fig. 3.7).

(g) Sherds from the Puna (4000 m ASL) and from Batungasta and its dispersion area (mesothermal valleys at 1500 m ASL) form a dense group due to their chemical similarity. Following the abundance criteria [3.1] and based on the valleys having the physical and cultural–environmental conditions for ceramic manufacture, the valleys are considered to be the ceramic artefact area of origin and the Puna to be the dispersion area. In this way, the hypothesis of the Chaschuil area as a trade, fuel and information corridor and the Batungasta site as a manufacturing centre is reinforced. The presence of similar elemental profiles for Puna and valley sherds and La Troya clays (Fig. 3.9) also supports the hypothesis considering the La Troya clays as local.

(h) The chemical profile of Puna sherds is more homogeneous than that of valley sherds (Figs 3.4 and 3.7, respectively). Although the La Troya clays are local, as they come from the same recovery area as the valley sherds, it can be said that some of them were manufactured with other clays: some of these are yet to be sampled and others are included in this paper. These sherd samples are mainly from the late period or cannot be dated, the latter group being formed of undecorated sherds (Fig. 3.10).

3.7. CONCLUSIONS

The analysis presented in this paper allows the following conclusions to be drawn:

(1) La Troya clay sources, located within the installation area of the Batungasta archaeological site, have a different elemental profile from those of Puna and other valley clays.

(2) Puna sources of ceramic raw materials at 4000 m ASL were not used for the manufacture of those sherds sampled at Puna sites, which were the most frequently found sherds with the highest density. This conclusion is also valid for those samples from 3800 m ASL (Las Lozas), with the difference that no sherds were recovered at this altitude.

(3) Clays from 3500 m ASL (Cazadero Grande) differ from other Puna clays in their chemical profile, which is more similar to that from the upper Guanchín valley areas (2800–3000 m ASL). According to XRD results [3.5], Cazadero Grande clays have the highest clay fraction of all the Puna clays, being suitable for ceramic manufacture, although the results of this work indicate that they were not used for pottery.

(4) Most Puna sherds (4000 m ASL) are similar in their elemental profile to the sherds from the Batungasta site dispersion area and were manufactured with ceramic raw materials from the valley area, mainly La Troya (1500 m ASL).

(5) Sherds from the valley area were manufactured principally with local raw materials (1500 m ASL) that included the already sampled sources and others still to be located, possibly at the Abaucán river basin.

(6) The results presented in this work show ceramic manufacture to be predominant in valley areas, with the sherds distribution being towards both Puna and valley.

(7) These results are in agreement with the fundamental hypothesis of this project, since:

   (i) Puna ceramic raw materials were not used for the manufacture of ceramic artefacts recovered in this area.

   (ii) The ceramic artefacts entering the Puna region were manufactured with ceramic raw materials from valley sources. The archaeological site of Batungasta is a possible manufacturing centre, since the valley sherds come from a 5 km radius around this site.

   (iii) These results strengthen the hypothesis of the Puna area serving as a corridor for trade, fuel and information, within a 765 year period determined using thermoluminescence dating. During the Inca occupation, mobility patterns possibly existing since the early ceramic–agricultural societies time were maintained. Further research is ongoing to find new evidence to test this idea.

REFERENCES

[3.1] BISHOP, R.L., et al., “Ceramic compositional analysis in archaeological perspective”, Advances in Archaeological Method and Theory, Vol. 5 (SCHIFFER, M., Ed.), Academic Press, New York (1982) 275–230.

[3.2] BISHOP, R.L., NEFF, H., “Compositional data analysis in archaeology”, Archaeological Chemistry IV (ALLEN, R.O., Ed.), Advances in Chemistry Series No. 220, American Chemical Society, Washington, DC (1989) 57–86.

[3.3] NEFF, H. (Ed.), Chemical Characterization of Ceramic Pastes in Archaeology, Monographs in World Archaeology No. 7, Prehistory Press, Madison, WI (1992).

[3.4] LIZZE, J.H., et al., “Clay acquisition and vessel distribution patterns: neutron activation analysis of late Windsor and Shantock tradition ceramics from Southern New England”, American Antiq. **60** 3 (1995) 515–530.

[3.5] RATTO, N., “Informe de Avance, Proyecto Arqueológico Chaschuil, PACh.1995–1996”, 2 vols, Secretaría de Ciencia y Técnica, Univ. Nacional de Catamarca (1997).

[3.6] RATTO, N., “Distributional archaeology and paleoecology in the Southern Puna, Catamarca, Argentina: Preliminary results”, Lithic Technology (Proc. 13th Congr. Int.

Union of Prehistoric and Protohistoric Sciences, Forli 1998) (ARIAS, C., et al., Eds), (1998) 261–270.

[3.7] RATTO, N., ORGAZ, M., La presencia inkaica en la cuenca superior del Valle de Chaschuil (in preparation).

[3.8] RATTO, N., et al., “La ocupación de pisos altura por sociedades agroalfareras tempranas: El caso de la cuenca superior del valle de Chaschuil”, paper presented at 4th Mesa Redonda sobre La Cultura de La Aguada y su Dispersión, San Pedro de Atacama, Chile, 2000.

[3.9] PLÁ, R., et al., “Provenience archaeological studies of ceramic raw material and artifacts using instrumental neutron activation analysis: the cases of Chaschuil and Bolsón de Fiambalá (Catamarca, Argentina)”, Nuclear and Related Techniques in Agriculture, Industry and Environment (Proc. 2nd Int. Symp. Havana, 1999) (CD-ROM).

[3.10] DIRECCIÓN NACIONAL DEL SERVICIO GEOLÓGICO, Mapa Geológico de la Provincia de Catamarca (Argentina), Secretaría de Minería, Ministerio de Economía y Obras y Servicios Públicos, Buenos Aires (1995).

[3.11] BELARDI, J.B., GARCÍA, M.F., “Primeros lineamientos teóricos para la comparación interregional desde una perspectiva distribucional”, Los Primeros Pasos (OLIVERA, D., RADOVICH, J.C., Eds), Instituto Nacional de Antropología y Pensamiento Latinoamericano, Buenos Aires (1994) 53–58.

[3.12] LANATA, J.L., “Cambios para evolucionar: Las propiedades del registro arqueológico y la evolución de los grupos humanos en Patagonia y Tierra del Fuego”, Arqueología. Solo Patagonia (GOMEZ OTERO, J., Ed.), Centro Nacional Patagónico, Consejo Nacional de Investigaciones Científicas y Técnicas, Chubut, Argentina (1996) 99–106.

[3.13] SCHOFIELD, A.J., “Artifacts distributions as activity areas: examples from Southeast Hampshire”, Interpreting Artifact Scatters: Contributions to Ploughzone Archaeology (SCHOFIELD, A.J., Ed.), Monograph 4, Oxbow Books, Oxford (1991) 117–128.

[3.14] MUNITA, C.S., et al., “Intercomparison among three activation analysis laboratories in South America”, J. Trace Microprobe Tech. **19** 2 (2000) 189–197.

[3.15] GONZÁLEZ, A.R., “Cultural development in Northwestern Argentina”, Aboriginal Cultural Development in Latin America: An Interpretative Review (MEGGERS, B., EVANS, C., Eds), Smithsonian Miscellaneous Collection, Vol. 146, No. 1, Smithsonian Institution, Washington, DC (1963) 103–117.

[3.16] BISHOP, R.L., Smithsonian Centre for Materials Research and Education, personal communication, 2000.

Chapter 4

TRIBES AND CHIEFDOMS: AN ANALYTICAL STUDY OF SOME BRAZILIAN CERAMICS

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Abstract

There is no evidence of urban civilization in Brazilian prehistory; most inhabitants lived in tribal organizations, probably with regional economic integration among several independent tribes. There is little evidence of seasonal migrations between the coastal and inland areas of southern Brazil. Some specialized horticulturists competed among themselves but other groups lived more in isolation, and probably peacefully, in the upper interfluvial regions.The chiefdom system is supposed to have existed only along the river Amazon. In this region, some pottery makers may have been specialized craftsmen, and the finest ceramics that could have been exported from one village or region to another can be found. Outside this region, pottery was generally plain, except the tupiguarani, which was partly decorated. In this study some limited possibilities were tested, in three different cultural and regional contexts, to find out if the application of chemical analysis to economically and politically 'simple' societies can produce any results of additional archaeological relevance.

4.1. INTRODUCTION

The prehistory of the last two millennia in Brazil was characterized by the co-existence of several cultures in each region. It is difficult to know what the level of integration was between the different tribes of the proto gê, proto tupi, proto aruaque, proto pano and proto carib populations. There is no evidence of urban civilization in Brazilian prehistory; most inhabitants lived in tribal organizations, probably with regional economic integration among several independent tribes as recent ethnographic examples suggest (as in the Upper Xingu or Rio Negro areas). There is little evidence of seasonal migrations, except for some examples between the coastal and the inland areas of southern Brazil.

Part of the population, mainly specialized horticulturists in the alluvial plains, competed among themselves but other groups lived, probably peacefully, in more isolated areas in the upper interfluvial regions.

Each tupiguarani family outside the region along the river Amazon was able to produce their own traditional decorated pots and some of these might have been given to their neighbours — proto gê people.

It can be seen that in this preliminary research, and with the existing collections, trade or large scale transportation of ceramics can hardly be totally proven. So we decided to test some limited possibilities in three different cultural and regional contexts to see if application of chemical analysis in economically and politically ‘simple’ societies could give any meaningful results (Fig. 4.1).

The first point was to verify the possibility of applying analytical procedures to lower Amazonian clays because we feared that the hydrological conditions could

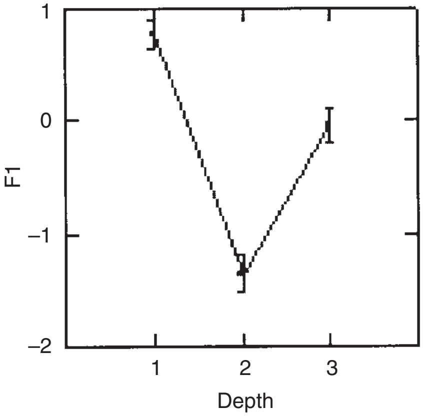

FIG. 4.1. ANOVA applied to the Amazon region ceramics. The depth scale is: 0, 30–40 cm; 1, 100–110 cm; 2, 140 cm; 3, 180–190 cm.

make the clay beds homogeneous. Analyses were made with sherds from three regions: Porto Trombetas, Marajo Island and Amapá (at the mouth of the Amazon), with the collaboration of the Museu Emilio Goeldi.

The second point was to see if contemporary tribes of the same region used the same raw material and exchanged pottery or pottery makers (probably women). The tribes studied are from different archaeological cultures but lived in a small area and might have been in contact. This study was made in the Peruaçu region (north of Minas Gerais State, in the valley of the river São Francisco), using the collection of the Museu de História Natural of Belo Horizonte.

The third point was to verify if there were differences among the households of one village. Did the members of different clans use distinct raw material sources? Were different clays used to make potteries for distinct uses? These questions were studied at the Guara site, with sherd samples of the Universidade Federal de Goiás.

4.2. DESCRIPTION OF THE SITES AND PROBLEMS

We have supposed that an interregional trade in ceramics was possible between Amazon chiefdoms. In central Brazil, we will probably be able to find evidence only of restricted intertribal exchanges, or of intratribal differentiation among ceramic vessels.

4.2.1. Amazonian sites

In the state of Pará we studied a sample of ceramics from open air sites in an archaeologically poorly known region near Porto Trombetas (Fig. 4.2). There are large occupation sites along the banks of the many lakes and rivers that flow to the Amazon. The cultural remains are found in deep dark soils of archaeological origin. Though they have been known since the beginning of the twentierth century, no systematic research was done until the late 1990s, when the University of São Paulo started a large archaeological project.

On Marajó Island at the mouth of the Amazon, most sites are earth mounds in low swampy areas (Fig. 4.3). In the 1950s, Meggers and Evans defined several archaeological phases, from the early ceramic period to the late prehistoric period. We chose samples of Anatuba ceramics (dating from about 900 B.C.) from the Marajoara culture (after the fifth century A.D.) and from the Formiga phase (intermediate period). We wanted to know if the same raw material was present throughout the centuries for more than a millennium, considering that many sites contain components from several cultures.

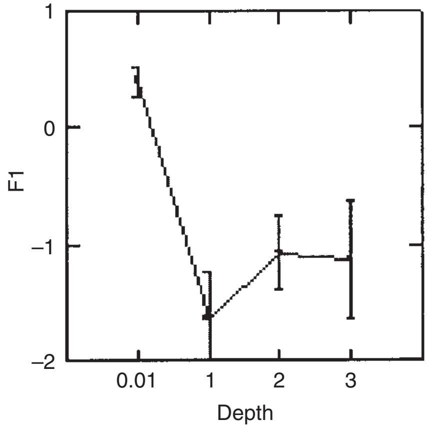

FIG. 4.2. Porto Trombetas ceramics: ANOVA applied to sampling at three levels of depth.

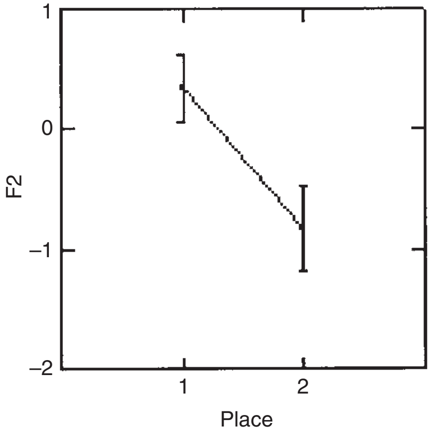

FIG. 4.3. ANOVA applied to different sites of Amapa samples. On the 'place' scale, 1 refers to habitation sites and 2 to cemeteries.

In the state of Amapa three main archaeological ceramic sites are known: Aristé in the north, and Mazagão and Maracá in the south. Mazagão pots come from habitation sites and the Maracá ones from cemeteries in the same region. Evans suggested two possibilities: (a) both types of vessel would have been produced by the same people for distinct purposes, (b) they originate from different tribes. To know whether they were made with the same clay or not would help to solve this problem and we could use the rich material recently excavated by the archaeologists of the

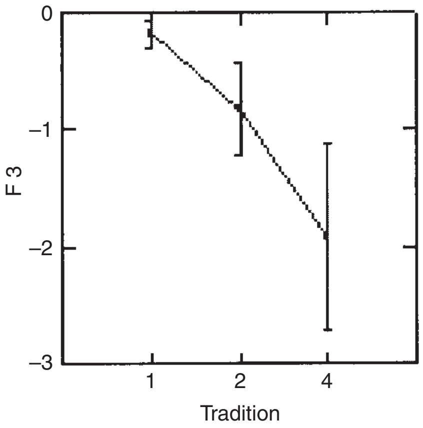

FIG. 4.4. ANOVA applied to different traditions from Peruaçu. On the 'tradition' scale, 1 refers to Una, 2 to Tupiguarani and 4 to Sapucai.

Museu Goeldi. So, we have compared domestic vessels from habitation open air sites identified as belonging to the Mazagao phase by Evans and the funerary ceramics from caves identified as belonging to the Maracá culture (Fig. 4.4).

In each region, a sample of a few sherds was sufficient to test the variability of Amazonian clay, but we also wanted to see if there were some local differences that should be used to compare close or successive occupations; so our samples included sherds from at least two sites from two different archaeological phases. Rings were not necessary, as the decorated sherds were typical of each archaeological culture and we were not comparing shapes.

4.2.2. Peruaçu sites

We also studied a sample of ceramics from a small region in the north of the State of Minas Gerais (about 15ºS and 44ºW). There, Prous and his team found more than 100 sites within 40 km from each other. The ceramic occupations are dated between 800 and 1400 A.D. One of the ceramic period sites is on the banks of the river São Francisco (Russinho) and the others are along the nearby valley of the river Peruaçu. We also studied samples of clay from several sites along the Peruaçu and São Francisco.

This region has three kinds of ceramic that are at least partly contemporary. The first belongs to the Una tradition and is found mainly in the shelter of the Peruaçu canyon, in the middle of the valley. Here, small globular pots or open bowls with charcoal or/and limestone temper that hold less than 1–2 L are found.

The second, Tupiguarani tradition, whose sites are found on the terraces in the upper part of the valley of the Peruaçu, has left small bowls and larger vessels such as small funerary urns for infants and open basins for storage of cassava flour (up to 7 L). Some urns are decorated with plastic motives and the basins were painted. They used crushed sherds and/or sand as temper (Fig. 4.5).

On the large low plain around the São Francisco we found sites belonging to a third (Sapucai) tradition. The vessels include mainly medium sized pots, of 5 or 7 L, and large globular and pear shaped pots used to store liquids and as burial urns.

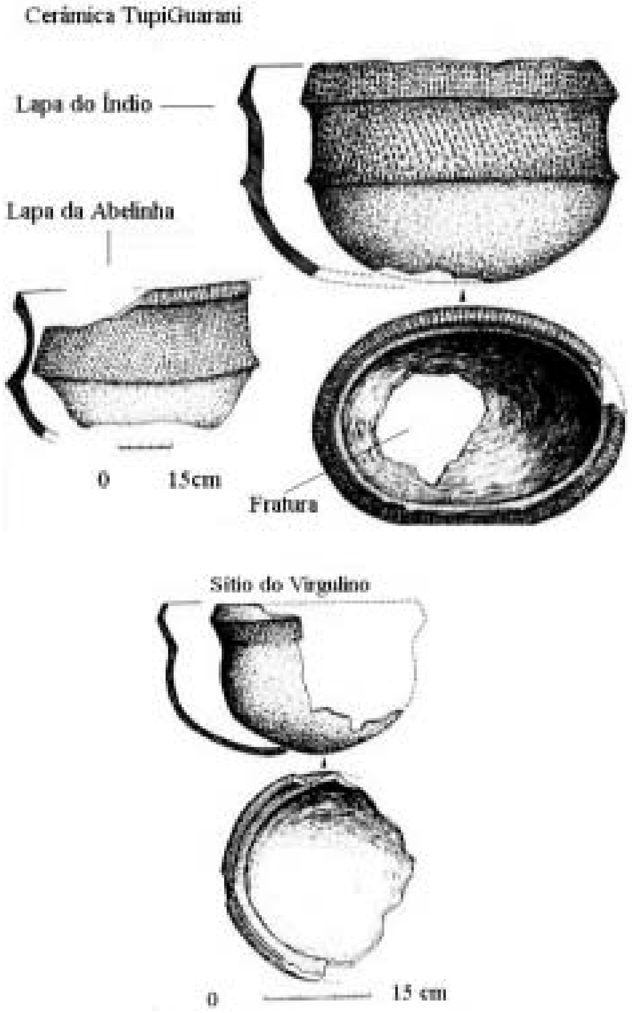

FIG. 4.5. An example of a ceramic from the Tupiguarani tradition.

At two open air sites of the canyon a few sherds of unknown attribution have also been found; some from the Terra Brava site have been analysed.

Our aim was to find the relationship between the three main regional traditions.

In some shelters, a few Tupiguarani decorated vessels are found among the dominant Una sherds. Were they produced by Tupiguarani women who lived among the Una tribe? In this case, the Una and Tupiguarani pastes should be the same. Or were the decorated vessels ‘imported’? In this case the pastes might show some differences, if the origin of the clays was distinct.

Some sherds from the Russinho site (Sapucai tradition) show some influence of the two other traditions, such as charcoal temper (like Uma) or sherd temper (like Tupiguarani). Were these sherds imported or were they made at the Sapucai site?

Our sample included dominant wares of each of the three main traditions and ‘unusual’ wares (e.g. isolated ceramics of one tradition found at a site where another culture was dominant). We therefore sampled two sectors of the Peruaçu valley (upstream and downstream) and a site in the São Francisco valley. At one site, Lapa do Boquete, we sampled sherds from the outer and inner parts of the shelter. As we had few rim sherds, we used other parts of the vessels, avoiding pieces found in the same part of the excavation, to reduce the chances of testing pieces of the same pot.

4.2.3. The Guará site

The Guará site is in the state of Goiás (50º1′37″W and 15º35′58″S) (Fig. 4.6). There, Wüst and Carvalho excavated the remains of two ring shaped villages on the same hillside. One belongs to the Uru tradition (site GO-NI-100, probably more recent than 1200 A.D.) and the other one to the Aratu tradition (site GO-NI-101, probably a little earlier). Ring shaped villages are formed by several collective large huts (each one for a extended family and/or a clan group) around a circular ceremonial place.

There were three main goals:

(1) To see if both traditions used the same clay;
(2) To know if there were differences between the households of the Uru site, suggesting differential access to the clay deposits;
(3) To verify if the different kinds of pot (eating/drinking vessels, cassava grids, containers and fire pots) were made with different clays.

Wüst showed that the plates used to process cassava flour were more numerous in one part of the ring — putatively near the house of a chief. Tribal chiefs had to supply a large amount of vegetal food for collective rituals and had several wives for this purpose. It was important to know if the main part of the cassava processing used vessels from the same source.

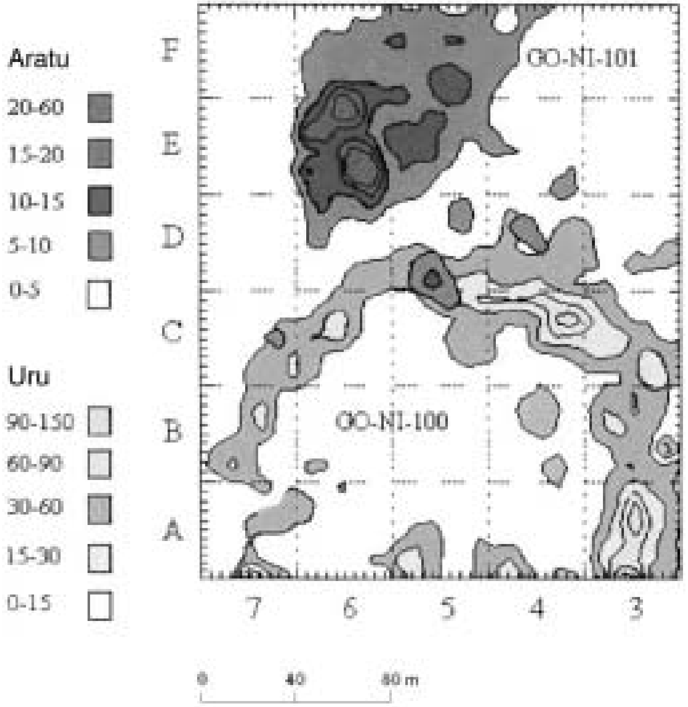

FIG. 4.6. Scheme of the Guará region. Ceramic density at the Guará site (number of fragments per small square (4 × 4 m)).

Having many available edges for each shape manufactured with several clay types, we selected seven shapes out of the 16 restored ones: shapes 1, 3, 4, 8, 10, 16 (Uru tradition) (Fig. 4.7) and 20 (Aratu tradition). Functional analysis suggests that vessels of shape 1, small pots, were for cooking activities, small open bowls (shape 3) for food serving and stocking, vessels of shape 4 and 5 for toasting flour and ‘beiju’, large carinated bowls (shape 8) for food processing (including cassava scraping), while jars (shape 16) were probably used to transport and stock liquids. We also selected samples of large pear shaped urns (shape 20) from the Aratu tradition. Table 4.1 gives the number of utensils analysed, their shape and the type of clay used.

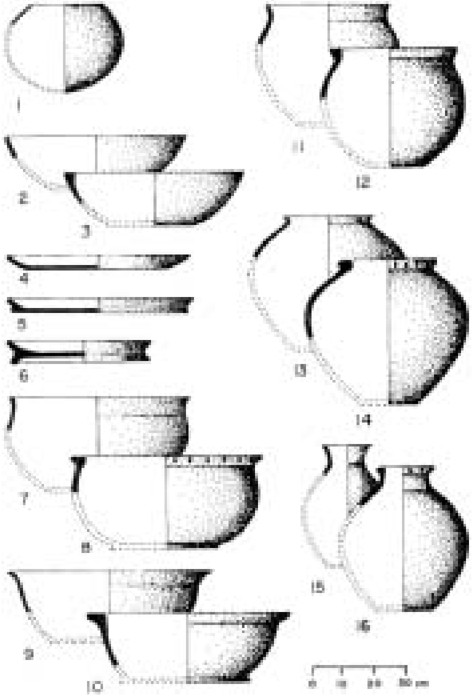

FIG. 4.7. Morphology of ceramics from the Uru tradition.

4.3. ANALYTICAL PROCEDURE

4.3.1. Sampling preparation

Before carrying out the analysis, sample data were recorded and sherds were prepared for irradiation. Each sherd was recorded according to its physical and stylistic characteristics and its archaeological sources:

(a) The lower Amazon, with site and intrasite stratigraphic localization;
(b) The Peruaçu region, with site and intrasite localization, vessel part and sampling date, temper, firing, decoration, and cultural attribution;
(c) The Guará region, with site and intrasite localization (excavation context), position in the habitation ring, hardness, temper, clay type, firing, shape, sherd thickness, presence of plastic decoration, volume of the recipient and colour, cultural attribution.

TABLE 4.1. SAMPLES BY TRADITION, RECIPIENT SHAPE AND CLAY TYPE

Recipient shape	Tradition	Clay type	Total number of edges per shape	Sample amount
Shape 1	Uru	1	34	15
Shape 3	Uru	1	103	15
Shapes 4 and 5	Uru	1	96	15
Shape 8	Uru	1	363	15
Shape 8	Uru	2	65	15
Shape 8	Uru	3	16	15
Shape 8	Uru	4	19	15
Shape 10	Uru	1	154	15
Shape 16	Uru	1	205	15
Pear shaped, inflected contour	Aratu (Mossâmedes phase)	5	40	15
Pear shaped, inflected contour	Aratu (Mossâmedes phase)	3	23	15
Total			1118	165

These data were imported into SYSTAT, a computer program, for archival and interpretative purposes.

The sherds were sampled using a motorized hand drill laid horizontally on a flat surface and secured with a vice. The following drilling technique was applied to the sherd sample:

(1) A rotary file was used to clean the section to be drilled.
(2) The powdered sample to be analysed was extracted from several perforations along the cleaned sections with a tungsten carbide drill.
(3) The powder was collected in a sheet of clean paper previously weighed and placed on a Petri dish. Three aliquots with 300 mg samples were weighed in polyethylene tubes: the first was used to determine short lived radionuclides (Al, Cu, Cl, Mn, Ti and V), the second for medium lived radionuclides (As, Au, Ga, K, La and Na) and the third for long lived radionuclides (Ce, Co, Cr, Cs, Fe, Rb, Sc, Ta and Zn). Of every eight samples one was taken in triplicate in order to check the reproducibility.

It was very difficult to sample some very small (1 cm^2) sherds. They are considered to be precious by the museum curators and were sent back to their collections.

Before preparation and analysis the clay samples were heated at 65ºC overnight. In each case the samples were collected in beds with homogeneous fine elements; some of these beds are, or were, still recently used by traditional potters. As Brazilian archaeological potteries are not very hard, marginal contamination by the drilling was expected.

4.3.2. Neutron activation analysis

The k_0 parametric neutron activation technique was applied to determine elemental concentrations. The nuclear research reactor TRIGA Mark I IPR R1 was used for the irradiation. At 100 kW, the thermal neutron flux is 6.61×10^{11} $n \cdot cm^{-2} \cdot s^{-1}$. For the determination of elements whose radionuclides have short half-lives (Al, Cu, Cl, Mn, Ti and V), the irradiation time was 5 min, 10 min for decay time and 600 s for measurements; for medium half-life radionuclides (As, Au, Ga, La, K, La and Na), 4 h for irradiation, 12 h for decay time and 3 h for measurements; and for long half-life radionuclides (Ce, Co, Cr, Cs, Fe, Rb, Sc, Ta and Zn), 20 h for irradiation, at least 10 days for decay time and 4 h for measurements.

The gamma spectroscopy was performed using one HPGe detector of the CANBERRA model GC1518, with a resolution of 1.85 keV for the 1332 keV peak of ^{60}Co and Maestro EG&G Ortec software.

Several reference materials were analysed with the samples IAEA/Soil-7, IAEA/Soil-5, GXR-1, GXR-3 and GXR-6 (United States Geological Survey). Of every eight samples one was taken in triplicate in order to check reproducibility.

4.3.3. Data analysis

All the statistical analyses were performed by means of SYSTAT 7.0 software. In the data analysis the elemental concentration data were first transformed to the natural logarithms base. Principal components were then calculated from the variance–covariance matrix of the (ln) concentration data. The data analysis was done using the ANOVA and *t* test methodologies.

4.4. RESULTS

4.4.1. Lower Amazonian ceramics

We studied 42 sherds: 11 from Porto Trombetas (about 2°S and 55°W), region 1, 13 from Marajo Island (about 1°S and 50°W), region 2, and 18 from Amapa (about 1°N and 51°W), region 3. The conclusions of the study are:

(a) The clay analysis showed clear differences between regional clusters (p = 0.0000). Therefore it will be possible to use analytical procedures to study evidence of interregional trade or gifts. Until now, typological analysis has never suggested the possibility of such ceramic exchange, but we know very little about Amazonian prehistory and new investigations may change our concepts. Figure 4.1 shows the different types of clay analysed according to its chemical composition, selected by means of the SYSTAT software as F1.

(b) The samples from Porto Trombetas came from four levels of one test pit (at depths of 30–40, 100–110, 140 and 180–190 cm) excavated at the Lago de Mura site. The composition of the sherds from the first level is completely different from that of deeper levels (p = 0.01). This shows that there is not only the possibility to separate the clays of the three regions tested (which are far from each other) but also that local modification occurs in the Porto Trombetas region. Figure 4.2 shows the different types of clay analysed according to its chemical composition, selected by means of the SYSTAT software, as F1, and depth.

(c) When studying the ceramics collected by Meggers and Evans in Marajo, we hoped to see the possibility of discriminating the clay from different sites and/or archaeological phases. The results were not conclusive, suggesting a high homogeneity of the clay and temper on the island or, at least, at both the PA-JO 26 and PA JO 28 sites, and in the three archaeological cultures that were represented (ancient Anatuba, intermediate Formiga and later Marajoara phases).

(d) Our analysis of Amapa samples shows differences both in the clay and in the temper between habitation sites and cemeteries, even between very close places such as Banal do Pocinho, Lapa do Pocinho and Gruta do Periquito. It is thus highly probable that distinct potters made Mazagão phase and Maraca style pottery (p = 0.000). Figure 4.3 shows the different types of clay analysed according to chemical composition, selected by means of the SYSTAT software as F2 and place (habitation sites and cemeteries).

The sites are earth mounds in low swampy areas (Fig. 4.3). In the 1950s, Meggers defined several archaeological phases, from the early ceramic period to the late prehistoric period. We have chosen samples of Anatuba ceramic (dating from about 900 B.C.), of Marajoara culture (after the fifth century A.D.) and of the Formiga phase (intermediate period). We wanted to know if the same raw material was present throughout the centuries for more than a millennium, considering that many sites have several cultural components.

4.4.1.1. Restrictions to the samples

Obviously, we do not know if the few sherds from each region or archaeological phase are representative. But we have reached our objective: we know that the variability of low Amazonian clay is sufficient from one region to the other to allow the use of analytical procedures in archaeology. In Amapa and in Porto Trombetas, at least, it is also possible to discriminate sherds from different phases even when they were locally produced.

4.4.2. Peruaçu region ceramics

We used 87 sherds and 6 clay samples from Peruaçu. The analytical study showed that the whole Russinho ceramic was made with a local clay (that can be collected some hundred yards from the site), suggesting that some Tupiguarani and Una or acculturated potters were living in the same Sapucai village. Una sherds from both cave and open air sites were made from the same clay.

In the Peruaçu canyon, both Tupiguarani and Una sherds from Malhador shelters have similar pastes and were made with a clay that is neither the one found at the Russinho site nor the one found in the nearest places where good clay is available in the canyon; once more, it is possible that potters from two distinct traditions worked together.

Some observations suggest that potters travelled some distance to choose their clay, because most Una sherds found in the Boquete shelter are made with clay that is not very different from the type found in Russinho, the most distant site of the region. In addition, Tupiguarani sherds from the upper part of the Peruaçu valley seem to be made with the same clay as sherds from the lower part of the river, being different from that in the canyon (middle valley) used by present day potters (p = 0.04). Figure 4.4 shows the types of clay from the different traditions, Una, Tupiguarani and Sapucaí analysed according to chemical composition, selected by means of the SYSTAT software as F3.

4.4.2.1. Restrictions to the samples

The analyses are not totally conclusive because of the small number of sherds we were allowed to use. In the Tupiguarani case, at each shelter only one or a few Tupiguarani vessels were found. It seems they do not belong to this site. The Tupiguarani occupied open air sites have not been excavated until now. Another problem is inaccurate dating; the last prehistoric occupation layers in the region suffered interference from cattle that occupied the shelters. So we could not demonstrate that the association of some Tupiguarani and Una sherds in the shelters during the late Una period was not the result of cattle stamping. Another limitation is that it was not possible to test the possible relationship between paste and use of pottery because only Tupiguarani tribes used cooking pots and, as we stated, we did not have a representative sample of their production in the region. It seems that in the Una culture, ceramic had the same uses (small containers) as *Lagenaria* cucurbit and in the dry shelters remains of *Lagenaria* are even more significant than ceramics. The Una peoples who intensively used the shelters for ceremonial purposes, and to preserve organic material (mainly food), probably left very few vessels in these places.

In conclusion, we consider that this initial project was an attempt to test statistical methods combined with nuclear analytical techniques to help in this type of research. To be assertive we would need stratigraphically intact sites with a great quantity of ceramics, a big challenge in this region.

4.4.3. Guará site (Goiás) ceramics

We studied 165 sherds from Guará, 150 from the Uru occupation and the others from the Aratu. Analytical procedures clearly showed that Uru and Aratu villages used different clay beds (p = 0.005). Figure 4.8 shows the different types of clay analysed according to chemical composition, selected by the SYSTAT software as F1.

In Uru villages, no difference was found in the sherds from different parts of the habitation ring; thus it seems that different moieties and clans shared the same clay deposits.

But we can see some differences related to vessel shape. It seems that the clay used to manufacture shapes 1, 3 and 4 (Fig. 4.7) was different from the clay used for the processing bowls (shapes 8–10) and also from the clay used to make jars. The reason may be that shapes 1 and 4 were used in fireplaces while shapes 8, 10 and 16 did not need to be resistant to thermal action. At the same time, there is a correlation between these shapes and the size of the vessels (cooking pots and grids are smaller than processing bowls and jars).

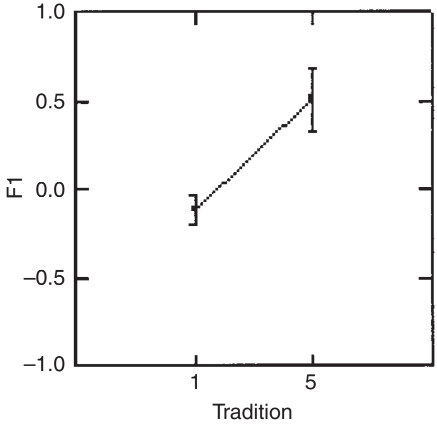

FIG. 4.8. ANOVA applied to different traditions from Guará. On the 'tradition' scale, 1 refers to Uru and 5 to Aratu.

Otherwise, we can state that potters used different types of clay for vessels used for food processing (shape 8). Classic optical analysis has previously demonstrated this. However, there is no difference between cooking pottery and other vessels. Figures 4.9 and 4.10 show the different types of clay analysed according to chemical composition, selected by means of the SYSTAT software as F2, and shape and size, respectively, related to ceramic from the Uru tradition.

4.5. CONCLUSION

The results of the analysis show that nuclear analytical techniques can be used to differentiate Lower Amazonian ceramics. This will probably be the most interesting area in Brazil to be studied by this method because more complex societies lived along the banks of the great river than elsewhere. Exchanges or population migration probably occurred during the last two millennia and pottery should be easily carried by canoe.

Study of the more ‘simple’ tribes that lived in central Brazil showed that potters might choose different clays for vessels that have distinct uses, as at the Guará site.

We did not find significant differences in the clay of vessels found in several households of an Uru village but we note that clan possession of clay beds is ethnographically documented in some places and should be established with the use of nuclear methods.

Definitive results were not achieved in this attempt to see if there was any exchange of vessels or of potters in the Peruaçu valley, mainly because the available amount of our sample was insufficient. We worked in a restricted area and it should

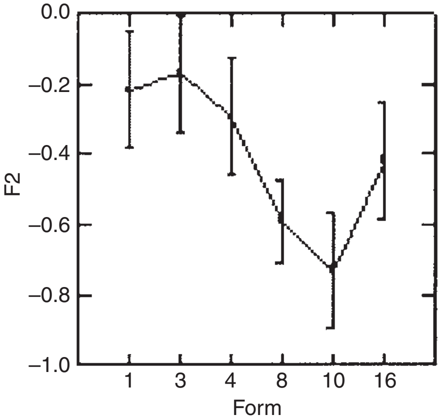

FIG. 4.9. ANOVA applied to different shape (see Fig. 4.7).

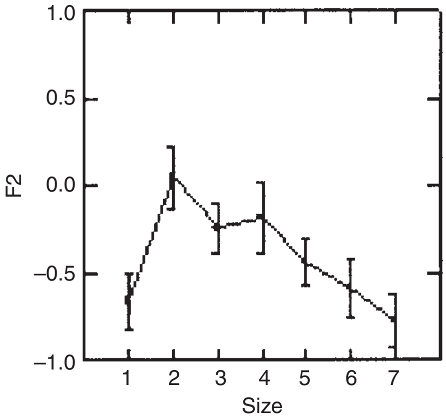

FIG. 4.10. ANOVA applied to different sizes. The pottery size scale (in litres) is: 1, 0–1; 2, 1–2; 3, 2–5; 4, 5–10; 5, 10–20; 6, 20; 7, up to 50.

be more interesting to use ceramic analysis in this region on a large scale to find boundaries between tribal territories. This study will be completed in the future.

After this first experience, the Universidade Federal de Minas Gerais (Federal University of Minas Gerais) and the Centro de Desenvolvimento da Tecnologia Nuclear (Nuclear Technology Development Center) of Belo Horizonte are undertaking a project to study the ceramics at Tupiguarani sites scattered along the river Rio Doce in the state of Minas Gerais. The objective of this project is to study the migration of tribes along the river (the Tupiguarani are believed to have been highly mobile) and the relationship between the sites found along the banks of the river and in the interfluves. We will also study the relationship within the same large village households and the possibility that different clays were used in pottery for different uses: ritual, cooking or storing purposes.

BIBLIOGRAPHY

BISHOP, R.L., NEFF, H., Compositional Data Analysis in Archaeology, Advances in Chemistry Series, American Chemical Society, Denver, CO (1987) 5–10.

JOBIM, P., “Os vestígios cerâmicos do vale do rio Peruaçu”, Coord. Relatório Parcial do Projeto de Estudo Arqueológico do Alto Médio São Francisco (PROUS, A., Ed.), FINEP7UFMG, pp. 39–53.

MEGGERS, B., EVANS, C., Archaeological Investigations at the Mouth of the Amazon, Bull. 167, Smithsonian Institution, Bureau of American Ethnology, Washington, DC (1957) 664 pp.

NEVES, E., GOES, O velho e o novo na arqueologia amazônica, Rev. USP **44** 1 (2000) 86–111.

PROUS, A., Fouilles de l'abri du Boquete, Minas Gerais, Brésil, J. Soc. des Américanistes, Paris, NS **77** (1991) 77–109.

PROUS, A., Arqueologia Brasileira, Universidade do Brasil, Brazil (1991) 604 pp.

PROUS, A., BRITO, M.E., LIMA, M., As ocupações ceramistas do vale do rio Peruaçu, Rev. Museu de Arqueologia e Etnologia, São Paulo, USP **4** (1994) 71–94.

SABINO, C., PROUS, A., WÜST, I., AMARAL, A., Utilização da técnica paramétrica k_0 no estudo da composição de cerâmicas arqueológicas brasileiras, paper presented at 1st Int. Symp. on Nuclear and Related Techniques in Agriculture, Industry, Health and Enviornment, Havana, 1997.

WÜST, I., CARVALHO, H.B., Novas perspectivas para o estudo dos ceramistas pré-coloniais do centro oeste brasileiro: A análise espacial do sítio Guará 1 (GO-NI-100), Goiás, Rev. Museu Arqueologia e Etnologia, São Paulo, USP **6** (1996) 47–82.

Chapter 5

CHEMICAL CHARACTERIZATION OF BRAZILIAN PREHISTORIC CERAMICS BY INAA

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Abstract

One hundred and forty-nine ceramic fragment samples from three archaeological sites were analysed using instrumental neutron activation analysis (INAA) to determine the concentration of 24 chemical elements: As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn. A multivariate statistical method, discriminant analysis, was performed on the data set. Discriminant analysis identified three compositional groupings and derived two discriminant functions that account for 100% of the variance between groups. The results show, at a confidence level of 98%, that the ceramics from each separate site are statistically similar so that it can be concluded that a common source of raw material was used independently at each of these sites.

5.1. INTRODUCTION

Over the last three decades, ceramic analyses have become central in deriving archaeological information and in helping to understand the way of life of different civilizations on the basis of the abundance and variety of the ceramics. The delineation of past systems of production and exchange lies at the core of this research [5.1].

The characterization involves numerous studies of sample typologies, i.e. from the study of shape, colour, presence of drawings, texture of material and decoration [5.2] to determination of the chemical composition. Typology has been very useful when applied to whole or reconstructed objects. However, it has proved to be less helpful for materials in fragmented condition as, although ceramic fragments constitute a large part of the materials recovered from excavations, these fragments happen to be very similar even under microscopic examination. The raw material constituents from ceramics are complex and include a variety of items: sand and granule sized igneous minerals, calcareous grains, sedimentary rocks, sourced sand and granule mineral grains such as quartz, mica, magnetite and chalcedony [5.3]. The concentration levels of a number of major elements, such as Al, Fe and Si, are usually similar for different samples of sand or clay. The clay, sand and other natural materials from which the ceramics were fashioned can have a chemical composition which is unique and which may serve as a diagnostic of the local source from which the ceramics were taken [5.4–5.9]. For this reason, it is necessary to consider the chemical composition and concentration levels of trace elements in the materials from which the pottery was manufactured [5.5–5.9].

Different techniques can be applied to determine the sample composition, including atomic absorption spectrometry (AAS) [5.4], ICP [4.5], proton induced X ray emission (PIXE) [4.6] and instrumental neutron activation analysis (INAA) [5.2, 5.7, 5.10, 5.11]. Among the various analytical techniques, INAA employing gamma ray spectrometry seems to be the most suitable because it does not require mineralization of samples and allows the determination of numerous elements simultaneously with high sensitivity, accuracy and precision. Sample preparation is relatively easy and fast [5.12].

The aim of this study was to characterize by means of inorganic elements Brazilian prehistoric ceramics from three archaeological sites as potential indicators of Indian culture. The data obtained helped archaeological studies already made in this region with the objective of making spatial, temporal and cultural reconstructions of this period. Samples from Água Limpa, Prado and Rezende were studied.

5.2. ARCHAEOLOGICAL BACKGROUND

The wide surface excavation technique was adapted to the tropical conditions of the Brazilian soil [5.13, 5.14]. The ceramics found in these sites were associated with food preparation, funeral urns and decorative uses. The three sites are superficially located in the intermediary part of a hill with a water course in its interior part [5.15]. The locations are indicated in Fig. 5.1.

The Água Limpa site is located at the confluence of three small farms, in the city of Monte Alto in the north of São Paulo state (21°15′40″S, 48°29′47″W). The site has been divided into two excavation zones. In zone 1, all that remains of the village is two dark spots. An area of primary burials of extended and semi-flexed youths and adults was detected. Ten other burials were exhumed, besides the exhumation of a secondary burial of an adult inside a globular urn with a lid [5.16]. There was one hearth on the spot, dated 476 A.D. All other hearths were external. In the internal and

FIG. 5.1. Map showing the location of the excavation sites.

external hearths there were ceramic vessels related to flakes, scrapers, mammalian, reptile and fish bones and shells, with indications of the preparation and consumption of food obtained through hunting, collecting and, on a smaller scale, fishing [5.17].

In zone 2, eight darks spots and several hearths, most of them inside houses, form the remains of the village. Only a secondary grave of a child was found and exhumed.

The ceramics are of two types: plain and painted. The paintings are in red and white, and without rearranging the painted fragments and the few whole painted sherds that were collected they have no forms. The selection of grains is good, with a predominance of thin and medium grains.

The Prado site is located at Engenho Velho farm, in the city of Perdizes, in the state of Minas Gerais (19°14′25″S, 47°16′00″W). It is formed of seven dark spots (housing structures), three hearths (one internal and two external to the spot), two concentrations of lithic remains and one primary burial inside a pyriform urn covered with a lid. Three stratigraphic profiles were excavated and indicate a single stratum: the litho-ceramic.

The archaeological vestiges collected are represented by two kinds: ceramic and lithic (polished and unpolished).

The few whole ceramic vessels collected and those partially reconstructed in the field or the laboratory are smooth, without plastic decoration or painting, with a predominance of medium to large granularity, and with a poor selection of grains. They were produced for utilitarian and funerary objectives, according to the archaeological evidence [5.18–5.21]. Their most expressive forms are globular vases and pots, spherical bowls and pyriform urns.

The Rezende site is located at the Paiolão farm at Piedade in the Paranaíba valley, 7 km from the city of Centralina in the state of Minas Gerais. Archaeological studies have found evidence of two occupations: the more recent one was ceramic production and was dated 810 ± 60 years A.D. The remains begin at the surface and go down to 35–40 cm in depth. The archaeological studies have demonstrated that the population lived in oval huts forming villages and made use of fire for light, heat and cooking. They also had an incipient agriculture–horticulture. The ceramics produced were plain, utilitarian and funerary. The oldest one is a pre-ceramic (or pure lithic) that is at a depth of 90–130 cm and was dated as 7300 ± 80 years B.P. (before present). They represent the first and oldest inhabitants of the Minas Gerais area, called ‘the Mineiro triangle’. This population consisted of hunter–collector nomads that made their living by fishing, hunting and collecting [5.15, 5.16].

5.3. MULTIVARIATE STATISTICAL ANALYSES

In order to elucidate the major variations in the set of compositional data obtained using INAA, it is necessary to employ multivariate statistics that use correlations between element concentrations as well as absolute concentrations to characterize sources of the samples. The basis for all multivariate analyses is that all the elements included are independent variables. This is not necessarily true, but it can be tested using the pooled within-groups correlation matrix provided by discriminant analysis.

Discriminant function analysis is a multivariate technique and is based on the assumption that the pooled variance–covariance matrix is an accurate representation of the total variance and covariance of the data set [5.22]. Bivariate plots of discriminant functions are useful for visually displaying group separation.

The statistical studies were made using three programs: SPSS, Statistical Package for Social Sciences version 8, Statistica version 5 and Excel version 97.

5.4. EXPERIMENTAL TECHNIQUE

Powder samples were obtained by cleaning the 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 the thickness, three or five 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 h 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 reference samples in all analyses. These materials were dried in an oven at 105°C for 24 h and stored in a desiccator until weighed. Analytical details and the precision attained have been published elsewhere [5.23–5.25].

5.5. RESULTS AND DISCUSSION

One of the basic premises underlying the use of analytical chemistry for ceramic analysis is that clay sources can be differentiated if a highly precise analytical technique is used. If an element is not measured with good precision real differences in concentration can be obscured and the discriminating effect of other well measured elements tends to be reduced. These differences can be used to form ceramic compositional groups because vessels manufactured from a given clay source will be more similar to each other than to other types of vessels which were manufactured from a different source. In this work all the elements with a relative standard deviation (RSD) of less than 10% were considered [5.24]. Although Co and Ta have RSDs around 3%, they were not included in the data set as their concentrations could have been affected by the tungsten carbide files [5.26]. The precision to which Cs, K and Rb concentrations were measured was better than 10%; however, they were not included because of missing values. The determination of Zn is not reliable due to the strong gamma ray interference from ^{46}Sc and ^{182}Ta. The interference of ^{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 extraordinarily low [5.11].

On the basis of these screening criteria, 13 elements — As, Ce, Cr, Eu, Fe, Hf, La, Na, Nd, Sc, Sm, Th and U — were used in subsequent data analyses. None of the elements considered contained missing values. The entire data set consisted of all 149 samples (Água Limpa, 82; Prado, 34; Rezende, 33). Eight samples were eliminated by evident outliers. Range, mean and standard deviation are presented in Table 5.1. Since INAA measures both bulk and trace elements, elemental concentrations were converted to log base 10 values to compensate for the large difference of magnitudes between major and trace elements [5.27, 5.28].

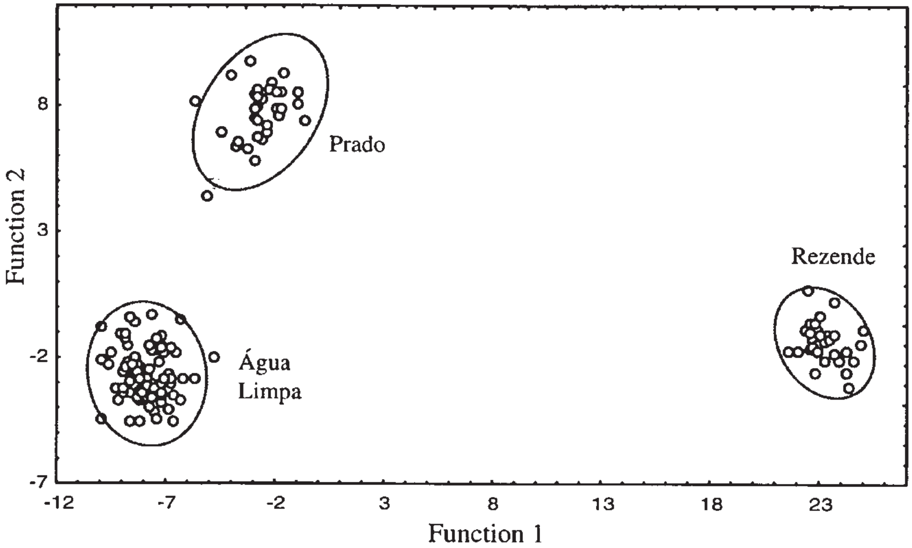

FIG. 5.2. Canonical discriminant functions for all the samples studied. The ellipses represent 98% confidence levels for sample inclusion in the clusters.

In order to examine questions of exchange and sociopolitical interaction among the prehistoric cultures of these three sites, the similarities among samples were studied by means of discriminant analysis. Since differences in chemical composition are typically interpreted as evidence for distinct production locations, our main purpose was to identify and distinguish the similarities among the samples analysed with the aim of defining one or more compositional groups, which presumably would represent one or more production sites. Such information helps the range of compositional variation that might be expected from a single production context. A bivariate plot obtained by canonical discriminant functions is presented in Fig. 5.2.

As can be seen the samples from each site form a very tight chemically homogeneous group, showing a high degree of chemical similarity among themselves. The results show that clay from ceramic fragments, which was collected and analysed from three sites, originated from three distinct raw materials. From the samples studied at least three centres of production may be identified in the area. Whether these sources are local or not will only become clear by means of a systematic local clay analysis. The idea of autonomous development without contact with neighbours could be supported.

On the other hand, when the data from each site are interpreted separately, two samples from Prado and Rezende and three samples from Água Limpa proved to be different from the group. However, when the data sets are studied together, they become similar to the other samples of each site. This means that the difference that occurs is not important. In other words, this proves the hypothesis that the raw material of the ceramics studied came from the same source, all suggesting that at these sites a single type of clay material was used in the manufacture of the vessels that have been analysed in this study. This does not necessarily mean that a single clay source was used, since there is the possibility that similar raw materials were available from different locations.

5.6. CONCLUSION

Inspection of the chemical data from ceramic fragments by the discriminant analysis method has demonstrated clearly that all the samples found in each of the archaeological sites were manufactured from a site specific raw material.

Statistically all the ceramics at each individual site have the same elemental chemical composition, even though a visual inspection of the data does not show any significant difference in their compositions. In addition, the samples showed no visible temper or gritty texture differences from their manufacture.

This suggests that a single type of raw material was used in the manufacturing of all of the ceramics analysed from each site or that the composition of the original raw material could have been altered during the overall ceramic manufacturing process by washing or adding temper or colouring agents. There is support for the idea of an autonomous development without contact with neighbours.

Finally, INAA studies have provided important contributions to the study of ceramic production and distribution in the prehistoric era. This information confirms previous hypotheses. The use of NAA has allowed ceramic analysis to reach a higher level of resolution, and allowed us to sharpen our understanding of the past.

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REFERENCES

[5.1] CARPENTER, A.J., FEINMAN, G.M., The effects of behaviour on ceramic composition: implications for the definition of production locations, J. Archaeol. Soc. **26** (1999) 783–796.

[5.2] PUNYADEERA, C., PILLAY, E., JACOBSON, L., WHITELAW, G., The use of correspondence analysis to compare major and trace elements for provenance studies of iron-age pottery from Mngeni river area, South Africa, J. Trace Microprobe Tech. **17** (1999) 63–79.

[5.3] REDMOUNT, C., MORGENSTEIN, M.E., Major and trace element analysis of modern Egyptian pottery, J. Archaeol. Sci. **23** (1996) 741–762.

[5.4] PEISSACH, M., PINEDA, C.A., JACOBSON, L., LOUBSER, J.H.N., Analytical study of pottery from Soutpansberg, J. Radioanal. Nucl. Chem. **151** (1991) 229–237.

[5.5] KILIKOGLOU, V., BASSIAKOS, Y., DOONAN, R.C., STRATIS, J., NAA and ICP analysis of obsidian from Central Europe and the Aegean: source characterization and provenance determination, J. Radioanal. Nucl. Chem. **216** (1997) 87–93.

[5.6] KUISMA-KURSULA, P., RAISANEN, J., Scanning electron microscopy-energy dispersive spectrometry and proton induced X ray emission analyses of medieval glass from Kproinen (Finland), Archaeometry **41** (1999) 71–79.

[5.7] HUGHES, M.J., MATTHEUS, K.J., PORTAL, J., Provenance studies of Korean celadons of the Koryo period by NAA, Archaeometry **41** (1999) 287–310.

[5.8] MOMMSEN, H., KRAEUSER, A., WEBER, J., A method for grouping pottery by chemical composition, Archaeometry **30** (1988) 47–57.

[5.9] BURTON, J.H., SIMON, A.W., Acid extraction as a simple inexpensive method for compositional characterization of archaeological ceramics, Am. Antiq. **58** (1993) 45–59.

[5.10] ROTUNNO, T., SABBATINI, L., CORRENTE, M., A provenance study of pottery from archaeological sites near Canosa, Puglia (Italy), Archaeometry **39** (1997) 343–354.

[5.11] GLASCOCK, M.D., “Characterization of ceramics at MURR by NAA and multivariate statistics”, Chemical Characterization of Ceramic Pastes in Archaeology, Monographs in World Archaeology (NEFF, H., Ed.), Prehistory Press, Madison, WI (1992) 11–26.

[5.12] BISHOP, R.L., CANOUTS, V., CROWN, P.L., DE ATLEY, S.P., Sensitivity, precision, and accuracy: their roles in ceramic compositional databases, Am. Antiq. **55** (1990) 537–546.

[5.13] LEROI-GOURHAN, A., Fuilles de pincevent. Essai d’analyse ethnographique d’un habitat magdalénien (La section 36), Vocabulaire, Annexe IV, Centre National de la Recherche Scientifique, Paris (1972) 321–327.

[5.14] PALLESTRINI, L., Interpretação das estruturas arqueológicas em sítios do Estado de São Paulo, Série Arqueológica No. 1, Universidade de São Paulo (1975).

[5.15] ALVES, M.A., As estruturas arqueológicas do Alto Paranaíba e Triângulo Mineiro — Minas Gerais, Rev. Museu de Arqueologia e Etnologia, São Paulo, USP **2** (1992) 27–47.

[5.16] ALVES, M.A., Metodologia e técnicas de campo e a evidenciação de áreas culturais, Coleção Arqueologia, Porto Alegre, EDIPUCRS **1** 1 (1995/1996) 255–270.

[5.17] ALVES, M.A., CALLEFFO, M.E.V., Sítio de Água Limpa, Monte Alto, São Paulo — estruturas de combustão, restos alimentares e padrões de subsistência, Rev. Museu de Arqueologia e Etnologia, São Paulo, USP **6** (1996) 123–140.

[5.18] ALVES, M.A., Estudo do sítio Prado: um sítio lito-cerâmico colinar, Rev. Museu Paulista, São Paulo, USP, Nova Série **19** (1983/1984) 169–199.

[5.19] ALVES, M.A., Culturas ceramistas de São Paulo e Minas Gerais: estudo tecnotipológico, Rev. Museu de Arqueologia e Etnologia, São Paulo, USP **1** (1991) 71–96.

[5.20] ALVES, M.A., Estudo técnico em cerâmica pré-histórica do Brasil, Rev. Museu de Arqueologia e Etnologia, São Paulo, USP **4** (1994) 39–70.

[5.21] ALVES, M.A., O emprego de microscopia petrográfica, difratometria de raios X e microscopia eletrônica no estudo da cerâmica pré-colonial do Brasil, Anais da VII Reunião Científica da Sociedade de Arqueologia Brasileira, Rev. Arqueologia **8** 2 (1994/1995) 133–140.

[5.22] GLASCOCK, M.D., BRASWELL, G.E., COBEAN, R.H., “A systematic approach to obsidian source characterization”, Archaeological Obsidian Studies, Method and Theory (SHACKLEY, M.S., Ed.), Plenum Press, New York and London (1998) 29 pp.

[5.23] MUNITA, C.S., PAIVA, R.P., ALVES, M.A., MOMOSE, E.F., SAIKI, M., Chemical characterization by INAA of Brazilian ceramics and cultural implications, J. Radioanal. Nucl. Chem. **244** 3 (2000) 575–578.

[5.24] MUNITA, C.S., PAIVA, R.P., ALVES, M.A., OLIVEIRA, P.M.S., MOMOSE, E.F., Contribution of neutron activation analysis to archaeological studies, J. Trace Microprobe Tech. **18** 3 (2000) 381–387.

[5.25] MUNITA, C.S., et al., Intercomparison among three activation analysis laboratories in South America, J. Trace Microprobe Tech. **19** 2 (2001) 189–197.

[5.26] ATTAS, M., FOSSEY, J.M., YAFFE, L., Corrections for drill-bit contamination in sampling ancient pottery for neutron activation analysis, Archaeometry **26** 1 (1984) 104–107.

[5.27] HARBOTTLE, G., “Activation analysis in archaeology”, Radiochemistry: A Specialist Periodical Report, Vol. 3 (NEWTON, G.W.A., Ed.), The Chemical Society, London (1976) 33–72.

[5.28] POLLARD, A.M., “Data analysis, in Greek and Cypriot pottery, a review of scientific studies”, Fitch Laboratory Occasional Papers 1 (JONES, R.E., Ed.), British School of Archaeology, Athens (1986) 56–83.

Chapter 6

REGIONAL CERAMIC PRODUCTION AND DISTRIBUTION SYSTEMS DURING THE LATE INTERMEDIATE CERAMIC PERIOD IN CENTRAL CHILE BASED ON NAA[*]

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Abstract

This research focused on the pre-Hispanic ceramic production and distribution systems of the Maipo region in central Chile by means of determining the concentration of the chemical elements in pottery of the Aconcagua culture (900–1450 A.D.) with instrumental neutron activation analysis (INAA). Pottery fragments from eight archaeological sites and natural clays from the study region were included. The differences in chemical composition between subsets of the sample (sites, paste group and ceramic type) were interpreted as indicators of resource and ceramic production locations as well as the imprint of the geological background. These results contributed to the understanding of the Aconcagua ceramic assemblage and helped to test some hypotheses about the Aconcagua social organization.

6.1. ARCHAEOLOGICAL BACKGROUND

From the late intermediate period (900–1450 A.D.) the Aconcagua culture provides the best known archaeological component in central Chile. Its geographical distribution stretches from the Aconcagua basin in the north (32°30′) to the Cachapoal basin in the south (34°10′) and from the Pacific coast (71°45′W) to the Andes mountains (70°E) (±150 km × 200 km) (Fig. 6.1). From a developmental point of view, this period represents a dramatic change in all aspects of culture: subsistence patterns, ceramics, funerary practices, lithic technology and morphology, personal adorment, etc., all of which have supported the interpretation of radical changes in the

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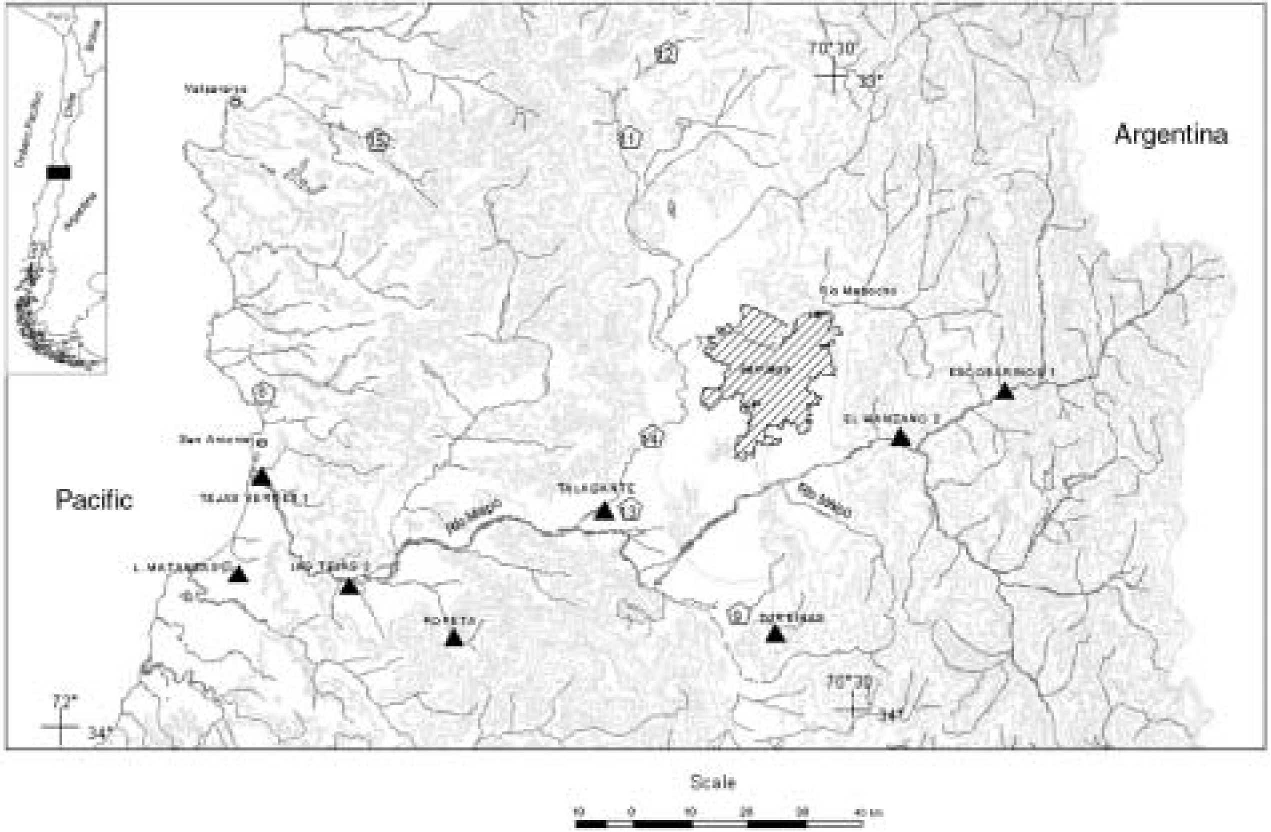

FIG. 6.1. Archaeological sites and clay sample locations in the Maipo valley. The triangles indicate archaeological sites and the pentagons indicate clay samples.

social, economic, ideological and political spheres. This sociopolitical scenario has been described as a system of chieftainships or chiefdoms, with a certain degree of centralization [6.1, 6.2].

The Aconcagua culture was an agricultural society. Horticulture and guanaco hunting were the main subsistence activities inland, as were collecting and fishing at coastal sites. There were probably minor mining activities in the Andean and coastal mountains. It has been argued that the Aconcagua people had permanent settlements only in the valleys (central and intermontane) while coastal and Andean sites were semi-permanent or occasional for task specific occupations. Also concentrated in the valleys were ritual activities such as mortuary practices in local cemeteries (small earthen burial mounds). There were minor social units linking kin groups living in communities dispersed in a recognized territory (socio-territorial units). At another level of integration, these units composed a regional system (in the Maipo basin, for example). The existence has been suggested of economic and craft specialization that would have promoted intra- and inter-regional interactions [6.1].

Contrary to these views we argue that there is very scant archaeological information to support these hypotheses, and that most are quite ‘intuitive’. A lot of fieldwork and analyses are still needed to verify the assumptions. This project is intended to open a new line of evidence (instrumental neutron activation analysis (INAA)) which, based on elemental composition analysis and other analytical procedures, will provide more solid arguments to infer where pottery was manufactured, helping to understand some aspects of Aconcagua economic, social and territorial organization.

6.1.1. Aconcagua ceramics

The definition of the Aconcagua culture relies to a large extent on the widespread distribution of a standardized set of wares or pottery types: Aconcagua Salmón, Aconcagua Rojo Engobado, Aconcagua Pardo Alisado and Aconcagua Tricromo Engobado (this last type being a late development probably stemming from Inca acculturation and found almost exclusively in the Aconcagua river area) [6.3]. The other types (pre-Inca and contemporary) are regularly associated with the same sites, middens and offerings. What is most distinctive of Aconcagua ceramics is the use of specific clays for specific wares and very standardized decorative and morphological styles [6.4]. There are two wares from the total Aconcagua assemblages that are most likely to have been distributed from special manufacturing centres, thus moving within the region: Aconcagua Salmón and Aconcagua Rojo Engobado. Both are likely to convey social information and carry icons of special significance. These have been selected for INAA. Although the distribution of natural resources and the variety of paste groups suggest that pottery could have been made by unspecialized potters at widely dispersed locations, the difference in variability between coastal and interior valley sites suggests the possibility that pottery was transported or exchanged within the region. Our hypothesis in fact is that at least some kinds of pottery were transported.

In terms of the organization of ceramic production, there is no evidence of state or special elite organized production. We think the technology used was simple, perhaps even without permanent facilities such as kilns. In central Chile all the natural resources necessary for making pottery, good clays, temper, water and fuel, are widely available and located near to most of the sites. It is likely that pottery could have been made throughout the year because of suitable weather conditions. The organization of pottery production (following Costin's criteria) should have been somewhere between:

(a) Unspecialized household production — Each household produces those items necessary for its own use.
(b) Dispersed individual specialization — A few individuals or households produce for their community.
(c) Community specialization — A few individuals in a few communities produce pottery for regional distribution.

6.2. RESEARCH PROBLEMS AND QUESTIONS

Our basic goal was to determine compositional groupings through INAA that would aid us to source pottery and trace its distribution in the Maipo basin, so as to contribute new evidence to the discussion of ceramic production and regional interaction in the Aconcagua society in central Chile. The main objective was to distinguish local from non-local production and to test the hypothesis of a centralized system of production for the Aconcagua Salmón ware.

Our working assumptions were (1) that the chemical composition of pottery is likely to reveal its geographic source since, following the 'provenience postulate' [6.5], variation within one source should be less than variation between sources, and (2) that the location of those sources could be inferred on the basis of the 'abundance criteria' [6.6], or the geological and natural clay characteristics.

Our specific research questions were:

(a) Is there a site specific subregional and/or regional patterning in the compositional data?
(b) Does the light clay matrix, so peculiar to Aconcagua Salmón, and the reddish clay of Rojo Engobado ware come from a limited number of or multiple clay sources and/or localities?
(c) Where are the clay sources most probably located?

(d) Do all settlements or production centres manufacture the whole range of wares or is there a specialized ware specific production?

(e) Were coastal and/or Andean site vessels locally produced or were they transported from other production centres (subregions)?

6.3. RESEARCH REGION, MATERIALS AND METHODS

Our study area was the Maipo basin (approximately 60 km north to south and 150 km east to west). From a geological point of view, the major differentiation is between Andean volcanic formations (to the east) and the coastal mountain granite formations (to the west) (Fig. 6.2). These two zones are separated by a Quaternary sedimentary basin (central valley). Although there is this difference, several factors contribute to homogenize the whole area. Some granite outcrops are also found in the Andean mountains, and volcanic rhyolitic formations are found in the coastal mountains. A widespread volcanic event dispersed a dense volcanic ash sediment along the Maipo basin, especially in the Pudahuel and Melipilla zones. Finally, clays and sand (temper) weather from the rock formations in the higher eastern mountains and drain down the effluents of the river Maipo and the river itself towards the coastal mountains and the Pacific, mixing with clay and sandy particles from different provenances on the way.

On the basis of geological and archaeological information, we stratified the region into four subregions and worked with pottery fragments from eight sites, two in each subregion: Tejas Verdes 1 (TV1) and Laguna de Matanzas (MZ) in the coastal area; Las Tejas 3 (LT3) and Popeta (Pt) in the intermediate valleys; Talagante 10 (T10) and Turbinas (CH) in the central valley; El Manzano 2 (Ma2) and Escobarinos 1 (E1) in the Andean area (Figs 6.1 and 6.2, Table 6.1). They are all

TABLE 6.1. NEUTRON ACTIVATION ANALYSIS — NUMBER OF SAMPLES

Ceramic ware	Site								
	MZ	TV1	PT	LT3	T10	CH	Ma2	E1	Total
Aconcagua Salmón	27	20	25	30	30	30	30	31	223
Rojo Engobado	9	10	2	10	—	10	10	10	61
Total	36	30	27	40	30	40	40	41	284
Clay									28

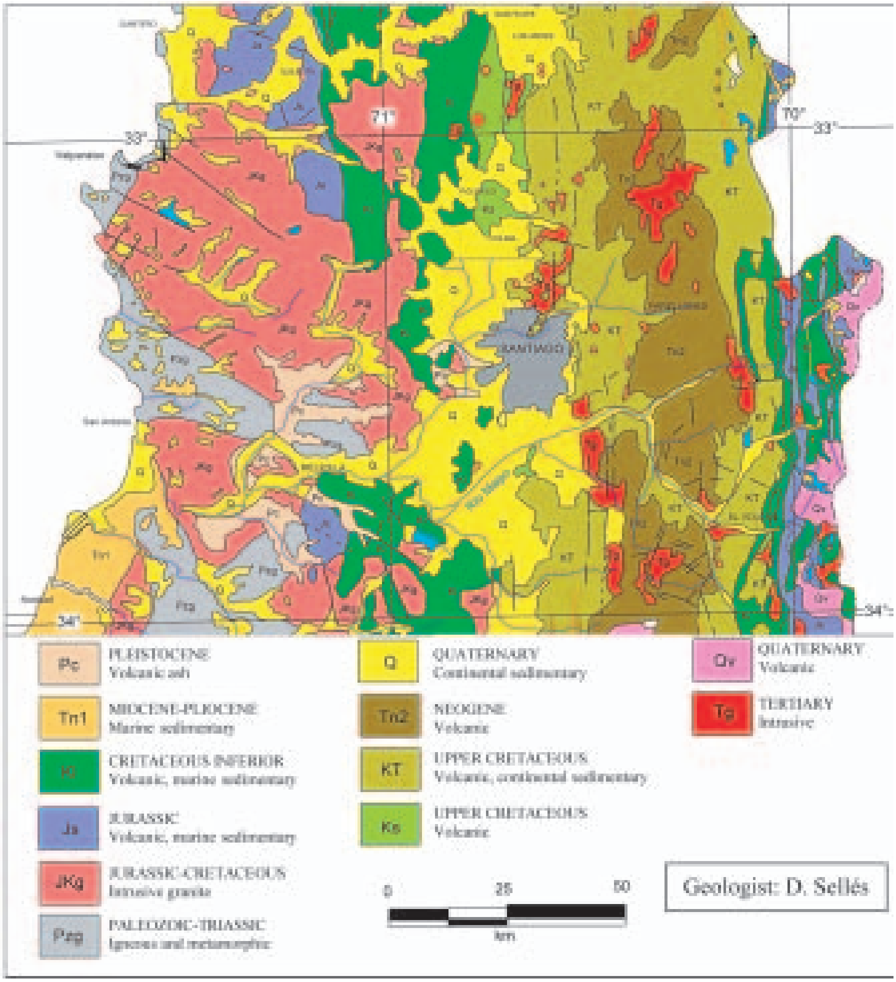

FIG. 6.2. Geological map of the Maipo valley (after D. Sellés).

domestic household sites that have similar cultural characteristics and spatial extent, where most debris comes from middens altered by post-depositional processes (mainly plowing).

For the data to be comparable, the ceramic context of each of the sites selected for this study was analysed with a systematic ceramic methodology. This included routine ceramic analyses (typological, attribute analysis (surface treatment, morphology, wear from use, decoration, low microscopic paste analysis and standards determination)) and petrography (mineralogical characterization). The age of the sherds was also determined.

Previous archaeological studies enabled four main Aconcagua Salmón fabric families (based on type of inclusions in the paste) to be determined, which we have correlated with the local geological formations. Fabric R includes andesitic–basaltic rocks from Andean formations and plagioclase; fabric G is a mineralogical mixture characteristic of the weathering of granite rocks which include mainly quartz, plagioclase feldspars, amphiboles, epidotes and mica; fabric F is a combination mainly of feldspars and quartz or feldspar and rhyolite that can be found in several regional environments; fabric C is dominated mainly by highly weathered feldspars and/or kaolin inclusions. Most of them are present at all the sites, although there are differences in regional distribution (Fig. 6.3). The granulometry (medium to coarse) and density (medium to high) are quite similar.

The paste (fabric) groups were our reference groups in selecting the samples. We chose, randomly, a proportionate number of samples from the main paste groups and subgroups at each site. This criterion selects for what is most abundant and leaves without consideration rare or infrequent pots, something to be taken into account in the final archaeological interpretation.

We also included 28 samples from natural clay sources, 9 from the coastal area, 3 from the central alluvial valley, 2 from the central valley and 14 from mountain deposits (four of them experimentally mixed by us) (Figs 6.1 and 6.2). We needed to have some idea of the chemical profiles of the natural clay resources in the area to evaluate some issues concerning the Aconcagua ceramic data. We especially wanted to know if different sources formed distinctive compositional groups, if coastal clays differed from valley clays and if coastal clays were as heterogeneous as the archaeological ceramic data. A non-systematic collection of clay samples was obtained from locations known to geologists or local potters. In three places, samples were taken at two different depths.

We prepared test tiles from each sampled source, with surgical gloves, adding deionized water, and fired them to 700, 850 and 1000°C in an electrical furnace. Some of the test tiles fired at 700°C were analysed by INAA. The raw clays were analysed by X ray diffraction to determine the clay minerals.

6.3.1. Sample preparation and techniques

We used the following strategy for sample preparation:

(1) Thin ceramic sherds, small fragments and sherds which did not have significant decoration as well as test tiles were prepared with a grinding technique. A piece of about 2 cm^2 of the fragment was used to homogenize the sample (usually it corresponded to a weight of 2–3 g). The area to be ground was cleaned with a rotary file (surfaces and sections), after which it was further cleaned with a brush and deionized water, dried, submerged for

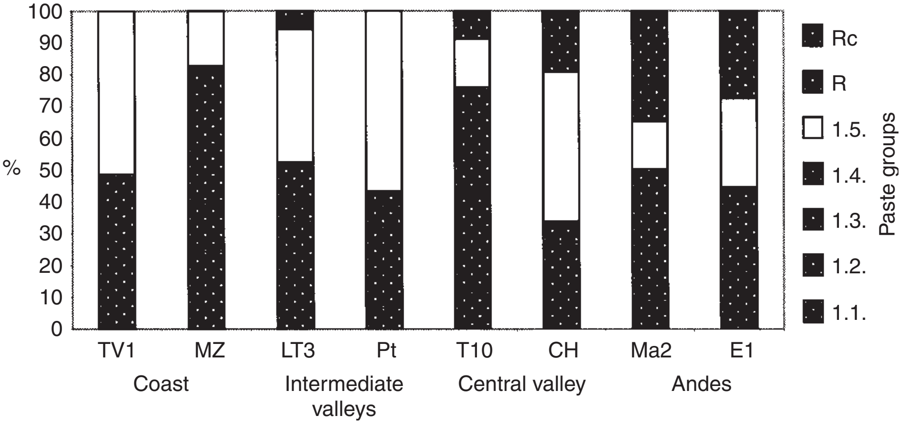

FIG. 6.3. Distribution of the main Aconcagua Salmón ceramic paste groups at the archaeological sites.

less than 1 min in liquid nitrogen and then crushed into a fine powder in an agate mortar.

(2) Decorated sherds, where it was important not to damage the surfaces because of their relevant archaeological information, were prepared with a drilling technique. The section to be drilled was cleaned with the rotary file, and the powdered sample was extracted from several perforations along the cleaned section with a tungsten carbide drill. The powder was collected in special inert weighing paper and then emptied into glass flasks previously hygienized with nitric acid (20%). Approximately 400 mg of material was extracted to homogenize the sample.

A detailed register and part of each specimen were retained for the archaeological laboratory archives.

6.4. ANALYTICAL PROCEDURES

After the samples were powdered, they were air dried in ovens at 105 ± 5°C for 22–24 h and then allowed to cool in a desiccator. An analytical balance was used to weigh the samples. Dried samples were of 150–250 mg poured into a polyethylene vial, which was surrounded with an iron wire used as a neutron flux monitor and then irradiated in the reactor.

The samples were irradiated in the reactor RECH-1 for 8 h, with a thermal neutron flux of 5.0×10^{12} $n \cdot cm^{-2} \cdot s^{-1}$. After a decay time of 6–8 d the samples were measured for a period of 1.0 h at a sample–detector distance of 6 cm. Then, after a decay time of 25–30 d, the samples were again measured for 2 h, in this case with a sample–detector distance of 1 cm. In both measurements, a Canberra HPGe detector of 15% efficiency coupled to a Canberra amplifier (model 1510) and a Canberra multichannel board (model S100) were used. The elemental concentrations of the samples were calculated using NIST SRM-1633b (coal fly ash). For non-certified elements of NIST SRM-1633b, the concentrations obtained from the Smithsonian Institute were used. NIST SRM-679, brick clay, NIST SRM-2704, Buffalo River Sediment and Ohio Red Clay were used for quality control. Sometimes a sample previously analysed was used for quality control. All the spectra were deconvoluted with SAMPO90 software.

In the first RCM, agreements were made relating to the analytical procedure to be used in the project and it was decided to attempt to analyse the following elements: As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, U, Yb and Zn. These 25 pre-established elements were analysed. In some samples we also analysed W in order to estimate drilling contamination.

From a chemical analytical perspective, the following observations are important:

(a) Zn: There is interference in some of the samples with high concentration of Sc. This increases the measurement error.

(b) W: The high measurement error in the samples is due mainly to the low concentration of W in the standard used. We do not have a standard with a higher concentration of this element.

(c) Many elements could not be used in the statistical analysis because of low detection limits in the majority of the samples (Ba, Ca, K and Sr). Others such as Cs, Rb, Sb, Ta and Tb, although quantifiable in many of the samples, were below detection limits in some, which precluded their utilization in the PCA.

(d) When all the samples were pooled together, or for the Aconcagua Salmón samples, the analyses were run using Na, Sc, Fe, As, Cs, La, Ce, Sm, Eu, Yb, Lu, Hf and Th, which included minor and trace elements. In the Rojo Engobado analyses we could use Co but had to exclude Cs because of some cases below the detection limit.

6.5. CONTAMINATION PROBLEMS

We found a significant rise in the W and Co values in the samples obtained by drilling ceramic sherds with a tungsten carbide bit, as expected, and found a rise in Co and Ta values in samples obtained with a tungsten carbide burr. This information led us to exclude Co and Ta from further analysis and to process most of the samples with the grinding technique where contamination, if present, is minimal.

Additionally we had an unexpected source of contamination. From sample CHI-219 onwards a Spex Certiprep 6750 freezer mill was used to grind the samples. The rod shaped steel impactor, which shuttles back and forth inside a stationary sample vial, heavily contaminated the samples with Cr. Therefore, this element was also discarded from most of the analyses.

6.6. STATISTICAL PROCEDURES

We looked into the chemical compositional data with an exploratory approach to find patterning related to sites, subregions, ceramic types and paste groups. It included visual inspection of raw data and biplot scattergram analysis crossing two elements at a time. Further multivariate statistical analyses were run after data were transformed to log base 10 values. We performed average linkage cluster analyses (Euclidean distance), principal component analysis (PCA) (using a correlation matrix) and discriminant analysis[1].

6.7. RESULTS FROM ARCHAEOLOGICAL AND CLAY SAMPLES

6.7.1. Aconcagua Salmón

The results did not show the discrete and separate clusters that are interpreted as the chemical compositional groups of the data set. Therefore we attempted to find some pattern in the data, identifying their position in the compositional space by site provenance and paste group.

When site provenance was coded we found different patterns for valley, coastal and Andean sites.

The chemical data plotted along principal components (PCs) 1 (rare earths) and 4 (As, Hf) revealed some overlap between the data sets of the valley sites but with an undoubted shift in the position of each of these sites on the graph (Fig. 6.4, Table 6.2). This trend for samples from the same site to be located in a specific quadrant of the graph should reveal the distinctive chemical pattern of each site. We interpreted this finding as evidence of different ceramic production loci. The low grouping reveals heterogeneity and general resemblance for all the samples. Only one site located in the intermediate valley, Popeta, did not follow this pattern.

Coastal samples behaved in a different way. There is a total overlap in the PCA plot, which indicates that sites could not be differentiated. Since prior evidence

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[1] All the statistical analyses were performed with SYSTAT 7.0 software.

TABLE 6.2. COMPONENT LOADINGS (ACONCAGUA SALMÓN, ROJO ENGOBADO AND CLAYS)

(PC1, rare earths; PC2, Sc, Fe; PC3, Na, Cs; PC4, As, Hf)

	PC1	PC2	PC3	PC4
Variance explained (%)	37.1	17.0	14.2	8.7
Na	0.152	0.110	**–0.758**	0.197
Sc	0.074	**0.812**	–0.053	–0.270
Fe	–0.043	**0.704**	0.256	0.296
As	0.009	0.265	0.521	**0.622**
Cs	0.013	0.118	**0.761**	–0.048
La	**0.815**	–0.264	0.318	–0.203
Ce	**0.828**	–0.263	0.290	–0.209
Sm	**0.907**	0.247	0.063	–0.211
Eu	**0.767**	0.451	–0.004	–0.227
Yb	**0.804**	0.251	–0.282	0.163
Lu	**0.793**	0.212	–0.290	0.242
Hf	0.618	–0.310	0.051	**0.523**
Th	0.613	–0.598	-0.021	0.091

Note: Bold numbers assign components of a principal loading/significance to explain the influence of the element.

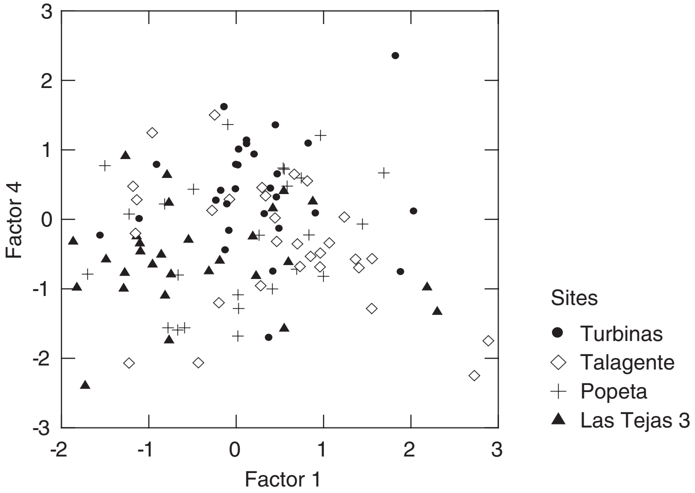

FIG. 6.4. Component loadings of Aconcagua Salmón pottery: valley sites.

suggested a seasonal pattern for coastal production [6.7], the coastal chemical data were plotted over the valley samples in order to trace the origin of the vessels from the data overlap over the whole area occupied by the valley sites. Thus we could not identify a specific provenance for the coastal samples.

Andean samples also showed a total overlap in the PCA plot.

When fabric group according to low microscopic paste characteristics (paste group) was coded, some trends were seen but this time along principal components 2 (Sc, Fe) and 3 (Na, Cs). The data showed some patterns that can be explained by the presence of the coarser fraction, especially in paste group F, which has feldspars and quartz or feldspars and rhyolite as the main inclusions (Fig. 6.5).

6.7.2. Rojo Engobado

The fuzziness of the Aconcagua Salmón (AS) ware data raised questions about whether all the clays in central Chile were difficult to model through compositional analysis and the extent to which local clays could be differentiated. Since the light coloured clay of AS is absolutely different from Rojo Engobado (RE) reddish brown clay we thought their study could help understand the compositional profiles in the region under study.

The results show that RE samples have a different behaviour from those of AS.

When plotted together RE samples can be distinguished from AS samples on a regional and a site by site basis but, instead of the expected absolute differentiation, the data only showed a trend to cluster in a specific area of the graph (Fig. 6.6). In the site by site analyses, the greatest distinctions were observed in coastal and Andean sites. Another difference between RE and AS wares is that RE samples, in each subregion, cluster together in tighter groups than AS samples (Fig. 6.7). The only exception is Las Tejas 3.

When only the RE samples are analysed (Table 6.3), the data plotted along principal components 1 (rare earths) and 3 (As) show a clear distinction between two compositional groups: one of them clusters the sites in or near the Andes range (Ma2, E1 and CH1) and the other groups the intermediate valley and coastal sites (TV1, MZ, LT3 and Pt) (Fig. 6.8). These groupings can be explained by the geological differences between the Andean deposits and the coastal mountains/coastal plains area.

6.7.3. Natural clays

The PCA plots show along principal components 2 and 3 (Table 6.2) that the valley samples (locations 9, 13 and 14) tend to cluster with the coastal samples (location 8) and that those at location 11 form a separate group. Natural El Belloto clays (location 15) that originate from the same deposit do not always cluster, nor do Montenegros clays (location 12) (Fig. 6.9).

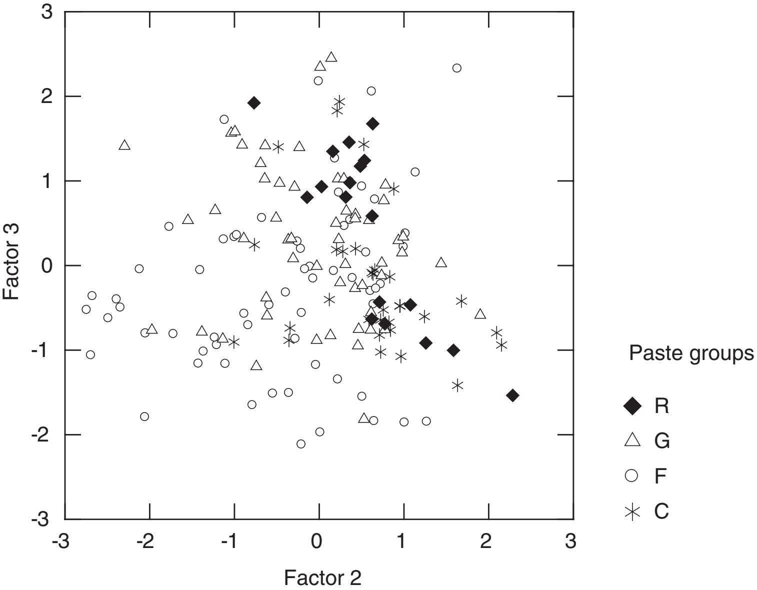

FIG. 6.5. Aconcagua Salmón wares: paste groups.

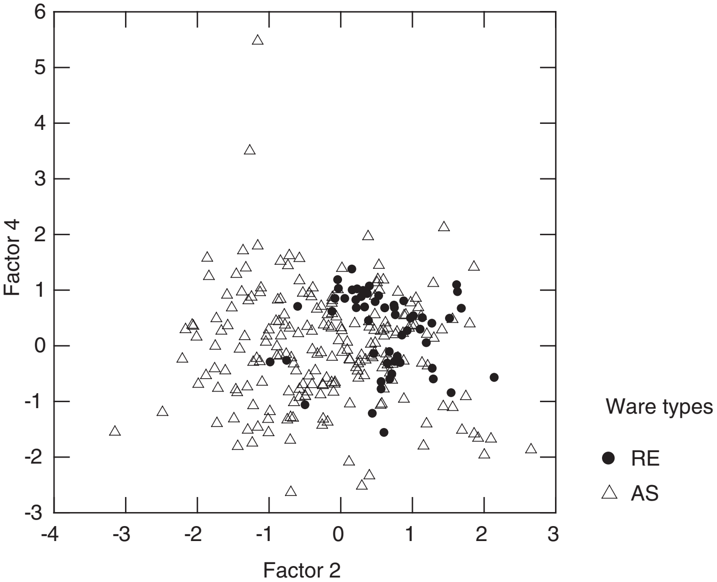

FIG. 6.6. Aconcagua Salmón wares: ware types.

TABLE 6.3. COMPONENT LOADINGS (ROJO ENGOBADO)

	PC1	PC2	PC3
Variance explained (%)	57.1	14.8	9.9
Na	0.482	–0.311	0.431
Sc	–0.728	**0.614**	–0.132
Fe	–0.380	**0.686**	0.532
Co	–0.754	0.474	–0.020
As	0.503	–0.281	**0.723**
La	**0.885**	–0.016	–0.247
Ce	**0.913**	0.002	–0.226
Sm	**0.934**	0.259	–0.096
Eu	**0.820**	0.272	0.241
Yb	**0.742**	0.493	0.074
Lu	**0.714**	0.521	0.008
Hf	**0.938**	0.113	0.009
Th	**0.770**	0.076	–0.302

Note: Bold numbers assign components of a principal loading/significance to explain the influence of the element.

The results also show that coastal clays group together in a tighter cluster than coastal archaeological samples. Since the clay samples cluster tightly, even those from different sources along the coast, it seems reasonable to think that the heterogeneity of the archaeological samples is due mainly to cultural factors. These might depend upon the manufacturing process like added tempers or the settlement systems and production loci.

In the central valley data, alluvial and lacustrine clay samples form a tighter cluster than the AS samples but are more dispersed than the RE samples. It is important to consider that even though the distance between two of these sources is more than 30 km (locations 9 and 13) they are not always clearly grouped apart. Only along principal component 4 (As, Hf) are the Hospital (location 9) samples (nearer to the Andes) differentiated (see also Fig. 6.10). There is a geological explanation since Andean volcanism is associated with S and As. The other element that distinguishes clay samples is Na (feldspars). This is clearly seen in the bi-plot of As against Na (Fig. 6.10).

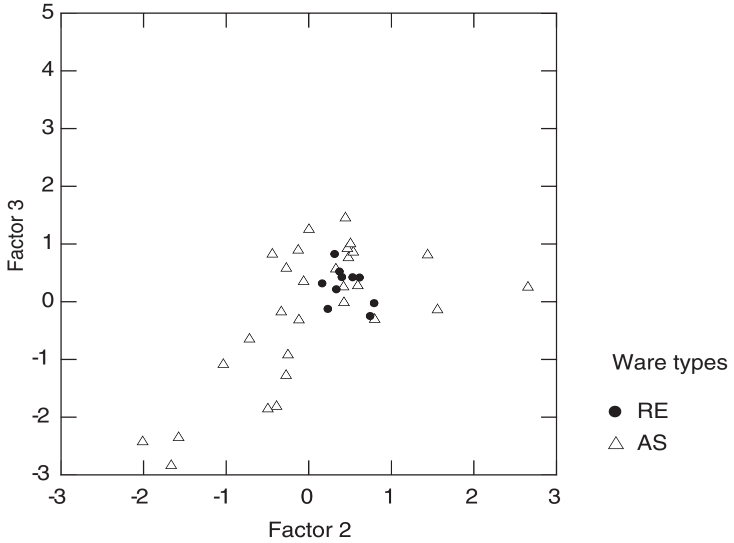

FIG. 6.7. Aconcagua Salmón wares: valley sites.

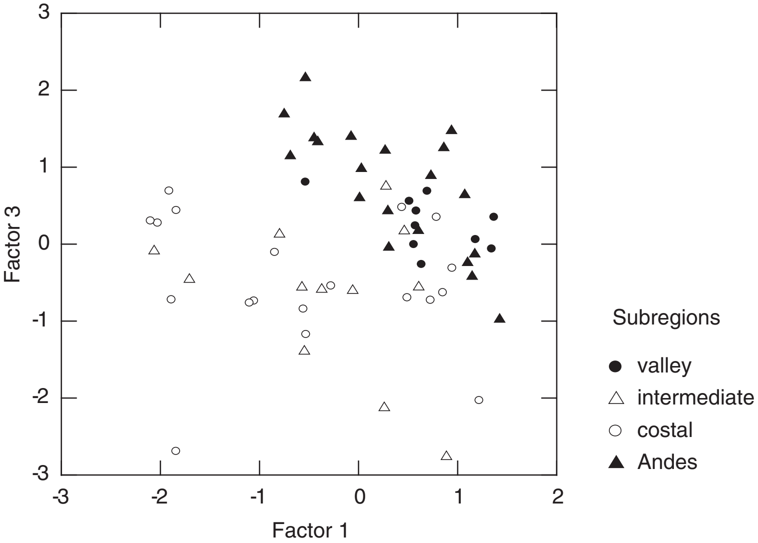

FIG. 6.8. Rojo Engobado wares: subregions.

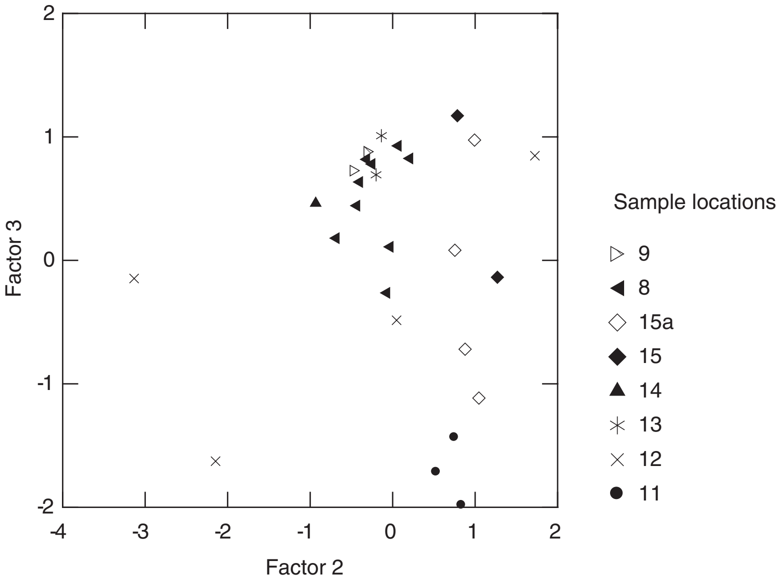

FIG. 6.9. PCA for clay samples.

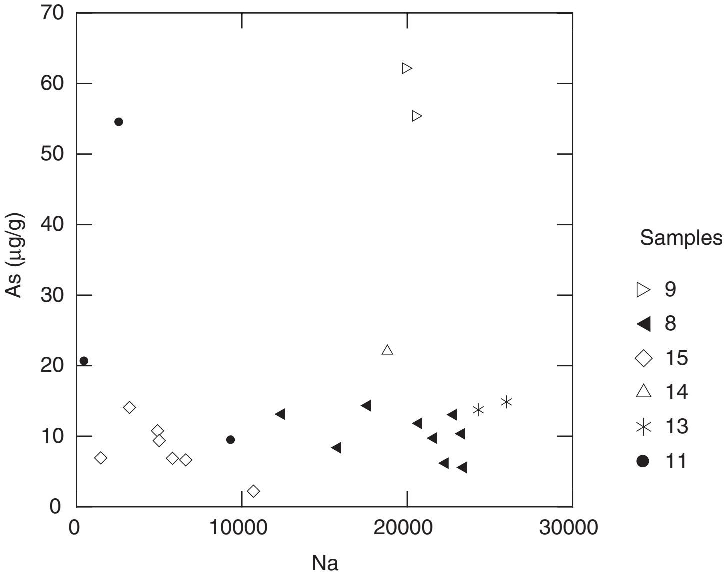

FIG. 6.10. Clay samples bi-plot: As–Na.

The mixed clays (Figs 6.9, location 15a) show a chemical signature as expected according to the raw clays mixed (Fig. 6.9, locations 15 and 11). This raises the problem that mixing clays (resources) of different origins (different chemical profiles) alters greatly their distribution in the compositional space.

6.8. INTERPRETATION OF RESULTS AND DISCUSSION

Although some subgroups were recognized among the data, the partial or total overlap in the majority of samples made our archaeological interpretation rather difficult.

The results show some chemical similarity of local clays. The 28 clay samples, although they are not a random sample of the study region, render the impression that subregional differentiation is not always to be expected in this area. What is especially puzzling, however, is that spatial proximity does not equate with chemical similarity. Hospital samples (lacustrine deposits in a central valley environment), Talagante and Peñaflor samples (alluvial deposits in a central/intermontane valley environment) plotted along principal components 1, 2 and 3 cluster with Las Cruces samples (coastal deposits). On the other hand, clays from the same natural formation and locality (i.e. El Belloto) can be quite dissimilar chemically.

The results also show a chemical similarity among many of the pre-Hispanic vessel fragments from all around the region. These similarities can be explained by several factors. Two major factors are the scale of analysis and the geological characteristics. We were working at a subregional level, comparing sites located along the same river axis, not more than 120 km apart. The major geologically based difference expected is between Andean deposits (near sites E1, Ma2 and CH1) and deposits from the coastal plains and mountains (sites TV1, MZ, LT3, T10 and Pt).

RE wares could be differentiated into two subgroups, each of them clustering samples according to this geographical provenance. For these wares, our interpretation is that at least two different production loci were responsible for RE vessels, one located near the Andean clay formations and another somewhere within the coastal mountains, valleys or plains. Some vessels from the Andes might have reached the coastal area, but not the other way around. However, the chemical characteristics of the Maipo basin's natural resources are not that much different as to enable us to state that there was not more than one procurement and production zone in each of them. The low microscopic characteristics of RE ceramic fabrics from LT3, MZ and TV1 are so similar that our initial hypothesis of a common origin is supported by the chemical pattern observed in the NAA results. However, the fabric patterns for RE of sites E1, Ma2 and CH1 are so different that they preclude a single source interpretation for them.

AS wares did not reveal the same distinction. There are four main differences:

(1) The AS chemical data are much more disperse than the RE data, i.e. the groups do not cluster as tightly.
(2) Some groupings were revealed according to valley site provenance (based on rare earths and As–Hf).
(3) Some wares were grouped according to paste characteristics (Sc–Fe and Na–Cs).
(4) Although analysing the same sites as for RE, no complete distinction was found between Andean and coastal plains, valley or mountain provenances.

We think one possible factor for (1) and (4) is the mixing of clays in the preparation of AS pastes in order to produce the light coloured effect. Experimental work mixing reddish clays with kaolinitic clays from the study region has produced matrix colour and fabric characteristics very similar to some paste groups in AS wares [6.8]. INAA chemical patterns for four of these mixed samples clearly 'blurred' the chemical profiles of the original clays. The partial overlap of some AS and RE data might be due to similar clays, some mixed with a white clay component (AS), others not (RE). Another factor might be the original chemical characteristics of the clays used for each ware (more or less homogeneous), or some culturally related issue involving the way artisans produced their vessels, but we have no way of testing these last alternatives.

The AS data, in spite of all the above mentioned problems (intraregional scale of analysis, geological homogenization, mixing of clays, access to similar geological formations from many sites, abundant medium to coarse temper and volcanic ash) showed some trends which enabled the identification of a characteristic chemical pattern for three of the valley sites analysed. Our interpretation of these data is that the ceramic source and production location in the valleys is usually site specific. Binocular paste analyses and petrography support this interpretation. This is coherent with a home based system of ceramic production in the Aconcagua culture. Even in geologically homogeneous environments and/or in pottery manufacture, where the mixing of clays is a technological tradition, we should expect more clustering of the data if specialized or centralized ceramic production existed.

The different dispersal range of AS samples between valley (more homogeneous) and coastal (more heterogeneous) sites, especially in TV1, is consistent with paste observations under a binocular microscope. Since we discarded a natural chemical heterogeneity in coastal clays we are inclined to support the interpretation that cultural factors are responsible for this difference. Such regional patterns have sometimes been interpreted in archaeology in terms of pottery making (homogeneous) and pottery consuming (heterogeneous) communities [6.9]. We think that a seasonal occupation of the coastal area, with no intergroup territorial boundaries, would also render the same results by mixing the debris from separate occupation events of people coming from different communities. If there was pottery manufacture at some places along the coast, a difference in the scale of production or temper related issues could also be responsible for such a pattern.

6.9. CONCLUSIONS

Although the resolving power of NAA did not enable us to solve all the research problems, some new ideas were put forward about the Aconcagua ceramic system.

(a) The Aconcagua Salmón clays do not seem to come from a single source but from many local sources where this kind of pottery would have been manufactured. The geological survey led us to confirm such diversity because we recognized different clay minerals (kaolin, montmorillonite and perhaps clays weathered from volcanic deposits) and sources that can contribute to light coloured clays in many locations in the study area.
(b) Different compositional patterns for the AS wares in three valley sites were found, which we interpreted as specific local production locations. This led us to argue for a home based system of production.
(c) At least two compositional groups for RE wares were found with evidence of some Andean vessels going to coastal sites.
(d) It was concluded that two ceramic wares produced and used by the same people might have different production and distribution systems.

REFERENCES

[6.1] DURÁN, E., PLANELLA, M.T., “Consolidación agroalfarera: Zona central (900 a 1470 d.C.)”, Prehistoria (HIDALGO, et al., Eds), Editorial Andrés Bello, Santiago (1989) 313–327.
[6.2] SÁNCHEZ, R., MASSONE, M., Cultura Aconcagua, Dirección de Bibliotecas, Archivos y Museos de Chile and CIDBA, Santiago (1995).
[6.3] MASSONE, M., Los Tipos Cerámicos del Complejo Cultural Aconcagua, Grade Thesis, Universidad de Chile, Santiago (1978).
[6.4] FALABELLA, F., El estudio de la cerámica Aconcagua en Chile Central: Una evaluación metodológica, Contribución Arqueológica **1** 5 (2000) 427–458.
[6.5] WEIGAND, P.C., et al., “Turquoise sources and source analysis: Mesoamerica and the Southwestern U.S.A.”, Exchange Systems in Prehistory (EARLE, ERICSON, Eds), Academic Press, New York (1977) 15–34.

[6.6] BISHOP, R.L., et al., “Ceramic compositional analysis in archaeological perspective”, Advances in Archaeological Method and Theory, Vol. 5 (SCHIFFER, Ed.), Academic Press, New York (1982) 276–329.

[6.7] FALABELLA, F., et al., “La cerámica Aconcagua: Más allá del estilo”, Actas 2° Taller de Arqueología de Chile Central, Universidad de Chile, Santiago (2001).

[6.8] FALABELLA, F., et al., “Una propuesta sobre la naturaleza de las materias primas de la cerámica Aconcagua Salmón”, paper presented at 15th Natl Congr. of Chilean Archaeology, Arica, 2000.

[6.9] LONGACRE, W.A., STARK, M.T., Ceramics, kinship, and space: A Kalinga example, J. Anthropol. Archaeol. **11** 2 (1992) 125–136.

Chapter 7

CLASSIFICATION OF THE REGIONAL ABORIGINAL CERAMIC PRODUCTION AND DISTRIBUTION IN THE CENTRAL REGION OF CUBA BASED ON INAA

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Abstract

Findings from the excavations of Cuban aboriginal Subtaíno and Archaic settlements in the central region (700–1500 A.D.) were analysed by neutron activation analysis (INAA). The exploration of the results obtained was performed using a principal component analysis (PCA) for the reduction of the dimensionality of the data space, and the definition of the chemical paste compositional reference units was aided by the application of the Davis discriminant analysis procedure. As final results, after the analysis of the geological characteristics of the zone and the interpretation of the archaeological contexts under study, the Subtaíno aboriginal pottery could be attributed to several compositional reference units and manufacture loci. The ceramic artefacts in some Archaic sites were also considered as to whether they have been produced locally or imported.

7.1. ARCHAEOLOGICAL BACKGROUND

Earlier aboriginal settlements in Cuba (4000–500 B.P.) were classified as Archaic (or Siboneyes in the literature up to the 1980s). These communities were mainly devoted to fishing, gathering and hunting activities, and in their latest settlements (proto-agricultures), there is evidence of an incipient agriculture. Large collections of lithic and shell tools were compiled from excavations throughout the whole island, and these communities were classified as Cayo Redondo (when the presence of stone daggers or balls was predominant) or Guayabo Blanco (when shell tools were predominant). Kozlowski [7.1] and Febles [7.2] studied the lithic industry at Aguas Verdes and Playitas, and suggested the possibility of these communities originating in the formative period (3000 B.P.), when a big migration might have taken place from Colombia towards the south of North America (Mississippi valley), passing through the Antilles arc. Samples of primitive pottery were found at some Archaic sites.

For some decades, Cuban archaeologists have accepted the generic classification in Taínos and Subtaínos proposed by Rouse [7.3] for the study of the groups with agricultural and pottery traditions (Agroalfareros). The first and earliest ones (twelfth to sixteenth centuries), according to Guarch [7.4], were spread in the eastern edge of the island and are usually associated with the series of Chicoide styles (Fig. 7.1). The Subtaínos, perhaps established as early as the eighth century [7.5], were distributed mainly in the eastern and central territories of Cuba. Their pottery is associated with the Meillacoide stylistic series. Their pottery shows a poorer decoration and elaboration (Fig. 7.2) when compared with the Chicoide techniques.

Archaeological research in Cuba has been oriented mainly towards the study of both the eastern and the western territories of the island: (a) the former province of Oriente, considered as the location with the higher density of communities with agricultural and pottery traditions; (b) the former provinces of Pinar del Río, La Habana and Matanzas, where mostly Archaic sites have been discovered. However, the central region of Cuba, in spite of its rich diversity and relevance, has been only partially and incompletely studied.

The variety in the landscape of the central region of Cuba (about 150 km west to east and 100 km north to south) was extremely favourable for the development of diverse social and economic structures. Located in the heart of the Cuban archipelago, the central region was the centre of the confluence of pre-Hispanic cultures with uneven levels of development, ideology and social organization. The communities arriving from the eastern territories, bearing strong agricultural and

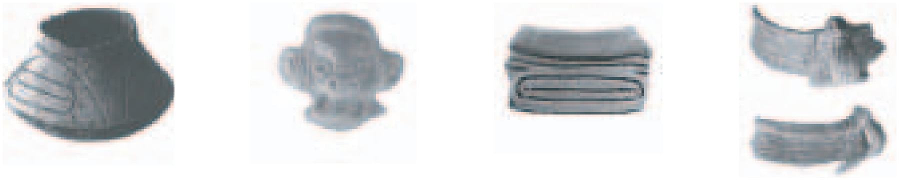

FIG. 7.1. Exponents of Chicoide pottery, Maisí, Oriente.

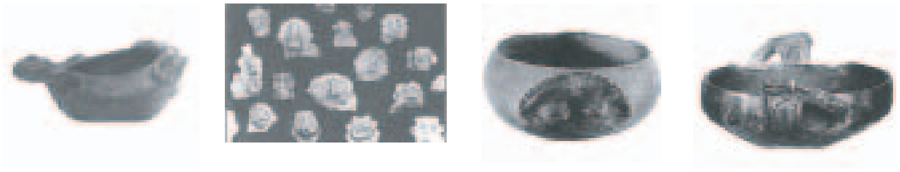

FIG. 7.2. Exponents of Meillacoide pottery artefacts.

pottery traditions, interacted with the Archaic society already established centuries previously in these territories, and successive transculturation and assimilation processes took place. In his second trip to Cuba, Christopher Columbus was impressed by the magnificent Jagua bay [7.6], but Sebastián de Ocampo made the first records about the native settlements around the bay during his navigation of the islands, and subsequently more information was recorded by the friar Bartolomé de las Casas, who lived in the region for many years [7.7].

The techniques and stylistic features of the ceramic wares from this territory show a certain unity with the Meillacoide series. The masters of the central region used the techniques of emptying successive cords to build up the vessels and of firing the artefacts in open sky kilns. The decoration motives became simpler when compared with the Meillacoide exponents from the eastern edge of the island. A tendency to schematize the represented themes seems to be the result of their contact with the Archaic culture, as well as the use of a decoration based on incisions and applications in panels. The handles are smaller, consisting of small pieces with an elementary moulding of abstract and geometric shapes, giving up the richness in anthropomorphic and zoomorphic motives from the eastern cultures. Population groups in the southwest, northeast and middle east of the central region show local variations that suggest the need to study their history and social development.

The chronological information about some Agroalfarero settlements and their interactions with the then existing by Archaic settlements [7.8, 7.9] that spread from the east (earlier sites) towards the centre of Cuba (late sites) suggest the hypothesis of two migration routes following that direction (Fig. 7.3).

The Agroalfarero colonization of the central region started at the southern limits of the provinces of Ciego de Ávila and Sancti Spíritus, with the sites of Palo Alto, Toma de Agua, Tayabacoa and Guayabalito. Some communities continued moving north to reach clear inland locations in the municipalities of Jatibonico (La Nata, Los Ranchos and Las Mulas y Guainabo) [7.10] and Sancti Spíritus (Pueblo Viejo) [7.11]. The unity in the style of decoration is the main reason for our association of their pottery with a local development we refer to as Yayabo.

Other settlements were established at many sites in the southwest of the central region in the provinces of Cienfuegos (Cantabria, Cayo Ocampo, Cayo Carenas, Punta de Ladrillos, Ojo de Agua, Rancho Club, Abra de Castellón and El Convento) and Trinidad (Cabagán, Guanayara, Río Cañas, Laguna de Algodones and El Masío), showing different patterns in the decoration motifs. Different aspects of life of the communities developing the Jagua pottery are widely described in the literature [7.12–7.15].

Finally, we observed a differently decorated pottery at sites including Playa Carbó and Júcaro II, located in the eastern part of the northern coast, which were studied by the members of the Caguanes group. We assume the wares were produced by local manufacture (Yaguajay) developing from the stylistic traditions found at the

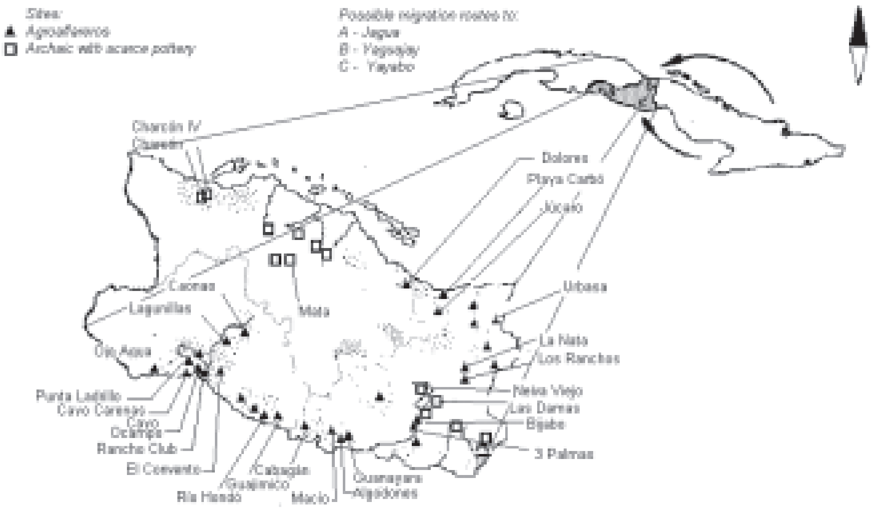

FIG. 7.3. *Settlement of the central region by the Agroalfarero culture arriving from the east.*

sites located further to the east on the north coast, in the provinces of Ciego de Ávila and Camaguey.

Classification into three stylistic variations (Jagua, Yayabo and Yaguajay) in the manufacture of most of the ceramics of the central region is described in detail in the latest interpretations by Celaya and Godo [7.17] of the origin and formal transformation of the themes represented in the pottery. The rich diversity of the geology of the zone, and therefore of the procurement materials for pottery manufacture, should also impose a source of difference in the paste composition of the aboriginal pottery.

7.2. RESEARCH PROBLEMS AND QUESTIONS

Our basic goals were to source pottery and trace its distribution in the central region to contribute new evidence to the discussion about ceramic production and regional interaction between Subtaíno and Archaic settlements.

Our working hypothesis and assumption was that the observed differences in stylistic features might be an indicator of the existence of different production loci; we posed the following specific research questions:

(a) Was the presence of ceramics in the Archaic settlements an indication of an incipient manufacture of pottery, or was it the result of the exchange with Subtaíno communities living in the region?

(b) Are there any compositional patterns in the pottery of the region which might reflect the existence of several production loci?

7.3. MATERIALS AND METHODS

Samples were collected following the traditional ceramograph technique (Ford’s method), and the analytical portion was taken by removal of around 300 mg of powder by drilling with a tungsten carbide burr. After the samples were powdered, they were air dried in ovens at 105 ± 5°C for 22–24 h and then allowed to cool in a dessicator. The values obtained for the concentrations of Co and Ta were disregarded due to possible contamination during the sampling procedure [7.18].

An INAA of more than 400 samples was carried out via the access granted to research facilities of several institutions in the region: ININ (Mexico), CAE (Argentina) and IPEN (Peru). Therefore, the characterization of aboriginal ceramic production was constrained to the interpretation, from all of the obtained data, of such chemical elements that were determined in all of the samples with adequate precision and accuracy. The time limitations imposed by the use of analytical facilities of other institutions, as well as by the differences in the established analytical protocols, resulted in the determination of different sets of elements in each analysis campaign.

The sampling and INAA procedures employed are described in Sections 1.3 and 1.4. Since the accuracy of the determinations varies from element to element, only 14 elements (Na, K, Sc, Cr, Fe, Rb, Ba, La, Ce, Sm, Hf, Cs, Yb and Th) were considered to be determined with an accuracy of better than 10% and were thus accepted for the statistical evaluation. The original concentration values were transformed to log base 10 in order to exclude the uneven influence on the data treatment of the differences in the concentration ranges.

Factor analysis was used for study of the data obtained. Since the concentration values were transformed to logarithmic values, the co-variance matrix was analysed instead of the correlation matrix in order to extract the principal components. An orthogonal rotation (Varimax) that minimizes the number of variables that have high loadings on each factor was applied to the extracted components, with the aim to make the interpretation easier. Factor scores were calculated by regression. The ordination of the cases in two or three dimensional scatter plots, defined in space by the extracted principal components, aided in the screening of our data.

Conformance to a predictive model of group membership was established according to the hypothesis formulated in accordance with the archaeological contexts and previous interpretations, as well as to relevant information obtained from other sources, such as the interpretation of the geology of the zones (and therefore the expected differences in the composition of the raw materials), the observation of the ceramic paste by optical and electronic microscopy and the petrography analysis of thin sections.

Once a set of groups for a given analysis was established, the procedure formulated by Davis [7.19] was used for discriminant analysis. A set of discriminant functions based on linear combinations of the predictor variables, which provides the best discrimination between the groups, is generated. The functions are generated from a sample of cases for which group membership is 'known', and are further applied to the rest of the cases, with measurements for the predictor variables but unknown group membership. The probability of belonging to a given group was set by the software from group sizes due to the observed uneven distribution of samples. The Mahalanobis distance from sample to each alternative group centroid provides the criteria for evaluating the relative probabilities of membership of the specimen in each of the groups.

7.4. DESCRIPTION OF THE ANALYSED SAMPLES

Three hundred fragments of aboriginal ceramic, selected by the traditional ceramograph technique (Ford's method), were analysed between 1997 and 1999. The results of 228 samples corresponding to 15 Agroalfarero and 12 Archaic sites from the central region (Table 7.1) underwent statistical evaluation in the search for compositional patterns, as well as for associations and exchange among the supposed loci.

As can be seen from Table 7.1, most of the fragments came from Jagua locus, which corresponds to the higher density of agricultural sites in the whole central region. Some Archaic sites were selected among the ones closely located to any of the three supposed loci, while others were sampled far enough from them, trying to reveal the scope of the Agroalfarero influence.

We did not analyse clays from the region due to the constraint imposed by the use of analytical facilities of third institutions. The extreme variability of the geology of the central region leads to the supposition of a consequent variation in the composition of the clays from the possible procurement of alluvial deposits, which cross formations containing ultrabasic, basic, intermediate and acid rocks. Therefore, to carry out research that involves finding correlation on results for both clays and ceramic samples would involve analysis of a larger quantity of samples. On the other hand, the intense programme of improvement of water resources developed in the region during the last 30 years has led to the construction of numerous artificial lakes and reservoirs that might have covered the original clay beds. To compensate for the lack of information on the composition of the clays, a detailed study of the geology of the region was performed.

TABLE 7.1. ANALYSED SAMPLES FROM THE CENTRAL REGION

Agroalfarero sites			Archaic sites with ceramic findings		
Locus	Site	Analysed fragments	Site	Analysed fragments	Possible interactions
Jagua	Ojo de Agua	25	Lagunillas	3	Jagua
	Punta de Ladrillos	14	Caunao	4	
	Rancho Club	3	Guajimico	2	
	Cayo Carenas	15	Tres Palmas	3	Yayabo
	Cayo Ocampo	32	Neiva Viejo	5	
	El Convento	30	Las Damas	3	
	Río Hondo	2	Bijabo	3	
	Cabagán	2	Urbaza	12	Yaguajay
	El Masío	1	Dolores	6	
	Guanayara	2	Mata	6	?
	Laguna de Algodones	2	Encrucijada	1	?
Yayabo	La Nata	10	Charcón	8	?
	Los Ranchos	11			
Yaguajay	Júcaro II	11			
	Playa Carbó	9			

7.5. RESULTS

The data obtained for the ceramic from the central region was subdivided into three groups, following the stylistic classification mentioned above [7.17] as well as the geographical distribution of the sites in the three respective territorial zones. The observed technological features, such as the use of open sky firing, a medium to large grain size and the absence of surface decoration, suggest that the ceramic production of the zone had a not very well specialized character. Therefore, we tried to emphasize the suspected differences in the raw materials available from the surrounding areas to differentiate the chemical composition of the pottery paste.

7.5.1. Jagua pottery

The results obtained for 142 fragments from the Jagua region underwent a principal component analysis. The concentration of 12 elements accounted for most of the variability in the data set for 67 samples, and the first four components extracted accounted for 85% of the variability of the data. The results in Table 7.2 reveal there is a complete association between the rare earth elements (REEs) since their loadings are high in the first component. As far as the REEs tend to concentrate on the sediments resulting from processes involving hydrolysis, such as clay beds, the presence of REEs in the first component also reveals that the main differences in the paste composition are conditioned by the use of clays from different procurement areas. Chromium is the element with a high loading in the first component, and its correlation with the REEs suggests its presence also in the clay fraction.

TABLE 7.2. FACTOR LOADINGS AFTER EXTRACTION OF PRINCIPAL COMPONENTS FOR THE JAGUA REGION

	Factor loadings						
	12 elements, 67 cases				10 elements, 142 cases		
	PC1	PC2	PC3	PC4	PC1	PC2	PC3
lg Ce	**0.901**	0.025	0.191	–0.036	**0.807**	0.187	0.233
lg La	**0.883**	0.080	0.349	0.045	**0.818**	0.222	0.385
lg Sm	**0.820**	0.016	–0.003	–0.050	**0.843**	0.191	0.152
lg Cr	**0.774**	–0.101	0.532	0.295	**0.756**	–0.066	**–0.634**
lg Yb	**0.760**	0.069	0.093	0.059	**0.732**	0.395	–0.031
lg Na	–0.286	**0.935**	0.130	–0.039	—	—	—
lg Fe	0.126	**0.845**	0.079	0.086	0.154	**0.916**	0.070
lg Sc	0.451	**0.673**	–0.075	0.180	0.342	**0.852**	–0.173
lg Th	0.146	–0.120	**0.745**	0.011	0.254	–0.047	**0.628**
lg Rb	0.137	0.078	**0.657**	0.171	0.038	0.074	0.402
lg Ba	–0.003	0.150	**0.521**	0.148	0.090	0.488	0.258
lg K	0.024	0.149	0.394	**0.894**	—	—	—

Note: Bold numbers assign components of a principal loading/significance to explain the influence of the element.

The observed correlation of the transition metals Sc and Fe with Na (high loadings in the second component) leads to the hypothesis that differences in the concentration of these elements are mainly due to the presence of several minerals in the temper fraction of the pottery of the region. The same conclusion can be inferred from the loadings for Th, Rb and Ba (third component) and for K (fourth component).

The study of the geology of the zone surrounding Jagua bay [7.20] suggests that the observed compositional differences might be due to the use of clays from different types of beds, among the three major procurement sources located around the bay.

Surrounding the Jagua bay clockwise, the first sources of clay are the red clay deposits from the Villa Roja formation (west bank of the bay), which originated from the weathering of calcareous and limestone rocks and contain, as natural non-plastic inclusions, sand landslide, boulder and pebble. Before starting factor analysis, the raw data have to be transformed into log to base 10 form. High contents of Ca, Mg, Ba and Fe are expected in these clays, due to the weathering of the limestone and calcareous rocks. The Th contents are high since this element is concentrated in the limestone rocks.

Next, there are the grey to brownish grey mud beds lying around the mouth of the river Damuji at the northwest of the bay, which contain sand as a natural impurity. The Damuji originates in a formation of limestone rocks with a strong presence of andesite (Brujas, not shown in Fig. 7.3) and cross-formations rich in limestone and dolomite, basic lava and conglomerates, among other kinds of rocks. As in the case of the Villa Roja clays, Ca, Mg, Ba, Fe and Th are concentrated in these clays. On the other hand, and as a result of weathering of the andesite massifs of the Brujas formation, these clays contain plagioclase impurities, and thus high concentrations of Na and Ca. The presence of sand impurities affects the abundance of quartz grains in the ceramic paste.

The last beds are found along the banks of the rivers Arimao and Caunao, the sources of which are located in the rocky mountains surrounding the bay from the northeast and east, and where basic and intermediate rocks such as lava, basalt, landsite basalt, breach and limestone abound. These rivers in their path to the eastern side of Jagua bay pass through formations of limestone, marl, conglomerates and sandstone. The clays that originated from the weathering of these rocks are higher in Cr and lower in Th than the ones originating from limestone rocks, due to the behaviours of Cr and Th being opposite during magma crystallization and differentiation. Indeed, the concentration of Cr is maximal in ultrabasic rocks, having an average value of several thousands of parts per million (ppm) that decreases along the differentiation of the magma to only some ppm in the granites [7.21]. On the contrary, the average concentration of Th in basic rocks is only 3.9 ppm, and rises to 14 ppm in acidic rocks.

To allow the classification of all of the samples of this zone, a second analysis was performed, this time excluding the concentrations of Na and K. The results obtained did not differ strongly from those previously obtained (Table 7.2).

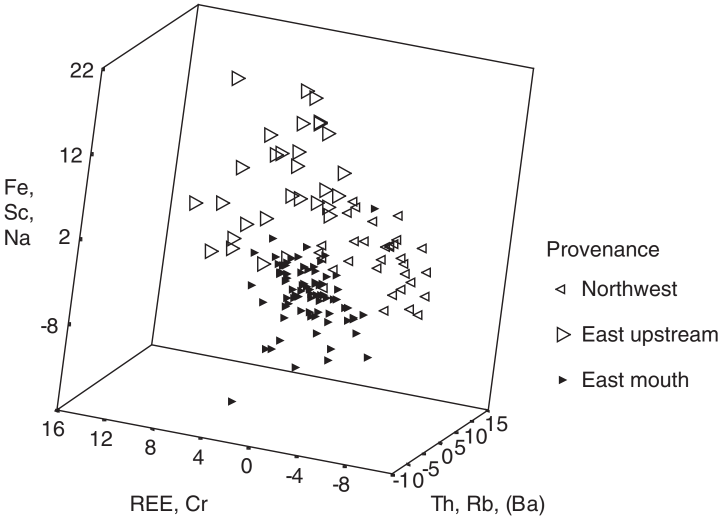

FIG. 7.4. Ordination of Jagua pottery in the principal component space.

Ordination of the samples in the principal component space shows three clearly differentiated groups. A group of thin sections from the samples corresponding to these three groups was studied by petrography analysis [7.22]. The size of the mineral inclusions varied from 0.02 to 1.5 mm, suggesting that they might be naturally present in the clay beds. The paste texture under optical and electronic microscopy was found to be coarse in general, with cavities and fissures as large as several millimetres and widths of tenths of millimetres.

The inclusions were found to be larger in the group represented by the right pointing open triangles in Fig. 7.4, suggesting that these clays were closer to the origin of the river and that therefore the particles suffered less erosion and weathering than those from the other two groups. Plagioclase was found to be the more abundant mineral, and crystals of potassium feldspar, quartz, biotite, epidote and clinopyroxene were also observed, as well as metallic inclusions. This group corresponds to the artefacts with the highest contents of REEs, Cr, Na, Fe and Sc; therefore, this pottery should be manufactured with clays from the beds located closely to the sources of the rivers Caunao and Arimao (‘east upstream’ data in Fig. 7.4). Indeed, being closer to the massifs of the Arimao, Matagua and Provincial formations that are rich in lava, basalt, landsite basalt, andesite basalt and breach rocks, the concentrations of REEs and Cr are higher, including the proportion of plagioclase in the clay composition.

The fragments represented by the right pointing solid triangles seem to be produced also with materials from the beds of the Arimao and Caunao, but located closer to the mouth of these rivers. Nearer to the river mouth, the proportion of plagioclase in the clays decreases, and the quartz inclusions become more abundant. The results of the petrography analysis revealed a higher proportion of quartz in the grain inclusions of this group, corroborating our hypothesis (east mouth data in Fig. 7.4).

The group of left pointing open triangles (northwest data) shows the lowest contents of REEs and Cr and the highest contents of Th, Rb and Ba. These artefacts might be elaborated with clays from Villa Roja or Damuji sources. However, the presence of plagioclase as a major mineral indicates that the materials should be from the Damuji beds.

The Archaic sites of Lagunilla and Caunao exhibit fragments with a composition corresponding only to the north upstream group. This can be interpreted as evidence of the transculturation process leading to the adoption of pottery manufacture practices by these communities. The Archaic site La Mata, located in a valley further to the north and surrounded by formations of ultrabasic rocks (serpentinites, harzburgites, therzolites, wherlites and dunites), shows a compositional pattern far from that expected but resembling the samples produced by potters from sites east of the bay. This community must have acquired the artefacts as the result of the exchange with communities from the southeast.

One of the analysed fragments consists of a handle showing features of a white man's face with beard and helmet, providing evidence of contact with Spanish conquerors. The composition of this fragment corresponds to the group of artefacts manufactured with materials from beds located close to the sources of the rivers (north upstream data in Fig. 7.4). On the other hand, the proportion of fragments of this compositional group in the stratigraphic levels of the El Convento site increases with time. These facts might be an indication of some displacement of the pottery activities to territories located inland.

7.5.2. Yayabo and Yaguajay pottery

Data reduction of the results obtained for the samples of the Yayabo and Yaguajay loci was performed following the same strategy as in the case of Jagua production. The first extraction of the principal components from the concentration values for 11 elements in 35 samples (Table 7.3) showed the existence of different associations. The first three extracted components account for 75% of the variability in the data set. The high factor loadings of the REEs in the first component indicate that the major variability in the compositional data set is conditioned by the use of clay deposits of different origins. The elements Sc and Fe are correlated with the heavy REEs, indicating their presence mostly in the clays. The elements Na and Cr

TABLE 7.3. FACTOR LOADINGS AFTER THE EXTRACTION OF PRINCIPAL COMPONENTS FOR YAGUAJAY–YAYABO POTTERY

	Factor loadings					
	35 cases			68 cases		
	PC1	PC2	PC3	PC1	PC2	PC3
lg Sc	**0.898**	-0.057	–0.081	**0.791**	–0.262	0.252
lg Yb	**0.839**	0.148	–0.021	**0.902**	0.139	0.042
lg Fe	**0.836**	0.093	0.022	**0.798**	–0.045	0.276
lg Ce	**0.783**	0.099	0.368	**0.593**	**0.660**	–0.087
lg Eu	**0.761**	–0.076	0.227	**0.846**	0.248	0.066
lg Sm	**0.657**	0.364	0.346	—	—	—
lg La	**0.610**	0.299	0.307	—	—	—
lg Na	0.200	**–0.892**	–0.013	—	—	—
lg Cr	**0.508**	**0.771**	–0.008	0.244	–0.130	**0.958**
lg Rb	–0.025	–0.101	**0.896**	–0.042	**0.613**	–0.282
lg Th	0.333	0.335	**0.495**	0.015	**0.891**	0.069

Note: Bold numbers assign components of a principal loading/significance to explain the influence of the element.

show higher loadings in the second component, suggesting that the second cause of variation is the difference in composition of the tempering fraction. However, some of the Cr seems to be associated with the clay composition (refer to the Cr loading in the first component). The different signs for these elements point to their opposite concentrations in the suspected groups. The elements Th and Rb are correlated in the third component, and also appear to be concentrated in the temper fraction. In a way similar to the case of the Jagua region, a second analysis was carried out for the elements present in all of the 66 samples of the region.

The geology of the eastern territories of the central region is even more complex [7.23]. Successive formations of ultrabasic, basic and acidic rocks constitute the Jatibonico mountain chain in the middle east and the Meneses and Bamburanao mountain chains in the northeast.

The rivers descending from the Bamburanao and Meneses mountain chains to the northern coast cross formations of basic and intermediate rocks of constitution and age similar to those in the area of the rivers Arimao and Caunao in Jagua. Some

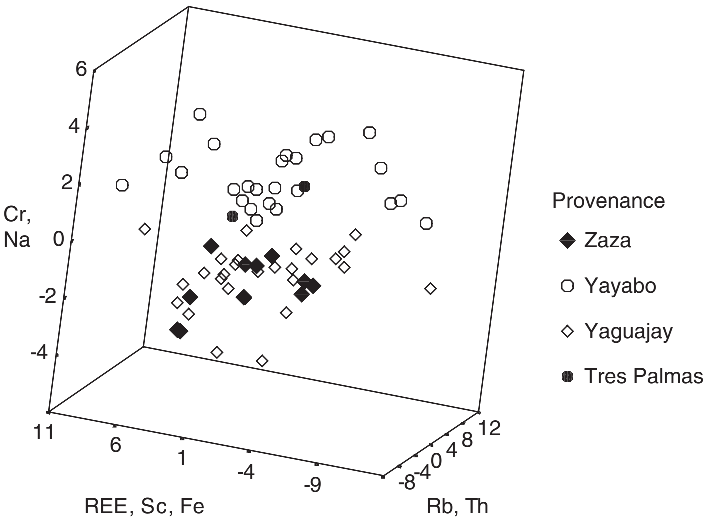

FIG. 7.5. Ordination of Yayabo and Yaguajay pottery in the principal component space.

ultrabasic massifs are also present in these mountain chains, although not so numerous as in the case of Sierra de Jatibonico. To the south, two major rivers convey sediments to the coastal areas: the Zaza to the southwest and the Jatibonico to the southeast.

Ordination in the principal component space (Fig. 7.5) shows several groups. The group showing the largest concentrations of Cr (open circles) and the lowest concentrations of Na corresponds to most of the fragments from Yayabo. Such large concentration values seem to be conditioned by the weathering of the ultrabasic and basic rocks (serpentinites, harzburgites, therzolites, wherlites and dunites) from the Sierra de Jatibonico. On the other hand, lower values for Cr and higher values for Na are found for the majority of fragments from the sites in Yaguajay (open diamonds).

Inspection of the paste texture of the Yaguajay fragments revealed a proportion of antiplastic particles of 50–80%, the most common constituent minerals being plagioclase, quartz, potassium feldspar and biotite, in decreasing order of abundance. Sometimes clinopyroxene and hornblende crystals were also observed. The relatively high abundance of plagioclase seems to be conditioned by its weathering from the Gabro massifs of the Meneses and Bamburanao mountains. The paste of Yayabo samples is not so heavily tempered, and the fraction of particles with sizes from 0.01 to 0.09 mm ranges from 45 to 60%. The most abundant minerals are quartz, plagioclase, potassium feldspar and, in the case of the samples with larger contents of

Cr, fragments of volcanic rocks (the four open circles in the upper left corner of Fig. 7.5). The petrography observations also confirmed the results for the concentration values determined by neutron activation analysis (NAA) for Yayabo pottery: lower concentrations of Na (due to the lower proportion of plagioclase) and higher contents of metals observed in this work, conditioned by the presence of clinopyroxene and volcanic rocks.

The fragments of the Archaic site Tres Palmas (solid circles in Fig. 7.5) show a composition similar to the ones from the Yayabo pottery. On the contrary, the composition of the fragments at the Neiva Viejo and Las Damas sites (solid diamonds) is more similar to the Yaguajay pottery.

The extreme complexity of the geology of the territory and the small quantity of analysed fragments do not allow more conclusive inferences.

7.6. CONCLUSIONS

The results obtained after interpretation of the compositional data have led us to several interesting conclusions:

(a) The communities living in the keys in the bay, as well as those occupying territories on its eastern bank, had well consolidated manufacturing processes. The potters from these sites employed clays from the beds located around the mouths of the Caunao and Arimao rivers, as well as from deposits located closer to the sources of the rivers. Finding a fragment that showed the features of a white man's face with beard and helmet confirmed their establishment until the arrival of the Spanish conquerors. An increase in the proportion of fragments with composition corresponding to the sources located upstream might be an indication of some displacement of their activities into territories located inland.

(b) The Ojo de Agua and Punta de Ladrillos sites, both located at the west side of the bay, exhibit some ceramic diversity, which includes fragments of the northwest and east mouth variations. Either the potters of these sites used raw materials of the two kinds described above, or they imported wares from the communities of the eastern territories. Whichever way, the proportion of ceramic fragments of the east mouth variation increased with time, as stated by their proportion in the latest stratigraphic layers of the Ojo de Agua site.

(c) The El Convento site, which has been described as being larger, exhibits the presence of pottery from the three Jagua variations, corroborating its role as a centre of intense exchange between the communities of the zone.

(d) Fragments found at the Mata Archaic site, located in the heart of an ultrabasic environment, show a composition similar to the east Jagua groups, thus indicating that they were probably acquired as a result of contacts with Agroalfarero communities.

(e) The Caunao and Lagunillas Archaic sites seem to have developed a local industry, since all of the samples found at these sites are exclusively of the Jagua east upstream group.

(f) The pottery from Yayabo investigated in this work shows higher concentrations of Cr, Sc and Fe, whereas the more abundant mineral present in the inclusions is the quartz. The ceramic from Yaguajay, although with average concentrations of the metals and REEs of the order observed in Jagua east mouth pottery, can be distinguished from the latter by its higher content of plagioclase. However, the scarcity of the material collected, as well as the scatter in the principal component space of the values observed, does not allow such a clear differentiation of the procurement areas as in the case of Jagua pottery.

REFERENCES

[7.1] KOZLOWSKI, J., Las Industrias de la Piedra Tallada de Cuba en el Contexto del Caribe, Serie Arqueología No. 5, Academia de Ciencias de Cuba, Havana (1975) 15 pp.

[7.2] FEBLES, J., "Estudio comparativo de las industrias de la piedra tallada de Aguas Verdes y Playitas. Probable relación de estas industrias con otras de Estados Unidos", Arqueología de Cuba y Otras Áreas Antillanas, Academia de Ciencias de Cuba, Havana (1991) 312–372.

[7.3] ROUSE, I., "Archaeology of the Maniabon Hills, Cuba", Anthropology, No. 26, Yale University Press, New Haven, CT (1942).

[7.4] GUARCH, J.M., El Taíno de Cuba, Academia de Ciencias de Cuba, Havana (1978) 263 pp.

[7.5] TABÍO, E., REY, E., Prehistoria de Cuba, 2nd edn, Academia de Ciencias de Cuba, Havana (1979) 269 pp.

[7.6] COLÓN, C., Códice Diplomático Americano de Cristóbal Colón, Colección de Cartas del Gran Descubridor del Nuevo Mundo, Almirante Mayor del Mar Océano, Virrey y Gobernador de las Islas y Tierra Firme de las Indias, Imprenta y Librería El Iris, Havana (1867).

[7.7] LAS CASAS, B., Apologética Historia Sumaria, 2 vols, Universidad Nacional Autónoma de México and Instituto de Investigaciones Históricas de México, Mexico City (1967).

[7.8] PICHARDO MOYA, F., Los Caneyes del sur de Camaguey, Rev. Arqueol. Etnol., Epoca II, Año III, No. 6–7, Enero–Diciembre, Havana (1948) 37–54.

[7.9] PICHARDO MOYA, F., Mapa Indoarqueológico de Camaguey, Rev. Arqueol. Etnol., Epoca IV, No. 1, Junio, Havana (1960) 7–25.

[7.10] GODO, P.P., RAMOS, J., GUADARRAMAS, R., Arqueología de Jatibonico, Museo Municipal de Jatibonico, Sancti Spíritus (1999).

[7.11] GONZÁLEZ ALEA, F.B., Localización de Pueblo Viejo: Sitio de fundación de Sancti Spíritus, Museo Provincial de Sancti Spíritus (1984).

[7.12] GONZÁLEZ MUÑOZ, A., AVELLO, I., Asiento Cantabria, Rev. Arqueol. Etnol., Epoca II, Año I, No. 3, Havana (1946) 11–27.

[7.13] MORALES PATIÑO, O., et al., Cayo Ocampo. Historia de un cayo, Rev. Arqueol. Etnol., Epoca II, Año II, No. 4–5, Havana (1947) 55–123.

[7.14] HERRERA FRITOT, R., "Estudio de las hachas antillanas", Comisión Nacional de la Academia de Ciencias de Cuba, Havana (1964) 146 pp.

[7.15] DOMÍNGUEZ, L., Arqueología de Centro-Sur de Cuba, Editorial Academia, ACC, Havana (1991) 102 pp.

[7.16] CHIRINO, J., Cerámica subtaína de Yaguajay, Vitrales, Suplemento cultural del periódico Escambray, Año VII, Sancti Spíritus (1992).

[7.17] CELAYA, M., GODO, P.P., Guacanayabo, Jagua, Yucayo: La variación local en la Cerámica, Centro de Antropología, Sancti Spíritus (1998).

[7.18] INTERNATIONAL ATOMIC ENERGY AGENCY, Report of the 1st Research Co-ordination Meeting of the Co-ordinated Research Programme on Nuclear Analytical Techniques in Archaeological Investigations, Smithsonian Institution, USA, Internal report, IAEA, Vienna (1998).

[7.19] DAVIS, J.C., Statistics and Data Analysis in Geology, 2nd edn, Wiley, New York (1986).

[7.20] INSTITUTO DE GEOLOGÍA Y PALEONTOLOGÍA, Mapa Geológico de la República de Cuba, Escala 1/250 000 (Editado por el Instituto de Geologia de la Academia de Ciencias de la URSS H-2111) Hoja 12 (F 17-7), Academia de Ciencias de Cuba, Havana (1980).

[7.21] RANKAMA, K., SAHAMA, T.G., Geoquímica, Editorial Águilar, Madrid (1962) 862 pp.

[7.22] INSTITUTO DE GEOLOGÍA Y PALEONTOLOGÍA, Petrología y Mineralogía. Descripciones petrográficas de muestras de cerámica, Rep. No. 43/2000 Laboratorio de Petrología y Mineralogía, Instituto de Geología y Paleontología de Cuba (2000).

[7.23] INSTITUTO DE GEOLOGÍA Y PALEONTOLOGÍA, Mapa Geológico de la Republica de Cuba, Escala 1/250 000 (Editado por el Instituto de Geologia de la Academia de Ciencias de la URSR, H-2111), Hojas 13 (F 17-80) y 21 (F 17), Academia de Ciencias de Cuba, Havana, 1980.

Chapter 8

CLASSIFICATION OF MAJOLICA POTTERY FROM COLONIAL HAVANA ON THE BASIS OF INAA

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Abstract

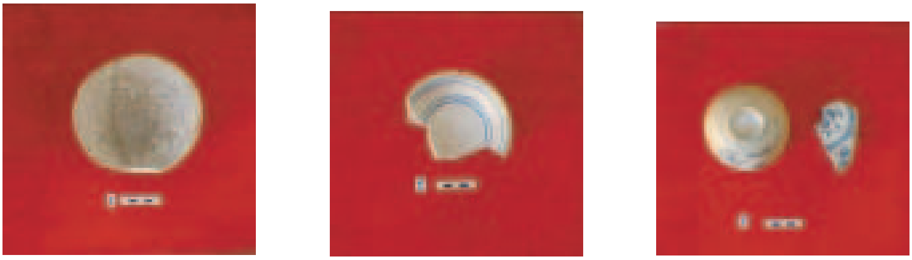
Fragments of pottery from the collections of Havana museums, corresponding to the Spanish colonial period (1600–1900 A.D.), were analysed by instrumental neutron activation analysis (INAA). Analysis of the results for the concentrations of 18 chemical elements was performed using principal component analysis (PCA) to reduce the data space size. Application of the Davis discriminant analysis procedure helped to define the chemical paste compositional reference units. For the final results, typological characterization of the colonial majolica pottery was complemented and enhanced.

8.1. ARCHAEOLOGICAL BACKGROUND

8.1.1. Presence of majolica from colonial Havana

Since the sixteenth century, and owing to its geographical location, Havana has been an important port for ships sailing between the Old and New Worlds. From the seventeenth century Havana, with its safe bay, was selected as a meeting point for the ships that awaited convoys departing for Spain. Havana was therefore an important trading and cultural centre in central America. Cuban museums have important collections of pottery from the colonial period. The large quantity of archaeological research conducted in the historic centre of Havana (Old Havana) since 1968 has revealed a marked presence of majolica pottery in the excavations performed in colonial contexts.

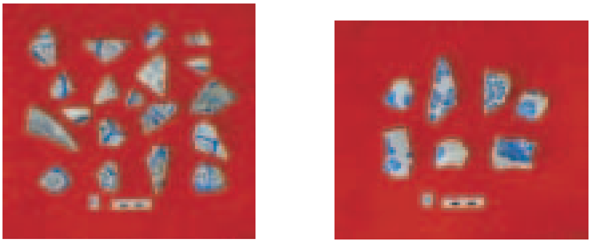
Majolica is a distinctively Hispanic category of glazed, wheel thrown ceramic, distinguished by its soft earthenware paste covered by an opaque vitreous enamel or glaze. Addition of tin oxide to the glaze produces an opacity which is also found on the technically related French faience and English and Dutch delftware.



Columbia simple

Yayal Azul
sobre Blanco

Catalana Azul
sobre Blanco



Puebla Polícromo

Puebla Azul
sobre Blanco

FIG. 8.1. Some of the majolica types found in colonial Havana.

FIG. 8.2. Santovenia Azul sobre Blanco.

Majolica pottery has been found at sites covering practically the whole period of the Spanish presence in Cuba [8.1], even in those corresponding to the earlier sixteenth century [8.2, 8.3]. Different researchers have identified ceramic artefacts in Havana and other major Cuban cities [8.4, 8.5], with the distinctive features described for the majolica types found in continental America and the Caribbean basin [8.6, 8.7], such as Isabella Polícromo, Santo Domingo Azul sobre Blanco, Columbia Simple, Yayal Azul sobre Blanco, Abó Polícromo, San Juan Polícromo, Caparra Azul, Ichtuknee Blue on White, Catalana Azul sobre Blanco, Puebla Polícromo and Puebla Azul sobre Blanco (Figs 8.1–8.3).

A group of ceramic artefacts that seemed to belong to an as yet undescribed majolica type was found during archaeological excavations performed in the house of the Counts of Santovenia. Typological features and a preliminary description of the ceramic were reported at the sixth Havana Symposium of Culture [8.8]. Further, similar fragments and artefacts were found at other Havana sites, and a more exhaustive study was carried out with the aim of characterizing these artefacts as belonging to a new (non-described) typology [8.9].

A pale cream paste distinguishes the Santovenia Polícromo type, with its variety of Santovenia Azul sobre Blanco showing light variations in its colour tone. The paste is covered with a very homogeneous, white bone thin tin–lead glaze. The most commonly identified utensils are deep and semi-deep dishes and plates, as well as cups and chamber pots. The colours used in the decoration motif of Santovenia Polícromo are blue, orange, violet and yellow. Some specimens show a very light green associated with the aforementioned colours. The combinations of colours in the designs are variable, the most frequent being blue with orange, although more complex designs include blue, orange, violet and yellow in a single piece. The typical decoration consists of simple circular lines, sinus circles, bands, chains of stylized leaves, floral motifs, concentric circles, spirals, garlands and semi-circles, sponge ovals and asps, among others. In the variety Santovenia Azul sobre Blanco, all the described typological features are present with the distinct use only of blue on white.

This type of majolica is found mainly in association with other types described for the late eighteenth and early nineteenth centuries. Our typological classification

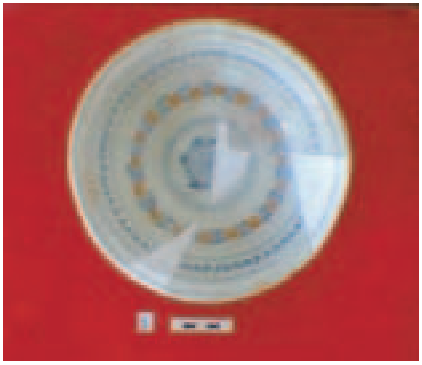


FIG. 8.3. Santovenia Polícromo.

points to a Spanish origin, probably from master workshops in Seville or Catalonia. The object of our research was to corroborate this hypothesis by establishing a specific compositional model that would enrich the characterization and help in finding a correlation with other compositional patterns that could indicate possible area(s) of provenance. The well known and described Sevilla Columbia Simple, Santo Domingo Azul sobre Blanco and Yayal Azul sobre Blanco, as well as the Catalana Azul sobre Blanco, seem to be the more probable related Majolica types.

8.1.2. San Francisco pottery

Large quantities of fragments of ordinary pottery are found in Old Havana churches and convents, where these fragments were used as light materials to fill the scallops over arcades. Some archival records mention the presence of local tile factories at several locations surrounding the city, but there is no evidence of their existence or of the manufacture of pottery. The ceramic fragments found in the arcades (especially over the chorus) seem to belong to a workshop established in Havana, since we found glazed (finished) and non-glazed specimens of similar typologies, as if the last were discarded after the first firing (Fig. 8.4).

The decoration is very simple, basically geometrical, with concentric circle design on the bottom. More complex designs include phytomorphic themes, with a central medallion on the bottom. Blue, green and black are the more frequent colours. The motifs appearing in most of the cases are sometimes not clearly defined, as testimony of failures in the preparation of pigments or in the firing process.

FIG. 8.4. San Francisco coarse pottery.

This ceramic ware provides the first reported evidence of a local glazed pottery where the workshop tried to follow the Spanish styles in Havana, and is at present under typological classification. A group of samples was analysed by instrumental neutron activation analysis (INAA) in order to start the characterization of its chemical composition.

8.2. RESEARCH PROBLEMS AND QUESTIONS

Our basic goals were to establish the provenance of the Santovenia type, as well as to corroborate the classification already performed on the basis of the stylistic features of several majolica types.

Our working hypothesis was that the observed features of the Santovenia majolica point to a Spanish origin.

8.3. MATERIALS AND METHODS

Samples were collected following the techniques of traditional ceramography, and the analytical portion was taken by removal of around 300 mg powder by drilling with a tungsten carbide burr. After the samples were powdered, they were air dried in ovens at 105 ± 5°C for 22–24 h and then allowed to cool in desiccators. The concentration values obtained for Co and Ta were disregarded owing to possible contamination during the sampling procedure [8.10].

INAA of more than 100 samples was carried out making use of access granted to the research facilities of several institutions in the region (Table 8.1). Interpretation of the results obtained was aided by comparing the values reported by Olin and Blackman [8.11] after analysis of 109 samples of different majolica types.

The interpretation of the results was performed using some of the tools for multivariate analysis included in the SPSS 7.5 package. The chemical compositional data were examined, with an exploratory approach, looking for patterning related to sites, subregions and procurement areas. A visual inspection of raw data and plots of scatter graphs crossing two elements at a time were included. To avoid the uneven influence of the differences in concentration ranges for some elements, the concentration values were transformed to base 10 logarithms. The dimensionality of the data matrix was reduced by extracting the principal components, and the components obtained were rotated with the Varimax method using Kaiser’s normalization. The latter allows enlargement of the loading of each element in the extracted components, and therefore makes interpretation of the results easier [8.12].

The discriminant analysis procedure described by Davis [8.13] was used to evaluate the distances between each individual sample and the centroids of the

TABLE 8.1. SUMMARY OF THE PERFORMED INAA DETERMINATIONS

Year/number of analysed samples	Irradiation/ measurement	Elements quantified
1998/50 Spanish and Puebla majolica	ININ, Mexico/ CEADEN[a]	25 Na, K, Sc, Cr, Fe, Co, Zn, As, Br, Rb, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U
1998/25 Domestic ware, supposed Havana	ININ, Mexico/ CEADEN	24 Na, K, Sc, Cr, Fe, Co, Zn, Br, Rb, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U
1999/34 Spanish majolica	NIST, USA	29 Na, K, Ca, Sc, Cr, Fe, Co, Zn, As, Br, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U, W
Total number of analysed colonial ceramics		109

[a] Centro de Estudios Aplicados al Desarrollo Nuclear.

supposed groups. As independent variables were used, the factor scores of the extracted components and the predicted probabilities for group membership were calculated by computing specific heights proportional to group size. The Mahalanobis distances from a sample to each alternative centroid provided the criteria for evaluating the relative probabilities of membership of the specimen in each of the groups.

8.4. DESCRIPTION OF THE ANALYSED SAMPLES

One hundred and nine samples of colonial pottery were analysed during 1998 and 1999. Table 8.2 summarizes the types of sample analysed. The results obtained by INAA were compared with the values reported by Olin and Blackman [8.11], thus enlarging the number of data for interpreting majolica samples to 196 cases.

8.5. RESULTS

The extraction of principal components for the matrix containing all the results obtained for majolica types (14 elements, 114 cases) is presented in Table 8.3. The

TABLE 8.2. SUMMARY OF THE ANALYSED COLONIAL SAMPLES

Type	Provenance	Number of analysed fragments
Majolica		
Santovenia Azul sobre Blanco	Supposed Spain	17
Santovenia Polícromo		7
Puebla Azul sobre Blanco	Puebla, Mexico	7
Puebla Polícromo	Puebla, Mexico	18
Sevilla Azul sobre Azul	Spain	20
Catalana Azul sobre Blanco	Spain	5
Columbia Simple	Spain	8
Coarse pottery		
Glazed Blue on White	Supposed Havana	1
Green Glaze		3
Thin walls, smooth surface		12
Unelaborated surface, middle to thick thickness		4
Acordelada, rough finishing		5
Results added to the interpretation [8.11]		
Mexico City White	Valley of Mexico	21
Columbia Plain (Mexican version)	Valley of Mexico	2
San Juan Polychrome	Valley of Mexico	5
San Juan Polychrome	Puebla, Mexico	17
San Luis Blue on White	Puebla, Mexico	17
Aucilla Polychrome	Puebla, Mexico	14
Mt. Royal Polychrome	Puebla, Mexico	4
Puebla Polychrome	Puebla, Mexico	2
Puebla Blue on White	Puebla, Mexico	1
Sevilla White	Spain	4
Columbia Gun metal	Spain	5
San Luis Blue on White (Spanish version)	Spain	3
Columbia Plain	Spain	14
Yayal Blue on Blue	Spain	5

first three extracted components accounted for 78% of the total variability in the data matrix.

The loadings of rare earth elements (REEs) in the first two principal components indicate that the main cause of the differences in the paste composition is conditioned by the use of different clays. There are also selective associations

TABLE 8.3. FACTOR LOADINGS (ALL MAJOLICA TYPES)

	Principal components (rescaled)		
	1	2	3
lg La	0.963	–0.069	0.081
lg Th	0.939	–0.004	–0.017
lg Ce	0.874	0.129	–0.278
lg Rb	0.810	–0.054	–0.099
lg Hf	0.801	–0.025	0.016
lg Sm	0.791	0.073	0.127
lg Cs	0.777	0.035	–0.011
lg Eu	0.569	0.222	0.016
lg Lu	0.557	0.488	–0.111
lg Fe	–0.058	0.769	–0.067
lg Cr	0.296	0.750	0.464
lg Sc	–0.234	0.750	–0.102
lg Yb	0.353	0.621	–0.366
lg Na	–0.034	–0.142	0.956

between the light and heavy REEs. This conclusion might seem to be trivial, since we are comparing samples from several loci in New and Old World kilns, but the goal of this first analysis was to test the validity of the typological classifications for majolica fragments and the hypothesis that the Santovenia type is of Spanish origin.

The Th and Hf contents are usually highly correlated due to their similar geochemical behaviour [8.14]. Use of volcanic ashes as tempering materials in the manufacture of Mexican pottery [8.15] and the presence of mica, biotite and muscovite in the temper used by the Spanish masters from Seville and Catalonia [8.16] are the causes of the highlighted differences in Th, Rb and Cs loadings in the first component extracted.

Our results confirmed the criterion proposed by Olin and Myers [8.15] to differentiate the manufacture of Puebla from the one established in the region of the Valley of Mexico, based on the differences in the concentrations of Cr and Fe. The factor loadings for Fe, Sc and Cr in the second component are conditioned by this observation. A third component, showing a high loading for Na, leads us to the assumption that, besides the already described causes of variation, there must exist a difference between some of the groups conditioned by an uneven proportion of plagioclase in the paste composition.

Ordination of the samples in the three dimensional space of the first components (Fig. 8.5) allowed corroboration of the provenance of all of the fragments classified as belonging to several majolica types by their close position to the samples analysed by Olin and Blackman. Only some of the samples initially classified as Sevilla Blue on Blue (12 from a total of 20) differ remarkably from the Spanish group. This group of samples has larger concentrations not only of Cr, Sc and Fe (open squares in the upper right corner of Fig. 8.5(a)) but also of Na (upper right corner in Fig. 8.5(b)). These features suggest that these samples belong to Italian Liguria [8.17], which also features Blue on Blue decoration.

The hypothesis of the Spanish origin of Santovenia majolica seems to be valid. All of the analysed samples from both Azul sobre Blanco and Polícromo types closely fit into the principal component space of the Spanish production.

An additional interpretation of the results obtained for the Spanish majolica was found in a similar way. Use of different clay resources is suggested by the loadings of some REEs in the first and second components. The influence of differences in the ratios of Na to K, Rb and Cs is highlighted by different signs of their loadings in the second and third components. One ought to suppose that the proportion of feldspar materials is the main cause of such differences. Petrography analysis of thin sections identified quartz as the major mineral constituent, as well as the presence of plagioclase. Crystals of biotite were also observed in some samples [8.18]. Nevertheless, a more detailed classification within the Spanish majolica based on the identification of some structure in the ordination of the results in the principal component space was not possible (Fig. 8.6) and Table (8.4).

8.5.1. Coarse pottery: local or imported?

The analysis of fragments of coarse crockery found in the fillings from the church scallops showed that this pottery could not be associated with any of the studied loci, from neither Mexico nor Spain. The pottery of this simple ware seems to have been established in Old Havana or in the surrounding areas, and local materials used for their manufacture. For only a few fragments were certain similarities in composition with some of the Puebla exponents noticed. On the basis of descriptions of shipment cargos, including imports to Havana, there are records of clays coming from Veracruz, Mexico; however, the small quantity of fragments analysed did not allow a conclusion to be drawn.

8.6. CONCLUSIONS

The application of NAA and statistical data evaluation allowed meaningful evidence to be found to help in the interpretation of several archaeological problems in the studied contexts. The main conclusions drawn are:

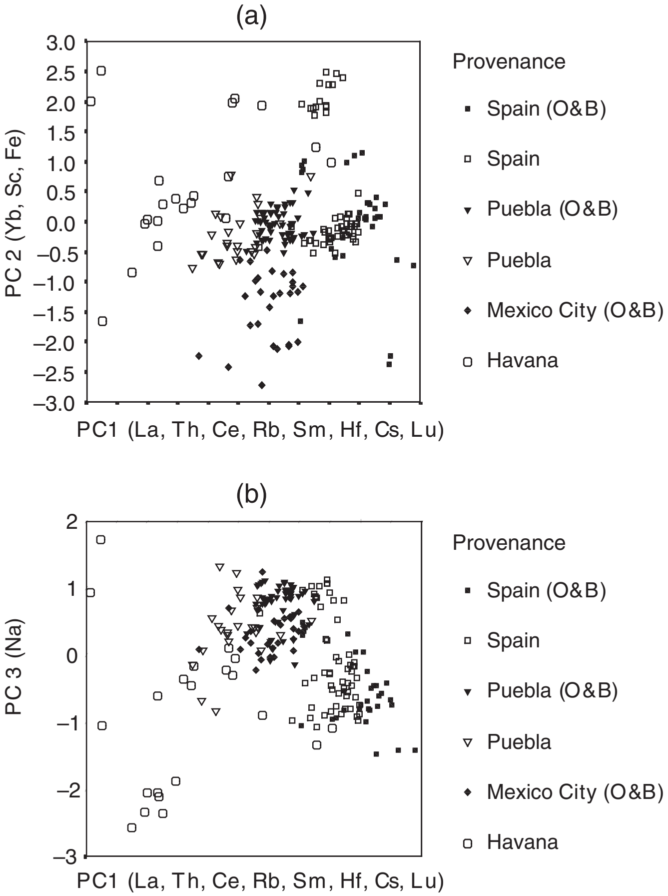


FIG. 8.5. Provenances of the classified majolica types: (a) differences in REE, transition metals (Sc, Cr, Fe), Rb and Th; (b) differences due to feldspar materials (Rb–K feldspar, Na plagioclase). O&B refers to data obtained by Olin and Blackman [8.11] for comparison.

(a) The study of Santovenia majolica served to prove its Spanish provenance.
(b) The classification of the fragments of some types of Spanish majolica was reinforced, and the presence of some Italian ware, wrongly classified as Sevilla Azul sobre Azul, was revealed.
(c) The common ceramics used in colonial Havana were produced by local masters, who exploited different procurement sources.

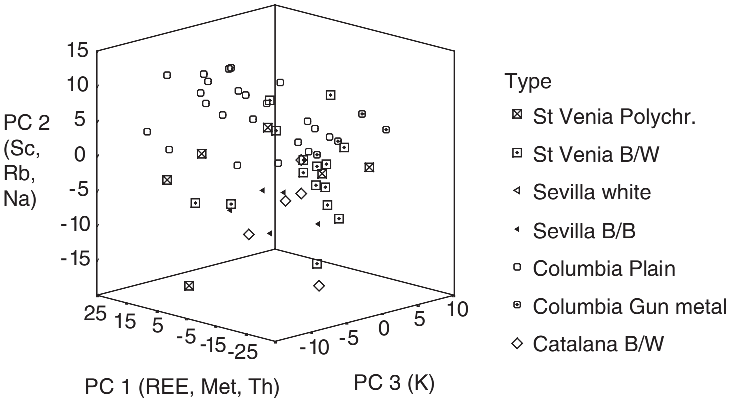


FIG. 8.6. Ordination of the Spanish majolica types in the principal component space.

TABLE 8.4. FACTOR LOADINGS FOR SPANISH MAJOLICA TYPES

	Principal components (rescaled)		
	1	2	3
lg Fe	0.893	0.132	0.039
lg Sc	0.878	0.214	0.026
lg Th	0.779	0.297	0.219
lg Ce	0.767	0.197	0.168
lg Cr	0.755	–0.176	–0.207
lg Hf	0.697	0.379	0.009
lg La	0.652	0.563	0.132
lg Sm	0.628	0.599	0.149
lg Lu	0.480	0.467	0.185
lg Yb	0.463	0.394	0.127
lg Eu	0.379	0.201	–0.090
lg Cs	0.230	0.931	0.020
lg Rb	0.164	0.912	0.156
lg Na	0.457	–0.493	–0.288
lg K	0.068	0.175	0.979

REFERENCES

[8.1] ROMERO ESTÉBANEZ LEANDRO, S., La Habana Arqueológica y Otros Ensayos, Editorial Letras Cubanas, Havana (1995) 243.

[8.2] PRAT PUIG, F., Significado de un Conjunto Cerámico Hispano del Siglo XVI de Santiago de Cuba, Editorial Oriente, Santiago de Cuba (1980) 147.

[8.3] DOMÍNGUEZ, L., “La transculturación en Cuba (siglos XVI–XVII)”, Cuba Arqueológica I, Editorial Oriente, Santiago de Cuba (1978) 33–50.

[8.4] PAYARÉS, R., “Informe de los trabajos de salvataje en el Morrillo”, Cuba Arqueológica II, Editorial Oriente, Santiago de Cuba (1980) 77–90.

[8.5] DOMÍNGUEZ, L., Arqueología Colonial Cubana: Dos Estadíos, Editorial Ciencias Sociales, Havana (1984) 112.

[8.6] GOGGIN, J.M., Spanish Majolica in the New World: Types of the Sixteenth to Eighteenth Centuries, Yale University Press, New Haven, CT (1968).

[8.7] DEAGAN, K., Artifacts of the Spanish Colonies of Florida and the Caribbean, 1500–1800, Vol. 1, Smithsonian Institution Press, Washington, DC (1987).

[8.8] ARRAZCAETA, R., “Estudio de la cerámica de una letrina en la casa de los condes de Santovenia”, paper presented at 6th Symp. on Culture, Havana, 1989.

[8.9] HERNÁNDEZ, O., CARLOS, A., ARRAZCAETA DELGADO, R., “Reporte de un nuevo tipo de mayólica del período colonial de Cuba”, paper presented at the 8th Symp. of Culture, Havana, 1992.

[8.10] INTERNATIONAL ATOMIC ENERGY AGENCY, Report of the 1st Research Co-ordination Mtg of the Co-ordinated Research Programme on Nuclear Analytical Techniques in Archaeological Investigations, Washington, 1997, IAEA, Vienna (1997).

[8.11] OLIN, J.S., BLACKMAN, M.J., Compositional classification of Mexican majolica ceramics of the Spanish Colonial Period, Adv. Chem. Ser. **171** (1978) 87–112.

[8.12] BISHOP, R.L., NEFF, H., Compositional data analysis in archaeology, Adv. Chem. Ser. **220** (1989) 57–86.

[8.13] DAVIS, J.C., Statistics and Data Analysis in Geology, 2nd edn, Wiley, New York (1986).

[8.14] BISHOP, R.L., “Aspects of ceramic compositional modeling”, Models and Methods in Regional Exchange (FRY, R.E., Ed.), SAA papers No. 1, Society for American Archaeology, Washington, DC (1980) 47–65.

[8.15] OLIN, J.S., MYERS, J.E., Old and New World Spanish Majolica technology, MRS Bull. **17** 1 (1992) 32–38.

[8.16] OLIN, J.S., HARBOTTLE, G., SAYRE, E.V., Elemental composition of Spanish and Spanish-Colonial majolica ceramics in the identification of provenience, Adv. Chem. Ser. **171** (1978) 200–229.

[8.17] BLACKMAN, M.J., Smithsonian Institute, Washington, DC, personal communication, 2000.

[8.18] IGP, Petrología y Mineralogía, Descripciones Petrográficas de Muestras de Cerámica, Informe No. 43/2000 (2000).

Chapter 9

ELEMENTAL COMPOSITION OF MEXICAN COLONIAL MAJOLICA USING INAA

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Abstract

Historic ceramics recovered in the Templo Mayor excavations in Mexico City were analysed by means of instrumental neutron activation analysis (INAA) to source 42 majolica sherds representing 20 different ceramic types and then compared with 85 samples analysed by Olin and Blackman. In previous archaeological interpretations, these types were assumed to have come from Spain, Mexico City and Puebla. The concentrations of 23 major, minor and trace elements were measured using INAA. A statistical treatment of the overall analytical data using cluster analysis (CA) and principal component analysis (PCA) methods was used to group the specimens according to the overall similarity of their compositional characteristics. Cluster analysis and PCA revealed two groups of ceramic types: Puebla and Mexico City. Our archaeometric results provide evidence that Spanish styles were copied in Mexico during the early colonial period, and that Mexico City and Puebla workshops shared a common stylistic tradition.

9.1. INTRODUCTION

Elemental and structural analyses of archaeological ceramics provide very useful information in three important areas: geographical origin, manufacturing technology and physical characteristics of fired materials. In this way the clay material can be analysed to identify which groups of clays determined typical pastes or typical ceramics whose homogeneity is related to a common origin. The original pieces are analysed, and their elemental composition can be compared with the composition of ceramic material collected at the archaeological site, of natural clay sources or of ceramics of known origin. In this way it can be determined, on the basis of whether a correlation exists, if they came from the same source [9.1]. Compositional analyses may provide the basis for archaeological interpretations of social interaction and consumption trends.

In this work two nuclear analytical techniques, instrumental neutron activation analysis (INAA) and proton induced X ray emission (PIXE), were used to study the manufacturing techniques and origin of ceramic materials found in the excavation work at Templo Mayor in Mexico City between 1978 and 1982. Ceramic fragments dating from the late fourteenth to the twentieth century were uncovered during archaeological work done by Matos [9.2]. Although colonial architectural features were scarce, more than 300 000 historic ceramic sherds were recovered in the architectural fills. Majolica collections consist of more than 18 000 fragments, sorted into more than 100 types based on conventional typological schemes, and further divided into fine, medium and common grades according to visual enamel differences [9.3, 9.4].

The manufacturing technique for majolica ceramic is of Arab origin and was introduced to Mexico by the Spaniards during the conquest. Through the sixteenth and seventheeth centuries ceramic vases made in Spain were sent to Mexico, and by the middle of the sixteenth century local production was started in Mexico City and Puebla [9.5–9.7]. Very little has changed in the manufacture of the base material for majolica, which is an earthenware with a vitreous opaque enamel surface made from tin oxide, lead oxide, sand (with a ratio of 25:4:4, respectively) and water, covering a terracotta ceramic body. Vessels of this ware are fired twice. The first firing process or biscuit fire (produces ceramics of biscuit colour) is carried out to produce the earthenware body. With the second firing process, the stanniferous enamel or glaze and the mineral oxides dissolved in water used to decorate the vessels are vitrified. Most majolica vessels are wheel thrown, except for large vessels, figurines and tiles, which are made with moulds [9.8].

Amongst the low quality ceramics produced in Mexico City during the sixteenth and seventeenth centuries, and considering their macroscopic characteristics [9.6], the best known of the common types are Mexico City, Mexico City Green on Cream, Mexico City Blue on Cream and San Luis Polychrome. Among the fine type ceramic, we have Mexico City White, San Luis Blue on White, Fig Springs Polychrome, La Traza Polychrome and Tacuba Polychrome. The less representative types are known as Valle earthenware, which are possibly the earliest in Mexico City, and Tlalpan White, Tlalpan Blue on White and Guadalupe Blue on White. It is possible that some of these types were also produced in the city of Puebla.

During the colonial period a pseudo-majolica in which tin was not used as an opacifier and known as Romita Sgraffito, and the monochromic version, as Romita Plain. It is deduced that this type of ceramic was produced in the Mexico City area, due to the similarity with Aztec pottery [6].

Towards the seventeenth century a new majolica style with improved quality was being produced, presumably in the city of Puebla. The most relevant types are Puebla Polychrome, Abo Polychrome, Castillo Polychrome and Puebla Blue on White. This last type of ceramic continued to be produced until the eighteenth century. According to records it is possible that the Puebla Polychrome and Abo Polychrome were also produced in Mexico City. Spanish majolica has a strong Morisco influence and corresponds to the types Columbia Plain, Santo Domingo Blue on White, Yayal Blue on White, Isabela Polychrome and Santa Elena Spotted Blue on White. The last three types are found in lesser amounts than the rest. The Morisco majolica is of low quality in manufacture and is decorated in the same way as the majolica known as Guadalquivir, which comes possibly from Seville in the types Seville White and Seville Blue. The most common type of majolica found in collections is the Ichtucknee Blue on White with its fine design inscribed on Chinese porcelain of the sixteenth and seventeenth centuries. There are also ceramic vases brought from Italy of the monochromic, bichromic and polychromic types and also of the types Fayenza White, Montelupo Polychrome and Ligurian Blue on Blue.

In archaeological terms majolica is considered a symbol of socioeconomic and ethnic status due to its relatively high cost. Its diverse style has been used as a basis for the development of typology [9.5, 9.6] and has been used as a chronological indicator of the types of occupation in different times.

Our goal is to achieve a better understanding of the origin, technological procedures and differences in clay formulas of the majolica vessels used by the inhabitants of Mexico City from the sixteenth to the eighteenth century. Our study focuses on the definition of compositional groups associated with clay sources, in order to address issues of production, exchange and consumption of majolica ceramics in the capital of the former New Spain.

9.2. EXPERIMENTAL PROCEDURE

From the types identified or established in the archaeological analyses of majolica collections from Templo Mayor [9.3], samples were sorted according to typological schemes previously developed [9.5, 9.6] on the basis of paste and decoration attributes. Specimens were mainly selected on the basis of macroscopic differences for paste composition and enamel quality — believed to represent grades recorded in historical documents, showing temporal variations as well as probable provenance.

The forty-two samples selected (Table 9.1) represent types commonly assumed to have been produced: in Mexico City (twenty-five fragments) dating from the sixteenth and seventeenth centuries; Puebla (ten sherds) dating from the seventeenth and eighteenth centuries; Spain (five sherds) dating from the seventeenth century; and probably Spain (two sherds) dating from the eighteenth century.

TABLE 9.1. SAMPLES OF MAJOLICA TYPES FROM THE TEMPLO MAYOR EXCAVATIONS IN MEXICO CITY

Number	Type	Century	Assumed provenance
001TM	Mexico City Green on Cream	16th	Mexico City
002TM	Huejotzingo Blue on White	18th	Puebla
003TM	San Luis Polychrome	16th–17th	Mexico City
004TM	Mexico City White	16th	Mexico City
005TM	Mexico City Cream	16th	Mexico City
006TM	Ichtucknee Blue on White	16th	Spain
007TM	San Luis Blue on White	16th–17th	Mexico City
008TM	Fig Springs Polychrome	16th	Mexico City
009TM	Tacuba Polychrome fine grade	16th	Mexico City
010TM	Tacuba Polychrome common grade	16th	Mexico City
011TM	Tlalpan Blue on White	16th	Mexico City
012TM	Fig Springs Polychrome common grade	16th	Mexico City
013TM	Mexico City Blue on Cream	16th	Mexico City
014TM	Mexico City Green on Cream	16th–17th	Puebla
015TM	Huejotzingo Blue on White	18th	Mexico City
016TM	San Luis Polychrome	16th–17th	Mexico City
017TM	Mexico City Cream	16th	Mexico City
018TM	Mexico City White	16th	Mexico City
019TM	Tacuba Polychrome	16th	Mexico City
020TM	Tacuba Polychrome	16th	Mexico City
021TM	Tacuba Polychrome	16th	Spain
022TM	Santo Domingo Blue on White	16th	Spain
023TM	Santo Domingo Blue on White	16th	Spain
024TM	Columbia Plain	16th	Spain
025TM	Columbia Plain	16th	Spain
026TM	Romita Plain	16th	Mexico City
027TM	Romita Plain	16th	Mexico City
028TM	Mexico City Blue on White	16th–17th	Mexico City

TABLE 9.1. (cont.)

Number	Type	Century	Assumed provenance
029TM	Puebla Blue on White	17th–18th	Puebla
030TM	Puebla Blue on White	17th–18th	Puebla
031TM	Puebla Polychrome	17th	Puebla
032TM	Tacuba Polychrome	17th	Puebla
033TM	Mexico City Polychrome	16th–17th	Mexico City
034TM	Mexico City Polychrome	16th–17th	Mexico City
035TM	Abo/Aranama Polychrome	18th	Puebla
036TM	Abo/Aranama Polychrome	18th	Puebla
037TM	La Traza Polychrome	16th	Mexico City
038TM	La Traza Polychrome	16th	Mexico City
039TM	Marine ware	18th–19th	Spain?
040TM	Marine ware	18th–19th	Spain?
041TM	Puebla Blue on White early Chinoiserie	17th	Puebla
042TM	Puebla Blue on White early Chinoiserie	17th	Puebla
043TM	Huejotzingo Blue on White	18th	Puebla
044TM	Mexico City Green on Cream	16th–17th	Mexico City

The ceramic pieces were analysed using NAA to study the elemental composition of the paste. It is important to note that X ray diffraction, electronic microscopy and proton induced X ray emission techniques were also used to analyse all the materials in order to obtain as much information about the composition and morphology of glazes and decorative pigments. However, these results are presented elsewhere [9.9, 9.10].

9.2.1. Neutron activation analysis

For NAA, a central portion from each sherd was crushed and homogenized in an agate mortar to obtain a fine powder. From the homogenized material, approximately 100 mg was sampled for each specimen. All samples were sealed in small polyethylene vials and placed in a polyethylene rabbit. The vials and rabbits were marked with India ink, cleaned with distilled water and dried. The reference material used was the standard reference material NIST SRM-1633b. The samples and reference material were irradiated in a Triga Mark III nuclear reactor at a flux of about 1.65×10^{12} neutrons·cm^{-2} ·s^{-1} for two periods: 1 min and 4 h.

After irradiation and a cooling period, the gamma rays of the samples and reference material were measured under identical geometrical conditions with a co-axial HPGe detector semiconductor (GEM 40190P, ORTEC), coupled to a multichannel pulse height analyser (ACE ORTEC with 32 thousand channels). The energy resolution F of the system was 2.5 keV for 1332 keV. Samples subjected to 1 min of irradiation were analysed after two cooling periods of 1 min and 3 h, and then counted for 100–500 s, respectively [9.9].

Samples subjected to irradiation for 4 h were stored for eight days, then counted for 1 or 2 h each. Eight days was chosen to allow the decay of short lived species (Mg, Ti, Ca, Na, K, Mn and Ba). For example, sodium is the strongest single contributor to the background at earlier measurement times. This analysis is programmed for radioactive species with half-lives in the range of 1–7 days and gives results for the following elements: U, Sm, Lu, La, Zn, As, Yb and Sb. The same samples were set aside for a further cooling period of at least two weeks. This process lowered the background even further to obtain a better analysis of the longer lived elements: Fe, Ce, Sc, Ta, Eu, Zn, Co, Cs, Sb, Cr, Hf, Th, Ba, Ni and Rb. The samples were counted for periods of more than 2 h [9.11, 9.12].

The spectra obtained from the counting were stored and processed using the ORTEC MAESTRO code for Windows software. The data were corrected considering the dead time, sample weights and half-lives. They were then compared with the mean value of the standard for the same peak. A computer program developed at the Instituto Nacional de Investigaciones Nucleares (ININ) was employed to calculate the concentrations in parts per million (ppm) or as percentages.

Of the forty-two samples, two (036TM and 037TM) were eliminated for the final analysis since they were contaminated as a result of the preparation process. In order to support our interpretation of the results, we compared them with the data reported by Olin and Blackman [9.13] for 85 samples of majolica, and seven majolica samples from Templo Mayor analysed in the University of Missouri Research Reactor Centre (MURR) laboratory (Table 9.2) [9.13, 9.14].

9.3. RESULTS AND DISCUSSION

9.3.1. Instrumental neutron activation analysis

Nineteen chemical elements were determined by INAA in the whole population (forty-two specimens): eight alkaline and alkaline earth elements (Na, K, Rb, Cs, Mg,

TABLE 9.2. NUMBER OF MAJOLICA SAMPLES ANALYSED BY OLIN AND BLACKMAN

Type	Provenance	Number of analysed samples
Mexico City White	Central Mexico	17
Columbia Plain	Central Mexico	2
San Juan Polychrome	Central Mexico	3
La Trinidad (modern ceramic)	Puebla, Mexico	9
San Juan Polychrome	Puebla, Mexico	8
San Luis Blue on White	Puebla, Mexico	16
Aucilla Polychrome	Puebla, Mexico	12
Mt. Royal Polychrome	Puebla, Mexico	4
Puebla Polychrome	Puebla, Mexico	2
Talimali Polychrome	Puebla, Mexico?	4
Fig Springs Blue on White	Puebla, Mexico	1
Mexico City White	Templo Mayor, Mexico City	6

Ca, Sr and Ba), eight transition elements (Ti, Hf, Cr, Mn, Fe, Co, Ta and Sc), one semi-metal (Al) and six rare earth elements (La, Lu, Ce, Sm, Eu and Th). The analytical precision of the reported data is satisfactory since, in general, the measurement uncertainty is about 10%, except for Th and Eu due to interference and unsatisfactory sensitivity for the countings.

9.3.2. Statistical analysis

In order to detect differences and similarities in elemental compositions, identify ceramic groups that enable meaningful archaeological interpretations and link ceramics analysed to groups previously established by Olin and Blackman [9.13], we made at first a visual inspection of the data; after that we generated binary scatter plots and used two multivariate data methods: cluster analysis (CA) and principal component analysis (PCA).

Visual inspection of the data revealed that significant variations exist in the elemental compositions. Evident differences in the concentrations of Cr, Fe, Sc, Na, K, Ca, Hf and Ta exist between the samples previously established as Puebla and Mexico City by Olin and Blackman [9.13]. In the case of Ce, Ba and Sr, these differences are less obvious, while the rare earth concentrations are in general very

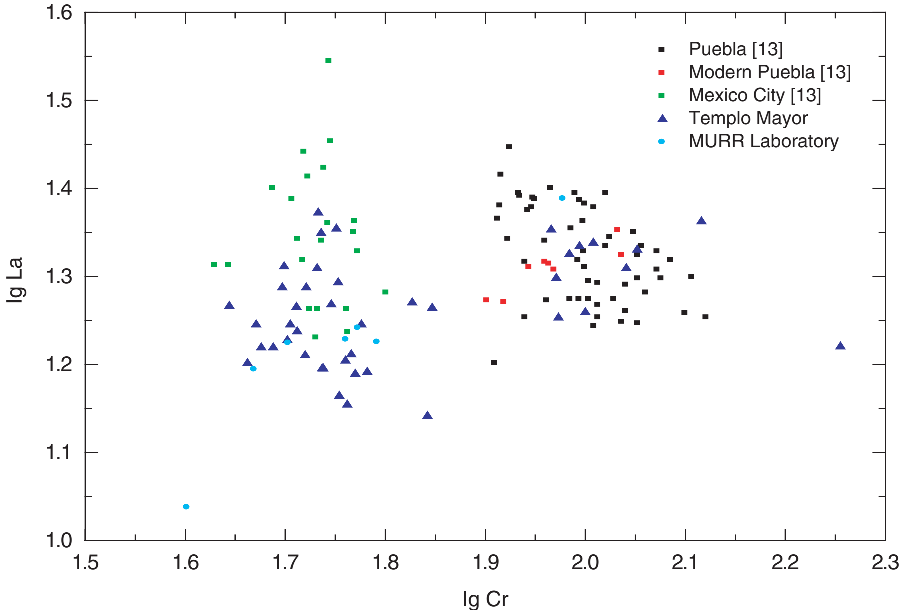

FIG. 9.1. Scatter plot for chromium versus lanthanum of majolica pot sherds from Puebla and Mexico City (Templo Mayor).

similar in the Puebla and Mexico City samples, apart from the Eu, Ce and Lu concentrations, which show a tiny dissimilarity. On the other hand, the *x–y* graphs generated for all combinations of elements show that the presence of chromium always results in the formation of two groups of ceramics: Puebla and Mexico City (Fig. 9.1). In addition, the correlation between the elements is highly significant in the case of the rare earths, between Sc and rare earths, Fe and Sc, Sc and Hf, and Hf and Fe. These high correlations can be explained from a geochemical point of view. For example, rare earths are chemically very similar to one another and consequently show notable similarities in their geochemical behaviour; this is why they correlate to each other. Scandium, although chemically resembling the lanthanides, differs materially from them in its occurrence in igneous surroundings as to weathering and formation of sediments. These differences are due to the smaller ionic size and weaker basic properties of scandium compared with the lanthanides. Therefore, scandium does not always accompany these metals in minerals if the lanthanide series is specially concentrated. The rule is that when the lanthanides accompany scandium in minerals, a relatively high content of ytterbium and lutetium is always to be expected. Nonetheless, the bulk of the scandium is concealed in the ferromagnesium minerals, explaining its high correlation with iron. Hafnium preferentially accompanies scandium and the lanthanides in minerals [9.15].

The presence of chromium in clays is certainly due to the fact that most of the usable clays found in nature contain iron (limonite) and other mineral impurities (e.g. quartz and dolomite). Because the chromium ion closely resembles the ferric ion in its chemical properties, ionic size and ionic charge, it follows iron during its exogenic cycle. Iron ores of igneous rock are often chromiferous, being mainly composed of chromite ($FeCr_2O_4$) [9.15]. On the other hand, it is important to note that chromium is notably enriched in coal ashes. Utilization of shrub ashes in manufacturing tin glaze, as well as the use of volcanic ashes as tempering materials in clays in the manufacture of Mexican ceramics, has already been documented [9.6, 9.13]. This type of volcanic ash contains a medium amount of silica, Fe and Mg and, consequently, also contains Cr. This could explain the differences in the Cr and Fe concentrations between the Puebla and Mexico City data. The Mexico City clays contain less Fe and Cr than do the Puebla clays. From that information we can suggest three interpretations:

(1) That volcanic ashes were added, as tempering materials in the clays, to both types of pottery (Puebla and Mexico City) in different proportions.
(2) That only Puebla clays contain volcanic ashes.
(3) That neither Puebla clays nor Mexico City clays contain volcanic ashes and therefore the differences in concentrations of chromium and iron depend upon the kind of clay minerals contained in each clay. Considering that the volcanic ashes are rich in iron, its addition in clays inevitably involves an increase in intensity of the colour of pastes, producing effects on the surfaces and the colour of glazes. The result is a larger addition of opacifier (tin) to the glaze in order to obtain an opaque white glaze, but at a higher cost. Economically, the use of volcanic ashes in this type of ceramic would not be profitable; on the other hand, according to our glaze analysis of the Templo Mayor samples, they contain low amounts of tin (<3%) [9.10].

In conclusion, we consider it less probable that volcanic ashes were widely used in the preparation of Templo Mayor pastes. Consequently, the differences between chromium and iron concentrations in the Puebla and Mexico City ceramics would mainly be caused by the use of different kinds of clay.

The first step in analysing the data in CA and PCA was to transform them to log base 10 values, which effectively scaled the data to account for the large differences in magnitude between major elements and trace elements [9.16]. After that, we established the elements that would enable the differentiation of clays in order to achieve a more reliable classification of the pottery samples.

It is important to take into consideration that the composition of the raw material is altered during the overall processing of the pottery due to the selection of materials, washing, and addition of a temper or of a colouring agent. For example, heating at 700–1000°C may modify the chemical composition of the pottery; elements such as Cl, Br, As and Sb may be volatilized. The concentrations of mobile ions such as Ca, Na or Mg may also be modified during the washing of the materials. Other alterations may occur during the burial of the samples, especially due to the phenomenon of phosphate ion retention [9.17]. The elements selected for the statistical analysis were therefore those which have a high stability in clay minerals, for example elements with a large radius, which may easily substitute for K, Na or Ca, or Rb, Cs and Ba as well as the rare earth and transition elements, strongly stabilized in octahedral sites by the influence of transition metals such as Cr, V, Ni and Co [9.17–9.19]. Thus, taking into account previous geochemical considerations, the visual inspection of data and the results obtained of the binary scatter plots, the elements which were found to be most useful in differentiating clays are: rare earth elements, Cr, Fe, Hf, Sc, Cs, Rb, Co, Ta and K.

In order to gain a preliminary notion as to the number of source groups that may be presented in the body of the 136 majolica samples, the results were subjected to cluster analysis by means of Ward's method, using the STATISTICA 5.1 statistical package. The dendrogram (Fig. 9.2) indicated the existence of two well defined

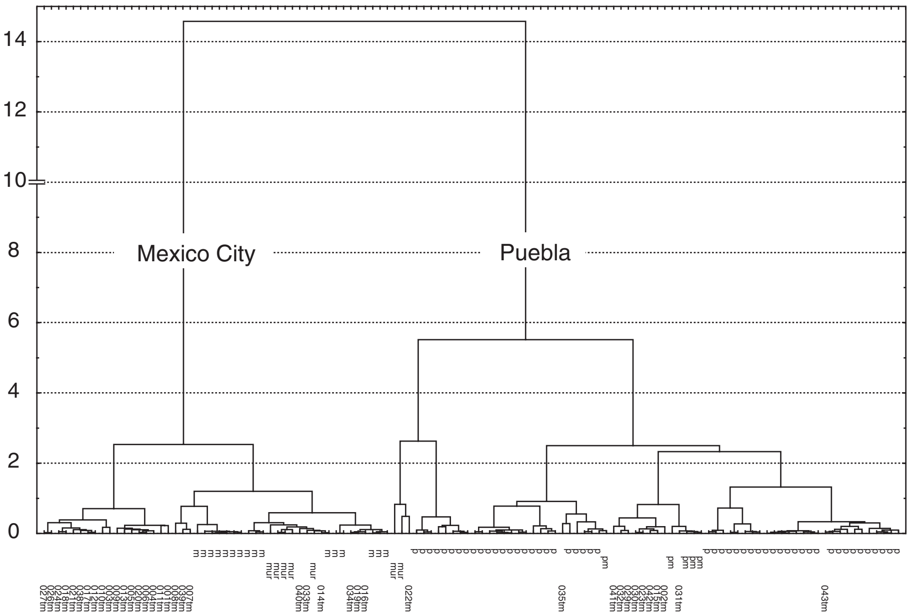

FIG. 9.2. Cluster analysis dendrogram of majolica samples from Puebla and Mexico City (Templo Mayor): p, Puebla; pm, modern Puebla; m, central Mexico; tm, Templo Mayor; MURR, MURR laboratory.

clusters: Mexico City and Puebla. Only two samples, assumed as having been manufactured in Mexico City (AZP25 and AZP29), are classified as Puebla. On the other hand, it is worth stressing that from our results it was not possible to identify a third group which in theory corresponds to a ceramic produced in Spain. The Spanish ceramics, Marine ware, Columbia Plain and Ichtucknee Blue on White, are classified, in these cluster analyses, as Mexico City ceramics. The Santo Domingo Blue on White type is assigned to a group of Puebla potteries. The modern Puebla samples are grouped in the Puebla cluster.

To increase the statistical significance and overcome the drawbacks of cluster analysis using Euclidean distances of raw elemental compositions, all the data were transformed to characteristic vector co-ordinates by means of PCA. The resulting components were rotated using the varimax method. Figure 9.3 shows the evident difference between Puebla and Mexico City samples using PCA. The modern Puebla samples could be considered as a subgroup of the Puebla cluster with similar characteristics as the bulk group but not with the same elemental composition. Thus, in the case of the analysis of pottery with highly dissimilar origins, the comparisons between ancient and modern Puebla pottery could be made only as a first approximation on the basis of visual inspection. The plot also shows samples assumed as manufactured in Mexico City that are classified as Puebla and vice versa. The Spanish samples from the Templo Mayor followed practically the same classification shown in the cluster analysis. Consequently, we identified these samples as ceramics made in Mexico following Spanish styles.

Our results confirm the criterion proposed by Olin and Blackman [9.13] to differentiate the manufacture of the Puebla ceramics and the Valley of Mexico ceramics from the concentrations of chromium and iron. It is important to note that a clay body is composed of clay minerals, not plastic and melting agents. It is therefore practically impossible to obtain similar chemical compositions using natural clay and paste ceramics. Consequently, the origin of an archaeological ceramic should not be based on this type of comparison. We considered it more advisable to use known origin ceramics in the identification of paste groups.

9.4. CONCLUSIONS

A ceramic body is a mixture of clay minerals, plastic agents and melting agents. In our case, the ratio of these materials contributes to the creation of a clay body that fits the enamelled surface, preventing it from crazing or shattering during the firing or cooling down processes. A proper enamel body fit is arrived at by sensible application of the principles of thermal expansion and contractions [9.20]. Ceramic bodies are highly vulnerable to mineralogical changes. The ratio of the three components affects the strength of the final product and its technical and functional

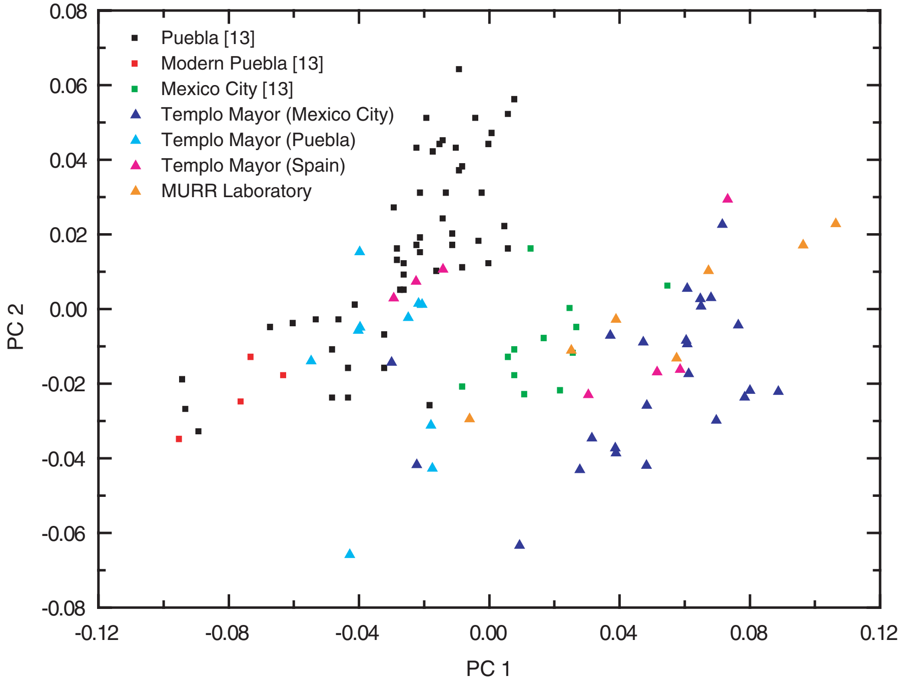

FIG. 9.3. Principal component plot of the characteristic vectors 1 (Fe, Cr, Sc, Ca, Ka and Co) and 2 (rare earth elements, Ta, Rb, Cs and Hf) of majolica samples from Puebla and Mexico City (Templo Mayor).

performance. This ratio is therefore a focal point in the description of the ceramic bodies of tin enamelled earthenwares.

Two major clusters based on INAA, corresponding to majolica from Mexico City and Puebla, composed the resulting dendrogram and plot of principal components (Fig. 9.2). The INAA results confirmed that most of the ceramic types archaeologists believed to have been produced in Mexico City or Puebla were indeed manufactured there. Two samples of a type assumed to come from Puebla turned out to be from Mexico City (Puebla Polychrome, 031TM, and Puebla Blue on White, 029TM). This result confirmed historical information recorded in the ordinances established to regulate majolica production in Mexico City between 1677 and 1681, which defined the quality and styles of majolica [9.21]. However, some samples believed to represent Mexico City majolica types fell into the Puebla group. This might be explained by the close proximity of these two potting centres, suggesting a similar composition of the clays used in these cities due to geomorphological similarities in the central Mexican highlands. Another possibility is that, contrary to previous assumptions, similar vessels were produced in Mexico City and Puebla.

The historical, archaeological and archaeometric evidence demonstrates that Mexico City not only used ceramics manufactured elsewhere but was an active majolica production centre for more than 350 years. Majolica potters assimilated global influences and created styles.

It is interesting to note that the specimens believed to represent Spanish majolica types formed part of the Mexico City or the Puebla group, as well as of the group whose source is either Puebla or Mexico City. We may infer that the Spanish styles were widely copied at these pottery centres during the early colonial period.

On the basis of the paste composition of the samples analysed, we were able to differentiate two majolica groups: one manufactured in Puebla and another manufactured in Mexico City. This confirms that both cities were pottery production centres, as historically and archaeologically recorded. It also confirms that during the colonial period they shared common stylistic traditions and emulated ceramics manufactured in Spain. Stylistic similarities between European and New World majolica industries provide evidence of the developmental trends.

We must emphasize that no Spanish specimens were analysed in the present study. Stylistic types copied from Europe and reproduced in both Mexico City and Puebla are related to the socioeconomic status or ethnic group of consumers, since ceramics were employed as status symbols in colonial New Spain [9.3, 9.4, 9.22], particularly at the capital of the viceroyalty.

According to archival information (mainly probate and store inventories) Spanish majolica was two to three times more expensive than Mexican majolica [9.23] and, probably, tin enamelled earthenwares from Puebla were more expensive than those produced in Mexico City. Copies were a result of economic and market variables as well as consumer choice.

Many styles may have been developed in Mexico City in the middle of the sixteenth century and later copied in Puebla. By the middle of the seventeenth century, both Mexico City and Puebla shared homogeneous styles, as shown in guild regulations and proven in our compositional analyses.

The compositional similarities of the Mexico City and Puebla groups may be attributed to the exploitation of clay sources from the volcanic deposits of the geomorphologically homogeneous central Mexican highlands. Another possibility is that potters from both centres intentionally mixed clays coming from sources different from those located in the Basin of Mexico or the Puebla valley to produce majolica. We dispute this since the transportation and energy costs involved would have had a negative effect on the market price of the finished products. In any instance, from the sixteenth to the eighteenth centuries the same clay sources were exploited and employed to manufacture majolica at these potting centres as proven by our analyses.

Archaeological inferences about cultural changes, economic trends and social interaction may be based upon differences in compositional analyses. The provenance of majolica is more complicated than visual studies alone can deal with. Future studies will provide further evidence about the complexity of majolica production in central Mexico during the colonial period.

REFERENCES

[9.1] ORTON, C.L., TYRES, P., VINCE, A., La Cerámica en Arqueología, Crítica, Barcelona (1997) 309 pp.

[9.2] MATOS, E., "Las excavaciones del Proyecto Templo Mayor, 1978–1981", El Templo Mayor, Excavaciones y Estudios, Instituto Nacional de Antropología e Historia, Mexico City (1982).

[9.3] FOURNIER, P., CHARLTON, T.H., "Correlatos materiales de diferencias socioétnicas en Nueva España", Historical Archaeology in Latin America (Proc. 15th Int. Conf. Columbia, 1996), Vol. 2 (SOUTH, S., Ed.), University of South Carolina, Columbia, SC (1996) 71–76.

[9.4] FOURNIER, P., CHARLTON, T.H., "La tradición de mayólica en México (siglos XVI al XIX)", Primer Congreso Nacional de Arqueología Histórica, Memoria (FERNÁNDEZ, E., GÓMEZ, S., Eds), Instituto Nacional de Antropología e Historia, Mexico City (1998) 419–426.

[9.5] GOGGIN, J.M., Spanish Maiolica in the New World, New Haven, Yale Publications in Anthropology No. 72, Yale University Press, New Haven, CT (1968).

[9.6] LISTER, F.C., LISTER, R., Sixteenth Century Maiolica Pottery in the Valley of Mexico, Anthropological Papers of the University of Arizona 39, University of Arizona Press, Tucson, AZ (1982).

[9.7] DEAGAN, K., Artifacts of the Spanish Colonies of Florida and the Caribbean, 1500–1800, Vol. 1, Ceramics, Glassware, and Beads, Smithsonian Institution Press, Washington, DC (1987).

[9.8] FOURNIER, P., "Mexican ceramic analysis", The Presidio and the River on the Borderlands, Vol. 1 (VIERRA, B.J., CHAPMAN, R.C., Eds), University of New Mexico, Albuquerque, NM (1997) 199–256.

[9.9] MONROY GUZMAN, F., FOURNIER, P., FALCÓN, T., DE LA TORRE, J., "Mexican colonial majolica analysis using neutron activation and X-ray diffraction techniques", Archaeometry (Proc. 32nd Int. Symp. Mexico City, 2000) (BARBA, L., Ed.), Universidad Nacional Autónoma de México, Mexico City (2001) (CD-ROM).

[9.10] MONROY GUZMÁN, F., GÓMEZ, MIRANDA, S.J., RUVALCABA, J.L., DE LA TORRE, J., "Manufacturing techniques of glazed pottery found at the ex-convent of Santo Domingo in Oaxaca", ibid.

[9.11] KULEFF, I., DJINGOVA, PENEV, R., Instrumental neutron activation analysis of pottery for provenience study, J. Radioanal. Nucl. Chem. **99** 2 (1986) 345–358.

[9.12] KILIKOGLOU, V., GRIMANIS, P., VASSILAKI-GRIMANI, M., GRIMANIS, A.P., Comparison between two INAA methods applied to chemical characterization of ancient ceramics, J. Radioanalyt. Nucl. Chem. **152** 2 (1991) 469–477.

[9.13] OLIN, J.S., BLACKMAN, M.J., Compositional Classification of Mexican Majolica Ceramics of the Spanish Colonial Period, Archeological Chemistry IV, American Chemical Society, Washington, DC (1989) 87–112.

[9.14] NEFF, H., Missouri University Research Reactor Centre, Columbia, MO, personal communication, 2001.

[9.15] GUNTER, F., Principles and Applications of Geochemistry, 2nd edn, Prentice-Hall, Englewood Cliffs, NJ (1997).

[9.16] WAKSMAN, S.Y., Les Céramiques Byzantines de Fouilles de Pergame. Caractérisation des Productions Locales et Importées par Analyse Elémentaire par les Méthodes PIXE et INAA et par Pétrographie, PhD Thesis, Université Louis Pasteur, Paris (1995).

[9.17] DE SENA, E., LANDSBERGER, S., PEÑA, J.T., WISSEMAN, S., Analysis of ancient pottery from the Palatine Hill in Rome, J. Radioanal. Nucl. Chem. **196** 2 (1995) 223–234.

[9.18] DIEBOLT, J., RICQ, J.C., An attempt to select suitable elements to characterize an ancient ceramic by neutron activation analysis, J. Radioanal. Chem. **39** (1977) 9–20.

[9.19] ROSSINI, I., ABBÉ, J.C., GUEVARA, B., TENORIO, R., Characterization of Costa Rican potsherds by neutron activation analysis, J. Radioanal. Nucl. Chem. **170** 2 (1993) 411–421.

[9.20] FOURNIER, P., “Tendencias de consumo en México durante los períodos colonial e independiente”, Approaches to the Historical Archaeology of Middle and South America, Monograph 38 (GASCO, J., SMITH, V., FOURNIER, P., Eds), University of California, Los Angeles, CA (1997) 49–58.

[9.21] CARRERA STAMPA, M., Los Gremios Mexicanos, La Organización Gremial en la Nueva España, EDIAPSA, Mexico City (1954).

[9.22] SEIFERT, D., Archaeological Majolicas of the Rural Teotihuacán Valley, Mexico, PhD Thesis, University of Iowa, Iowa City, IA (1977).

[9.23] FOURNIER, R., Illustrated Dictionary of Practical Pottery, Van Nostrand Reinhold, Princeton, NJ and New York (1977).

Chapter 10

CHEMICAL CHARACTERIZATION OF ARCHAEOLOGICAL CERAMICS USING k_0 BASED INAA: A STUDY IN THE PRODUCTION AND DISTRIBUTION OF MIDDLE HORIZON POTTERY FROM CUZCO, PERU

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Abstract

The objective of this research was to establish, in general terms, the provenance of certain pottery styles that are found in the Peruvian southern highlands, in the Cuzco region. Previous work allowed identification of ceramic influences from outside Cuzco, namely from the Peruvian central highlands, the heartland of the Wari culture, and from the high plateau region of Bolivia and Peru (the Altiplano), the centre of Tiwanaku society. One of the goals was to determine which of these ceramic styles were made in other regions and brought to Cuzco, and which of them were locally manufactured imitations. In addition, an attempt was made to compare their patterns of production and distribution with those of local ceramic styles. These data, in turn, were found helpful in understanding some aspects of the social, economic and political dynamics of the Middle Horizon period at Cuzco. To realize this objective, a set of about 350 ceramic samples was chemically analysed using instrumental neutron activation analysis (INAA) and the results processed by multivariate statistical methods. From the pioneering works of Sayre, INAA has become a major tool in multielement compositional characterization of archaeological ceramics. One of the best ways to carry out INAA is the k_0 standardization method, first developed by De Corte et al. [De Corte, F., Habil. Thesis, University of Gent (1987), De Corte, F., et al., J. Radioanal. Chem. **62** (1981) 209 pp.]. It was very effective in accurate multielement analysis of large numbers of samples and has been employed in the Instituto Peruano de Energía Nuclear (IPEN) laboratory since 1993. Special care was taken in our research to maintain quality control of the analytical results, which were produced in duplicate for every sample, and for repeated analysis of NIST SRM-2704 (Buffalo River Sediment) and other reference materials such as the well known Old Ohio Red Clay.

10.1. INTRODUCTION

A very important period of Andean prehistory known as the Middle Horizon (540–900 A.D.) is associated with the widespread expansion of the Wari state from the region of Ayacucho. During this time, the Wari occupied much of Cuzco, building the large settlement complex of Pikillacta and a large settlement located in the Huaro valley (southeast of Pikillacta), including the elite cemetery of Batan Urqu and a complex of domestic structures referred to as Ccotocotuyoc (Fig. 10.1).

Pikillacta is one of the largest and best preserved archaeological sites dating from the Middle Horizon. Strategically located in the centre of the region and situated above the valley's southern basin, Pikillacta is laid out on a grid and is composed of over 700 structures, many of which stood three storeys high. The site is believed to have served as the southern provincial capital of the Wari empire. A network of smaller Wari sites located in the general vicinity of Pikillacta probably contributed to its operation. McEwan excavated Pikillacta in 1982, 1990 and 1991. His excavations generated approximately 55 000 sherds and a few intact vessels. Pottery recovered at Pikillacta from various sites was analysed by Glowacki and her research identified nine ceramic styles that comprised the majority of the collection.

The site of Batan Urqu, situated on a hill overlooking the valley of Huaro, is located 10 km southeast of Pikillacta. It is one of a number of sites in this area which, during the Middle Horizon, formed a large Wari settlement complex. The earliest investigation of Batan Urqu was made by Chávez Ballón, whose exploration of the site in 1952 revealed the presence of Tiwanaku style pottery. Using Chávez Ballón's research as a guide, Zapata performed excavations at Batan Urqu in 1988, 1992 and 1994. Zapata's research demonstrated the presence of an elite Wari cemetery containing many elaborate interments and numerous funerary and other ritual offerings. These excavations generated about 80 000 pottery fragments of various local, local imitation and foreign ceramic styles and a number of whole vessels that represent different phases of the site occupation. Batan Urqu is an important site because it is one of the few known Middle Horizon cemeteries which have been systematically excavated. In 1996, Glowacki and Zapata carried out excavations of two architectural complexes at the site of Ccotocotuyoc in the Huaro valley, obtaining about 2000 fragments of pottery. A preliminary analysis of this material revealed a new family of ceramic styles, referred to as Ccotocotuyoc, which corresponds to the late phases of the Middle Horizon. These three ceramic collections recovered from well controlled archaeological excavations a total of approximately 137 000 fragments and vessels that allow a thorough and accurate ceramic representation of this period of Cuzco prehistory.

10.2. EXPERIMENTAL PROCEDURE

10.2.1. Sample selection

In addition to the approximately 137 000 fragments that constitute the aforementioned collection of pottery, a number of samples were recovered from the

FIG. 10.1. Archaeological sites sampled: 1, Pampailla; 2, Q'Otakalli; 3, Wimpillay; 4, Señorpa; 5, Batan Urqu; 6, Q'Oripata; 7, Isla Estévez; 8, Sunturbay; 9, Tiwanaku; 10, Conchopata; 11, Kullupata; 12, Pikillacta.

surface of the following Middle Horizon archaeological sites (Fig. 10.1): (a) Q'Otakalli, Wimpillay and Araway in the Cuzco valley; (b) Pampailla, Señorpa, Q'Oripata and Sunturbay in the Huaro valley; (c) Kullupata in Pomacanchi; (d) Conchopata in the Ayacucho valley, (e) Tiwanaku pottery in Isla Estévez (Puno Department); (f) Tiwanaku in La Paz, Bolivia. Of all these, about 250 samples were selected during the first stage of the project, taking into account the criteria of abundance at archaeological sites, style variability, presence of exotic styles and sherd size. In the second stage of the research it was decided to exclude from the study all samples of Tiwanaku pottery (42 samples) because they complicated a lot of the statistical analysis. In addition, approximately one hundred additional samples were collected, analysed and added to our database. These new samples were from some Cuzco and Paruro ceramic styles dating to the Late Intermediate Period (900–1473 A.D.), such as Killke, Colcha and black incised wares, which were chosen to help compositionally distinguish Cuzco Middle Horizon styles from one another. In addition, about six samples were discarded because they showed outlier behaviour, perhaps because of a doubtful archaeological characterization. Finally, a set of 306 samples constituted the work database, as can be seen in Table 10.1. Some selected samples are shown in Fig. 10.3.

10.2.2. Sample preparation and chemical analysis

10.2.2.1. Preliminary processing of samples

Before carrying out the analysis each sherd was cleaned, coded, photographed and recorded in a digital form for archival purposes. Pertinent information for each sherd was recorded in a spreadsheet database. These data included: (a) site provenance; (b) intra-site provenance (i.e. excavation context, when applicable); (c) ceramic style; (d) ware quality; (e) decoration; (f) vessel part; (g) inferred vessel form.

10.2.2.2. Comparators and neutron flux monitors

Mixed comparators of Au and Na were prepared using 250 μL of a primary standard containing 20.0 ppm of Au (III) and 20 000 ppm of Na (I) in 1M HCl medium. The solution was dried on high purity cellulose contained in small polyethylene capsules (11), producing a well defined cylindrical disc of 9.0 mm in diameter and 2 mm in height. For the determination of f and α, high purity zirconium foil discs of 10 mm diameter and 100 mg weight were used with the standards. The values of the parameters f and α were determined using the classic methods of two and three terminus tecyhniques, metal foils or wire, respectively.

10.2.2.3. Sample preparation

The surface of each selected sample was carefully removed using a motorized hand drill and special high purity tungsten carbide drill bits. The sherd was then frozen in liquid nitrogen for 20 min and pulverized in an agate mortar. The pulverized samples were collected in glass vials, dried for 24 h at 105ºC and homogenized for

TABLE 10.1. STYLES AND A PRIORI PROVENANCE OF SELECTED SAMPLES

Code	Style	Found in (site)	Number of samples
CTA	Araway	Ccotocotuyoc (Huaro)	3
COA	Araway	Collasuyo (Cuzco)	16
QPA	Araway	Q’Oripata (Huaro)	2
BUB	Bandoja	Batan Urqu (Huaro)	6
PKB	Bandoja	Kullupata (Pomacanchi)	3
WIB	Bandoja	Wimpillay (Cuzco)	2
MURON	Black incised	Muyurocco (Cuzco)	16
BUCC	Ccoipa	Batan Urqu (Huaro)	3
CTCC	Ccoipa	Ccotocotuyoc (Huaro)	2
RPCC	Ccoipa	Paruro	18
WICC	Ccoipa	Wimpillay (Cuzco)	1
CTCT	Ccotocotuyoc	Ccotocotuyoc (Huaro)	18
TPC	Colcha	Paruro	25
BUH	Huaro	Batan Urqu (Huaro)	11
COK	Killke	Collasuyo (Cuzco)	26
BUM	Muyu Orqo	Batan Urqu (Huaro)	12
PKM	Muyu Orqo	Kullupata (Pomacanchi)	3
CC_LL	Plain	Ccotocotuyoc (Huaro)	3
BUPU	Pucara	Batan Urqu (Huaro)	2
BUQ	Q’Otakalli	Batan Urqu (Huaro)	22
CQK	Q’Otakalli	Cuzco	19
QKH	Q’Otakalli	Huaro	1
ACW	Wari	Ayacucho/Conchopata	25
BUW	Wari	Batan Urqu (Huaro)	13
CTA	Wari	Ccotocotuyoc (Huaro)	1
HUW	Wari	Huaro	52
QPW	Wari	Q’Oripata (Huaro)	1

3 h. The analytical samples, weighing approximately 250 mg, were then placed inside polyethylene capsules (like those used for comparators) and sealed.

10.2.2.4. Irradiation and counting

All samples were irradiated at a nominal neutron flux of 1.4×10^{13} $n \cdot cm^{-2} \cdot s^{-1}$ using a pneumatic transfer system to rigorously control irradiation and decay times. A well thermalized irradiation site was employed to ensure a high value of the f parameter. For every f and α determination, a zirconium foil disc was irradiated between two standards for 30 min. Every sample was irradiated with a mixed standard. Special care was taken to ensure that each sample and comparator was irradiated in a reproducible manner and with nearly identical neutron flux. Irradiation times varied from 5 s to 40 min, depending on the elements analysed. After appropriate decay times had elapsed, samples and comparators were counted using high resolution gamma spectrometry with a moderately low efficiency HPGe detector (15%) and a source–detector distance of at least 7 cm to minimize self-coincidence effects. The maximum dead time allowed was 10%, which was kept constant during the counting process. Data reduction of the gamma spectra was accomplished using DBGAMMA V5.0 software. The efficiency curve of the gamma detector was periodically determined using ^{152}Eu, ^{241}Am and ^{133}Ba sources.

10.2.2.5. Data processing and quality control of analytical results

Calculations were made with an ad hoc computer program which interacts with DBGAMMA. To assess the quality of the analytical results, the analysis of precision technique was used, ensuring statistical control. Accuracy was assessed by frequent analysis of reference materials and the use of the α, β and t tests recommended by the National Institute for Standards and Technology (NIST). Special care was taken during the overall analytical process to obtain a set without any missing data.

10.2.3. Statistical analysis

The analytical results, in logarithmic units, were further processed using the multivariate statistical analysis methods of: (a) extraction of a set of principal components (without rotation); (b) hierarchical clustering – dendrogram formation using the method of averaged linkage (between groups) and Euclidean distance measures (not squared ones). The first five principal components were used as independent variables for clustering. Many weeks were spent during the preliminary statistical analyses determining which elements were useful in characterizing and identifying ceramic groups. The following were ultimately selected: Ce, Cr, Dy, Eu, Fe, La, Sm, Sc, Th and Yb. This selection was made because these elements led to a set of principal components, the first three of which explained (after rescaling) almost 90% cent of the observed variance in the data.

10.3. RESULTS AND DISCUSSION

10.3.1. Extraction of principal components

The general results obtained in the extraction of the principal components are shown in Tables 10.2–10.6. It can be seen that the first three rescaled components explain more than 88% of the observed variance (Table 10.4) and that in spite of the low eigenvalues the six components constitute an almost perfectly orthogonal set (Table 10.6).

10.3.1.1. Dendrogram formation

The dendrogram obtained using average linkage and Euclidean distance is shown in seven parts of one page each in Figs 10.2(a)–(g) in addition to digital images of some selected examples of the different styles. Visual inspection of Fig. 10.2 leads to a quite logical organization, allowing the following possible groups to be proposed:

(a) Group 1: The main core of this large group (143 samples) is located in the first three parts of the dendrogram, constituted by local pottery produced and found at different places in the Cuzco and Huaro valleys. This group includes abundant cases of Wari style pottery of local manufacture. It is very noteworthy that the main core of this group includes five cases of Wari pottery found in Ayacucho (M179, M177, M178, M193 and M174). Each of these samples shows a close chemical affinity with one or more cases of a priori clearly local production. The only other apparent intrusions in this core are six cases of black incised pottery, but these also constitute local pottery, at least compared with Ayacucho. In addition to the main core it seems there are four small tails of the proposed local group. These tails, with 17, 6, 3 and 12 cases, are located in parts 4 and 5 of the dendrogram, being constituted by a mixture of different local styles, each one linked to a more specific local pottery group.

(b) Group 2: This group consists mainly of black incised pottery, which is a small Cuzco local subgroup. It is located in part 4 of the dendrogram, constituted by two small clusters of seven cases with some intrusions of local pottery. One of these small clusters has one intrusion and shows a notable chemical affinity with the first part of group 3. The other small cluster is linked to the main core of the large local group.

TABLE 10.2. DESCRIPTIVE STATISTICS

	Mean	Standard deviation	*N*
lg Fe	0.6442	0.1002	306
lg La	1.4864	0.1511	306
lg Sc	1.1607	9.815×10^{-2}	306
lg Sm	0.8260	0.1352	306
lg Th	1.0057	0.2424	306
lg Yb	0.4460	0.1081	306
lg Ce	1.8470	0.1663	306
lg Cr	1.6385	0.3396	306

TABLE 10.3. CORRELATION MATRIX

		lg Fe	lg La	lg Sc	lg Sm	lg Th	lg Yb	lg Ce	lg Cr
Correlation	lg Fe	1.000	0.076	0.650	0.161	–0.166	0.110	0.055	0.272
	lg La	0.076	1.000	0.318	0.937	0.827	0.658	0.959	0.621
	lg Sc	0.650	0.318	1.000	0.444	0.151	0.372	0.289	0.522
	lg Sm	0.161	0.937	0.444	1.000	0.764	0.778	0.898	0.575
	lg Th	–0.166	0.827	0.151	0.764	1.000	0.569	0.892	0.718
	lg Yb	0.110	0.658	0.372	0.778	0.569	1.000	0.644	0.332
	lg Ce	0.055	0.959	0.289	0.898	0.892	0.644	1.000	0.681
	lg Cr	0.272	0.621	0.522	0.575	0.718	0.332	0.681	1.000
Sigma (one tailed)	lg Fe		0.094	0.000	0.002	0.002	0.027	0.167	0.000
	lg La	0.094		0.000	0.000	0.000	0.000	0.000	0.000
	lg Sc	0.000	0.000		0.000	0.004	0.000	0.000	0.000
	lg Sm	0.002	0.000	0.000		0.000	0.000	0.000	0.000
	lg Th	0.002	0.000	0.004	0.000		0.000	0.000	0.000
	lg Yb	0.027	0.000	0.000	0.000	0.000		0.000	0.000
	lg Ce	0.167	0.000	0.000	0.000	0.000	0.000		0.000
	lg Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	

TABLE 10.4. TOTAL VARIANCE EXPLAINED

Component		Initial eigen-values, total	Percentage of variance	Cumulative (%)	Extraction sums of squared loadings, total	Percentage of variance	Cumulative (%)
Raw	1	0.203	73.936	73.936	0.203	73.936	73.936
	2	3.967E–02	14.470	88.406	3.967E–02	14.470	88.406
	3	1.918E–02	6.995	95.401	1.918E–02	6.995	95.401
	4	5.460E–03	1.991	97.392	5.460E–03	1.991	97.392
	5	3.030E–03	1.105	98.497	3.030E–03	1.105	98.497
	6	2.502E–03	0.913	99.410	2.502E–03	0.913	99.410
	7	1.069E–03	0.390	99.800	—	—	—
	8	5.496E–04	0.200	100.000	—	—	—
Re-scaled	1	0.203	73.936	73.936	4.400	55.001	55.001
	2	3.967E–02	14.470	88.406	1.317	16.461	71.461
	3	1.918E–02	6.995	95.401	1.398	17.478	88.940
	4	5.460E–03	1.991	97.392	0.380	4.751	93.691
	5	3.030E–03	1.105	98.497	0.213	2.664	96.354
	6	2.502E–03	0.913	99.410	0.212	2.655	99.009
	7	1.069E–03	0.390	99.800	—	—	—
	8	5.496E–04	0.200	100.000	—	—	—

Note: Extraction method, PCA, when analysing a covariance matrix, the initial eigenvalues are the same across the raw and the rescaled solution.

(c) Group 3: This is an impressive homogeneous group that joins the samples of the Colcha and Ccoipa styles of the Paruro pottery, the Colcha style of the Late Intermediate Period. It is composed of two clusters of 18 and 26 cases including two and five intrusions, respectively. In addition there are very few tails of just two samples in part 5 of the dendrogram and four cases spread over the tails of group 1.

(d) Group 4: This group constitutes ten cases of Killke pottery, which is the main local Cuzco group from the Late Intermediate Period, and five cases of Wari pottery found in Huaro. All these 15 samples exhibit intense chemical affinity. The remaining 16 cases of Killke pottery are distributed in the main core of group 1. Four of these cases consist of a very near subcluster that includes one of the samples of Wari pottery found in Ayacucho (M178).

(e) Group 5: This group comprises the pottery of the Ccotocotuyoc style. The main core includes 16 cases, 12 of them of Ccotocotuyoc pottery and the remaining four including three cases of the Wari style from Huaro, and one case of the Q’Otakalli style found in Batan Urqu. So this core is completely consistent. The

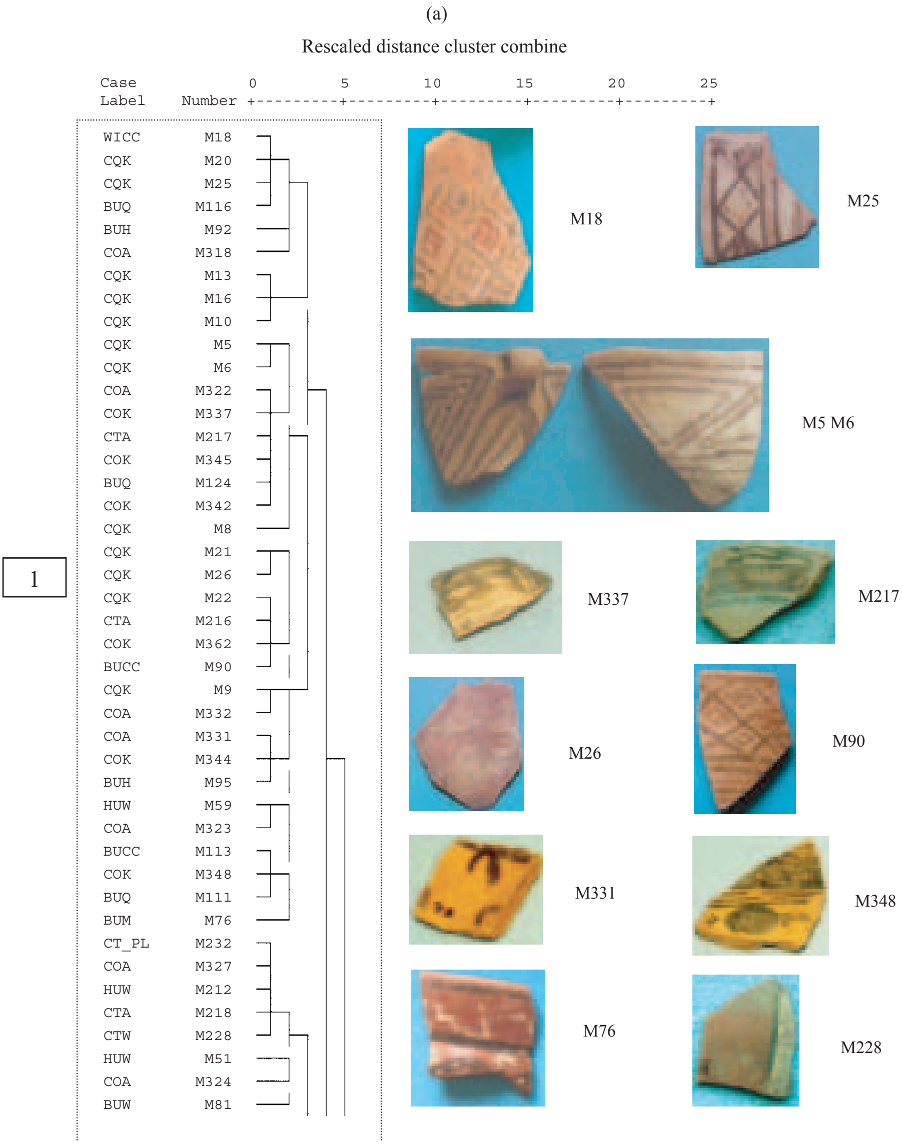

FIG. 10.2(a). Hierarchical cluster analysis (part 1 of 7): a dendrogram using average linkage (between groups).

(b)

Rescaled distance cluster combine

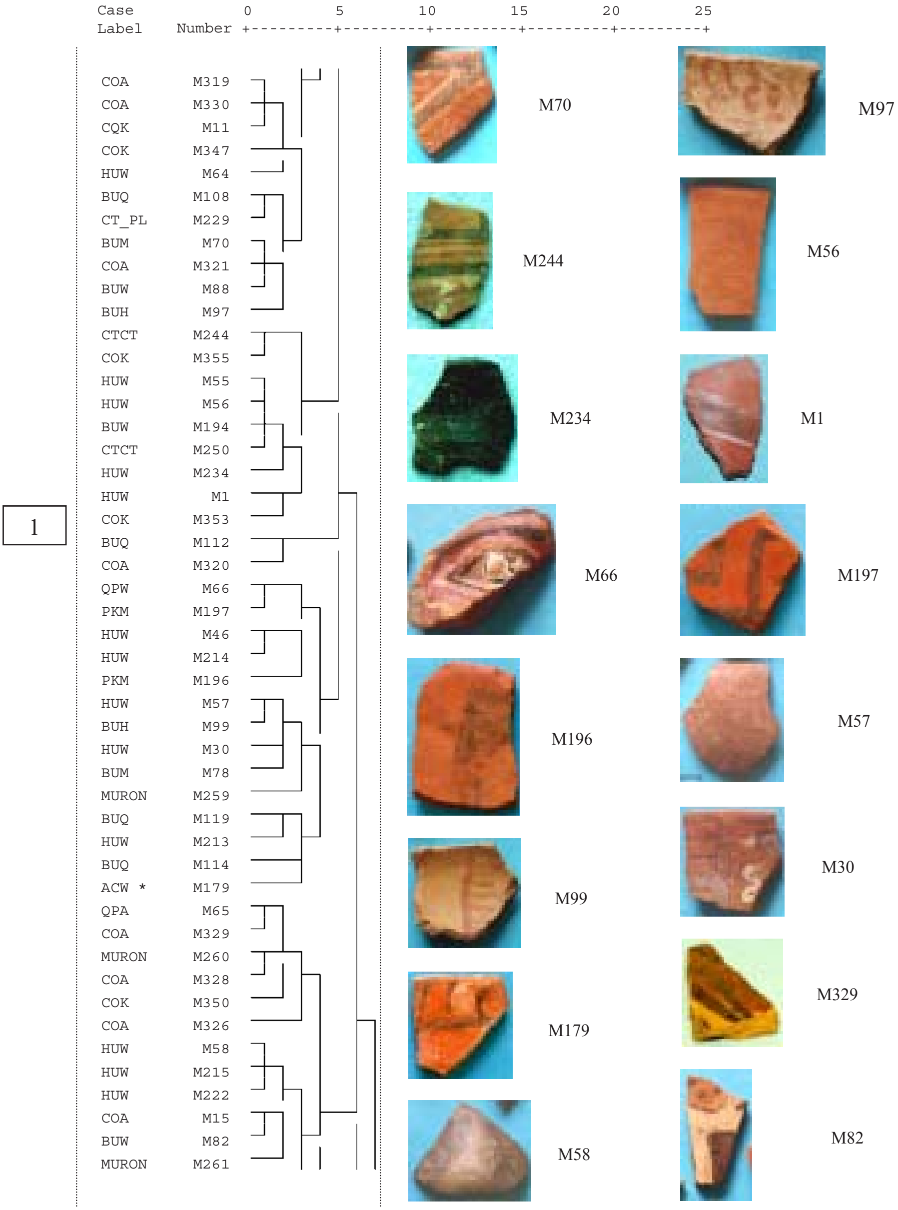

FIG. 10.3(b). Hierarchical cluster analysis (part 2 of 7).

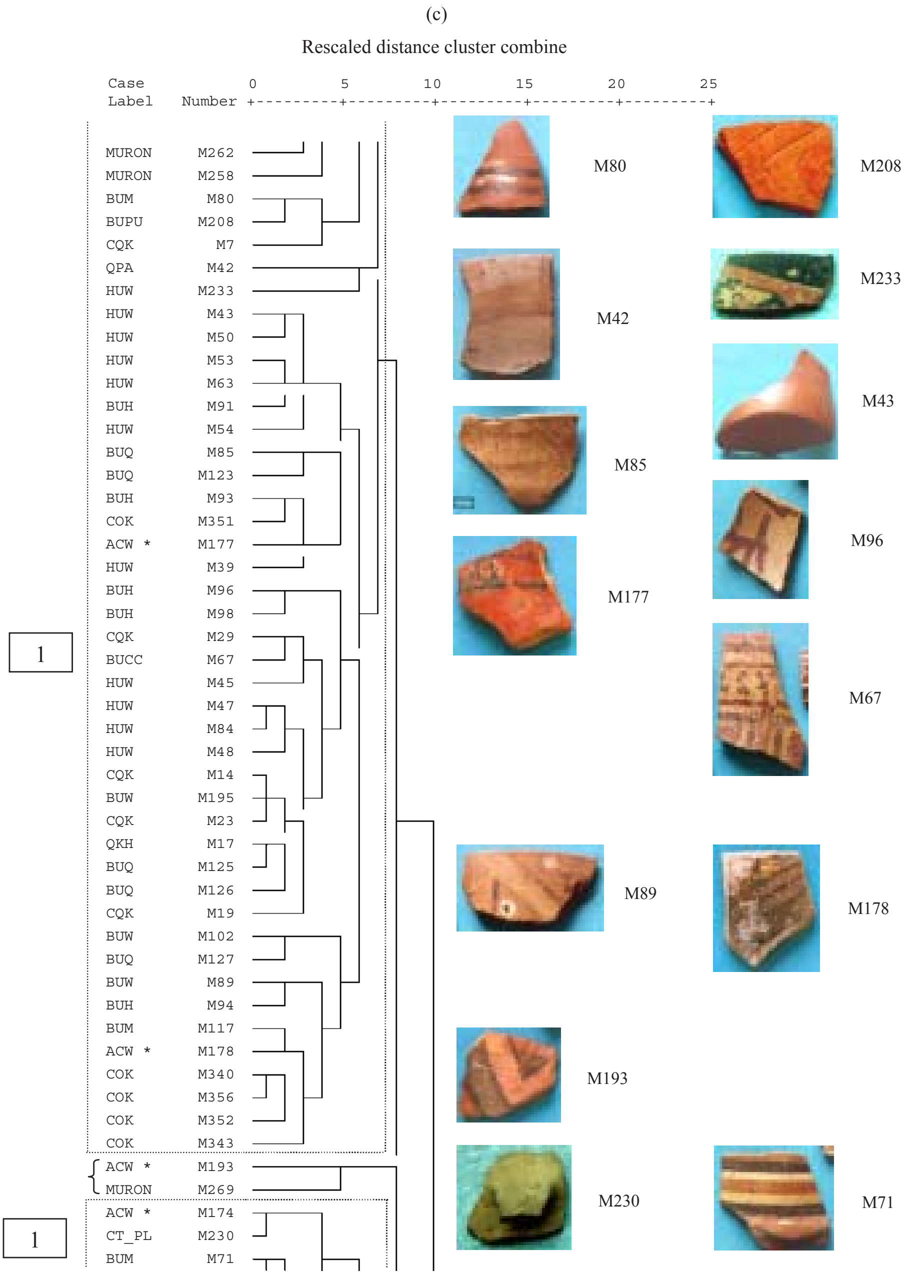

FIG. 10.2(c). Hierarchical cluster analysis (part 3 of 7).

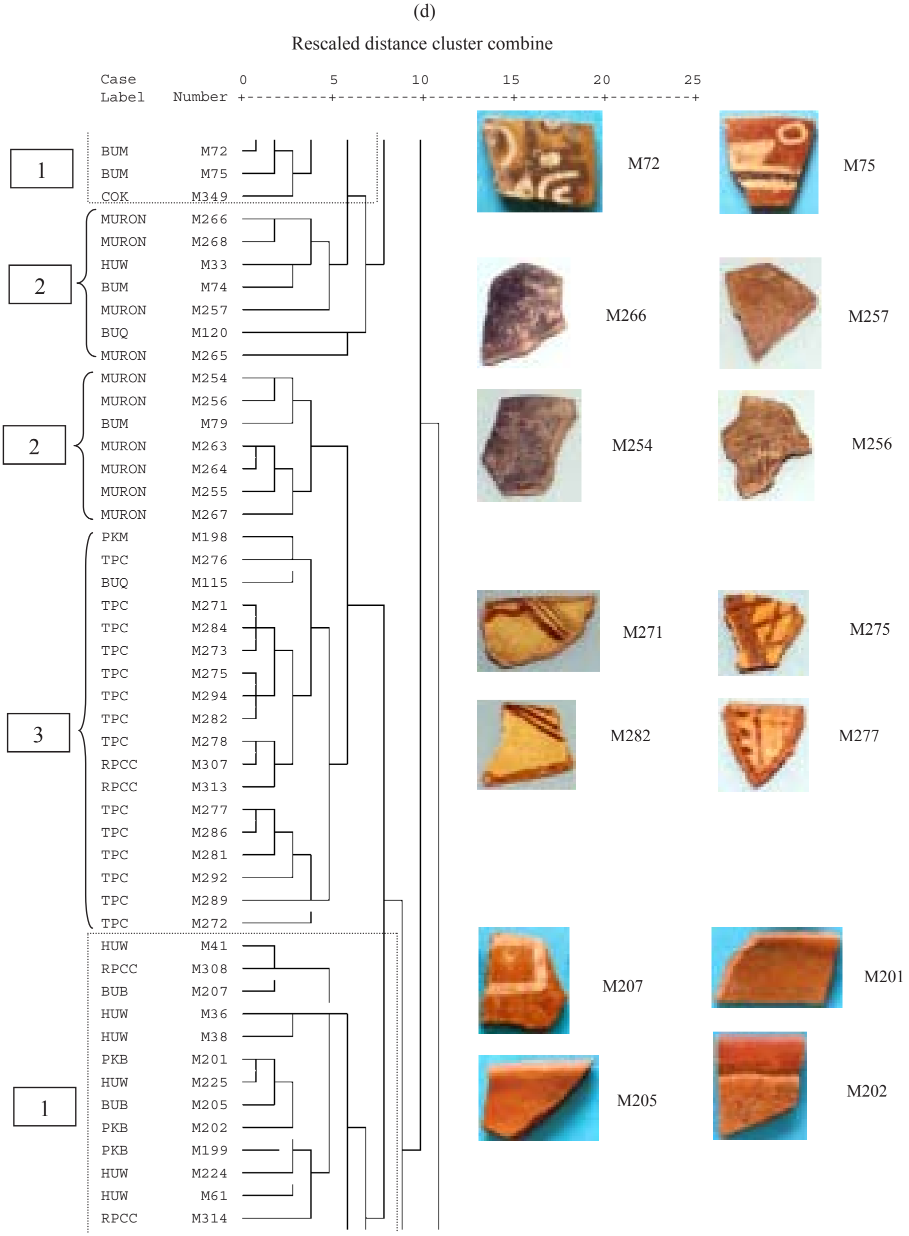

FIG. 10.2(d). Hierarchical cluster analysis (part 4 of 7).

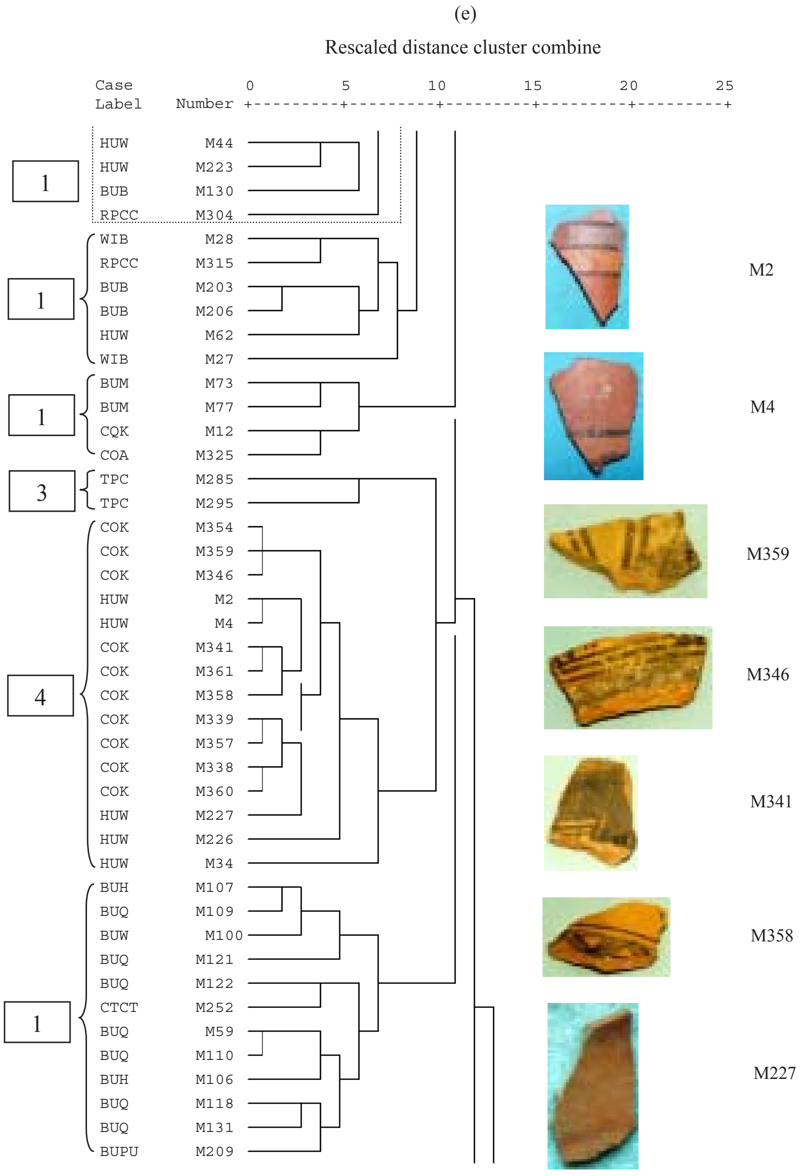

FIG. 10.2(e). Hierarchical cluster analysis (part 5 of 7).

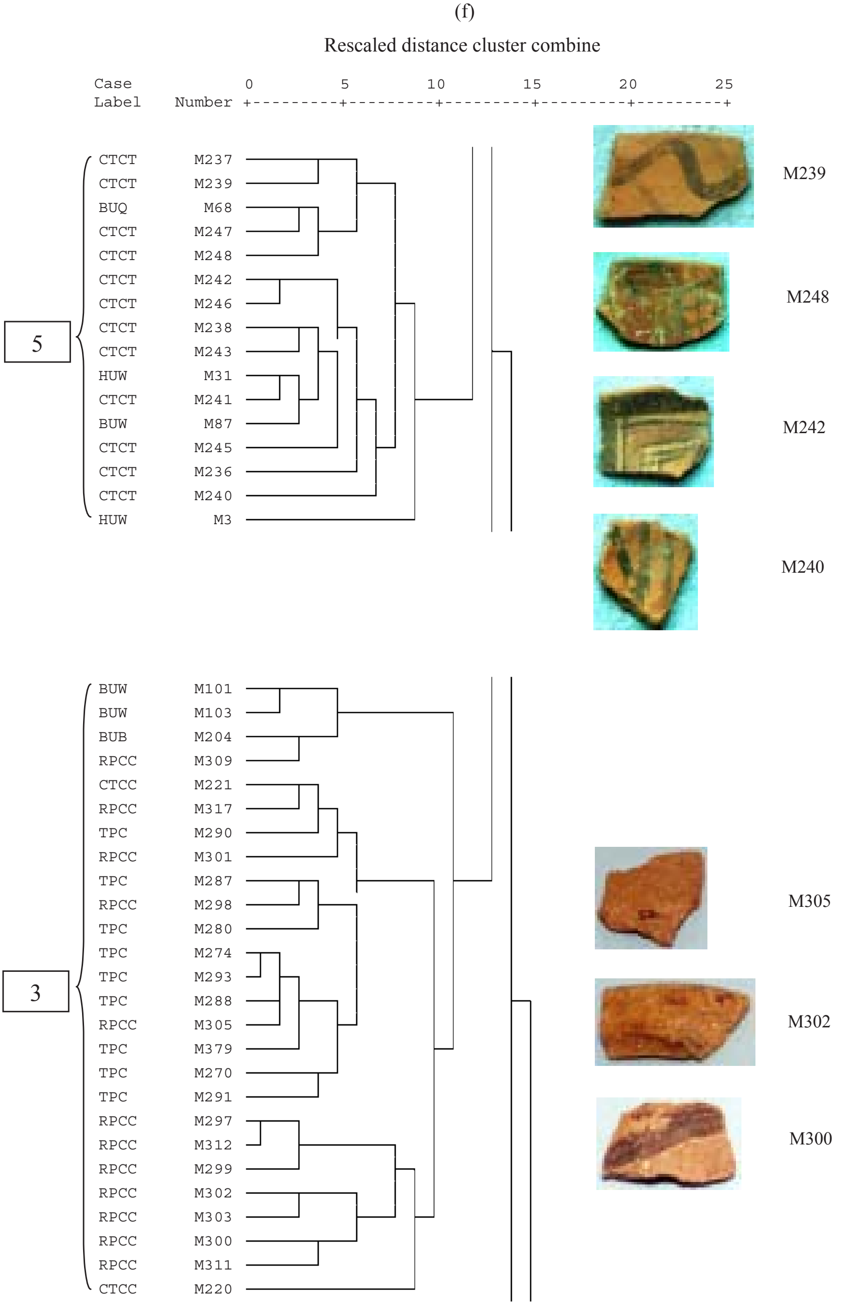

FIG. 10.2(f). Hierarchical cluster analysis (part 6 of 7).

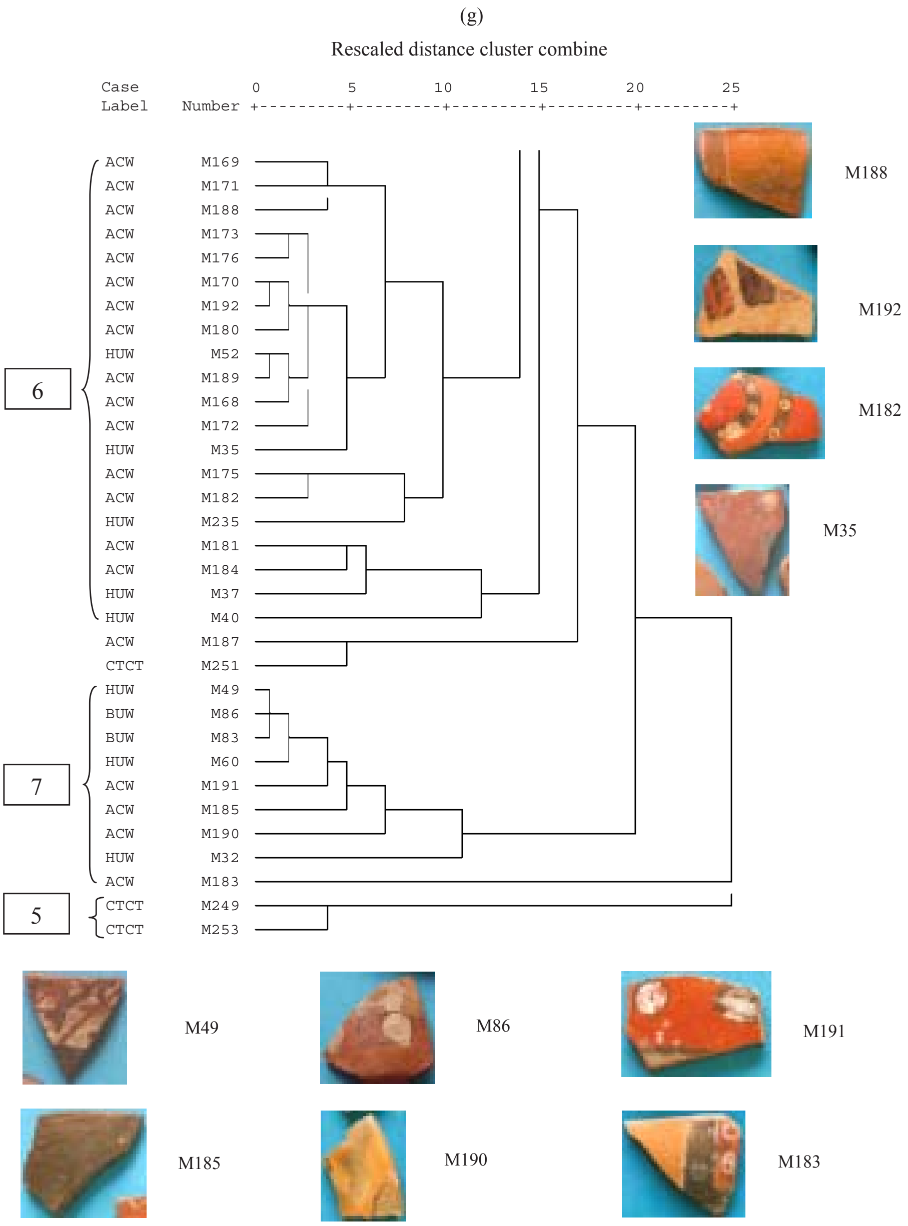

FIG. 10.2(g). Hierarchical cluster analysis (part 7 of 7).

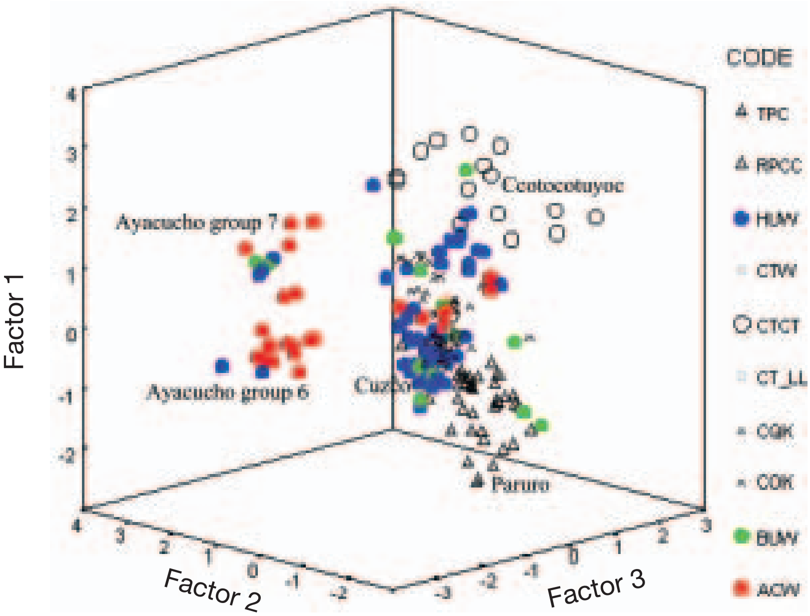

FIG. 10.3. Graphical representation of the first three principal components for selected pottery styles.

TABLE 10.5. COMPONENT SCORE COEFFICIENT MATRIX

	Component					
	1	2	3	4	5	6
lg Fe	0.007	–0.125	0.380	–0.298	1.373	–0.258
lg La	0.096	0.232	0.250	–0.861	–0.762	–0.152
lg Sc	0.021	–0.099	0.328	0.354	–0.256	1.494
lg Sm	0.073	0.183	0.359	–0.042	–0.649	0.075
lg Th	0.262	0.482	–0.720	0.765	2.120	1.653
lg Yb	0.032	0.131	0.265	1.046	–0.018	–1.056
lg Ce	0.123	0.255	0.148	–0.832	0.163	–0.215
lg Cr	0.524	–1.108	–0.369	0.131	–1.048	–1.378

Note: Extraction method, PCA/component scores, coefficients are standardized.

TABLE 10.6. COMPONENT SCORE COVARIANCE MATRIX

Component	1	2	3	4	5	6
1	1.000	0.000	0.000	0.000	0.000	0.000
2	0.000	1.000	0.000	0.000	0.000	0.000
3	0.000	0.000	1.000	0.000	0.000	0.000
4	0.000	0.000	0.000	1.000	0.000	-1.233×10^{-16}
5	0.000	0.000	0.000	0.000	1.000	0.000
6	0.000	0.000	0.000	-10.233×10^{-16}	0.000	1.000

Note: Extraction method, PCA/component scores.

Ccotocotuyoc pottery shows a notable variability in chemical composition and there are some cases of Ccotocotuyoc pottery spread as intrusions in different groups.

(f) Group 6: This is a perhaps a triple core group. The first comprises 20 cases from which 15 are Wari pottery found in Ayacucho and the other five are Wari pottery found in Huaro (but exhibiting a strong chemical affinity with the Wari samples from Ayacucho). The second has nine cases, four of them of Wari pottery found in Ayacucho and the other five of Wari pottery found in Huaro. This is group 7 (Fig. 10.2(g)). Finally, two samples, M187 (Wari style from Ayacucho) and M251 (Ccotocotuyoc style from the Ccotocotuyoc site), show a notable chemical affinity but are apparently quite isolated from the other samples.

The three first principal components for some selected pottery styles are represented in Fig. 10.3. It can be appreciated that the samples of Wari pottery found in Ayacucho (solid red circles) form at least three compositional groups, one of which corresponds to the group numbered as 7 in the dendrogram. This figure also includes the five samples of Wari pottery which are located in the main core of group 1 of the dendrogram. These samples show a marked compositional affinity with diverse non-Wari local pottery (represented by small black characters such as small crosses, void triangles and void circles for the Cuzco, Paruro and Ccotocotuyoc styles, respectively). It can also be seen that Wari style samples recovered from the Batan Urqu cemetery (solid green circles) spread along the compositional space suggesting its diverse provenance, including Cuzco, Huaro, Paruro and Ayacucho sources. Finally, the spatial distribution of the Wari samples found in Huaro (solid blue circles) also suggests up to four sites of manufacture, including two different places in Ayacucho, one in Cuzco and the other perhaps in Huaro. This proposition is in general agreement with the results from Glowacki's analysis of pottery from Pikillacta, which identified two possible centres of Wari ceramic production, one of which was Paruro.

Ceramic styles of the Late Intermediate Period also helped clarify the compositional groupings of local Cuzco Middle Horizon styles. Production patterns of Q'Otakalli pottery, the principal local Middle Horizon ceramic style of Cuzco, were found to be very similar to that of Wari pottery recovered in the Huaro valley, with possible centres of manufacture in the Cuzco basin and in Huaro. Glowacki's earlier study of Middle Horizon pottery recovered from Pikillacta likewise indicated a production centre for Q'Otakalli pottery in the northern sector of the Cuzco valley, supporting our current findings. These results further suggest that the Wari and Q'Otakalli societies utilized or even shared the same clays and other resources in ceramic manufacture.

With respect to other local Cuzco ceramic styles, our analysis was likewise facilitated by Late Intermediate pottery. Ccoipa pottery, speculated to be a substyle of Q'Otakalli, exhibited no evidence of this relationship but appears to be a local Cuzco Middle Horizon ceramic style manufactured mainly in the province of Paruro. The compositional patterning of Bandoja pottery indicated that this was, in fact, a local ceramic style whose production was separate from that of Wari pottery. Muyu Orqo, another Cuzco ceramic style previously thought to be influenced by Tiwanaku culture, showed a composition pattern that suggests it is a locally manufactured ceramic style whose centre of production was the Cuzco basin area. Finally, black incised pottery, defined by Bauer, and speculated to have been influenced by Wari, and possibly a locally Wari produced ceramic style, exhibited a compositional character distinct and separate from all the other local Cuzco groups but within the range of local production. Consequently, this ceramic style was classified as local but no association was made with other ceramic styles of the region.

10.3.1.2. Interpretation of Wari–Ayacucho pottery

The use of Late Intermediate pottery in assessing compositional groups additionally helped clarify the compositional groupings of Wari–Ayacucho pottery. Araway pottery, considered a Wari–Ayacucho ceramic style known as 'Wamanga', showed compositional characteristics that suggested its centre of production was located in the northern end of the Cuzco valley. Glowacki's analysis of Pikillacta pottery produced similar results, further strengthening the view that this style was principally produced in this zone. Five examples of Wari Viñaque pottery recovered in Ayacucho, at the site of Conchopata, were shown to be clearly associated with

Cuzco manufactured Wari pottery. Its composition suggested it was produced in the Cuzco basin area.

10.3.1.3. Archaeological implications

The results of this investigation illuminated many aspects of early ceramic production in Cuzco, particularly those associated with the Middle Horizon period. Our study suggests that patterns of ceramic production during the Middle Horizon were quite different from those of the succeeding Late Intermediate Period. Wari ceramic production in the Cuzco province does not appear to be nearly as standardized as previously thought. Production occurred in different parts of the region and was exchanged between centres for local distribution. This pattern was probably initiated at the outset of the Wari occupation of Cuzco, which was centred in the Huaro valley. The Wari Cuzco occupation appears to have taken place gradually and with less state domination than earlier proposed. After becoming firmly established the Wari designed and built Pikillacta, a highly structured architectural complex located a few kilometres north of Huaro. Further changes were probably imposed on the Cuzco territory in the form of state political and economic control mandated by Wari administrators in Ayacucho. This theory would explain the diverse ceramic production patterns identified for Cuzco Wari pottery during the early stages of the Middle Horizon. It would further explain a more centralized pattern of ceramic production and distribution associated with the later site of Pikillacta, as indicated by Glowacki's research.

Our study likewise indicates considerable diversity of local Cuzco ceramic production, in both ceramic styles and production areas. We can infer from our data that local Cuzco groups co-existed with the Wari, sharing ceramic resources in pottery production and use. The appearance of certain ceramic styles, such as black incised ware and a related orange ware, suggests that, while the Wari may have influenced the production of some local ceramic styles, they did not control either local Cuzco pottery production or its use. This relationship may have had its roots in the Early Intermediate Period when Cuzco and Ayacucho populations were first in contact, as suggested by shared similarities of the ceramic styles of these regions, namely, Q'Otakalli and Huarpa.

Finally, our research confirms a bidirectional exchange of pottery between the Wari capital, Ayacucho, and its southern province, Cuzco. This finding is particularly interesting in light of the fact that the Wari-Ayacucho ceramic samples used in this study were recovered from the site of Conchopata. Research conducted by Pozzi-Escot at Conchopata indicates that the site functioned as a centre of pottery production for settlements in Ayacucho. Perhaps it likewise served as a distribution centre where many sources of pottery were collected and stored for later allocation.

BIBLIOGRAPHY

BAUER, B., Muyu Orqo y Ccoipa: Dos nuevos tipos de cerámica para la región del Cusco, Rev. Andina **7** 2 (1989) 537–542.

BAUER, B., The Early Ceramics of the Inca Heartland, Fieldiana No. 31, Field Museum of Natural History, Chicago, IL (1999).

BECKER, D., et al., NIST Special Publication 829, National Institute of Standards and Technology, Gaithersburg, MD (1992).

BLAAUW, M., BODE, P., DE BRUIN, M., J. Radioanal. Nucl. Chem. **152** 2 (1991) 435–445.

DE CORTE, F., Habil. Thesis, University of Ghent (1987).

DE CORTE, F., et al., J. Radioanal. Chem. **62** (1981) 209 pp.

GLOWACKI, M., The Wari Occupation of the Southern Highlands of Peru: A Ceramic Perspective from the Site of Pikillacta, PhD Thesis, Brandeis University, Waltham, MA (1996).

GLOWACKI, M., Análisis Instrumental por Activación de Neutrones de Cerámica Wari y Otras Pastas Wari Coetáneas: Una Investigación Preliminar Sobre la Producción Cerámica en Cuzco, Perú Durante el Horizonte Medio, National Institute of Culture, Cuzco (1996).

HEYDORN, K., Rep. Risoe-R-419, PhD Thesis, Risoe National Laboratory, Denmark (1980).

MONTOYA, E.H., MSc Thesis, Universidad Peruana Cayetano Heredia, Lima (1995).

MONTOYA, E.H., “Selected topics about applications of k_0 method and other parametric methods in neutron activation analysis”, paper presented at IAEA/IACS Workshop, Lima, 1995, Internal Report, IAEA, Vienna.

POZZI-ESCOT, D., Excavaciones en Conchopata, Gaceta Arq. Andina **1** 4–5 (1982) 9.

POZZI-ESCOT, D., “Conchopata: A community of potters”, Huari Administrative Structure, Prehistoric Monumental Architecture and State (ISBELL, W.H., GORDON, F., Eds), Dumbarton Oaks Research Library and Collection, Washington, DC (1991) 81–92.

PUBLICATIONS RESULTING FROM THE CRP

ALVAREZ, R.P., et al., Compositional classification of archaeological pottery based on INAA and SEM-DEX, Int. J. Trace Microprobe Tech. (in press).

BISHOP, R.L., NEFF, H., Compositional data analysis in archaeology, Adv. Chem. Ser. **220** (1989) 57–86.

FALABELLA, F., El estudio de la cerámica Aconcagua en Chile central: Una evaluación metodológica, Contribución Arqueológica **1** 5 (2000) 427–458.

MONROY-GUZMÁN, F., FOURNIER, P., “Estudios de cerámicas coloniales con técnicas nucleares”, paper presented at Proc. Symp. on Archaeometry, Zamora Michoacán, México, 2000.

MONROY-GUZMÁN, F., FOURNIER, P., FALCÓN, T., DE LA TORRE, J., “Mexican colonial majolica analysis using neutron activation and X ray diffraction techniques”, Archaeometry (Proc. 32nd Int. Symp. Mexico City, 2000) (CD-ROM).

MONROY-GUZMÁN, F., GÓMEZ, S., MIRANDA, J., RUVALCABA, J.L., DE LA TORRE, J., “Manufacturing techniques of glazed pottery found at the exconvent of Santo Domingo in Oaxaca”, ibid.

MUNITA, C.S., et al., Intercomparison among three activation analysis laboratories in South America, J. Trace Microprobe Tech. **19** 2 (2001) 189–197.

MUNITA, C.S., PAIVA, R.P., ALVES, M.A., DE OLIVEIRA, P.M.S., MOMOSE, E.F., Contribution of neutron activation analysis to archaeological studies, J. Trace Microprobe Tech. **18** 3 (2000) 381–387.

MUNITA, C.S., PAIVA, R.P., ALVES, M.A., MOMOSE, E.F., Chemical characterization by INAA of Brazilian ceramics and cultural implications, J. Radioanal. Nucl. Chem. **244** 3 (2000) 575–578.

MUNITA, C.S., PAIVA, R.P., ALVES, M.A., OLIVEIRA, P.M.S., MOMOSE, E.F., Major and trace element characterization of prehistoric ceramic from Rezende archaeological site, J. Radioanal. Nucl. Chem. (in press).

PADILLA, R., ARRAZCAETA, R., HERNÁNDEZ, C.A., HERNÁNDEZ, A.T., “INAA characterization of colonial pottery from Old Havana collections”, Nuclear and Related Techniques in Agriculture, Industry and Environment (Proc. 2nd Int. Symp. Havana, 1999) (CD-ROM).

PADILLA, R., PLÁ, R.R., ESTÉVEZ, J., JOURAVIEVA, I., "Introduction of nuclear analytic techniques in archaeological researches in Cuba", paper presented at 1st Int. Symp. on Nuclear and Related Techniques in Agriculture, Industry and Environment, Havana, 1997.

PLÁ, R., RATTO, N., "Provenience archaeological studies of ceramic raw material and artifacts using instrumental neutron activation analysis: The cases of Chaschuil and Bolsón de Fiambalá, Catamarca, Argentina", paper presented at 2nd Int. Symp. on Nuclear and Related Techniques in Agriculture, Industry and Environment, Havana, 1999 (CD-ROM).

SABINO, C.S., PROUS, A., AMARAL, A.M., "Utilização da técnica paramétrica k_0 no estudo da composição de cerâmicas arqueológicas Brasileiras", paper presented at 1st Int. Symp. on Nuclear and Related Techniques in Agriculture, Industry and Environment, Havana, 1997.

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