

Chapter 2

CERAMIC IN ANCIENT SOCIETIES: A ROLE FOR NUCLEAR METHODS OF ANALYSIS

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Abstract

The application of the instrumental neutron activation analysis (INAA) in support of provenance research of archeological ceramics has been largely used over the past few decades. INAA is a sensitive technique useful for quantitative multi-element analysis of major, minor, and trace elements. Among these, trace elements can be particularly useful to determine provenance of the mineral components in the paste of archaeological ceramics or to distinguish different ceramic groups, better differentiating diverse raw materials. The chemical characterization of the regional potential raw materials is particularly important in the case of the lack of kilns structures in archaeological excavations, and if the ceramic artifacts study points to local productions. This is the case of Bracara Augusta (nowadays Braga), a Roman town located in the north of Portugal, recognized as a center of production and distribution of pottery. In this chapter chemical data (major and specially trace elements) of the different types of clay materials of Braga region obtained by instrumental neutron activation analysis are used to establish the geochemical profiles of raw materials, which can be used as indicators of provenance of several ceramic types found in Bracara Augusta. Among the chemical elements studied rare earth elements play an important role differentiating resources and their correlation with ceramics. The results obtained suggest that during Roman times two main resources were used to produce different types of ceramics: (1) the sedimentary clays of the Prado basin (located near Braga) to produce common wares, amphorae, as well as imitations of “Pompejanish-roten slip”, and “Terra Sigillata Hispanica” and “African Red Slip Ware” forms; and (2) sedimentary kaolin deposits located 30 km west of the town, near the coast, for the production of the “Bracarense” ceramics, a fine yellow-pale paste covered with a brownish yellow slip. Until the finding of archaeological evidence of pottery workshops in the area, one may assume that potters, already settled in Bracara Augusta, may have went further west to look for especial clays to answer specific needs, functional and aesthetic. The chemical characterization of the ceramics pastes and their comparison with ceramics of well established origin also point to imports of several types of ceramics from other locations of the Roman Empire, such as Italic “Pompejanish-roten” production (Campania) as well as imitations of “Pompejanish-roten slip” produced in Lucus Augusti (NE Braga).

1. Introduction

Ceramics enclose messages about the society that manufactures and uses that must be clarified within a broader context of the ancient society, its cosmological structures, ritual behavior, overall productive systems, resources exploitation strategies and the interactions with neighboring areas. The objectives of ceramic research in archaeological studies are at inferring how the ceramic might have been used and determining the chronology, and the location and techniques involved in its manufacture - that is what for, when, where and how was a ceramic piece done. In this way pottery can be seen as a source of insights into people and cultures.

Identification of archaeological ceramics based on visual inspection may not allow distinguish different production sites or different productions of the same site. Technological properties of pottery – the physical, mineralogical, and chemical characteristics of ceramic materials – constitute an irreducible minimum of detail on ceramic objects supplementing morphological and stylistic criteria. Pottery was the first synthetic material humans created, and the discussion of its history must begin with the recognition of clay itself as a raw material. For potters the term clay means the basic ingredient in ceramic manufacture, composed of plastic particles (clay) and natural non-plastic grains. In archaeology the term ceramics usually refers to cooking and serving utensils and art objects manufactured of clay. The chemical analysis of archaeological ceramics and raw materials in support of provenance research has grown rapidly over the past few decades. Technological information together with classical archaeological approaches has been largely used in solving a broad variety of questions and an overview of these types of studies is well described and summarized in the literature (Rice, 1987, Chappell, 1991, Hector, 1992, and Velde & Druc, 1999) and a review of ceramic production, provenance and use was recently published (Tite, 2008). Compositional profiles of ceramics and raw materials (clays and temper) are used to trace individual artifacts from their find spot to their origin. Chemical analysis, together with statistical data treatment, has been used extensively to supplement archaeological investigations when provenance studies or socioeconomic aspects are concerned. The information obtained is used by archaeologists to investigate questions regarding the location of production areas, the identification of routes of trade and exchange of raw materials and artifacts, and the mobility patterns in ancient times.

In chemical-based provenance studies of archaeological ceramics important issues must be considered. Among the materials and processes involved in making a pot, the most important is clay and its manipulation to make the vessel body. Hence a discussion of pottery must include clay and its origin, composition and properties. Therefore it is important to know how the different elements make clays, what the leftovers are in the clay-making process, and the geochemical and mineralogical fingerprints which can give one a clue to the geographic origin of the clay and temper materials found in the ceramics. Thus, the use of resources is very important to deciphering the provenance of a ceramic object, i.e., the geographic area where the object was produced, especially when no archaeological evidence of pottery workshops are found. The resources should be compared with care to the possibilities of a given production site. Today clay and other ingredients used for ceramic production can come from sites thousands of kilometers from the production site. However, in the past, the potter was more tied to the local/regional resources for his production, since in

general clays did not travel more than several kilometers. In this way the potter would have adapted local resources to answer specific needs. In ancient times, sources of clays tended to be those easily available. Soils or surface sediments are likely candidates, which can be adapted to form a ceramic without further treatment. By their natural mixture of plastic and non-plastic components, they can be used to form pottery. If the proportions of clay, silt and sand are not adequate, tempering by mixtures of materials of the same source or from different sources can be done. All these procedures during manufacture, together with eventual modifications of the ceramic composition during use and burial, can lead to compositional alterations that can complicate the establishment of provenance.

Technological data are independent of other common categorizations of pottery used by archaeologists, such as styles, type classes, or shape categories, yet they can be used for comparing such groupings or creating new ones (compositional groups). In combination with ceramic ecology, ceramic technology can, for example, characterize properties of both resources and pottery and permit comparisons between them. Furthermore, these objectives can be achieved on broken fragments as well as intact vessels. Compositional data provide a basis for understanding many questions about production techniques and organization, functional relationships between specific resource manufacturing combinations, and patterns of local, regional, or extra regional distributions of pottery. Thus, better understand a culture, time period or human interaction. These are the main research issues of ceramic technological (and ecological) analysis.

The methodological approaches to study archaeological ceramics vary depending on the nature of the raw materials used and the manufacturing techniques. Research began by a careful examination of the broken pottery fragments that archaeologists recover in their excavations. Ceramic characterization is done with three main objectives – classification, production technology and provenance. The more commonly used techniques to characterize archaeological vessels focus on the chemical and mineralogical constituents. There are several methods that can be employed. However it should be noted that special considerations in applying these methods to archaeological pottery must be taken into account. The objectives of the analysis must be defined so they can be translated into compositional (geochemical and mineralogical) terms.

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.

Within their composition, ceramics preserve a record of their raw materials, so chemical analysis of the ceramics pastes, determining the larger number of chemical elements as possible, is particularly useful in provenance studies. In this way, large data sets are generated, which need to be processed by computer with statistical programs. One important thing to not forget is that statistical analysis is only a tool to help us with very large amount of data matrixes (variables and samples) and remember that the results obtained are an approximation of the reality. The attribution of one pot to one particular site or composition group is based on statistical probabilities. The results obtained by statistical analysis must be checked taking into account geochemical (and mineralogical) considerations.

In some cases, an important step prior to any statistical analysis is normalization of the chemical elements contents. To compensate for grain-size and mineralogy effects on trace element concentrations, thus diminishing erroneous interpretation of ceramic provenance, a

common approach used in determining regional geochemical baselines is to normalize geochemical data using one element as grain-size and mineralogical proxy, that is to express the ratio of the concentration of a given element to that of the normalizing factor (Sanei et al. 2001; Prudêncio et al., 2007b). Normalization in archaeological ceramics studies is defined as a procedure to compensate for the influence of natural (geological and ceramic burial time) and anthropogenic (technology of production) processes on the measured variability of the concentration of elements, emphasizing the importance of taking into account geochemical behavior of the element chosen for normalization. So, the selection of the normalizing element should be not purely based in statistical considerations (Prudêncio et al., 2006; Dias & Prudêncio, 2008). In this way, normalization of elemental concentration to an immobile, conservative element provides deeper insights about other elements distribution than the consideration of the absolute concentration itself alone. The criteria used to choose the normalization factor must be supported by geochemistry. Considering that it is well established that more relevant information can be derived from the concentration of any element when it is compared with some reference element, the question arises is which element should be chosen to normalize concentration. When dealing with ancient pottery production, whenever a possible anthropogenic input of a grain-size proxy is suspected, preliminary investigation of the nature of the added temper is recommended before choosing the reference element. The variable of time burial is important, as it may induce element mobilization / lixiviation. Therefore, the best option appears to be the use of a conservative element, and among these, Sc appears to be the more appropriate to normalize chemical data than other elements; even their variability is higher, since the raw materials are related with a specific geological context which has to be considered. Sc^{3+} easily hydrolyzes and is structurally combined in clay minerals and micas, being a good tracer of phyllosilicates, particularly in sediments containing Al-silicates in all size fractions. Normalization of chemical elements contents to Sc was successfully employed to distinguish production centers using raw materials within the same geological context of estuarine sediments of the Tagus River, Portugal (Dias & Prudêncio, 2008).

Several multivariate statistical methods can be employed by using programs like Statistica (Statsoft, 2003). Each value in the series is standardized: $x = (x-M)/SD$, where M and SD are the overall mean of each variable and the standard deviation for the untransformed series, respectively. Clustering methods, using the absolute concentration of the chemical elements as variables, or the ratios of elements, like element/Sc, are commonly employed, including hierarchical methods such as joining tree clustering and non-hierarchical, particularly the k-means clustering. Principal components analysis (PCA), involving a transformation of the dataset on the basis of eigenvector methods to determine the magnitude and direction of maximum variance in the dataset distribution in hyperspace, is also commonly employed. The PCA transformation provides a new basis for viewing the entire data distribution to reveal structure not readily observed when plotting the original variables (Baxter, 1994; Sneath and Sokal, 1973). The results obtained with different statistical methods must be integrated and interpreted taking into account the significance of correlations between the chemical elements (variables) found in ceramics and their meaning in terms of raw materials composition, and possible alterations due to the production technologies (sieving, sedimentation, add of temper, mixing clays, etc.) and to eventual modifications during the use of pots and post-depositional processes.

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. Although a number of techniques have been employed to characterize archaeological materials, the analytical method with one of the longest and most successful histories of application for provenance research has been neutron activation analysis (NAA). The real success story of this technique, however, comes from the investigation of ceramics dating from throughout archaeological times. NAA is a sensitive technique useful for quantitative multi-element analysis of major, minor, and trace elements, which concentration can have different meanings in minerals or in rock descriptions, as well as in ceramics. Major elements may give an idea of the type of mineral material which makes up the ceramic. Minor elements indicate the variations between different sources of material and major mineral abundance, which varies according to its geologic source. Trace elements can be used to determine provenance of the mineral components in the paste or to distinguish different ceramic groups, better differentiating diverse raw materials even within the same geological context.

Among trace elements, rare earth elements (La-Lu, Y and Sc) distributions can be particularly useful in distinguishing clayey materials resources. Among rare earth elements (REE), lanthanide elements, La ($Z=57$) through Lu ($Z=71$), are a particularly coherent group of elements that is usually used in geochemistry. Yttrium ($Z=39$) is commonly included because its similar chemical behavior; scandium ($Z=21$) is small enough to have a distinct chemical behavior. In this chapter lanthanides will be referred as REE. The subtle variations in the properties of REE make them sensitive to mineral/melt equilibria, as well as to weathering conditions after the breakdown of primary minerals and the formation of new mineral phases, sedimentary sorting, and diagenesis (McLennan, 1989). These elements have very similar chemical and physical properties, which is the result of the nature of their electronic configurations. The dominant oxidation state is the +3 state, and there is a small but steady decrease in ionic radius with increasing atomic number (for a given co-ordination number). The REE, therefore, tend to occur in nature as a group. They are lithophile, in that they concentrate predominantly in the silicate rather than the metal or sulphide phases when they coexist. The differences existing among the REE lead to differences in their relative behavior in response to the chemical environment, making this group particularly useful in geochemistry since they can be a pointer of the genesis processes of the rocks and minerals and subsequent alterations.

The REE are usually divided in two or three groups: (a) light REE (LREE) - those from La to Sm (i.e. lower atomic numbers and masses) and heavy REE (HREE) - those from Gd to Lu (higher atomic number and masses); (b) LREE - La to Nd, middle REE (MREE) - Pm to Ho, and HREE - Er to Lu. The fractionation between LREE and HREE is measured by the $(La/Yb)_{ch}$ ratio, i.e. the ratio between the La and Yb concentrations normalized relative to chondrites (Haskin, 1971). As referred above, REE occur in a trivalent state in most of the temperature-pressure conditions of the earth. There are two exceptions in nature to this: Ce and Eu. Under oxidizing conditions, Ce^{3+} may be oxidized to Ce^{4+} leading to a decrease in the ionic radius of about 15%. This reaction occurs on a large scale in the marine environment, associated with the formation of manganese nodules, with a consequent depletion of Ce in ocean waters. On a smaller scale, this reaction also occurs in superficial environments during weathering (Prudêncio et al. 1993; 1995; Gouveia et al. 1993). The Ce anomaly degree is measured by the Ce/Ce^* (Ce is the concentration measured and Ce^* is the value obtained at

the cerium position by straight-line interpolation between the plotted points for La and Nd). Under reducing conditions, europium may exist in the divalent state, resulting in an increase of the ionic radius of about 17%. Europium is the only element for which a significant proportion of the ions in igneous systems are likely to be present in valences other than 3+, leading to an anomalous behavior. Anomalous behavior of Eu can be expected for many minerals, but is most pronounced for plagioclases, because Eu^{2+} is similar to Sr^{2+} and substitutes much more easily for Ca and Na in the large feldspar site than does Eu^{3+} . The amount of feldspars (particularly plagioclase) or the fate of Eu after the breakdown of these primary minerals during weathering and sedimentary processes, have an important control of the Eu anomaly of residual or sedimentary clayey materials. Thus Ce and Eu anomalies may occur depending on several factors, and may be used as indicators of geological formations. The sum of the elements concentrations (ΣTR) can also be used for comparison purposes.

A more controversial control on REE distributions in geological samples is the so-called “tetrad” or “double-double” effect in which REE representing quarter, half, three-quarter, and completely filled 4f shells have increased stability with resulting anomalous behavior. In geological samples it has been suggested that the tetrad effect is most apparent in natural waters and other aqueous liquids, and in rocks it results from interaction with aqueous solutions (McLennan, 1994). Sea water and precipitates from sea water would process a “W-type” to the REE pattern; the interaction water-rocks would result in “M-type” effects to the REE pattern of the rock (Masuda et al, 1987).

A very large proportion of REE contents may be found within heavy minerals. There are minerals in which the REE are essential constituents (e.g., bastnaesite, monazite, xenotime, aeschynite, allanite), although the chemical mechanisms and limits of REE substitution in some rock-forming minerals (e.g., zircon, apatite, titanite, garnet) are also derived (Burt, 1989). These minerals are resistant to weathering and may be concentrated during sedimentary sorting processes. Many heavy minerals have high concentrations of elements, other than the REE, that are found in trace levels in most residual and sedimentary clayey materials. Accordingly, in some cases it is possible to evaluate the influence of heavy mineral fractionations on REE patterns by examining other geochemical data like, Hf, Zr and Th contents (McLennan, 1989). Also a correlation between REE contents and the clay minerals present in sediments has been found pointing to the incorporation of REE especially in kaolin minerals (Prudêncio et al., 1993; Marques, 2007).

With the exception of inductively coupled plasma- mass spectrometry (ICP-MS) on liquid samples, NAA offers sensitivities that are superior to those possible by all other analytical methods. Even compared with ICP-MS, INAA is more sensitive and accurate method for certain trace elements such as middle and heavy REE, particularly when these elements are present in very low amounts in the samples as shown by Dai Kin et al. (1999) in a comparative study using instrumental NAA (INAA) and ICP-MS. As mentioned above, REE are very good indicators of geological contexts, particularly the differentiation between light REE (LREE) and heavy REE (HREE). Thus, the precise and accurate determination of both LREE and HREE is fundamental for a good characterization, INAA being the most appropriate method. Besides the difficulty of achieving complete digestion of geological samples for analysis by ICP-MS is known the same happens with artifacts like archaeological ceramics.

The INAA technique involves the irradiation of a sample by neutrons to make the sample radioactive followed by gamma spectrometry to determine the amounts of different elements present in the sample. INAA has a number of advantages over most other analytical methods when investigating archaeological specimens. In fact the preparation of archeological materials, particularly ceramics, for analysis by INAA is extremely easy in most instances a representative sample may be only a portion of the sample weighed and placed in an appropriate container, which is very important when dealing with cultural materials that must be preserved. INAA is a sensitive, precise and accurate technique for quantitative multi-element analysis and the potential of this method as an archaeological tool to establish the provenance of archaeological ceramics was first recognized by Robert Oppenheimer in 1954 (Sayre and Dodson 1957; Harbottle 1976). Since then numerous works have been done based on this method. Although nuclear reactors are becoming less available, INAA applications on archaeological materials proceed, still being considered one of the most appropriate methods to analyze artifacts. A brief history of NAA and its application to archaeology, and a description of the physics behind the analytical method can be found in Glascock & Neff, 2003. After fifty years of successful NAA applications to archaeology, a special issue of *Archaeometry* (vol. 49, 2007) was published with contributions describing the history of several NAA laboratories and case studies of archaeological artifacts. Among these, several case studies concerning ceramics provenance were presented (Dias & Prudêncio, 2007; Hancock et al., 2007; Kilikoglou et al., 2007). A brief review of the 50th anniversary of NAA applications was done by Pollard (2008).

The application of the INAA method in support of provenance research has been largely used over the past few decades in the Instituto Tecnológico e Nuclear (ITN). The first analyses of archaeological ceramics were conducted in the late 1970's by using the Portuguese research reactor (RPI), and proceeded generating a large database for ceramics and raw materials from different chronologies and archaeological sites (Cabral & Gouveia, 1979; Cabral et al., 1983, 1988; Dias et al., 2001; 2002; 2003a, 2003b; 2005a; 2005b; Prudêncio et al., 1989; Prudêncio et al., 2003; 2006). In the late 1990's, a research group especially devoted to archaeometry (measurements techniques in archaeology), particularly compositional and dating studies (TL-OSL) of ceramics and raw materials, was formed in ITN – “Cultural Heritage and Sciences”. INAA has been used not only to help answer questions related to ceramics provenance but also to study the degradation of stones in archaeological monuments and historical buildings, and to determine the provenance of the stones in order to perform conservation products tests and restoration of buildings with a similar geological material (Prudêncio et al. 1995; 1998; 2000; Romão et al. 2000; Sequeira Braga et al., 2000; Nasraoui, 2002). INAA has also been used for precise and accurate determination of the contents of natural radioactive elements such as potassium, rubidium, thorium and uranium aiming to evaluate the dose rate, which is fundamental for TL-OSL dating of cultural materials and archaeological contexts, as well as geological contexts (Richter et al. 2003; Prudêncio et al, 2007a).

In this chapter the INAA technique (comparative method) used in the ITN laboratory of the Chemistry Unit to characterize archaeological ceramics and clayey materials is described. The chemical data obtained for shards and potential raw materials used for their production of the NW Iberian Peninsula are discussed, particularly for ceramic production during the Roman occupation Bracara Augusta and vicinities, where no archaeological evidence like kilns or wastes has been found. The importance on the application of techniques of nuclear

chemistry to ceramics and raw materials to solve archaeological problems mainly related to the location of production sites in this area during Roman times is enhanced, which is fundamental to pursue studies of distribution and exchange. Among the chemical elements studied, special attention is paid to the importance of the precise and accurate determination of the REE contents by nuclear methods, allowing geochemical patterns in ceramics and raw materials that can be used to identify provenance.

Chemical Characterization of Archaeological Ceramics and Clays by INAA

The theory of neutron activation analysis can be found in Parry, 1991. In this chapter a brief description of procedures for archaeological ceramics and clays in the INAA laboratory of the Chemistry Unit of ITN is given.

To obtain powder samples of ceramics, the procedure is as follows: the inner and outer surfaces of the shard are scraped using a drill burr made of tungsten carbide (Fig. 1). The scraped specimens are subsequently brushed clean, washed, boiled for 30 min in deionized water, and then dried for several hours at 30°C.

After drying, a planetary agate mortar for small samples is used to crush and homogenize ~2 g of pottery sample into a fine powder (<53 μm). Potential source clays (500-1000 g depending on the grain size) are dried at 30°C and ground in agate mortars into a fine powder (<53 μm).

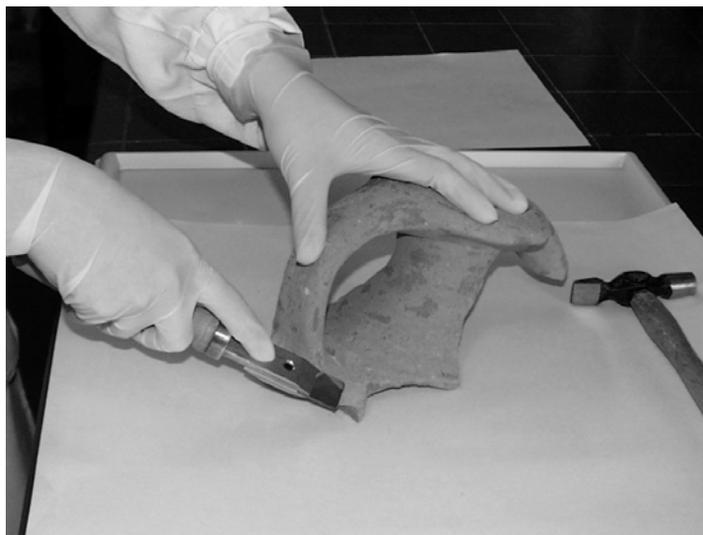


Figure 1. Photograph showing the scraping of the surfaces of the shard.

For INAA, aliquots of ~1 g of powder of ceramics are then dried in an oven at 110°C for 24 h and stored in a desiccator until the samples can be weighed for irradiation. The same procedure is performed for clays and reference materials. Two multi-element reference materials are normally used. All powdered samples (ceramics, clays and standards) are prepared by weighing 200-300 mg of powder into cleaned high-density polyethylene vials (Fig. 2).

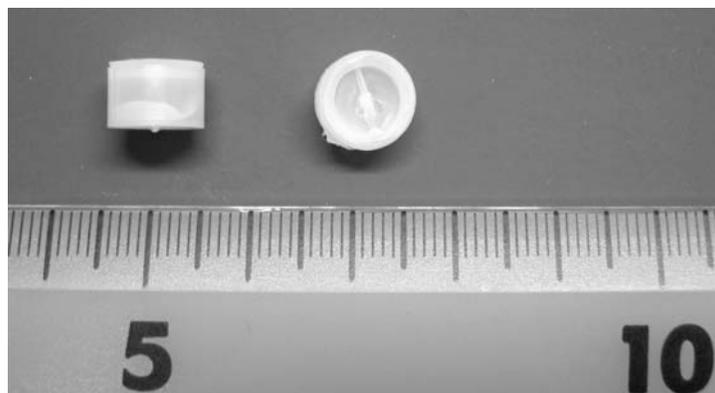


Figure 2. Photograph of the polyethylene vials used for irradiation.

Long irradiations (7 h) on pottery and clay specimens are performed in batches of 20 unknowns along with four standards (Fig. 3) in the core grid of the Portuguese Research Reactor at a thermal flux of $3.346 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$; $\phi_{\text{epi}}/\phi_{\text{th}} = 1.4\%$; $\phi_{\text{th}}/\phi_{\text{fast}} = 12.1$. The bundles are rotated continuously during irradiation to ensure that all samples received the same exposure to neutrons. Even so, Fe flux monitors are placed in appropriate plastic containers for irradiation together with the samples for neutron flux variation corrections.

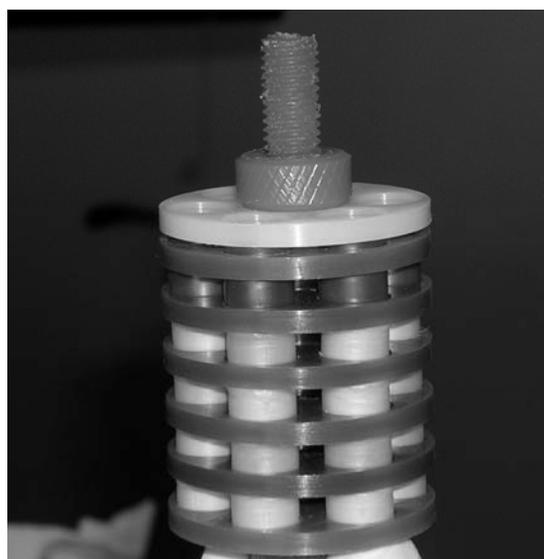


Figure 3. Container used for long irradiations in the RPI.

Two γ -ray spectrometers are used: (1) one consisting of a 150 cm^3 coaxial Ge detector connected through a Canberra 2020 amplifier to an Accuspec B (Canberra) multichannel analyzer. This system has a FWHM of 1.9 keV at 1.33 MeV; and (2) the other consisting of a low energy photon detector (LEPD) connected through a Canberra 2020 amplifier to an Accuspec B (Canberra) multichannel analyzer. This system has a FWHM of 300 eV at 5.9 keV and of 550 eV at 122 keV (Fig.4).



Figure 4. Counting room of the INAA laboratory of the Chemistry Unit at ITN.

Different cooling times were selected to determine radionuclides with different half-lives. These cooling times and energies of γ rays, as well as the type of detector used are given in Table 1. Na, K, Fe, Sc, Cr, Co, Zn, As, Br, Rb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th and U abundances are obtained. Relative precision and accuracy are, in general, to within 5%, and occasionally within 10%.

Table 1. Radionuclides, cooling times, energies of γ rays, and type of detector used.

Element	Radionuclide	Decay time (d)	Energy of γ -rays used (keV)	Detector Coaxial Ge(Li)	LEPD
Na	^{24}Na	3	1368	x	
K	^{42}K	3	1524	x	
Sc	^{46}Sc	27	889	x	
Cr	^{51}Cr	27	319	x	x
Fe	^{59}Fe	27	192;1099	x	x
Co	^{60}Co	27	1332	x	
Zn	^{65}Zn	27	1115	x	
As	^{76}As	3	559	x	
Br	^{82}Br	3	776	x	
Rb	^{86}Rb	27	1077	x	
Zr	^{95}Zr	27	756	x	
Sb	^{124}Sb	27	1690	x	
Cs	^{134}Cs	27	796	x	

Table 1. Continued

Element	Radionuclide	Decay time (d)	Energy of γ -rays used (keV)	Detector Coaxial Ge(Li)	LEPD
Ba	¹³¹ Ba	27	496	x	x
La	¹⁴⁰ La	3	1596	x	
Ce	¹⁴¹ Ce	27	145	x	x
Nd	¹⁴⁷ Nd	27	91; 531	x	x
Sm	¹⁵³ Sm	3	103	x	x
Eu	¹⁵² Eu	27	1408	x	x
Tb	¹⁶⁰ Tb	27	881; 1178	x	x
Yb	¹⁶⁹ Yb	27	177; 198	x	x
Lu	¹⁷⁷ Lu	27	208	x	x
Hf	¹⁸¹ Hf	27	482	x	
Ta	¹⁸² Ta	27	1222	x	x
Th	²³³ Th	27	300; 312	x	x
U	²³⁹ Np	3	106; 228	x	x

The spectra are processed by using the programs GELI and DAISY, adapted respectively from GELIAN and OLIVE programs (Op de Beek 1972/74). In general, two pairs of standards are used in order to obtain an internal calibration.

Corrections are made for the interference from uranium fission. It is well known that the presence of U in samples interferes in the determination of several elements concentration by instrumental neutron activation analysis. This is partly due to the identity of some ²³⁵U fission products with radionuclides formed by radioactive capture of neutrons on those elements (nuclear interference), and also to the fact that the γ -rays emitted by some fission products cannot be resolved from γ -rays emitted by radionuclides of interest produced by (n, γ) reaction (spectral interference). The extent to which the interference may affect the accuracy of the determination depends on the ratio of the concentrations of the element to be determined and of U in the sample, as well as on the irradiation conditions and cooling time. In this chapter corrections for the determination of rare earth elements (REE), zircon and barium were done. The determination of the concentration of the light rare earth elements (LREE), Zr and Ba in geological materials containing U must be done with great care in this respect. A numerical procedure to correct for U interference in this determination is necessary, based on the Runge-Kutta algorithm, for solving the differential equations governing the growth and decay of nuclides during and after the irradiation. The interference factors for element X is defined as the ratio $F = N^*(^aX)/N(^aX)$, where $N(^aX)$ = number of nuclei of the radionuclide ^aX produced by (n, γ) reaction in 1 gram of the natural element X; $N^*(^aX)$ = the number of nuclei of the same radionuclide produced by fission of ²³⁵U in 1 gram of natural U. The values of $N(^aX)$ and $N^*(^aX)$ may be obtained by solving the systems of differential equations that govern the number of nuclei ^aX present at time t, during and after the irradiation. Experimental values were obtained by irradiating an uranyl nitrate solution with U₃O₈ previously verified by alpha-spectrometry as being of natural isotopic composition and

REE, Zr and Ru standards also in the form of solution prepared with pure REE oxides and Zr and to account Ru chlorides. The determination of Ba based on the reaction $^{130}\text{Ba}(n,\gamma)^{131}\text{Ba}$ must take into account the spectral interference from fission due to ^{103}Ru . The results obtained in the experiments performed in the RPI showed a good agreement between experimental and calculated values. Especial attention must be paid to the irradiation conditions, since the correction factors depend particularly on the $\phi_{\text{epi}}/\phi_{\text{th}}$ ratio (Martinho et al., 1991; Gouveia et al., 1987). More details of the analytical method can be found elsewhere (Gouveia et al. 1988; Prudêncio et al, 1986; 1988).

NW Iberian Peninsula - Production and Trade of Pottery in Bracara Augusta

Bracara Augusta, Braga (NW Portugal), was a Roman town recognized as a centre of production and distribution of pottery to a wide regional area (Martins & Delgado, 1995). The morphological analysis of Roman ceramics established the existence and chronology of different production types used during the five centuries of Roman occupation (1st – 5th century). The location of the town is shown in Fig. 5.

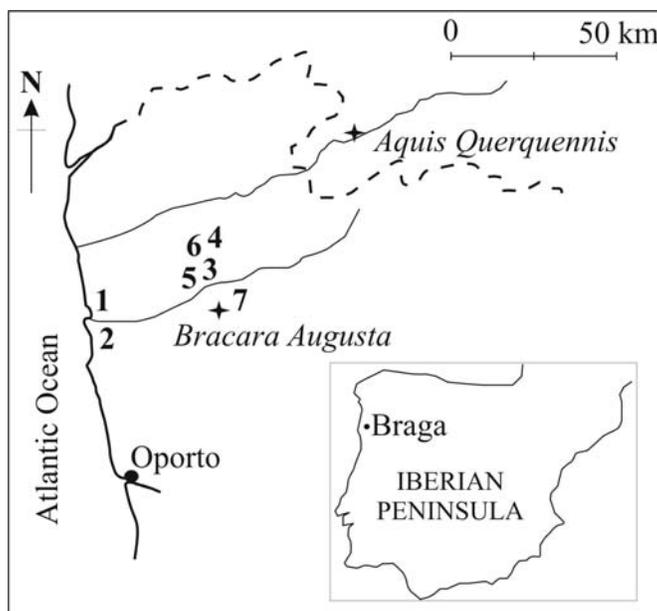


Figure 5. Map of the studied area, with the location of the archaeological sites - *Bracara Augusta* and *Aquis Querquennis*, and raw materials sampling. 1 – Campados; 2 – Barqueiros; 3 – Prado; 4 – Bustelo; 5 – Espinheira, Ucha; 6 – Quebrosas; 7 – Braga.

The study of thousands of shards found in Braga allowed the identification of different types of Roman pottery, such as Bracarense, polished fine gray painted ceramics, late gray ceramics, local amphorae production, non-vitrifiable red slip ware and also several types of common ware (Martins & Delgado, 1989-90a; 1989-90b). The location of production sites was first made by the so-called criterion of abundance or gravity model (Rice, 1987), since

there is little evidence of pottery workshops in the Braga region. In this way a compositional study of the different types of ceramics and the inventory and the compositional features of regional clay deposits is crucial in order to identify local/regional productions and also imports. The chemical characterization by using INAA, and complemented with mineralogical studies, of the pastes of different types of ceramics found in Bracara Augusta has been done in an attempt to confirm the morphological classification by macroscopic observation of the pastes. Chemical-based provenance studies can be performed aiming to identify the raw materials used to produce the several types of ceramics, and thus delimiting the geographic source region by tracing the clay source used to infer the most probable location of production. While provenance studies may be able to identify the kinds of clay material used in a particular kind of pottery, they do not provide information on the cultural or socioeconomic context, such as the locations of workshops, which depends on the finding of kilns, deposits of raw materials, wasters, etc. at a site. Thus, the approach adopted for the establishment of the existence of ceramic production in Bracara Augusta (town and vicinities areas) has been a combination of the abundance of the types of potteries (forms and paste types) and comparisons of the ceramic composition with clay resources available in the area to establish local/regional production, and thus creating “ceramics reference groups” to be used for provenance studies. Besides, an important achievement is to distinguish imports from imitations of imports locally produced (Prudêncio et al, 2006, Oliveira, 1997; Oliveira et al, 2005; Gomes, 2000; Gaspar, 2000).

Ceramics from Bracara Augusta

Among the ceramics found in Bracara Augusta, special attention is paid in this chapter to several types of ceramics, namely the “Bracarense” (B), common wares (C), the “non vitrifiable red slip” wares including imitations of “Terra Sigillata Hispanica” and “African Red Slip Ware” forms and stamp-types (IS), and imitations of “pompejanish-rotten” slip (IP). Also chemical composition of ceramics of known origin, namely Lugo (Galicia, Spain), Cadiz (Andaluzia, Spain), and Italy (Oliveira, 1997; Oliveira et al., 2005; Gaspar, 2000; and Dias et al, 2003c) are compared with ceramics found in Braga in order to identify imports and imitations of imports.

The “Bracarense” ceramics paste is characterized by a very fine- to medium-grained yellow-pale paste covered with a brownish yellow slip that is clearly different from other ceramic types found in the town (Alarcão and Martins, 1976). A similar fine yellowish paste is also found in some common wares and special ceramic pieces, suggesting the use of the same clay source type used to produce ceramics of different typologies (Oliveira, 1997; Prudêncio et al., 2006). The designation – Bracarense - was due to the fact that it was located and identified first in Bracara Augusta and vicinity. However, shards with a similar fine paste were found later on in other archaeological sites of the NW Iberian Peninsula region, such as Aquis Querquennis (Galiza, Spain) (Fig. 5). In fact, the textural and mineralogical features of the Bracarense ceramics from both archeological sites, Bracara Augusta and Aquis Querquennis, are very similar, pointing to the possible use of the same type of raw material. This finding together with the absence of kilns near Braga, question the production centre’s location. Aquis Querquennis is a large archaeological complex, including several structures, namely the military camp, a possible inn facing the XVIII vía, one thermal waters bath complex, local pre-Roman settlements and Roman villae.

As referred above, some pieces of common wares and other typologies present a fine yellowish paste like the one used to produce the so-called “Bracarense” ceramics type. However, the majority of the “Common ware” found in Bracara Augusta present a reddish-brown to yellowish-brown and pale brown paste. The same paste type is also found in ceramics of the so-called “non vitrifiable red slip” ware, which is also very frequent in Braga and vicinity. The same technique of manufacture and the typical non vitrifiable red slip occurred in different types that lasted from the 1st to the middle of the 5th century. This large span of time can explain the significant particularities of the fabric and shapes which determined their inclusion in different groups, according to well defined criteria (Delgado, 1993/94).

A multivariate statistical approach, using the chemical contents obtained by INAA, of the several ceramics found in large amounts in the Braga region point to two main compositional groups of pastes, each of them including different typologies: (i) Group 1 - the fine yellowish paste mostly found in Bracarense ceramics – the “Bracarense paste” – of Bracara Augusta and Aquis Querquennis, and also in common wares and other typologies of Bracara Augusta; and (ii) Group 2 - the “common ware paste” found in the majority of the common wares of Bracara Augusta and also in imitations of “Terra Sigillata Hispanica”, “African Red Slip Ware”, and stamp-types (all these three types made with the non vitifiable red slip technique), and ceramics with imitations of the “pompejanish-rotten” slip found in this Roman town.

The chemical composition obtained by INAA showed that the “Bracarense paste” differs from the “common-ware paste” mainly due to a lower REE fractionation and a greater intermediate and heavy REE relative to the light REE, as can be seen in the chondrite-normalized REE patterns (Haskin et al., 1971) of both pastes groups presented in Fig. 6 and 7. Greater U and Ta, and smaller Fe, Na and Ba contents were also found. The Aquis Querquennis pottery shards analyzed present the same geochemical pattern as those from Bracara Augusta.

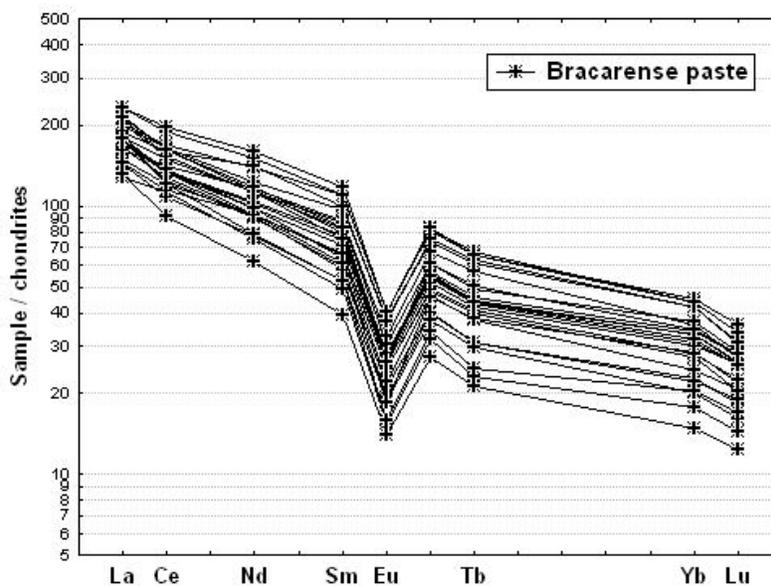


Figure 6. REE patterns shards with the “Bracarense paste”.

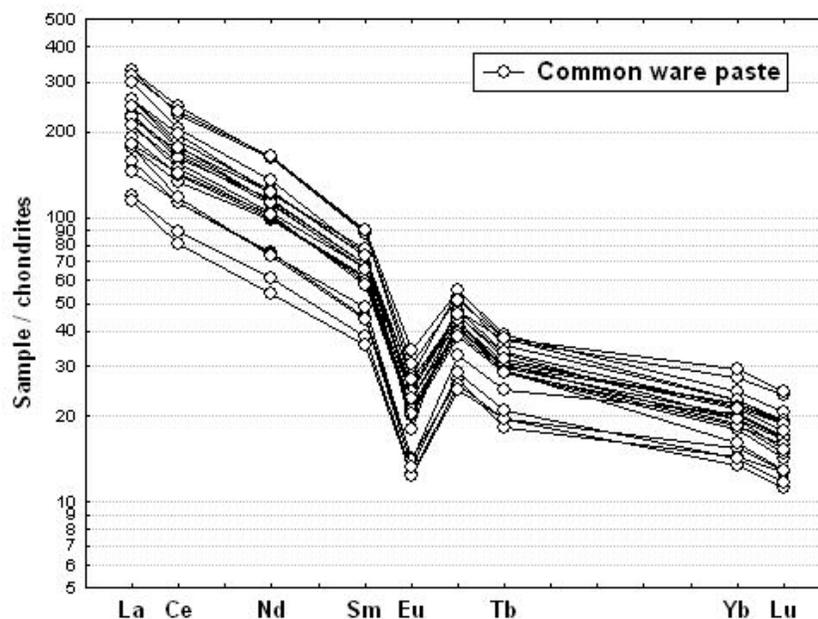


Figure 7. REE patterns shards with the “common ware paste”.

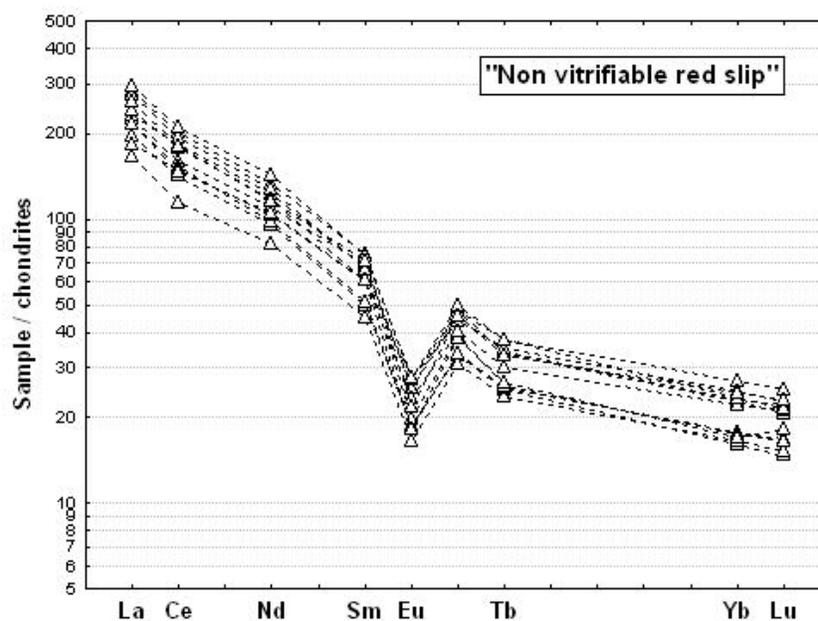


Figure 8. REE patterns of shards of the “non vitrifiable red slip” wares – imitations of “*Terra Sigillata Hispanica*”, “African Red Slip Ware” and stamp-types.

The composition of the pastes of “non vitrifiable red slip wares” (IS) analyzed is similar to the common ware paste, as shown by the REE patterns (see Fig. 7 and 8). Assuming that the production of the majority of the common wares is local, the similarity presented by the IS ceramics suggests that the same clay resource was used in the Braga region to produce

imitations of imports. It should be noted that the paste of ceramics with “non vitrifiable red slip” present in general higher contents of Fe and other transition metals of the 1st transition series (Fig. 9) which can be due to their incorporation into the paste (for instance as iron oxides) during the technological procedures to obtain the red slip.

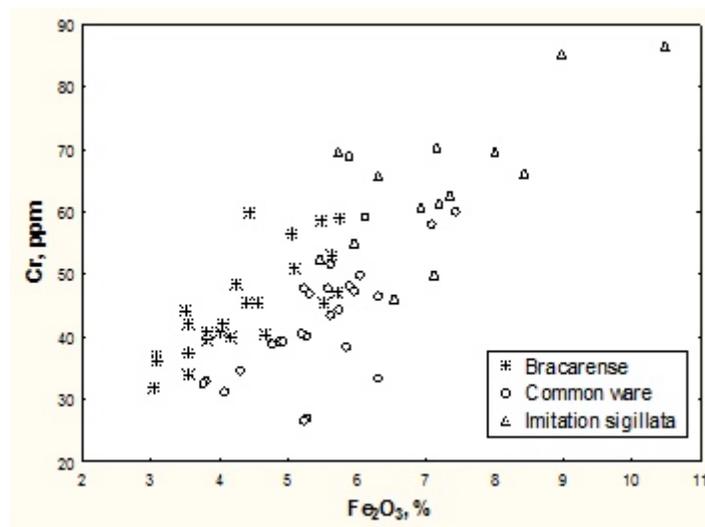


Figure 9. Fe vs. Cr contents plot of the “Bracarense paste”, the “common ware paste” and the “non vitrifiable red slip” wares (IS).

In this way, two main types of pastes appear to exist in shards of different typologies found in large amounts in Bracara Augusta and vicinity (the “Bracarense paste” and the “common-ware paste”), pointing to local/regional productions with the use of two main types of local/regional raw materials. The absence of archaeological evidence of ceramic production justifies the clay tracing to confirm local/regional productions.

Local and Regional Raw Material Sources

The regional clay materials between the city of Braga and the shoreline were previously studied by Sequeira Braga (1988), Sequeira Braga et al. (2002) and Ferreira et al. (2000). These previous geological studies, including the inventories of regional clay materials and their mineralogical characterization have been used in tracing the clays. Clay materials are more concentrated in the Cávado river basin (NW Portugal), between the city of Braga and the shoreline, corresponding to sedimentary deposits, as well as residual clays derived by weathering from granites and schist.

The strategy procurement for clays to study was directed to the more adequate raw materials. In this way, fine grain size and the yellow-pale color characteristics of the “Bracarense paste” was taken into account, and kaolin deposits located near the coast were collected. In the case of the brownish “common ware paste”, clay materials deposits located near the city of Braga were selected for compositional analysis. The sampling locations of the clays are shown in Fig. 5: (a) residual kaolin (#1); (b) sedimentary kaolin (#2); (c)

paleoweathered schist (#4,5); (d) sedimentary deposits (small temporary basins) (#6); (e) Prado sedimentary formation (#3); and (f) clays derived by weathering of granite (#7).

The chemical results obtained for the clay materials clearly differentiate the samples according to the geological environments. A first multivariate statistical approach of the clay materials using the chemical contents obtained by INAA as variables (except Br due to its mobile character) show that samples gather according to the nature of the deposit (Fig. 10): (a) near Braga - (1) clays derived by weathering of schist (Espinheira and Bustelo) and sedimentary deposits of small temporary basins (Ucha and Quebrasas); (2) clays derived by weathering of the Braga granite and the upper level of the Prado formation; (3) Prado sediments; and (b) near the coast - (4) residual kaolin; and (5) sedimentary kaolin.

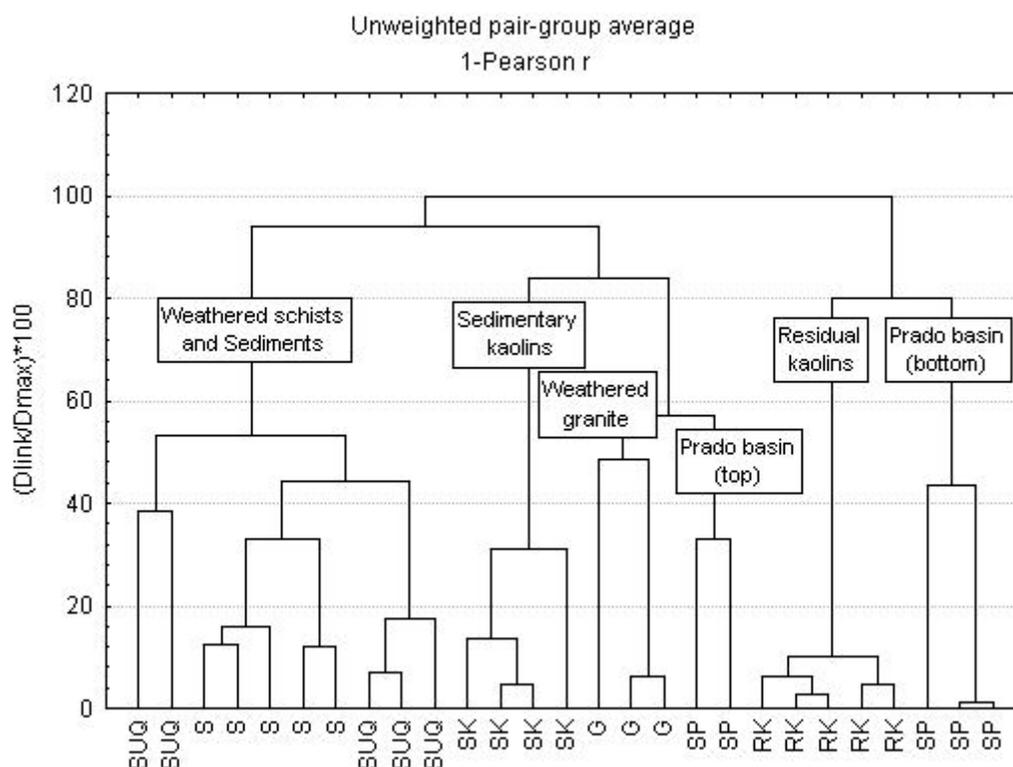


Figure 10. Phenogram resulting from the joining tree clustering applied to clay materials, using the Pearson correlation coefficient and the UPGMA amalgamation method.

Among the chemical elements studied, REE patterns well characterize and differentiate the two main compositional groups of ceramics pastes found in large amounts in Braga - the Bracarense and the common ware paste (see Fig. 6 and 7). The REE patterns of the clay materials are shown in Fig. 11-14. The REE patterns of residual kaolin (Fig. 11) are clearly different of the remaining clay materials studied, including the sedimentary kaolin of Barqueiros, as well as the clayey materials collected in different geological environments near the city of Braga. Residual kaolin samples present low REE contents and relative enrichment of the MREE relative to the LREE and the HREE. Also, the results obtained point to the existence of Yb-Lu anomalies, with inflexion of the REE distribution curves in Yb, which can

be explained by the "tetrad" effect (McLennan, S.M., 1994; Masuda et al., 1987). Concerning the sedimentary kaolin, REE are more concentrated and the MREE and HREE contents vary more than the LREE, particularly La and Ce (see Fig. 11).

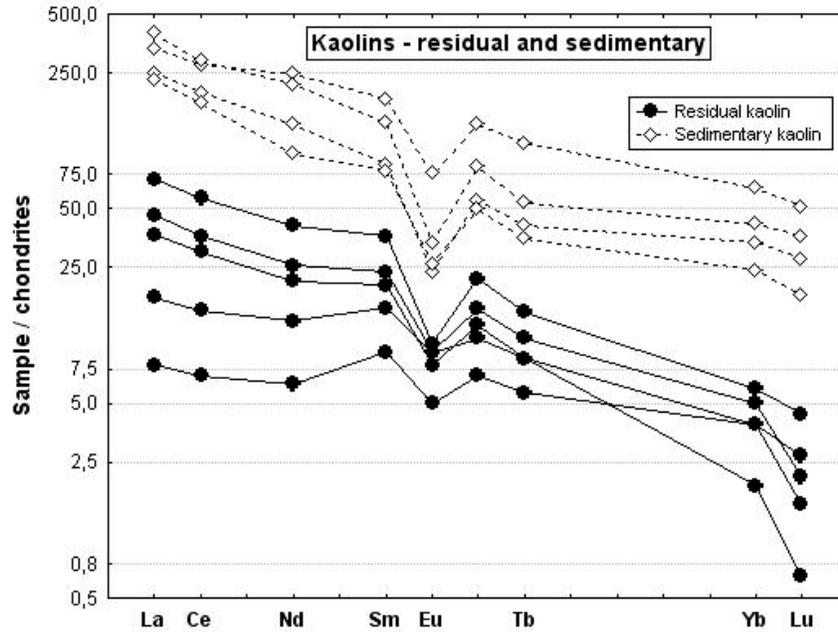


Figure 11. REE patterns of residual and sedimentary kaolin deposits located near the coast.

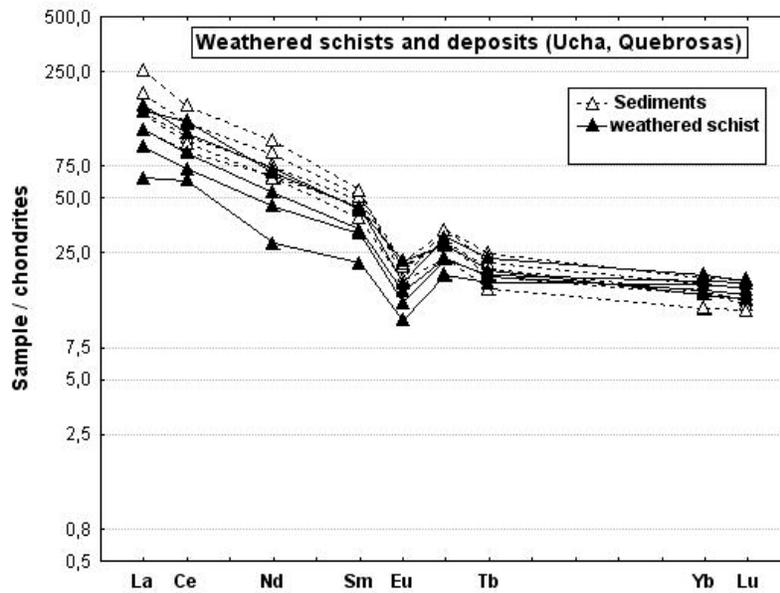


Figure 12. REE patterns of weathered schist and sediments of small sedimentary basins near Braga.

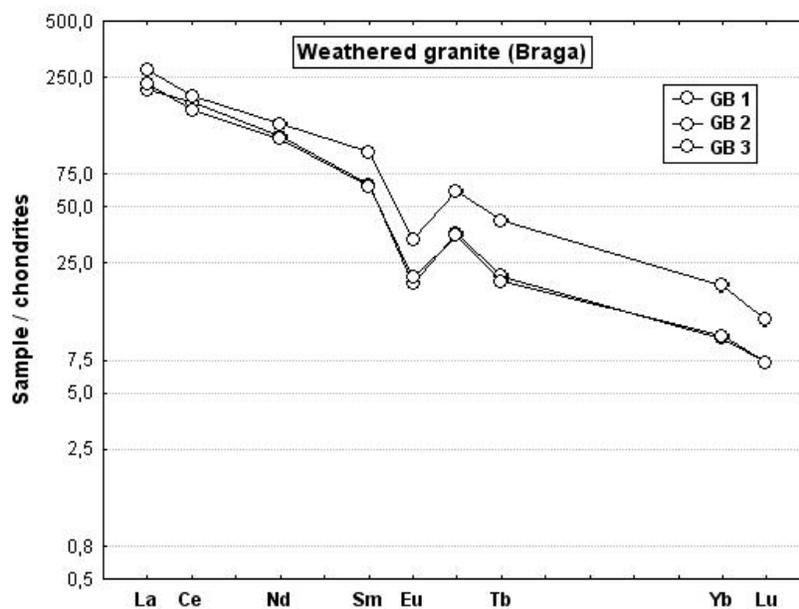


Figure 13. REE patterns of weathered granite located near Braga.

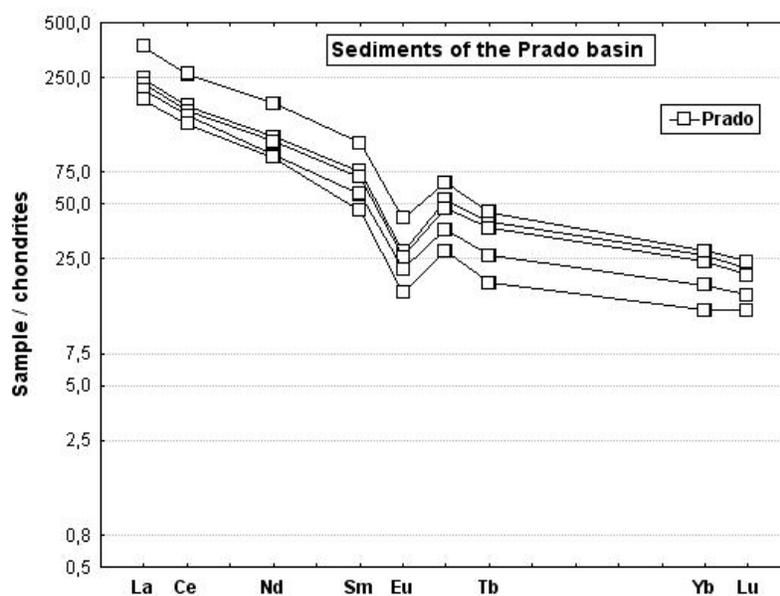


Figure 14. REE patterns of sediments of the Prado basin located near Braga.

The REE patterns of the clay samples from the vicinities of Braga are shown in Fig. 12-14. The sedimentary deposits of Ucha and Quebrasas show an enrichment of the LREE relative to the HREE when compared to the clays derived by weathering of schist (Fig. 12). The weathered granite materials present a higher LREE/HREE ratio due to lower HREE contents (Fig. 13). The sediments of the Prado sedimentary basin (Fig. 14) present in general higher REE contents, when compared with the small basins of Ucha and Prado. However,

La/Yb ratios are not as high as observed for the clay materials derived by weathering of the granite of Braga. In this way, the REE patterns of the Prado sediments point to a more important contribution of granites as source materials than of schist. On the contrary, the geochemical pattern of the sediments from the small basins of Ucha and Quebrasas point to a composition more similar to the weathered schist.

Thus, the REE patterns of the kaolin samples, both residual and sedimentary, collected near the shoreline are clearly different of the patterns found for the clay materials derived by weathering of granites and schist, as well as sedimentary deposits located near Braga. Also a clear distinction can be made of the several deposits studied in both regions. Among the other elements studied, thorium and chromium contents are also good indicators, and can be used to differentiate the geological formations.

The residual kaolin can be clearly differentiated due to lower contents of Hf, HREE, Sc, Co, and particularly Cr. Low Fe concentrations were also found, but of the same magnitude of those found in the sedimentary kaolin. High contents of K, Cs, and particularly Rb also differentiate the residual kaolin.

Ceramics and Clays

Multivariate statistical analysis of the clays and the ceramics by using the chemical elements contents as variables (except Br due to its possible modifications after the ceramic manufacture) showed that the ceramics with the “Bracarense paste” gather with the sedimentary kaolin. The composition of “common ware paste” presents more similarities with the clay materials collected near Braga. However, using a multivariate statistical approach it is not possible to relate the ceramics compositional group with one particular type of raw materials (see Fig. 15). For this purpose geochemical considerations must be considered. As referred above, some trace elements are good indicators to distinguish the clay deposits, namely the REE, Th and Cr contents. In this way these elements were used in an attempt to identify the most probable raw materials used to obtain the “common ware paste”, and among the clay materials occurring near Braga, the results obtained so far point to the clays of the Prado sedimentary basin (see Fig. 16).

Thus, the results obtained so far suggest that in Roman times, clays from the Prado sedimentary basin located near Braga appear to have been used to produce ceramics of different typologies with the “common ware paste”. On the other hand, the similarity between the “Bracarense paste” and the sedimentary kaolin deposits occurring along the NW Iberian Peninsula point to the procurement of this type of special clays to obtain a fine paste to produce different types of pots, including the Bracarense ceramics and also other special pots like thin walls from the Augustus Tiberius period, as well as common wares. Although no ceramic kilns were found in Braga, given the large number of occurrences of ceramics with these two types of pastes, as well as the importance of the site, production centers probably did exist in the area. To produce pottery with finer pastes, the procurement of appropriate raw materials may have led to the exploitation of the kaolin deposits which occur near the coast of the north of Portugal and Galiza. White fine clays are rare and valuable, not only nowadays, but also in antiquity. This might explain its use in the area, even though the source is not very close (~40 km away) to the Bracara Augusta archeological site, especially considering that the manufacture could have taken place in Bracara Augusta. However the transport of raw materials by boat up the river should be considered.

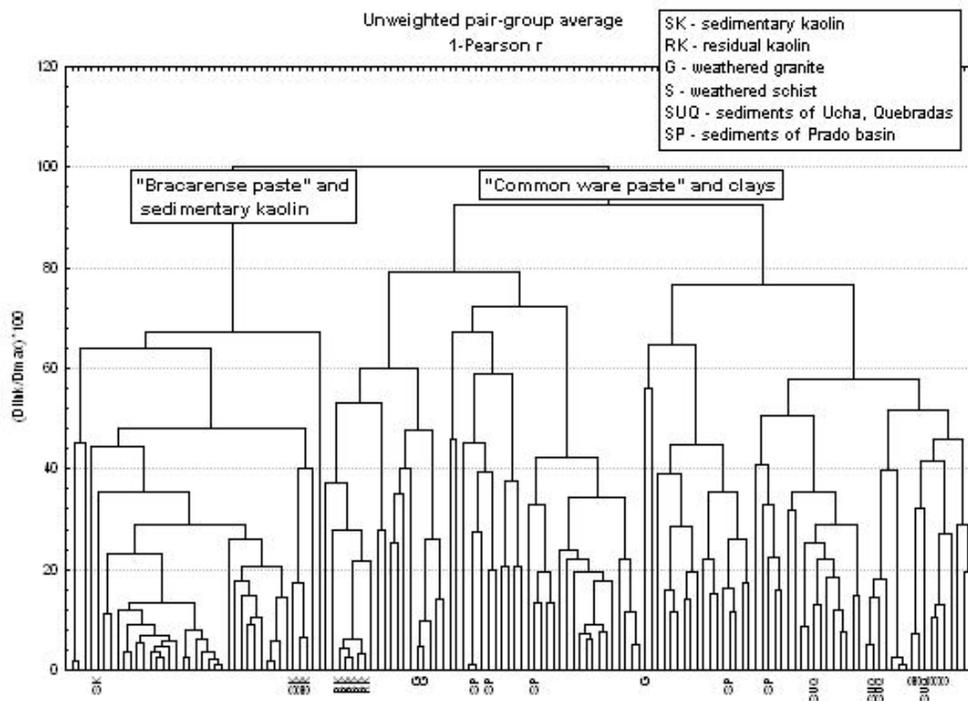


Figure 15. Phenogram resulting from the joining tree clustering applied to clay materials and ceramics from Braga, using the Pearson correlation coefficient and the UPGMA amalgamation method.

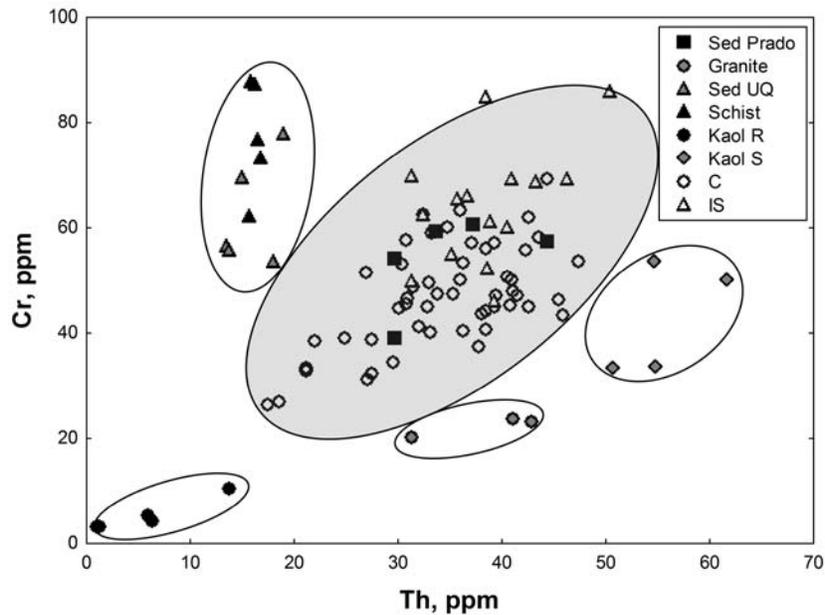


Figure 16. Th vs. Cr plot of the “common ware paste” compositional group and the clay deposits. The grey ellipse includes “the common ware paste”, the “non vitrifiable slip” wares and the clays of the Prado basin.

The Bracarense ceramics from Aquis Querquennis and Bracara Augusta archeological sites present the same geochemical and mineralogical features, pointing to the use of the same type of raw material. The differences found between the ceramics from both sites can be explained by compositional variations along the same sedimentary kaolin deposit which is widespread along the NW Iberian Peninsula coast, as well as differences in clay processing and/or differences in the pottery use and burial environment. A comparison of Bracarense ceramics from the two sites and regional clay materials reinforces the suggestion that sedimentary kaolin were exploited in their manufacture. Mullite, spinel and hematite were the newly crystallized minerals in the shards, indicating firing temperatures near 900°C, inferred by the reaction series of the kaolin minerals and associated minerals (illite and goethite) during firing (Prudêncio et al., 2006).

Concerning the imports, the chemical analysis of the pastes of samples of Italic production (Pompejanish-rotten Platen) found in Bracara Augusta and of imitations of the “pompejanish slip” also found in this town confirmed that the imitations have a paste with distinct chemical composition. Two different types of composition were identified – one similar to the “common ware paste” pointing to a local production of these imitations, and the other with a completely different composition, suggesting a different provenance. In this way a comparative study with ceramics from other Roman sites, namely Lugo (L) and Cadiz (CD) in Spain, and also Italic ceramics (I) including the one found in Bracara Augusta, was performed. The result of the joining tree clustering using the chemical contents as variables and the UPGMA amalgamation method is shown in Fig. 17. The sample of Pompejanish-rotten Platen (P) found in Bracara Augusta is similar to other ceramics from Campania, Italy. The Imitations of “pompejanish-rotten” slip (IP) found in Bracara Augusta gather with ceramics from Lugo (located NE of Braga) indicating these imitations were produced in the Roman town of Lucus Augusti and imported to Bracara Augusta, except one shard analyzed which appears to have been produced in Bracara Augusta since the paste is similar to the “common ware paste”. The REE patterns the Italic shard and the imitations of the “pompejanish slip” found in Braga are shown in Fig 18, together with the REE patterns of ceramics from Lugo. The REE pattern presenting the lower REE contents and the higher negative Eu anomaly corresponds to the imitation with a composition similar to the “common ware paste” of Braga and the one with the smaller negative Eu anomaly corresponds to the Italic ceramic found in Braga. Despite some similarities found between composition of the Italic and Cadiz ceramics (see Fig. 17), the REE patterns differentiate well these two groups of ceramics due to lower REE contents and a slightly lower $(La/Yb)_N$ ratio as shown in Fig. 19 and 20.

Significant differences among the several provenances were also found for other chemical elements determined by INAA, as shown in Fig. 21-23.

The study confirmed the importation of “Pompejanish-rotten Platen” from Italy (Campânia) as well as imitations of this production made in Lucus Augusti. Also evidence of production in Bracara Augusta of imitations of “Pompejanish-rotten Platen” and forms of “Terra Sigillata Hispanica”, “African Red Slip Ware” and stamp types was found.

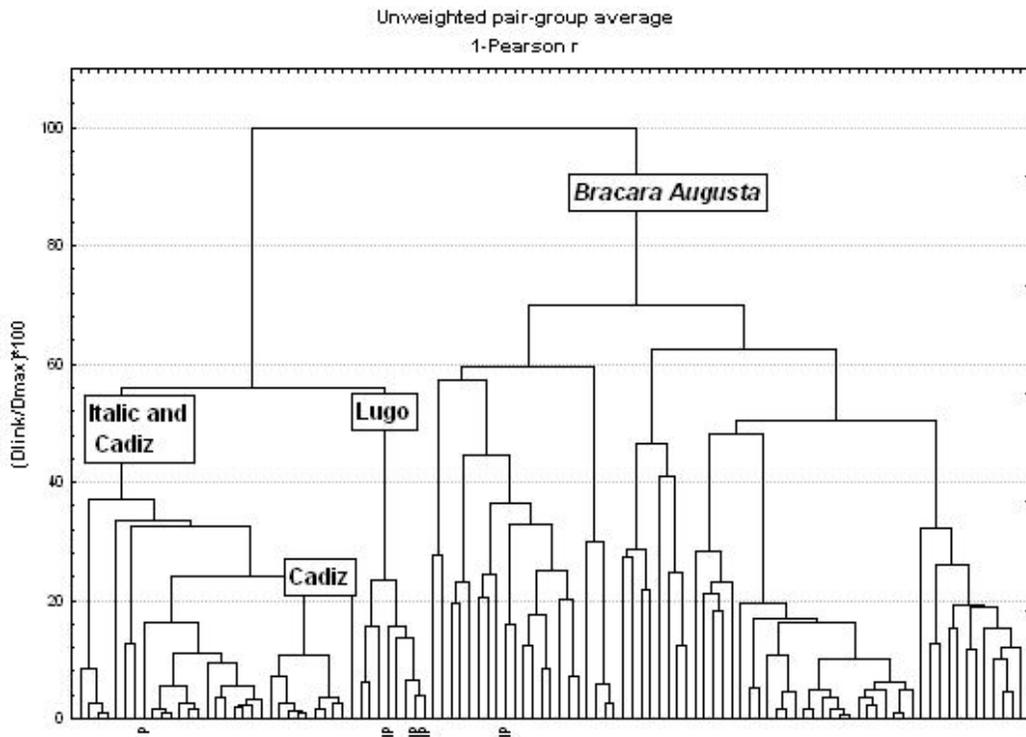


Figure 17. Phenogram resulting from the joining tree clustering applied to ceramics from Braga and imports, using the Pearson correlation coefficient and the UPGMA amalgamation method.

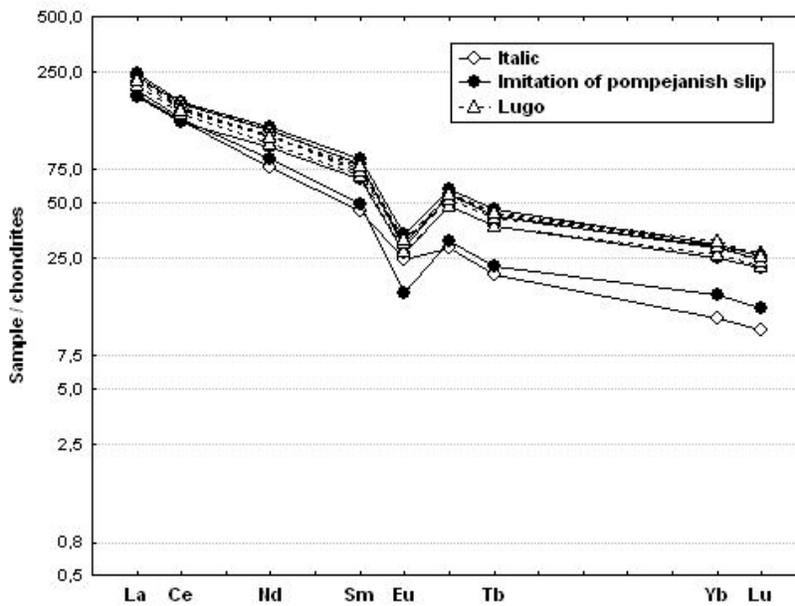


Figure 18. REE patterns of shards with imitation of the pompejanish slip and ceramics from Lugo (Spain).

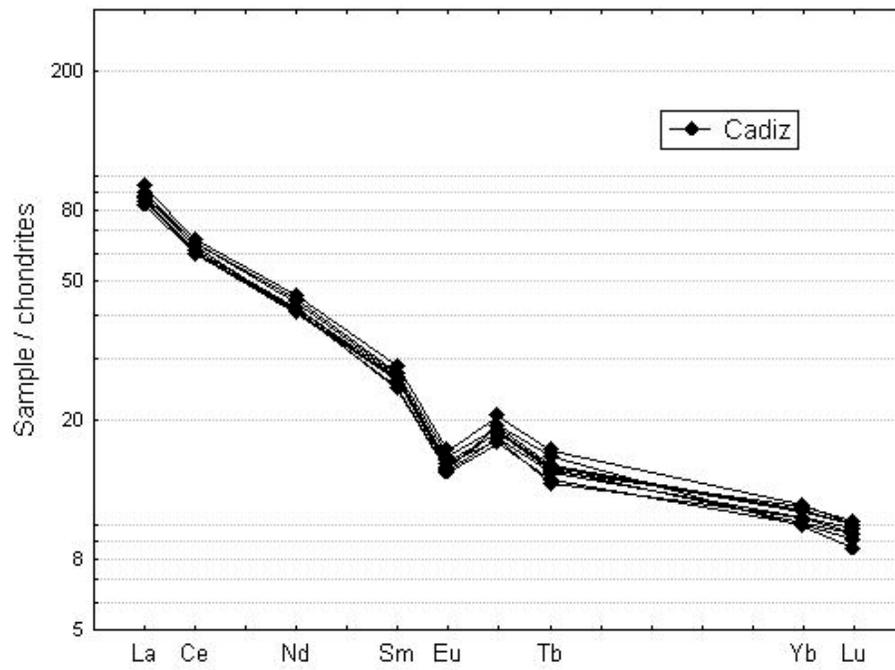


Figure 19. REE patterns of ceramics from Cadiz (Spain).

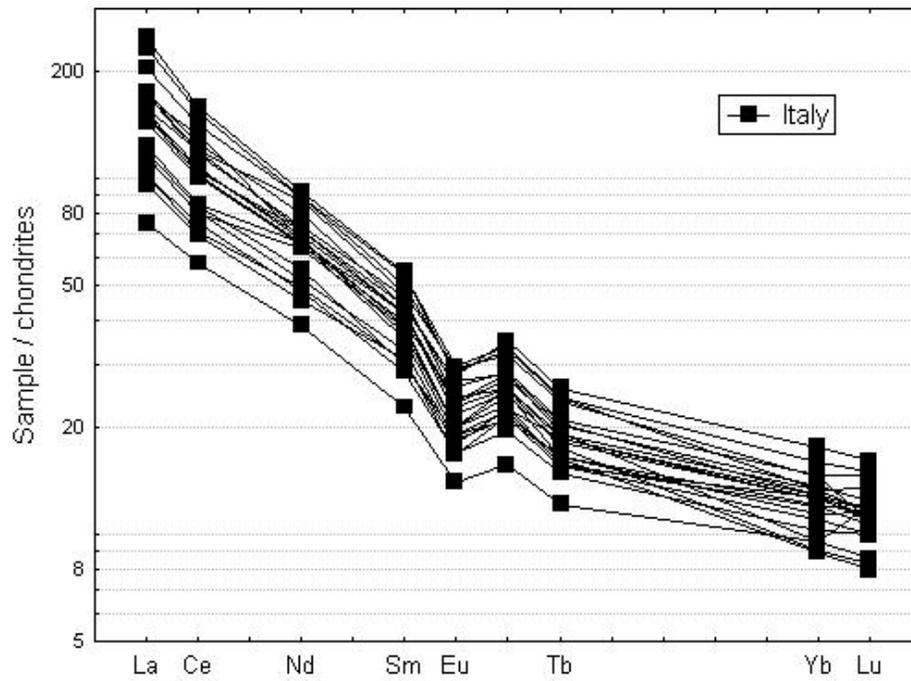


Figure 20. REE patterns of ceramics from Campania (Italy).

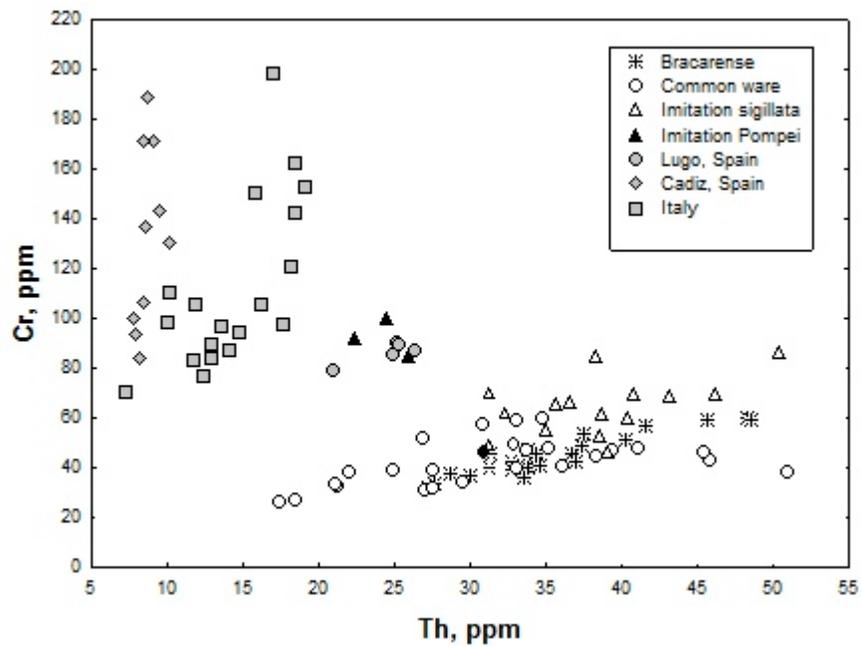


Figure 21. Th vs. Cr plot of the ceramics from Cadiz, Italy, Lugo, and ceramics found in Braga.

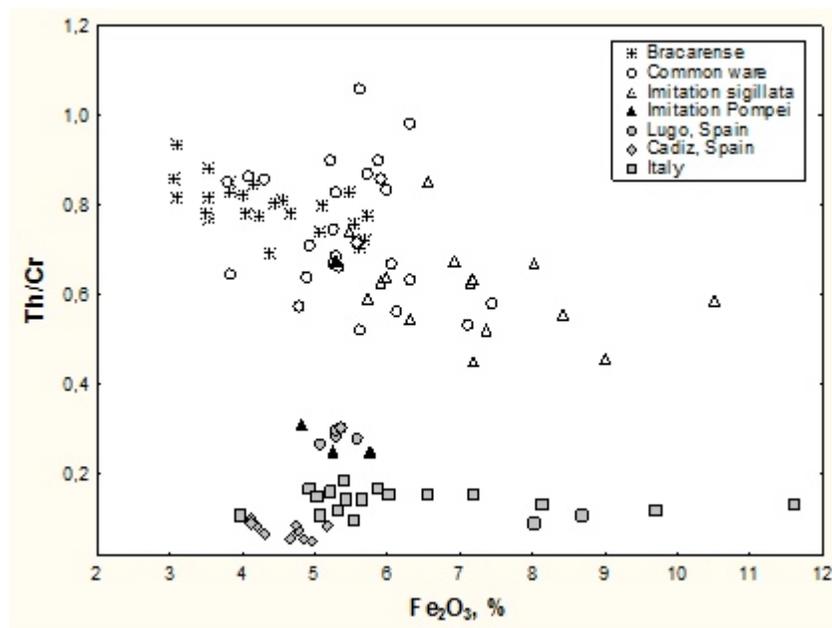


Figure 22. Fe vs. Th/Cr plot of the ceramics from Cadiz, Italy, Lugo, and ceramics found in Braga.

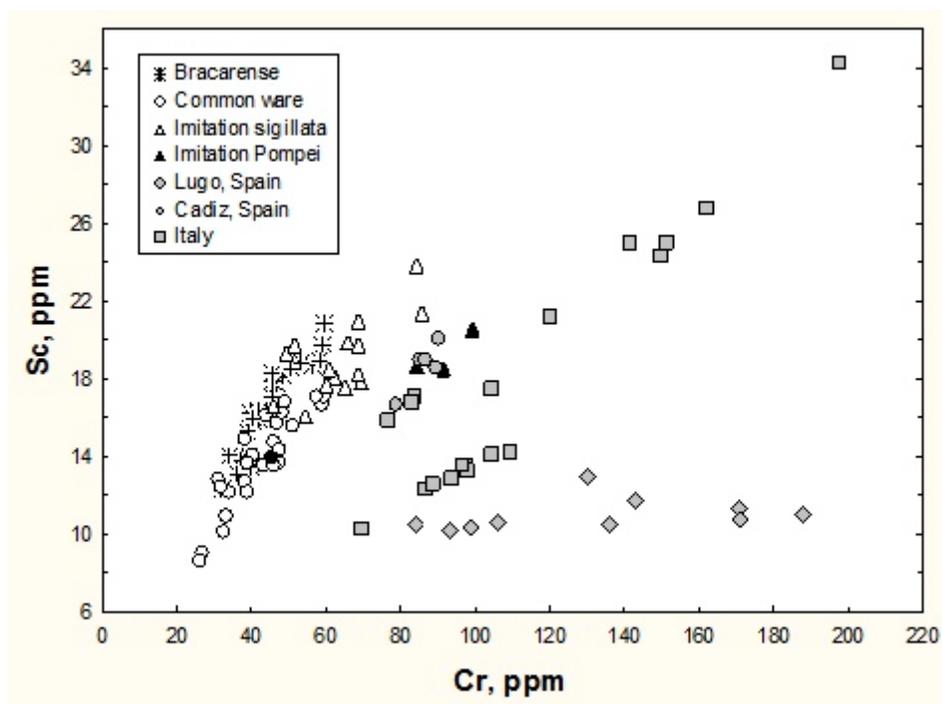


Figure 23. Sc vs. Cr plot of the ceramics from Cadiz, Italy, Lugo, and ceramics found in Braga.

Conclusion

Chemical analysis by instrumental neutron activation analysis of the paste of archaeological ceramics found in the Braga region (NW Portugal) showed that there are two main compositional groups of ceramics – the “common ware paste” and the “Bracarense paste”. A comparative study with the chemical composition of regional clays allowed identifying local/regional productions, and distinguishing regional productions and imports:

- The clays of the Prado sedimentary basin, located near Braga, were used to obtain the “common ware paste” to produce most of the common wares typologies and also imitations of different types of imports of other regions of the Roman Empire (“Terra Sigillata Hispanica”, “African Red slip ware”, stamp types, and “Pompejanish-roten slip”).

- The sedimentary kaolin deposits occurring along the north coast of Portugal and Galiza (Spain) appear to have been used to obtain the “Bracarense paste” to produce the Bracarense ceramics and other types of ceramics. The shards collected in Aquis Querquennis have the same geochemical pattern than those found in Bracara Augusta, i.e. they all appear to have been manufactured with the same clay type, reinforcing the suggestion that sedimentary kaolin deposits were exploited in their manufacture.

- The compositional analysis confirmed the importation of “Pompejanish-roten Platen” from Campania (Italy) as well as of ceramics with imitations of the “pompejanish-roten slip” made in Lucus Augusti.

It is important to enhance that different geochemical patterns found in clays from different geological context obtained by the precise and accurate results of INAA, consists on an important basis for the comparison with ceramics since the identification of the clays used for certain productions can contribute to delimit a potential area of clay resources and thus establishing provenance. This is particularly useful when no archaeological evidence of production exists. Among the chemical elements obtained by INAA, the precise and accurate determination of REE contents and other trace elements with diverse geochemical behavior is very important for the characterization of ceramic productions and their relation with raw materials, which is crucial to pursue studies of provenance establishment and trade routes reconstruction in ancient times.

Technological styles incorporate materials and behavior. Compositional analysis of archaeological ceramics and raw materials, particularly the chemical characterization by using INAA, together with classical archaeological methods is a powerful approach to solve questions dealing with provenance, and also some indications of the technology and use in ancient times. Clay analysis plays a crucial role in studies of ancient ceramics, contributing with answers to better understanding resource exploitation strategies, production technologies, and regional and interregional interaction patterns. The vessels are made essentially by clays, the composition of the ceramics reflecting the origin of the clay materials used and conclusions may be inferred concerning the type of raw materials and the establishment of the geographic area of production. However, a special care has to be paid to the interpretation of the results obtained by the compositional analysis of the archaeological ceramics, since the composition of the broken fragments that archaeologists recover in excavations is the combination of several parameters, starting with the initial composition of the raw materials, its manipulation to make the vessel, the use and the burial environment.

The application of nuclear methods of chemical analysis has been contributing to a large extent to resolve questions related with the production of ceramics in Bracara Augusta. The chemical results obtained allowed to establish two compositional groups of local/regional productions that can be used as “ceramic reference groups” in further studies involving imports and exports of pottery of this Roman town.

Acknowledgments

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