
Trace element geochemistry and mineralogy for solving problems in provenance and production technologies of Pre-historic ceramics

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Abstract

Compositional analysis of archaeological ceramics and raw materials, together with archaeological data is a powerful approach to solve questions dealing with provenance, production technology, and regional and interregional interaction patterns. The chemical and mineralogical characterization of the regional potential raw materials is very important when there is a lack of kilns structures, which is the case of prehistory. The vessels are made mostly by clays, the composition of the ceramics reflecting the original raw materials. Conclusions may be inferred concerning the type of raw materials and the establishment of the resource procurement zones. A special care has to be paid when interpreting the compositional results 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. Compositional studies of Chalcolithic ceramics from archaeological sites in Portugal played a very important role, particularly the trace elements distribution, to determine provenance. In general, the results point to local productions, and thus to the circulation of the idea rather than the products. These results help to conceptualize the diffusion models and to recognize the importance of certain typologies and their significance in an archaeological point of view.

Resumen

El análisis composicional de las cerámicas arqueológicas y sus materias primas, junto a los datos arqueológicos, son una potente herramienta para resolver cuestiones relativas a la proveniencia, tecnología de producción y modelos de interacción regional e interregional. La caracterización química y mineralógica, de las materias primas potenciales de la región, es muy importante cuando se carece de estructuras de hornos, como es el caso de la prehistoria. Los recipientes se han realizado principalmente con arcillas, en los que la composición de la cerámica refleja las materias primas originales. Se pueden extraer conclusiones, teniendo en cuenta el tipo de materias primas, estableciendo las zonas de aprovisionamiento de recursos. Hay que considerar como un caso especial la interpretación de los resultados de composición de las cerámicas arqueológicas, ya que los fragmentos rotos que recuperan los arqueólogos en sus excavaciones suponen una combinación de varios parámetros, desde la composición inicial de las materias primas, su manipulación para realizar la vasija, el uso y finalmente el ambiente de enterramiento. Los estudios composicionales, y en especial los de distribución de elementos traza, de la cerámica del Calcolítico de yacimientos arqueológicos portugueses, han jugado un papel muy importante para determinar la proveniencia. En general, los resultados apuntan a producciones locales y por tanto, a la circulación de la idea, más que de los productos. Estos hallazgos ayudan a conceptualizar los modelos de difusión y a reconocer la importancia de ciertas tipologías y su significado en el punto de vista arqueológico.

Key-words: *ceramics, clays, trace elements, mineralogy, production technology, provenance, pre-history*

1. Introduction

Ancient ceramics are well known for their enormous potential of information in archaeological studies, being used to date sites, trace trade patterns, understand social and economic relationships, and so forth. In archaeology the term ceramics usually refers to cooking and serving utensils and art objects manufactured of clay. For potters the term clay means the basic ingredient in ceramic manufacture, composed of plastic particles (clay) and natural nonplastic grains. Compositional analyses of pottery together with classical archaeological approaches have been largely used in solving a broad variety of questions. In fact, the application of the techniques of chemistry, physics, geology, and materials science provide a basis for understanding many questions about manufacturing techniques, history of technology, production organization, functional relationships between specific resource manufacturing combinations, and patterns of local, regional, or extraregional distributions of pottery. Thus, better understand a culture, time period or human interaction. These are the main re-search issues of ceramic technological (and ecological) analysis. An overview of these types of studies is well shown in the literature (Rice 1987; Chappell 1991; Hector 1992; Velde & Druc 1999).

The compositional analysis of ceramic materials in archaeological studies is carried out aiming particularly to understand how the ceramic might have been used and to determine the location and techniques involved in its manufacture. Furthermore, these objectives can be achieved on broken fragments as well as intact vessels. Numerous issues deserve significant attention at the start of a mineralogical and chemical characterization study:

- the objectives of the analysis must be defined so they can be translated into chemical and mineralogical terms;
- the requirements of sample selection for each technique must be understood;
- the understanding of the limitations of the

conclusions one can get from the results; and

- the translation of mineralogical and geochemical data to archaeological proposals.

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 which is the case of the majority of prehistory. Compositional characterization, as applied to pottery, is oriented toward quantitative and qualitative description of its mineral and chemical components. Establishing local and regional patterns needs a regional clay deposits inventory, followed by studies of mineralogical and chemical characterization.

Mineralogical analysis of ancient pottery is particularly useful in the understanding of the manufacture process, and appropriate techniques may provide information about temper addition, oxidation-reduction conditions and temperatures of firing. Results may also be obtained about post-depositional processes.

Petrographic analysis is an important tool in the determination of pottery provenance by the identification of fingerprint minerals, when comparing different clay deposits.

Chemical analysis of sherds, especially concerning trace elements, is a powerful approach in ceramics characterization and provenance studies, since geochemical interpretations may contribute largely to solve archaeological problems.

Among the materials and processes involved in making a pot, the most important is clay and its manipulation to make the vessel.

Therefore it is important to know how the different elements make clays, what the leftovers are in the claymaking process, and the mineralogical and geochemical fingerprints which can give one a clue to the geographic origin of the clay and temper materials found in the finished product. Hence a discussion

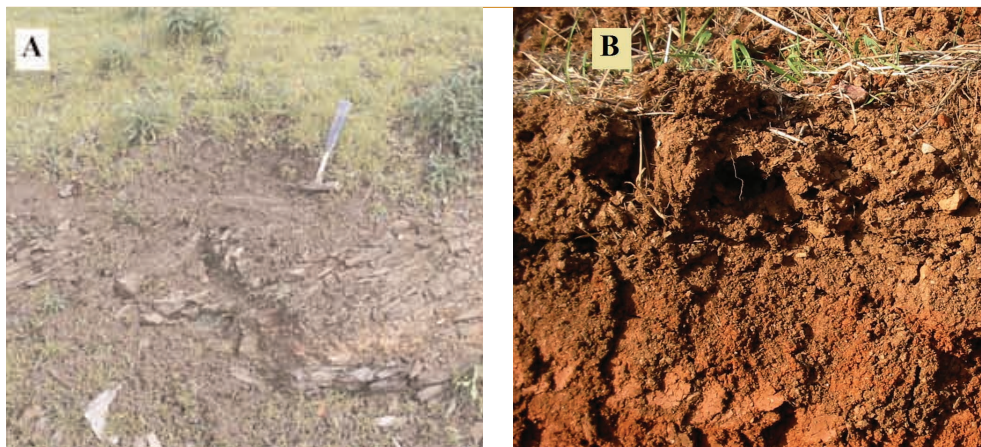


Fig. 1. Surficial clay materials derived by weathering of schists (A) and sediments (B).

of pottery must include clay and its origin, composition and properties.

In ancient times, sources of clays tended to be those easily available. Soils or surface sediments are likely candidates (Fig. 1). Some soils or sediments can be adapted to form a ceramic without further treatment. 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 difficult the establishment of provenance.

Studies of the mineral transformations of clays induced by firing and their comparison with the mineralogical composition of sherds may help to determine the type of clay used and the temperatures range they could have been exposed to during their production. In this comparison it is necessary to take into account that ceramics are not merely fired clays. Their composition depends not only on the chemical and mineralogical composition of the clays, but also on the grain size distribution, possible addition of different types of nonplastic grains as temper, mixture of clays, maximum heating temperature, heating ratio, duration of firing, redox atmosphere and post-depositional alteration (Maggetti, 1982; Rice, 1987; Moropoulou et al., 1995; Velde & Druc, 1999; Trindade et al, 2010).

Compositional 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. In combination with ceramic ecology, ceramic technology can, for example, characterize properties of both resources and pottery and permit comparisons between them. 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 kilometres from the production site. However, in the past, the potter was more tied to the local resources for his production, since clays did not travel more than several kilometres; tens at most if water transport did not intervene, sands and so forth even less. In this way the potter would have adapted local resources to answer specific needs, functional and aesthetic.

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 cha-

racterize archaeological vessels focus on the mineralogical and chemical 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 very first step (and one of the most important) in an archaeological ceramics study concerning a compositional study, is the selection of sherds from a large collection. In general there is an enormous range of recognized variation in visible characteristics, and it is a difficult task to break down a collection into a much smaller number of sherds that represent the variations in the entire collection. The ideal starting point is the identification of a problem and the categories of archaeological pottery from which the sample will be drawn are generally those traditionally used in archaeology - types, decorative classes, and wares, as well as



Fig. 2. Pre-historic sherds with different pastes and decorations (photographs by António Valera).

chronological and regional variations (Fig. 2). Compositional analyses of the archaeological ceramics aim to know texture features, and the mineralogical and chemical composition. Several techniques can be used such as optical microscopy, X-ray diffraction (XRD), Mössbauer spectroscopy, instrumental neutron activation analysis (INAA), X-ray fluorescence, among others. Chemical analysis of ceramics and of raw materials, 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 statistics 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 considerations.

In some cases, an important step prior to any statistical analysis is normalization of the chemical elements contents. To compensate for grainsize 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 grainsize and mineralogical proxy, that is to express the ratio of the concentration of a given element to that of the normalizing factor.

Normalization using a conservative element has been commonly used in environmental studies, especially in verifying whether the variation of elements in sediments is indeed the result of anthropogenic and/or natural activities. Hence 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 behaviour of the element chosen for normalization, and not purely based in statistical considerations (Prudêncio *et al.*, 2006; Dias & Prudêncio, 2008).

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. Therefore, the best option appears to be the use of a con-

servative 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 is structurally combined in clay minerals and micas, being a good tracer of phyllosilicates, particularly in sediments containing Al-silicates in all size fractions.

Several multivariate statistical methods can be employed by using statistic programs (e.g. *STATISTICA*, *Statsoft*, 2011). The results obtained 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.), eventual modifications during the use of pots, and postdepositional processes.

A number of different analytical techniques have been applied with varying degrees of success to characterize archaeological materials, but all of them need to have multielement capability and sufficient sensitivity to detect traces of elements in the various matrices. Among them the analytical method with one of the longest and most successful histories of application for provenance research has been instrumental neutron activation analysis (INAA). The real success story of this technique, however, comes from the investigation of ceramics dating from throughout archaeological times. INAA is a sensitive technique useful for quantitative multielement analysis of major, minor, and trace elements, which concentration can have different meanings in minerals or in rock descriptions, as well as in ceramics (Prudêncio, 2009; Glascock & Neff, 2003).

Among trace elements, rare earth elements distributions can be particularly useful in distinguishing clayey materials resources. 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. 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 coordination 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 behaviour 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 (Prudêncio et al. 1993, 1995; Gouveia et al. 1993; Burt, 1989).

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 (IST/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

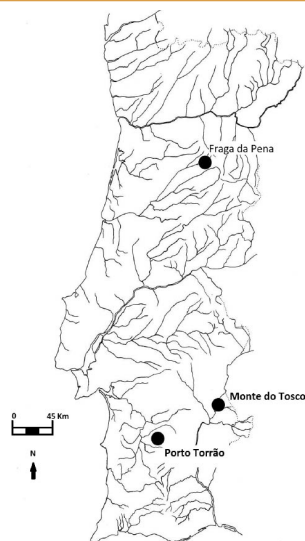


Fig. 3. Map of Portugal, with the location of the archaeological sites - Fraga da Pena, Monte do Tosco and Porto Torrão.

chronologies and archaeological sites (Dias et al., 2000; 2001; 2002; 2003a, 2003b; 2005; 2007; 2010; Prudêncio et al., 1988; 2003; 2006; 2009). 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”, nowadays named “Applied Geochemistry & Luminescence on Cultural Heritage” (GeoLuC). 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 (Prudêncio et al., 2007; Burbidge et al., 2009; 2010).

The making of pots in pre-history

Potter's clay is a material of “high” clay content, with a high or certain plasticity when wetted and worked. In addition to clay minerals, nonplastic grains may occur in different proportions. Also non-plastic grains may be added by the potter to the clay material to improve the working to make the pot that is reducing the plasticity of the waterloving clay particles. The material added is in general termed as temper. Inclusion is also a term used by archaeologists to refer any nonplastic material in the paste (mineral grains, rock fragments, grog or crushed shells).

The manufacturing process include several steps (forming, drying and firing), which lead to physical and chemical reactions influencing ceramic production: plasticity and the role of temper, shrinkage during firing, and nonplastic expansion during firing. The “visible” reactions are mainly change in colour, and retraction and expansion processes related to the quality of the paste, the type and quantity of the raw materials, the particle size, the amount of water present, the preparation of the paste and the forming techniques used.

The function or quality of a pot is influenced by the raw materials used. A coarse paste, fairly

porous, with poorly oriented particles, and low-firing, is more defected resistant. It is a multi-purpose paste often found in prehistoric wares. However in some cases a careful selection of the clays or a preparation of the materials to obtain a particular paste for the production of a specific kind of ware was also done in pre-history (Velde & Druc, 1999).

2. Case studies. Geochemical and mineralogical characterization of Chalcolithic ceramics from Portuguese sites

Three relevant case studies of ceramics from Chalcolithic to early Bronze Age archaeological sites from Southern and Central Portugal (more recent up to north) are presented (Fig. 3). They are specially focused on a chemical and mineralogical characterization of both pottery and potential raw materials from the region, aiming the establishment of provenance and production technology, thus contributing to the discussion of the circulation /diffusion of this kind of pottery (Cabral et al., 1988; Dias et al., 2000; 2002; 2003a; 2005; Dias et al., in press; Valera, 2006).

Chalcolithic ceramics from the three sites include the typical typologies of this chronology, particularly the combed incisions and the Bell Beakers. These typical pots were decorated with patterns stamped on the surface in parallel bands, sometimes filled with white paste, but there are often traces of lime and paint decoration as well. Cord impressions are common, some are all over cord or all over ornamented, others are incised or stamped with various geometric motives, often arranged in zones (Valera, 2006).

Classical archaeological studies regarding the prehistoric ceramics together with laboratory research has been providing significant results concerning questions related with production technology, raw materials exploitation strategies, provenance and mechanisms of circulation.

2.1. Porto Torrão, Ferreira do Alentejo

Bell Beakers from the Chalcolithic settlement of Ferreira do Alentejo (Beja, Portugal), Porto Torrão archaeological site, as well as pre-

Beaker ceramics, modern ceramics, and potential raw materials from site surrounds were studied in order to establish whether the Bell Beakers found at the site were imported or produced locally (Fig. 4).

The geological context of the site comprises gabbrodiorites, quartz, porphyries, Silurian and Devonian schists, greywackes, Palaeogene-Miocene and Pliocene sediments. Nowadays local potters prefer to use raw materials derived by weathering from gabbros and diorites, the so called “Barros de Beja”.

The materials studied included:

- sherds from two different archaeological contexts - the pre-Beaker and the Beaker levels;
- clay samples from available geological background in the area, including soils derived by weathering from gabbros and diorites, and from schists and greywackes, as well as Palaeogene-Miocene and Pliocene sediments; and
- samples of modern ceramics made by local potters.



Fig. 4. Sherds from Porto Torrão archaeological site, Ferreira do Alentejo (photographs by António Valera).

Among the chemical elements studied REE patterns, particularly the europium anomaly, showed that weathered gabbros and diorites were used as raw materials to produce Bell Beakers and also pre-Beaker ceramics. The geographic area of origin of this type of geological materials is shown in Fig. 5. The same type of surficial soils is still used to produce ceramics by the local potters.

Thus the results obtained for ceramics from Porto Torrão Chalcolithic site and for available clay materials, give an important contribution to the Bell Beakers circulation problematic, as they clearly indicate that they were not introduced in the area as a result of some trade or “prestige good” distribution network, but were produced locally.

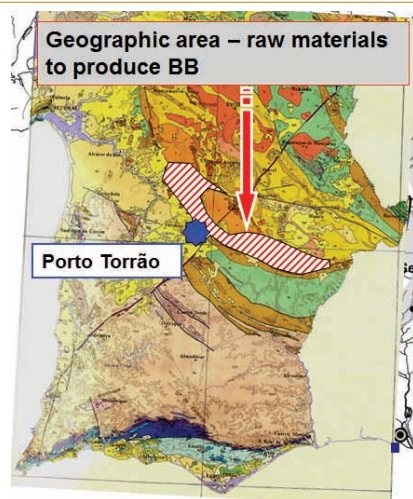


Fig. 5. Geological map of southern Portugal with the location of the Porto Torrão archaeological site and the area of the gabbro-diorite complex (red dashes).

2.2. Monte do Tosco, Alentejo

Monte do Tosco is an enclosure Chalcolithic site, reoccupied during the early Bronze Age, where a late Bell Beaker context has been excavated (Fig. 6). The sherds studied include Chalcolithic ceramics, Bronze Age ceramics from the Bell Beakers context, common ware, and crucibles. Raw materials samples were collected from regional/local clays (weathered schists, greywackes, diorites and gabbros and Tertiary sediments).

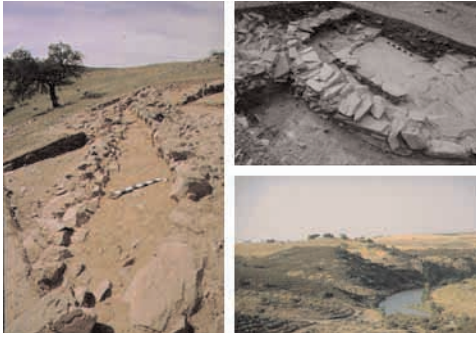


Fig. 6. Monte do Tosco archeological site (Alentejo, Portugal) (photographs by António Valera).

Ceramics from Monte do Tosco were divided in three chemical groups (Fig. 7):

- Group one (1) embraces 80% of Chalcolithic ceramics;
- the second group (2) comprises all the Bronze Bell Beakers (60%) and other Bronze and Chalcolithic ceramics;
- the third group (3) is mainly composed of Bronze Age ceramics (80%)

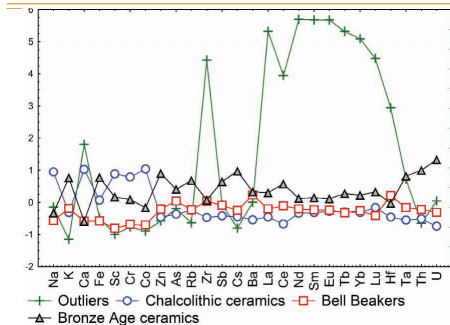


Fig. 7. Plot of means for each cluster (K-means method) using chemical results of Monte do Tosco ceramics as variables.

Chalcolithic ceramics can be differentiated from Bronze Age ceramics by a chemical composition more correlated with the basic rocks of the region, namely clays derived by weathering of quartzdiorites, diorites and gabbros. Bell Beakers ceramics have a more homogeneous composition than other Bronze Age ceramics. Bell Beakers and other Bronze Age ceramics present a similar chemical composition, with a chemical signature also found in local clay - weathered schists and sedimentary clays.

Hence, at Monte do Tosco site, a local pro-

duction for all ceramic typologies can be delineated, including Bell Beakers. Still a few outliers are defined comprising the analysed crucibles and three Bell Beakers (Fig. 7), pointing to the use of different raw materials, probably a different provenance.

2.3. Fraga da Pena, Beira Alta

The Fraga da Pena archaeological site is a fortified settlement located in a huge granitic tor, impressively conspicuous in the surrounding country, occupied at the transition Chalcolithic - early Bronze Age (last quarter of the third millennium BC) (Fig. 8).

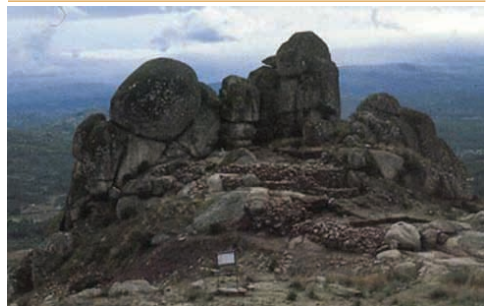


Fig. 8. Fraga da Pena archeological site, central Portugal (photograph by António Valera).

The material culture indicates an occupation where symbolic activities could overcome the domestic ones (Valera, 2006).

Among the several typological groups identified, four were selected for an archaeometric study: Bell Beakers (Fig. 9) decorated vessels with combed incisions; vessels with morphological and decoration patterns of Chalcolithic tradition; and Bronze Age new morphologies.

Clays available in the settlements



Fig. 9. Bell Beakers from Fraga da Pena archaeological site, central Portugal (photographs by António Valera).

surrounding area are residual materials of granites, veins of quartz, aplitedolerite, and schists. Dolerites provide the most clayey samples. The aplite pegmatite veins also provide argillaceous materials, very rich in alkali feldspars. Plagioclase reaches the higher levels in granites. Iron oxides and pyroxenes reach the higher levels in dolerites. Micas occur in all cases. A good differentiating indicator within these samples is the phyllosilicates, plagioclase, iron oxides and pyroxenes proportion.

Clays derived by weathering of granite and dolerite can be distinguished by their Na and K contents related to plagioclase and alkali feldspar, and other elements with geochemical affinity to ferromagnesian minerals, such as Cr, Co, Sc and Fe. Although it is possible to clear differentiate these geological materials, significant variations of the REE contents may occur within the same type of clays depending on the weathering degree of the parent rock.

Macroscopic observation and petrographic analysis showed significant amounts of nonplastic grains, a high irregularity of the grain size distribution, lumps of clay joined to form the paste, giving a very irregular texture, and a very nebulous and irregular

aspect of the orientation of the clays. Thus the claytemper mixture materials used to make the vessels were certainly not ground and sieved.

Compositional studies of all ceramic typologies from Fraga da Pena revealed that Bell Beakers have in general a similar composition. The main geochemical features enhance three main groups, which are related with the regional geological materials:

- Group 1 comprises mostly Bell Beakers;
- Group 2 is mainly composed of Chalcolithic and Bronze Age typologies, combed incisions ceramics, and a few Bell Beakers;
- Group 3 includes Bell Beakers and Chalcolithic and Bronze Age typologies (Fig. 10).

Phyllosilicates, mainly mica, illite, chlorite and smectite occur in Fraga da Pena ceramics. XRD allowed the identification of significant amounts of smectite and interstratifieds in some sherds. The results obtained point to low temperature firing processes, not higher than 500 °C – 600°C (Dias *et al.*, 2005).

The chemical patterns of the Bell Beakers are

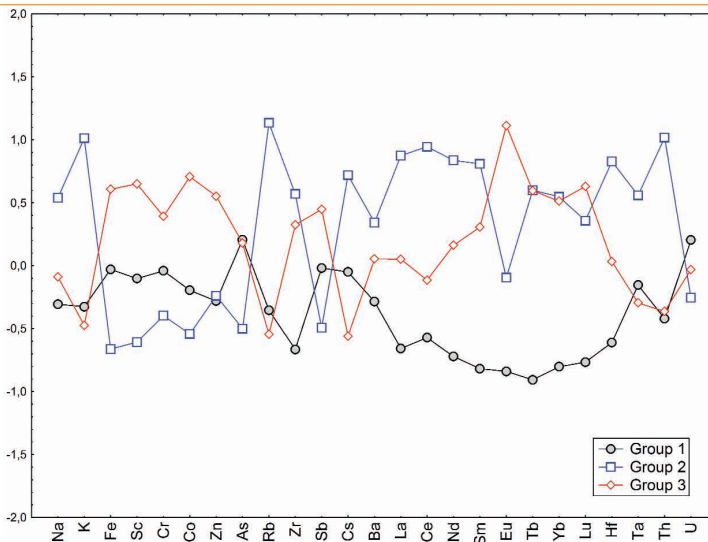


Fig. 10. Plot of means for each cluster (K-means method) using chemical results of Fraga da Pena ceramics as variables.

similar to the dolerites samples, with significant amounts of elements associated to ferromagnesian minerals. The dissimilarities found may be due to the differences among different dolerite veins and/or different stages of weathering as revealed by the REE fractionation. The chemical composition of Chalcolithic and some Bronze Age typologies points to the use of more acid rocks, like local/regional granites, with higher contents of elements related with the presence of feldspars (Na, K, Rb, Cs), higher amounts of REE, specially LREE, Zr, Hf, Ta and Th, and a depletion in elements of the first transition series.

Textural features obtained by petrography, together with mineralogy and chemistry, indicate that weathered dolerites were used for the production of fine pottery. Coarser pastes appear to have been done using weathered granites. In both cases non-plastic grains of granite origin are found. For the production of the Bell Beakers, specially the “nail printed” ones, a careful production technology occurred, with the use of well selected materials of dolerite origin.

In general non plastic grains occur in great amounts added by the potter in the process of assembling the paste to produce ceramics. The high irregularity of grain size distribution, the irregular texture, and the very nebulous and irregular aspect of the orientation of the clays indicate that raw materials were not ground or sieved and well mixed.

Bell Beakers, especially the “nail printed” ones, present a thinner paste with well selected nonplastic grains, indicating a careful mixing and working of the clay resource and temper grains, thus a different process of making the pot. Therefore most of the Bell Beakers from Fraga da Pena, especially the “nail printed” ones, were produced using a careful local production technology.

3. Contribution of compositional data for solving archaeological problems related with pottery circulation

The methodological approach by using compositional data and archaeological evi-

dence to solve ceramics mechanisms of circulation, including the Bell Beakers issue, has been very useful. In the three case studies (Porto Torrão, Fraga da Pena and Monte do Tosco archaeological sites), local production was ascertained for the majority of the cases. Nevertheless some exogenous ceramics were found.

The mineralogical assemblage of pre-historic ceramics in general does not present high temperature mineral phases, pointing all of them to low firing temperatures - below 500°C.

In general, the results obtained point to local productions including Bell Beakers. However in some cases a careful selection of the clays and/or a different preparation of the raw materials to obtain a more fine paste for the production of special wares like “nail printed” were also done in the Fraga da Pena archaeological site.

In a few cases the circulation of the “Product” was suggested. In the three archaeological sites most of the outliers found are Bell Beakers. The transport of these fragile ceramic objects over great distances, enhance the importance of these typologies over a certain period. This approach helps to conceptualize the diffusion models of ceramics.

Thus, the results indicate that several ceramic types including Bell Beakers were made with local/regional resources and only occasionally imported.

Acknowledgements

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