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Analytical and multivariate study of roman age architectural terracotta from northeast of Spain

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Abstract

Roman culture employed architectural terracotta made from baked clay as original material to manufacture ceramic pieces. It was often used as a basis for construction of functional and/or decorative elements in roofs, such as plane and curve tiles as well as antefixes with their corresponding "imbrexes". Some of them are conserved nowadays. They were collected in Roman quarries discovered in old cities and villages sited in the *Hispania Citerior* (northeast of Spain in Roman age). A study of the origin and manufacturing process (moulding, baking, touching up and painting) of these terracotta pieces has been made on the basis of the data obtained from a physicochemical characterization of samples. The used techniques were mainly flame absorption and emission spectrometry for the elemental analysis (major and minor elements), dilatometry for the study of thermal behaviour, scanning electron microscopy (SEM) for observation of thin layers and X-ray diffraction spectrometry (XRD) for mineralogical composition. In addition, a supervised pattern recognition programme was applied to the results for a selected group of 85 samples and five variables (chromium, copper, lead, nickel and zinc contents). Dilatometry and SEM results showed baking temperatures of these materials below 900 °C and the existence of zones with very different porosity in the same ceramic piece. Results obtained from multielemental analysis and multivariate statistical study by linear discriminant analysis lead us to the following conclusions: (i) the high content of lead found in a large number of antefixes demonstrates the use of lead oxide as an additive in the lime grout treatment, (ii) different contents of Cu, Zn, Cr, and Ni were indicative of the use of varied clay types in the manufacture process (even in the same production centre) as well as of the existence of a pigmentation process, although this last affirmation is not corroborated by the presence of remains of evident painting in the ceramic pieces, (iii) samples can be classified according to the places where these pieces came from and (iv) more variety in their composition was found in Roman age terracotta production centres.

Keywords: Multivariate analysis; FAAS; XRD; SEM; Thermal analysis; Archaeometry; Terracotta

1. Introduction

Ancient architectural terracotta comprises all of those pieces made from baked clay and used as functional and/or decorative elements in construction. There is not much information about the production, employment and evolution of ancient architectural terracotta but it seems that Roman culture acquired from Etruscan the habit of employing terracotta elements for covering and decorating their house's roofs [1]. Among these ceramic pieces, plane and curve tiles as well as antefixes were the most often used in roof construction [2]. In particular, antefixes were ornamental pieces located at the end of a tile-line, placed in vertical position and fixed to the

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corresponding curve tile with the aid of an intermediate piece called "imbrex". They could be made of diverse forms (circular, square, triangular, lobed, etc.) and could represent varied figures (head, palm, etc.) [1]. In particular, Fig. 1 shows an example of roof construction indicating the locations of the different elements.

Terracotta was made in most cases of clays from sedimentary type, which had a variety of colours and paste qualities depending on the origin zone. Potters used to wash the clay with water and purify it trough a decantation process. Then, they usually mixed it with sand or other substances (chamotte, fragments of volcanic rocks, etc.) in order to decrease the plasticity of the ceramic pastes or to prevent cracks during baking. They left to dry all pieces into their moulds before the baking process took place in kilns at 600–1000 °C during several days under an oxidant atmosphere [3]. The process was continued by filling the pores of the ceramic pieces using the "engobium", a lime grout (sometimes with addition of lead oxide) or fine clay suspended in water in order to obtain a homogeneous and very smooth surface. Finally, the ceramic material was subject to a second baking process at 600–900 °C [4]. After this, some of the ornamental pieces, like antefixes, were touched up and painted [5] using natural substances such as ochre, cinnabar, minium and several iron hydroxides (red and yellow colours), carbon (black colour), copper compounds (blue and green colours), kaolin (white colour), chromium compounds (yellow shades), nickel substances (greenish-blue shades), etc. However, these colours have seldom withstood the passing of time, because of this pigmentation usually took place after the baking process.

Traditionally, archaeological methods used for characterization of ancient terracotta [6,7] did not enable us to obtain enough information about several aspects regarding to their nature and origin. On the other hand, information about archaeological sites [8] where fragments of ancient architectural terracotta were collected is usually vague, imprecise and sometimes many of the archaeological pieces were located far from their original source. Taking into account all these aspects, chemical and mineralogical data obtained from them help us to establish relations between the composition of the ceramic materials and the raw materials employed, the technological aspects of manufacture process and the origin zone [9–11].

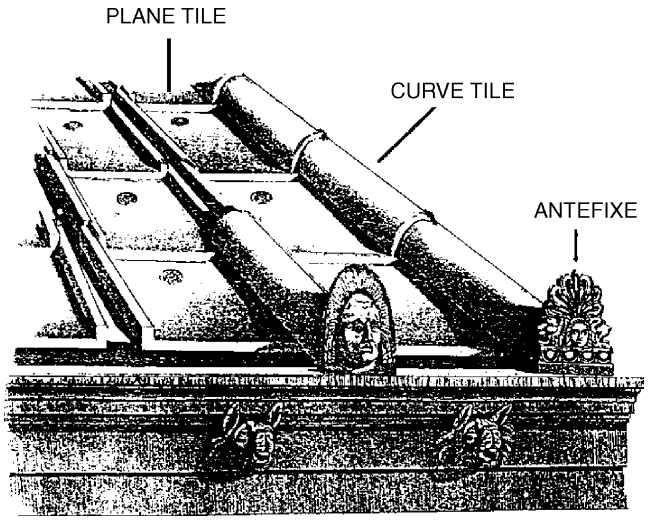

Fig. 1. Terracotta elements in a Roman roof construction.

The aim of this work was to obtain mineralogical, chemical and dilatometric information about ancient terracotta samples collected in Roman quarries discovered in old cities and villages sited in the *Hispania Citerior* (northeast of Spain in Roman age). These results allowed us to compare the original materials used with the clay from the surrounding areas where archaeological samples were collected, with the purpose of knowing whether the analysed pieces were made of raw materials from the surrounding areas of the corresponding ancient village or were imported from other areas. In the same way, the presence of large amounts of not typical substances, such as chamotte and fragments of volcanic rock, was indicative of a deliberated addition of these components in the manufacturing process in order to improve the physical properties of the ceramic paste. In addition, the presence of relative high amount of other elements such as zinc, cooper, chromium, nickel, etc. in antefixes could prove the use of different clay types in the fabrication process and the existence of a pigmentation process, in spite of the absence of remains of painting in the pieces.

Due to the high number of variables involved in the manufacturing process, it is often very difficult to establish a connection between the ceramic object and the raw materials [12,13]. This circumstance, joined to the large number of samples analysed, drove us to use statistical procedures that provide a way to find possible connections among a high number of variables and classify samples into compositional groups [11,14–17]. In this paper a multivariate statistical study by linear discriminant analysis using the SPSS program was applied to 85 architectural terracotta samples with the purpose of classifying these samples into groups sharing similar chemical composition in order to establish how the manufacturing process of these architectural terracotta pieces took place and when it was possible to establish their origin. It introduces us to the importance of chemical data and chemometrics in classification of terracotta pieces within architectural realm, where the traditional archaeological methods used for characterization of ancient terracotta did not enable us to obtain enough information.

2. Experimental

2.1. Description of the samples

The ceramic analysed were fragments of Roman age terracotta coming from old cities and villages sited in the *Hispania. Citerior* [18] and located, at present, in different National Archaeological Museums of Spain and catalogued by