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Archaeometry and Analysis of Ceramic Materials from Ávila (Spain): Late-Vetton Evidence

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Abstract: From the archaeological excavations carried out during 2019/2020 in the walled Ávila city (Spain), numerous ceramic fragments of different chronologies have appeared that have allowed us to find settlement sequences in this city that place its beginnings before Romanization. The latest interventions allow us to know that the wall of Ávila has a Roman origin, and it was developed on an indigenous nucleus from the 1st century BC that received the Romanizing influence during the 1st century AD. In addition, it was possible to establish that the materials used for their preparation are consistent with the materials of the geological environment, which suggests a local origin. This paper presents the study of a set of ceramic samples using XRD, ICP/MS, SEM/EDX, and linescan analysis. A statistical analysis of the samples using the minor elements concentrations has suggested that even though the local origin, there were several production centers within painted ceramics that until now were always included as a single set. Finally, due to the importance of the "late-Vetton" or "late Iberic" ceramics (mid-1st century BC—middle of the 1st century AC) from the archaeological aspect, for the first time, these ceramics are studied in detail from chemical and mineralogical tests. It was discovered that these samples had been made in an oven that had not exceeded 800 °C due to the persistence of different phases after cooking.

Keywords: archaeometry; Ávila; chemometry; late Vetton; pottery; Spain; wall

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1. Introduction

Archaeometry and archaeological science correspond and refer to the application of scientific techniques to the analysis of archaeological materials, as well as the processes involved in their manufacture [1–3]. It was in the 19th century that sporadic chemical analysis began to be carried out on archaeological samples. However, it is not until the mid-twentieth century when the foundations of archaeometry are established. The first to use these physicochemical techniques in archaeology was the English researchers, in 1958, with "Archaeometry" journal foundation, in Oxford. These techniques were used to solve the problems that, from a purely archaeological viewpoint, they were not capable of solving. For example, the study of the ancient ceramic materials' origins and their manufacturing processes [4,5]. At present, this science has acquired an important development due to the rapid evolution of modern analytical techniques, which is demonstrated by the numerous publications on the subject [6,7].

Ceramic materials provide information on the clay materials employed in their manufacture [8,9], thus facilitating the assignment of their autochthonous or allochthonous character [10–12]. In the same way, they allow the technique description followed in the elaboration [13,14] and the ovens types employed [15], together with the utility that is attributed to each container pottery [16,17], with all this, it is possible to make copies [18–22]. The techniques used have been very diverse from spectroscopic to thermal analysis, including the most recent optical observations and the chemical analyses [23–25]. Nowadays, mineralogical and chemical techniques and further statistical treatment of the results are the most commonly applied.

The mineropetrographic study is carried out mainly by microscope analysis (optical and electronic) and X-ray diffraction techniques [2,5,26]. In both cases, it is intended to discover the mineralogical composition of the ceramic samples, taking into account that the initial clay may have undergone modifications by the ceramic firing process due to the destruction and formation of new phases. Therefore, these techniques can provide very valuable information on firing temperature samples when studying minerals newly formed from minerals present in the initial clay paste. On the other hand, electron microscopy analysis (scanning electron microscope. SEM, and transmission electron microscope, TEM) allows obtaining information on the samples (texture and microstructure) and the minerals recognition by electron backscattered diffraction [4], without destruction of the specimen.

Chemical analyzes also provide information about the origin of ceramics since they are like a "fingerprint" of the same [1]. The chemical study is carried out with one of the following techniques: neutron activation (NAA), optical emission spectrometry (OES), atomic absorption spectrometry (AAS), inductively coupled plasma spectrometry (ICPS), proton-induced X-ray emission (PIXE), proton-induced gamma-ray emission (PIGME) and X-ray fluorescence spectrometry (XRF) [4–27], and others.

To finalize the study of ceramics, after analyzing the samples, it is very important to interpret the results and draw conclusions. Due to the high number of samples studied and that multiple variables have been determined in each of them. Statistical analyzes are essential tools in this type of study [28].

In relation to archaeological interventions in urban centers, these offer enriching knowledge of the historical evolution of cities. However, they provide evidence of a different nature that must be selected. Materials such as bones, ceramics, metals, textiles, and others are collected. Ceramic samples present special importance because they can indicate chronologies and stylistic details that, sufficiently interpreted, shed light on the different settlements in a specific place.

This circumstance has occurred in the walled Ávila city (Spain). During the 2019/2020 archaeological excavations campaign of the city and the Ávila wall, numerous ceramic fragments of different chronologies have appeared. These archaeological samples have allowed studying the settlement sequences in this area. Many have been the works that have tried to unravel the origin of it, possibly being one of the favorite subjects for historians and archaeologists, who have debated for years about its Vetton, Roman, or medieval origin. The "Vettons" people were a pre-Roman people located on the Northern plateau, in the Ávila, Salamanca, and Northern Cáceres provinces, in Spain [29]. Thanks to the latest interventions, it is known that the wall has a Roman origin, and it was developed on an indigenous nucleus from the 1st century BC that received the Romanizing influence during the 1st century AD [30–32].

In order to expand this knowledge, it was decided to carry out a more in-depth analysis of the materials found in the latest archaeological interventions in the area, both common pottery and construction ceramic materials (curved tile, plane tile, clay ball). The study of the ceramics by mineralogical, chemical, and spectroscopic analysis, with the subsequent statistical treatment of data, has made it possible to establish the different phases through which the history of the Ávila wall has passed. For the first time, a set of ceramics called "late Vetton" or "late Iberic" has been identified and characterized in this work. It is important to characterize separately the painted ceramics of indigenous tradition linked to the late-Vetton settlement stage, and those found of the painted Clunia type found together.

The aim of this research is to try to justify the late-Vetton age of the initial settlement on which the Roman nucleus of "Abula" developed through the ceramics and differentiate them from the Clunia type. The subject in question is of great interest to the archaeological community, which, in the Special Issue: Frontiers of Archaeological Studies on Ancient Ceramics, collects this type of research.

2. Materials and Methods

2.1. Materials

The ensemble group is made up of 67 ceramic fragments collected in archaeological interventions (2019–2020). Eleven groups were identified according to typology by visual examination: Chalcolithic pottery, Hispanic terra sigillata, Clunia-type indigenous painted pottery, late-Vetton painted pottery, fine-walled pottery, shiny Hispanic terra sigillata, late Hispanic terra sigillata, ceramic imitation of Hispanic terra sigillata late burnished stamped, beaded edged ceramic, common ceramic (without any surface treatment), and building materials, such as tiles and clay (Table 1).

However, although eleven groups have been identified, from the archaeological criterion, the ceramics known as "late Vetton" deserve special attention since they would corroborate the pre-Roman nucleus on which the Roman Ávila. For this reason, in this paper, a more detailed study of these samples was performed for the first time in the history of the city. They are very fine paste ceramics with painted decoration. The object of a further study has been to verify the differences or analogies between Clunia-type ceramics and late Celtiberian or late Vettonian pottery.

Another relevant group appears in the analyzed ensemble. They are black or gray ceramics, as its name indicates, with reductive firing, with decanted pastes and burnished or smoothed finishes. Sometimes they can be decorated with prints. It is a documented production in the Madrid, Zamora, Segovia, Salamanca, and Ávila provinces with dates ranging from the 5th century to the end of the 8th century [33,34].

In relation to the situation of the samples, they come from the nuclear zone of Ávila city, both inside and outside the wall: eastern and western canvas of the wall, San Segundo and San Miguel hermitages (Figure 1).

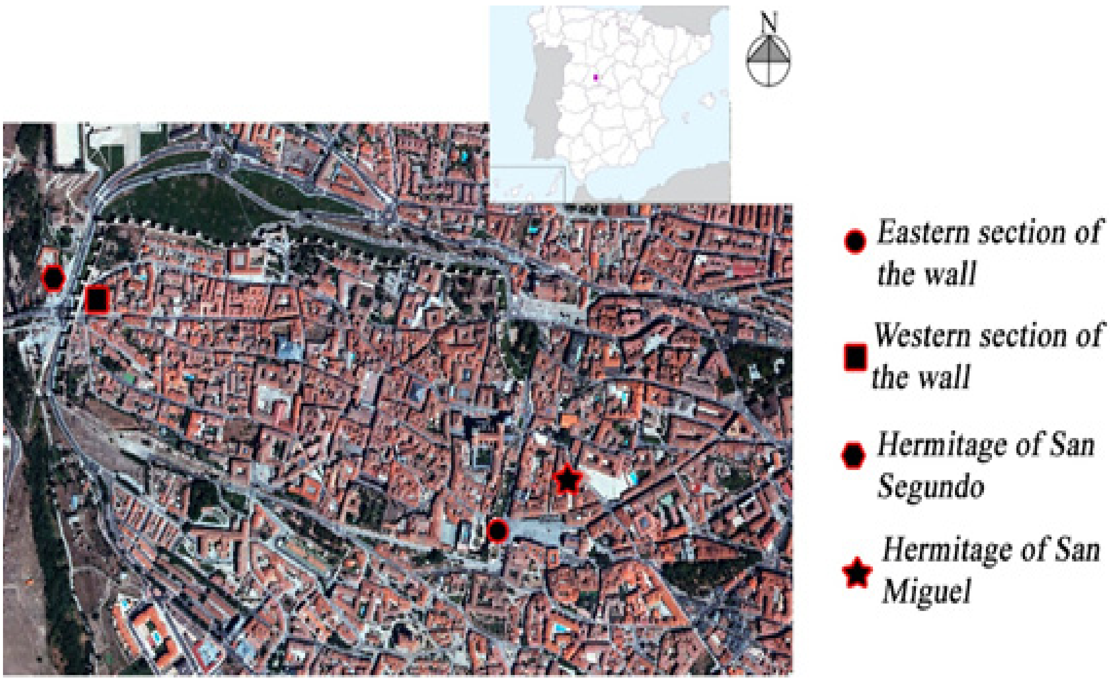

Figure 1. Aerial photograph of Ávila city with the excavations for collecting samples.

Table 1. Material description: typology and Münsell color in ground sample.

Sample	Tipology	Münsell Color
MU-OR-01	Hispanic terra sigillata	10 YR 6/6 light red
MU-OR-02	Clunia-type indigenous painted pottery	7.5 YR 7/4 pink
MU-OR-03	Hispanic terra sigillata	10 YR 6/6 light red
MU-OR-04	Hispanic terra sigillata	10 YR 6/8 light red
MU-OR-05	Late-Vetton painted pottery	7.5 R 7/4 pink
MU-OR-06	Shiny Hispanic terra sigillata	10 YR 7/6 yellow
MU-OR-07	Late-Vetton painted pottery	5 YR 7/8 reddish yellow
MU-OR-08	Late-Vetton painted pottery	10 YR 7/6 yellow
MU-OR-09	Hispanic terra sigillata	10 R 6/6 light red
MU-OR-10	Fine-walled pottery	5 YR 6/2 pinkish gray
MU-OR-11	Fine-walled pottery	5 YR 6/2 pinkish gray
MU-OR-12	Shiny Hispanic terra sigillata	5 YR 7/2 pink
MU-OR-13	Hispanic terra sigillata	10 R 6/6 light red
MU-OR-14	Hispanic terra sigillata	10 R 6/6 light red
MU-OR-15	Fine-walled pottery	2.5 YR 6/4 reddish brown
MU-OR-16	Late Hispanic terra sigillata	10 R 6/6 light red
MU-OR-17	Hispanic terra sigillata	10 R 6/6 light red
MU-OR-18	Late-Vetton painted pottery	2.5 YR 6/8 light red
MU-OR-19	Chalcolithic pottery	5 YR 5/2 reddish gray
MU-OR-20	Ceramic imitation of Hispanic terra sigillata, late burnished stamped	10 YR 6/2 light brownish gray
MU-OR-21	Slipped ceramic	5 YR 7/6 pink
MU-OR-22	Clunia-type indigenous painted pottery	5 YR 8/2 pinkish white
MU-OR-23	Shiny Hispanic terra sigillata	5 YR 7/6 reddish yellow
MU-OR-24	Hispanic terra sigillata	2.5 YR 6/6 light red
MU-OC-01	Clunia-type indigenous painted pottery	5 YR 7/1 light gray
MU-OC-02	Clunia-type indigenous painted pottery	5 YR 5/1 gray
MU-OC-03	Shiny Hispanic terra sigillata	5 YR 5/1 gray
MU-OC-04	Hispanic terra sigillata	5 YR 6/4 light reddish brown
MU-OC-05	Clunia-type indigenous painted pottery	10 R 6/6 light red
MU-OC-06	Clunia-type indigenous painted pottery	10 R 6/6 light red
MU-OC-07	Construction material. Clay ball	2.5 YR 6/8 light red
MU-OC-08	Construction material. Clay ball	5 YR 5/2 reddish gray
MU-OC-09	Common Ceramic	10 YR 6/2 light brownish gray
MU-OC-10	Common Ceramic	5 YR 8/4 pink
MU-OC-11	Common Ceramic	5 YR 8/4 pink

Table 1. *Cont.*

Sample	Tipology	Münsell Color
MU-OC-12	Common Ceramic	5 YR 6/4 light reddish brown
MU-OC-13	Common Ceramic	5 YR 7/4 pink
MU-OR-25	Common Ceramic	5 YR 6/2 pinkish gray
MU-OC-26	Common Ceramic	5 YR 5/1 gray
MU-OR-26	Common Ceramic	5 YR 8/4 pink
MU-OC-27	Common Ceramic	5 YR 8/4 pink
MU-OR-27	Common Ceramic	5 YR 6/4 light reddish brown
MU-OC-28	Construction material. Plane tile, tegula	5 YR 7/4 pink
MU-OR-28	Chalcolithic pottery. Hemispherical bowl	5 YR 6/2 pinkish gray
MU-OC-29	Common Ceramic	5 YR 5/1 gray
ESS01	Clunia-type indigenous painted pottery	5 YR 5/1 gray
ESM01	Clunia-type indigenous painted pottery	5 YR 6/4 light reddish brown
MU-OC-22	Ceramic imitation of Hispanic terra sigillata, late burnished stamped	5 YR 7/1 light gray
MU-OC-23	Common Ceramic	5 YR 5/1 gray
MU-OC-24	Common Ceramic	5 YR 5/1 gray
MU-OC-25	Construction materialCurved tile	5 YR 6/4 light reddish brown
MU-OC-26	Construction material. Plane tile, tegula	10 R 6/8 light red
MU-OC-27	Ceramic imitation of Hispanic terra sigillata, late burnished stamped	5 YR 5/1 gray
MU-OC-28	Ceramic imitation of Hispanica terra sigillata, late burnished stamped	5 YR 6/1 gray
MU-OC-29	Common Ceramic	5 YR 5/2 reddish gray
MU-OC-30	Common Ceramic	5 YR 5/4 reddish brown
MU-OC-31	Shiny Hispanic terra sigillata	5 YR 7/1 light gray
MU-OC-32	Clunia-type indigenous painted pottery	5 YR 8/4 pink
MU-OC-33	Clunia-type indigenous painted pottery	5 YR 8/4 pink
MU-OC-34	Common Ceramic	5 YR 6/4 ligh reddish brown
MU-OC-35	Common Ceramic	5 YR 7/4 pink
MU-OC-36	Common Ceramic	5 YR 6/2 pinkish gray
MU-OC-37	Ceramic imitation of Hispanic terra sigillata, late burnished stamped	5 YR 5/1 gray
MU-OC-38	Common Ceramic	5 YR 4/1 dark gray
MU-OC-39	Common Ceramic	5 YR 4/1 dark gray
MU-OR-30	Ceramic imitation of Hispanica terra sigillata, late burnished stamped	5 YR 6/2 pinkish gray
MU-OR-31	Ceramic imitation of Hispanica terra sigillata, late burnished stamped	5 YR 5/1 gray

Eastern section of the wall: Area located next to Santa Teresa Place or "El Grande place". The samples come from the excavation carried out between cubes 84–85 and the Alcazar door. They are ceramics of high imperial, late ancient, high medieval chronology and a fragment of Chalcolithic pottery (it was recovered in a sedimentary deposit for leveling the surface and preparing it for the provision of a pavement/ground). Their chronology is late medieval. Residual fragments of the clay layer mixed with Chalcolithic material were found at the base of the stratigraphic sequence.

Western section of the wall: area near the Roman Bridge and San Segundo hermitage. In the area, cubes 44–45 were intervened within the walls, and the materials collected are from high imperial, low imperial, late ancient, and high medieval chronologies. The intervention occurred next to the door of the Roman Bridge that crosses the Adaja River, and that made it possible to document the historical evolution of the city from the 1st century BC to the present. In addition, a section of the Roman wall, at the cementation level, was recognized on which, later, the medieval fence that appears today would be superimposed. A lot of ceramic material was found of late Celtiberian tradition that was called "tardo Vetton" or "late Vetton".

- San Segundo Hermitage: This small hermitage is located outside the walls, next to the gate of the wall near the bridge over the Adaja River. A single fragment of high empire chronology comes from the excavation there.
- San Miguel Hermitage: It is a hermitage that has now disappeared and was located in the current San Miguel Place. A single fragment of high empire chronology comes from this intervention.

In general, the strata where they were recovered are Roman-Late Roman strata, so ceramic productions from earlier chronologies, such as Chalcolithic pottery, are a later inclusion residual.

2.2. Methods

The chemical composition of the samples was performed by the dissolution of the samples with hydrofluoric acid in an open vessel and heated on a hot plate until dry. This was followed by the addition of aqua regia and heated again until dry. The residue was dissolved with 1 mL of concentrated hydrochloric acid and diluted with water in Teflon volumetric flasks bringing the dilution to 25 mL [35]. Chemical analyses of both major, minor, and trace elements were performed by inductively coupled plasma-mass spectrometry (ICP-MS) in a SciexElan 6000 Perkin Elmer spectrometer equipped with an AS91 autosampler (Perkin Elmer, Waltham, MA, USA). Inductively coupled plasma spectrometry is one of the most important chemical techniques for the characterization of solid materials in recent studies and is becoming more popular in archaeological studies, as it provides information on a huge number of elements [1]. Each sample has been replicated twice. All reagents used in chemical analysis are test grade.

The mineralogical composition of the samples was resolved by X-ray diffraction (XRD) on a PANalytical X'Pert PRO X-ray diffractometer (Malvern Panalytical, Cambridge, UK) fitted with a Cu anode. Their operating conditions were 40 mA, 45 kV, divergence slit of 0.5°, and 0.5 mm reception slits. The samples were scanned with a step size of 0.0167° (2θ) and 150 ms per step. The characterization of samples was carried out using the random power method operating from 5° to 80° (2θ). Measured patterns were qualitatively and quantitatively analyzed using Match v.3 and Fullprof software for Rietveld analysis, respectively [36]. Crystallography open database (COD) reference patterns have been used to identify the different phases.

Due to the importance of late-Vetton samples, for the first time, a complementary detailed analysis has been carried out on the unpolished surface of the MU-OR-05 sample in order to detect the chemical changes that present from the outer edge to the interior of the ceramic. This linescan, at each point, offers a value of the elements present throughout the entire route. The technique used for this purpose has been scanning electron microscopy (SEM) in an FEI QUANTA 200 unit (FEI, Hillsboro, OR, USA), which operates with three vacuum modes (high vacuum, low vacuum, and environmental mode) with secondary and backscattered electron detectors for all vacuum modes. An unpolished section was subjected to a sequential sweep, Linescan analysis, along the transept. SEM/EDX analysis was performed with point mapping at 2.10, 4.20, 6.30, 8.40, 10.50, 12.60, and 14.70 mm depth. The EDX analysis was performed using a long and wide window of 552 and 470 m, respectively. The linear sweep along each specimen requires about 27 fields, and the measurements were averaged to form 7 contiguous profiles. The radiation exposure time in each field was 30 s. The chemical composition at each point was calculated using the mean value of 10 individual analyzes and adjusted for the standard deviation. These analyzes were carried out on clean surfaces to avoid all possible sources of contamination.

SEM analysis has an integrated OXFORD INSTRUMENTS Analytical-Inca analysis system with two X-ray detectors that can be used simultaneously and alternatively, one EDS (energy dispersive) and the other WDS (wavelength dispersive) (FEI, Hillsboro, OR, USA). The analyses have been carried out by scanning from the free edge of the ceramic to its interior in order to detect the relative variation of the main components, which will be described in each case. The evolution of the major elements in the ceramic sample (reliably detectable) has been followed: potassium, sodium, calcium, silicon, aluminum, iron, and titanium. Their evolution provides maximums and minimums that coincide with the material addition and firing phases to which these ceramic has been subjected.

Statistical analysis was performed using SPSS 27 software (SPSS Inc., Chicago, IL, USA) and Origin 75E version by box-and-whisker graphics and linear discriminant analysis. This analysis is commonly used in archaeology, and some mathematics and statistics studies have been used over the past 50 years [37].

Box-and-whisker graphics (boxplots) are among the most commonly used methods for univariate data display. These graphs help to understand the distribution of the variables because the center, spread, and overall range are represented. In this plot, each box encloses the middle 50%, and the median is drawn as a horizontal line inside the box. Vertical lines extending from each end of the box (called whiskers) enclose data within the 1.5 interquartile ranges. Values falling beyond the whiskers but within three interquartile ranges are plotted as individual points (suspect outliers) as well as points that are further away (outliers). In addition, they are very useful when there a large number of observations. For that, these graphs have been widely used in archaeological studies for data representation [35,38–43]. Linear discriminant analysis was used in many science fields for classification purposes because this approach allows classifying or identifying unknown groups characterized by quantitative and qualitative variables [44–46]. In this paper, this analysis was used for trying to establish possible connections between minor elements content of the samples and the typology of the sample (Chalcolithic pottery, terra sigillata, ceramic painted type Clunia, ceramic painted type "late Vetton", fine-walled pottery, ceramic imitation of Hispanic terra sigillata late burnished stamped, slipped pottery, common pottery and construction material). The values of minor or trace elements have been used in this analysis because; the concentration of minor elements in the ceramic samples provides very valuable information about the origin of the ceramics since they are like a "fingerprint" of the same [1].

3. Results and Discussion

3.1. Mineralogical Analysis

The minerals identified are mainly phyllosilicates, quartz, calcite, dolomite, Ca/Na feldspar or plagioclase, K feldspar, calcite, and maghemite. In some samples, XRD analysis recognizes dolomite, diopside, biotite, amphibole, hematite, and pyrite. The geology of the area [47] includes all the minerals described, only maghemite and diopside; they are foreign minerals but originate during cooking. These results coincide with those obtained in previous archaeological campaigns, in which it was observed that the materials used in the mortars of the wall of Ávila city also came from a nearby area [48].

The minerals that have been identified correspond to minerals common in the local area of the Ávila region, given the silicate nature (quartz, phyllosilicates, and feldspars appear) and in nearby areas carbonates (limestones and dolomites) that, suitably prepared, constitute the raw materials of the clays for the ceramics. Samples of building materials such as the tiles that require a local manufacturing process have a composition similar to that of ceramics. In the same way, the clay pellets have been analyzed, corresponding to uncooked natural materials in which the same minerals are recognized with, in addition, kaolinite, a clay mineral that disappears in the cooking processes in ovens with temperatures above 450 to 600 °C [49]. Due to the carbonate's permanence and clay minerals' disappearance, the firing range in most of the ceramics studied is between 600 and 850 °C, the latter temperature corresponding to calcite destruction.

Figure 2 shows the mineralogical composition of the studied samples in a box-and-whisker plot. These graphs are among the most widely used methods for displaying univariate data. Therefore, in this work, they were used to evaluate the homogeneity or heterogeneity of the samples in relation to their mineralogical composition. It can be seen that the samples were quite heterogeneous due to the fact that a notable variability was found for quartz, K feldspar, plagioclase, and phyllosilicates concentrations. In addition, the variability of calcite, maghemite, and biotite content was moderate.

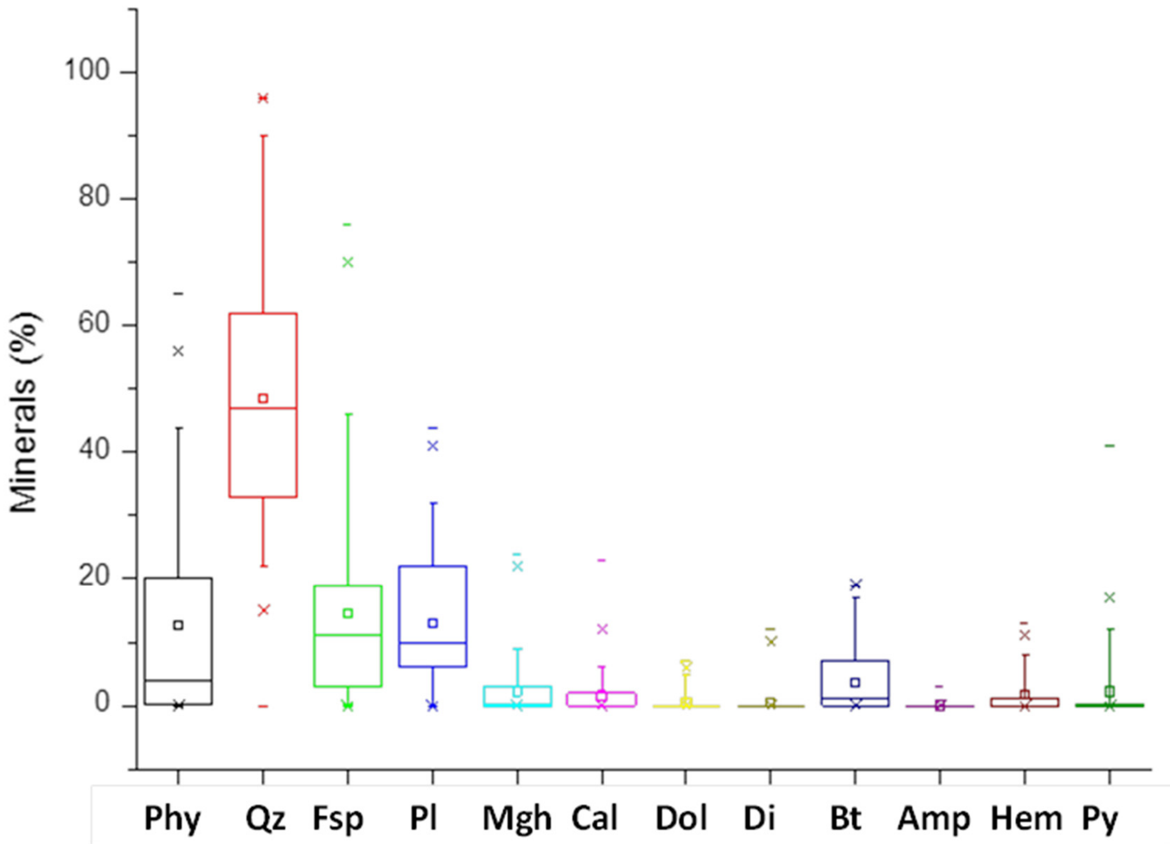

Figure 2. Box and whiskers plots of the mineralogical phases in the studied samples (Phy = phyllosilicates; Qz = quartz; Fsp = potassium feldspar; Pl = plagioclase; Mgh = maghemite; Cal = calcite; Dol = dolomite; Di = diopside; Bt = biotite; Amp = amphibole; Hem = hematite; Pr = pyrite).

3.2. Chemical Analysis: Major and Trace Elements

For the concentration of the major elements (Na_2O, MgO, Al_2O_3, K_2O, TiO_2, Fe_2O_3, and SiO_2), the samples are quite homogeneous (Figure 3 and Supplementary Table S1). In the box-and-whisker plot, carried out with the results of ICP/MS chemical analysis, it can be seen that silica is the one with the highest concentration, followed by alumina, which suggests the silicate nature of the samples (coinciding with the geological environment). The other oxides concentration is quite similar since SiO_2 is high, and the rest oxides distribution is compressed at lower concentration values.

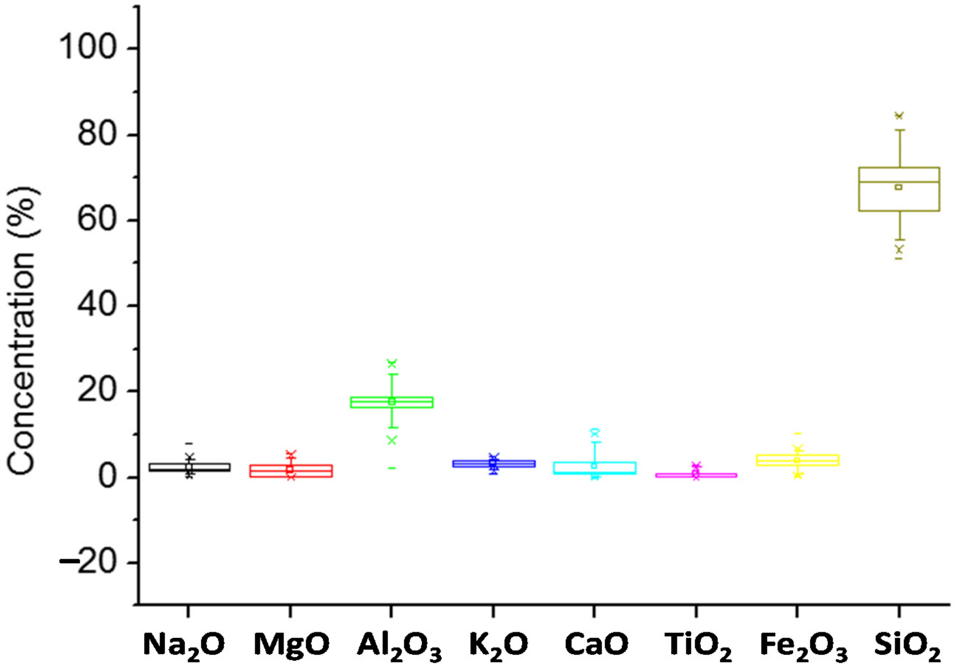

Figure 3. Box-and-whisker plot for the major oxides in the studied samples (%).

The minor or trace elements were also studied using statistical techniques with the calculation of the mean, maximum and minimum values (Table 2 and Figure 4). In addition, to study minor and trace element concentration, a linear discriminant analysis was used to establish possible connections between groups of samples and variables and between all ceramic samples with each other. Table 3 includes the coefficients of the discriminant analysis functions. It generates a small number of quantitative measurement functions, which are linear combinations of standardized standard variables with weights. The procedure assumes that the variables are drawn from a population with multivariate normal distributions and that the variables have equal variances.

Table 2. Mean, maximum and minimum values of trace elements in the studied samples (ppm) (X = arithmetic mean; M = maximum value; m = minimum value).

	Li	**Be**	**B**	**P**	**S**	**Sc**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Rb**	**Sr**	**Y**
X	45.4	2.7	92.8	206.3	1306.2	5.0	37.6	30.4	199.9	5.6	20.6	51.2	57.6	17.3	1.1	6.8	1.6	79.5	157.7	11.9
M	108.0	10.0	710.0	1402.0	5500.0	18.0	79.0	85.0	595.0	17.0	50.0	1113.0	315.0	39.0	5.0	32.0	18.0	270.0	3450.0	60.0
m	5.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	2.0	0.0	1.0	0.0	0.0	0.0	3.0	16.0	0.0
	Zr	**Nb**	**Mo**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Cs**	**Ba**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**
X	42.2	8.7	0.4	1.0	0.2	0.1	27.9	0.9	4.3	365.4	22.8	46.6	5.5	21.3	4.1	0.6	3.3	0.4	2.4	0.4
M	112.0	21.0	5.0	13.0	3.0	9.0	1425.0	19.0	22.0	1851.0	70.0	176.0	19.0	76.0	14.0	2.0	12.0	2.0	9.0	2.0
m	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	50.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Er	**Tm**	**Yb**	**Hf**	**Lu**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Tl**	**Hg**	**Au**	**Pb**	**Bi**	**Th**	**U**	**Pt**		
X	1.1	0.0	0.9	1.7	0.0	2.2	11.0	0.0	0.0	0.0	0.4	0.0	0.3	31.7	0.2	7.4	2.0	0.0		
M	5.0	1.0	4.0	12.0	1.0	6.0	51.0	0.0	0.0	0.0	1.0	0.0	12.0	731.0	1.0	27.0	12.0	0.0		
m	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		

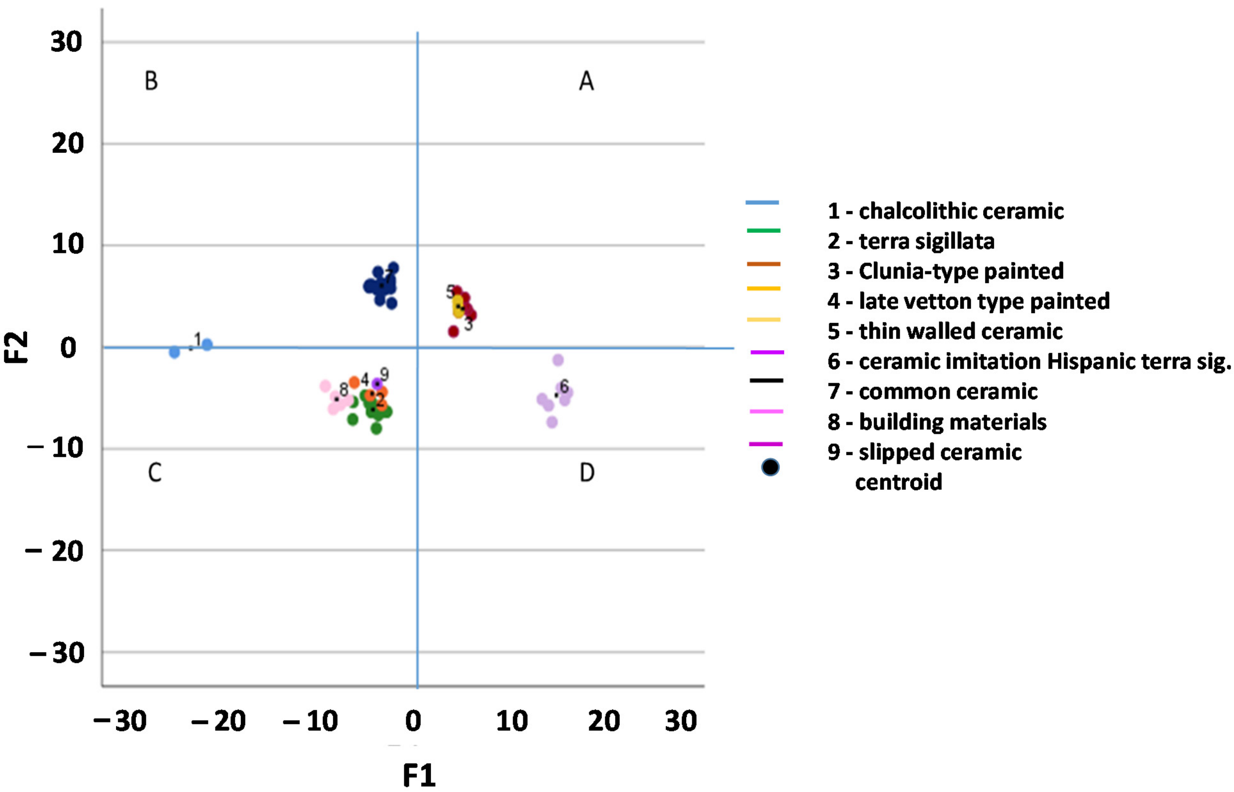

Figure 4. Ceramic groups of the samples from linear discriminant analysis according to the fragment typology: Chalcolithic ceramic, terra sigillata, Clunia-type painted ceramic, late-Vetton-type painted ceramic, fine-walled ceramic, ceramic imitation of Hispanic terra sigillata late burnished stamped, slipped ceramic, common ceramics and construction materials.

According to the discriminants, the samples have been grouped into level groups according to the fragment typology: Chalcolithic ceramic, terra sigillata, Clunia-type painted ceramic, late-Vetton-type painted ceramic, fine-walled ceramic, ceramic imitation of Hispanic terra sigillata late burnished stamped, slipped ceramic, common ceramics and construction materials.

Figure 4 shows that the samples tend to form four main groups:

- Group A: with samples of painted Clunia type and ceramics with thin walls. It is characterized by Li, Nb, Nd, Sb, Ho, and Er contents.
- Group B: is represented by the samples of common ceramic pottery and Chalcolithic productions, characterized by similar Rb, Pr, Sm, Sb, Ho, and Er content.
- Group C: includes samples of terra sigillata, late-Vetton-type painted ceramics, construction materials, and slipped ceramics, being the elements Rb, Pr, Sm, Pb, Se, and Tm, which group them.
- Group D: ceramic imitation of Hispanic terra sigillata late burnished stamped, being Li, Nb, Nd, Pb, Se, and Tm content, those that separate them.

The most important fact of these results is that painted Clunia type ceramics (group A of the discriminant) are not in the same group of the late-Vetton-type painted ceramics (groups C of the discriminant), which means that there are several production centers within painted ceramics that until now were always included as a single set. In addition, the ceramic imitation of Hispanic terra sigillata late burnished stamped (group D of the discriminant) are in a different group of the common ceramic pottery, which also means several production centers or at least a differentiation of raw materials at the time of its elaboration or some production processes in terms of paste preparation [20]. In addition, samples of building materials such as the tiles that require a local manufacturing process have a composition similar to that of ceramics. Therefore, the discriminant analysis suggested that even though the local origin of raw materials (clays), there were several production centers near the Ávila city. In relation to the manufacturing process, the XRD analysis has suggested that the firing range in most of the ceramics studied was between 550 and 850 °C due to kaolinite disappearance and calcite presence in most of the samples; furthermore, diopside appears in some samples, a neoformation mineral that forms below 900 °C [50]. This suggests that the manufacturing process was similar in all of these different production centers. To date, no ceramic production centers have been found near the city.

Table 3. Coefficients of the discriminant analysis functions for the minor and traces elements.

	Function							
	1	2	3	4	5	6	7	8
Li	15.378	0.715	−2.352	4.793	−1.837	−1.390	0.012	0.436
Be	−12.204	2.890	2.174	−4.694	2.009	1.298	1.114	−1.119
B	4.030	0.853	−0.589	0.277	1.150	0.280	0.410	−0.151
P	7.091	4.088	−2.143	0.474	1.168	−1.095	−0.015	1.243
S	2.452	3.073	0.316	−1.186	0.633	−0.466	0.144	0.979
Sc	14.432	−6.562	4.372	3.201	−0.540	0.502	−0.533	−1.464
V	−4.792	−0.152	−1.517	−2.004	−7.801	0.717	1.633	1.154
Cr	−11.717	0.282	−0.254	−2.601	0.518	0.291	−0.044	2.078
Mn	−3.074	−1.357	1.986	0.610	3.484	0.817	0.135	−2.085
Co	−5.478	0.292	−0.218	−1.138	0.899	0.502	0.365	0.830
Ni	−2.171	0.185	−0.587	−0.829	0.565	−1.501	−1.783	−0.945
Cu	0,815	−0.866	−1.495	−0.699	−1.789	0.589	0.862	1.072
Zn	0.429	1.362	−0.799	1.010	2.794	−0.340	−0.130	−0.753
Ga	4.572	−4.681	0.208	5.369	−2.307	−0.957	−2.422	3.245
Ge	11.692	−1.094	−0.240	2.074	1.700	−0.355	0.406	−0.277
As	−2.956	1.104	−3.242	1.174	1.001	−0.612	−0.027	0.416
Se	−3.461	−1.487	1.844	−2.861	0.736	0.252	−0.690	−0.493
Rb	−16.686	−1.915	0.609	−5.174	−2.480	0.186	−0.265	−0.633
Sr	2.184	−0.601	2.021	−0.274	−0.358	1.523	−0.700	−0.628
Y	1.441	−0.682	2.261	2.007	0.028	−0.241	−0.840	−0.681
Zr	−3.741	−1.792	2.371	2.438	−2.027	0.380	−0.060	−1.135
Nb	14.436	−3.902	2.696	0.569	5.509	−0.365	−1.054	−2.671
Mo	−3.775	−0.491	0.030	0.758	1.437	0.304	0.275	−0.231
Ag	−0.744	2.743	−0.998	0.090	1.219	1.040	0.225	−0.579
Cd	−2.967	−0.116	1.110	0.422	−0.857	0.336	0.371	−0.800
In	−2.572	0.777	0.087	−0.122	1.040	−0.347	−0.151	0.326
Sn	9.688	4.166	−0.594	−5.894	1.491	0.261	6.664	2.865
Sb	5.440	5.564	4.602	2.871	−0.741	0.009	−0.684	−6.307
Te	1.746	1.422	0.113	0.877	−0.047	0.051	−0.063	−0.253
Cs	10.432	1.834	−1.879	2.773	1.889	−0.413	0.755	1.280
Ba	−1.410	−0.172	−0.692	−1.237	3.271	0.637	1.257	−0.118
La	−7.354	5.292	−0.785	−5.497	−0.582	0.024	0.923	−1.325
Ce	4.720	1.729	−1.799	−10.744	−0.060	−1.070	−1.167	3.154
Pr	−13.842	1.151	−10.280	13.785	7.707	−1.075	1.414	5.122
Nd	14.406	1.246	16.053	4.830	−3.116	3.746	1.643	−6.271
Sm	−12.738	−4.365	−2.555	1.776	−2.812	−2.159	−3.626	0.037
Eu	−4.172	0.138	−1.582	−1.471	0.389	−0.446	−0.059	0.650
Gd	15.748	−1.575	3.022	−9.195	−7.839	2.897	3.395	−4.250
Tb	1.117	−2.662	0.678	−0.891	−1.978	1.163	1.007	−0.116
Dy	−4.806	−1.322	−5.086	−1.034	6.844	−1.956	−1.655	0.715
Ho	5.630	4.846	−1.248	−1.261	1.761	−1.790	−1.327	1.012
Er	−9.774	4.816	1.389	0.957	0.200	1.038	0.819	1.022
Tm	5.534	−5.939	2.545	3.956	−0.333	−0.599	−1.938	−0.432
Yb	1.043	1.475	−1.847	1.602	−2.115	−0.198	0.401	1.666
Hf	−0.171	3.398	−0.313	−1.254	0.096	0.461	0.851	0.536
Lu	5.279	1.261	0.304	0.032	0.528	−0.567	0.352	0.216
Ta	−10806	4.202	−2.936	−2.959	−2.822	0.579	0.949	1.546
Tl	2.249	2.399	0.551	0.489	0.323	−0.464	−0.410	−0.296
Pb	−10.708	−10.826	−4.147	4.423	−3.260	−0.141	−5.505	4.296

3.3. Linescan in the Late-Vetton Pottery

As an example of the technique used to control the variation of the major chemical elements in ceramics, the late-Vetton ceramics (“tardo Vetton”) of Figure 5 (MU-OR-05 sample of Table 1) has been studied, given its importance in answer to ceramics excavated in Ávila city.

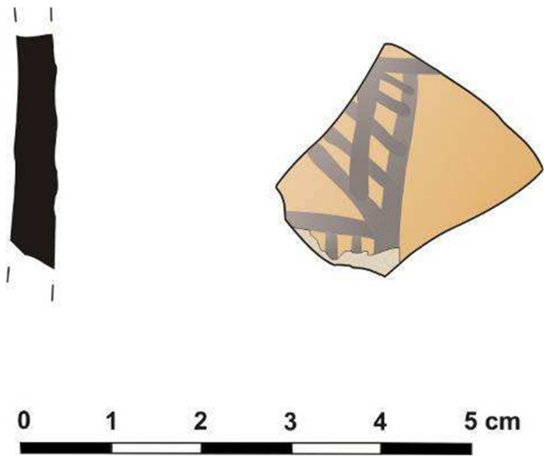

Figure 5. Section and external wall views for late-Vetton sample number MU-OR-05.

Figure 5 represents a painted ceramic fragment from the indigenous tradition. Both its morphology and its decoration follow the tradition of autochthonous ceramics, in the present case “late Vetton”, “late Iberic”, or “late celtiberic” belonging to the “late vacceas” or “late Iberian” in other territories of high-imperial chronology (1st century AD). It is a fragment of galbo, with a slight orange slip on the outer surface, decorated in brown with triangular motifs filled with reticulates. The paste is 7.5 R 7/4 pink (Table 1), compact and well refined, with few inclusions made up of feldspars and iron oxides. In Figure 6A, which shows the SEM observation, the homogeneity of the paste is appreciated (some holes are recognized), with few inclusions that have already been detected in the view with the binocular magnifying glass.

SEM images in each of the examined spots and by analyzing the elements described in Figure 6, allow and following the trace of the calcium analysis, to appreciate an external calcareous slip, where the calcium carbonate is the main component. In general, lines and by SEM analysis can be said that it is a uniform ceramic with some pores corresponding to the shrinkage processes associated with firing. According to the analyzed transept, the composition is homogeneous, although Figure 6A allows identifying some large grains corresponding to the inclusions described with a binocular magnifying glass and corresponding to feldspars (sharp) and quartz (rounded).

Variation of titanium, iron, silicon, sodium, aluminum, potassium, and calcium has been followed in all ceramics (Figure 5), according to the transept represented in Figure 6A. The variation in the concentration of these elements is related to the ceramic pastes prepared for this pottery typology. In all the elements considered, there appear two separated maxima at a distance from the surface of approximately 1.1 mm. The appearance of a slip layer as evidenced by the behavior of calcium, where at 0.3 mm, a maximum is identified in this element, then continuing with the trace observed for the rest of the elements studied.

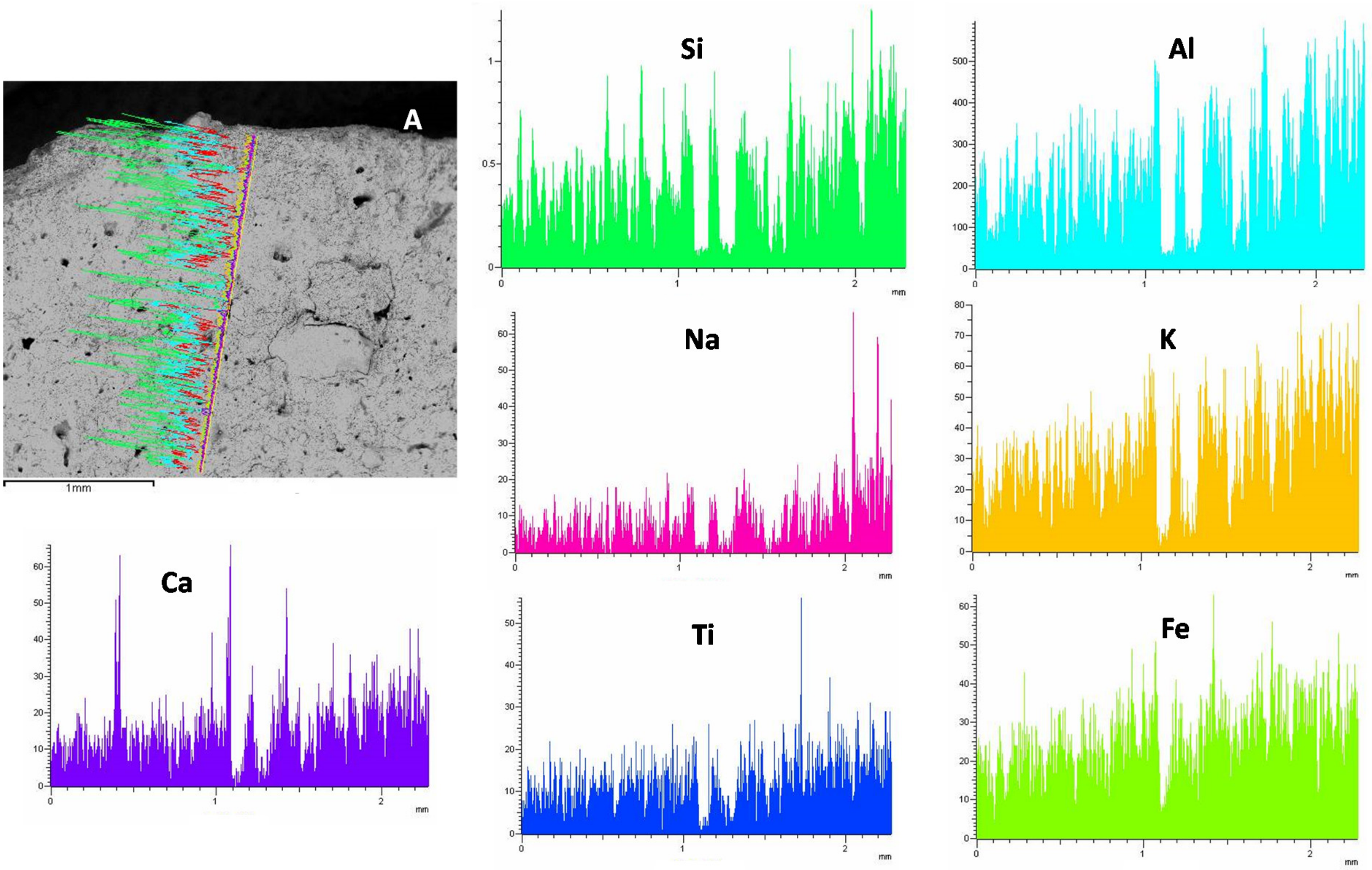

Figure 6. Observation of pottery by SEM/EDX. (**A**) General view. Others: Variation for major elements.

4. Conclusions

Archaeometric study of a set of 67 ceramic fragments from interventions carried out in the Ávila city, Spain, has shown that the materials employed for their preparation are consistent with the materials of the geological environment. Mineralogical study shows the samples' natures are uniform. The most abundant minerals are phyllosilicates, quartz, calcite, dolomite, plagioclase, K feldspar, calcite, and maghemite. From an archaeological viewpoint, it was established 11 groups based on the typology sample. These groups have made it possible to establish the different phases of the history of the Ávila wall, which began before Romanization. The most important fact is that late Vetton, late Iberian, or late Celtic ceramics have appeared that indicates this age, and their origin dates back to the 5th century.

Chemometrically, four possible groups are established according to their composition by the statistical study. However, the most important fact is that the difference between the painted ceramics of the indigenous Clunia tradition and the painted ceramics of the late-Vetton indigenous tradition stands out. The object of a further study has been to verify the differences or analogies between Clunia-type ceramics and late Celtiberian or late Vettonian pottery. The clay differentiation between both productions shows that all the painted indigenous productions do not come from the same workshop.

This fact allows us to think about the existence of several production workshops within painted ceramics that until now were always included as a single set or production technologies in terms of raw materials area of collection or production procedure. It is also relevant to highlight the differentiation according to their chemical composition of common ceramics and the ceramic imitation of *terra sigillata* Hispanic late burnished stamped, the latter production identified and studied in recent years.

Finally, for the first time, it was studied in detailed the "late-Vetton"-type ceramics, which are refined, sometimes with simple decoration on a slip. This sample has been made in an oven that has not exceeded 800 °C.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su13115910/s1, Table S1: Composition of the major elements in the all samples.

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