Regular Article

Composition and technological features of ceramics manufactured by Benito de Valladares in the seventeenth century from the *Alcazar* Palace in Seville, Spain

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Abstract The walls of the *Alcazar* Palace in Seville have been covered with ceramic tiles of different styles that were manufactured with different techniques. Several studies have been carried out on these ceramics, but no interest has been paid to the tiles manufactured by the workshop of the Valladares family, one of the most productive ceramic workshops in *Triana* (Seville). In this work, tiles that were made in the Valladares workshop are studied for the first time. The tiles from the *Cenador del Leon* built in 1645–1646 were chosen. The experimental studies suggest that the ceramic body was manufactured with silico-calcareous clay. This raw material was heated to a temperature of ca. 900 °C. A nondestructive and on-site analytical procedure was applied first. Microsamples were also taken and studied through microanalytical techniques. The *maiolica* style was used by Benito de Valladares for tile manufacture. The glaze phases were constituted by two layers. The pigments and doping elements used to obtain different colors were characterized. Valladares' work is considered as a continuation of Augusta's work; therefore, a comparison between both ceramists has been realized to better understand the ceramics production in southern Spain during the sixteenth to seventeenth centuries.

1 Introduction

The *Alcazar* Palace of Seville is the most ancient royal palace in Europe and is still in use. It was built over Roman ruins in different steps during the emiral, califal, taifa-abbadit, almoravides, almohad and Castilian-medieval stages. After the Christian conquest in 1248, the Gothic Palace was constructed. Afterward, in the fourteenth century, the *Mudejar* Palace was built [1]. During the following centuries, the construction of new buildings and gardens have enlarged the architectural area.

Unlike other monuments and despite multiple historical vicissitudes, the original ceramic wall tiles of the *Alcazar* Palace of Seville have largely been preserved. Pleguezuelo [2] has carried out important historical and artistic studies on these tiles. Works on the compositions and technological features of ceramic fragments from the eleventh to fifteenth century, mainly from the Islamic period, that were found in some archaeological excavations in the area of *Alcazar* Palace have been studied by Garofano et al. [3]. Three of the ceramic body groups studied in this paper were manufactured from marly clays near Seville, and one group had a different composition [3]. The glassy phase of the ceramics revealed variable amounts of PbO and SnO_2. Green, blue, black and yellow colors in the glazes were associated with the presence of Cu, Co, Mn-Fe and Sb-based compounds, respectively [3]. One ceramic luster from the eleventh century was also found to have a composition and color similar to those from Middle Eastern production [3]. Archaeometric characterizations of tiles from the *Mudejar* Palace of Seville *Alcazar* have been recently performed by several authors [4–7]. The compositions and manufacturing techniques of these ceramics and their periods of application in different areas of the Palace were studied. De Viguerie et al. [8] studied the technological evolution of the Renaissance ceramics of *maiolica* style located in the Altarpiece and the Gothic Palace, which were made, respectively, by Niculoso Pisano in 1504 and Cristobal de Augusta in approximately 1578. In addition, the arista tiles made by Polido brooders in the *Cenador de Carlos Quinto* were also studied by these authors. The *maiolica* technology was learned by Niculoso Pisano, who brought it to Seville, and disappeared with his death. Later, the *maiolica* technology was reborn by Cristobal de Augusta, who learned the technique from Frans Andries and arrived in Seville from Antwerp [8].

An important ceramic manufacture in *Triana*, Seville, is that produced in the Valladares workshop, which has monopolized a large part of the demand for ceramics for churches and civil architecture in Seville since the end of the sixteenth century. These ceramics were also exported to other Spanish cities and convents in Mexico and Lima. The founder of this workshop is Juan Valladares, who was dedicated to the manufacture of earthenware and not tiles. His son Hernando had two sons, Hernando and

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Benito, who were dedicated to the manufacture of tiles until the middle of the seventeenth century. This workshop made ceramics for the *Alcazar*. Hernando de Valladares supplied tiles for the *Apeadero* and the *Jardín de las Damas* between 1609 and 1625, some of which have disappeared or are in a very degraded state. Tiles from the old Assumption convent in Seville have been attributed to Hernando de Valladares and can be considered prototypical of his work [9, 10]. Years later, Benito de Valladares was in charge of the manufacturing of tiles for the *Cenador del Leon* within the *Alcazar*, built in 1645–1646 [2, 11]. On the pavement of this building, an ornate composition was developed as starry shape. Benito de Valladares offered new compositional designs and a more delicate sense of ornamentation through which the hard profiles of the ceramics transformed from mannerism to Baroque tastes, more in line with seventeenth century artworks. The style of the ceramics made in this workshop can be considered a continuation of the techniques of Cristobal de Augusta, although there is no known link between the two workshops [12].

The various kinds of ceramic technology employed in the manufacturing of the pieces from the *Alcazar* and involved in Seville's workshops and their comparisons with other European ceramics have been discussed by several authors [3–8]. However, the technology of the ceramics manufactured by Benito de Valladares has never been studied; little attention has been given to this artist and his workshop until now, and a comparison of these ceramics with other ceramics from Seville has not been carried out to date. The intervention of conservation and restoration carried out recently in *Cenador del Leon*, which contains the most important ceramics made by Benito de Valladares, created a good opportunity for the study of these ceramics.

The analyses of these tiles will provide information on the ceramic technology involved in the Valladares workshop and facilitate comparisons with other ceramics manufactured in Seville. This paper provides information on the ceramic body, glaze phases and their colors, as well as the glaze surface and the interphase glaze body of these tiles. We will also try to confirm whether or not Valladares ceramics are a continuation of the techniques of Cristobal de Augusta. For the characterization of these ceramics, on-site (noninvasive) techniques and other laboratory techniques, such as scanning electron microscopy coupled to energy dispersive of X-rays (SEM–EDX), will be applied to microsamples taken from the tiles.

2 Materials and experimental methods

2.1 Materials

Figure 1a shows a photo of the ceramics studied in this work. The shape of a Greek cross and octagonal inner corners containing vegetable motifs, flowers and animals are observed. An important section of Benito de Valladares's tiles on the pavilion's interior of the *Cenador del Leon* contained a thick layer of salts (mainly carbonates, according to the X-ray diffraction-XRD-results) resulting from the presence of water from the fountain (Fig. 1a). This layer was up to 8 mm high and was hardened and highly adhered to the glazes and ceramic parts. In addition, extensive black spots were observed due to the effects of cyanobacteria. Fortunately, a section of the decorated tiles remained. Figure 1b–g shows the different colors of the glazes. Before starting our study on-site or taking microsamples, the carbonate layer of this zone was removed through the application of chemical solutions completely controlled and executed by the restoration team, and the surfaces were subsequently treated with biocides.

The samples of the tiles manufactured by Benito de Valladares were studied. A stratigraphic study was performed on the cross sections of twelve microsamples containing the glaze phase and the body of the ceramic. Some of the sampling zones taken from the pavilion pavement are shown in Fig. 1c–g. In four of them, the ceramic paste is apparent due to the loss of glaze. In these zones, samples were taken for studies of the ceramic body.

2.2 Experimental methods

First, the analysis of the glazes was quantitatively performed on-site using portable X-ray fluorescence (XRF) equipment. The XRF apparatus has a Pd-anode tube that functions at 3 W power and 30 kV. In addition, another type of equipment that combines XRF with XRD using a Cu anode was employed [4, 13]. For the quantitative analyses with these portable equipments, spectra were processed by using PyMCA software.

Afterward, cross sections were prepared using small samples of collected ceramics, which were embedded in a polyvinyl resin block and polished. The micromorphology and chemical analysis of the different layers observed in the cross sections were studied by optical microscopy (using a Nikon Optiphot microscope with magnifications of $\times 20$, $\times 50$, $\times 100$ and $\times 200$ and equipped with a Nikon Coolpix 4500 camera) and scanning electron microscopy (SEM, HITACHI S-4000 microscope) coupled with energy dispersive X-rays equipment (EDX Bruker XFlash 4010 analyzer), and the results were used for qualitative and quantitative analyses; elemental punctual analyses and elemental chemical mappings were also performed. The morphological analyses were performed by using optical and electron microscopes on the cross sections as were prepared in the laboratory. For the chemical and mineralogical characterizations of the ceramic pastes, XRD and XRF were used. The X-ray diffractometer used was a PANalytical, Model X'Pert Pro MPD (0.5 g of sample was ground in an agate mortar). Grazing-incidence X-ray diffraction was also performed using the same equipment in order to obtain information about the glaze surfaces and about ceramic paste surfaces when unglazed. XRF analytical equipment (AXIOS model) with a Rh tube was used. AXIOS is a WD-XRF, considered the most high-resolution system among the different XRF instruments. The powdered samples were sieved at 50 μm and dried in an oven for 24 h at 105 °C; 0.8 g of sample and
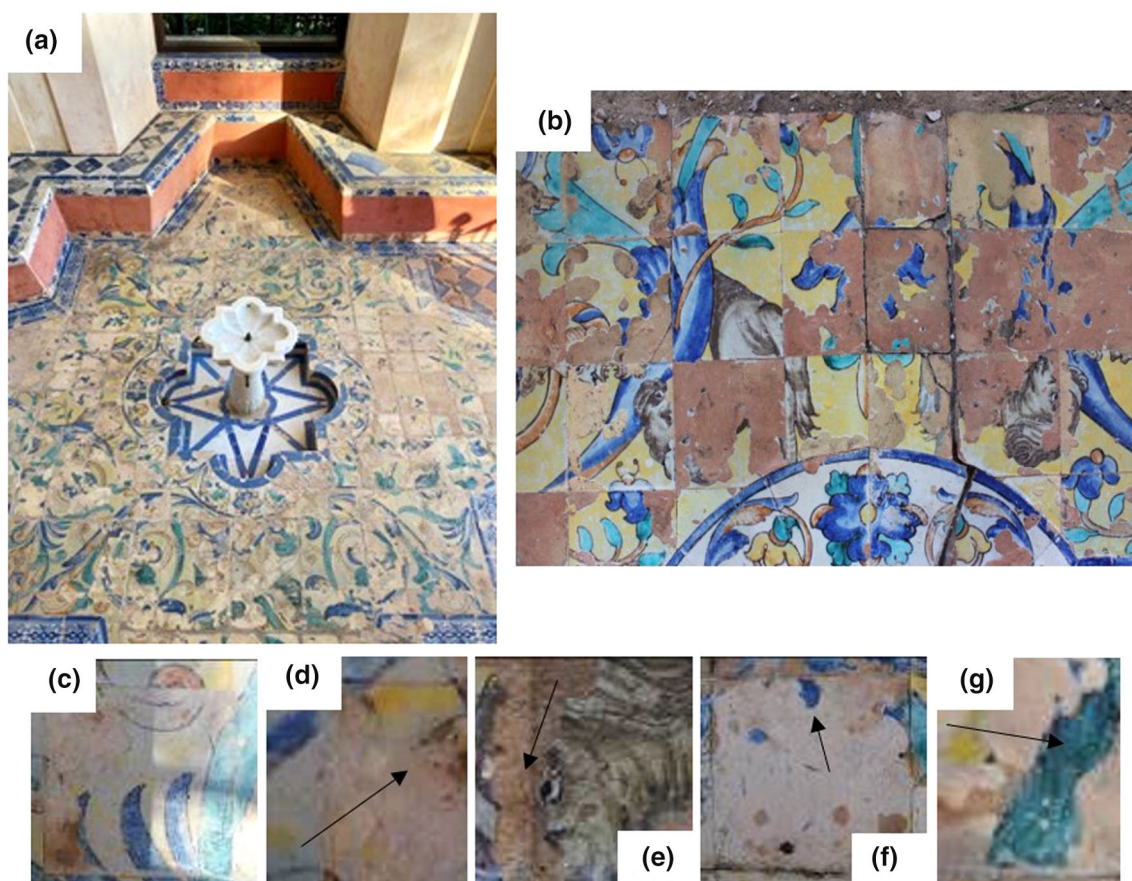
Fig. 1 a Tiles of the pavement of the *Cenador del Leon*, manufactured by Benito de Valladares; **b** Photo showing the different colors of the ceramic tiles; some of the zones of sampling are shown with arrows: **c, d** white and yellow glazes; **e** brown glaze; **f** blue glaze; **g** green glaze

4.7 g of $Li_2B_4O_7$ were processed to obtain molten beads using Philips Perlx'2 radio frequency induction equipment. Conventional procedures have been used to determine the oxide concentrations of the major elements (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2 and P_2O_5), which are given in values of % by weight. The chemical analyses of the ceramic pastes in the cross sections were also performed with SEM–EDX using standards from the Oxford Instrument Society. These techniques have been described in previous publications about the ceramics and wall paintings of the *Alcazar* by some of the authors of this work [3, 4, 8, 13].

## 3 Results and discussion

3.1 Ceramic body

3.1.1 Chemical analyses

The tiles of the *Cenador del Leon* made by Benito de Valladares showed a great state of alteration that resulted in parts of the tiles being unglazed, which have been used to study the ceramic body. High percentages of SiO_2 (ca. 40.00%), CaO (between 27 and 37%) and Al_2O_3 (ca. 11%) were observed. MgO, Fe_2O_3, K_2O and Na_2O are present in percentages of ca. 3.25, 4.25, 2 and 1.75%, respectively (Table S1). These data suggest that the ceramic body was manufactured with silico-calcareous clays. The iron oxide content is responsible for the pink ochre color of the ceramic pastes [14]. The color of the ceramic paste is as such because this element is present mainly as liberated oxide and is not incorporated into the new phases formed during heating. Iron oxides can be formed in different phases regarding the use of reducing and oxidative atmospheres.

3.1.2 Mineralogical analyses

The X-ray diffraction study showed that the predominant mineralogical component was quartz (SiO_2), followed by calcite ($CaCO_3$) with a medium abundance. In addition, wollastonite ($CaSiO_3$), anorthite ($CaAl_2Si_2O_8$) and gehlenite ($Ca_2Al_2SiO_7$) were detected,

Fig. 2 XRD diffractograms corresponding to two ceramic body from Valladares tiles (*Q*: quartz; *C*: calcite; *W*: wollastonite; *A*: anorthite; *G*: gehlenite; *H*: hematite)
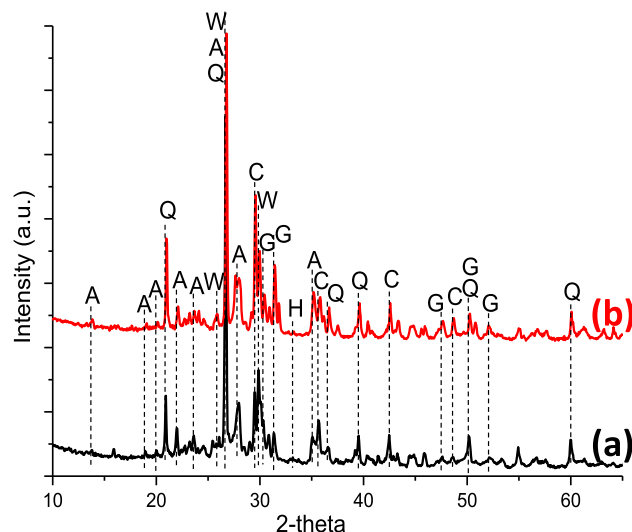
as well as hematite (Fe_2O_3). The presence of these phases and the absence of illite suggests that firing temperatures higher than 850 °C were used. The manufacturing temperature of the ceramic will be discussed later. These chemical analyses match the data provided by Gonzalez Garcia and Garcia Ramos [15] and Gonzalez Garcia et al. [16] in the studies of clays from Guadalquivir Valley.

Calcite is formed mainly by the recarbonation of CaO from the decomposition of primary calcite, although an external contribution of calcium carbonate cannot be ruled out [17]. These ceramics were located next to the fountain (Fig. 1a), and the water from the fountain produced a surface layer of calcium carbonate (characterized by XRD), which may have affected the CaO contents in the ceramic body. In this form, the percentages of CaO between 27 and 37% corresponded from both the ceramic body (inner zones) and the surface of the body for unglazed ceramics.

Wollastonite was detected in the ceramic body studied in this work by the diffraction signals at 3.84 Å, 3.52 Å, 3.32 Å, 30.9 Å, 2.98 Å, 2.31 Å, etc. (Fig. 2) and is formed by the reaction of calcite and quartz (SiO_2). Anorthite, also detected by the diffraction signals at 6.41 Å, 4.69 Å, 3.26 Å, 3.19 Å, 3.12 Å, etc., is formed by the reaction of illite ($KAl_4(Si_7Al)O_{20}(OH)_4$) and calcite at temperatures higher than 850 °C. Gehlenite, detected by the diffraction signals at 3.06 Å, 2.84 Å, 2.73 Å, 1.92 Å, 1.81 Å, etc., was found in addition to wollastonite and anorthite (Fig. 2 and Table S2). Gehlenite is formed by the reaction between illite and calcite at a temperature of approximately 800 °C; it begins to form at 800 °C. These data confirm that the raw material would have been heated at a temperature of ca. 900 °C.

3.1.3 Optical microscopy observations

Through studies performed with optical microscopy, the ceramic body showed a heterogeneous matrix of dark green and isotropic colors. The detected quartz and feldspar grains are more associated with the raw material than with the materials added to decrease plasticity, which are frequently used for the application and manufacture of this material. From the SEM observations, the absence of phyllosilicates and the existence of edges of contact reaction between the beginning of the formation of new phases and the pre-existing ones can be deduced.

3.1.4 Thermal study

The differential thermal analysis (DTA) and thermogravimetry (TG) curves of one ceramic body (the others showed very similar features) are shown in Fig. 3. The carbonates present in the ceramic body was detected by an endothermic effect and a mass loss between 620 and 780 °C. This mass loss may be used to determine the calcite content in the studied ceramics. Monocrystalline calcite undergoes complete decarbonation at temperatures higher than 750 °C, while polycrystallines, such as limestone or chalk, start to decompose at temperatures lower than 650 °C, as shown in our samples, and so we suggest that the calcite observed is secondary calcite [18–21]. XRD patterns of the samples with high carbonate contents showed an increase in gehlenite and a decrease in quartz after heating to ca. 1000 °C in the DTA/TG instrument. The calcite disappeared after this heating. An endothermic effect occurred at 575 °C, which was attributed to the polymorphic transformation of the α-quartz phase into the β-quartz phase. These data agree with the high concentration of quartz detected by XRD. The mass loss between 200 and 600 °C is attributed to the thermal degradation of organic matter and structural water.

The percentage of $CaCO_3$ deduced from the results of the thermogravimetric analysis is approximately 10.00%, which does not correspond to the amount of CaO determined by chemical analysis (between 27 to 37%), confirming that the higher percentages

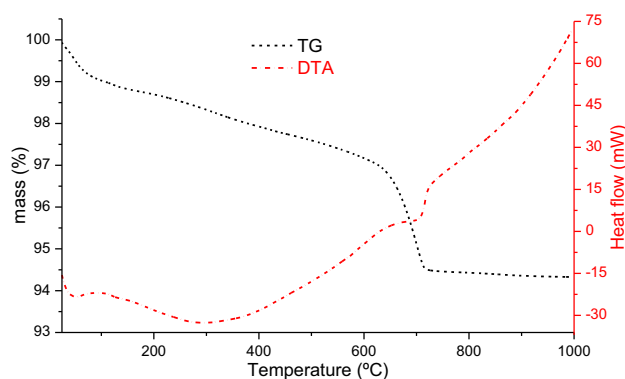**Fig. 3** DTA and TG curves of the ceramic body from Valladares tiles

Table 1 Quantitative chemical analysis of glaze and pigments by using portable XRF equipments

	Yellow	Orange	Brown	Blue	Green	White	Black
SiO_2							
K_2O	7.75	7.35	6.95	7.30	5.05	6,96	5.53
CaO	4.90	4.82	4.34	4.57	9.75	4.78	2.94
MnO	0.05			0.07	0.25		1.53
Fe_2O_3	1.10	2.65	3.01	1.55	0.92		1.43
CoO				1.65			
ZnO	7.01	0.14	0.12				
SnO_2 K	4.50	4.45	4.60	4.43	5.63	5,03	2.58
SnO_2 L	8.50	8.53	9,3	7.70	6.57	8.01	5.85
Sb_2O_5 K	7.35	7.55	7.95		0.10		
Sb_2O_5 L	12.35	11.58	13.49		0.15		
PbO L	28.02	24.65	25.65	23.10	25.15	29.3	32.00
PbO M	48.35	47.52	48.32	46.95	31.15	57.51	
As_2O_3				2.75			
CuO					2.69		

The values are expressed as the average of oxides wt.%

detected in the chemical analyses by EDX and XRF arise from other Ca-containing mineral phases, such as calcium silicates, wollastonite and gehlenite.

The materials used to manufacture the bricks that were used to build the Seville from Arabic times are clayey materials from the Guadalquivir River valley that have been studied by Gonzalez Garcia and Garcia Ramos [15]. Blue marls are used, mixed with clays from recent sediments from the *Vega de Triana*, which is close to the Guadalquivir River; the latter was employed to reduce the plasticity of blue marls. It is concluded that the main components of these clays are minerals of the smectite group and illites in an advanced stage of transformation to montmorillonite. They contain small quantities of kaolinite and impurities of free silica and hydroxides. Substantial amounts of mica have also been found. The clays from the Guadalquivir Valley contain substantial amounts (approximately 30%) of finely grained calcite [15]. Technological tests suggest that these materials have good ceramic properties. In this work, we have characterized ceramic body that were very possibly manufactured using these clayey materials.

3.2 Ceramic glaze and pigments

The chemical compositions of the glaze layers were first determined by X-ray fluorescence. A Pd-anode apparatus was used for the study of green glazes. For the other color glazes, the Cu-anode of the other equipment was employed. Silicon was detected but was not able to be quantified in either portable system due to absorption in air. The dominant colors are blue (Fig. 1a, b and f), which was used for drawing, and yellow to orange (or white) (Fig. 1a–e), which were mainly used for the background. Other colors, such as green and brown, have also been observed and studied. Black color is used in the borders of the drawing. Yellow to orange colors have also been observed in the vegetables and flowers (Fig. 1a, b). The percentages of different components of the glaze colors, obtained by portable XRF, are reported in Table 1.

The XRF spectra provided excellent information about the elemental chemical compositions of the glaze phases of the ceramic tiles that allowed comparisons between the compositions of the different colored glazes [8, 22, 23]. The thicknesses of the glaze layers affected the results of the analyses. The percentages calculated from XRF lines with energies less than 10 keV, such as Pb-M 2.3, K-K 3.3, Sn-L 3.4, Sb-L 3.6, Ca-K 3.7, Mn-K 5.9, Fe-K 6.4, Co-K 6.9, Zn-K 8.6 and Cu-K 8.0, correspond to elements found in the first approximately 5 to 20 μm of the glaze layers. The percentages calculated from XRF lines with energies of approximately
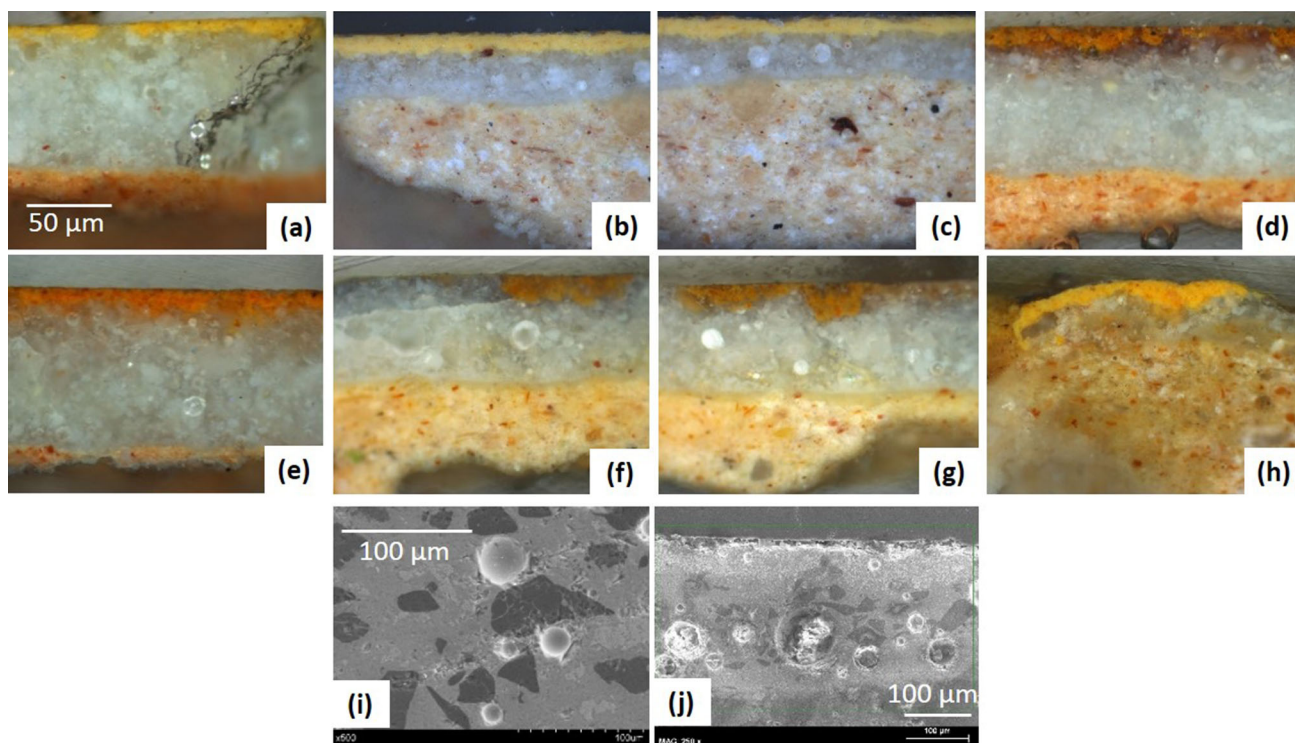
Fig. 4 Optical micrographs corresponding to **a–c** yellow glazes; **d, e, h** orange glazes; **f, g** brown glazes; SEM micrographs corresponding to **i, j** yellow glazes

10 keV and higher, such as As-K 10.5, Pb-L 10.6, Sn-K 25.2 and Sb-K 26.4, correspond to elements found at depths of more than 50 μm of the glaze layers [8]. For some elements, the quantification was performed by using two emission lines at different energies. For high-energy lines, such as Pb-L, Sn-K or Sb-K the concentrations of the surface layers can be neglected [8].

The thicknesses of the glaze layers in the ceramics studied in this work were higher than 100 μm in all cases (Fig. 4). The optical microscopy and SEM studies of the cross sections gave in-depth information about the different layers and their chemical compositions. The elemental punctual analyses and elemental mappings produced by EDX provided information about the stoichiometries and/or partial chemical substitutions in crystalline phases formed during heating.

3.2.1 Yellow, orange and brown colors

The yellow, orange and brown glaze colors showed higher percentages of Sb_2O_5-L, PbO-M and SnO_2-L than Sb_2O_5-K, PbO-L and SnO_2-K, respectively (Table 1). These differences suggested the presence of two layers in the glazes of these colors. The micrographs of the cross sections with these glaze colors showed two types of glaze layers: one with a surface of yellow (Fig. 4a–c), orange (Fig. 4d, e, h) or brown (Fig. 4f, g) colors and thickness of 20–40 μm, and another inner and opaquer layer with a thickness of 80–100 μm, both followed by the ceramic body. Similar results were shown in a study of two sixteenth century ceramics by Tite [24]. The microphotography study performed by SEM of the samples studied in this work shows clear differences between both layers (Fig. 4i, j).

The EDX analyses of the surface layers of the yellow, orange and brown colors showed Sb as the main element responsible for the colors. The presence of three different Sb oxides or their mixtures with another chemical element may be responsible for this color range. Naples yellow ($Pb_2Sb_2O_7$) has been produced as a synthetic pigment since antiquity in the Middle East and has been applied in paints. This yellow pigment is doped with other elements, such as Fe, Zn or Sn, as has been previously studied [25–28] and found in ceramics. Naples yellow has a cubic pyrochlore crystal structure with a general formula of $A_2B_2O_7$, including Pb^{2+} and Sb^{5+} cations. Deformations occur when a third cation (Fe, Zn or Sn) is introduced into the structure [28]. The presence of Sb oxide doped with these elements and the formation of compounds during the heating treatment of manufactured *maiolica* ceramics may be responsible for the color range depicted in these artworks. The study of small fragments by grazing incidence X-ray diffraction ($\Omega = 2°$) to obtain information about the surface crystalline structure of the glaze ceramic did not give information about the doped Sb oxide.

The thicker inner layers showed abundant bubbles and inclusions of quartz, seen as darker and angular particles. The EDX analyses (Fig. 5a) of these particles showed the presence of Si and O. Some punctual chemical analyses of this layer (Fig. 5b)

Fig. 5 EDX analyses corresponding to **a** the dark particles shown in Fig. 4b, 4i; and the **b** opaque zones of the yellow layer in Fig. 4j
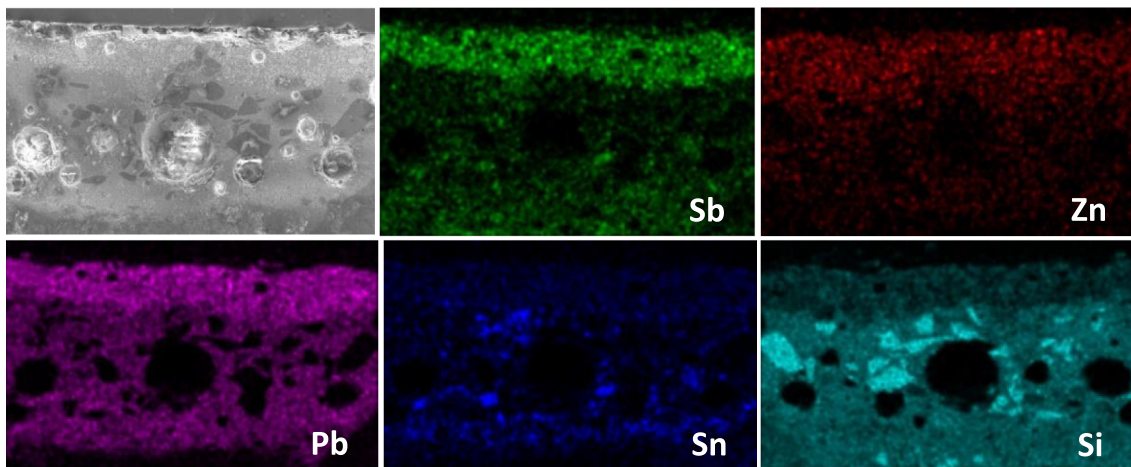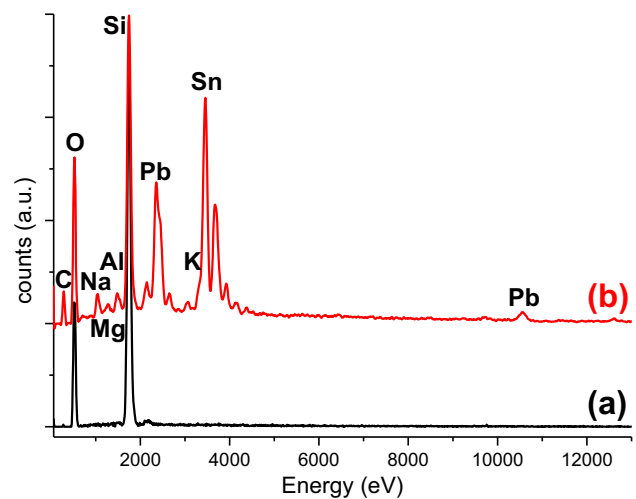

Fig. 6 SEM micrograph and mappings of Sb, Zn, Pb, Sn and Si corresponding to a sample of yellow glaze
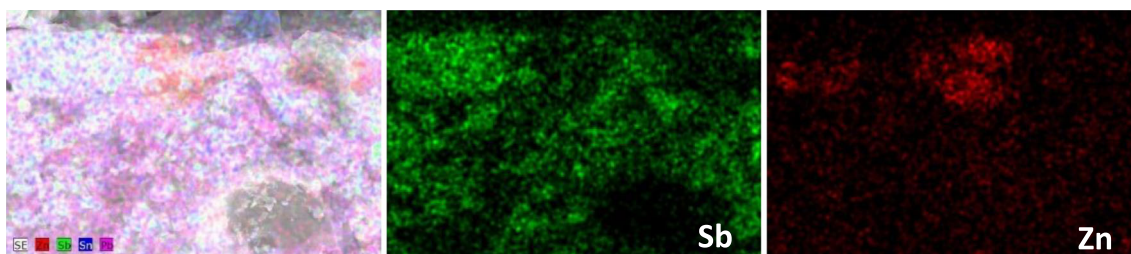

Fig. 7 Mappings of Zn, Sb, Sn and Pb corresponding to another sample of yellow glaze

showed high contents of Sn together with Si and Pb. These data suggest that sand was possibly added to the glaze phases to modify their physical properties [24]. SiO_2 was also present in the color layer.

Yellow color

EDX analyses of the yellow layer observed on the top of some of the cross sections (Figs. 4a–c, i, j) showed the presence of Si, Pb, Sb, Sn, Al, K, O, Na and Zn. The presence of Zn in the yellow layer was also detected by XRF. The cross section and mappings of one of the yellow glaze samples (Fig. 4j) are shown in Fig. 6. The mapping showed Sb at the top of the cross section together with Zn. Pb appeared along the entire glaze. Sn was more accumulated at the bottom. This implies a close relationship between Sb and Zn. In other cross sections (Fig. 7), the Zn distribution was irregular along the surface of Sb, appearing in zones with higher Zn contents. In this sample glaze, $Pb_2Sb_2O_7$ may be doped with Zn, similar to other glazes in the literature [25–29], and Zn-based particles also appeared.

Fig. 8 EDX analyses
corresponding to different
particles within the yellow glazes
containing **a** Sb, Pb and Zn; **b** Sb,
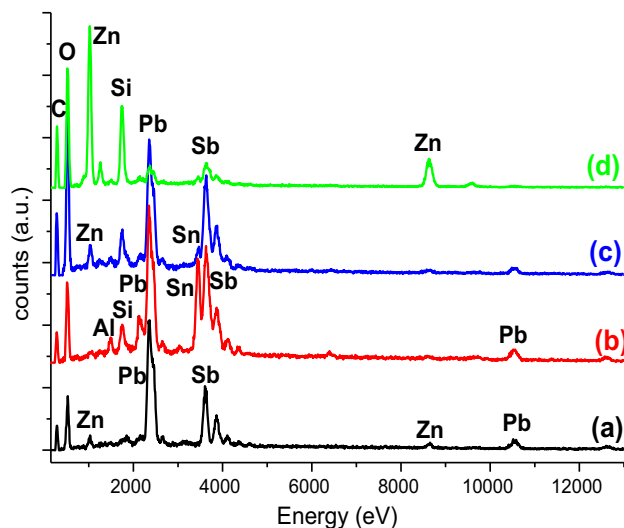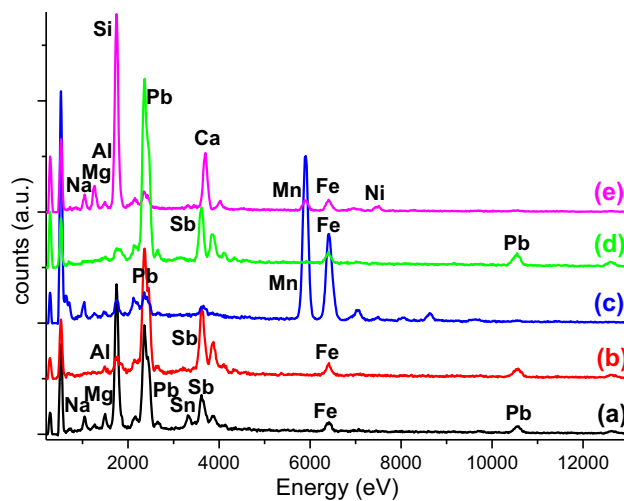Pb and Sn; **c** Pb, Sn, Sb and Zn;
and **d** Zn and Si

Fig. 9 EDX analyses
corresponding to orange and
brown glaze layers containing
a Si, Pb, Sb, Al, Mg, Na and Fe
(orange); **b** Pb, Sb and Fe
(orange); **c** Mn and Fe (orange);
d Pb, Sb and Fe (brown); and **e** Si,
Ca, Al, Mg, Na, Fe, Mn and Ni
(red particles)

A fragment with yellow color glaze was analyzed by SEM to study its yellow surface. The punctual chemical analyses showed the presence of particles composed of Sb, Pb and Zn (Fig. 8a). Other particles were composed of Sb and Pb with high contents of Sn (Fig. 8b) or Pb, Sn, Sb and Zn (Fig. 8c). In addition, the particles mainly consisted of Zn accompanied by Si (Fig. 8d). These data could indicate the presence of different compounds based on Naples yellow but with inclusions in their pyrochlore structure of Zn, Sn or both cations simultaneously.

Orange and brown colors

EDX analyses of the orange color showed the presence of Si, Pb, Sb, Al, Mg, Na and Fe. Sn was also present (Fig. 9a). Punctual chemical analyses showed the presence of Pb, Sb and Fe (Fig. 9b). These analyses also showed that the particles were mainly composed of Mn and Fe (Fig. 9c).

Regarding the brown color, the EDX analyses showed the presence of Pb, Sb and Fe (Fig. 9d). Punctual analyses of small particles of reddish color (Fig. 4h) showed that they were constituted by Si, Ca, Al, Mg, Na, Fe, Mn and Ni (Fig. 9e); the last three elements are responsible for the reddish color. Important iron oxide quantities (ca. 2.7 and 3.0% for orange and brown, respectively) have been found in these colors (Table 1).

As described in the results provided by EDX, iron was also present in variable amounts as a chromophore of the glassy matrix. This element may be included in the structure of $Pb_2Sb_2O_7$ and form an Fe-modified pigment during the ceramic firing process [27]. The incorporation of Fe inside the pigment lattice was largely described by Cartechini et al. [28]. The punctual chemical analyses carried out in our study (Fig. 9d) suggest the possibility of the formation of the abovementioned phase in the orange and brown glazes. The light Naples yellow darkens with exposure to iron. The punctual chemical analyses also showed the presence of Fe-based compounds are not associated with Pb and Sb but with Mn (Fig. 9e). In other ceramics from the *Alcazar* [3], Mn and Fe were detected in the darkest color areas.
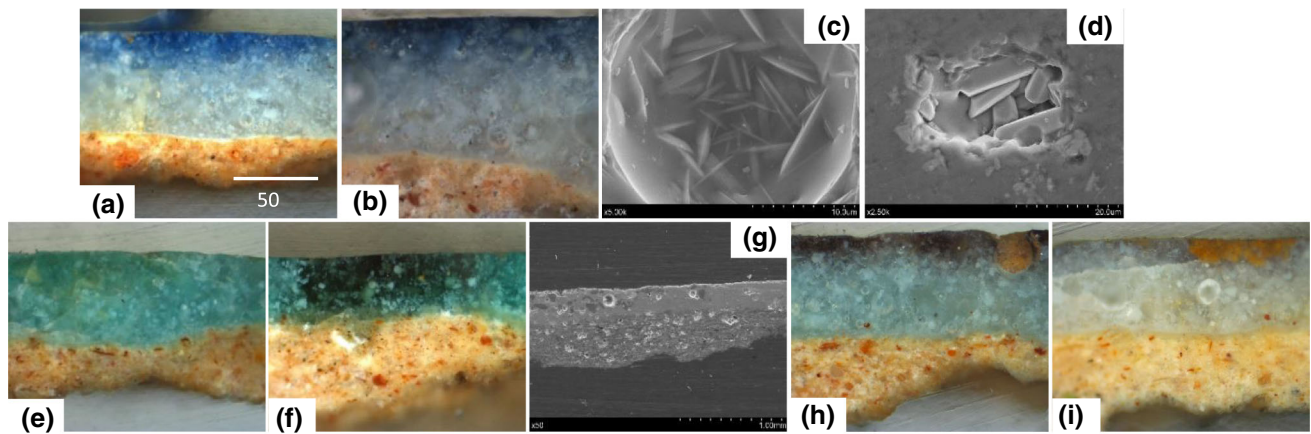
Fig. 10 Micrographs of cross sections of blue color glazes by optical microscopy (**a**, **b**); morphology of particles constituted by P, Ca and As within the blue glazes by SEM (**c**, **d**); green color glazes by optical microscopy (**e**, **f**) and by SEM (**g**); black color glaze (**h**) and white color glaze (i) by optical microscopy

Fig. 11 EDX analyses corresponding to the **a** general analyses of blue glazes showing the presence of Si, Pb, Al, Mg, K, Ca, Sn, Na, Co, Ni and Fe; **b** punctual chemical analyses of blue glazes showing As, Co, Pb and Ca; **c** general analyses of the upper layer of the lightest green glaze showing the presence of Cu, Fe, Si, Pb, K and Ca; **d** general analyses of the darkest green hue glaze showing Cu, Fe and Mn; **e** punctual chemical analyses of the black glaze showing Fe, Mn, Pb, Si and Ca
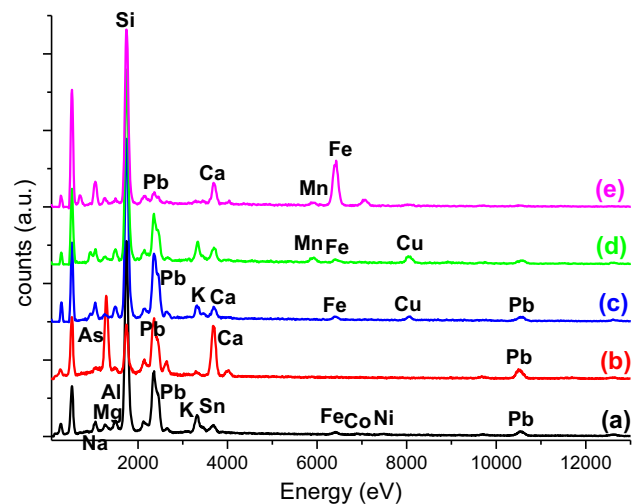
3.2.2 Blue color

The chemical analyses performed with XRF showed that the manufacture of these glaze colors was realized using Co as a chromophore (amounts of 1.65% cobalt oxide were detected, Table 1). In all the studied blue samples, arsenic was present. Similar to the yellow, orange and brown glazes, differences appeared between the percentages found from the Sn-K and Sn-L emission lines and from the Pb-L and Pb-M emission lines (Table 1), which suggests the possibility of two layers in the blue glazes.

The micrographs of these cross sections (Fig. 10a, b) clearly showed the presence of two layers as inferred from XRF results: a thin surface blue layer of approximately 30 µm thickness and another inner and opaque layer with a thickness of approximately 100 µm.

The general EDX analyses of the blue glaze performed with SEM showed a strong Si peak together with Pb, Al, Mg, K, Ca, Sn and Na peaks. In addition, weak lines corresponding to Co, Ni and Fe appeared (Fig. 11a). Punctual chemical analyses showed the presence of Sn in higher amounts. Co was difficult to detect by SEM due to its low content in the samples. The EDX analyses showed the presence of As, accompanied by the presence of Co, and of Ca and Pb in all the blue colors (Fig. 11b). The morphology of the particles constituted by P, Ca and As are shown in Fig. 10c and d.

The presence of As is in agreement with the data of manufactured Co-based pigment found in the literature. The pigment CoAs was obtained before 1520 as a byproduct of the processes to obtain Ag in which As was lost. After 1520, this pigment was obtained by roasting complex arsenides and sulfo arsenides of Co and Ni obtained from veins rich in Co; these minerals rich in Co were roasted, recovering part of the As during heating [30–33]. The ceramic tiles of the *Alcazar* manufactured after 1520 contain both Co and As; in the ceramic tiles studied in this work, Ni also appeared, whereas tiles manufactured in 1504, such as those in the Altarpiece by Pisano in the Royal Oratory, do not contain As [8], so other sources of Co are still possible. A study of the Islamic ceramics from the eleventh to fifteenth centuries from Seville *Alcazar* detected Co-based compounds as pigments [3]. Co deposits

are known in Morocco and Persian. Ceramists from this zone journeyed to the Peninsula to obtain this chemical element during the Muslim occupation of Seville [34]. Co was discovered in Spain in the eighteenth century [35].

3.2.3 Green color

The chemical analyses performed with XRF showed that the green color of the glazes was obtained using Cu-based compounds as colorants. The amount in CuO was ca. 2.7% (Table 1). The presence of two layers was suspected due to the different concentrations deduced from the Pb-L and Pb-M lines (Table 1).

The cross section of one green sample showed a surface green layer at the top followed by another inner layer with a lighter green color (this was also observed in the blue glazes); the total thickness was approximately 200 μm (Fig. 10e). EDX analysis showed the presence of Cu and Fe in the upper zone (Fig. 11c) together with Si, Pb, K and Ca. The Cu content decreased in the light green zones. The distribution of Cu along the glaze phase, with the highest amounts on the surface, suggested that this element emigrated from the top of the layer.

The green color glaze of the other sample showed zones with the darkest color (Fig. 10f). EDX analysis of the darkest color showed the presence of Cu, Fe and Mn (Fig. 11d), which were probably responsible for the darkest green hue. In the lightest green zones of this cross section, Cu was detected, and Fe and Mn were absent. The micrograph produced by using SEM with backscattering electrons (Fig. 10g) shows the presence of particles of SiO_2 (darker color) in the lightest green color.

From all these results, we can conclude that the green glazes were produced by adding copper oxide to the glaze as a colorant. Lead oxide was used as flux for all the glazes.

3.2.4 Black and white colors

Regarding the black glazes, XRF analyses showed high contents of MnO (ca. 1.5%) (Table 1). The micrograph of one of the black cross sections showed, as is usual in these ceramics, two different layers: one was black, with a thickness of approximately 10 μm, and the other was opaque, with a thickness of ca. 100 μm (Fig. 10h). The chemical analyses performed with EDX showed the presence of Mn and Fe. Punctual chemical analyses performed with EDX (Fig. 11e) showed the presence of Fe in the black layer (Mn, Si, Pb and Ca were also detected).

Regarding the white glazes, the microphotography of one white cross section (Fig. 10i) showed a high content of siliceous particles. The white color zones appeared next to the orange color zones, and the morphology differed from that of the other white color zone that was present underneath. They were probably not added in the same manufacturing process. However, both layers showed very similar compositions based on Si.

3.2.5 Bubbles in the glaze

SEM micrographs of all the studied glazes in this work showed the presence of small bubbles. The presence of bubbles may be attributed to the use of lead carbonate in the manufacturing process to produce lead oxide, releasing carbon dioxide [36–38]. These bubbles appear frequently in glazes that have been heated at temperatures between 900 and 1000 °C [37]. Needles were observed inside the bubbles (Figs. 12a–c). Silicon and oxygen were the elements composing the needles. The formation of this silica compound (SiO_2) during heating in the manufacture of the tiles may be favored by the presence of Na and K in the glaze phase [39]. In some bubbles and in their vicinity, prismatic crystals made up of P and Ca were detected (Fig. 10c, d, 12d–f). As-, Pb-, Na-based compounds with spherical morphologies (Fig. 10c, d, 12g, h) were also detected inside of the bubbles in the glaze phase of blue enamels [40, 41].

3.3 Comparison of ceramics manufactured by Benito de Valladares and Augusta

The Valladares technique is considered a continuation of Augusta's work [8]. This is the reason why it would be interesting to compare the microstructure and composition of the tiles manufactured by both ceramists. Augusta covered the *Palacio Gotico* of the *Alcazar* with *maiolica* ceramics using the techniques developed in Antwerp. These tiles have been considered as one of the most important instantiations of this genre existing in Spain; they reflect flowers, birds, fantastic animals, warriors, and other motifs. Two saloons, the *Salon del Baile* and *Salon Cantarera,* belonging to the *Palacio Gotico,* were previously studied by some authors of this work [8]. The study revealed differences between both saloons. The name Augusta appeared in many places in the *Salon del Baile* and was absent in the *Salon Cantarera,* so for a comparison between both ceramists, the *Salon del Baile* was selected. Benito de Valladares manufactured (within the workshop of Hernando de Valladares in *Triana*, Seville) the tiles of the *Cenador del Leon*; they represent plants, flowers and fantastic animals.

The glazes of the *Cenador del Leon* made by Benito de Valladares have a double layer, as seen in some glaze cross sections: yellow, orange, brown (Fig. 4a–h), blue (Fig. 10a, b), green (Fig. 10e) and black (Fig. 10h). The glazes of the *Palacio Gotico* made by Augusta at the end of the sixteenth century have a single layer for all colors except yellow and some samples of blue [8]. This fact is the most important difference between the tiles made by Augusta and Benito de Valladares. The differences between the
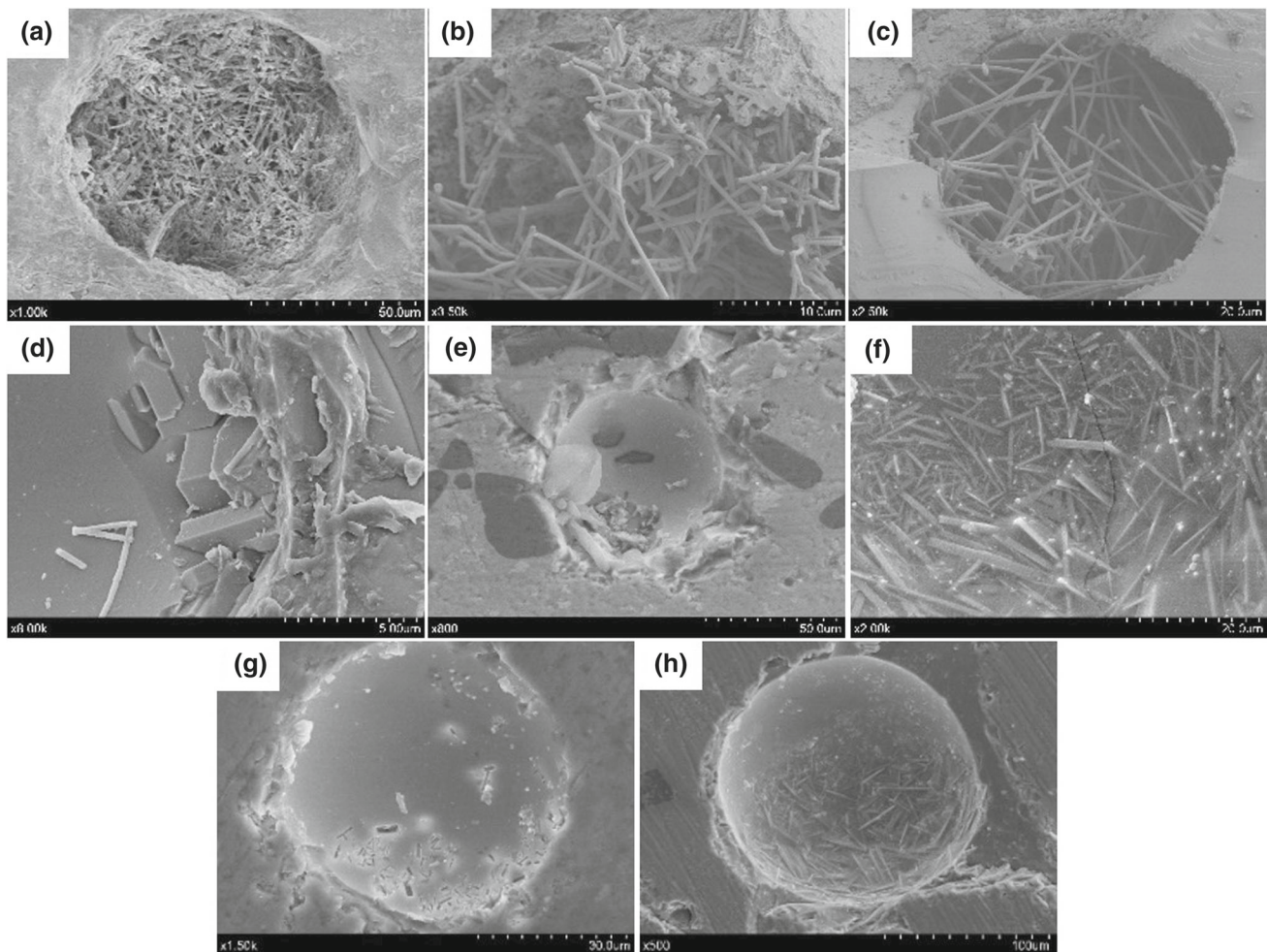
Fig. 12 SEM micrographs of glazes corresponding to needles **a–c**; prismatic crystals **d–f**; spherical compounds (**g**, **h**)

formation of one or two layers may be attributed to the manufacturing processes. The colors obtained using Sb (mainly yellow but also orange and brown) always showed two layers; the remaining upper layer separated due to this chemical element not dissolving into the glazes, whereas Co or Cu used to obtain blue or green colors dissolved easily in the glaze phase and may be distributed along the entire glaze layers [42]. A coperta layer, added specifically to yellow–orange glazes [42, 43], was not observed in the Benito de Valladares or Augusta tiles. Perez-Rodriguez found a coperta layer in the ceramics of the *Santa Paula* convent gate in Seville, which were manufactured by Niculoso Pisano at the beginning of the sixteenth century (data not published). The main advantage of applying a coperta layer lies in its effectiveness for filling pores and making color more luminous [44]. Double-layer glazes seem to become less frequent in Italy at the end of the sixteenth century [24]. However, Benito de Valladares made the tiles of the *Cenador del Leon* in the middle of the seventeenth century, continuing with this manufacturing practice.

Important differences appear between the quantifications obtained by using the Sn-K and Sn-L emission lines in yellow glazes of tiles manufactured by Augusta [8] and Benito Valladares (Table 1) due to the presence of two layers in the glazes made by both ceramists. The differences also appear in the orange and brown glazes of Valladares, which are constituted by two layers. However, there were no differences in Augusta orange and/or orange glazes, which was attributed to the presence of only one layer. Similar trends are found between Pb-L and Pb-M, and Sb-K and Sb-L, attributed to the number of layers in the glaze phases.

$Pb_2Sb_2O_7$ (Naples yellow), dissolved in the upper zone of the glaze, is the pigment responsible for obtaining the yellow glazes. It was used in the earliest *maiolica* tiles from the fifteenth to sixteenth century. This pyroantimonate may be doped to modify the color. $Pb_2SnSbO_{6.5}$ was found in the glaze phase of the ceramics of the *Palacio Gotico* [8]. Other elements, such as Zn and Fe, have also been found doped into the Naples yellow in Renaissance *maiolica* [26, 27]. In this sense, Zn was detected in the five yellow glazes studied in this work, with an average amount of ZnO of ca. 7.01% by XRF portable equipment (Table 1). By Augusta, tiles were found to contain 6% ZnO in the *Salon del Baile* [8], a value very similar to that found in Valladares tiles. Zn was probably added to the Sb by both ceramists to obtain a warmer hue [45, 46]. Additionally, lead antimoniates doped with Sn and simultaneously with Sn and Zn were detected by EDX analysis in some other punctual chemical analyses on yellow Valladares glazes. The orange and

brown colors of Benito de Valladares were also obtained by the formation of Pb-antimoniate in the glaze phase. Important iron oxide percentages were found by XRF analysis to be approximately 2.65 and 3.01% (Table 1). Fe was found to be included in the structure of $Pb_2Sb_2O_7$ and appeared as Fe_2O_3. The orange color of the ceramic tiles of the *Salon del Baile*, manufactured by Augusta, also showed a high quantity of Fe.

The compositions of the blue-colored glazes were found to be similar in the two types of ceramics, and this observation implies similar glaze process evolutions, as was previously discussed in this work. The study of the green color made by Augusta revealed the presence of Cu-based compounds as pigments accompanied by Sb, although at lower concentrations than in yellow, between 1 and 2% [8]. In the green tiles made by Benito de Valladares, Sb was present in a very low content (ca. 0.1%) (Table 1). Cu may produce a dark greenish color [47] when accompanied by Mn and Fe, as shown in the Valladares ceramics. Both ceramic types had similar proportions of Sn in this glaze color. The presence of Pb-antimoniate in green glaze has been described by several authors [24, 29].

Black and white glaze were not compared between the two ceramists. Black glazes were not present in Augusta production, and white glazes were relatively rare in Augusta tiles.

4 Conclusions

The *maiolica* style was used by Benito de Valladares for tile manufacturing. The ceramic body employed by Valladares contained high amounts of SiO_2, CaO and Al_2O_3 and low amounts of Fe_2O_3, MgO, K_2O and Na_2O. The presence of high amounts of CaO and anorthite means that calcium-rich clays were used as raw material. The material used to manufacture the ceramic body of the tiles studied in this work was similar to the clays used to make ceramics in Seville in Arabic times. The existence of anorthite and gehlenite and the absence of illite indicated that the tiles were fired at approximately 900 °C.

Regarding the composition of the glaze tiles made by Valladares, yellow, orange and brown colors were made using Naples yellow pigment. Zinc oxide and iron oxide were mainly added to the Naples yellow pigment to obtain a light-yellow color or orange-dark color, respectively. Zn and Fe (and Sn) were included in the pyroantimonate phases formed during firing but also appeared as free oxides. CoAs and CuO were used to obtain blue and green colors, respectively. The presence of As in the blue glazes is in agreement with the data of manufactured Co pigment. Black color was made using iron and manganese oxides. The glazes of the different colors were constituted by two layers: a top layer with a thickness between 10 and 20 µm containing the pigment and an inner opaquer layer with a thickness between 80 and 100 µm.

Valladares' style is considered a continuation of Augusta's work. Augusta covered the *Palacio Gotico* of Seville *Alcazar* with *maiolica* ceramics. The manufacture of both types of tiles and the pigments used by both ceramists were similar. However, the glazes of the Augusta tiles were constituted by one layer except for the yellow color glaze. The presence of two layers was responsible for differences between the percentages of PbO, SnO_2 and Sb_2O_5 calculated by using the different emission lines of Pb, Sn and Sb. Sb was used by Augusta, not by Valladares, to obtain green color.

The presence of secondary calcite was the primary cause of the ceramic coating detachments, which determined large lacunae in the decorative motifs. Restoration treatments were applied in order to preserve this remarkable ceramic.

Data Availability Statement This manuscript has associated data in a data repository. [Authors' comment: The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request].

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