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EXPLORING THE TECHNIQUE OF GLAZING USED BY THE POTTERS OF BARCELONA

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ABSTRACT

The application of glazes on pottery became common in Western Europe from the late 12th century / early 13th century onwards. However, the process of "glazing" entails different degrees of complexity which might involve a great variety of raw materials. Accordingly, simple glazing process consists of a single layer applied over the surface of the body, becoming a shiny and transparent coat after firing. The addition of pigments would result in a coloured glaze that can be translucent or even opaque. The more complicated sequence occurs in decorated glazed pottery, where opacifiers, pigments and metals are added to produce an opaque white glaze to enhance the decoration. This glaze is applied to the bisque pottery and manufactured, usually, in a second or third firing.

To deepen our knowledge of the glazing technique, we have studied glazes from coarse pottery, cooking ware, polychrome coarse pottery and majolica from Barcelona (13th to 18th centuries AD). The application of the glaze, the thickness, and the composition of glazes (including opacifiers, pigments and/or metals) have been examined, through Scanning Electronic Microscopy (SEM). This study has revealed the high diversity in the glazing technique.

KEYWORDS: Tin lead glazed, lead glazed, coarse ware, Black and Green, Blue on White, Lusterware, Polychrome decoration.

1. INTRODUCTION

Since 2009, in the framework of the Tecnolonial project, a research program focused on the archaeometric characterisation of tin lead glazed (commonly named *majolica* or *pisa* in the Iberian peninsula and Italy), transport jars, lead glazed coarse ware, and cooking ware among others, is being developed at the Material Culture and Archaeometry UB (ARQUB, GRACPE) research unit, at the University of Barcelona. The main goal of the project is to improve the knowledge and to understand the interaction, influence and cultural change during the colonisation process in the Americas, through the assessment of the impact of the pottery produced in the Crown of Castile, and, on a lesser extent, that of the Crown of Aragon in the new colonial societies. In this context, the main production centres of the Iberian Peninsula are under consideration. This is necessary to identify the reference groups related to each production centre, but also to assess the technical features as well as the technological changes that occurred through time. These changes and the existing complexity must relate to relevant changes in these societies.

In the case of Barcelona, the archaeometric characterisation was designed as a diachronic study where all the artefacts selected covered a broad period from the 13th century to the 18th century. Chemical and mineralogical study reveals a very complex structure with the presence of several groups that enables us to hypothesise the use of at least four different base clays (labelled A, B, C and E[1]). The three base clays here studied (A, B, and C) are further diversified in turn exhibiting different amounts of calcium, a differentiation that has significant implications from the technical point of view. A summary of the results, which are the basis for this study, is presented below.

The products of the 13th century are classed all through the groups A1, A2 and A3 (Buxeda et al. 2009, 2011, 2015, Madrid et al. 2015). Those groups differ basically by their CaO content, enabling us to distinguish among low calcareous ceramics (A1), border calcareous ceramics (A2) and calcareous ceramics (A3). Regarding the ceramic products, groups A1, A2 and A3 include green lead glazed and lead glazed coarse pottery, transport jars, jugs and archaic tin lead glazed (commonly named majolica arcaica o pisa arcaica in the Iberian peninsula and Italy) (Beltran de Heredia 2007, Iñañez and Buxeda 2007, Berti and Capelli, 1994, 217-219). However, while green glazed and glazed coarse pottery is well represented in all groups, archaic tin lead glazed, transport jars and jugs are just included in groups A2 and A3, i.e., the border calcareous and the calcareous groups, being more abundant in the latter. That seems to suggest that there was not a specific recipe for the preparation of the paste of green glazed and coarse glazed pottery, while for archaic tin lead glazed, transport jars and jugs the seeking of calcareous pastes is clear. But this search would not lead to differentiate recipes since the three groups exhibit a continuum in the CaO variations without a clear cut.

At the end of the 13th century, a significant change is observed with the advent of clay B, which will be the base clay for producing pottery during the 14th and 15th centuries. The B1 group exhibits an increase in the CaO content compared to the previous group A, and it is the one in which the production of tin lead glazed starts. This advancement in tin lead glazed production (from archaic tin lead glazed to tin lead glazed) does not mean a specialization of the production at this stage because the same paste B1 is used to produce coarse green and honey-coloured lead glazed pottery and transport jars. In the 15th century, a new significant change took place. Besides the B1 products, group B2 reached the market. B2 implied a new increment in the CaO content but, from the technical point of view, the most significant change is that this paste B2 will only be used for tin lead glazed production, while paste B1 will be still in use for lead glazed coarse ware. It was also at that time, the beginning of the 15th century, that the potters' guild (called *Confraria de Sant Hipòlit*) is established in the town (García-Oses, 2018).

The guild was run under the regulations of *Ordinacions d'ollers, gerrers i rajolers* (which translates as 'Ordinances for potters producing cooking ware, coarse wares and transport jars, and tiles and bricks'), and tin lead glazed potters (*escudellers*) were also included. The founding of the guild and the regulation of their activities was a significant step in the process of change and improvement. During the 16th century new groups like C1 and C2, showing low calcareous pastes, are employed in the elaboration of glazed and unglazed coarse pottery and cooking ware. This change would appear to be in line with the separation of *escudellers* potters from the guild of *Sant Hipòlit* and the establishment of a new specific *escudellers* potters' guild in 1531. This seems to be a new step in the process of specialization of ceramic production in Barcelona. Finally, concerning the 17th and 18th centuries, it is clear that ceramic ware from the B2 group was not produced anymore. New ceramic groups B4a, B4b that show a very high CaO content in their pastes, were created. That implies, again, an increase in the

[1] Group E, the earlier one is still in progress and will not be included in this paper (Di Febo et al. 2011)

CaO content. The new pastes will be used for the elaboration of tin lead glazed, but also for imitations of Ligurian *blue berettino* pottery. Besides, from the 18th century onwards, group C2, a part of being employed in the elaboration of lead glazed and unglazed pottery, is also used for the production, among others, of polychrome glazed pottery as will be shown below.

2. BARCELONA AS A PRODUCTION CENTRE

The city of Barcelona lived its magnificence period between the 15th and the 17th centuries, where the city became the main political centre of Catalonia. These centuries meant a significant change in terms of trade, the exportation of raw materials were substituted by the trade of manufactured products made in Barcelona, which at the same time had consequences in the process of production in all Catalonia, and what is more, in the network exchange. In this sense, the city of Barcelona became the main centre of manufactures, as well as several luxury items, were arriving from the whole Mediterranean. In this context, pottery was one of the most demanded products by the social elite from Barcelona, where ceramics from Italy, France or Flanders arrived in huge quantities (Beltran et al. 2010). On the contrary, ceramics made in Barcelona were highly spread over the city, even though these ceramics were probably not much demanded in the Mediterranean area.

The importance gained of pottery production is well documented among numerous legal and commercial manuscripts referring to these activities, as in the old and current names of the streets, like the contemporary *escudellers* st. (i.e., potter producing tin lead glazed vessels), from the word *escudella*, which means porringer, one of the most characteristic shapes of this tableware. Nevertheless, archaeological surveys conducted in Barcelona in the last decades have provided us with many pottery ensembles, as well as with the discovery of some kilns, reinforcing the written sources and enabling us to date the potting production between the 13th and 18th centuries (Figure 1).

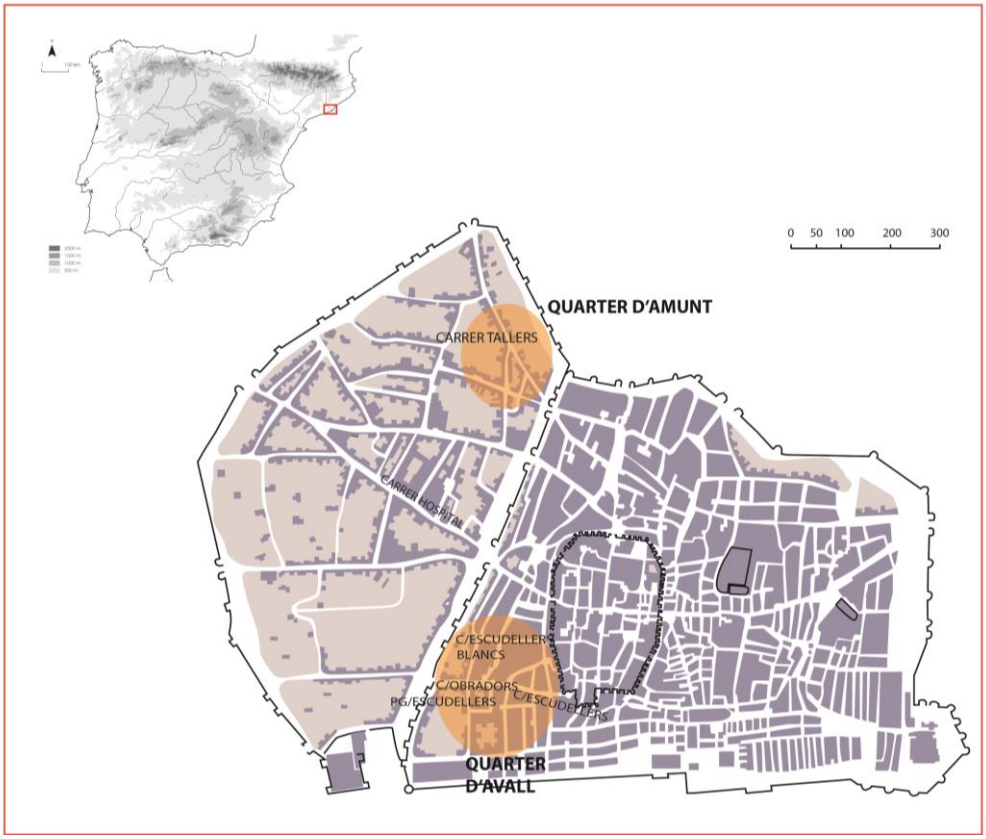

Figure 1. The situation of Barcelona in the Iberian Peninsula with the main pottery production areas highlighted. On the top "Quarter d'Amunt area" with Hospital st., and Tallers st.; on the bottom "Quarter d'Avall area" with Escudellers st., Escudellers Blancs, st., and Obradors st.

Focusing our attention on pottery produced in Barcelona; up to now, several kilns have been archaeologically excavated. Pottery from the 12th century was produced in *Carders* st. kiln, while pottery from the 13th century was produced in *Hospital* st. kiln. Both base clays -E for *Carders* kiln and A for *Hospital* one- were probably collected from Quaternary deposits closer to the two workshops (Buxeda et al. 2009; Di

Febo et al. 2012). Afterwards, from the 14th century onwards, workshops started being moved from the outskirts to the centre of the city. Some workshops from 14th to 18th centuries are well known, such as those from *Avinyó* st., *Tallers* st. or *Rull* st. (all of them in the process of study), located at the Quarter *d'Avall* area. From the 14th century, the same base clay —but different from those used during the 12th/13th centuries— was used for the elaboration of many products, linked with the beginning of the tin lead glazed productions. The next step, in the 17th and 18th centuries, would involve the standardization of manufactures having yet a specific clay for a specific product. The archaeological contexts, together with the archaeometric information, enabled us to infer into the circulation of pottery, the evolution of traditions, or the insight of workshops.

The previous studies have been focused on the characterization of workshops and the pottery distribution around the city. The next step, and what is presented in this article, has been the characterization of glazes, allowing us identifying different ways of preparation and application, and additionally, the possibility of discerning potters as well as workshops.

As has been previously observed, to obtain a good tin lead glaze pottery, calcareous pastes and a double firing process is required (Molera et al. 1996, 2001a, Tite et al. 1998, Iñañez et al. 2007, Iñañez 2007). In contrast, lead glazed coarse ware is commonly the result of one firing process (Molera et al. 2001b). The identification of single or double firing process in tin lead glazed vessels is, sometimes, complicated. During the firing process, ceramics undergo mineralogical phase transformations and densification of the microstructure depending on their composition (at the atomic, mineralogical, and petrological level) (Buxeda and Madrid 2016), the firing temperature, the duration of firing, and the firing atmosphere (Heimann and Maggetti 2014). Firing temperature and firing atmosphere can only be tentatively estimated after the evaluation of the possible changes undergone for a given composition. However, there is no way to estimate — unless written sources exist— the duration of firing and, because of that, only the equivalent firing temperature (EFT), and only for pastes, can be estimated (Roberts 1963).

Nevertheless, for glazes and the development of interfaces between matrix and glaze, experimentation is the only way to get an approach on temperature, atmosphere and duration of firing (Molera et al, 1999, 2001b, 2013, Pradell et al. 2004, Roqué et al. 2005, Ben Amara and Schvoerer 2006, Molera et al. 2007, Fortina et al. 2008, Pradell et al. 2010, 2012, Godet et al. 2019). Those studies point out that with a single firing process, crystals of potassium-lead-aluminium-silicate are formed at the body-glaze interface, and the interaction between the glaze mixture and the body is significantly greater than when the same glaze suspension is applied to a biscuit-fired body. Taken those studies into account, we have paid special attention to the examination of the interface trying to contribute to a better understanding of one of the most complicated steps to identify in archaeological materials.

3. MATERIALS AND METHODS

Selected individuals representing most of the different products mentioned above were investigated to improve the knowledge of glazing techniques (Table 1). For this purpose, the study of the glazes and decorations has been undertaken through SEM coupled to an energy dispersive X-ray detector and using the backscattered electrons detector (SEM-BS-EDS). The emphasis was given to the following features: the thickness of the glazes, their composition (including the presence of tin oxide particles, bubbles, quartz and alkali feldspar inclusions, responsible all of them for the opacity of glazes), observations of the interface between paste and glaze to infer whether the application of the glaze was made on the ceramic body before firing or after a first firing, in an already biscuit ceramic, and, finally, nature of pigments used for decorations.

SEM observations were performed on polished sections. Bulk specimens were fixed on metal specimen stubs using silicone adhesive, and the non-conductive ceramic specimens were made conductive. Colloidal silver paint was applied on excess silicone adhesive and lateral sides of the ceramic bulk specimen. Then, the specimen surface was coated with a thin carbon film (~ 10 nm) by vacuum evaporation. The observations were made by using a JEOL JSM-6510 in high vacuum conditions. Microanalyses were carried out with an Energy-Dispersive X-ray spectrometer (EDS) INCA 250 (Oxford Instruments). The observations were performed using an acceleration voltage of 20 kV, a working distance of 15 mm, and the microanalyses are counted for 100 live seconds. All the analyses to determine the composition of the glazes of this study have been carried out on homogeneous areas, avoiding possible altered parts. Each chemical analysis is the result of the mean of 5 microanalyses by SEM-EDS performed at 5 different areas at 3000X. Interfaces for the assessment of single or double firing processes all the samples have been observed at 1000X.

Table 1. Individuals sampled in the present study (by chemical group, ceramic class, and decoration). Technical features observed by Scanning Electronic Microscopy (SEM). RG: reference group. PCRU: paste compositional reference unit. X: between 2 and 4 inclusions/bubbles; XX: between 4 and 8 inclusions/bubbles; XXX: > 8 inclusions/bubbles.

Group (RG/PCRU)	Ceramic class	Individual	Decoration	Chronology	Thickness	Interface	(S) Stripe/(s) slip	Relict inclusions	Bubbles
A3	archaic majolica	BCN082	white glaze	13th century	irregular. 30- 60-300µm	irregular. Possibly two firings			
		BCN248	white glaze	13th century	irregular. 60-100µm	irregular. Possibly two firings. One line between the interface and the glaze			
B2a	majolica	MJ0091	black and green	13-14th century	homogeneous. 80-100µm	possibly two firings. One line between the interface and the glaze in some areas		xx	x
B1a		MJ0191	black and green	13-14th century	homogeneous. 80-100µm	one firing. Feldspat crystals and lead between the interface and the glaze. 10µm		xx	xx
		MJ0196	black and green	13-14th century	homogeneous. 80-100µm	one firing. Crystals between the interfase and the glaze. 10-30µm		x	x
B2c		BCN262	blue on white	15-16th century	homogeneous. 100-120µm	two firings. One line between the interface and the glaze. 50µm	S-black	x	x
B2c		BCN251	blue on white	16th century	irregular. 100-110µm in white areas, 100-20µm in the blue ones.	irregular. White glazed has a line between the interface and the glaze, showing two firings. Nevertheless, blue areas presents a high interaction	S-black	xxx	xx
B2a		BCN179	blue on white	16-17th century	homogeneous. 110-120µm	two firings. One line between the interface and the glaze. 20-30µm		xx	x
		BCN174	blue on white	16-17th century	homogeneous. 110-120µm	two firings. One line between the interface and the glaze. 20-30µm		xx	x
		DIA650	blue and yellow	17th century	irregular. 80-300µm	Irregular. One line between the interface and the glaze. 15-20µm, but with crystals		xxx	xxx
		DIA649	blue on white	17th century	irregular. 300-200µm	two firings. 10µm		x	x
		BCN177	blue on white	16-17th century	homogeneous. 100µm	one firing. 10µm		x	x
		MJ0114	lustreware	17th century	homogeneous. 200µm	two firings. 10µm		xx	x
B2c		BCN250	blue on white	undated	homogeneous. 50-80µm	irregular. One line in some areas, in other areas 80 µm	S-black	x	x
		BCN261	blue on white	15th-16th century	100-150µm	two firings. 10µm		x	x
B2out		MJ0117	blue on white	17th century	homogeneous. 200µm	irregular. interface with crystals. 20 µm		xx	xx
B1out	coarse ware	BCN117	green glaze	15th century	irregular. 150-300µm	one firing. high presence of crystals		xx	xx
B1c		BCN156	honey-colored glazed	16-17th century	homogeneous. 100-200µm	one firing. high presence of crystals		x	x
B1b		BCN157	honey-colored glazed	16-17th century	homogeneous. 150-200µm	one firing. high presence of crystals		x	x
C2		BCN236	brown and yellow	17-18th century	irregular. 100-250 µm	one firing. Neoformation crystals10-20µm	s-100µm	x	x
B2d		BCN290	polychrome	18th century	irregular. 70-110µm	one firing. Crystals in the whole glaze	s-50µm	x	x
		BCN237	polychrome	17th century	irregular. 50-100µm	one firing. Neoformation crystals10-20µm	s-50µm		

4. RESULTS AND DISCUSSION

4.1. 13th century - Archaic Tin lead glazed

Archaic tin lead glazed was the first tin-glazed produced in the city of Barcelona in the 13th century (Iñañez and Buxeda, 2007). This product represents a period of experimentation before the tin lead glazed as such was achieved. The process observed by SEM for the elaboration of the glazes consisted of the double firing process, which means that the potters had already good know-how of the tin lead glazed technique. Hence, the application of the glaze on the ceramic body was made after the first firing phase, in an already biscuit calcareous ceramic. This practice avoids problems as bubbling, due to the release of carbon dioxide that occurred during the biscuit firing, as well as other difficulties related to retractions and porosities (Tite et al. 1998). This process can be observed at the interface of ceramics, where no interaction between the matrix and the glaze could have been detected. Furthermore, two different ways of glazing have been observed. As can be seen in Figure 2 (A to G), the sample presents a glaze on both sides —in the external and the internal part of the vessel— identifying an alteration process resulting in the loss of lead in some areas of the glaze (darker parts) (Figure 2, A, C and D; C and F). The base of the glaze (Table 2) contains a significant amount of tin oxide (10.65%) poorly distributed and concentrated in specific areas, visible

mainly in those parts where lead is lost (Figure 2, F). Besides, the decoration would correspond to black bands, badly preserved. Due to the small part of the sample preserved after the chemical and the mineralogical analysis, we could only observe one of the bands of the decoration, marked with a red square (Figure 2). Manganese and iron oxide were responsible for the black decoration (Table 2). These pigments were identified partially dissolved in the glaze, partially as accumulations on the upper part of the glaze (Figure 2, E and G), and several amounts of crystals of manganese were also observed in the lower part of the glaze, where lead underwent a leaching process. (Figure 2, G).

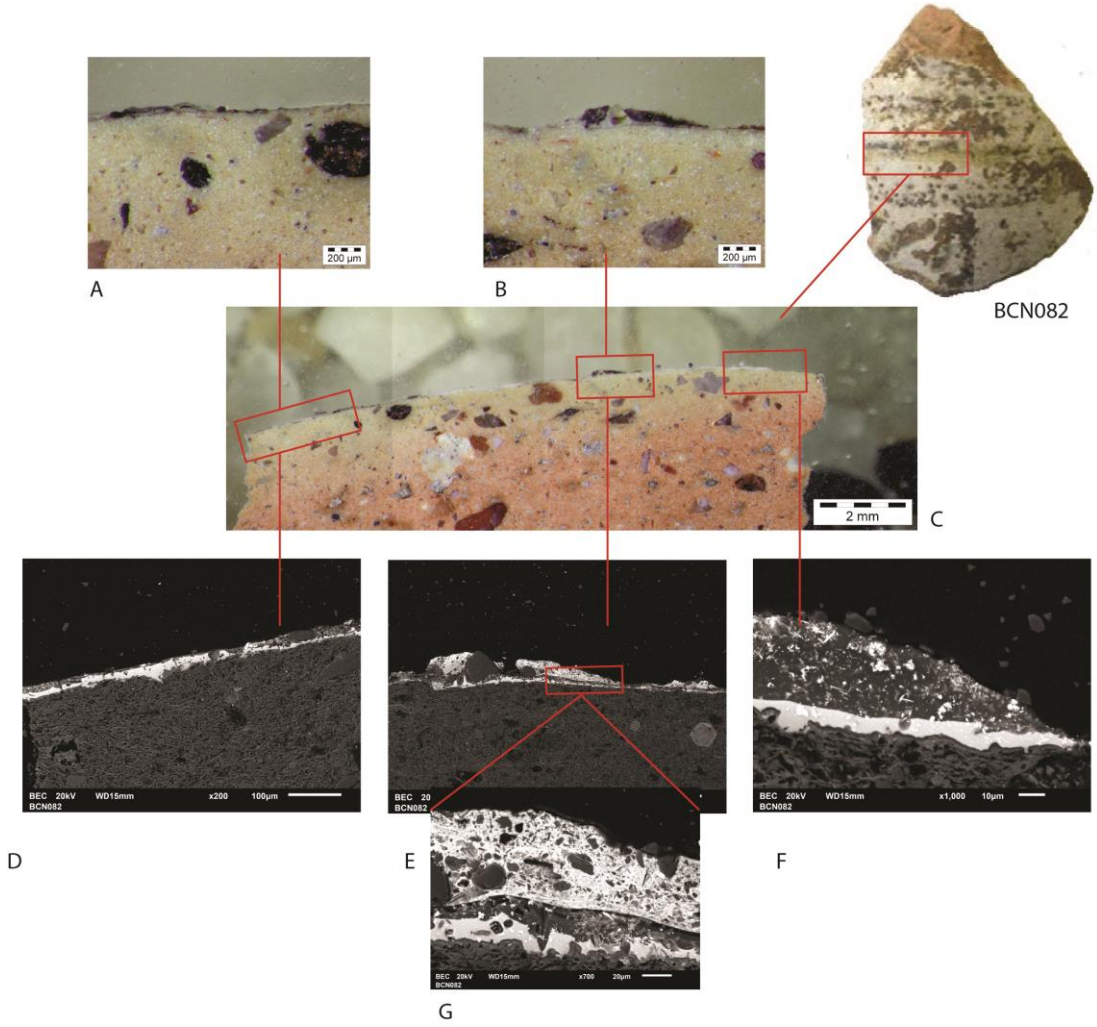

Figure 2. Archaic majolica BCN082. The red square on the sample indicates the area analysed by SEM-EDS, corresponding to one of the black decorative bands. C corresponds to the total polish section analysed, viewed by the optical microscope. A and B: well-preserved parts of the black decoration. D: microphotograph by SEM where an altered glaze that lost lead can be observed (darker areas). E and G: black decoration. Manganese crystals were detected in the lower part of the glaze (darker area). F: microphotograph by SEM of the altered white part of the glaze, where many crystals of tin oxide can be observed.

The second case, shown in Figure 3, presents slight differences. The glaze was only applied in the internal part of the ceramic (Figure 3, BCN248 INT., A to F) and, as in the previous case, the interface shows no interaction between the glaze and the body (Figure 3, B and C), as a result of a double firing process. The result is a well-produced glaze, containing a higher quantity of tin than in the previous individual (18.68%, Table 2), but distributed along the glaze with a thickness between 60 µm and 100 µm (Figure 3, A and B). In this way, the opacification (Vendrell et al., 2000) is produced due to the distribution of small particles of tin oxide within a colourless glaze, which produced a reflection and the scattering of the light. The more particles added into the glaze (increasing the path length for the light), the more size of particles and the higher refractive index between crystals and glass matrix, the better is the result. Furthermore, the glaze seems to be altered in some parts, presenting

some crack areas where lead has been leached, leaving the siliceous compound, darker, visible (Figure 3, BCN248 INT., A and E). The alteration of glazes is a complicated process that requires extensive and in-depth studies. However, it is interesting to point out that studies carried out on archaeological glasses shows that the most serious alterations occurred for those materials high lead content (Zacharias et al., 2020). Returning to our study, iron and copper were applied to obtain green colour, and, similar to the other individual, the pigment was concentrated mainly on the upper part of the glaze (Figure 3, BCN248 INT., D, E and F).

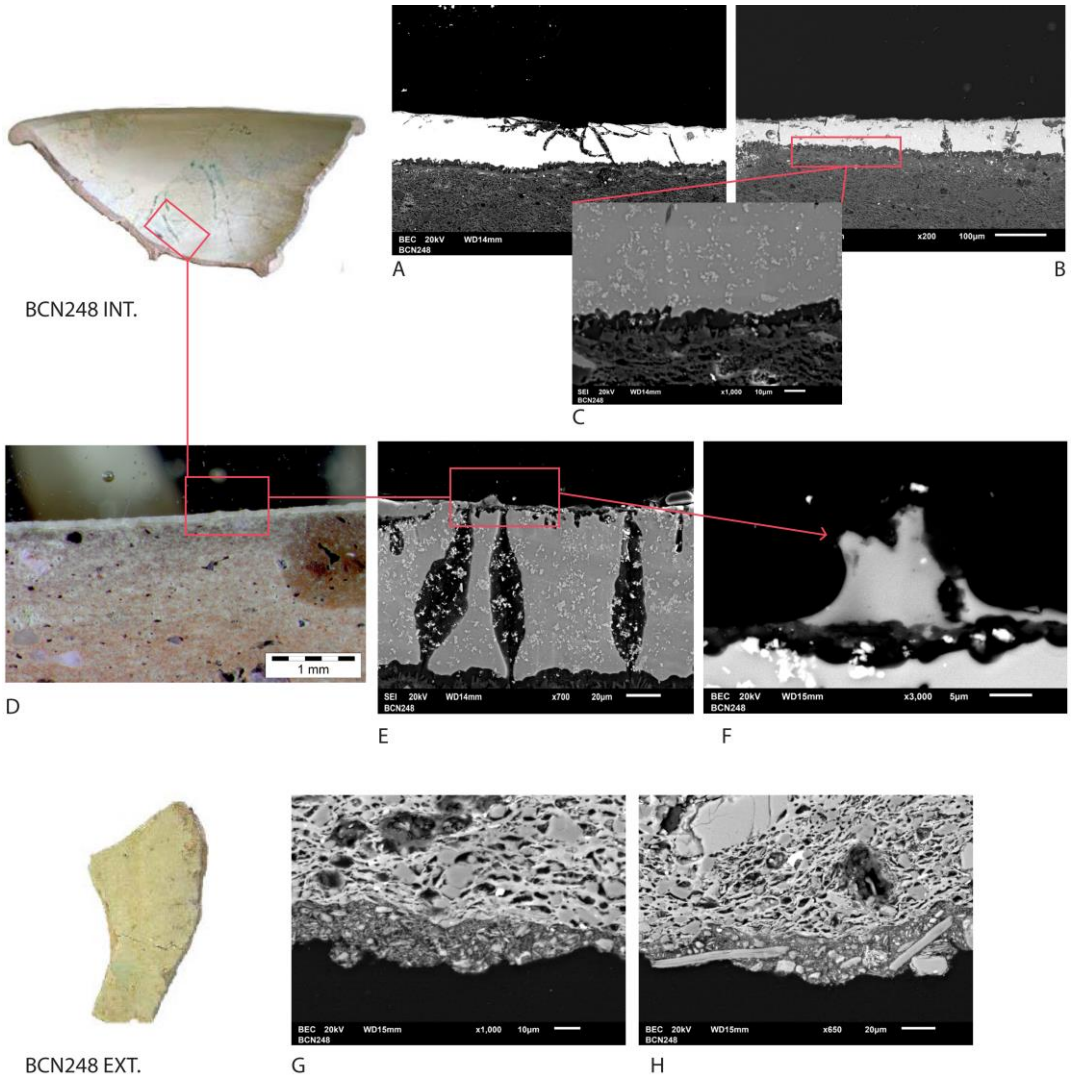

Figure 3. Archaic majolica BCN248. Vessel glazed in the internal part (BCN248 INT.), and with a slip in the external part (BCN248 EXT.). A and E: cracked areas of the glaze. B: glaze of the internal part showing a double firing (C). D, E and F: accumulations of copper dissolved in the glaze corresponding to the green decoration. E: concentration of crystals of tin oxide. BCN248 EXT. G and H: white slip applied in the external part of the vessel.

The external part can be considered as a slip, made of silicon, aluminium, potassium, calcium and iron oxides (Figure 3, BCN248 EXT., G and H). This preparation must have been intended, probably to save expensive raw materials, such as tin and lead. It is important to point out that until the 15th century, archaic tin lead glazed and tin lead glazed, with rare exceptions, were only glazed in the internal part, probably considering not necessary to waterproof the external part.

Table 2 Chemical composition of the glazes measured by SEM-EDS. All the amounts represent mass % (mean obtained after the microanalyses of 5 homogeneous areas at 3000X). RG: reference group. PCRU: paste compositional reference unit. Int: interior. Ext: exterior. BG: Black and Green. BL: Blue on White. LS: lusterware. DEC: decoration. POL: polychrome decoration.

Group (RG/PCRU)	Ceramic class	Individual	Na2O	MgO	Al2O3	SiO2	K2O	PbO	FeO	CaO	SnO2	MnO	P2O5	CuO	CoO	ZnO	TiO2
A3	archaic majolica	BCN082	0.17		4.29	32.03	1.46	33.63	3.35	7.56	10.65	0.26	6.6				
		BCN248 (Int)	0.68		2.43	37.84	4.29	33.48	2.59		18.68						
		BCN248 (Ext)*			9.78	24.92	3.58		6.76	54.96							
B2a	majolica	MJ0091 (BG)	1.83		2.68	46.74	6.45	26.6		0.51	15.18						
B1a		MJ0191 (BG)	0.56		2.51	29.7	1.87	37.89		2.48	18.5	0.43	6.06				
		MJ0196 (BG)	0.72		3.35	36.92	2.09	35.03	1.68	1.21	15	0.67		3.32			
B2c		BCN262 (BL)	1.62		3.1	50.19	9.21	27.82	0.43	2.01	5.62						
B2c		BCN251 (BL)	0.17		2.16	42.04	5.28	38.53			11.83						
B2a		BCN179 (BL)	1.18		2.47	48.5	5.73	35.64		0.98	5.5						
		BCN174 (BL)			2.84	46.68	5.15	35.78	0.27	0.32	8.78				0.2		
		DIA650 (BL)	2.15		3.58	48.14	3.6	37.22		1.58	3.73						
		DIA649 (BL)	2.06	0.14	2.85	48.83	5.53	31.05		2.49				7.04			
		BCN177 (BL)	0.8		2.88	50.16	5.5	40.67									
		MJ0114 (LS)	0.57		2.36	45.64	4.71	40.37		0.78	5.57						
		MJ0114 (DEC)			1.79	44.89	4.26	33.37	1.57	1.59				12.54			
B2c		BCN250 (BL)	0.75		2.59	45.79	5.43	36.74	1.03	2.54	4.91				0.21		
		BCN261 (BL)	1.35		3.23	56.37	6.47	28.38	0.73	2.45	0.9				0.12		
B2out		MJ0117 (BL)	0.18		3.46	57.73	7.53	27.29	1.52	1.74						0.22	0.32
B1out	coarse ware	BCN117			3.48	34.75	1.32	52.67	2.45	2.11				3.23			
B1c		BCN156			3.71	36.31	1.81	55.2		2.97							
B1b		BCN157		0.17	5.58	35.5	1.32	50.58	3.39	3.34							0.13
C2		BCN236			5.76	36.67	0.23	52.08	3.73	0.55				0.98			
B2d		BCN290 (POL)			8.02	36.98	1.64	49.22	1.94	2.03				0.16			
		BCN237 (POL)		0.39	3.9	33.48	0.54	58.35	1.27	0.91				0.96			0.2

It is interesting to highlight that although shapes and decorative patterns applied to the frames, necks and handles of the vases are like those utilized on the 13th-century Italian archaic tin lead glazed (Berti, Capelli, 1994, 217-219), the technique of glazing clearly shows differences. In this sense, Italian vessels present a fine white layer, a slip, between the clay body and the glaze, probably to save tin oxide for opacifying and obtain a white surface for applying the decoration (Capelli, 1996; 1999a; 1999b; Capelli and Di Gangi, 2000; Alaimo et al., 2004).

4.2. 14th / 15th centuries - Black and Green decoration

Even if small attempts were done before, as we have seen above, true tin lead glazed could be considered to start in the Mudejar ceramic tradition, representing green and manganese patterns on a white glaze, which exhibited mainly geometric designs from the end of the 13th century and during the whole 14th century. Most of the individuals with this decoration analysed in Barcelona belonged to the chemical group B1 (Table 1), the first clearly calcareous, which also contains coarse glazed pottery and transport jars, pointing out what was said above that, at this moment, there was not still a specialization in pottery production, using the same paste preparation for most of the ceramic classes.

Notwithstanding, at the beginning of the 15th century a change in the paste is archaeometrically detected, and potters started using what we called paste B2 —slightly more calcareous than B1— restricted to prepare tin lead glazed products, in particular, Blue on White and Lustre decorations. However, few of the Black and Green individuals analysed in this work correspond to the paste B2. This study tends to observe whether the differences established chemically, corresponds also to a different way of applying glazes. A detailed research focused on Black and Green decoration has been recently published (Peix Visiedo et al. 2021).

The individuals belonging to the chemical group B1 (Figure 4 and 5 respectively) were the result of one firing, as we were capable of observing a great layer of interaction in the interface between the body and the glaze where many feldspar and lead crystals grew up (Figure 4, G and H, Figure 5, E). Glaze thickness varies between 80 and 100 µm (Table 1). The amounts of lead, silicon and tin are the same as the concentrations documented on archaic tin lead glazed pottery (Table 2). Like archaic tin lead glazed, some parts of the glaze underwent the leaching of lead due to an alteration process (Figure 4, F and G). The black decoration is identified not only because of accumulations in the upper part of the glaze (Figure 4, A to D; Figure 5, A to D) but also for the manganese dissolved into the glaze (in this case there is no crystallisation of manganese). Indeed, crystals of kentrolite (Pb_2Mn_3+2(Si_2O_7) O_2), a lead silicate and Bustamite ($CaMnSiO_6$), a calcium manganese pyroxene, developed in the interface of the black areas (Figure 4 E; Figure 5, F). Kentrolite crystals are formed due to the reduction of Mn4+ first to Mn3+ and then to Mn2+, and the reaction with the lead (Molera et al. 2013). This transformation is observed to happen at the low temperature of 650 ^{o}C, remaining stable at least at 840 ^{o}C. As these authors observed, the high contents of lead in these productions may have helped the formation of kentrolite. Bustamite is formed when large amounts of manganese are applied to the glaze facilitating the grown of acicular crystals as those shown in Figures 4E.

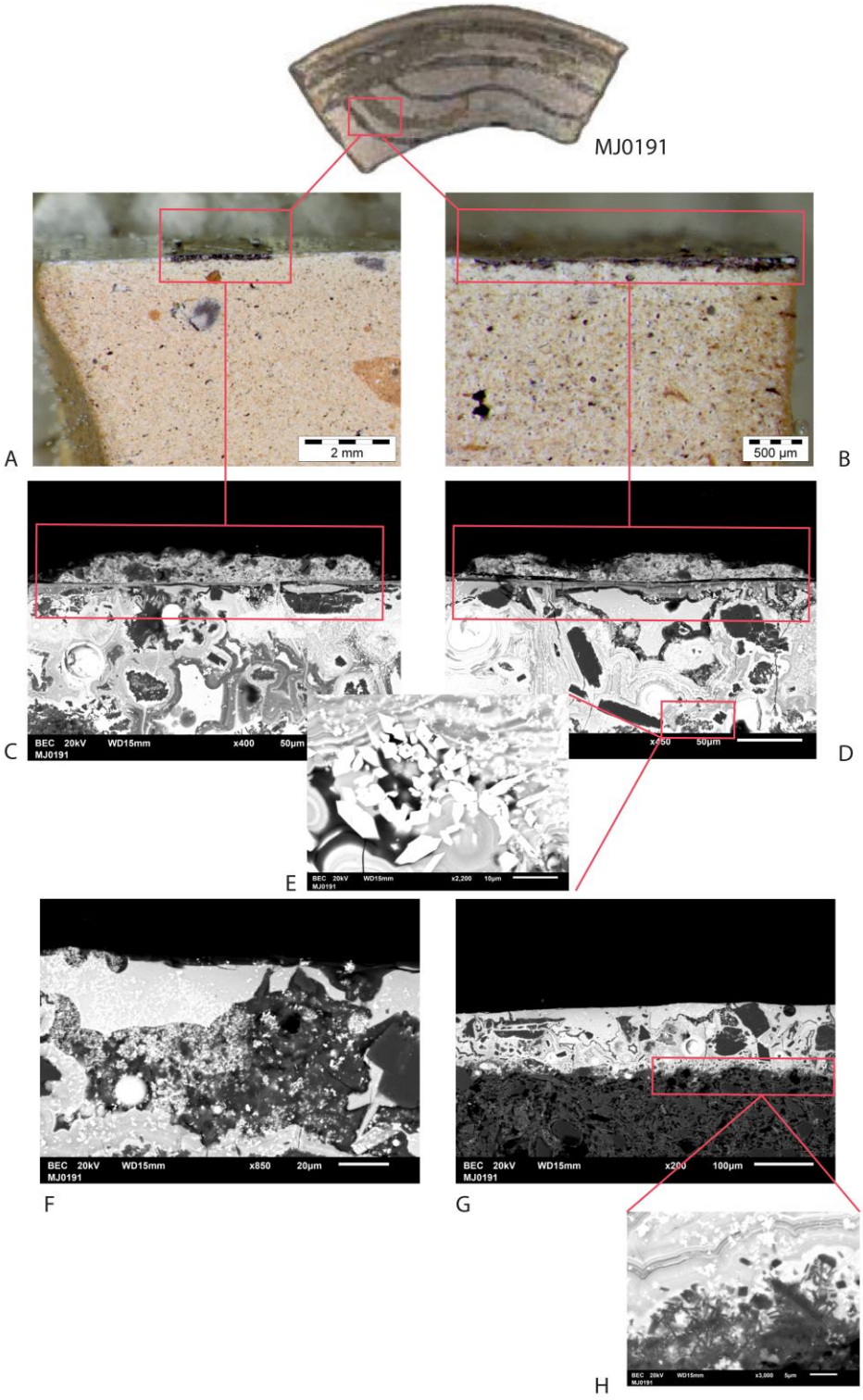

Figure 4. Black and Green majolica MJ0191. A and B: black decoration observed by an optical microscope. C and D: black decoration observed by SEM. E: crystals of kentrolite near to the interface. F: microphotograph by SEM where an altered glaze that lost lead can be observed (darker areas), tin oxide crystals accumulations. G and H: interface resulted from one firing process.

In contrast, Black and Green from group B2 show a double firing process and a well-fired glaze (Figure 6, A and C). A change in the composition of glaze has been identified, with an increase of 10% of silicon oxide, and a decrease of 10% in the use of lead, although the use of tin remains very high (>15%) (Table 2). Like in the previous cases, some parts of the glaze are altered, as can be observed by the formation of crystals of lead and calcium phosphate (Figure 6, B). Unfortunately, ceramics from this group only preserve the

non-decorated part, therefore we were not able to check whether the black decoration would have been prepared in the same way as decorations from group B1. The thickness is the same observed in the previous individual from B1 (80-100 µm, Table 1).

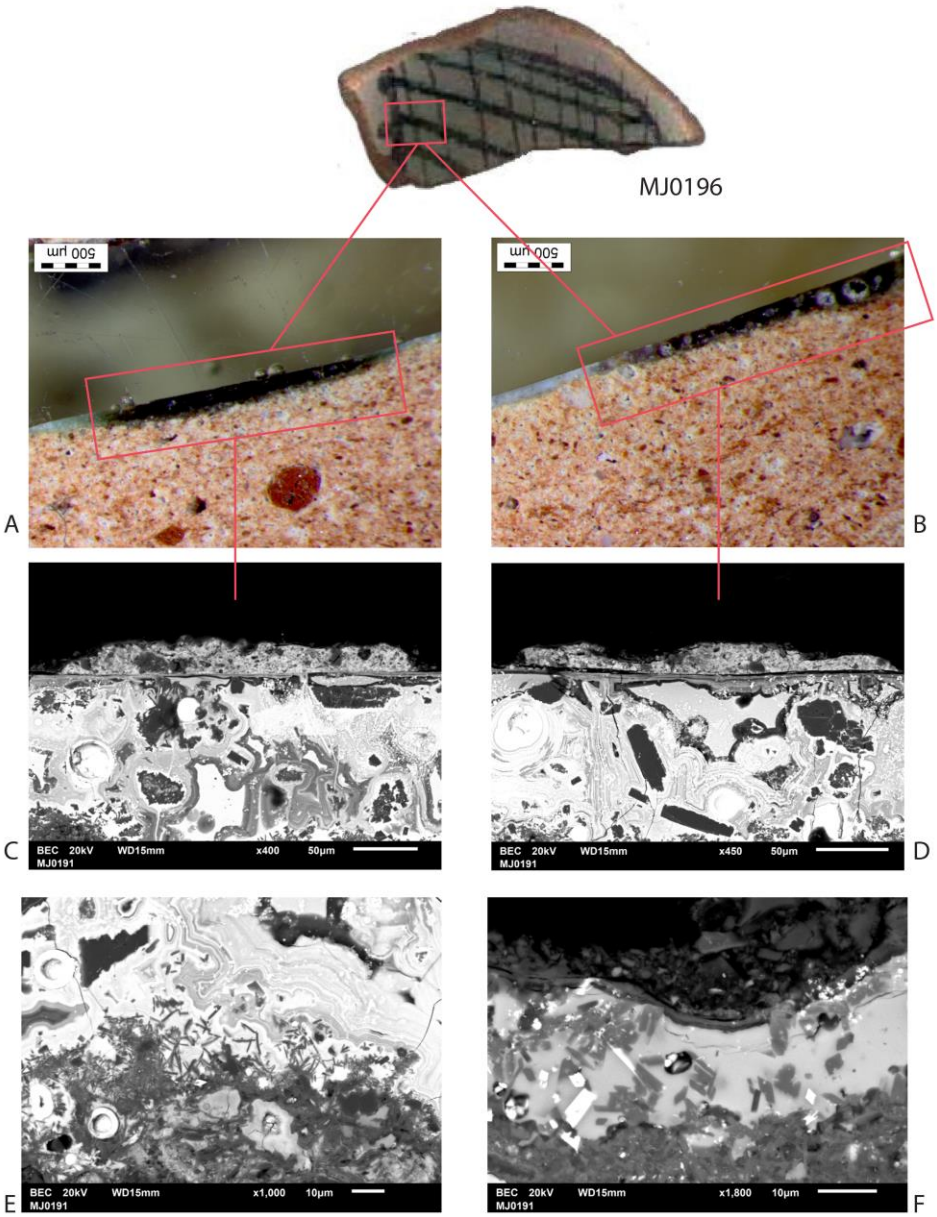

Figure 5. Black and Green majolica MJ0196. A and B: black decoration observed by an optical microscope. C and D: black decoration observed by SEM. E: interface resulted from one firing process. F: bustamite (dark crystals), kentrolite (bright crystals).

Since very recently, the most common way of identifying MnO for black decorations was as a dissolution into the glazes of medieval and postmediaeval tin lead glazed (Fortina et al., 2005; Iñañez, 2007; Pérez-Arantegui et al., 2007). However, lately, crystals of kentrolite and bustamite have been observed for brown and for Black and Green products of the Iberian Peninsula, such as Andalusia (Molera et al. 2013, 2018). Nevertheless, magnetoplumbite was identified in Guatemala and Mexican products, thought as a specific autochthonous solution for the adaptation of the European tradition for the application of black pigments in decorations (Iñañez et al. 2013).

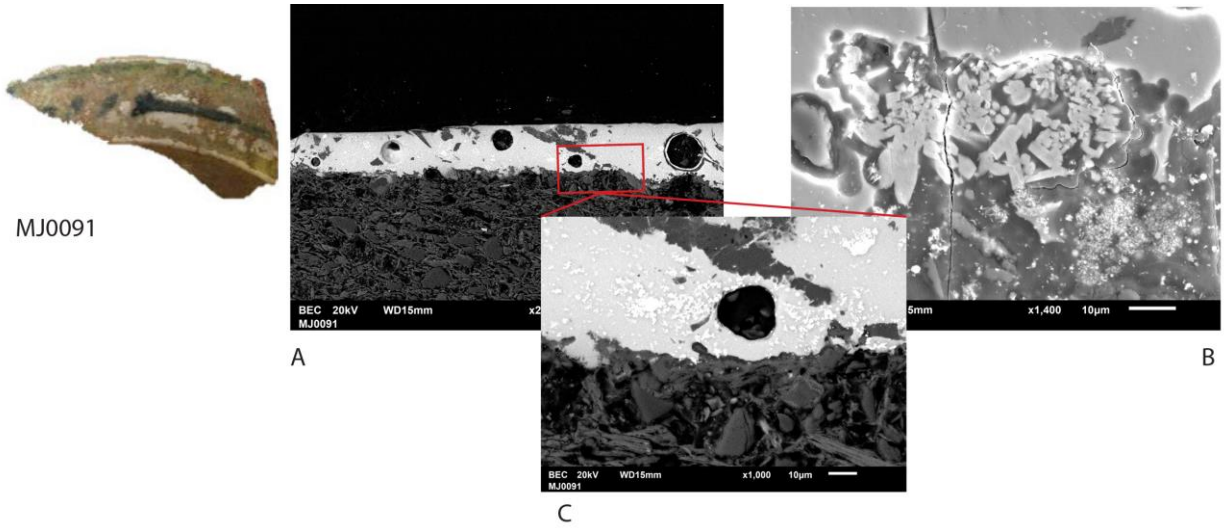

Figure 6. Black and Green majolica MJ0091. A and C: interface resulted from a double firing process. B: crystals of lead and calcium phosphate due to alteration.

4.3. 15th/17th centuries - Blue on White and Lustre decoration

During the 15th century, the production of Black and Green was no longer continued, and the appearance of Blue on White and Lustre productions followed. Renaissance style, due to the Italian influence, replaced the geometric patterns, introducing new decorative motifs (human figures, animals, or plants among others) and new colours (blue and yellow). These colours, together with metallic Lustre, became the most characteristic during the 16th and 17th centuries (Farwell et al. 2003, Panagopoulou et al. 2018). Besides, glazed coarse wares and transport jars played an important role also as utilitarian pottery. Starting with the first one, Blue on White ceramics were manufactured from the 15th to the 18th century, being the period between the 15th and the beginning of the 17th the goal of this paper. In this sense, a study focused only on blue decorations from the 15th to the 18th century is ongoing. The study of this kind of pottery (Figure 7 and 8) reveals an increase in the average of silicon and a significant decrease of the average of tin oxide (Table 2) when compared to archaic tin lead glazed and Black and Green decorations. In this case, the blue decoration is always due to cobalt although other components such as copper have also been detected to achieve the blue color (Sadek 2016). Blue on White productions from Barcelona show a double firing process (Figure 7), and the glaze and colour would be applied after the first firing.

However, some differences observed between the first Blue on White products are worth mentioning. Some individuals exhibit a glaze with a significant presence of inclusions and bubbles (Figure 7, C to G, BCN251 and BCN250). At the same time, these individuals show a black stripe just under the blue decoration identified even macroscopically, by an optical microscope (Figure 7, A and B). This stripe is made up of iron, having a variable width (between 100 µm and 120 µm thickness, Table 1), that sometimes reaches the upper part of the glaze (Figure 7, BCN250, F and G). In our opinion, this would be indicative of a marker, easing the application of the blue decoration. As it can be seen clearly in Figures 7, C and E, the black stripe cannot be observed in those areas where the glaze is white. On the other hand, some individuals show a glaze free of inclusions and bubbles, and no sign of stripe is detected in the blue decorated area (Figure 7, BCN262 A to C). The differences in the application of the decoration, together with the presence of two different tones of blue, would suggest two recipes for applying the blue decoration, maybe by the same potter to get different tonalities of blue, or maybe these differences would correspond to two different workshops. Regarding the blue, the pigment is in both cases dissolved into the glaze and related to the presence of iron and cobalt, which sometimes are not detected together. In fact, in some cases, only iron, or only cobalt was identified. Some samples are related to Co+Fe+Ni+Mn, a combination characteristic of asbolane ($(Ni, Co)_2$-xMn_4+$(O, OH)_4$ nH_2O), although manganese can also be added as an antiflux for preventing the diffusion of cobalt during the firing process (Roldán et al. 2006).

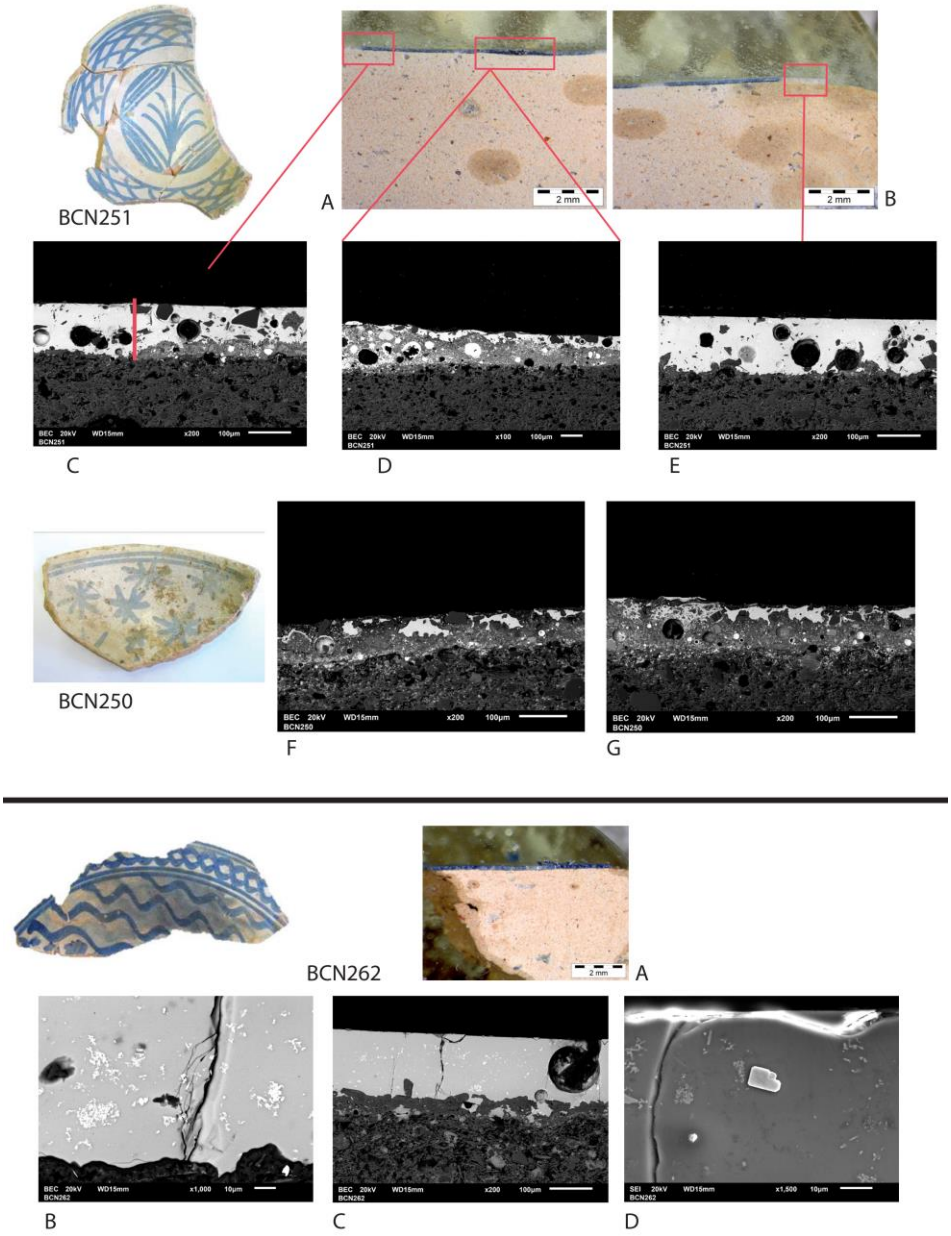

Figure 7. Blue on White majolica BCN251, BCN250. A and B: blue and white decoration observed by an optical microscope. C: the line indicates the beginning of blue decoration with a black stripe in contact with the interface. D: black stripe in the blue part. E: white part of the glaze. F and G: black stripe in the blue areas of BCN250. Blue on White BCN262. A: blue decoration observed by an optical microscope. B and C: interface resulted from a two-firing process. D: containing bismuth crystal in the glaze.

Moreover, crystals containing bismuth, characteristic of hydrothermal environments, were identified in most of the samples from Barcelona studied in this paper regardless of their decoration (Figure 7, BCN262, D). This point is interesting since the written sources told that potters from Barcelona bought the lead used to produce glazes to Falset (Garcia-Oses, 2018). The lead came from galena of the Bellmunt del Priorat (Falset) mine, an epigenetic low-temperature site, where constant mineralizing flow during the genetic process, of subvolcanic morphology and a rich hydrothermal environment. The mineralizations of lead-zinc are the most important of the Mediterranean system (Abella, 2008). In this hydrothermal environment, bismuth is also abundant and probably would arrive mixed with lead. Although the melting point of bismuth (271 ^{o}C) is lower than the firing temperature of vessels, bismuth is a chalcophile element and combines readily with sulphur and/or some other chalcogen other than oxygen. When any of those elements are available, as happens in the case of bismuth found in the glazes of tin lead glazed pottery, the recrystallization of bismuth as it, is produced. Besides, it must be highlighted that bismuth might also be related to the mine of Erzgebirge (Germany), from

where cobalt was obtained (Roldán et al., 2006). However, in the case of Barcelona, where bismuth has been found not only in blue decorations but also in Black and Green and coarse glazed pottery, we think that bismuth is related to the acquisition of lead from Falset, pointed out in the written sources.

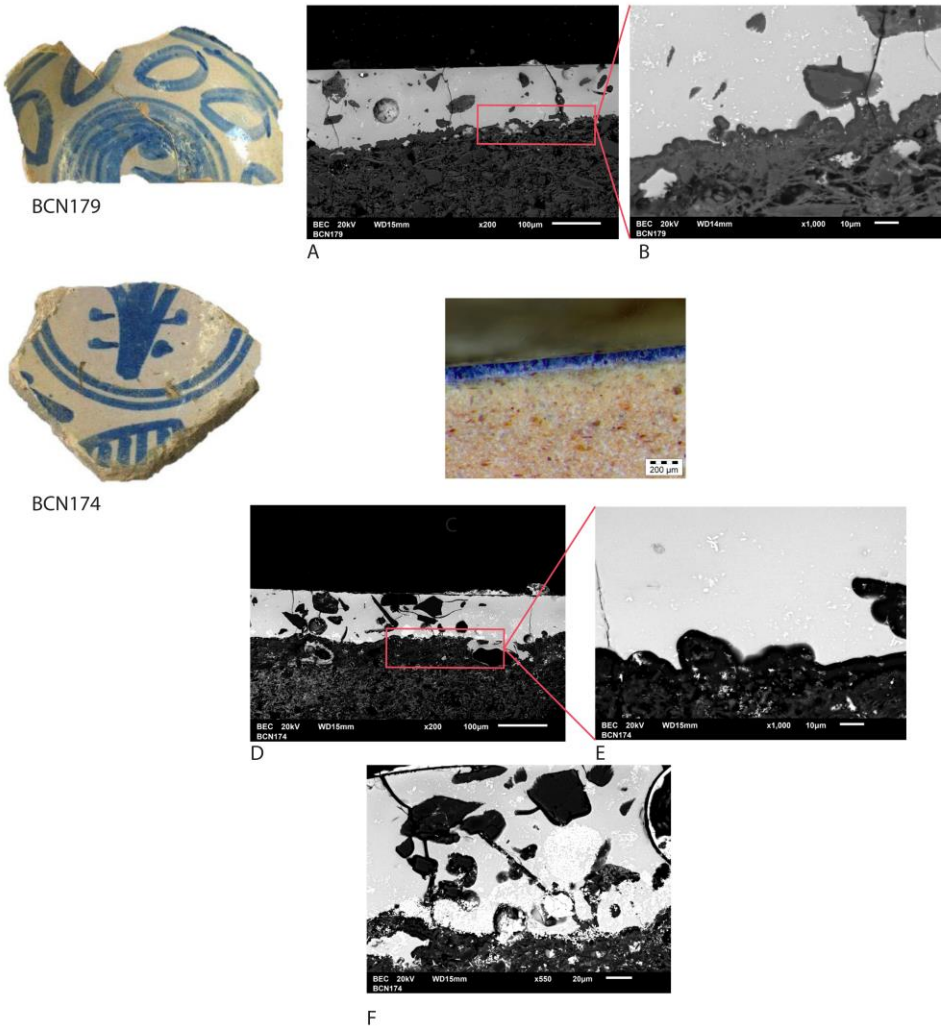

Figure 8. Blue on White majolica BCN179 and BCN174. A and B: glaze and interface resulted from one firing process. C: blue decoration of BCN174 observed by an optical microscope. D and E: glaze and interface resulted from a double firing process. F: lead and calcium arsenate crystals near the interface.

Moving to individuals with Blue on White decoration dated at the 16th, they show similar features to those explained above, such as an interface characteristic of double firing (Figure 8, BCN179, B; BCN174, E), a homogeneous glaze, at around 100 µm and 120 µm (Table 1), containing feldspar inclusions and bubbles (Figure 8, BCN179, A; BCN174, C), as well as tin oxide inclusions to get more opacity in the ceramic surface, and a whiter result (Table 2). However, no stripe is observed, and the blue decoration area presents accumulations of lead and calcium arsenate crystals, possibly originated during the process of firing (Figure 8, BCN174, F). Although As is difficult to see by EDS in high Pb materials like tin lead glazed glazes, given that arsenic shares some spectral lines with Pb (Kα1-Kα2 vs Lα1-Lα2, around 10.5 keV), in these blue decoration areas noticeably can be distinguished As peaks Lα1, Lα2 and Lβ1 (1.28-1.3 keV). These crystals, contrary to the mineral used during the previous period, can be related to roselite/erythrite ($Co_3(AsO_4)2 \cdot 8H_2O$) ore, as well as to cobaltite mineral (CoAsS), whose source might be in Saxony (Germany), as well as in Huesca (Aragon, Spain) (Zucchiatti et al. 2006).

At this point, is interesting to compare the utilization of minerals for the preparation of the blue pigment in Barcelona and Valencia. As proposed by Roldán and collaborators (2006), there are asbolane ores in Valencia itself, and although there is no written evidence of their exploitation in the modern ages, the hypothesis that Barcelona potters would be supplied with Valencian asbolane is feasible. Besides, like in Barcelona, the presence of arsenate is identified in

16th-century Valencian Blue on White individuals (Perez Arantegui et al., 2008, Coll, 2009), suggesting that the mineral ore would be the same in both centres. If this is right, both cities would be in the same network exchanges purchasing cobalt probably from Germany (Gratuze et al., 1996, Roldan et al., 2006, Perez Arantegui et al., 2008, Coll, 2009). Thereby, the presence or the absence of arsenic seems to be indicative of the use of two different minerals during two different periods; during the 15th century, the combinations Co+Fe, Co+Fe+Ni+Mn could be related to asbolane, maybe coming from Valencian ores, whilst ceramics with arsenic would be the result of the use of erythrite, from Saxony already from the 16th century onwards.

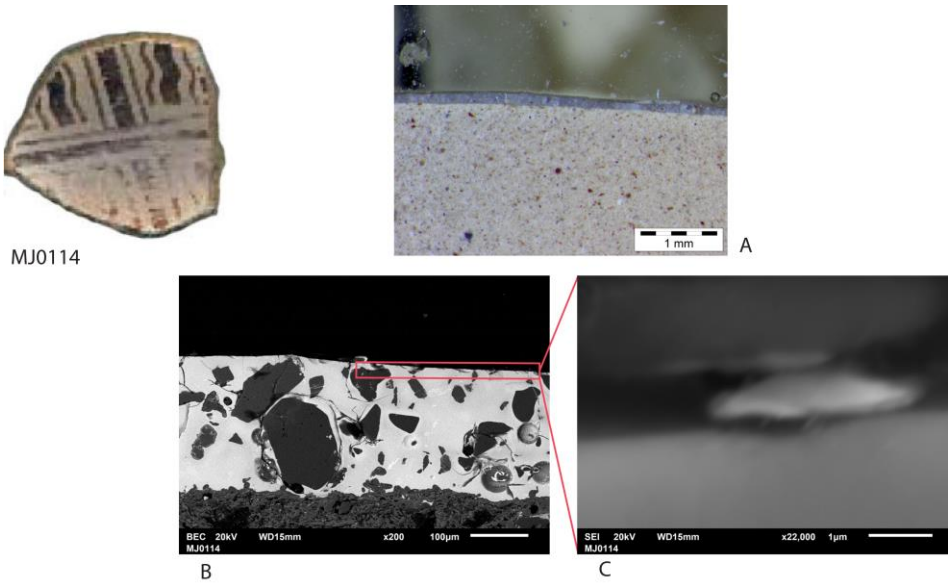

Figure 9. Lusterware majolica MJ0114. A: Lustre part observed by an optical microscope. B Lustre area observed by SEM. C: layer with the Lustre decoration.

Proceeding with Lusterware, this decoration consisted of white and golden colours, with the idea of trying to get a metallic effect. To achieve that, the use of copper and silver was added into the glaze, creating a nanostructured layer composed mainly of small particles of metallic copper and silver, and in some cases cuprite (Molera et al. 2001, Pradell et al., 2013). Although the glaze (Figure 9, A and B) is thicker than the one observed for the blue decorations —at around 200 µm—, the thin lustre layer makes the determination of the compounds hardly difficult. In this case, only copper is detected (Figure 9, C). This product is supposed to be made in three firings, where the last one was destined only to get the lustre. As it is mentioned in Alvaro (1982), based on the sources of Enrique Coock in *Relación del viaje hecho por Felipe II en 1585, a Zaragoza, Barcelona y Valencia*, in contrast with the other two firings, the third was made with much fumes and with a reduction atmosphere. A successful application requires temperatures in the range of 650 ºC for three hours following by a reduction with simultaneous decrease of temperature at 500 ºC for three more hours. Although this explanation is related to Muel, it seems that this centre was the referent for potters of Barcelona and Valencia among others (Alvaro, 1982, Pinto Monte et al. 2021).

Despite the differences between Blue on White and Lustre decorations, it is interesting to highlight that the recipe of the glaze is similar, suggesting the standardisation of the proportions of the specific components at this period (SiO_2, between 40% and 50%; PbO, between 30% and 40%; and SnO below 10% and sometimes below 5%, Table 2).

4.4. 15th/18th centuries: coarse and polychrome glazed pottery

Considering coarse glazed pottery (Figure 10), all the individuals studied show an interface characteristic of one firing, regardless of chronology (Figure 10, BCN117, C, BCN157, F; Figure 11, BCN290, H). Although three different pastes were used to produce those products: calcareous ones corresponding to group B (produced during the 15th century), low calcareous pastes to the group C1 and C2 (between the 16th and 17th centuries) and again calcareous pastes of the group B2d (during the 18th century) —different from those of the 15th century—, it is interesting to highlight that the lead/silicon ratio for the elaboration of glazes remains stable (Table 2). Those results seem to point out that potters would use a standardised receipt (with an average of 52.58 % of lead and 35.64 % of silica) for the preparation of glazes.

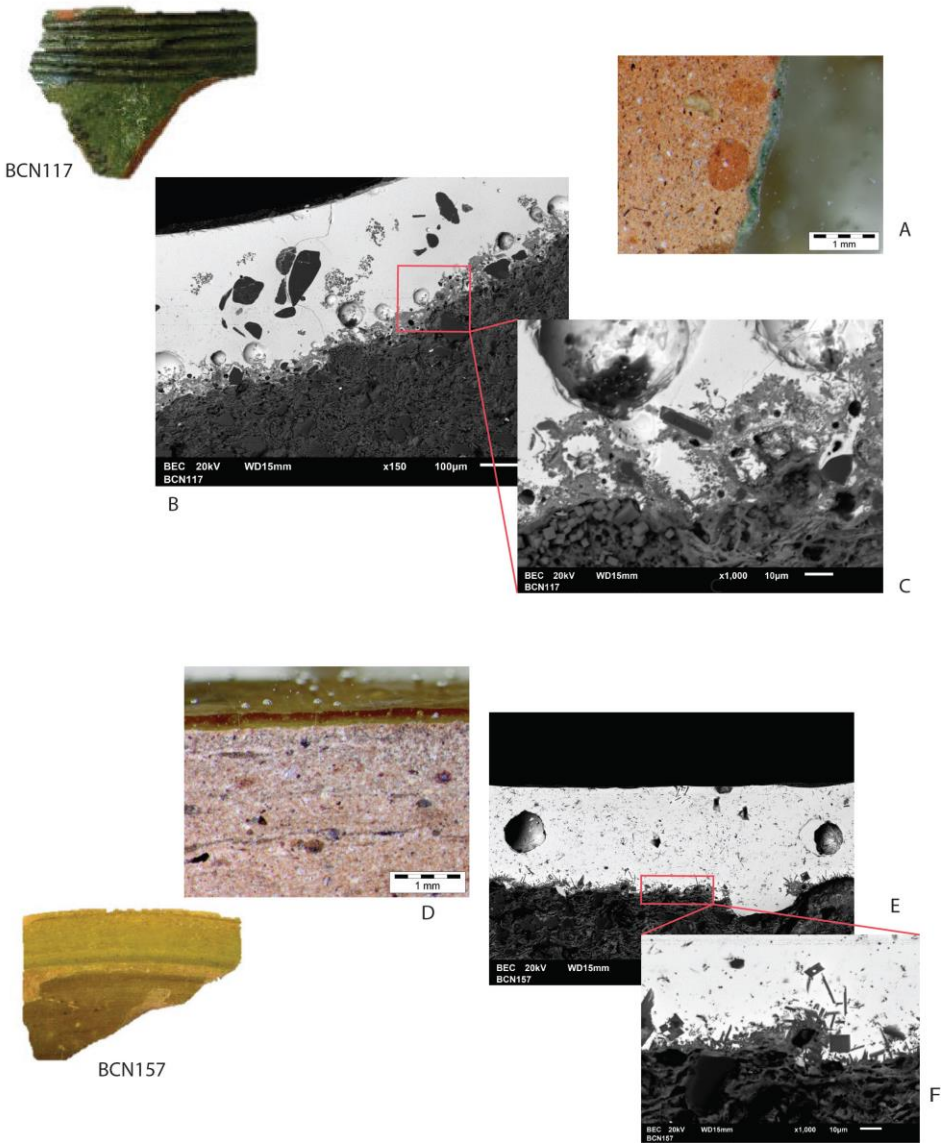

Figure 10. Coarse ware pottery BCN117 and BCN157. A: green decoration observed by an optical microscope. B and C: green decoration observed by SEM and an interface resulted from a single firing process. D: brown decoration observed by an optical microscope. E and F: brown decoration observed by SEM and an interface resulted from a single firing process.

Pigments used in that production where mostly consist of iron in the totality of the glaze, and copper to get a green tonality. Areas with a yellowish decoration did not have any pigment, but iron. Vessels present a clear glaze, with few inclusions and bubbles (Figure 10, BCN117, B; BCN157, E), probably accidentals since there is no purpose of opacifying. All the pastes are the result of an oxidating firing process. It is interesting to highlight differences between similar Valencian products from Paterna (13th to 15th centuries), where the green colour is the consequence of the iron diffused from the paste to the glaze after a reduction firing process, providing a grey or dark brown paste (Molerat et al. 1997).

Coarse ware corresponding to polychrome glazed pottery presented a clear glaze, without inclusions nor bubbles (Figure 11, BCN236, B and C; BCN 290, G). Black parts were made by manganese dissolved in the glaze, yellow parts with iron, and green areas with copper. Most of the cases are the result of a single firing process. These vessels presented a slip between the paste and the glaze, which can be detected even macroscopically (Figure 11, BCN236 A; BCN290, E and F). In all the cases, the white slip was always in contact with the parts of the glaze with a light-coloured decoration (only in the external part since no decoration occurs on the internal side) (Figure 11, BCN236, A; BCN290, F). This is probably because the colours of the paste in coarse ware tended to be darker than for tin lead glazed products, and therefore they need a white slip to get the glaze brighter in the selected parts. The slip would have the function

of enhancing the whiteness in these areas, to get the effect of a light glaze. In contrast, for brown and black areas, sometimes two layers of slip were applied under the transparent glaze (one white and one brown) (Figure 11, BCN290, E), and sometimes brown and/or black is directly in contact with the matrix (Figure 11, BCN236, D). It was not possible to visually detect this slip by SEM (Figure 11, BCN236, C), as it has the same chemical composition as the paste, and this provides a similar grey aspect by SEM. The only difference between the paste and the slip is the calcium and iron content, having the slip a larger amount of calcium and a minor presence of iron, providing a lighter tone to the clay used as slip when is fired.

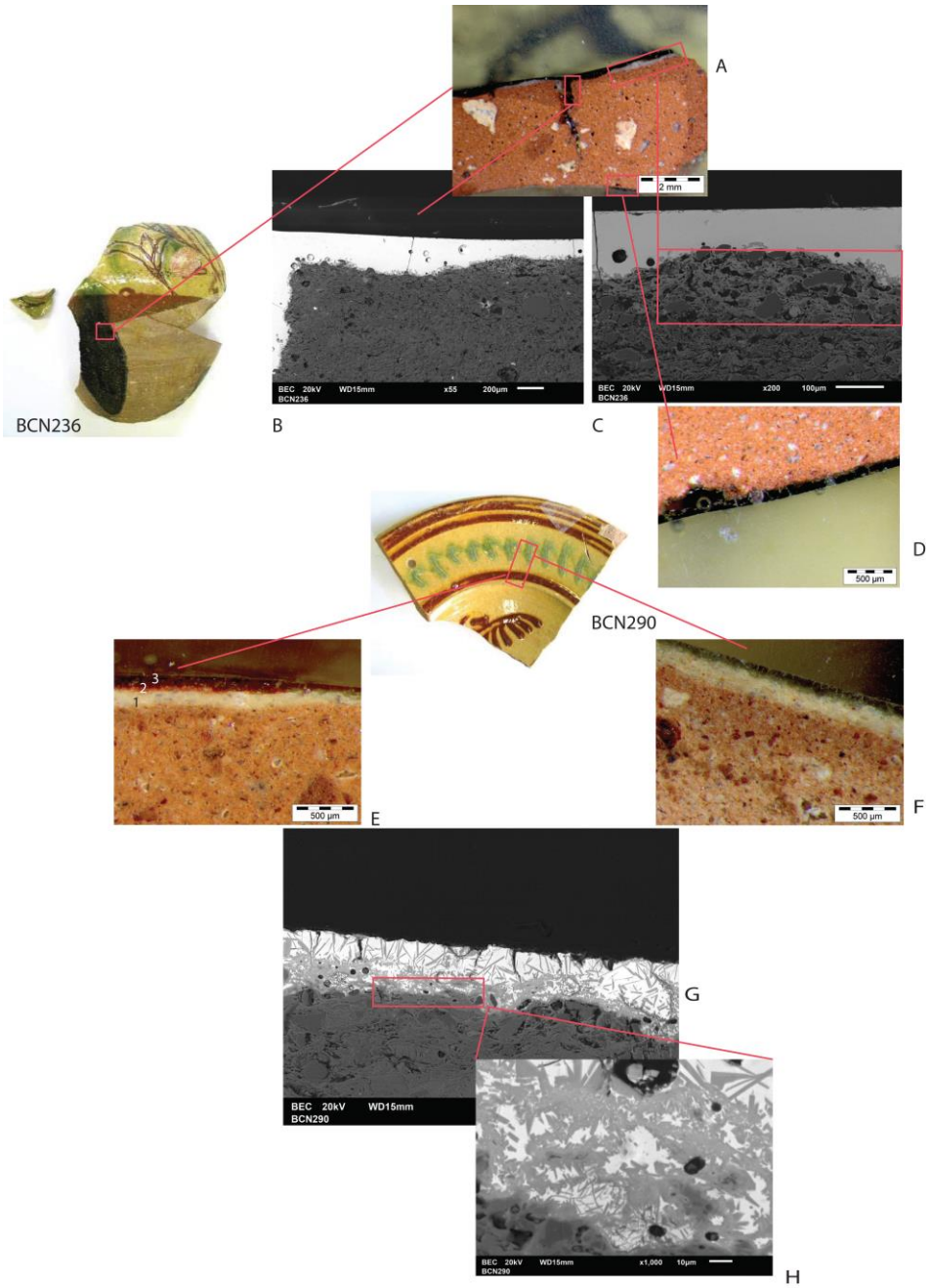

Figure 11. Polychrome glazed pottery BCN236. A: decoration observed by an optical microscope. B: green glaze. C: white slip marked with a red square undifferentiated from the matrix. D: black decoration without slip by an optical microscope. Polychrome glazed pottery BCN290. E: brown decoration. 1: white slip; 2: brown slip; 3: glaze. F: white slip and green decoration by optical microscope. G and H: interface resulted from one firing process.

5. CONCLUSION

The study by SEM-EDX on illustrative individuals from the main ceramic groups previously identified at Barcelona supports our assumption that high diversity in glazing techniques confirms the complexity observed in the city as a production centre. That sug-

gests the elaboration of different recipes and the participation of several workshops in the elaboration of tin lead glazed as well as glaze coarse and polychrome pottery, reinforcing the information provided by the written sources, which pointed out that hundreds of potters were active in the city, especially between the 15th to 17th centuries.

There is no doubt that Barcelona went through a large process of experimentation until good quality tin lead glazed was achieved. However, it is surprising that the first attempt known so far, which is archaic tin lead glazed from the 13th century, already entailed a double firing process. Moreover, ceramics from this period contain a high amount of tin oxide as an opacifier. The amounts of tin (with a mean of 14.84 %) observed in the older products (archaic tin lead glazed, and tin lead glazed dated back to the 13th and 14th centuries) will not be repeated. In all cases studied from this period, manganese, iron, and copper oxides were responsible for the Black and Green decoration, when detected. These pigments were identified on the upper part of the glaze.

Unexpectedly, what is considered to be the first true tin lead glazed from Barcelona, the one with Black and Green decoration, was produced for over a century -from the end of the 13th century to the beginning of the 15th century- only glazed on the internal part and using one firing process. The composition of glazes, including tin, is similar to the archaic tin lead glazed one. The same can be said for the black decoration, which is identified because of accumulations in the upper part of the glaze, but in this case, showing crystals of kentrolite and bustamite. Besides, manganese is also found dissolved into the glaze. Already in the 15th century, the last Black and Green products show a double firing process and a good quality glaze with a higher amount of silicon oxide, and a lower amount of lead, but continuing with the use of a significant amount of tin oxide. Unfortunately, black and green decoration were no preserved in the specimens analysed.

The last step on tin lead glazed products analysed in this article is the Blue on White and Lustre decoration objects. The recipe becomes stable during the 17th century, showing a clear decrease of tin oxide in the composition of the glazes. At the same time, they exhibit an increase in intended bubbles and inclusions to achieve the opacification. All the individuals show the characteristic interface of a double firing process. During the first period of production -15th century and part of the 16th century-, a black stripe made of iron under the area where the blue decoration is applied has been identified in some specimens, perhaps related to the drawing of the decoration before applying the final colour, the blue one. Regarding the pigment used for obtaining the blue colour, asbolane from Valencian ores could have been used. During the 16th and 17th centuries, individuals do not show any stripe, and the blue decoration is now related to the presence of lead and calcium arsenate crystals, possibly originated during the process of firing. These crystals can be related to roselite/erythrite ore, the source of which might be in Saxony (Germany), according to the written sources (Garcia Oses, 2018).

The most remarkable results in coarse and polychrome glazed pottery are, on the one hand, the ratio of lead to silicon, which remains stable from the 15th to the end of the 17th century. And on the other hand, the use of a one firing process with an interface full of neo-formed crystals. Moreover, some of the polychrome glazed pottery presented a slip between the paste and the glaze, which can be detected even macroscopically, and that it only appears in the parts of the glaze with a light-coloured decoration, being missing in those areas of the glaze presenting dark colours, such as black or brown. The slip was applied to enlighten the tone of the glaze in areas where decoration would be used. The pigments used in these products were mostly iron in the totality of the glaze, and copper to get a green tonality. Surprisingly, areas with a yellowish decoration did not have any pigment, but iron, being really important to get a light colour in the ceramic paste. The slip would have the function of enhancing the whiteness in these areas, to get the effect of a light glaze, and avoiding using other pigments such as antimony.

Finally, the presence of crystals containing bismuth in a large number of individuals, from different classes and centuries, is remarkable. As it is said before, this compound is characteristic of hydrothermal environments and can reinforce the evidence of the written sources indicating that potters from Barcelona would have bought the lead used in glazes to Falset.

AUTHOR CONTRIBUTIONS

Conceptualization, M.M.F. and J.B.G.; investigation, M.M.F. and J.P.V.; writing—original draft preparation, M.M.F. and J.P.V.; writing—review and editing, M.M.F., J.P.V. and J.B.G.; project administration, J.B.G.; funding acquisition, J.B.G. All authors have read and agreed to the published version of the manuscript.

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