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Commentary

Potters and pigments: preliminary technological assessment of pigment recipes of American majolica by synchrotron radiation micro-X-ray diffraction (Sr-μXRD)

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ABSTRACT

This paper assesses the impact of European ceramics on preexisting American potting technologies. Specifically we investigate the technological features of pigments used for production of colonial American majolica. In order to achieve this goal, majolica sherds from Puebla (4), and Oaxaca (2), both in Mexico, from Antigua (Guatemala) (2), from Panama (1), and from Mission San Luis (Florida) (5) were analyzed by synchrotron micro-X-ray diffraction (μ-XRD). Eleven out of these fourteen samples were also analyzed by scanning electron microscopy (SEM). The combination of micro-chemical and micro-structural techniques provides a cross sectional profile of the constituent minerals present ultimately providing information about the nature and distribution of the pigments used in their decorations, their dissolution in the glassy matrix, and the formation of crystalline compounds. Our results reveal significant differences among productions.

1. Introduction

Majolica is a tin lead glazed earthenware, also known as, *loza*, *faience*, or delftware, characterized by a creamy light-buff colored ceramic body and an opaque white tin–lead glaze covering the entire outer surface of the vessel. Perhaps, the most characteristic feature of majolica pottery lies in the metallic oxide decorations that typically are applied on top of the opaque white glaze coat. The opaque white glaze is composed of silica and lead oxide—a flux that serves to lower the temperature needed for melting silica. The glaze is opacified with particles of tin oxide (SnO_2) and also by the action of extant quartz and feldspar inclusions. These inclusions, and the bubbles that result from the firing process, absorb, scatter, and/or reflect incident light, thereby giving the transparent glaze a white appearance (Molera et al., 1999; Tite et al., 2008).

Historically, majolica ware is one of the most recognizable European artifacts traded to the Americas during the European colonial period, especially from the 16th to the 18th centuries. The introduction of this new ceramic technology into the preexisting American societies is one of the major Europeans technological innovations at that time. Rapidly, majolica replaced many pre-Hispanic potting traditions and ultimately became a social prestige item unto itself. The establishment of European masters in key locations, such as Puebla, Mexico, facilitated the development of majolica pottery production in the Americas. At the same time, these local workshops successfully replicated the main features of European majolica wares, primarily those of Spanish origin, replacing significant aspects of indigenous ceramic identity, especially as local markets attempted to produce ceramics that visually and functionally could compete with higher valued Spanish imports. A well-known example is represented by the so-called

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Romita ware, a hybridized Mexican ware which combines aspects of the pre-Hispanic Purepecha pottery tradition and European majolica technology (Iñañez et al., 2010a; Iñañez, in press). These shifts in production strategies resulted in a very significant transculturation role, with majolica emerging as one of the first icons of globalization and a symbol of European influence in the Americas.

Although majolica production generally is considered a highly standardized technological process, differences among production centers may be traced archaeometrically as seen in the literature regarding the most important centers from the Iberian Peninsula among others (Buxeda and Iñañez, 2010; Buxeda et al., 2011; Hughes and Vince, 1986; Iñañez et al., 2009, 2008; Iñañez et al., 2010c; Molera et al., 1996; Pérez-Arantegui et al., 2007). Thus, diversity in the nature of glazing technology and, especially, the pigments used for the decoration of majolica glazed coatings might be related to different potting traditions, not only European, but also influenced by preexisting pre-Hispanic traditions in the Americas.

The present study represents the initial steps toward the characterization of the different technologies used for colonial majolica production in the Americas. The emphasis of this work lies in the identification of the different nature of the pigments that craftsmen used in order to achieve the outstanding decorations of the majolica pottery produced in the Americas. In order to carry out this preliminary assessment, a sampling strategy was adopted in which archaeological specimens from well-established American production centers were examined (for a thorough discussion see Blackman and Bishop, 2007; Fournier et al., 2009; Iñañez et al., 2010b; Iñañez and Speakman, 2011; Rovira et al., 2006).

2. Materials and experimental procedures

Fourteen majolica sherds (Table 1) from Puebla ($n = 4$), and Oaxaca ($n = 2$), both in Mexico, from Antigua in Guatemala ($n = 2$), from Panama Viejo in Panama ($n = 1$), and from Mission San Luis (Florida, USA) ($n = 5$) were analyzed by means of synchrotron micro-X-ray diffraction (μ-XRD); 11 of these specimens also were examined by scanning electron microscopy (SEM) to assess the technological features and technical adaptation on colonial majolica production in the Americas (Fig. 1).

SEM is commonly used for the visual examination of the morphology, size and distribution of the crystallites. When combined with energy dispersive (EDS) or wavelength dispersive (WDS) spectroscopy it is possible to measure the chemical composition of a given sample. Body-glaze polished cross sections were prepared to analyze the interface paste–glaze reaction region and the distribution of the crystalline phases inside the glaze. However, quite often the identification of the crystallites is difficult mainly because they are smaller (below the micrometer) than the electron beam probe volume or because routine chemical analyses cannot distinguish specific polymorphs. The structural information of the crystallites may be obtained by means of X-ray diffraction directly on the surface of the glazes, but the small size and low volume fraction of the crystallites make their detection difficult in conventional XRD instruments.

Synchrotron radiation has a high brilliance and small probe size adequate for the identification of the crystalline phases including nanocrystals and polymorphs. Using a thin cut of the polished cross sections, it is also possible to study the nature and spatial distribution of the crystalline compounds. The size of the beam must be selected taking into account the size of the crystallites. It must be bigger than the size of the typical crystallites (few micrometers) to avoid a spotty single crystal like X-ray diffraction pattern, but small enough to permit mapping of the glaze cross sections at the micro scale (few hundreds of micrometers). We can take advantage of the bidimensional structure of the glazes (layered structure) using rectangular spots (40 μm × 100 μm), which permit scanning through the glaze layer from the paste–glaze interface to the glaze surface (Pradell et al., 2010). Considering that the glazes from the studied historical period are of mixed lead-alkaline type, and may contain up to 50 wt% of PbO, the use of 14 keV energy X-rays, transmission geometry and a spot of about 20–40 μm size supplies the adequate experimental conditions (Pradell et al., 2010).

3. Results and discussion

The analytical study of the colonial majolica ceramics from the production centers in Mexico, Antigua, and Panama Viejo, and the reception center of Mission San Luis in the United States, tentatively produced in Puebla (Iñañez et al., 2010b), has enabled the identification of distinct differences among the technological choices adopted by ancient craftsmen in a context of colonization and culture transformation and adaptation. Along these lines, technological choices are evidenced especially in the nature of the pigments used to decorating majolica glazed coats.

3.1. White

In all cases, the opaque white glaze of American-produced majolica is achieved by the recrystallization of cassiterite (SnO_2), which reflects and disperse incident light in the glaze coat (Molera et al., 1999), as assessed by μ-XRD (Fig. 2) and confirmed by SEM–EDS micro-chemical data (Table 2). Additionally, some productions may intentionally introduce the use of other particles, such as quartz and/or feldspars, along with the cassiterite crystals (Molera et al., 1999). The utilization of SnO_2, along with the tradition of lead glazing to achieve a high degree of waterproofing on the vessel

Table 1
Individuals analyzed with indication of their provenance and archaeological information.

ANID	Origin	Provenance	Chronology	Majolica type	Decoration
MXF202	Puebla, Mexico	Puebla	16th–18th centuries	Puebla Polychrome plate	Black on white
MXF206	Puebla, Mexico	Puebla	16th–18th centuries	Puebla Polychrome plate	Green and black on white
MXF030	Puebla, Mexico	Puebla	16th–18th centuries	Puebla Polychrome plate	Blue and yellow on white
MXF026	Puebla, Mexico	Puebla	16th–18th centuries	Puebla Polychrome plate	Blue and yellow on white
SDM117	Antigua, Guatemala	Antigua	17th–18th centuries	Polychrome jar	Black and green/yellow on white
SDM306	Antigua, Guatemala	Antigua	17th–18th centuries	Polychrome plate	Blue and yellow on white
OP0018	Panama City, Panama	Panama Viejo	17th century	Panama Polychrome plate	Blue, green and black on white
MSL027	Mission San Luis (FL, USA)	Puebla	1650–1700	San Luis Polychrome plate	Green and yellow on white
MSL039	Mission San Luis (FL, USA)	Puebla	1650–1700	Abo Polychrome plate	Blue, green, yellow and black on white
MSL014	Mission San Luis (FL, USA)	Puebla	1650–1700	Puebla Polychrome bowl	Blue and black on white
MSL015	Mission San Luis (FL, USA)	Puebla	1650–1700	San Luis Blue on White porringer	Blue on white
MSL030	Mission San Luis (FL, USA)	Puebla	1650–1700	Fig Springs Polychrome plate	Blue, orange and black on white
MXX127	Oaxaca, Mexico	Oaxaca	18th century	La Taza Polychrome plate	Yellow and blue on white
MXX132	Oaxaca, Mexico	Oaxaca	18th century	La Taza Polychrome plate	Yellow and blue on white

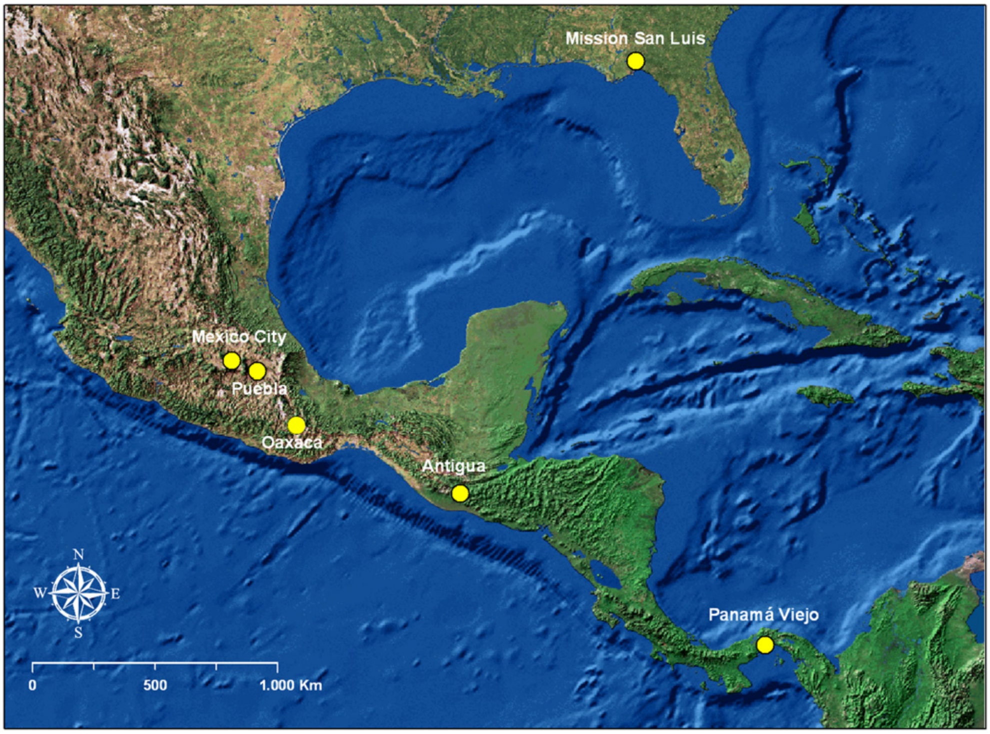

Fig. 1. Map showing the sites cited in the text.

performance, is common in medieval and postmedieval majolica pottery tradition in Europe, but not documented in the Americas until the arrival of the Europeans (Deagan, 1987). Therefore, this technological feature is clearly linked to the new potting technologies brought by European colonizers, which arguably was adopted in New World pottery.

3.2. Blue and green pigments

Blue and green decorations were used in Puebla and Antigua; whereas ceramics studied from Oaxaca only show green pigments in their decorations. Analytically, these decorations do not show any evidence of visible particles or crystals that might be related to

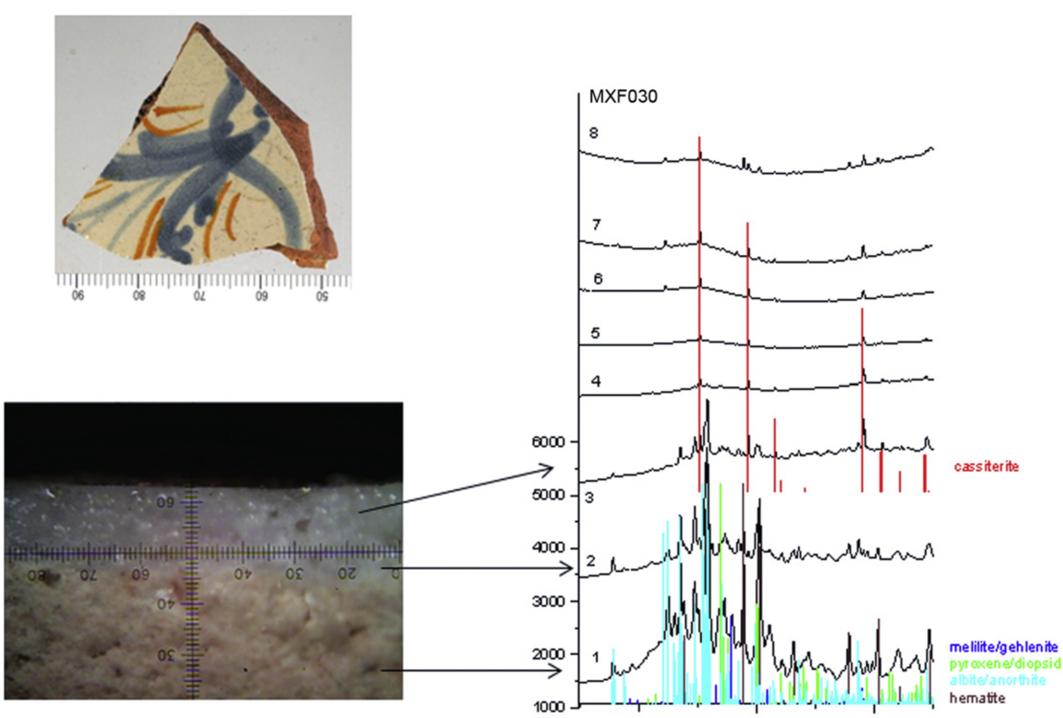

Fig. 2. Photograph, optical microphotograph and µ-XR diffractograms of the white glazed area of the individual MXF030 from Puebla (Mexico). Arrows show the main analyzed areas on the sample.

Table 2
SEM–EDS chemical data in weight % for majolica glazes and decorations.

Sample	Color	Origin	Al_2O_3	BaO	CaO	CoO	CuO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	PbO	Sb_2O_3	SiO_2	SnO_2	TiO_2
OP0018	Black	Panama	6.5	bdl	0.8	bdl	0.9	0.5	0.6	0.2	1.7	1.9	49.1	bdl	34.6	3.0	0.1
MXF202	Black	Puebla	6.0	bdl	0.6	bdl	0.3	28.6	0.7	0.6	0.2	2.3	35.0	bdl	23.7	1.8	0.1
MXF206	Black	Puebla	8.3	bdl	1.6	bdl	0.6	17.4	1.6	0.5	bdl	2.3	31.4	bdl	35.4	0.8	0.0
MSL014	Black	M S Luis	7.0	bdl	1.1	0.1	0.4	37.3	1.3	0.4	0.4	2.9	20.5	bdl	27.2	1.0	0.2
MSL039	Black	M S Luis	5.2	bdl	1.4	bdl	bdl	40.8	1.1	0.6	bdl	2.2	23.1	bdl	25.7	0.2	bdl
SDM117	Black	Guatemala	8.2	0.6	bdl	bdl	bdl	24.0	1.2	0.5	bdl	2.3	29.4	bdl	31.8	2.0	bdl
MSL014	Blue	M S Luis	11.2	bdl	3.1	0.3	0.1	1.3	2.7	0.7	bdl	8.8	18.1	bdl	52.5	0.5	0.1
MSL015	Blue	M S Luis	8.9	bdl	1.2	0.3	0.2	1.1	2.7	0.4	bdl	4.5	27.1	bdl	51.2	2.3	0.0
OP0018	Blue	Panama	5.8	bdl	0.7	0.2	bdl	0.6	0.9	bdl	bdl	1.8	48.5	bdl	38.0	3.2	0.1
MXF026	Blue	Puebla	9.2	bdl	0.6	0.6	0.1	1.0	2.0	0.3	bdl	2.8	35.2	bdl	43.8	3.9	0.1
SDM306	Blue	Guatemala	8.7	0.6	bdl	0.2	bdl	1.2	1.4	0.4	bdl	2.0	41.7	bdl	41.7	2.1	0.1
MXX132	Green	Oaxaca	11.4	bdl	0.5	0.1	0.3	0.6	3.2	0.2	0.2	3.6	27.9	bdl	50.3	1.3	0.1
MXX127	Green	Oaxaca	9.8	bdl	1.0	0.1	0.5	0.8	2.9	0.2	0.1	3.0	31.8	11.5	36.9	1.0	0.1
OP0018	Green	Panama	7.4	bdl	1.0	bdl	1.1	0.6	1.1	0.3	bdl	1.9	45.5	bdl	36.8	4.0	0.1
MXF030	Green	Puebla	11.4	0.9	0.6	bdl	4.9	0.7	2.1	0.3	0.2	3.1	27.9	bdl	42.6	5.0	0.1
MXF206	Green	Puebla	8.7	bdl	3.1	bdl	1.7	0.8	1.5	0.6	0.1	2.6	42.3	bdl	37.6	0.6	0.1
SDM117	Green	Guatemala	8.3	0.5	bdl	bdl	0.1	0.6	1.2	0.3	bdl	2.0	44.7	0.6	39.7	1.9	bdl
MSL014	White	M S Luis	11.2	bdl	0.6	bdl	0.2	0.6	2.2	0.3	0.1	3.8	28.9	bdl	48.1	3.7	0.0
MSL015	White	M S Luis	11.4	bdl	1.0	bdl	0.2	0.7	2.3	0.3	bdl	3.7	32.2	bdl	45.8	2.1	0.0
OP0018	White	Panama	7.4	bdl	0.9	bdl	bdl	0.4	0.6	0.2	bdl	2.0	46.4	bdl	37.5	4.4	0.1
MXF202	White	Puebla	11.1	bdl	0.7	bdl	bdl	0.6	2.2	0.3	bdl	3.7	30.8	bdl	47.1	2.8	0.1
MXF206	White	Puebla	10.0	bdl	2.0	bdl	0.2	0.6	2.1	0.4	bdl	3.0	36.0	bdl	44.1	1.4	0.0
SDM306	White	Guatemala	8.9	0.5	bdl	bdl	bdl	1.0	1.0	0.5	bdl	1.6	44.4	bdl	39.1	2.9	bdl
SDM117	White	Guatemala	8.2	0.3	bdl	bdl	0.3	0.5	1.3	0.5	bdl	2.1	46.4	bdl	38.0	2.2	bdl
MXX132	Yellow	Oaxaca	9.9	bdl	0.8	bdl	0.2	1.1	2.3	0.3	0.1	3.2	36.1	1.0	43.0	1.4	0.1
MXX127	Yellow	Oaxaca	9.7	bdl	0.8	bdl	0.2	1.0	2.3	0.2	bdl	3.2	37.8	0.6	42.5	1.1	0.0
MXF026	Yellow	Pueba	6.6	bdl	1.5	0.2	bdl	2.0	0.9	0.2	bdl	2.5	47.5	5.7	30.2	2.3	0.0

the original raw pigment. According to the SEM–EDS analyses (Table 2), cobalt is used for obtaining blue pigment, while copper is responsible for green decorations. Besides, they look dissolved in the glaze in every production, as evidenced by μ-XRD (Fig. 3), which do not show any trace of crystallization that may play this green or blue pigmentation role. Additionally, significant BaO content is found in two samples from Antigua and one from Puebla (Table 2). Interestingly, the three of them are green decorated and will be the subject of future studies. Unfortunately the raw materials responsible for these pigments may be linked to a broad number of

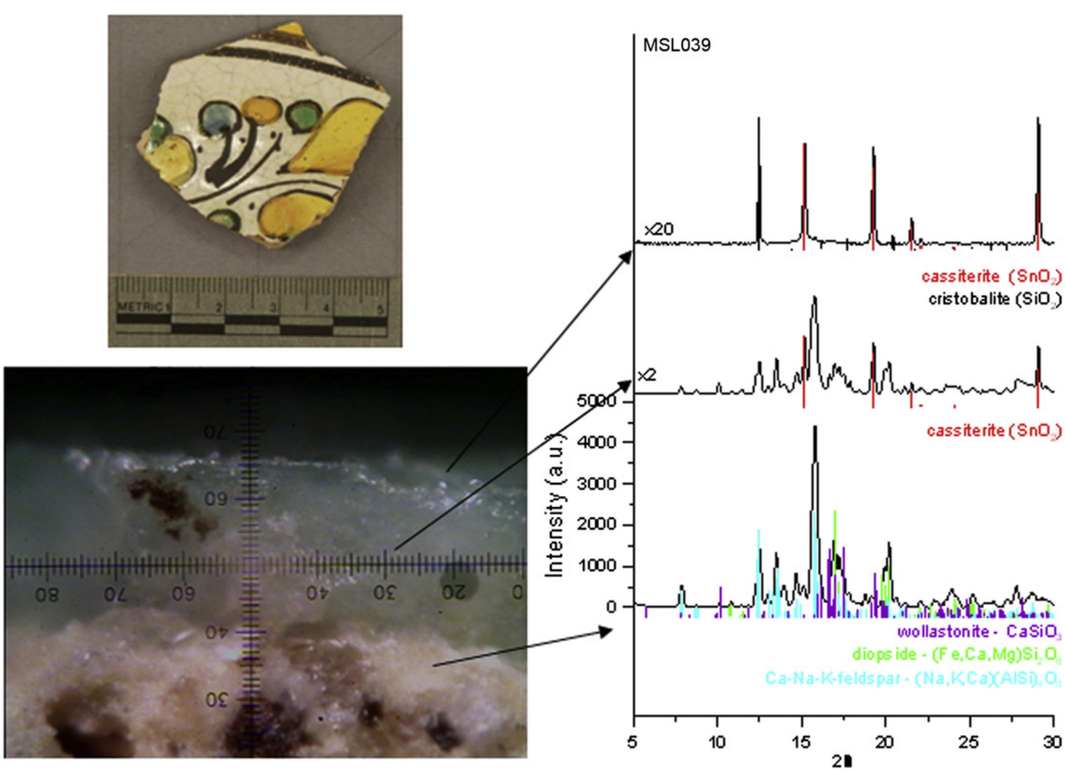

Fig. 3. Photograph, optical microphotograph and μ-XR diffractograms of the green glazed area of the individual MSL039 from Mission San Luis (Florida). Arrows show the main analyzed areas on the sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

minerals and the assessment of their original nature is presently not possible. Archaeologically, the use of cobalt for blue, and copper for green in majolica, is directly connected to the European medieval and postmedieval technological tradition of majolica production, and can be considered to indicate innovation brought by Europeans into the Americas.

3.3. Yellow pigment

In the current study, yellow pigments are visible in the decoration of majolica from Puebla, Oaxaca and samples found in Mission San Luis. Technologically, yellow pigment is achieved by the formation or the presence of iron containing lead antimonate ($Pb_2Fe_{0.5}Sb_{1.5}O_{6.5}$), as evidenced by μ-XRD (Fig. 4). Although SEM–EDS examinations were only conducted on samples from Oaxaca, these analyses also confirmed the presence of lead antimonate in the yellow areas (Table 2). Historically, the use of lead antimonate as pigment is frequently documented in the Western European craftsmen tradition to obtain yellow. The reintroduction of the use of this pigment is already documented at the end of the 15th century in Italy, referred also as potter's yellow (Dik et al., 2005), being also used in paintings, glass, and related arts and crafts (Borgia et al., 2007; Bultrini et al., 2006; Hradil et al., 2007; Iñañez, 2007; Rosi et al., 2009; Rosi et al., 2011; Viti et al., 2003). Furthermore, there is no evidence of the use of lead antimonate as a pigment in pre-Hispanic ceramic decorations in the Americas. The presence of iron in the lead antimonate in Fig. 4, has to be related to the reaction between the yellow pigment and, as shown further in the text, the iron oxide containing black pigment applied on the top of the yellow decoration.

3.4. Black/brown pigment

Perhaps, black and brown pigments provide with the most striking results in terms of technological choices and cultural

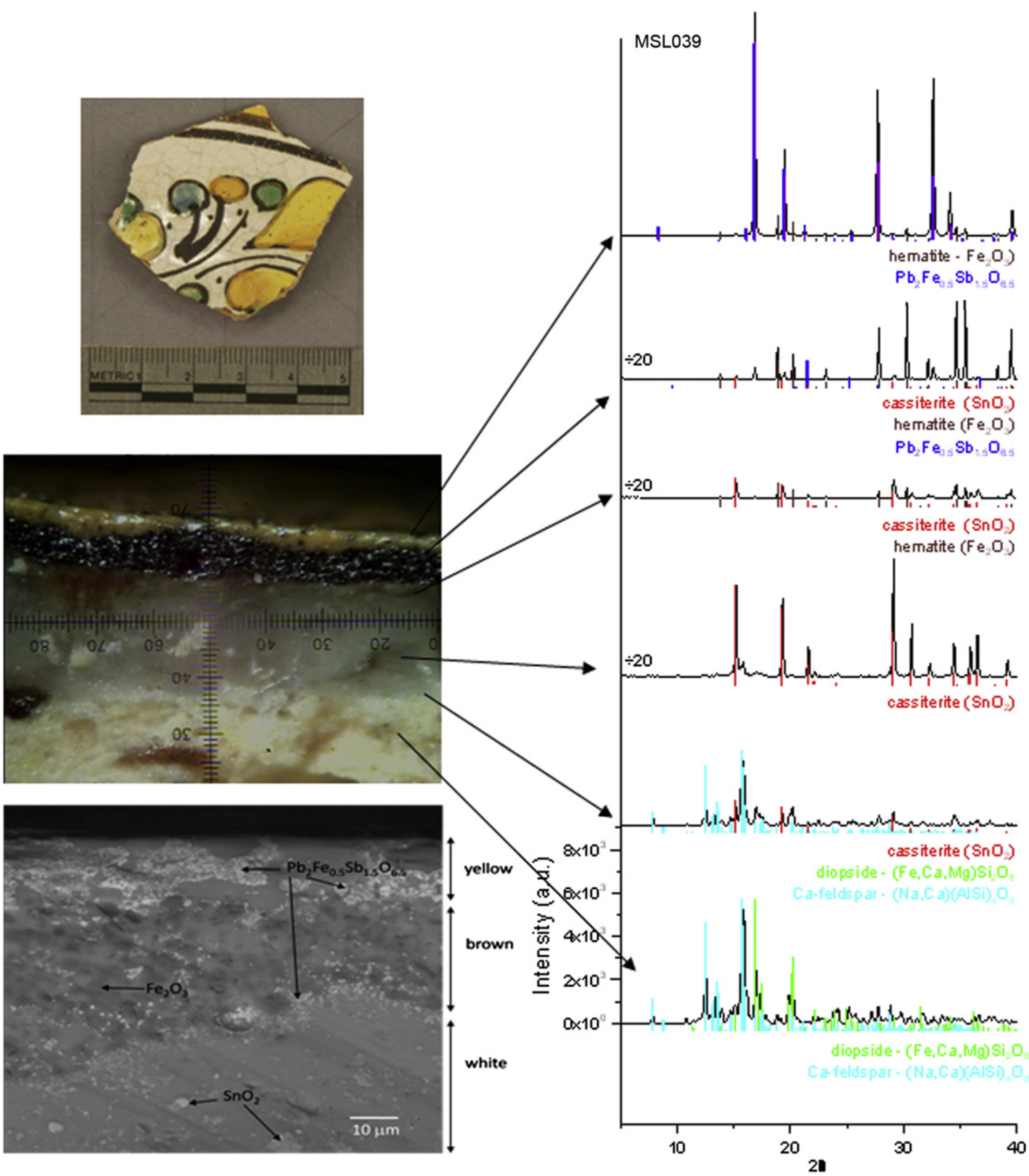

Fig. 4. Photograph, optical microphotograph and μ-XR diffractograms of the yellow glazed area of the individual MSL039 from Mission San Luis (Florida). Arrows show the main analyzed areas on the sample. On the left bottom side, SEM microphotograph with indication of lead antimonate, hematite, and cassiterite crystals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adaptation on American majolica. Interestingly, the choice of ancient potters regarding the nature of black pigments in the Americas reveals technologically different strategies that produce visually similar results.

In Panama, in order to achieve a black pigment on majolica decoration, potters used the same technological choice that was commonly employed at that time by European majolica potters, which is the use of manganese oxide (MnO) (Table 2). In agreement with previous literature, MnO is commonly found as dissolution into the glaze of European majolica in medieval and postmedieval times for black decorations (Fortina et al., 2005; Iñañez, 2007; Pérez-Arantegui et al., 2007). Additionally, the degree of blackness is directly correlated to the quantity and form of the Mn dissolved in the glaze, the oxidation state, and the formation of Mn compounds during firing. Generally speaking, Mn^{2+} produces a yellow-brownish color, Mn^{3+} purple and Mn^{4+} dark brown. Moreover, the color obtained depends not only on the oxidation state of the metal but also on its coordination in the glassy matrix (tetrahedral or octahedral coordination) and on the nature of the glassy matrix (alkali or lead glasses). Moreover, the more manganese the darker, whereas lower amounts result in a lighter black color instead.

However, the technological choice followed in majolica from Puebla and Antigua did not use MnO, as in European and Panamanian majolica, but consisted in the application of iron oxides for black decorations (Table 2). The content of iron oxides in these black decorations ranges from 17 to 30 wt%. Specifically, the study of the μ-XRD diffractograms has enabled the characterization of magnetoplumbite ($PbFe_{12}O_{19}$) as the main component found in the black pigment for these ceramics (Fig. 5). This phase is formed during firing from the use of a high concentration of iron oxide in a lead-rich glaze. Thus, magnetoplumbite is identified in the blackish areas of the glaze whereas hematite is identified in brownish areas. Although the presence of hematite is normally related to the red color of iron rich clays, the red color is actually associated to the presence of colloidal hematite. Large crystallites of hematite are black. The use of a high amount of iron oxide in the glaze decoration leads to the growth of large hematite crystallites and consequently to the black-brownish color shown by those decorations.

It must be pointed out that the use of synchrotron μ-XRD has allowed the detection of magnetoplumbite unquestionably; otherwise, such identification alone by SEM would be uncertain. Since the main component of the glaze is lead, and given that lead is

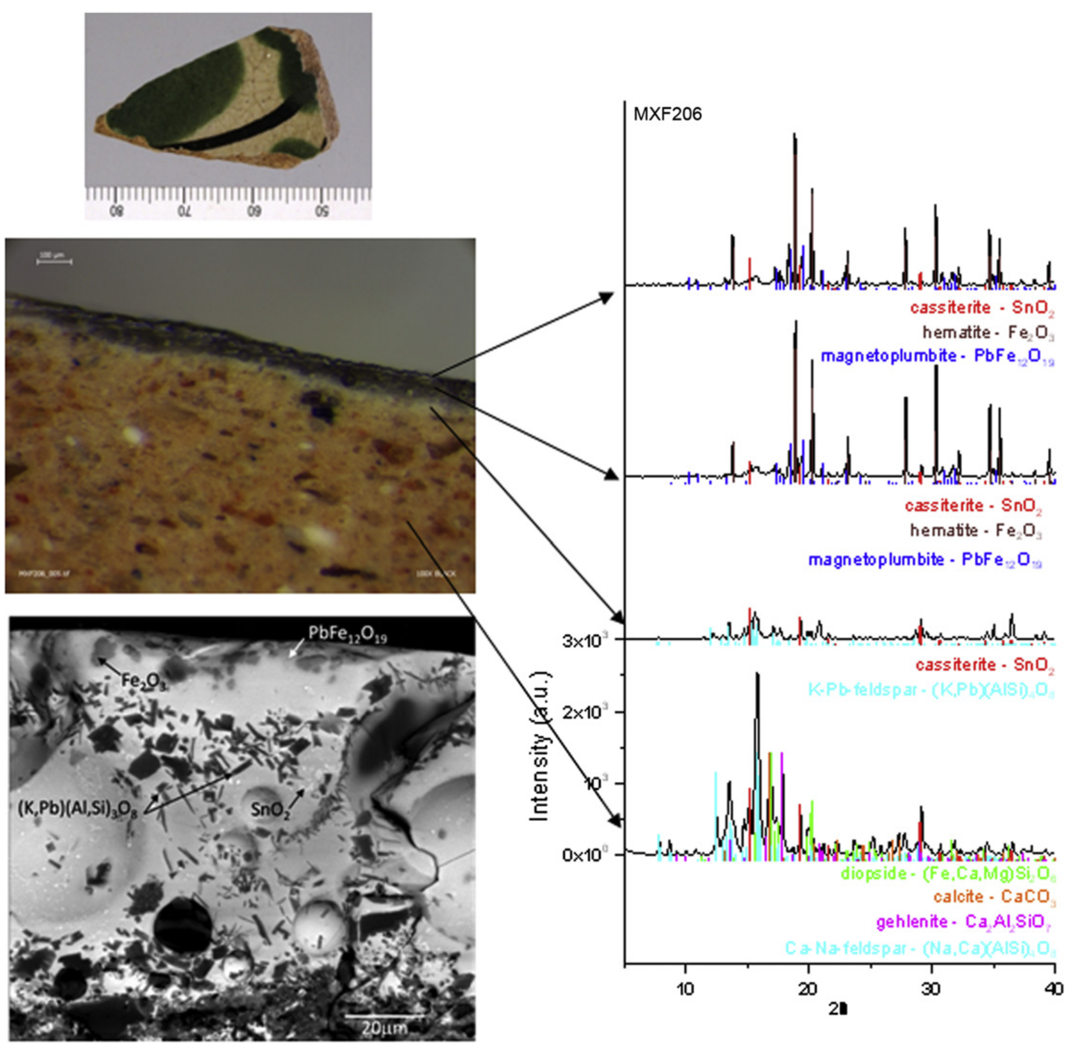

Fig. 5. Photograph, optical microphotograph and μ-XR diffractograms of the black/brown glazed area of the individual MXF206 from Puebla (Mexico). Arrows show the main analyzed areas on the sample. On the left bottom side, SEM microphotograph with indication of magnetoplumbite, hematite, feldspars, and cassiterite crystals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

a major component of magnetoplumbite as well, the latter compound would not show a significant contrast against the glaze in the SEM images.

Interestingly, the nature of brown or blackish pigments on decorations of the majolica specimens found in Mission San Luis shows a slight difference relative to the Puebla and Antigua ceramics. While magnetoplumbite is responsible for the deep black color achieved on these latter productions, hematite, which forming large crystallites shows a metallic black color, is the main crystal phase identifiable in the black painted areas on Mission San Luis majolica (Fig. 4). In these samples the iron content is higher than in Puebla and Antigua samples and ranges from 35 to 40 wt% of Fe_2O_3.

4. Conclusions

The examination of the different decorations on majolica pottery by μ-XRD and SEM techniques has enabled the characterization of the phases responsible for the different decorations, as well as the identification of the chemical compounds that play a main role in those pigments dissolved into the glaze coat.

Although the main characteristics of the European majolica technology can be seen in their American counterparts, there are also analytical data supporting the existence of autochthonous features used in colonial American productions. In this manner, the use of SnO_2, along with the tradition of lead glazing, is confirmed in the colonial majolica productions. Therefore, this technological feature is clearly linked to the new potting technologies brought by European colonizers, which arguably was adopted in the New World pottery. The use of cobalt for blue and copper for green pigments in colonial majolica also is related to the European medieval and postmedieval technological tradition of majolica making. Furthermore, the use of lead antimonate in order to achieve yellow pigment, is confirmed which follows the European tradition.

In contrast, the main differences regarding the autochthonous technology for the production of majolica pigments are found in the nature of the black color. Even though MnO is the black pigment used in the productions from Panama, following the European tradition, this study accounts for the first identification of iron oxides as a typical technological choice for black pigments on majolica ceramics. Specifically, the development of magnetoplumbite, an iron lead oxide phase, has been identified in this study as responsible of this color in Guatemalan and Mexican productions. Although the use of iron oxide as black pigment was tentatively suggested previously for the majolica production from Antigua (Iñañez and Speakman, 2011), it has only now been absolutely confirmed and the nature of such compound clearly identified.

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