NEW INSIGHTS IN TECHNOLOGY CHARACTERIZATION OF MEDIEVAL VALENCIA GLAZES

Journal:	*X-Ray Spectrometry*
Manuscript ID:	XRS-14-0127.R1
Wiley - Manuscript type:	Research Article
Date Submitted by the Author:	n/a
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Keywords:	SEM-EDX, Raman Microscopy, Lustre, Manufacture, Valencian Ceramics

New insights in technology characterization of medieval Valencia glazes

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Abstract

This study shows the first Raman Microscopy (RM) and SEM-EDX characterization of two 14th and 15th century lead-glazes and lustre ceramics from the Manises and Paterna workshops (Valencia, Spain) produced after the Aragon Christian conquest of the Iberian Peninsula (14th century). According to experts, these coetaneous ceramics were most probably involved in a process of technological transfer from the Islamic area of Southeast Spain to the Christian area of Valencia (East Spain) at the beginning of the 14th century; later on the celebrated Manises and Paterna workshops were formed. Although these ceramics have been studied widely in terms of production technology (ceramic body, glazes and lustre) using an array of diverse analytical techniques, until now a RM study has not been carried out. This paper presents results regarding the complex chemical composition of the glaze and lustre coloring agents and the quality of color manufacturing processes, elucidating firing conditions via spectral components analysis (i.e. Q^n for stretching/bending components) and polymerization index (*I*p), emphasizing chronology and pigment technology changes between both Valencian workshops. Coloring agents identified in glazes and lustres were cobalt present in blue glazes, copper in greenish glazes, copper and cobalt in

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the turquoise glaze and pyrolusite in black glazes. Tin oxyde was used as an opacifier in white glazes. Two lustre manufacture recipes were recognized mainly based on copper and silver compounds. Calculated firing temperatures were up to 1000ºC for white glazes and up to 600ºC for lustre and color glazes.

Keywords: Raman Microscopy; SEM-EDX; Lustre; Manufacture; Valencian Ceramics

1. Introduction

There is twofold interest in performing in-depth archaeometric studies of 14th and 15th century glazed ceramics from Valencia (Spain). On the one hand, the beginning of their production was linked to a process of technology transfer from Islamic culture and, on the other hand, these ceramics opened new Mediterranean commercial routes. The territory of the Christian Kingdom of Valencia, specifically in the towns of Paterna and Manises, developed ceramic activities during the Late Middle Ages (c. 1300–1500), as shown by archival documentation and archaeological interventions carried out in this territory [1-10]. Originally, the demand for Valencian ceramics was limited to the immediate surroundings, but they soon gained popularity in distant places. Indeed, these ceramics could be found in Mediterranean markets such as those in Northern Africa (*Ifriqiya*) or *Al-Andalus* (Islamic culture in Iberian Peninsula) [9,11]. Due to the geographic location of Valencia, as well as the political, social and economic evolution of this area, commercial links were developed facilitating the advancement of these ceramic activities. Manufacturing processes, ornamentation and chronological sequence of ceramic series have been researched in order to clarify stylistic criteria, specific epochs and different ceramic recipes [10, 12-17].

Archaeometric studies of ceramics have allowed identification of their intricate chemical composition, raw materials and manufacturing methods including elucidation of firing temperatures [18-22]. Characterization of glazes is challenging due to their complex disordered nanostructure, which is thermodynamically unstable with no crystallographic restrictions or stoichiometric ratios. Moreover, it is worth noting that glaze recipes are variable, both in terms of raw materials and available technologies among cultures, historical periods and workshops [16, 20-25]. In most cases, glazes are produced by specific and controlled smelting (from 600ºC to 1450ºC) and cooling methods for different compounds. Glazes are generally formed by the addition of feldspar-rich sandstones and clays with variable amounts of oxides such as alumina (Al_2O_3), calcium, sodium, potassium and magnesium oxides (i.e. CaO, Na_2O, K_2O and MgO) and iron oxides (Fe_2O_3 or Fe_3O_4), which contribute to diverse glaze functions and properties [2,20,22,24,26]. Other substances such as opacifiers and fluxes are used to obtain specific characteristics [23]. For instance, the traditional opacifier tin oxide (SnO_2, cassiterite) increases optical properties, while the main fluxes such as lead oxides (from diverse lead sources) avoid glaze devitrification and improve color development [2, 18, 20, 21, 22, 27-29].

Another finishing ceramic decoration is the so-called lustre, produced by metallic oxides such as silver and/or copper in an overglaze finish. Lustre is obtained at low temperature (<600ºC) under a reducing atmosphere to attain metallic sheen (effect of iridescence). The Hispano-Moresque lustres are mainly based on Ag_2S, tenorite (CuO), haematite (Fe_2O_3) and cinnabar (HgS) mixed with vinegar [2,16]. Most of these compounds are vulnerable to firing and cooling conditions, suffering mineralogical modifications or complete decomposition and volatilization (e.g. silver-compounds, cinnabar, etc.), which complicate their mineral characterization. Lustre could exhibit a broad range of colors from yellow, green to brown and shines from gold-like to copper-like depending on the type, size, structure and distribution of metal nanoparticles, Cu/Ag ratios, firing conditions, etc. The previously mentioned topics are commonly investigated in order to shed light on the role of diverse ingredients in glaze recipes, firing temperatures and pigments used in ceramic decoration [2, 4, 5, 10, 15-18, 20, 24, 29, 30].

The analytical characterization of glazes and lustre has been performed using an array of analytical techniques [3-5,10,19,20,22,23,25,26,29,31,32]. Particularly, Fourier Transformed Infrared Spectroscopy (FTIR) and Raman Microscopy (RM) are exceptionally apt to explain their complex composition, offering molecular information (in a non-destructive way with high spatial resolution) that retrieve knowledge about production process [20,23,25,26,31-33]. Specifically the polymerization index (*I*p) and different spectral components (Q^n for stretching components, $Q^{n'}$ for bending ones) derived from Raman spectra are used to clarify glass composition and nanostructure, such that they serve as a parameter for unraveling firing temperatures[21,22]. However in spite of the well documented archaeological and scientific benefits obtained from applying vibrational techniques to characterize Muslim, Italian, Ottoman, Iznik, Majolica or Vietnamese glazed ceramics, among others, to our knowledge glazes and lustres of Valencian ceramics have not been studied by means of RM [19,32,34-37]. Consequently, this paper focuses on applying RM combined with SEM-EDX to improve information concerning coloring recipes (pigment compositions) and manufacturing processes (e.g. firing temperatures) of glazes and lustres of 14th and 15th ceramics workshops from Manises and Paterna (Valencia, Spain). This will help unravel changes in coloring processes and establishing a chronology for the ceramics.

2. Materials and Methods

2.1. Investigated objects

Eleven pieces of glazed and lustre coetaneous (temporal and geographical) ceramics from Manises (MP) and Paterna (PP) workshops housed in the *González Martí* National Museum of Ceramics and Decorative Arts of Valencia were analyzed. Ceramics were taken from different archaeological sites in Manises and Paterna, in particular, *Testar del Molí* (*Olleríes Majors*) and *Barri d'Obradors*, respectively [28]. According to previous archaeological and archaeometric studies, the ceramic bodies from both workshops show similar ceramic-making procedures [9,28]. Thus, we present the results in chronological order to enable the determination of a timeline for the evolution of glaze manufacturing and changes in pigments technology. The characteristics, illustrations and reference numbers of previous works of the studied samples are shown in Table 1 and Figure 1 [9]. All fragments of bowls and dishes are decorated with four colored glazes of floral decorations in black, green, turquoise, blue and gilded lustre on a white background (i.e. white glaze) (Fig.1). Decoration of these ceramics has great interest since it has allowed leading archaeologists to establish a well-accepted chronology. Hence, in this work a rigorous sample selection was performed considering the ceramic glaze's color, stylistic criteria and chronology. Four groups of samples were selected for our analyses: 1) glazed ceramics decorated in green and black; these are the first pieces manufactured after the Aragon Christian conquest in the eastern coastal region of the Iberian Peninsula (beginning of the 14th century); 2) ceramics showing blue glaze and gilded lustre; this type of iridescent decoration with blue lines started to be manufactured also at the beginning of the 14th century; 3) turquoise glazed ceramics decorated with black lines produced during the 14th and 15th centuries and, 4) blue glazed ceramics comprising the most popular Valencian ceramics during the 14th and 15th centuries, with a decoration based on varied blue designs with no other colored lines [24,38-39].

Table 1

According to previous studies performed with optical microscopy by the authors [9,39], the analyzed ceramic bodies of pieces from both workshops show similar composition, largely of magnesium-rich carbonates with tempers of mainly quartz and feldspars displaying angular shapes. Calcareous microfossils are also present attesting to the use of marine sediments, although the use of other types of clays is not ruled out. Matrix colors typically range from yellow to orange indicating that ceramic bodies were fired under oxidizing conditions. The presence of few micrometer size diopside crystals ($MgCaSi_2O_6$) and anorthite ($CaAl_2Si_2O_8$) in the ceramic bodies suggest that they were fired well above 900°C [9,12,39]. In fact, the technology and manufacturing process for the ceramics bodies were comparable in both Valencian workshops.

Figure 1

2.2. Analytical Methods

2.2.1. Scanning Electron Microscopy

Polished thin (~30 µm thick) sections were prepared from resin-embedded samples to analyze the micro-texture and chemical composition of the glazes and lustres with a Scanning Electron Microscope equipped with an Energy-dispersive X-ray (EDX) detector (Philips SEM515–EDAX PV9100). For this purpose the polished thin sections were carbon-coated. Single-point elemental analyses were acquired linearly at equidistant points (several micrometers) from the ceramic body towards the surface of the decoration avoiding inclusions and neoformed phases such as alteration minerals. The SEM–EDX working conditions were 500 pA filament current, 20 keV beam energy, and 10 eV/ch resolution. Quantitative elemental analysis from SEM–EDX spectra were done normalizing to 100% in weight.

2.2.2. Raman Microscopy

RM identifies amorphous, poorly ordered, and crystalline compounds with high spatial resolution (few microns). RM analyses were performed on the surface of ceramic fragments by a *Renishaw InVia* Raman microscope system fitted with a Peltier-cooled CCD detector and a Leica DMLM microscope to identify the nature of the glaze and lustre compounds. Two lasers were used, i.e. 532 and 785nm, though finally samples were excited with a 785 nm diode laser to minimize fluorescence. Laser power ranged from 0.15 to 150 mW (0.05% to 50% respectively). Further information and specific working conditions for each Raman analysis − laser power (LP), numbers of accumulations (acc), seconds of irradiation exposure time (s) and the selected objective − are cited in the figure caption. Spectra were collected within the maximum wavenumber range of 200-3200 cm^{-1} with an average spectral resolution of 1 cm^{-1}. To improve signal/noise ratios, a series of recorded spectra (n = 10) with exposure time = 20 s, were collected from each sample spot and averaged. A silicon standard was used to fit the exact peak position of Raman bands. Spectra were taken by placing the samples on the microscope stage and observing them using long-working-distance 20X and 50X objectives. A video camera was used to identify particular locations in the samples. Key Raman bands for the different compounds were identified using the *Renishaw* commercial database. To clarify the presence of some mineral phases, Raman mappings were acquired using a 50X objective and series of recorded spectra (n =20) with an exposure time of 3s during an average of three hours. The remaining spot measurements were carried out with a 20X objective.

In addition, in order to characterize the glazes and lustre (kind of glassy silicates), the spectral deconvolution of the Si-O stretching/bending peaks into its components was carried out for: a) the identification of different spectral components (Q^0 or SiO_4; Q^1 or Si_2O_7; Q^2 or silicate chains; Q^3 or sheet-like region and Q^4 or SiO2 and tectosilicates) [21], and b) the polymerization index (*I*p) calculated as the ratio (A_{500}/A_{1000}) of the Si-O bending (~500 cm^{-1}) and stretching (i.e. ~1000 cm^{-1}). Raman spectra deconvolution was performed with the use of OPUS Spectroscopy Software Version 7.0 and PeakFit Software Version 4.11. Number of peaks was held constant and fitted to a Lorentzian and a mixed Lorentzian+Gaussian functions. The degree of smoothing was set at 25%. Peak amplitude was allowed to vary within 5%, while curve shape and width were allowed to vary freely. Previously, baseline corrections were performed on all Raman spectra sections. The processing temperatures of the glazes and lustre will directly influence the ratios of such above mentioned areas and the specific position of Q^n species.

3. Results and Discussion

3.1. Scanning Electron Microscopy

SEM-EDX analyses were performed to gain information on elemental composition and texture of the glazes and lustres. Results showed diverse surface finishing textures according to color decoration; likewise thickness varied from ca. 50 to 100 µm. Contacts between surface finishings with ceramic bodies were often irregular and frequently abundant bubbles were observed (Fig.2). Table 2 shows the SEM-EDX chemical composition of the glazes, which varied among samples. In general glazes are rich in SiO_2 (33-54%) and PbO (27-50%). Thus, samples PP-21 (green and black decoration), PP-27 (blue and gilded lustre), PP-15 (turquoise decoration) and MP-6 (blue decorations) can be considered high lead glazes since Pb contents range from 42.1% to 50.4% (Table 2). Amounts of alkalis (Na_2O < 2.9% and K_2O < 7.5%) are moderate in the glazes which have diverse quantities of Al_2O_3, CaO, FeO, MgO and TiO_2 (Table 2). No correlation between Na_2O and K_2O was observed. In all samples cassiterite (SnO_2 = 3.8-19.2%) was found to have been used as opacifier, in agreement with the findings of other authors [27]. Our results also revealed that SiO_2, K_2O and Al_2O_3 contents increased from the glaze surface towards the ceramic body (Fig. 3) while the PbO (added as a flux to lower the firing temperature of the silica) diminishes in content.

Table 2

Figure 2

Figure 3

On the other hand, various elements such as Fe, Mn, Co, Cu, Zn and/or Ni were detected in the glazes according to the colored regions, i.e. green, black, turquoise, blue and gilded lustre (Table 2). These elements could be either intentional additives to produce the glaze (e.g., in traditional glaze recipes Mn was added to prevent Co diffusion through the glaze during firing), or simply impurities associated with Co ores [23, 40]. Additionally, traces of As (not shown in Table 2) were detected in lustre layers of PP-25 and PM-27 samples and in color layers of MP-4 and PP-15. Regarding color agents, green decoration was due to dispersed Cu in the glaze, with SEM-EDX CuO values ranging from 1.25 to 4.77%. In the black regions SEM examination revealed that Mn was also dispersed in the glaze and that MnO amounts were lower than 1.63%. The turquoise color (sample PP-15) was obtained using Cu and Co immersed in a low K_2O glaze (2.64%, see Table 2). According to SEM-EDX analysis, in PP-25 the CuO value was found to be ca. 1.99%. Cobalt was responsible for the blue color in samples showing blue color (MP11, MP6, PP33 and MP2) and samples showing blue and lustre decoration (PP-25, PP-27 and MP-4). In these latter Ag, Hg and/or Cu were identified in the gilded areas. However, other elements such as Fe, Mn, Cu, Zn and Ni were identified together with Co in the blue region. It is worth mentioning that Borgia and co-workers suggested a complex composition made of Co-Ni-Fe-As ores for manufacture of blue smalt [24], afterward confirmed by other authors [7,10,21,41]. The SEM observations also revealed that the blue pigment was applied over the glaze in ceramics showing blue decoration, though it was applied at the ceramic body in samples displaying blue and lustre decoration, as suggested by aggregates of small angular Co-rich granules (<10 µm) or acicular crystals at the glaze base (Fig. 2).

In glazed ceramics there is a well-accepted chronological evolution for Co blue pigments according to their composition. Thus, Co is associated with Zn in pigments from the 12th and 13th centuries, while Ni is also present in pigments from the late 14th and early 15th centuries [42, 43]. In the Medieval Valencian ceramics experts also have indicated a chronological evolution for the glaze ceramics [7]. Hence, in ceramics from the Paterna workshop, Fe-Co-Zn were identified in the first blue decorations; indeed, this was the common composition of the first Co-rich blue pigments used in the Valencian area [2,10]. Therefore, samples PP-25, MP-4 and MP-6 can be ascribed to this period of the early 14th century. In periods later than the mid-14th century, the common associations were Mn-Fe-Co-Zn and Mn-Fe-Co-Ni. Correspondly, samples PP-27, MP-11, PP-33 and MP-12 showing different Ni contents but no Zn, belong to this later period [5,7,17,44]].

The origin of the cobalt used to prepare the blue smalts for medieval Iberian ceramics is a complex archaeological question not yet resolved. Cobalt mines have been abundant since antiquity in both the Iberian Peninsula and North Africa. Therefore cobalt could originate either from local quarries next to the Manises and Paterna ceramic factories, or it could have been imported, probably from Saxony (Germany) via Venetian traders. This option is reliable considering that Venetian merchants often traded in the ports of Valencia and Málaga. Additionally, it is alleged (webs) that cobalt has been extracted since antiquity from the Monte Horquera mine in Villamarchante (Valencia) to prepare blue smalts for the Manises ceramics. The minerals present in this mine are asbolite ((Ni, Co)xMn^{4+}(O,OH)$_4$•nH$_2$O), with Fe impurities), azurite ($Cu_3(CO_3)_2(OH)_2$), malachite ($Cu_2(CO_3)(OH)_2$) and Olivenite ($Cu_2(AsO_4)(OH)$). This paragenesis confirms the presence of impurities such as Ni, Mn and Fe in the Co ore, although the intentional addition of these elements to the Co-rich smalt cannot be ruled out. Neither of these two possibilities are supported by scientific references.

3.2. Raman microscopy

3.2.1. Green and black glazes (early 14th century)

The RM study of the green areas performed on MP-1, MP-2 and PP-21 samples revealed the presence of cassiterite in the glaze (478, 634, 778 cm^{-1}), Co-O Raman bands at 578 and 667 cm^{-1} and O-Si-O bending modes, whose bands appear at ca. 450-550 cm^{-1} (Fig.4). In this regard, the existence of a narrow Raman band at 545 cm^{-1} could suggest a firing temperature up to 450ºC due to the presence of Pb_3O_4 yet not dissolved in the glazes (Fig.4)[33] .Other key Raman bands allowed identification of haematite at 290, 410 and 614 cm^{-1} and quartz at 213, 365 and 465 cm^{-1} In this green region, we did not succeed in obtaining a specific signature for this color. This finding corroborates our SEM observations and suggest that the high Cu content identified with EDX (CuO=2.29%) must be dispersed within the glaze network as ionic coloration [23,45]. Consequently, no precise Raman signature is expected for the green color [23]. In this regard, it is worth noting that previous studies have reported green glazes in Ottoman ceramics where Cu is dispersed in a lead-based glaze due to a fast cooling process, and no specific Raman bands were obtained for the green color [35].

Figure 4

Additionally, in samples displaying black decoration in surface a thorough study which comprise deconvolution of specific bands around 800-1200 cm^{-1} was performed. The characteristic Raman band of Pb-based glass was found at 980 cm^{-1} in MP-1, at 985 cm^{-1} in MP-2, and at 978 cm^{-1} in PP-21 sample. It is well-accepted that this procedure allows identification of the Q^n species of the silicate network (n=1 to 4, meaning the number of bridging oxygens which constitute the silicate chains), where tetrahedra can be identified thanks to n = 0 (Q^0, monomer, i.e. isolated SiO_4, 800–850 cm^{-1}), n = 1 (Q^1, Si_2O_7 groups, 950 cm^{-1}), n = 2 (Q^2, silicate chains, 1050–1100 cm^{-1}), n = 3 (Q^3, sheet-like region, 1100 cm^{-1}) and n = 4 (Q^4, SiO_2 and tectosilicates, 1150–1250 cm^{-1}) [21,22,26]. This Raman information has been crucial in the present study since it has allowed estimation of the temperature and firing conditions for our samples (taking into account traditional ceramic glass recipes). For all three samples the stretching region of Q^n species of the silicate network showed similar bands. In particular, the position of the Q^3 unit for MP-2 (1080 cm^{-1}) sample suggests a temperature between 450 and 600ºC [20,33]. In addition, we identified in all samples the slight Raman band attributed to the Q^2 unit at ca. 1040 cm^{-1}, and the Raman band of Pb-based glazes located at 985 cm^{-1} which suggested a firing temperature ca. 450ºC (Fig.5a). In fact, the estimated polymerization index proposed A_{500}/A_{1000} rations around 0.2-0.3, which suggest a firing temperature lower than 600ºC for these samples [21,22]. The similar glaze-firing temperature for MP-1 and MP-2 (Manises workshop) and PP-21 (Paterna workshop) samples may suggest that these ceramics are contemporary (from the early 14th century according to leading archaeologists), and that knowledge transfer between both Valencian ceramic workshops occurred, which is to be expected considering the proximity of the two localities (~4 km), as proposed by Pérez-Arantegui and co-workers [5]. However this conclusion should be considered with caution since sample compositions are different, mostly in terms of Mn, Co, Cu and Zn contents.

In these black glazes we identified other minerals as well (Fig.5b). In particular, pyrolusite (MnO_2), responsible for the black color, was recognized thanks to its characteristic band at 637 cm^{-1}. This finding corroborates our SEM-EDX results (MnO content up to 1.63%), and agrees with those of Pérez-Arantegui and co-workers for black areas in glazes [5]. In addition the RM analyses identified the bands at 436 cm^{-1} and 323 cm^{-1} that corroborate the presence of zincite (ZnO), the Raman bands of Co-O molecule at 578 and 667 cm^{-1} and an intense Raman band at 540 cm^{-1} attributed to the Si-O-Si bending modes (Fig.5b).

Figure 5

3.2.2. Blue glaze and gilded lustre (late 14th century).

Samples PP-25, PP-27 and PM-4 show areas with blue glaze and gilded lustre. To simplify reading comprehension of decoration manufacture it should be recalled that their corresponding SEM-EDX analyses (see Table 2) revealed an elemental composition based mainly on Cu (CuO = 0.33-1.14%), Co (CoO = 0,04-0.2%), Zn (ZnO = 0.2-0.3%), and Ni (NiO = 0.11-0.4%). Additionally, traces of As and Ag were found in samples PP-25 and MP-4, unlike PP-27 where only As was detected and Zn is absent. As mentioned already, in Medieval Valencian glazes there is a well-accepted chronological evolution for blue decoration based on different element association. Thus, Fe-Co-Zn composition is typical for the first blue decorations (early 14th century) followed by Mn-Fe-Co-Zn and Mn-Fe-Co-Ni associations in later periods dating since the mid-14th century (see Table 2). Zn contents have only been found with SEM-EDX in samples PP-25 and MP-4. Likewise only in these two samples zincite was detected using RM thanks to identification of Raman bands at 436 cm^{-1} and a slight band at 515 cm^{-1}. These findings suggest that sample MP-4 should be ascribed to the early 14th century contrary to the archaeologists´ proposal. In the blue glaze regions of all samples the RM analyses identified Co-O Raman bands that corroborate the presence of cobalt blue –as a coloring agent– together with cassiterite. However these Raman bands showed low intensities in blue area of MP-4, possibly due to small amount of components, which complicate the interpretation as shown in Fig. 6a [23].

Regarding lustre decoration, Pérez-Villar and co-workers [44] indicated that silver nitrate was traditionally added to glazes (of low thickness ca. < 200 μm) to attain metallic effects or lustre. As cited by Pradell and co-workers, silver nitrate is the main source of Ag in traditional lustre recipes [5]. On the other hand it should be mentioned that lustres in ceramics from the 14th century have subtle thickness and low metal contents, which support the ascription of our samples (with thickness decoration from 50-100 μm) to this epoch [10,25,38]. In the lustre of sample PP-25 the RM analyses revealed, in addition to quartz, other Ag-compounds such as argenthite (Ag_2S) and sulfarsenide (Ag_3AsS_3) via recognition of key Raman bands at 330 and 350 cm^{-1}, respectively (Fig. 6b) [46]. According to Pradell and co-workers the above mineral phases are present in an amalgam of Ag and Hg formed during lustre firing at 500°C [17]. Consequently, these compounds could be considered remnants of an inadequate or incomplete firing and cooling of the lustre. Also in the lustre of sample MP-4, Ag_2O was identified, in addition to haematite. The presence of Ag_2O should be related to the oxidation of the Ag ion (Ag^+) to the oxide species due to the presence of Fe_2O_3 in the lustre, as proposed by Pérez-Villar and co-workers [43]. In this regard it should be recalled that As is volatilized during roasting when Co, Ni and Fe oxides are melted together with siliceous sand [24]. This suggests the use of early Islamic lustre recipes for sample PP-25, which include red and yellow arsenic sulfide – realgar (AsS) and orpiment, respectively –, as cited by Pradell and co-workers [17,29]. Instead, the luster of sample PP-27 should be related to a copper-based lustre considering the absence of Ag and Zn compounds in its composition.

Regarding the estimated firing temperature for lustres of samples PP-25, PP-27 and MP-4, the detailed study of the Q^n species showed similar position for the Q^3 species between 1072 and 1085 cm^{-1}, which suggests a firing temperature ranging from 450ºC to 600ºC (Fig.6a,b). On the other hand, the Q^2 species at 1040 cm^{-1} identified in the white glazes of PP-27 sample (Fig. 6 c) suggest a firing temperature of 990ºC [20,33]. Indeed, our predicted lustre firing temperature is supported by the findings of Pradell et al. (2005) which suggest that Cu and Ag ionic molten compounds are placed in contact with the glaze surface at temperatures of 300º–500ºC for Ag and 500º–600ºC for Cu [29]. Consequently, our estimated lustre firing temperatures and compositions for samples PP-25, PP-27 and MP-4 are in agreement with those proposed by experts in lustre ceramics, which propose a melting temperature between 450º–600ºC [2, 17, 18, 29]. In fact, the corresponding estimated polymerization index for these lustres showed A_{500}/A_{1000} rations around 0.3 associated to a firing temperature ~ 600ºC [21,22]. Finally, our RM analyses revealed the typical Pb-based glasses Raman bands at 986 and 980 cm^{-1} for samples PP-27 and MP-4 respectively, though these bands were not clearly identified in sample PP-25 [2,42].

Figure 6

3.2.3. Turquoise glaze (late 14th century)

In sample PP-15 the RM analyses discerned the Raman signatures of cassiterite in the white areas, while in the turquoise region smaltite $(Co, Fe, Ni)As_2$ was identified at 830 cm^{-1} (Fig.7). These results agree with the SEM-EDX data revealing that the coloring agents for the turquoise glaze were made of Co (CoO=0.17%), Fe (FeO = 0.82%), Ni (NiO=0.07%) and Cu (CuO=1.99%). The EDX analysis also showed that this is a Pb-alkali glaze with traces of As. These results agree with the well-known procedure to manufacture turquoise glaze by mixing Cu oxides in an alkaline glaze [23]. However, we did not find a specific Raman signature for the turquoise color, likely because Cu is dispersed in the glaze network, as seen under SEM observation [20, 23, 24]. Moreover, by means of RM we could not identify Co-O vibrations.

According to Roldán and co-workers [7], smaltite can be attributed either to the cobalt blue source or to a neoformed phase due to an oxidizing atmosphere. Although as mentioned earlier, some authors have suggested that the turquoise color in glazes are due either to Cu ions dispersed throughout the glaze [23] or to the presence of smaltite [7], we found in our sample that both components occurred together in order to achieve this color. Additionally, in sample PP-15 the Q^n species of the silicate network were recognized and evaluated. The identified RM bands suggested a firing temperature up to 600ºC due to the position of the Q^2 recorded at 1044 cm^{-1} and the Q^3 unit at 1088 cm^{-1}, as shown in studies performed in model samples elsewhere [33]. Nonetheless in our sample the complex region between 950 and 1000 cm^{-1}, related to Raman bands from glassy phases and Pb-based glasses at 981 cm^{-1}, also suggested a temperature around 600ºC (Fig.7).

Figure 7

3.2.4. Blue glaze (late 14th and 15th centuries)

The RM analyses performed on these blue glazes (MP-11, MP-6, PP-33 and MP-12) revealed a large variety of Raman spectra. In all four samples cassiterite was identified and its harmonic modes of Sn-O stretching at 1240 cm^{-1}, while in the blue regions we mainly detected Co-O Raman band at 665 cm^{-1} (which was assigned to cobalt blue pigment) and slight CuO Raman bands at 620 cm^{-1} (except MP-12). Furthermore, haematite and calcite were found in samples MP-12, MP-6 and PP-33, and quartz in sample MP-11 (Fig.8 a). Unlike Roldán and co-workers [7] and Borgia and co-workers [24], we did not recognize Raman bands in the blue glaze regions that could be attributed to rythrite $(Co,Ni)_3(AsO_4)_2.8H_2O$), which is a mineral claimed to be present in Ni-rich glaze blue decorations.

In addition, on sample MP-11 we identified Si-O-Si stretching/bending modes in the blue region (Fig.8 a,b), in particular the bending mode at 488 cm^{-1}, the Si-O stretching modes from silicate chains at 1051 cm^{-1} (Q^2 species) and those from tectosilicates (Q^3 species) at 1086 cm^{-1}. Likewise we found the characteristic Raman band of Pb-based glass at 985 cm^{-1}, while in the white areas a relevant shift of the identified Q^n species was observed (Fig.8c). As indicated elsewhere, the absence of Q^3 units implies a firing temperature higher than 600ºC, while the presence of Q^2 and Q^4, located at 1040 cm^{-1} and 1146 cm^{-1}, respectively, indicate a firing temperature up to 990ºC, as it was found in our white glazes (Fig.8c) [33]. Indeed, the estimated polymerization index for this sample was ca. 1.02 which is associated to a firing temperature around 1000ºC [21,22]. Considering these results, we suggest two successive decorations executed at different firing temperatures for sample MP-11 (see Fig. 2). Firstly, to manufacture the white background of the glaze an immersion into the opacificant agent solution (cassiterite) took place around 900-1000ºC. Later on, to achieve the blue decoration a lower firing temperature up to 450ºC was applied.

Figure 8

As well, the Q^n species from the silicate network were identified in samples MP-12, MP-6 and PP-33, helping to clarify a specific firing temperature for blue areas of each sample. In particular the Q^2 and Q^3 species recognized in MP-12 and MP-6 imply a glaze-firing temperature of up to ca. 600ºC while it suggest a lower temperature of around 450ºC for sample PP-33. In fact, the value of the polymerization index (0.2) reveals a firing temperature lower than 600ºC for blue glazes [21,22].

4. Conclusions

This work represents the first characterization of Middle Aged Valencian ceramics using RM combined with SEM-EDX. Our results demonstrate that knowledge and technology transfer took place during the 14th and 15th centuries between the Manises and Paterna ceramic workshops (Valencia, Spain), and that their production was influenced by Islamic recipes, as proposed by leading archaeologists. RM results revealed different coloring agents, color recipes and manufacture processes for the surface decorations of the studied samples, as well as the inadequate or incomplete firing/cooling of glazes. Furthermore, by recognition of Raman bands of specific silicate networks and the polymerization index we could suggest firing temperatures for the white glazes (up to 1000ºC) as well as lustre and color glazes (up to 600ºC) without using standards. Analytical results also enabled grouping the ceramic pieces into different periods, which mostly agree with the archaeologists´ conclusions.

For color glazes different coloring agents were identified. While pyrolusite was used in black areas, no specific Raman signatures were obtained neither for turquoise glaze nor for green glazes (since Cu is dispersed in the glaze network as ionic coloration). Two recipes were identified to manufacture lustre based on either Cu or Ag. Blue glazes were made of cobalt blue together with Mn, Cu, Zn and/or Ni.

Finally, considering that ceramic technology transfer took place during the Middle Ages in the Iberian Peninsula, it would be interesting to extend this type of study to other Mediterranean archaeological sites, other historical periods and even other archaeological objects. The aim would be to gain knowledge concerning historic trade routes and to better understand relationships among cultures considering the role of materials technology.

Acknowledgements

This work was supported by Research Groups RNM-179 and HUM-162 (JA, Spain), Research Projects HUM2006-06210, P08-RNM-04169, CGL2012-30729 and P12-FQM-1889, and the Bilateral Spanish-Flemish Project (BOF-2008-13). We thank C. Capelli of the *Università degli Studi di Genova* (Italy) for SEM-EDX discussion, P. Alvarez-LLoret for helping with Raman deconvolution and A. Kowalski for English revision.

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Figure Captions

Figure.1. Studied ceramic pieces from the Manises (MP) and Paterna (PP) workshops (Valencia, Spain) dated from the Middle Ages.

Figure 2. SEM microphotograph of sample a) MP1 and b) MP-6 (Manises workshop), and c) PP-15 and d) PP-25 (Paterna workshop). Notice the bubbles in MP-1 and PP-25 glazes, the contact at the glaze base in MP-1 and MP-6 (irregular) and PP-15 (regular), the lustre in PP-25 and the blue decoration applied over the glaze in MP-6.

Figure 3: BSE images and EDX microanalysis of: a) Pb; b) S; c) Si; d) Al; e) Ca; f) Fe and g) Mg in the profile of MP-4 sample.

Figure 4. Representative Raman spectra of green glazed area in MP-2 sample from 200 to 700 cm^{-1}. Inset: Raman spectrum deconvolution in the region between 500 and 700 cm^{-1}. Spectrum was collected with a 50% LP, 100 acc, 3 s and an objective of 50X. For interpretation of the bands the reader is referred to the text of the article.

Figure 5. Raman spectra of black glazes of: a) MP-2 from 950 to 1100 cm^{-1}; b) and PP-21 from 300 to 700 cm^{-1}. Spectra were collected with 50% LP, 7 acc, 10 s and an objective of 50X. For interpretation of the bands the reader is referred to the text of the article.

Figure 6. Raman microscopy results of: a) blue decoration of MP-4, b) gilded lustre of PP-25, and c) deconvoluted spectra of white glazed of PP-27. Spectra were registered at 50% LP, 7 acc, 10 s using an objective of 50X. For interpretation of the bands the reader is referred to the text of the article.

Figure 7. Deconvoluted Raman spectra for sample PP-15. Specific conditions working: 0.5% LP, 7 acc and 10 s with an objective of 50X. For interpretation of the bands the reader is referred to the text of the article.

Figure 8. Deconvoluted Raman spectra for sample MP-11. Blue decoration a) from 850 to 1100 cm^{-1}, b) from 450 to 700 cm^{-1}, c) white glazes from 400 to 1150 cm^{-1}, d) Raman optical image of the blue-white interface area in the glaze. Blue glaze spectra were acquired using an objective of 50X, 5% PL, 7 acc and 10s. White region spectrum was collected with an objective of 50X, 0.5% PL, 7 acc and 10s. For interpretation of the bands the reader is referred to the text of the article.

Table. 1. Description of samples studied from the Manises (MP) and Paterna (PP) ceramic workshops (Valencia, Spain) from the Middle Ages.

Table 2. Elemental composition obtained with SEM-EDX of the ceramic glazes from Manises (MP) and Paterna (PP) workshops (Valencia, Spain).

Table 1. Description of studied samples from the Manises (MP) and Paterna (PP) ceramic workshops (Valencia, Spain) from Middle Ages.

Sample	Museum ref.	Chronology*	Color	Morphology	Ornamental decoration
MP-1	CM01	1st half 14thc.	Green and Black	bowl	Triskele
PP-21	CM21	1st half 14thc.	Green and Black	bowl	Metopa
MP-2	CM02	2nd half 14thc.	Green and Black	dish	Parallel lines
PP-25	CM25	1st half 14thc.	Blue and lustre	bowl	Radial
PP-27	CM27	2nd half 14thc.	Blue and lustre	bowl	No determined
MP-4	CM04	2nd half 14thc.	Blue and lustre	bowl	Radial
PP-15	CM15	2nd half 14thc.	Turquoise	bowl	Cross
MP-11	CM11	End 14th-early 15thc.	Blue	bowl	Palm Leaves
MP-6	CM06	3rd quart 14thc.	Blue	bowl	Fishes
PP-33	CM33	End 14th-early 15thc.	Blue	bowl	Fishes
MP-12	CM12	End 14th-early 15thc.	Blue	dish	No determined

* According to archaeologists. c=century.

Table 2. Elemental composition obtained with SEM-EDX of the ceramic glazes from Manises (MP) and Paterna (PP) workshops (Valencia, Spain).

Chronology*	Surface colors	SiO_2	PbO	Na_2O	K_2O	CaO	MgO	Al_2O_3	FeO	SnO_2	TiO_2	MnO	CoO	CuO	
1st half 14th c.	Green and black	46.2	35.8	1.58	3.02	4.08	0.57	4.41	0.99	9.40	0.25	0.74	0	2.29	
1st half 14th c.	Green and black	33.5	50.4	0.74	1.34	2.86	0.26	2.85	1.12	5.40	0.28	1.63	0.22	4.77	
2nd half 14th c.	Green and black	49.5	35.2	2.17	4.37	2.39	0.42	3.01	0.72	4.53	0.27	0.15	0.32	1.25	
1st half 14th c.	Blue and lustre	46.6	37.7	2.31	3.92	2.87	0.57	2.88	0.61	3.80	0.40	0.19	0.04	1.14	
2nd half 14th c.	Blue and lustre	42.6	44.3	0.17	6.11	2.40	0.43	1.99	1.50	6.84	0.16	0.18	0.05	0,80	
2nd half 14th c.	Blue and lustre	54.3	27.3	2.04	7.47	3.88	0.64	2.58	0.67	19.24	0	0	0.20	0.33	
2nd half 14th c.	Turquoise	41.3	43.9	2.37	2.64	2.65	0.60	2.86	0.82	3.76	0.42	0	0.17	1.99	
End 14th-early 15th c.	Blue	47.1	40	0	5.97	2.29	0.44	2.11	0.67	5.90	0.21	0.15	0.17	0.63	
3rd quart 14th c.	Blue	40.1	42.1	2.02	5.01	2.18	0.35	1.87	3.53	5.60	0.17	0	1.03	0.70	
End 14th-early 15th c.	Blue	50.4	39.2	0.55	4.97	1.62	0.26	1.56	0.48	6.31	0	0	0.36	0.48	
End 14th-early 15th c.	Blue	49.4	34.3	2.89	6.57	2.51	0.62	2.47	0.67	9.90	0.1	0.14	0.28	0	0

* According to archaeologists. c=century.

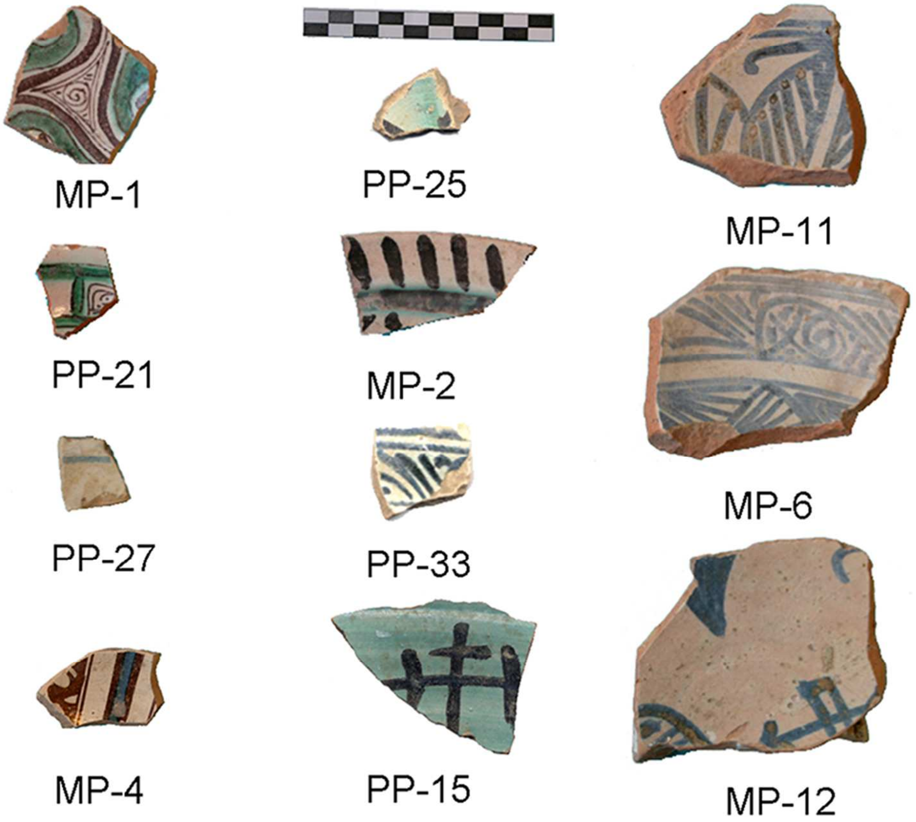

Figure 1. Studied ceramic pieces from the Manises (MP) and Paterna (PP) workshops (Valencia, Spain) dated from the Middle Ages.
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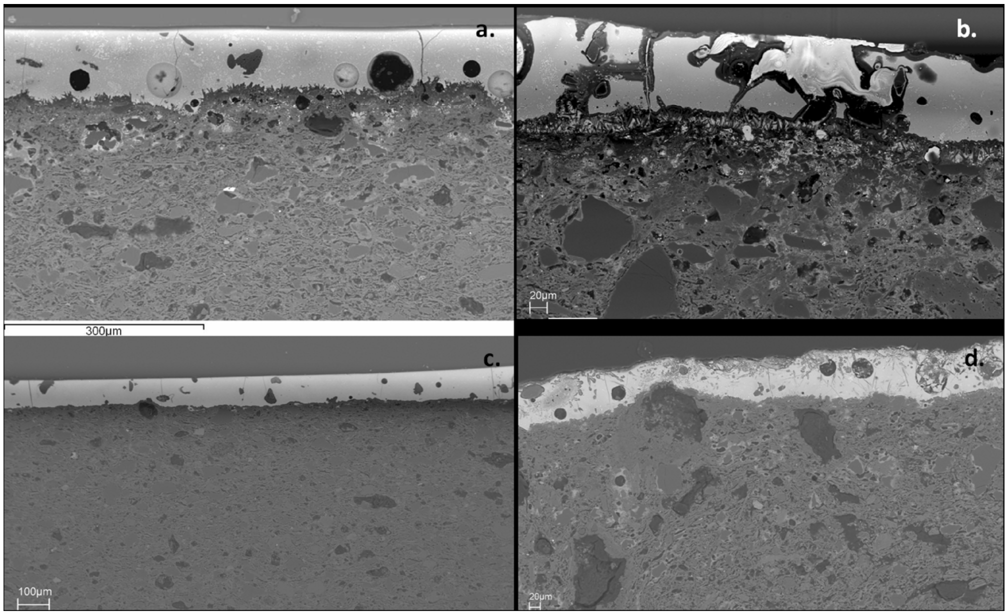

Figure 2. SEM microphotograph of sample a) MP1 and b) MP-6 (Manises workshop), and c) PP-15 and d) PP-25 (Paterna workshop). Notice the bubbles in MP-1 and PP-25 glazes, the contact at the glaze base in MP-1 and MP-6 (irregular) and PP-15 (regular), the lustre in PP-25 and the blue decoration applied over the glaze in MP-6.
170x103mm (300 x 300 DPI)

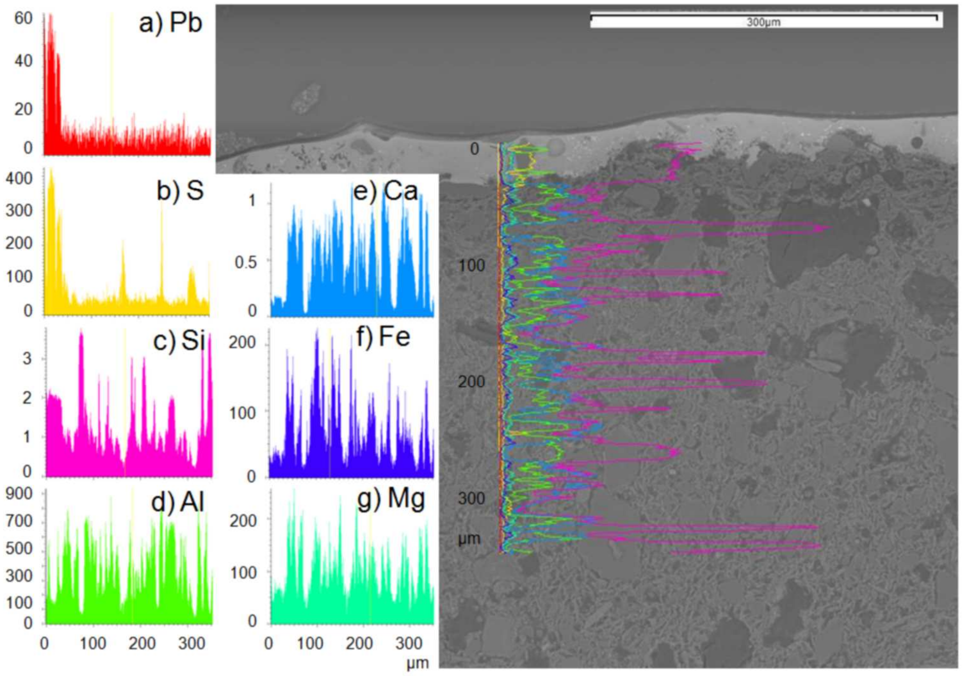

Figure 3: BSE images and EDX microanalysis of: a) Pb; b) S; c) Si; d) Al; e) Ca; f) Fe and g) Mg in the profile of MP-4 sample.
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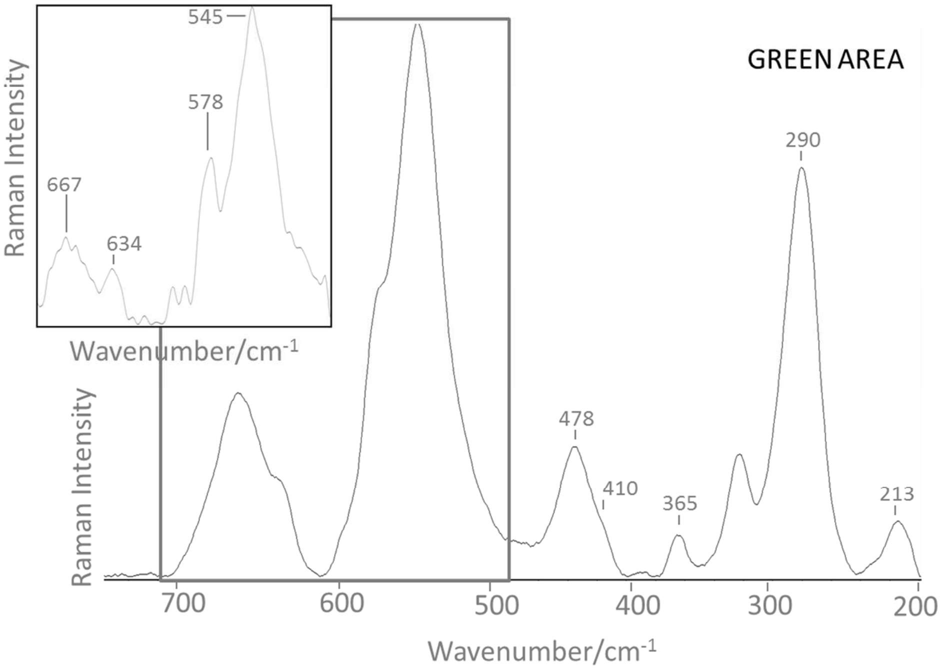

Figure 4. Representative Raman spectra of green glazed area in MP-2 sample from 200 to 700 cm-1. Inset: Raman spectrum deconvolution in the region between 500 and 700 cm-1. Spectrum was collected with a 50% LP, 100 acc, 3 s and an objective of 50X. For interpretation of the bands the reader is referred to the text of the article.
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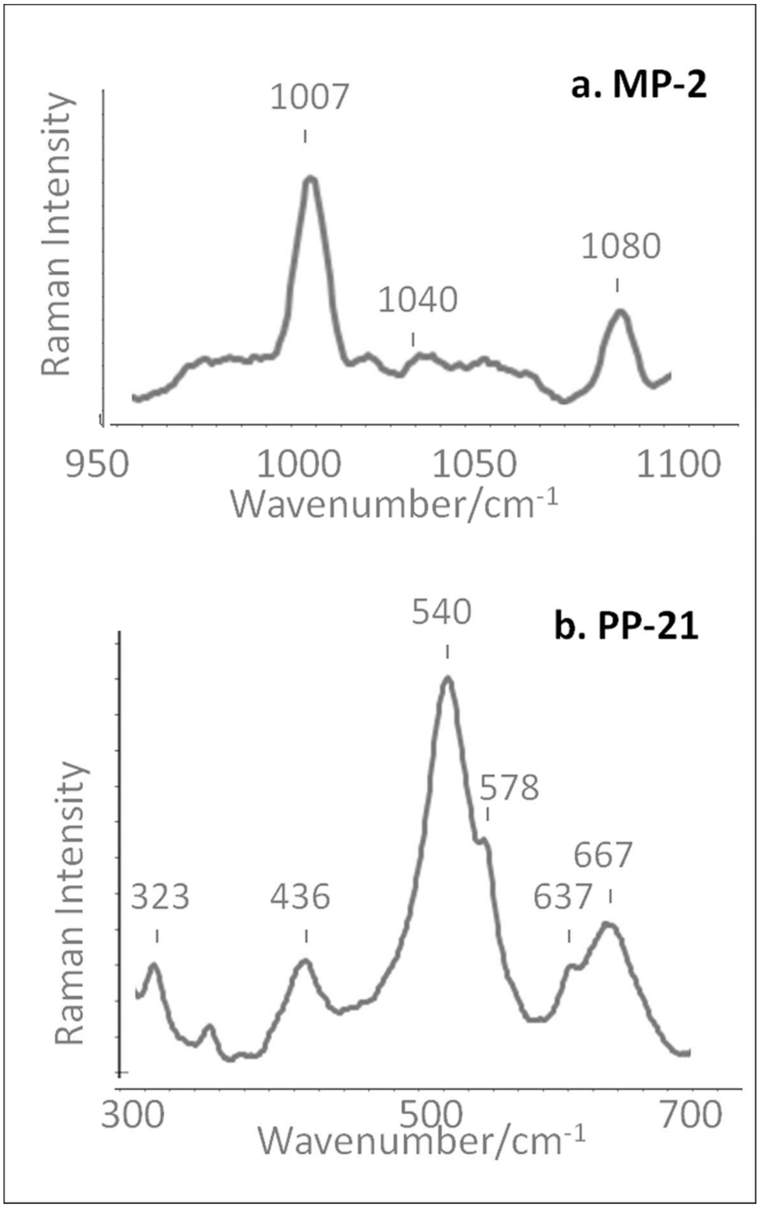

Figure 5. Raman spectra of black glazes of: a) MP-2 from 950 to 1100 cm-1; b) and PP-21 from 300 to 700 cm-1. Spectra were collected with 50% LP, 7 acc, 10 s and an objective of 50X. For interpretation of the bands the reader is referred to the text of the article.
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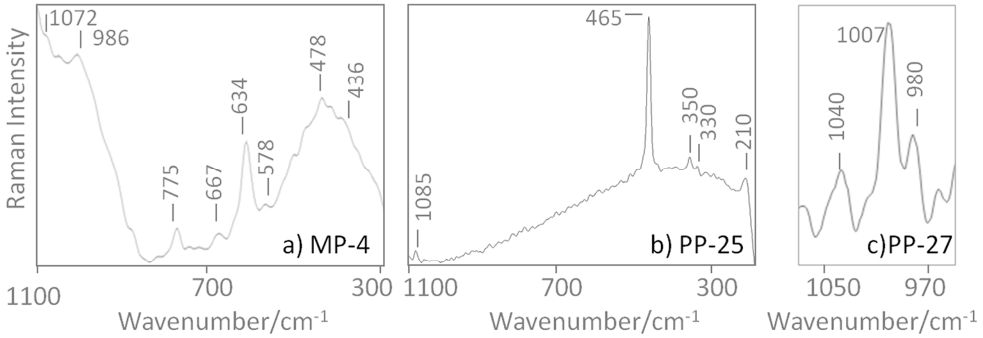

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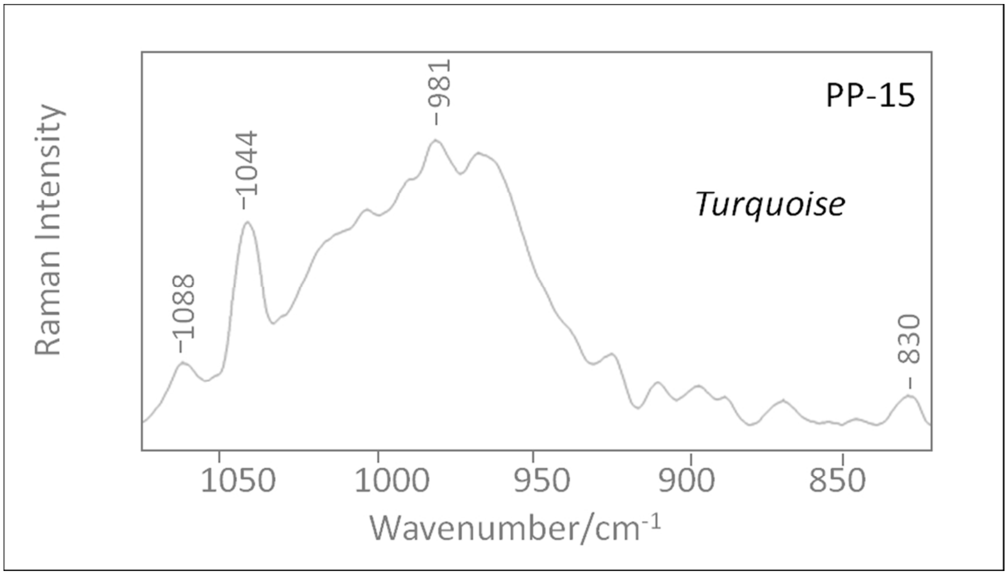

Figure 7. Deconvoluted Raman spectra for sample PP-15. Specific conditions working: 0.5% LP, 7 acc and 10 s with an objective of 50X. For interpretation of the bands the reader is referred to the text of the article.
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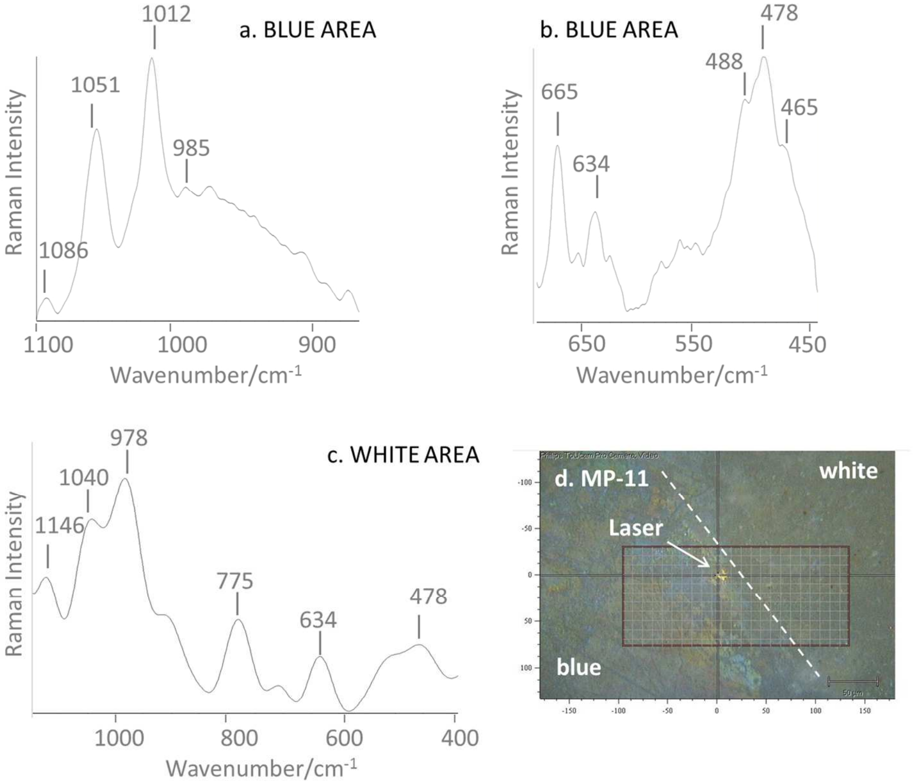

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254x205mm (200 x 200 DPI)