

Eleonora Odelli\*/\*\*/§, Giuseppe Tumbiolo\*, Federico Cantini\*,  
Anastasia Rousaki\*\*\*, Peter Vandenaabeele\*\*/\*\*\*, Simona Ranerj\*\*\*\*

\* Department of Civilization and Forms of Knowledge, University of Pisa, via dei Mille 19, 56126 Pisa, Italy.

\*\* Archaeometry Research Group, Department of Archaeology, Ghent University, Sint-Pietersnieuwstraat 35, 9000 Ghent, Belgium.

\*\*\* Raman Spectroscopy Research Group, Department of Chemistry, Ghent University, Krijgslaan 281, S12, 9000 Ghent, Belgium.

\*\*\*\* ICCOM-CNR, Via Moruzzi 1, 56124 Pisa, Italy.

§ Corresponding author (eleonora.odelli@phd.unipi.it).

## ITALIAN MAIOLICA AND SGRAFFITO POTTERY FROM VOLTERRA: A NON-INVASIVE AND NON-DESTRUCTIVE RAMAN AND XRF ANALYTICAL INVESTIGATION

**Abstract:** This paper reports on the preliminary results of the ongoing research on Medieval and Renaissance ceramic corpus from a cistern placed under the *Incontri-Viti* Palace in Volterra, Italy. The potteries found in the cistern are dated between 14<sup>th</sup> and 16<sup>th</sup> centuries; this period is marked by the transition between the late Middle-Ages and the Renaissance, and it is characterized by the introduction of technological and stylistic innovations in glazed ceramic productions. The work is part of a wider research program which involves the study of Volterra from the Late Antiquity to the Early Modern Age, through the detailed characterization of ceramic finds. Among samples from *Incontri-Viti* Palace, thirty-three fragments were selected for this investigation based on shape and decoration, including Maiolica and Graffita (or *Sgraffito*) productions. Micro-Raman and X-ray fluorescence analysis were carried out on both glaze and body, providing – for the first time – the non-invasive and non-destructive characterization of Maiolica and Graffita productions from Volterra. The investigation allowed the discrimination among studied productions based on glaze components and colouring agents, identifying one main compositional group credibly linked to local workshops. The analysis of ceramic paste enabled differentiating Italo Moresca among Maiolica productions for the higher tenor of Ca, which is a marker of the technological innovation optimised for obtaining a creamy coloured paste.

**Keywords:** Maiolica, Sgraffito, Raman Spectroscopy, XRF, Non-destructive analysis.

### 1. Introduction

Italian Maiolica, which appears in Tuscany in the first half of 13<sup>th</sup> century AD, is the first ceramic tableware since the disappearing of the African *Sigillata* (Grassi, 2010; Tite, 2009).

The main characteristic of Maiolica is the tin-opacified glaze, often decorated with the use of various colouring agents (Martin et al., 2018; Tite, 2009). This layer of tin-opacified glaze is applied on the cooked body. Afterwards, a coloured decoration could be applied on the unfired powdery glaze and then fired a second time (hence the term *bisquit*). The technique was introduced in Italy from the Arabic world, as tin-glazed pottery was first produced in Iran during the 8<sup>th</sup> or 9<sup>th</sup> century AD (Mason & Tite, 1997). The technique then spread to the Mediterranean area and to Italy, mainly thanks to commercial contacts, and flourished in various regions. Production of

Maiolica is attested in Tuscany, Sicily (Tite, 2009), Liguria (Capelli et al., 2007), Latium, Emilia-Romagna and Lombardia (Tite, 2009). As far as it concerns Tuscany, Pisa is attested as the first production centre of Maiolica in the region (Grassi 2010); the production propagated quickly in the overall regional context, as testified by well-known maiolica workshops in Siena, Volterra, Massa Marittima (Grassi, 2010), and Montelupo Fiorentino (Baldi, 2003).

The first manufacture circulating in Tuscany is known as Maiolica Arcaica, characterised by tin oxide (cassiterite) glazes and greenish-blue and brown colours. This kind of Maiolica usually exhibited a decorative motive only on one side or in a precise portion of the whole object. The part bearing the decoration was covered by tin opacified glaze, while the other plain parts were only covered by the glaze, without the presence of opacifier. Glass modifiers, as Pb oxide or feldspars, were added to lower the firing temperature (Colomban et al., 2006; Tite, 2009). Later, in the late 15<sup>th</sup> century, the slow decay of Maiolica and technological and stylistic innovations introduced the Graffita, even if the two productions usually co-existed for a long time. Graffita, also known as *sgraffito* slipware, is characterized by the application of a white engobe, decorated by engraving with various tools before the first firing phase, then covered by lead-rich glaze before a second firing phase. Sometimes, colours were added after the first firing phase to obtain polychrome effect (Brianese et al., 2008; Moore Valeri, 2004); in this production, the use of opacifiers is no longer needed. According to destructive archeometric analysis carried on Graffita from Castelfiorentino, the white engobe can be due to different clay mixtures which compositional features can help in tracing of raw materials sources (Brianese et al., 2008). The technological evolution in Maiolicas imprints the compositional features of glazes, namely fluxing, colouring agents colouring agents, and opacifiers, which characterization might allow discriminating different productions and tracing manufacturing changes in Italian Maiolica evolution (Brianese et al., 2008; Colomban et al., 2006; Hein & Kilikoglou, 2020; Tite, 2009).

Among the analytics for glazed ceramics (Cuomo di Caprio, 2007), various approaches are used for the direct analysis of works of art. X-ray fluorescence (XRF) is a well-established method in ancient ceramics' studies, mainly used for the geochemical characterization of ceramic paste in provenance issues (Bonizzoni et al., 2010; Hein & Kilikoglou, 2020) and for the compositional studies of glazes (Simsek et al., 2015). In the last decades, the developing of portable systems, as the ones used in this research, resulted in a wider use of this technique, also in the archaeology field. Even if the use of portable XRF determines various advantages, it must be kept in mind that those portable and completely non-destructive systems can suffer of some limitation comparing with destructive benchtop techniques, which have to be taken into account in order to provide improved results (Forster et al. 2011; Speakman et al. 2013). XRF data are usually treated with chemometric approaches (Bonizzoni et al., 2010; Ikeoka et al., 2018; Papachristodoulou et al., 2006; Van Pevenage et al., 2015; Forster et al., 2011), which represent a very useful tool in comparative studies when considering numerous samples and different variables. Raman spectroscopy is widely used in the analysis of cultural heritage objects, both as portable and benchtop instrumentation (Colomban et al., 2001, 2004, 2006; De Waal, 2009), especially in the analysis of glazes (Colomban et al., 2001, 2004, 2006), enabling the characterization of glass composition, colouring and opacifier agents in non-invasive way. In addition, micro-Raman spectrometers might provide insights on the mineralogical composition of ceramic paste, improving knowledge on firing environment and technological aspects (Legodi & De Waal, 2007; Odelli et al., 2021). The coupling of mobile XRF and Raman spectroscopy can provide complementary information and can help the archaeologists to answer questions about technological aspects and raw materials provenance in a direct and non-destructive way. As these techniques are becoming more and more widespread, it can be useful to incorporate such protocols in routine investigations, discriminating productions and characterising technological markers. Moreover, the characterization of reference groups of materials with certain provenance can offer interesting inputs for further comparative studies aiming to trace commercial networks and unveil the circulation of technological knowledge.

Portable XRF and Raman equipment have been used for studying Maiolica and Graffita productions from the *Incontri-Viti* Palace in Volterra. The main aim of this investigation was – for



fig. 1. Drawing from the archaeological survey of the cistern, finding place of the analysed materials (elaboration from Galluccio 1999, p. 86).

the first time – the non-destructive and non-invasive characterization of a reference group of local workshops, underlying the existing similarities and differences in the ceramic corpus, and creating reference materials for further studies. In addition, the results enabled enriching knowledge on glazed ceramics in mid-south Tuscany between the 14<sup>th</sup> and 16<sup>th</sup> centuries and trace chemical markers of the different studied productions.

### 1.1 Archaeological context and studied corpus

The *Incontri-Viti* Palace in Volterra, located on *Via dei Sarti*, was commissioned by the noble *Attilio Incontri* at the end of 16<sup>th</sup> century. According to *Fiumi*, who had the opportunity to see a series of arches and ancient openings on the ground floor, the building also incorporated pre-existing structures (Fiumi, 1983, p. 53). In 1850, a rich alabaster merchant, *Benedetto di Giuseppe Viti*, purchased the property and completed the construction of the palace (Calafati, 2013, p. 343.). We owe the discovery of the ceramic material to a member of the *Viti* family who is still the owner of the property. In the 1970s and the early 1980s, a renovation project in the cellar of the palace led to the discovery of two cisterns. The cistern that contained our materials is carved into the rock and has a bottle shape. It is about 4 meters deep, about 2 meters at the base and it shrinks to about 60 cm at the mouth (fig. 1). The inside is covered with blocks of stone and a layer of clay which function as a waterproofing layer. The structure of the cistern resembles that of the cisterns of the Acropolis, which dates to the 3<sup>rd</sup> century B.C.; this indicates the likely age of the site (Furiesi, 1999, pp. 31-32). According to its small size, it served a single house showing the urbanization of the area during Etruscan age. Unfortunately, the data in our possession do not allow us more insight into the development of the settlement in the area. Once the cistern had lost all its function, it was progressively filled with accumulation of material.

Among potteries from the cistern (fig. 2), thirty-three fragments were selected for this investigation (fig. 3, tab. 1). They are dated between the 14<sup>th</sup> and 16<sup>th</sup> centuries AD and include Maiolica production (specifically *Maiolica Arcaica* (*Marc*), *Zaffera a rilievo* (*Zaff*), *Italo Moresca* (*Im*)) and Graffita one, or *sgraffito* slipware (namely *Graffita a punta policroma* (*Gapp*), *Graffita a stecca* (*Gas*) and *Graffita a fondo ribassato* (*Gfr*)). In tab. 1 information about typologies, colour of paste, decorations and dating are summarised.

According to comparisons with other ceramics locally produced in Volterra, the *Maiolica Arcaica* from *Incontri-Viti* Palace is ascribable to a period between mid-14<sup>th</sup> century and the end of the 15<sup>th</sup> century. Both open forms (bowls) and closed forms (jugs) are attested, presenting the typical decorations of the ceramic class (chain motif or bands near the rim, stylized vegetal patterns or geometric patterns on the body) realized in green and brown (Berti et al., 1986; Pasquinelli, 1987). The ceramics are characterised by a tin-opacified glaze coating (on

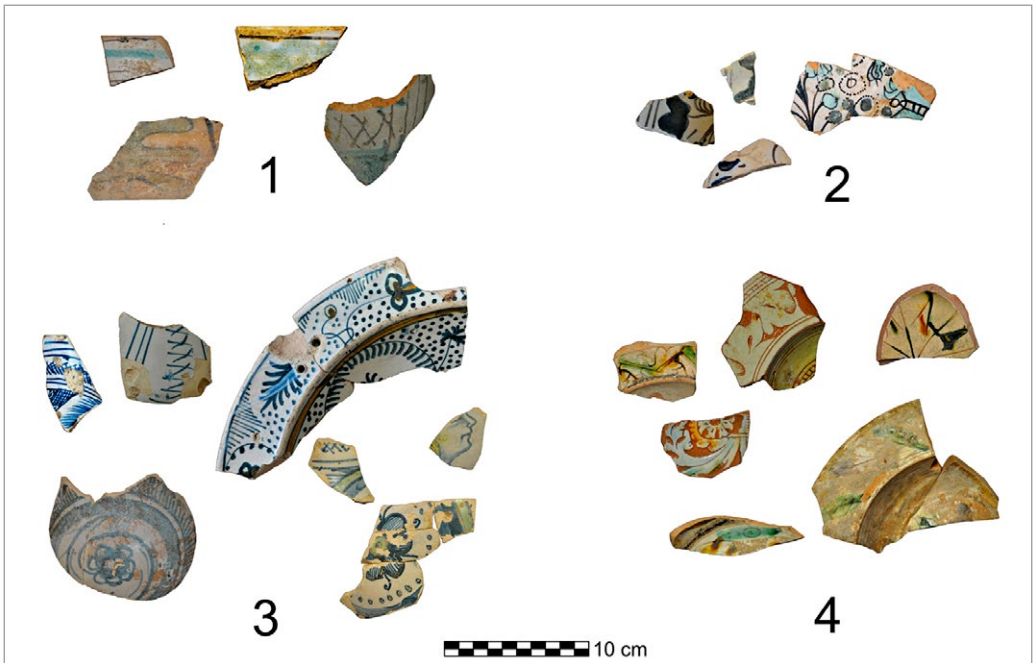


fig. 2. Fragments of pottery collected from Incontri-Viti Palace in Volterra: 1 Maiolica Arcaica, 2 Zaffera 3 Italo-Moresca, 4 pottery with engobe and Graffita. The material was recovered by Umberto Viti and then delivered to the Guarnacci Museum.

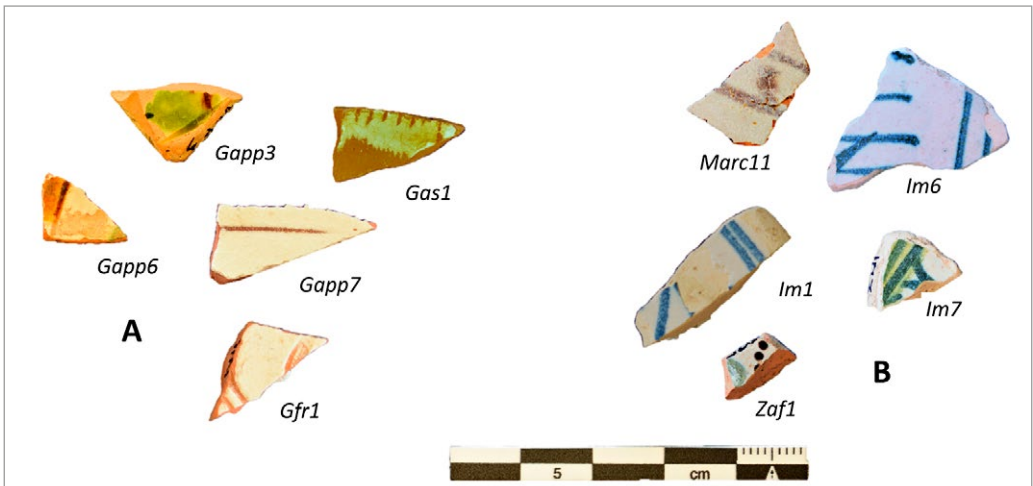


fig. 3. Some of the fragments selected for the archeometric analysis. All the samples' pictures are available in the MOD repository.

the interior of open forms and on the exterior of closed forms) with a lead-glaze coating on the rest of the surface. The *Zaffera a rilievo* found in the cistern dates to 14<sup>th</sup> century-early 15<sup>th</sup> century and it is known for its productions of in the Florentine area. In *Incontri-Viti* Palace, this ceramic class is attested both in the blue variant, exclusively jugs with drops or stylized vegetal pattern and in the green, blue, brown tricolor variant (only open forms with stylized and anthropomorphic patterns). The white glaze covers both the surfaces. Up to the literature,

	Name	Paste	Coating	Date	
Maiolica Arcaica	MARC1	5YR 6/8	White and brown//slip	XIV-XV cent AD	
	MARC2	2.5YR 6/8	White // slip	XIV-XV cent AD	
	MARC3	2.5YR 6/8	Whitish	XIV-XV cent AD	
	MARC4	2.5YR 6/8	White	XIV-XV cent AD	
	MARC5	2.5YR 7/6	White, ruined	XIV-XV cent AD	
	MARC6	2.5YR 6/8	Whitish and brown//slip	XIV-XV cent AD	
	MARC7	2.5YR 7/6	White, ruined// slip, ruined	XIV-XV cent AD	
	MARC8	5YR 6/8	White, ruined// slip	XIV-XV cent AD	
	MARC9	5YR 6/8	slip	XIV-XV cent AD	
	MARC11	2.5YR 5/8	white with brown stripes//slip	XIV-XV cent AD	
	MARC13	2.5YR 5/8	Whitish//slip	XIV-XV cent AD	
	Zaffera	ZAF1	5YR 8/4	White with blue and brown decoration// ruined	XIV-XV cent AD
		ZAF2	10YR 8/3	White and blue and brown lines//white	XIV-XV cent AD
ZAF3		5YR 7/8	Blue//white	XIV-XV cent AD	
Italo Moresca	IM1	7.5YR 8/6	White, blue lines//white	XV cent AD	
	IM2	2.5YR 8/4	White and brown line//white	XV cent AD	
	IM3	7.5YR 8/4	Blue lines on white	XV cent AD	
	IM4	7.5YR 8/4	Blue lines on white //white	XV cent AD	
	IM5	7.5YR 8/4	Blue lines on white //white	XV cent AD	
	IM6	7.5YR 8/4	Blue lines on white//white	XV cent AD	
	IM7	5YR 8/4	White, green, and light green lines//ruined	XV cent AD	
	IM8	7.5YR 8/4	White//ruined	XV cent AD	
Graffita a Punta Policroma	GAPP1	5YR 6/8	Green, white//white poor	XV-XVI cent AD	
	GAPP2	2.5YR 5/8	White	XV-XVI cent AD	
	GAPP3	5YR 6/8	Bright green, brown stripe//white	XV-XVI cent AD	
	GAPP4	5YR 6/8	Whitish, engraved stripe// glaze	XV-XVI cent AD	
	GAPP5	5YR 6/8	Green, white// glazed, ruined	XV-XVI cent AD	
	GAPP6	5YR 6/8	Light blue, white, brown//white ruined	XV-XVI cent AD	
	GAPP7	2.5YR 4/8	White, engraved line// white	XV-XVI cent AD	
	GAPP8	7.5YR 8/4	White with spots// white	XV-XVI cent AD	
Graffita a Stecca	GAS1	2.5YR 8/4	Whitish and ochre//ruined	XV-XVI cent AD	
	GAS2	5YR 7/8	White ruined	XV-XVI cent AD	
Graffita a Fondo Ribassato	GFR1	5YR 7/8	White engraved// thin whitish	XV-XVI cent AD	

tab. 1. Description of the analysed ceramic corpus.

the main new element that characterizes the *Zaffera a rilievo*, when compared to previous late Middle Age productions (*Maiolica Arcaica*), is the introduction of cobalt-blue in the decoration (Berti, 1997, pp. 115-117; Moore Valeri, 1984). The *Italo Moresca* is well documented among from *Incontri-Viti* Palace fragments, including different potsherds ascribable to both the first and the second production phase of this ceramic class (Berti & Pasquinelli, 1984, pp. 26-28). It is very popular in the mid-Valdarno area, where it is mainly produced in Montelupo, Bacchereto and Florence workshops (Perrazzi & Poggesi, 2011). The first phase of production (from the first half of the 15<sup>th</sup> century) includes open forms (bowls) and closed forms (jugs) entirely covered by a white glaze and decorated with geometric or floral patterns which are exclusively blue.



Some potsherds which are covered by a white tin-glaze over the entire surface with polychrome decorations in blue, yellow, green, and brown belong to the second phase of production in the second half of the 15<sup>th</sup> century (Berti, 1997, pp. 185-186). From a technical point of view, the *Italo moresca* represents a change compared to the old method of production, especially as concerns the whitening of the body fabric (Berti & Pasquinelli, 1984, p. 26.).

The *Graffita a punta*, *a stecca* and *a fondo ribassato* ceramics from Pozzo-Viti (open forms and one closed form) refer to a chronological period between the late 15<sup>th</sup> century and the beginning of the 16<sup>th</sup> century and it is most likely a local production (Pasquinelli, 1987, pp. 58-62; Wentkowska, 2004, pp. 187-193). Compared to the other classes, they present both technical and aesthetic innovations. Indeed, the ceramic body no longer displays a white-glaze (partially nor entirely), but rather a white engobe later decorated with incisions (realized with a pointed or *a stecca* tool) and covered with a lead-glaze. The frequent decorative patterns are stylized vegetal elements enriched with green and yellow-brown pigmentation.

## 2. Methods

### 2.1 Raman Spectroscopy

Micro-Raman spectra have been acquired by a Bruker Senterra R200-L spectrometer equipped with an Olympus microscope with 5×, 20×, 50× and 100×, and 785nm and 532nm excitation sources. 532nm line and 20x magnification (obtaining a spot size of about 10μm) were used for the analysis. Spectral ranges chosen were 60-1560cm<sup>-1</sup> or 60-2750cm<sup>-1</sup> while the spectral resolution was set at 3-5cm<sup>-1</sup>. The laser power was kept at 0.11 mW; time and acquisitions varied. Interpretation of the data has been obtained with Grams and Opus software. Baseline correction of the glass spectra has been performed with a point subtraction in the region of 200-1200 cm<sup>-1</sup> according to Colomban et al. (2006).

### 2.2 X-Ray Fluorescence (XRF)

X-ray fluorescence analysis have been performed by using two instruments. Preliminary data on a selection of samples have been collected with an Olympus™ Innov-X Delta Premium hXRF spectrometer, a handheld instrument, equipped with a Rh X-ray tube. It was possible to record both the low-Z (Mg to Mn) and high-Z (V and up) elements, by applying a 10 kV and a 40 kV voltage, respectively. Measuring time was set at 300 sec.

In depth analysis on all the ceramic corpus, both on ceramic paste and glazes, have been performed with a Bruker Elio portable spectrometer. Voltage was set at 30 kV while current at 90 μA (Odelli et al., 2020). On the glazes, almost two measurements were collected on each colour (acquisition time 180 s), while on ceramic past almost three measurement points were analysed to avoid errors due to the possible inhomogeneity of the matrix (Forster et al., 2011) (90 s acquisition time).

Post processing of the data was performed by AXIL (analysis of X-ray spectra by iterative least squares software) (Vekemans et al., 1994) and by Elio Bruker ® proprietary software.

Statistical principal component analysis (PCA) was performed on XRF spectra on peak areas. Data have been centred and scaled before performing the PCA with CAT (Chemometric Agile Tool), an additional package to R software environment.

## 3. Results and discussion

### 3.1 Glazes

Raman spectroscopy of glass and glazes usually gives back two broad bands centred around 1000 cm<sup>-1</sup> and 500 cm<sup>-1</sup> and attributed to Si-O stretching and bending modes, respectively (Colomban et al., 2006). The shape and dimension of those two bands is strictly correlated

with the Si-O glass network, in particular with the firing conditions and the presence of glass modifiers (Colomban et al., 2003, 2006).

In the present investigation Raman analysis revealed – in almost all Maiolica productions (*Maiolica Arcaica*, *Zaffera* and *Italo Moresca*) – the presence of cassiterite ( $\text{SnO}_2$ , Raman bands at 778, 635  $\text{cm}^{-1}$ ) which was used as opacifier (Ricciardi et al., 2009; Zaho et al., 2013), except for samples *Marc5* (no glass still present on the surface) and *Marc 9* (transparent, only the glassy part was found) (fig. 3). As expected from our knowledge on manufacture process, cassiterite was not detected in Graffita production, except for *Gapp8* fragment. The occurrence of cassiterite in sample *Gapp8* could be attributable to possible contamination in the workshop, producing also Maiolica in a moment of transition between the two productions. Diopside ( $\text{CaMgSi}_2\text{O}_6$ , Raman bands at 1013, 668, 391, 324  $\text{cm}^{-1}$ ) was also frequently found only in Maiolica Arcaica (samples *Marc1*, *Marc2*, *Marc3*, *Marc6*, *Marc7*, *Marc8*, *Marc9*, *Marc13*) and Italo Moresca productions (*Im1*, *Im3*, *Im4*, *Im8*) (fig. S1) while it was not detected in Zaffera or Graffita. The presence of diopside could be due to glass devitrification processes, during the cooling of the glaze (Pawłkiewicz et al., 2017; Sorli et al., 2004). The presence of diopside in Maiolica glazes has been reported in previous studies, also in the original Maiolica from the Arabic world (Mason & Tite, 1997). A mix of feldspars ( $\text{X}(\text{Al}, \text{Si})_4\text{O}_8$ , Raman bands at 510-514, 473-463  $\text{cm}^{-1}$ ) quartz ( $\text{SiO}_2$ , Raman bands at 465, 356, 206, 129  $\text{cm}^{-1}$ ) and anatase ( $\text{TiO}_2$ , Raman bands at 141, 399, 514  $\text{cm}^{-1}$ ) were identified in the surface of Graffita production, regardless the ceramic classes and attributable to the white engobe composition (fig. S2); as for anatase, it is an accessory mineral usually present in white kaolinitic clays.

The typical glass fingerprint has been detected in all studied samples, except for few fragments due to the intense degradation of the original glaze which is no more recognizable (*Im8*, *Marc5* and *Marc7*). Overall, the Raman fingerprint of glass is quite uniform, except for Zaffera (*Zaf1* and *Zaf2*; fig. 3), which exhibit a different Raman signal in the stretching region, which splits in two bands clearly visible. This is characteristic to the  $\text{Na}_2\text{O}$ -rich glass or  $\text{Na}_2\text{O}$ -Pb glass, according to Colomban et al. (2006).

The  $A_{500}/A_{1000}$  ratio, namely the polymerization index ( $I_p$ ), is the ratio between the areas of the two main bands of the glass and is strongly correlated with the glass composition and the firing temperature (Colomban et al., 2006, 2003). The polymerization index is generally varying with the glass composition, particularly with the Al/Si rate and the presence of glass modifiers; thus, it has been used to discriminate productions and define chronologies (Colomban et al., 2006). Polymerization Index was calculated, and it was averagely 0.75 in Graffita and 0.8 in Maiolica. In all the studied samples the  $A_{500}/A_{1000}$  ratio is lower than 1.3, suggesting temperatures between 600 and 1000°C during the glaze firing phase. According to empirical attribution based on Polymerization Index (Colomban et al., 2006), both Graffita and Maiolica samples can be classified as lead-based silicates glass processed at medium temperature (around 800°C), as  $A_{500}/A_{1000}$  ratio is in the range from 0.5 to 0.8 (Colomban et al., 2006). This attribution confirms the previous results. Nevertheless, for Graffita production and Maiolica production a slight difference in  $A_{500}/A_{1000}$  ratio can be observed, as evidenced by the student t test ( $p < 0.05$ ) where *Gapp8* is excluded from the analysis due to its borderline features (contamination with cassiterite).

X-ray fluorescence analysis enabled detecting Sn in all Maiolica samples (*Maiolica Arcaica*, *Zaffera* and *Italo Moresca*) and in sample *Gapp 8*, related to the identification of cassiterite with Raman spectroscopy. Lead has been detected on all studied samples; however, Pb tenors differ among different productions.

Principal Component Analysis was performed on the XRF fitted peak areas to highlight possible compositional differences among all the studied productions; Sn was excluded, as cassiterite is the known discrimination criteria among Maiolica and Graffita productions (fig. 4). The PCA results suggest that Graffita (*Gapp. Gas, Gfr*) and Maiolica (*Marc, Zaf, Im*) can be well distinguished, also based on Pb tenors, as revealed by the loading plot. Glazes in Graffita production exhibit quite homogenous composition; among Maiolica productions *Italo Moresca* and *Zaffera* seems well grouped for their different Si and Fe tenor, respectively, while Maiolica Arcaica samples are more scattered within the two compositional fields.

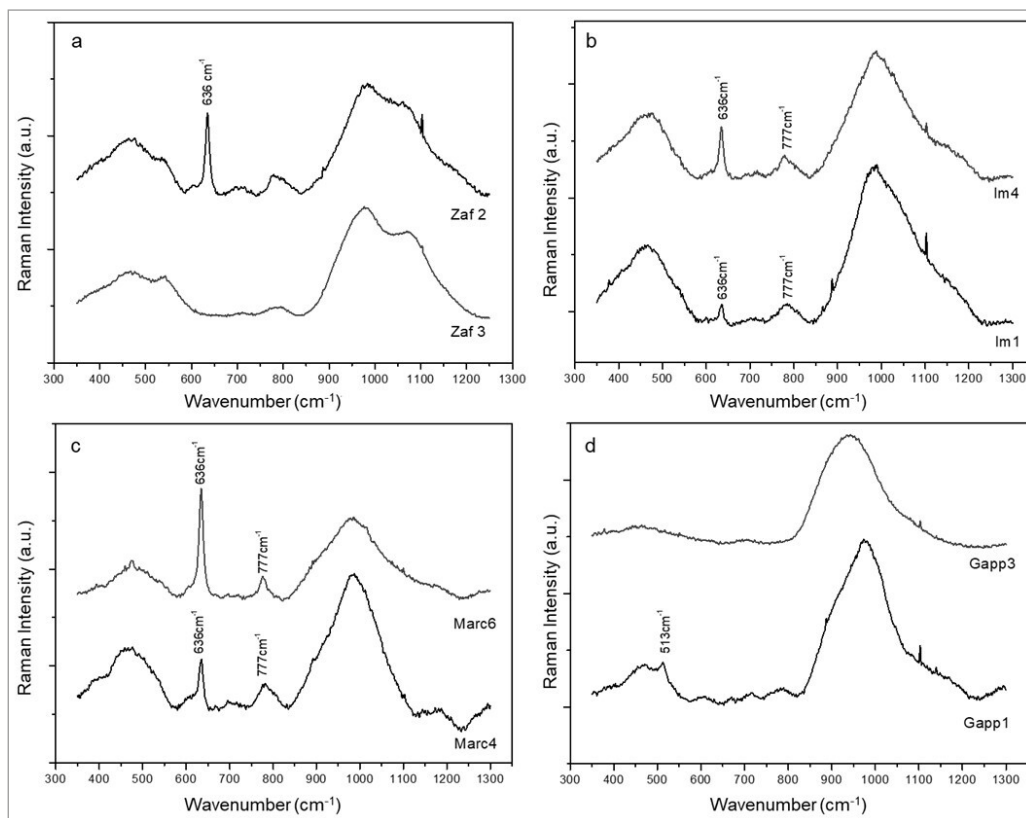


fig. 4. Raman spectra collected on glazes and main spectroscopic features, as representative of the different productions. (a) Zaffera samples, characterised by cassiterite (at  $636\text{ cm}^{-1}$ ) and the split of stretching mode in two bands, typical of  $\text{PbO}+\text{Na}_2\text{O}$  glasses. (b) Italo Moresca and (c) Maiolica Arcaica, characterised by cassiterite signal at  $777$  and  $638\text{ cm}^{-1}$ ; (d) Graffita samples, where the band at  $513\text{ cm}^{-1}$  from engobe is visible. 5 points baseline subtraction has been performed on raw spectra to better visualize the two broad bands. Points were set around  $200$ ,  $500$ ,  $700$ ,  $850$  and  $1200\text{ cm}^{-1}$ .

### 3.2 Colouring agents

Among the studied samples, coloured decorations made by blue, greenish blue, brown and green were observed and analysed (tab. 2).

Blue colour is more frequently attested in Maiolica production, while green in Graffita production (see tab. 1). It was usually obtained by using cobalt (bright blue) or copper (greenish blue) dispersed ions (Lightbown and Caiger-Smith, 2007; Tite, 2009). Raman spectroscopy cannot provide useful information on blue decorations, as it is a molecular spectroscopic technique. XRF analysis detected both Co and Cu in Maiolica samples, except for *Zaf1* and *Gapp6* where only Cu is detected; in the majority of the cases, a mix of cobalt and copper was likely used to obtain the blue colour.

Brown colour was observed and analysed on both Maiolica (*Zaf1*, *Zaf2*, *Im2*, *Marc1*, *Marc11*) and Graffita (*Gapp3*, *Gapp6*) productions. Raman spectra collected on brown decoration on Maiolica samples (*Zaf1* and *Im2*) revealed the presence of a broad band centred around  $632\text{ cm}^{-1}$ , which can be attributed to a manganese oxide (Angeli et al., 2018, 2019; Bersani, 2010). In Graffita samples (*Gapp6*), haematite ( $\text{Fe}_2\text{O}_3$ , typical Raman bands at  $1319$ ;  $411$ ;  $294$ ;  $246$ ;  $227\text{ cm}^{-1}$ ) was also detected on brown decoration (Colomban, 2017; Liou, 2011). XRF analysis revealed the presence of Mn and Fe on both productions, in accordance with the compounds



detected by Raman spectroscopy. It is noteworthy that brown decorations in Graffita are characterised by higher Fe tenors and lower Mn ones than in Maiolica.

Finally, green decorations were prevalent in Graffita production (especially in *G. punta policroma*, *Gapp1*, 3, and 5 samples) and in *Italo Moresca* (*Im7* sample). According to Piccolpasso (Lightbown, Caiger-Smith, 2007; Tite, 2009), green colour could be due to “burnt copper” also called “*ramina*” or a mix of copper, antimony, and lead oxides, producing a green colour without bluish hue. Both procedures are obtained by dispersing ions in the glass matrix, and therefore cannot be detected by Raman spectroscopy (Colomban et al., 2001). In *Italo Moresca* (*Im7*) Raman analysis on green decoration revealed the presence of a graphite type, carbon structure with Raman bands centered at 1577, 1348  $\text{cm}^{-1}$ ; the use of carbonaceous matter including graphite is attested since prehistory to obtain dark hues on pottery surfaces. XRF analysis on green decorations in Graffita revealed the presence of Cu, while no Sb detected, suggesting the use of “*ramina*” for obtaining the hue. In *Italo Moresca* Cu and Co was detected, which would indicate a specific recipe, encompassing also the use of graphite to darken the green hue (Coccatto et al., 2015).

### 3.3 Ceramic paste

In archaeological ceramics micro-Raman spectroscopy can be very useful to investigate firing conditions (Barillano et al., 2014; Perez et al., 2004; Sendova et al., 2015), as the presence of both hematite ( $\text{Fe}_2\text{O}_3$ , with characteristic peaks around 1326, 293, 228  $\text{cm}^{-1}$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ , broad signal centred around 669  $\text{cm}^{-1}$ ) can indicate the firing atmosphere, namely oxidizing or reducing respectively. In some cases, both hematite and magnetite can be observed, credibly due to changes of atmosphere occurred in the furnace (Barillano et al., 2014; Medeghini et al., 2014). Samples collected from *Incontri-Viti* Palace exhibit both hematite and magnetite signals,

	Sample	Colour	Elements	
Maiolica	Im1	Blue	Co; Cu	
	Im2	Brown	Mn; Fe	
	Im3	Blue	Co; Cu	
	Im4	Blue	Co; Cu	
	Im5	Blue	Co; Cu	
	Im6	Blue	Co; Cu	
	Im7	Green	Co; Cu	
	Zaf1	Blue	Co; Cu	
	Zaf1	Brown	Mn; Fe	
	Zaf2	Blue	Co; Cu	
	Zaf2	Brown	Mn; Fe	
Marc	Zaf3	Blue	Co; Cu	
	Marc1	Brown	Mn; Fe	
	Marc2	Blue	Co; Cu	
	Marc6	Brown	Mn; Fe	
	Marc11	Brown	Mn; Fe	
	Graffita	Gapp1	Green	Cu
		Gapp3	Green	Cu
Gapp3		Brown	Mn; Fe	
Gapp5		Green	Cu	
Gapp6		Blue	Cu	
Gapp6		Brown	Mn; Fe	

tab. 2. Summary of the colouring agents detected thanks to XRF.

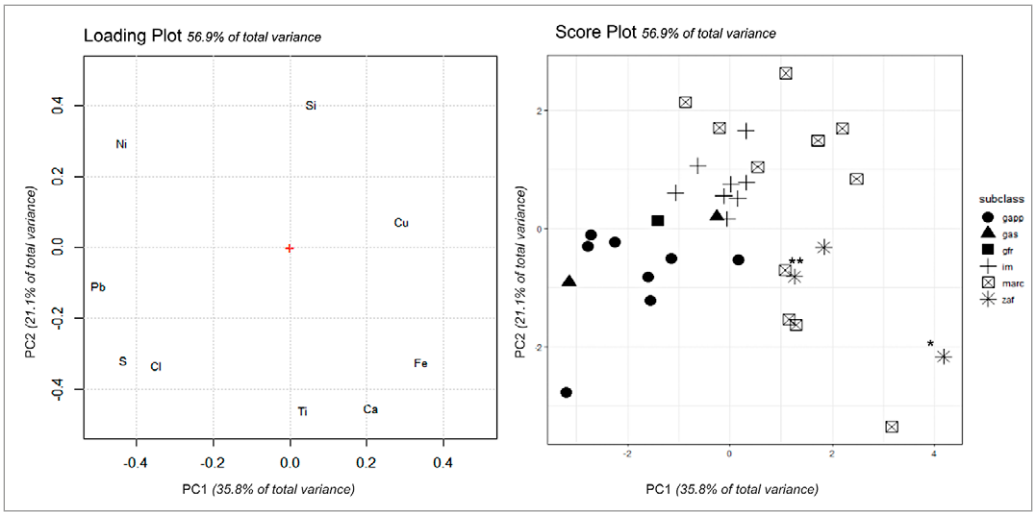


fig. 5. Principal component analysis on glaze composition. Data were centred and scaled before applying PCA. Graffita (full) and Maiolica (empty) samples are well separated. Among Maiolica, Italo Moresca and Zaffera seems to have a slightly different glaze composition, while Maiolica Arcaica is scattered. Data have been collected on the white surfaces, except for blue-Zaf3 (\*) and colourless-Marc9 (\*\*) missing white areas.

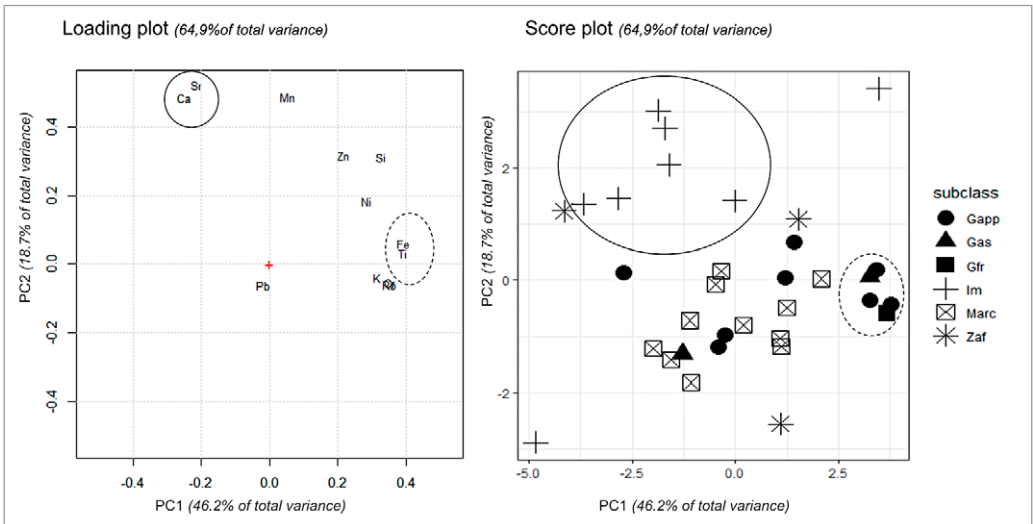


fig. 6. Scores and loading plots of XRF data collected on ceramic paste.

but the uniform colour without bi-fabric and the high degree of specialization, suggests a homogeneous oxidizing atmosphere, while magnetite is probably from the raw materials.

XRF data collected on ceramic paste revealed a quite homogenous composition among the studied productions. PCA performed on XRF peak areas did not evidence clear chemical clusters, except for Italo Moresca, which is discriminated for its Ca and Sr contents (see Loading plot), and few Graffita samples characterised by higher Fe tenors than other productions (fig. 5). Most of the samples classified as Maiolica Arcaica and some of the Graffita samples overlap, representing a third group where no clear differences between Graffita and Maiolica Arcaica can be remarked. This group could be recognized as a local production where similar sources were exploited through time. For the other two groups, the Ca and Sr in Italo Moresca

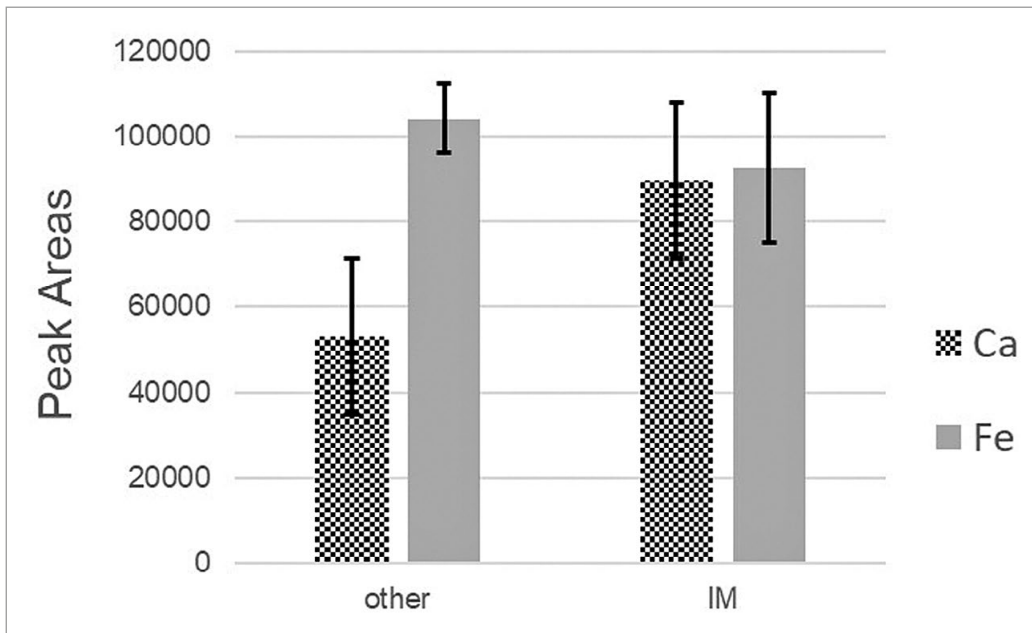


fig. 7. Area counts of Ca and Fe peaks evidencing differences between Italo Moresca and the other productions.

can be interpreted as a technical feature rather than a provenance marker; in fact, it is known that calcium carbonate was added to the raw material to better contrast the iron colouring effect (Berti Pasquinelli, 1984, p. 26.; Molera et al., 1998; Tite, 2009). Lighter ceramic pastes were easier to cover in white without spoiling the desired hue. For Graffita production a light paste was no longer required, as the red paste makes clearer the engraving under the engobe.

Since the PCA on XRF data pointed out the importance of Ca and Fe in the ceramic paste, a t student test was then performed on the two elements responsible for the ceramic paste colour; looking at *Italo Moresca* versus other samples, a significative difference in Ca ( $p < 0.01$ ) can be observed, while there is no difference in Fe contribution ( $p > 0.1$ ) (fig.6). This can point out to an intentional addition of Ca-rich additives to the clay pastes where Fe tenors are quite similar in the overall studied productions.

#### 4. Conclusions

- The investigation on Maiolica and Graffita ceramics from *Incontri-Viti* Palace in Volterra (central Italy) enabled providing – for the first time – the non-invasive and non-destructive characterization of these productions, constituting a reference group.
- Maiolica is characterised by cassiterite, while Sn was not identified in Graffita glazes. In Graffita, the white engobe is characterised by mix of feldspars, quartz and anatase, which find comparison with similar productions from Castelfiorentino; nevertheless, raw materials sources were still not identified. Thus, it is possible to propose a common clay source – probably kaolinitic – for making the engobe, which futures studies would locate and identify.
- Among Maiolica productions, diopside has been identified in *Maiolica Arcaica* and *Italo Moresca*, revealing the glass devitrification during cooling; it was not detected in *Zaffera* samples.

- *Zaffera* samples exhibit a specific glass fingerprints, which find comparison with soda-lead-rich glass (PbO+Na<sub>2</sub>O glass; Colomban, 2006).
- The polymerization index ( $A_{500}/A_{1000}$ ) overall suggest temperature between 600-1000 °C for the glaze firing phase; nevertheless,  $A_{500}/A_{1000}$  ratio further helps characterizing glazes of Maiolica and Graffita (lead-based silicate glass) productions.
- Apart from Sn, chemical data collected on glazes and processed by statistical methods enable discriminating Graffita and Maiolica productions, claiming for technological differences which imprints the overall chemical composition of the glaze. Although Pb is present in all glazes, it can be noticed that it is more correlated with samples belonging to Graffita.
- Based on Raman spectroscopy and XRF, coloring agents were due as following: blue in Maiolica is due to copper and cobalt, except for samples *Zaf1* and *Gapp6* where only copper was found; brown is due to iron-manganese oxides, with different relative amount in iron and manganese as per Maiolica and Graffita; green decoration, frequently found in Graffita, is due to copper, while in the only green Maiolica sample (*Im7*) cobalt, together with copper was found. Moreover, carbon black was also detected by Raman spectroscopy in *Italo Moresca* green decoration, probably mixed to the ingredients to deepen the color hue.
- Raman analysis on the ceramic body revealed the presence of both hematite and magnetite, claiming for an oxidizing atmosphere during the whole firing process together with the presence of magnetite in the raw materials.
- Chemical analysis on ceramic paste did not reveal clear compositional groups, likely indicating a quite homogenous local production exploiting the same raw materials for the manufacturing of ceramic bodies. Exceptions seem to mark technological fingerprint; in fact, *Italo Moresca* samples are very well grouped due to the higher amount of calcium, and few Graffita samples are characterized by higher iron tenors.
- The applied physicochemical analysis successfully provided compositional markers which can be determined by a completely non-destructive and non-invasive approach.
- Raw data collected in the frame of this study are available in form of datasets for future research, to facilitate comparative studies within the glazed ceramics production in central Italy and promoting the use of portable and non-invasive methods for provenance and technological investigations on ancient ceramics.

## Acknowledgements

A.R. wishes to thank FWO-Vlaanderen for her postdoctoral grant (12X1919N).

E.O. acknowledges the Tuscany Region for her PhD fellowship under the project *Giovani Sì*, Pegaso.

The study of the ceramics found in *Incontri-Viti* palace is part of a larger project involving the city of Volterra. The activity began in 2017 during the “Laboratorio Universitario Volterrano” a week of study promoted by the University of Pisa and held by the professor Federico Cantini for the teaching of Christian and Medieval Archaeology, and made possible by the willingness to study materials given by the Soprintendenza Archeologica della Toscana and the Guarnacci Museum (Cantini et al. 2018).

## References

Angeli, L., Brunetti, A., Legnaioli, S., Fabbri, C., Campanella, B., Lorenzetti, G., Pagnotta S., Poggialini, F., Palleschi, V., & Radi, G. (2019). Analysis of the middle Neolithic trichrome pottery: characterization of the decoration using X-Ray fluorescence and Raman spectroscopy. *Journal of Archaeological Science: Reports*, 24, 192-197.

- Angeli, L., Legnaioli, S., Fabbri, C., Grifoni, E., Lorenzetti, G., Guilaine, J., Palleschi, V., & Radi, G. (2018). Analysis of Serra d'Alto figuline pottery (Matera, Italy): Characterization of the dark decorations using XRF. *Microchemical Journal*, *137*, 174-180.
- Ballirano, P., De Vito, C., Medeghini, L., Mignardi, S., Ferrini, V., Matthiae, P., Bersani D., & Lottici, P. P. (2014). A combined use of optical microscopy, X-ray powder diffraction and micro-Raman spectroscopy for the characterization of ancient ceramic from Ebla (Syria). *Ceramics International*, *40*(10), 16409-16419.
- Bersani, D., Lottici, P. P., Virgenti, S., Sodo, A., Malvestuto, G., Botti, A., Salvioli-Mariani, E., Tribaudino, M., Ospitali F., & Catarsi, M. (2010). Multi-technique investigation of archaeological pottery from Parma (Italy). *Journal of Raman Spectroscopy*, *41*(11), 1556-1561.
- Berti F. (1997). *Storia della ceramica di Montelupo. Uomini e fornaci in un centro di produzione dal XIV al XVIII. Volume II, Le ceramiche da mensa dal 1480 alla fine del XVIII secolo*. Aedo.
- Berti, G., Cappelli, L., & Francovich, R. (1986). La maiolica arcaica in Toscana. In *La ceramica medievale nel Mediterraneo occidentale. Atti del III Congresso Internazionale organizzato dal Dipartimento di Archeologia e Storia delle Arti dell'Università degli Studi di Siena e dal Museo delle Ceramiche di Faenza (Siena-Faenza 1984)* (pp. 483-510).
- Berti F., & Pasquinelli G. (1984), *Antiche maioliche di Montelupo, secoli XIV-XVIII, Montelupo*. Bandecchi & Vivaldi Pontedera.
- Bonizzoni, L., Galli, A., & Milazzo, M. (2010). XRF analysis without sampling of Etruscan depurata pottery for provenance classification. *X-Ray Spectrometry*, *39*(5), 346-352.
- Calafati M. (2013). «Tanta gran machina di pietre» Alfonso Parigi il giovane e palazzo Incontri (ora Viti) a Volterra, *Bollettino della Società di studi Fiorentini*, *21*, 338-48.
- Cantini F., Fatighenti B., & Tumbiolo G. (2018). Ceramiche e merci a Volterra tra la tarda antichità e il Cinquecento. Note preliminari di uno studio in corso, *Quaderno del Laboratorio Universitario Volterrano*, *XVIII*, 75-82.
- Capelli, C., Cabella, R., & Waksman, S.Y. (2007). Archaeometric investigation on 13th century glazed and slipped pottery found in Liguria and Provence. In S.Y. Waksman (eds.), *Archaeometric and Archaeological Approaches to Ceramics* (vol. 1691, pp. 149-154). BAR Publishing.
- Coccatto, A., Jehlicka, J., Moens, L., & Vandenabeele, P. (2015). Raman spectroscopy for the investigation of carbon-based black pigments. *Journal of Raman Spectroscopy*, *46*(10), 1003-1015.
- Colomban, P., Sagon, G., & Faurel, X. (2001). Differentiation of antique ceramics from the Raman spectra of their coloured glazes and paintings. *Journal of Raman Spectroscopy*, *32*(5), 351-360.
- Colomban, P., March, G., Mazerolles, L., Karmous, T., Ayed, N., Ennabli, A., & Slim, H. (2003). Raman identification of materials used for jewellery and mosaics in Ifriqiya. *Journal of Raman Spectroscopy*, *34*(3), 205-213.
- Colomban, P., Milande, V., & Lucas, H. (2004). On-site Raman analysis of Medici porcelain. *Journal of Raman Spectroscopy*, *35*(1), 68-72.
- Colomban, P., Tournié, A., & Bellot-Gurlet, L. (2006). Raman identification of glassy silicates used in ceramics, glass and jewellery: a tentative differentiation guide. *Journal of Raman Spectroscopy*, *37*(8), 841-852.
- Colomban, P., Zhang, Y., & Zhao, B. (2017). Non-invasive Raman analyses of Chinese huafalang and related porcelain wares. Searching for evidence for innovative pigment technologies. *Ceramics International*, *43*(15), 12079-12088.
- Costa, M., Rousaki, A., Lycke, S., Saelens, D., Tack, P., Sánchez, A., Tuñón, J., Ceprián, B., Amate, P., Manuel Montejo, M., & Vandenabeele, P. (2020). Comparison of the performance of two handheld XRF instruments in the study of Roman tesserae from Cástulo (Linares, Spain). *The European Physical Journal Plus*, *135*(8), 1-17.
- Cuomo di Caprio, N. (2007) *Ceramica in Archeologia 2. Antiche tecniche di lavorazione e moderni metodi di indagine*. L'Erma di Bretschneider.
- De Waal, D. (2009). Micro-Raman and portable Raman spectroscopic investigation of blue pigments in selected Delft plates (17-20th Century). *Journal of Raman Spectroscopy*, *40*(12), 2162-2170.
- Fiumi, E. (1983), *Volterra e San Gimignano nel Medioevo*, Cooperativa Nuovi Quaderni.
- Forster, N., Grave, P., Vickery, N., & Kealhofer, L. (2011). Non-destructive analysis using PXRF: methodology and application to archaeological ceramics. *X-Ray Spectrometry*, *40*(5), 389-398.
- Furiosi A. (1999). *L'acqua a Volterra. Storia dell'approvvigionamento idrico della città*. NIE.
- Galluccio F. (1999). Volterra etrusca alla luce delle nuove scoperte, *Opuscula Romana: Annual of the Swedish Institute in Rome*, *24*, 83-98.
- Grassi, F. (2010). *La ceramica, l'alimentazione, l'artigianato e le vie di commercio tra VIII e XIV secolo. Il caso della Toscana meridionale*. BAR Publishing.
- Hein, A., & Kilikoglou, V. (2020). Ceramic raw materials: how to recognize them and locate the supply basins: chemistry. *Archaeological and Anthropological Sciences*, *12*(8), 1-17.
- Ikeoka, R. A., Appoloni, C. R., Rizzutto, M. A., & Bandeira, A. M. (2018). Computed Radiography, PIXE and XRF analysis of pre-colonial pottery from Maranhão, Brazil. *Microchemical Journal*, *138*, 384-389.



- Lightbown, R., & Caiger-Smith, A. (2007). *Cipriano Piccolpasso's The Three Books of the Potter's Art*. Editions la revue de la ceramique et du verre.
- Liou, Y. S., Chang Liu, Y., & Huang, H. Y. (2011). Micro-Raman spectroscopic study of cord-marked pottery decorated with red coatings from Taiwan, ca 2600-1700 BC. *Journal of Raman Spectroscopy*, 42(5), 1062-1068.
- Mason, R. B., & Tite, M. S. (1997). The beginnings of tin-opacification of pottery glazes. *Archaeometry*, 39(1), 41-58.
- Matin, M., Tite, M., & Watson, O. (2018). On the origins of tin-opacified ceramic glazes: New evidence from early Islamic Egypt, the Levant, Mesopotamia, Iran, and Central Asia. *Journal of Archaeological Science*, 97, 42-66.
- Medeghini, L., Lottici, P. P., De Vito, C., Mignardi, S., & Bersani, D. (2014). Micro-Raman spectroscopy and ancient ceramics: applications and problems. *Journal of Raman Spectroscopy*, 45(11-12), 1244-1250.
- Moore Valeri A. (1984) Florentine "zaffera a rilievo" maiolica: a new look at the "oriental influence", *Archeologia Medievale*, XI, 477-500.
- Moore Valeri, A. (2004). *Ceramiche rinascimentali di Castelfiorentino: l'ingobbiata e graffita in Toscana*. Polistampa.
- Odelli, E., Palleschi, V., Legnaioli, S., Cantini, F., & Raneri, S. (2020). Graph clustering and portable X-Ray Fluorescence: an application for in situ, fast and preliminary classification of transport amphoras. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 105966.
- Odelli, E., Raneri, S., Cantini, F., Mattiello, S., Salvioli-Mariani, E., Lottici, P. P., & Bersani, D. (2021). Micro-Raman spectroscopy to investigate production techniques: A focus on fine ware potteries. *Journal of Raman Spectroscopy*, 52(1), 199-207.
- Papachristodoulou, C., Oikonomou, A., Ioannides, K., & Gravani, K. (2006). A study of ancient pottery by means of X-ray fluorescence spectroscopy, multivariate statistics and mineralogical analysis. *Analytica Chimica Acta*, 573, 347-353.
- Pasquinelli G. (1987). *La ceramica di Volterra nel medioevo (sec. XIII-XV)*. All'Insegna del Giglio.
- Ricciardi, P., Colomban, P., Tournié, A., & Milande, V. (2009). Nondestructive on-site identification of ancient glasses: genuine artefacts, embellished pieces or forgeries?. *Journal of Raman Spectroscopy*, 40(6), 604-617.
- Roberta, S., Gaetano, R., Robin, J. H., & De Francesco, A. M. (2017). Scientific investigation on the provenance of the black glazed pottery from Pompeii: a case study. *Mediterranean Archaeology & Archaeometry*, 17(2).
- Sendova, M., Zhelyaskov, V., Scalera, M., & Ramsey, M. (2005). Micro-Raman spectroscopic study of pottery fragments from the Lapatsa tomb, Cyprus, ca 2500 BC. *Journal of Raman Spectroscopy*, 36(8), 829-833
- Simsek, G., Colomban, P., Casadio, F., Bellot-Gurlet, L., Zelleke, G., Faber, K. T., Milande, V., & Tilliard, L. (2015). On-Site Identification of Early Böttger Red Stoneware Using Portable XRF/Raman Instruments: 2, Glaze & Gilding Analysis. *Journal of the American Ceramic Society*, 98(10), 3006-3013.
- Speakman, R. J., & Shackley, M. S. (2013). Silo science and portable XRF in archaeology: a response to Frahm. *Journal of Archaeological Science*, 40(2), 1435-1443.
- Pawelkowicz, S. S., Rohanová, D., & Svora, P. (2017). Gothic green glazed tile from Malbork Castle: multi-analytical study. *Heritage Science*, 5(1), 1-16.
- Pérez, J. M., & Esteve-Tébar, R. (2004). Pigment identification in Greek pottery by Raman microspectroscopy. *Archaeometry*, 46(4), 607-614.
- Perrazzi, A., & Poggesi, G. (eds.). (2011). *Carta archeologica della provincia di Prato. Dalla preistoria all'età romana*. All'Insegna del Giglio.
- Tite, M. S. (2009). The production technology of Italian maiolica: a reassessment. *Journal of Archaeological Science*, 36(10), 2065-2080.
- Van Pevenage, J., Verhaeven, E., Vekemans, B., Lauwers, D., Herremans, D., De Clercq, W., Vincze, L., Moens, L., & Vandenabeele, P. (2015). Illustration of compositional variations over time of Chinese porcelain glazes combining micro-X-ray Fluorescence spectrometry, multivariate data analysis and Seger formulas. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 103, 106-111
- Vekemans, B., Janssens, K., Vincze, L., Adams, F., & Van Espen, P. (1994). Analysis of X-ray spectra by iterative least squares (AXIL): New developments. *X-Ray Spectrometry*, 23(6), 278-285.
- Wentkowska A. (2004). Fornaci per stoviglie a Volterra, in Caciagli C. (ed.), *Beni culturali e ambientali nella città storica*. Pisa University Press.
- Wentkowska A. (2010). Pomarance e Volterra due centri di produzione della ceramica ingobbiata e graffita. Le famiglie committenti, in Ciampoltrini G. (ed.), *Peccioli e la Valdera dal Medioevo all'Ottocento: Itinerari archeologici fra Pisa e Volterra* (pp. 111-144). Fondazione Peccioli per l'arte.
- Zhao, H. X., Li, Q. H., Liu, S., & Gan, F. X. (2013). Characterization of microcrystals in some ancient glass beads from China by means of confocal Raman microspectroscopy. *Journal of Raman Spectroscopy*, 44(4), 643-649.

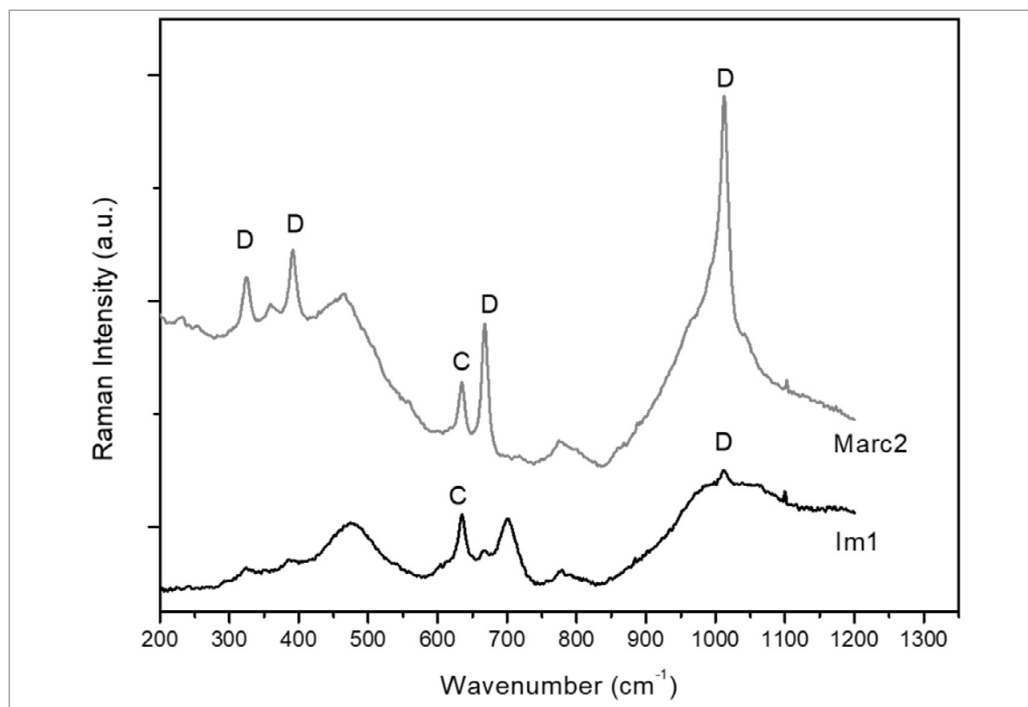


fig. S1. Examples of Raman spectra collected from maiolica glazes. D= diopside (1013, 668, 391, 324  $\text{cm}^{-1}$ ), C= cassiterite (636 $\text{cm}^{-1}$ ).

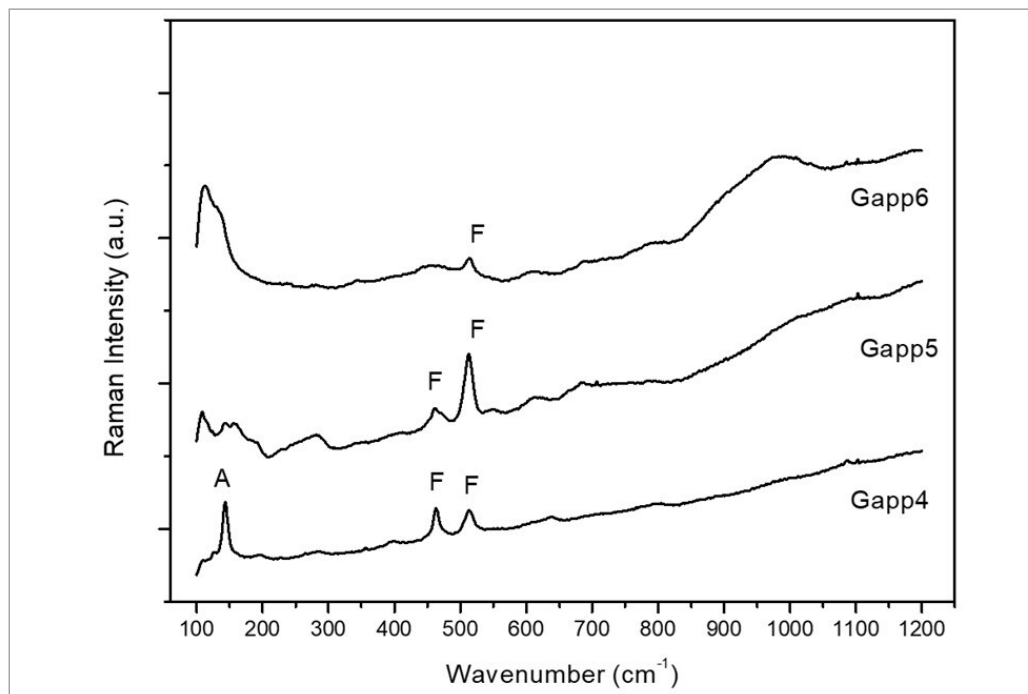


fig. S2. Examples of Raman spectra collected from maiolica glazes. A= anatase (144 $\text{cm}^{-1}$ ), F= feldspar (460, 513  $\text{cm}^{-1}$ ).