



1 (Thornton and Wilson 2009; Campbell 2012), also thanks to the famous treatise *The three books*  
2 *of the potter's art*, written by Cipriano Piccolpasso in c.1557 (Conti 1976). Ceramologists  
3 based the attribution of every artefact discovered in these territories on the knowledge of  
4 these two productions, whereas, concerning the town of Urbino (located some 12 and 36 km  
5 from *Casteldurante* and Pesaro, respectively; Fig. 1) the debate has focused on the *istoriato*  
6 (historiated) production and on the related famous painters of pottery (Guido Durantino and the  
7 Fontana family, Nicola da Urbino, Francesco Xanto Avelli etc.).

8 The admission of the archaeological methodology in the discussion about attributions has  
9 (partly) clouded the accepted axioms, causing more doubts than clarity. The archaeological  
10 methods have caused some perplexity about several attributions, yet they have often proved to be  
11 insufficient to establish a certain local attribution. This happened for the findings of second-class  
12 ceramic artefacts, dated from the mid-15th to the early 16th centuries, in the 'Salone del Trono'  
13 (Throne room) vaulted ceiling of the Ducal Palace of Urbino: at the time of the discovery, a local  
14 attribution was proposed by archaeologists (Ermeti 1997a,b) for these findings, but with some  
15 doubt. Until this discovery, the history of Urbino ceramic production was unknown; on the other  
16 hand, these artefacts were very similar, even stylistically, to those from Pesaro, where a strong  
17 tradition of ceramic production, from the end of the 15th century to the beginning of the 16th  
18 century, had long since been well known. In any event, why should second-class products (with  
19 firing and decoration imperfections) have been transported from Pesaro to Urbino? To answer this  
20 important question, an archaeometric approach was considered necessary. Samples discovered in  
21 the Ducal Palace of Urbino and coeval maiolica samples found in archaeological excavations in  
22 Pesaro (Campbell 2012) and kept in the city's Municipal Museum were submitted to laboratory  
23 analyses.



25 Figure 1 A simplified map showing the Italian maiolica production centres (solid circles) of the Marche region cited  
26 in the text.

1 Up to now, the Renaissance maiolica attributed to the Urbino production centre has been  
2 considered for analysis by Tite (1991), Hughes (1991), Myers (1992) and Hughes *et al.* (1995,  
3 1997), but without providing specific chemical data for the ceramic bodies of each sample  
4 considered, and reporting only the compositions of a few objects. Recently, Tite (2009) published  
5 a useful reassessment of the production technology of Italian maiolica, in which he also presented  
6 the results of chemical analyses (major elements only) carried out by SEM–EDS on five maiolica  
7 objects attributed to Urbino (two of which came from the Hugo Blake collection and three from  
8 the British Museum) dating from the second half of the 16th century to the early 17th century. To  
9 the authors' knowledge, no other archaeometric studies reporting chemical analyses of ceramic  
10 bodies have been published up to the present time.

11 In this paper, the results are reported of a trial study on a restricted number of samples, aimed  
12 at verifying the usefulness of some mineralogical–petrographic and chemical parameters in order  
13 to distinguish between the maiolica fragments found in Urbino and those manufactured in Pesaro.

14 The *Casteldurante* production has been intentionally excluded in this study, since this centre  
15 did not experience high-volume production until the late 15th century, as has also been confirmed  
16 by recent excavations executed beneath the city walls,<sup>1</sup> where mainly 16th century ceramics  
17 have been found (the innovative narrative pictorial style known as 'istoriato', for which the  
18 *Casteldurante* workshops are famous, was introduced in the second half/end of the 15th century  
19 and developed primarily in the 16th century).

#### 20 *The maiolica from the 'Salone del Trono' of the Ducal Palace of Urbino*

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22 In 1992, the finding of a large number of maiolica fragments in the 'Salone del Trono' vaulted  
23 ceiling of the Ducal Palace of Urbino (Ermeti 1997a,b; Ermeti 2005; Cecconi and Lippera 2005)  
24 raised many questions that are still partly unanswered. The most important discovery, which  
25 unfortunately was carried out only partially with archaeological methodologies, is related to the  
26 second layer of the vault filling: even if this layer represents a 'secondary position' layer, it is very  
27 interesting for its homogeneity, which is due to the one single filling dated to the beginning of the  
28 16th century. This is proved both by the ceramic typology and the recovery of 13 coins of  
29 Guidubaldo the First, dated between 1502 and 1508.

30 The pottery consists mainly of dishes with decorative typologies characteristic of the  
31 period from the late 15th century to the early 16th century (Fig. 2): 'gotico-floreal', 'alle  
32 geometrizzazioni', 'a bianco su bianco', 'a quartieri e girali', 'alla porcellana' and 'a zaffera'  
33 (Ermeti 2005). These valuable glazed ceramics include a number of whole objects (though in  
34 fragments) and their decorative typologies are well known in the Pesaro production (Berardi  
35 1984, 1989; Ermeti 1997a,b).

36 The fact some almost intact objects, a firing tripod and some biscuit sherds have been found  
37 allows us to suppose that they belong to a complete ceramic store that was destroyed at the same  
38 time. It could be a storage facility related to a nearby furnace and, in this case, these ceramics  
39 would represent real evidence of a 15th century production in Urbino, which is still unknown  
40 today. In fact, most of all, the presence of biscuit sherds (as sample U 675) and a tripod stilt  
41 (unfortunately now lost) is quite undoubtedly proof of the existence of a workshop in Urbino.  
42 Whereas finished items with slight or even serious imperfections could be commercialized and  
43 used, it makes little sense to suppose that unglazed slipped dishes and, in particular, furnace  
44 furniture were transported to Urbino.

45 <sup>1</sup>Close to the 'Porta del Mulino' in Urbania, known as Casteldurante in ancient times, archeological excavations were carried out in summer  
46 2003 by M. L. Ermeti, with the authorization of the 'Soprintendenza per i Beni Archeologici ed Architettonici delle Marche'. The  
47 excavation yielded thousands of ceramic fragments, mainly dating to the 16th and 17th centuries AD.



Colour online. B&W in print

Figure 2 The (greater part of the) maiolica sherds from Urbino and Pesaro selected for analysis. The numbers of the investigated samples are noted on the images. 5

Actually, in spite of the archival documentation testifying the presence in Urbino of a large number of potters during the 14th century, and especially the 15th century (Negroni 1994), in the great number of archaeological excavations (still unpublished) carried out in the historical centre of the town, ceramic items univocally related to that period have never been recovered. In the second half of the 15th century, surely many ceramic producers existed in Urbino who were able to satisfy the requirements of the Ducal Court, but at the present time we still have no tangible evidence (such as furnace remains) that could confirm this consideration. On the contrary, it has been mentioned above that, during the 15th and 16th centuries, the Court of Urbino imported ceramics from Pesaro, the greatest production centre of pottery in the vicinity.

The discovery of the maiolica fragments in the vaulted ceiling of the Urbino Ducal Palace testifies to a significant and uniform production inside the court itself (Ermeti 1997a,b), as also suggested by the very similar paste of the various ceramic fragments (hard, compact, fine grain-sized and very pale brown in colour: Munsell 10YR 8/3-8/4).

1 These maiolica samples present distinctive characteristics: in spite of the general high quality  
2 of the objects, they always show some imperfections due to the firing and/or decoration pro-  
3 cesses; moreover, all of these items were destroyed at the same time, before being used. Why  
4 should such valuable objects (even if with some slight imperfections) have been destroyed?  
5 Ermeti (1997a,b, 2005) supposed that this ceramic production was expressly committed to the  
6 Montefeltro Court and so was considered unsuitable for sale, even as a second-class product.  
7 Once these materials were destroyed, they were used as recycled building materials to fill the  
8 vaulted ceiling of the Ducal Palace.

9 So, if some stylistic characters should lead us to presume ceramic production from Pesaro,  
10 other clues (a coeval production exists in Urbino, as reported in the archive documentations; they  
11 represent a second choice, so there was no reason to transport goods from Pesaro to Urbino) allow  
12 us to suppose possible or probable ceramic production from Urbino workshops.

13 Although this study concerns a relatively small number of samples, it is the first investigation  
14 on the Urbino maiolica reporting comprehensive analyses made on this typology of samples, and  
15 it is the first significant step in the understanding of the ceramic production in Urbino between the  
16 end of the 15th century and the first half of the 16th century.

#### 17 18 EXPERIMENTAL PROCEDURES

19 Samples for the analyses (size generally around  $2 \times 1 \times 0.5$  cm) were taken from 19 large  
20 maiolica sherds dating from the late 15th to the early 16th centuries, coming from the storerooms  
21 of the Ducal Palace of Urbino (10 items; Fig. 2) and the Museum of Pesaro (nine items, some of  
22 which are kiln remains: e.g., samples P615 and P480; Fig. 2). The analysed samples are repre-  
23 sentative of all the typologies found both at Urbino and Pesaro. A detailed morphological and  
24 style description of the sampled artefacts is reported in Ermeti (1997a,b, 2005).

25 Samples were investigated using different techniques at the LAMA laboratory (Venice,  
26 Italy), with the exception of the chemical analyses of the ceramic bodies, which was performed  
27 at Activation Laboratories Ltd (Ancaster, Canada). Polarized-light optical microscopy (OM) on  
28 thin sections, using a Nikon Mod. TK-1270E microscope equipped with a digital camera for  
29 image acquisition, has been employed to describe the skeleton fragments, their characteristics/  
30 relationships, to provide data on their modal amounts (by using comparison charts for visual  
31 estimation), to illustrate the features of the matrix and to measure the thickness of coverings  
32 (e.g., glazes and slips). X-ray powder diffractometry (XRPD) has been employed to analyse  
33 the fine-grained bulk ceramic bodies, using a PANalytical Empyrean diffractometer with  
34 Cu-K $\alpha$  radiation at 40 kV and 40 mA, to obtain qualitative mineralogical data and to detect the  
35 presence of newly formed phases due to the firing processes. With the aim of better evidencing  
36 the presence of clay minerals, orientated powder-mount XRD analyses have also been per-  
37 formed by placing a suspension of the bulk sample on a glass slide, and drying at room  
38 temperature.

39 The quantitative chemical composition (major, minor and some trace elements) of the ceramic  
40 bodies was determined on 18 samples (sample P613 was excluded due to its very small size) by  
41 inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled  
42 plasma–mass spectrometry (ICP–MS). Samples (~3 g) for the ICP–OES–MS analysis were  
43 mixed with a lithium metaborate and lithium tetraborate flux and melted in a platinum crucible  
44 in a inductive furnace. The melts were poured directly into a solution of 5 vol% nitric acid  
45 containing an internal standard, and stirred continuously until completely dissolved. The sample  
46 solutions were run for major oxide and trace elements on a ‘Thermo Jarrell-Ash ENVIRO II ICP’

1 and a 'PerkinElmer SCIEX ELAN 6000 ICP-MS', respectively. Errors were 1 wt% for major  
2 oxides and 3 wt% for minor and trace elements.

3 Small fragments representative of the different glaze colours (e.g., colourless, blue, green,  
4 yellow and orange) were dry cut from sherds (two from Pesaro and three from Urbino), embed-  
5 ded in cross-section in polyester resin, then ground, polished and carbon coated for analysis by  
6 scanning electron microscopy (SEM, Philips XL30) and energy-dispersive X-ray microanalysis  
7 (EDS, EDAX New XL30). SEM images in backscattered mode were used to distinguish areas  
8 with different chemical compositions, and quantitative chemical analyses of the glazes were  
9 carried out. The instrument was typically run at 25 kV and 1 nA, with overall counting times of  
10 200 s. The compositions of the glazes were determined by scanning the electron beam on areas  
11 as large as possible, up to 0.3 mm × 0.3 mm, to ensure a composition representative of the glaze  
12 and to minimize alkali drift (ion migration) during the irradiation. The analyses of the opaque  
13 glazes included also tin oxide crystals. At least two (transparent glazes) or three (opaque glazes)  
14 different areas of each glaze were analysed in each sample and the average values were consid-  
15 ered. The net X-ray intensities (peak minus background) were quantified by means of a ZAF  
16 correction program supplied by EDAX. Reference glasses of known composition were measured  
17 in the same analytical conditions and the standardization coefficients, resulting from the differ-  
18 ence between the true values and the measured values for each element, were used to improve the  
19 accuracy of the analyses. The relative errors estimated were of the order of 5% for the oxides of  
20 Si, Pb, Al, Na, K, Mg and Sn, 10% for Ca and up to 15% for the oxides of P, Cl, Ti, Cu, Co and  
21 Ni. Larger values were found for Fe<sub>2</sub>O<sub>3</sub> (30%). The lower limit of detection was in the range  
22 0.1–0.2 wt% for most of the oxides. Yellow and orange particles were semi-quantitatively  
23 analysed by means of SEM-EDS.

## 24 RESULTS AND DISCUSSION

### 25 *Ceramic body*

26 *Optical microscopy and XRD analyses* Observation under the optical microscope of thin sec-  
27 tions (Table 1), combined with X-ray diffraction analysis (Table 2), indicates that all of the  
28 examined samples (both groups from Urbino and Pesaro) show a very similar mineralogical  
29 composition of the skeleton. The homogeneity in composition does not allow the samples to be  
30 divided into groups. Nevertheless, some considerations can be suggested. All of the samples are  
31 characterized by a serial fine grain size of the detrital fraction of the clay, which is slightly more  
32 abundant in the samples from the Ducal Palace of Urbino (15–22vol%) with respect to those from  
33 Pesaro (10–18vol%); moreover, the grain size always ranges from fine (0.2–0.035 mm) to very  
34 fine (≤0.035 mm) in the case of Urbino, and sometimes coarser (from silty to average sandy) in  
35 the Pesaro maiolica (Table 1 and Figs 3 (a) and 3 (b)). Quartz, which represents the more  
36 abundant mineralogical phase in all of the examined samples, is predominantly angular in the  
37 Urbino samples, with a minor amount of sub-angular individuals, whereas angular and sub-  
38 angular shapes are present in comparable quantities in the Pesaro samples. Polycrystalline quartz  
39 has been observed in many samples from Urbino, but in only one sample (P561) from Pesaro.  
40 Other phases, detected in almost all of the samples in variable amounts, consist of small  
41 fragments of K-feldspars, hematite, muscovite/illite and primary pyroxene; the latter and the  
42 K-mica are generally more abundant in the Urbino samples. Opaque minerals and rock fragments  
43 (micro-sparitic/sparitic limestone and quartz-arenite) are very rare and in trace amounts in both  
44 groups. Primary calcite is homogeneously distributed in the clay fraction in many samples  
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Renaissance maiolicas from Urbino and Pesaro (the Marches, Italy)

Table 1 The main results of the minero-petrographic observations (by means of optical microscopy) of the ceramic bodies

Sample	Matrix (microscopic aspect)	Illite	Microscopic analysis of the temper										Other minerals									
			Quantity			Grain			Quartz				K-Feldspar	Plagioclase	Muscovite	Biotite	Calcite	Pyroxene	Hematite	Opaque Minerals	Rock Fragments	
Abundant	Average (≥20% ≤35%)	Scarce (≤20%)	Very fine (≤0.035 mm)	Fine (0.2–0.035 mm)	Average (0.4–0.25 mm)	Angular	Sub-angular	Polycrystalline	Chert	Total												
<i>Urbino—Ducal Palace</i>																						
U617	SI	±	X	X-X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U639	AP	±	X-X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U649	AP	+	X	X-X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U640	AP	+	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U629	AP/SI + ARF/C	±	X	X-X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U675	SI + ARF/C	±	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U579	AP/SI	±	X	X-X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U594	AP + ARF/C	+	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U668	AP + ARF	+	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
U609	SI + ARF/C	±	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
<i>Pesaro—Municipal Museum</i>																						
P615	SI/AP	±	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
P613	SI + ARF	±	X	X-X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
P566	SI/AP	±	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
P564	AP	±	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
P571	AP	±	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
P501	SI + ARF	+	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
P304	AP + ARF	±	X	X-X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
P494	AP/SI	±	X	X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±
P480	AP + ARF	±	X	X-X		++	+	±	++	++	±	±	±	±	±	±	±	±	±	±	±	±

Symbols and abbreviations: +, ++, very abundant; ++, abundant; +, present; ±, traces. AP, aggregate polarization; SI, semi-isotropic; ARF, argillaceous rock fragment; ARF/C, argillaceous rock fragment, also calcareous; s, serial granulometry; Cl, belonging to the clay; 2ty, secondary spathic or microspartic calcite filling porosities.

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Table 2 The results of the mineralogical analysis (by X-ray powder diffraction) on the ceramic bodies

Sample	Qtz	Cpx	Gh	Cal	Kfs	Pl	Hem	Km	Ill (orientated)
<i>Urbino—Ducal Palace</i>									
U617	++	+++		+	±	+	±	±	±
U639	+++	++	++			±			
U649	+++	++	+++	+	±	+	+		
U640	+++	+++	++	±	±		±		±
U629	+++	++	+++	++	±		±		
U675	++	++	+++	++				±	±
U579	+++	+++	+++		±	±	±	±	
U594	+++	+	++			+	±		±
U668	++			+++		+	±	+	+
U668 Engobe	+++			++		+		±	+
U609	+++	++	++	±	+	±	+	+	
<i>Pesaro—Municipal Museum</i>									
P615	+++	++	+	±	±	+			±
P566	+++	++	+	+		+	±		±
P613	+++	+	+++	++	±		+		
P564	+++	+++	++		±		±		±
P571	+++	++	±	+	+		±	±	
P501	+++	++	±	+		+	+	±	±
P304	+++	++	++	+			±	±	
P494	+++	+++		+		+	+	±	±
P480	+++	+++	++	±		±	±	±	±

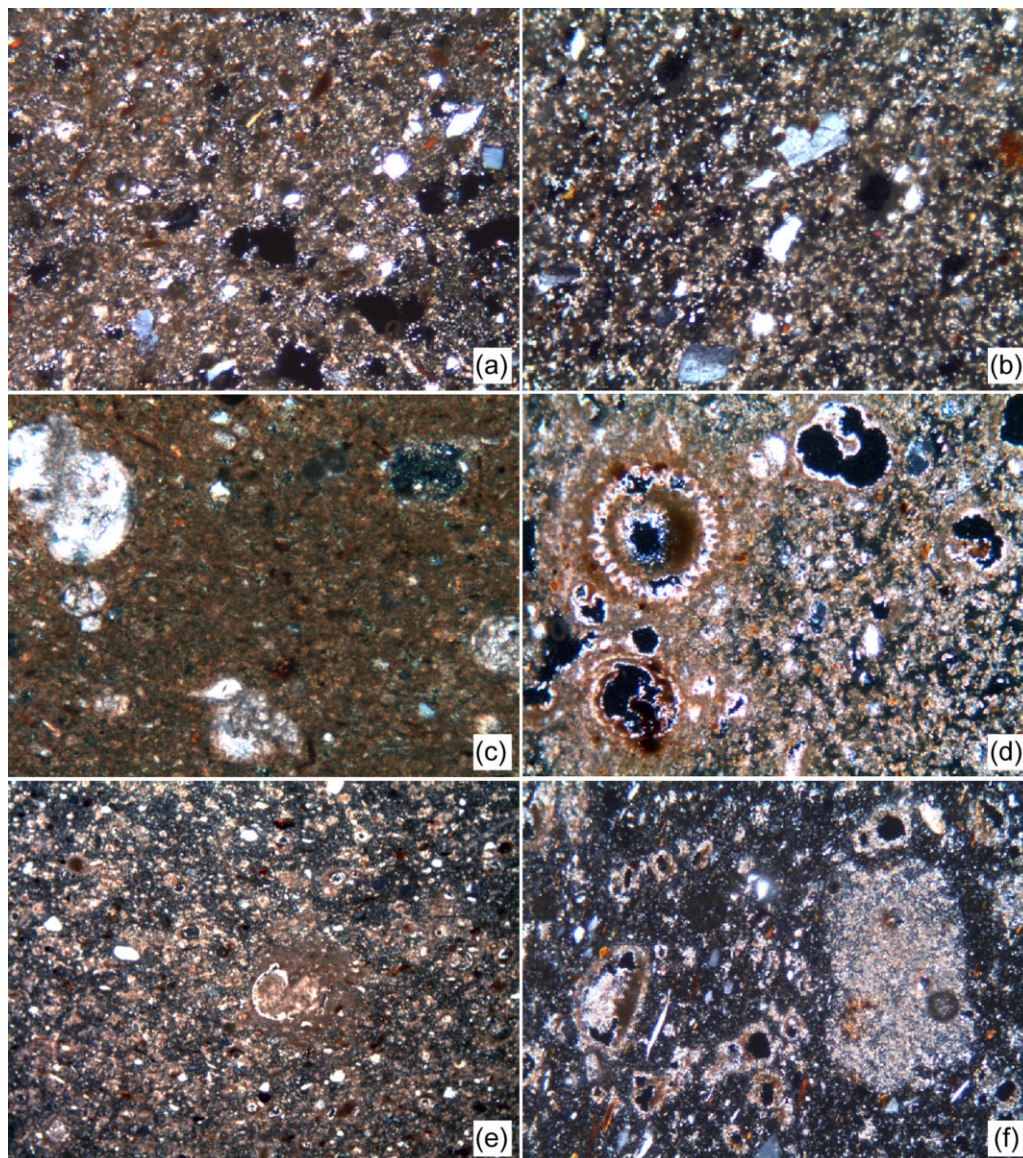
Symbols and abbreviations: +++, very abundant; ++, abundant; +, present; ±, traces. Qtz, quartz; Cpx, clinopyroxene; Gh, gehlenite; Cal, calcite; Kfs, K-feldspar; Pl, plagioclase; Hm, hematite; Km, potassic mica; Ill, illite.

(Table 1): the presence of reaction rims and the ‘ghosts’ shape (Fig. 3 (d)) allow us to suggest that calcite is probably related to the presence of biogenic components (Pliocene Foraminifera) in the raw materials. This is clearly the case with regard to samples U668 and P613, where intact Foraminifera with the chamber replaced/filled by sparite were observed in the skeleton fraction of the ceramic body (Figs 3 (c) and 3 (d)). In two samples from the Museum of Pesaro, the pores and the fractures are partially filled by secondary calcite.

The matrix is generally characterized by aggregate polarization, in some cases versus semi-isotrope, both in Urbino and Pesaro samples (Table 1). Argillaceous rock fragments (ARFs; Whitbread 1986), sometimes with a calcareous matrix, were observed in several samples belonging to both groups (Figs 3 (e) and (f)). Residual platy fragments of illite (grain size > 4 µm) were observed in thin section in many samples, but they sometimes appear more abundant in those from the Ducal Palace of Urbino.

By comparing diffraction data with optical microscopy observations, it results that calcite is more abundant in the Urbino samples than in the Pesaro sherds, reaching very high amounts in sample U668 (Table 2). Moreover, the XRD analyses allow identification of phases that were newly formed during the firing process (Maggetti 1981, 1982; Maggetti *et al.* 1984; Bertolino and Fabra 2003; Eramo *et al.* 2004), that is, abundant gehlenite (mainly in the Urbino samples), diopside clinopyroxene and plagioclase (the latter in lower amounts) (Table 2), confirming the





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Figure 3 Micrographs of the thin sections of some selected ceramic sherds. (a, b) The typical serial fine granulometry characterizing the ceramic bodies of the maiolica from Urbino (a, sample U640) and Pesaro (b, sample P304), (c, d) The presence of primary calcite in the bodies of the maiolica from Urbino (c, sample U668: intact Foraminifera are evident in the skeleton fraction) and Pesaro (d, sample P613: bioclasts and ghost shapes of Foraminifera are visible). (e, f) Argillaceous rock fragments with calcareous matrix present in the semi-isotropic whole matrix of samples U675 (e) and P613 (f). Crossed polars; the long side of the images measures 1.05 mm.

1 general reaction of CaO with the amorphous phases due to the dehydroxylation of clays (Shoval  
2 1988; Shoval *et al.* 1993; Riccardi *et al.* 1999), mainly in the 850–900°C range (relatively low for  
3 the maiolica production; Tite 2009). This maximum firing temperature seems to be confirmed for  
4 many sherds by the contemporaneous occurrence of relics of illite and calcite (Table 2). The  
5 slipped sample U668 differs from the maiolica samples (gehlenite and clinopyroxene were not  
6 found; Table 2), pointing to a lower firing temperature.

7 We assume that the composition of the used clays, which contained high amounts of illite,  
8 quartz and calcite (the high CaO content was also confirmed by the quantitative chemical  
9 analyses; Table 3), facilitated the formation of these new phases (Cultrone *et al.* 2001).

10 U668 is the only sample that shows the presence of a white engobe (slip) without a covering  
11 glaze. White slips were generally produced using kaolinitic clays (quite rare in Italy) or other  
12 kinds of pure or impure clays, in order to apply a white colour during firing. The white slip of  
13 sample U668 (Table 2, U668 Engobe) is mainly composed of quartz with lower amounts of illite,  
14 calcite, and traces of plagioclase. This composition is compatible with the use of the Terra di  
15 Vicenza (improperly also called ‘Caolino of Schio’ or ‘Terra Bianca o Ver Terra Visentina’, as  
16 stated by Piccolpasso; Conti 1976), an illitic clay very rich in quartz (unpublished XRD data: see  
17 also Lazzarini 1975; Dondi *et al.* 2003) used in Italy in that period.

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19 *The chemical composition of the ceramic body* The ICP–MS/AES chemical analyses of the  
20 ceramic bodies are reported in Table 3. Before we present the chemical data, it is worth recalling  
21 that the burial environment of archaeological ceramics may modify the chemical composition  
22 of their bodies. In particular, solutions migrating from the soil to buried samples can deposit  
23 extraneous matter on the ceramic body (phosphorous is notoriously the most common contami-  
24 nant) or lead to the extraction of some original chemical compound (Maggetti 1982; Fabbri  
25 1997). The sherds from Urbino were preserved from this possible contamination. By contrast,  
26 sample P566 represents an example of such contamination: it shows high contents of both  
27 secondary calcite (as confirmed by optical investigation) and phosphorous (P<sub>2</sub>O<sub>5</sub> 5.31%), as well  
28 as anomalous Ba and Sr values with respect to the other samples of the Pesaro set.

29 In general, the composition of the maiolica bodies from both sites is characterized by a  
30 high Ca content, varying over a wide range (CaO 17–30%), indicating the use of calcareous  
31 clays.

32 Moderately high contents of iron (Fe<sub>2</sub>O<sub>3</sub> ~ 5–6%) and magnesium (MgO 2.5–5%) were found,  
33 the values being quite similar for both sets of samples. The low MgO to CaO ratio may suggest  
34 the use of raw materials containing a carbonate fraction that is rich in calcite with possible minor  
35 amounts of dolomite. The high Ca content is consistent with the use of the Pliocene marly clays  
36 that outcrop widely in the natural deposits of the province of Pesaro–Urbino, which is crossed by  
37 the Foglia and Metauro rivers, and in the surroundings of Urbino (Centamore and Micarelli 1991;  
38 Carta Geologica d’Italia n.d.).

39 Table 3 shows some differences concerning calcium and magnesium oxides (Fig. 4 (a)): they  
40 are more scattered in the Urbino ceramic bodies (CaO 19–31%; MgO 2.5–5%) than in the Pesaro  
41 sherds (CaO 17–21%; MgO 3.6–4.6%). Similar trends are obtained by reporting CaO versus the  
42 silica, alumina, iron, titanium, barium and strontium concentrations.

43 Samples belonging to the two sites are clearly separated in the Na<sub>2</sub>O versus K<sub>2</sub>O diagram  
44 (Fig. 4 (b)), where the Urbino samples show higher potassium and lower sodium contents, as well  
45 as higher total alkali amounts, than those from Pesaro (Na<sub>2</sub>O + K<sub>2</sub>O 3.3–5% and 2.7–3.7%,  
46 respectively). A differentiation between the two groups was also observed for some minor and  
47 trace elements, such as Ti versus Zr and Sr versus Ba (Figs 4 (c) and 4 (d)).

Renaissance maiolicas from Urbino and Pesaro (the Marches, Italy)

Table 3 The chemical compositions of the maiolica bodies (analyses normalized to 100%)

Sample	Urbino—Ducal Palace										Pesaro—Municipal Museum									
	U649	U675	U579	U594	U617	U629	U640	U609	U668	U639	P304	P571	P566	P480	P494	P564	P615	P501		
<i>Major elements (wt%)</i>																				
SiO <sub>2</sub>	48.24	46.62	48.25	51.29	49.35	46.89	50.79	47.64	45.31	49.15	52.30	51.43	48.73	52.24	52.12	51.81	49.98	51.93		
Al <sub>2</sub> O <sub>3</sub>	13.96	12.96	13.68	14.70	14.82	13.33	14.71	15.24	12.25	14.75	13.90	14.68	14.27	13.30	15.45	14.16	14.58	14.65		
Fe <sub>2</sub> O <sub>3</sub>	5.38	4.90	5.24	5.59	5.66	5.15	5.72	6.21	4.73	5.88	5.68	6.01	5.94	5.21	6.19	5.64	5.86	5.84		
MnO	0.11	0.09	0.11	0.12	0.11	0.11	0.12	0.11	0.09	0.10	0.09	0.14	0.13	0.08	0.14	0.14	0.14	0.14		
MgO	3.73	3.18	3.43	3.47	3.93	3.62	4.53	4.87	2.84	4.60	3.65	4.02	3.45	4.64	4.04	4.07	3.78	4.05		
CaO	24.07	28.17	24.50	19.35	21.26	25.09	19.08	20.23	30.48	20.46	20.64	19.39	18.23	20.87	16.94	19.76	19.97	19.26		
Na <sub>2</sub> O	1.14	0.85	1.03	1.08	0.98	1.33	1.30	1.14	0.71	1.19	1.53	1.09	1.25	1.88	1.68	1.71	2.06	1.94		
K <sub>2</sub> O	2.53	2.46	2.91	3.25	3.03	3.67	2.92	3.68	2.77	3.00	1.29	2.30	2.05	0.88	1.47	1.83	1.66	1.13		
TiO <sub>2</sub>	0.62	0.57	0.60	0.66	0.65	0.59	0.65	0.67	0.55	0.66	0.73	0.70	0.65	0.70	0.72	0.67	0.69	0.69		
P <sub>2</sub> O <sub>5</sub>	0.22	0.21	0.25	0.51	0.19	0.23	0.20	0.22	0.26	0.22	0.19	0.27	0.31	0.19	1.25	0.21	1.28	0.35		
LOI	6.58	7.68	3.98	5.73	3.31	5.25	3.29	6.87	18.40	2.46	6.18	6.45	5.11	5.87	3.16	6.50	6.09	6.65		
<i>Trace elements (ppm)</i>																				
Be	2	2	2	2	2	2	3	3	2	2	2	2	2	2	2	2	2	2		
Sc	11.2	10.4	11.6	12.0	12.3	11.1	12.4	12.7	9	12.4	11.1	11.8	11.7	11.2	12.7	11.1	11.7	11.6		
V	111	107	113	111	123	114	119	130	94	124	106	107	96	108	102	115	98	101		
Cr	106	100	124	120	130	117	124	127	100	124	137	119	115	133	128	115	116	125		
Co	17	15	16	14	16	16	16	17	12	17	16	16	15	17	17	16	17	16		
Ni	73	75	75	71	74	70	68	73	67	73	80	72	64	75	79	67	69	72		
Cu	45	44	195	53	72	70	45	55	37	49	115	108	78	65	54	142	118	91		
Zn	87	91	89	95	82	83	79	79	85	82	75	99	113	70	96	237	85	82		
Br	2	2	2	2	2	2	2	3	2	2	2	3	7	2	6	3	7	4		
Rb	80	90	90	110	110	80	110	110	70	90	80	90	100	70	110	90	80	60		
Sr	570	731	612	512	557	599	446	451	664	480	406	468	735	426	553	451	482	472		
Y	26	27	26	26	25	26	26	25	23	26	26	25	26	26	26	26	26	26		
Zr	109	103	106	111	109	108	115	101	87	115	167	123	101	160	125	129	126	132		
Sb	4.2	0.9	1.1	1.5	2.5	2.3	1.4	7.9	0.8	4.7	6.3	1.2	2	1.9	1.9	1	2.8	1.1		
Cs	6.3	6.2	6.2	7.4	7.7	5.4	6.5	6.9	5.7	5.3	6.7	5.3	6.1	5	6.8	5.3	5.6	5.6		
Ba	605	874	692	487	417	655	507	400	831	508	427	401	790	264	417	402	419	383		
La	27.2	25.9	27.9	28.7	29.9	26.8	28.7	28.6	23.3	28.8	27.9	29.4	28.4	27.5	31.1	27.4	28.8	28.5		
Ce	44	43	50	50	52	45	51	51	41	54	48	50	48	45	51	48	47	48		
Nd	16	20	22	24	23	18	24	22	19	20	19	22	22	22	17	20	17	22		
Yb	2.2	2.3	2.3	2.3	2.3	2.2	2.4	2.3	2.0	2.3	2.2	2.2	2.1	2.3	2.2	2.2	2.2	2.1		
Lu	0.30	0.34	0.35	0.35	0.32	0.34	0.34	0.34	0.31	0.38	0.34	0.32	0.34	0.32	0.36	0.32	0.32	0.35		
Hf	2.6	2.1	2.4	2.6	2.4	2.3	2.7	2.3	2	2.4	3.9	2.7	2.5	3.3	2.8	2.6	2.8	3		
Th	9.4	9	9.9	10.2	10.4	9.2	10.2	11.2	7	10.3	10.1	9.6	9.5	9.4	10.6	9.6	9.1	9.4		
U	3.1	3.2	2.9	2.8	2.7	3.1	2.7	3.5	2.7	2.7	3.2	2.1	2.5	2.9	3.6	2.3	3	2.3		

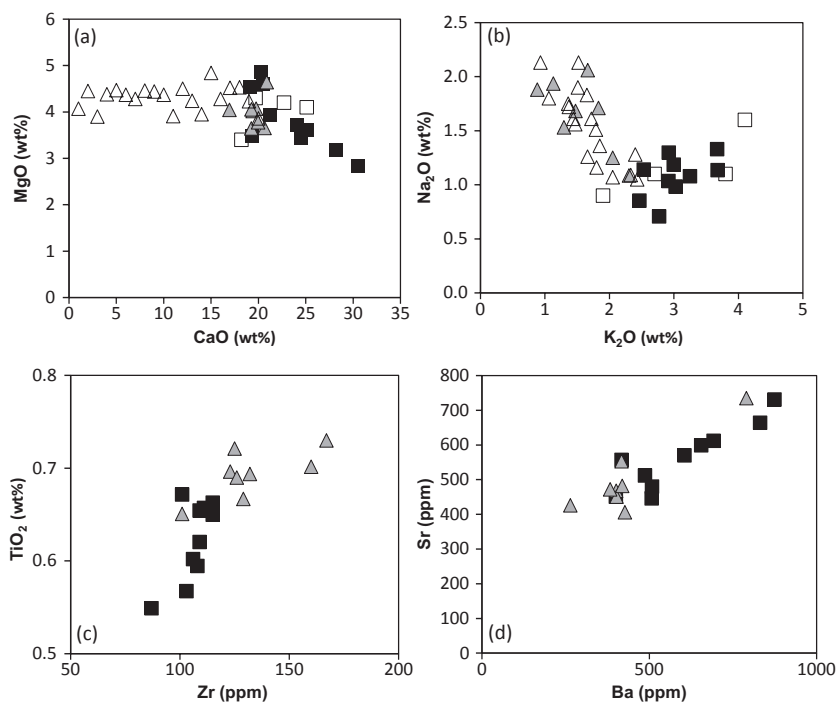


Figure 4 Bivariate plots of (a) MgO versus CaO, (b) Na<sub>2</sub>O versus K<sub>2</sub>O, (c) TiO<sub>2</sub> versus Zr and (d) Sr versus Ba contents for the 18 samples analysed. ■, Urbino maiolica; △, Pesaro Maiolica. The MgO, CaO, Na<sub>2</sub>O and K<sub>2</sub>O values are compared with those found for other coeval maiolicas from Pesaro (△; data after Amadori et al. 2002) and 16th century maiolica from Urbino (□; data after Tite 2009).

Myers (1992) and Hughes (2009) found that the Yb and Lu contents are useful for distinguishing the Urbino ceramic production from that of *Casteldurante* (only a few kilometres from Urbino). A similar result was not found using the same elements for the maiolicas of Urbino and Pesaro.

These chemical differences between the two groups are probably related to the most abundant presence of K-mica/illite in the clay fraction of the maiolica from Urbino, as already found by optical microscopy observations (Table 1) and X-ray diffraction analysis (Table 2). Furthermore, the chemical compositions of the ceramic body of the sherds from Pesaro included in this study are within the range of those determined (major elements only) by Amadori *et al.* (2002) for other coeval maiolica fragments that come from the same Museum of Pesaro (even if the latter are more scattered). The fragments analysed by Amadori and co-workers are also chemically different from both the maiolica sherds from Urbino examined in this work and the 16th century maiolica, attributed to Urbino production, recently analysed by Tite (2009) (cf., Figs 4 (a) and 4 (b)).

### Glaze

**Microstructure and EDS analyses** The average thickness of all of the glazes (opaque and transparent) is comparable in the Urbino and Pesaro samples: it varies from 300 to 750 μm in the

1 first case, and from around 250 to around 850  $\mu\text{m}$  in the latter (Table 4). In general, the glazes of  
 2 the Urbino potteries are thicker on the outer (*recto*) than on the back (*verso*) surface; the opposite  
 3 is the case for the Pesaro sherds (Table 4).

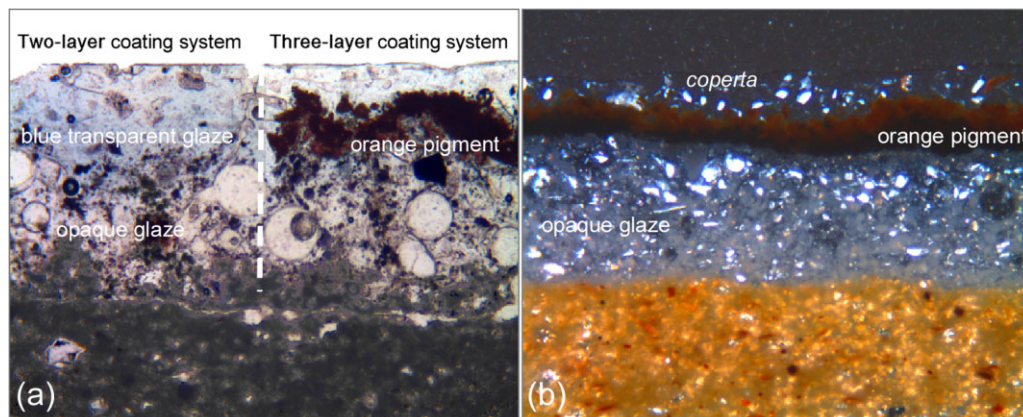
4 When observed in polished cross-section by optical microscopy and SEM, the maiolica  
 5 coatings consist generally of two layers: an opaque whitish glaze in contact with the ceramic  
 6 body, covered by a transparent glaze (coloured or colourless; Fig. 5). A three-layer system was  
 7 observed for the pigment-coloured white, yellow and orange areas (Fig. 5 (a)). These pigments  
 8 were applied on the opaque glaze and, to ensure a bright smooth reflective surface, they were  
 9 covered with a transparent glass layer (*coperta*, according to Piccolpasso's terminology), which  
 10 was colourless in the case of the white ground (Fig. 6), and had a yellow–brown colour when the  
 11 yellow and orange pigments were used. A single opaque glaze layer was observed only in few  
 12 cases.

13 When the glaze-polished cross-sections are observed by SEM–BSE, several phases can be  
 14 distinguished. In the two-layer glazes, white particles (tin oxide) are observed only in the opaque  
 15 glaze, while angular dark particles (quartz, K-feldspars and few Na-feldspars) are also dispersed  
 16 (lower amounts) in the *coperta* (Fig. 7 (a)). Usually, 50  $\mu\text{m}$  sized angular particles prevail and  
 17 larger grains up to 100  $\mu\text{m}$  are observed (Fig. 7 (e)).

18 In the three-layer glazes, a coating of pigment particles (tin oxide in white layers, lead  
 19 antimonate in yellow layers; white in colour in Figs 7 (b), 7 (c) and 7 (f)) is also observed between  
 20 the opaque glaze and the *coperta*. The opaque glazes appear to be quite heterogeneous due to the  
 21

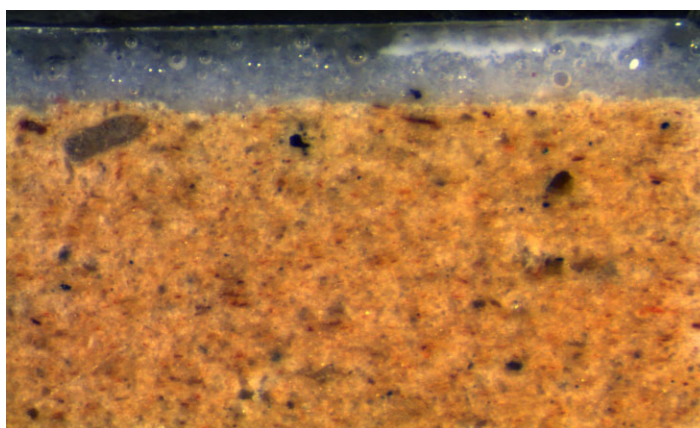
22 Table 4 The maximum thicknesses of the glazes and the glaze–body interaction depths (np, not present;  
 23 w, weathered): samples U668 (with white slip) and U675 (biscuit) are not considered

Sample	Thickness of the opaque glaze ( $\mu\text{m}$ )		Transparent glaze ( $\mu\text{m}$ )	Glaze–body interaction depth ( $\mu\text{m}$ )
	Recto	Verso		
<i>Urbino—Ducal Palace</i>				
U617	600	np	150	$\leq 20$
U639	250	np	130	40
U649	450	200	300	$\leq 20$
U640	250	250	150	30
U629	300	180	150	$\leq 20$
U579	320	250	220	$\leq 20$
U594	210	np	90	$\leq 20$
U609	200	np	100	$\leq 20$
<i>Pesaro—Municipal Museum</i>				
P615	250	np	150	$\leq 20$
P566	850	850	w	$\leq 20$
P613	250	np	w	$\leq 20$
P564	400	100	120	$\leq 20$
P571	250	400	180	$\leq 20$
P501	200	np	100	$\leq 20$
P304	300	380	200	$\leq 20$
P494	300	370	150	$\leq 20$
P480	400	420	250	$\leq 20$



Colour online, B&W in print

1 Figure 5 A micrograph of the P304 glaze in thin section, showing the opaque glaze covered by a blue transparent 5  
2 glaze (a, on the left) and a well-defined layer of orange particles covered by a transparent glaze (a, on the right; b,  
3 a different area of the same thin section). Parallel (left) and crossed (right) polars; the long side of the images  
4 measures 2.7 mm.



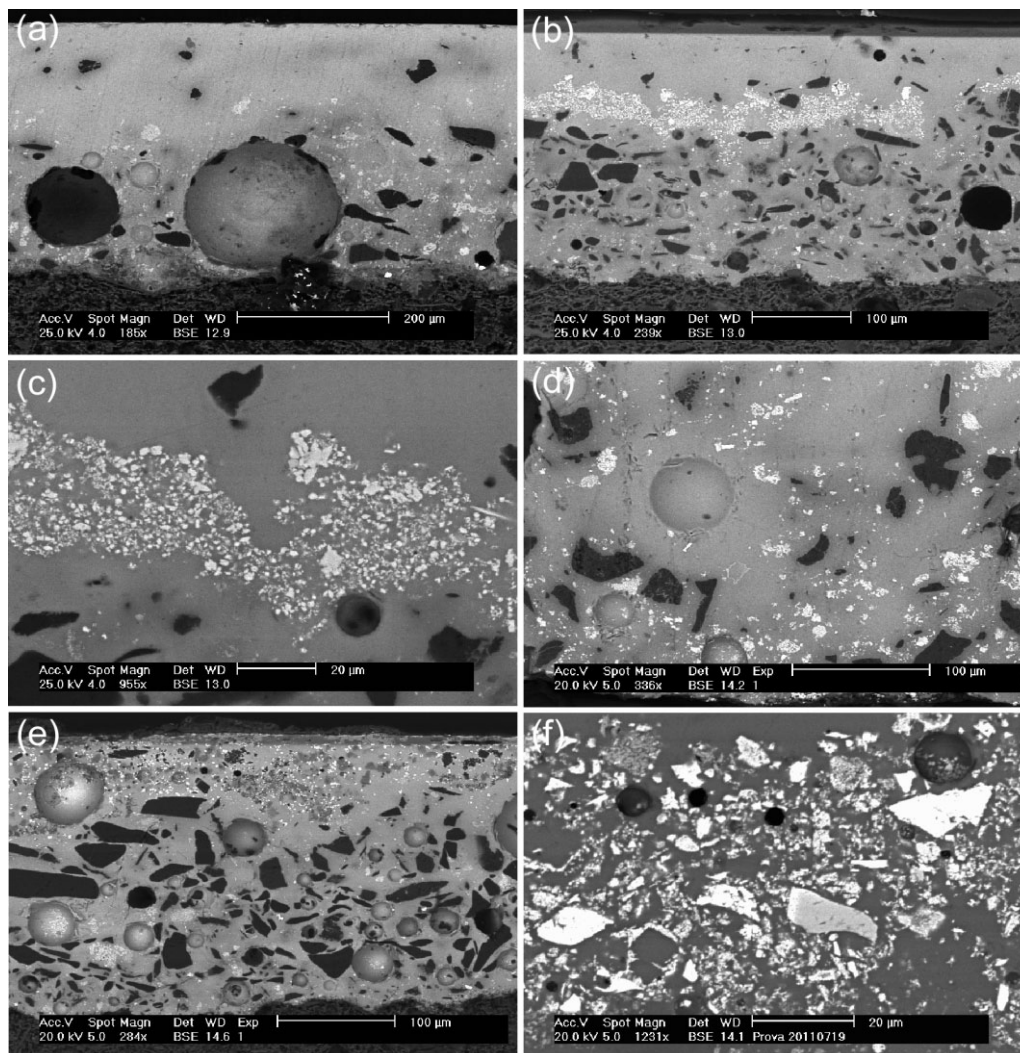
Colour online, B&W in print

6 Figure 6 An optical micrograph in polished cross-section, showing (in the left half of the image) the two layers of the 8  
7 U649 glaze (inner opaque glaze and outer transparent glaze) and (in the right half) a white layer at the interface between  
8 the opaque and transparent glazes. Reflected light; the long side of the image measures 2.7 mm.

9  
10 presence of large bubbles and fine crystals of tin oxide (<1  $\mu\text{m}$  in size), which are often associated  
11 in clusters up to 20  $\mu\text{m}$  in size (Fig. 7 (e)).

12 These observations are consistent with the results obtained by other studies on Renaissance  
13 maiolica (Kingery 1993; Tite *et al.* 1998; Tite 2009).

14 The glazes were applied directly on to the ceramic body; no white slip has been detected  
15 in the glazed samples examined. Only a scant diffusion of chemical species from the body  
16 into the glaze (Al) and vice versa (Pb) was observed, and no new phases were formed at the  
17 interface. These data indicate that a poor glaze–body interaction occurred during firing (Fabbri  
18 *et al.* 2001). Such a thin interface could indicate that the maiolica was exposed to a two-step  
19 firing process (an initial one for the ceramic body and a final one for the glaze) or to a low



1 Figure 7 SEM–BSE micrographs of polished cross-sections of the (a) U617, (b, c) U649, (d) P304, (e) U609 and (f)  
2 P615 glazes. (a) A scatter of tin oxide particles (white) and the outer glaze essentially free of particulate phases. (b) A  
3 scatter of small tin oxide (white) and angular quartz and feldspar (dark grey) particles. The white layer already shown  
4 in Figure 6 is evident at the interface between the opaque and transparent glazes. (c) Magnification of a detail of the layer  
5 with white particles (pigment) in the U649 glaze. (d) A scatter of tin oxide (white) and of angular quartz and feldspar  
6 (dark grey) grains in the P304 opaque glaze. (e) Bubbles (circles) and a scatter of tin oxide (white) and angular quartz  
7 plus feldspar (dark grey) particles in the blue area of the U609 glaze. (f) The yellow pigment (lead antimonate) involved  
8 in the P615 glaze.

9  
10 firing temperature. An advantage of using biscuit-fired bodies is that the decomposition of  
11 calcium carbonate in the calcareous clay used would already have occurred during the biscuit  
12 firing, reducing the risk of CO<sub>2</sub> gas bubbles being trapped in the glaze layer or passing through  
13 the glaze, leaving porosity.

1 *Chemical composition* The analyses of the transparent and opaque glazes are reported in  
2 Table 5. Angular particles were excluded and were identified separately by punctual X-ray  
3 analysis.

4 The glazes of the samples from both sites show a silica–lead–alkali type composition: SiO<sub>2</sub>  
5 40–60%; PbO 20–35.5% (except for U609, with PbO 37–41%); and Na<sub>2</sub>O + K<sub>2</sub>O 5.4–9.5%;  
6 with potassium (K<sub>2</sub>O 3.7–6.2%) prevailing over the sodium content (Na<sub>2</sub>O 1.7–3.4%). Signifi-  
7 cant amounts of alumina (Al<sub>2</sub>O<sub>3</sub> 1.7–4.5%), variable contents of lime (CaO 1.6–4.2%; slightly  
8 higher in the Pesaro glazes) and low quantities of magnesium (MgO 0.4–0.9%) were also  
9 found. These characteristics are typical of the Renaissance maiolica glazes (Tite *et al.* 1998;  
10 Tite 2009).

11 It is worth noting that in the glazes of one sample from Pesaro (P304) and one from Urbino  
12 (U649), the potassium contents (K<sub>2</sub>O 3.7–4.3% and 5.5–6.2%, respectively) are higher than in the  
13 other three samples (U609, U617 and P615), while the alumina content of the two groups is  
14 comparable (Al<sub>2</sub>O<sub>3</sub> 3–5%), with the exception of sample U609 (Al<sub>2</sub>O<sub>3</sub> ~ 2%).

15 These results suggest that part of the potassium in samples U649 and P304 was added not as  
16 K-feldspar but as a different compound; for instance, as calcined tartar (potassium carbonate, the  
17 deposit of wine barrels) or wine lees, as indicated by Piccolpasso.

18 Traces of chlorine (Cl ~ 0.1%; close to the detection limits of the instrument) seem to  
19 indicate that small amounts of sodium chloride were added only in opaque glazes. The addition  
20 of small amounts of sodium chloride to the raw materials is a procedure suggested in the  
21 Piccolpasso treatise. Most probably, the purpose of this addition was to facilitate the firing of  
22 the opaque glazes through a decrease in the surface tension and viscosity of the melt, so  
23 helping the refining (elimination of bubbles) and distension of the glaze (Volf 1984) on the  
24 ceramic body. In contrast, it is known that NaCl is unable to react with silica during the  
25 melting of glass; therefore, the sodium of the frit (Na<sub>2</sub>O 1.7–3.5%) has to be related to another  
26 source (probably plagioclase/Na-feldspar present as a secondary component in the sand used to  
27 melt the *marzacotto*).

28 In general, a low iron content was found (Fe<sub>2</sub>O<sub>3</sub> 0.5–0.6%), except for the coloured glazes,  
29 where iron oxides were voluntarily added or entered the glaze associated with cobalt ore  
30 (Table 5). A significant amount of tin oxide is present in the opaque glazes (SnO<sub>2</sub> 4.7–10%,  
31 clearly related to the cassiterite crystals), while its content is very low (SnO<sub>2</sub> < 1%) in the  
32 transparent glazes.

33 The angular grains present in the glazes were analysed separately. As mentioned above, they  
34 are mainly made of quartz, with a subordinate extent of K-feldspar and smaller amounts of  
35 plagioclase (Na-feldspar). The angular shape of these grains suggests that they were obtained by  
36 crushing coarse sand, and excludes the possibility that they could be unmelted particles belonging  
37 to the sand used to prepare the *marzacotto*.<sup>2</sup> As suggested by Tite (2009), these grains are  
38 probably the result of the supplementary sand that was sometimes added to the glazing mixture  
39 of *marzacotto* and lead–tin calx, and that underwent only limited dissolution during the second  
40 firing. The reason for the addition of variable amounts of sand to the glazing mixture is still  
41 unclear. Because the refractive indexes of quartz and feldspars are slightly lower than that of the  
42 glaze, their contribution to the opacity of the glaze should be modest. It could work to make the  
43 glaze more translucent (Kingery and Aronson 1990), or to improve the suitability of the unfired  
44

45 <sup>2</sup>According to Piccolpasso, the *marzacotto* was produced by firing a mixture of sand, wine lees (or tartar, the deposit from wine casks) and,  
46 sometimes, common salt. The melt was poured into water, milled, mixed with a lead–tin calx and then applied on the biscuit and fired to  
47 form the opaque glaze, the base for the painted decoration.



Renaissance maiolicas from Urbino and Pesaro (the Marches, Italy)

Table 5 The chemical compositions (by SEM-EDS) of some representative opaque and coloured glazes of the studied maiolica (analyses normalized to 100%)

Glazes	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	P <sub>2</sub> O <sub>5</sub>	Cl	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CuO	PbO	SnO <sub>2</sub>	CoO	NiO	MnO	Sb <sub>2</sub> O <sub>3</sub>
U609 Opaque	45.7	1.70	1.70	3.70	1.90	0.45	bd*	0.10	bd	0.50	bd	37.0	7.20	bd	bd	bd	bd
U609 Blue	40.5	2.30	2.20	4.00	1.90	0.30	0.30	bd	bd	3.40	1.20	41.5	0.40	1.20	0.80	bd	bd
U617 Opaque	54.5	4.50	2.20	4.20	2.20	0.90	0.50	0.15	bd	0.65	bd	25.5	4.70	bd	bd	bd	bd
U617 Blue	50.0	4.40	2.90	4.30	1.80	0.60	0.40	bd	bd	1.80	0.30	31.5	1.10	0.60	0.25	bd	bd
U617 Over orange	49.0	3.40	2.70	4.00	1.80	0.60	0.30	bd	bd	2.50	bd	35.5	bd	bd	bd	bd	0.20
U649 Opaque	60.3	3.60	2.00	5.50	1.60	0.40	0.40	0.20	bd	0.35	bd	21.0	4.60	bd	bd	bd	bd
U649 Colourless	50.5	3.60	2.90	5.50	2.50	0.65	0.30	bd	bd	0.65	bd	33.0	0.40	bd	bd	bd	bd
P304 Opaque	52.0	3.80	2.40	6.20	3.50	0.40	0.40	0.25	bd	0.70	bd	22.0	8.30	bd	bd	bd	bd
P304 Colourless	54.7	3.30	3.40	5.70	4.20	0.70	0.15	0.10	bd	0.70	bd	27.0	bd	bd	bd	bd	bd
P304 Blue	54.3	3.90	3.30	6.20	3.30	0.60	0.30	bd	bd	5.00	0.60	20.0	bd	1.30	1.20	bd	bd
P304 Green	52.0	4.30	3.20	6.20	3.50	0.50	0.30	bd	bd	1.50	4.00	24.5	bd	bd	bd	bd	bd
P615 Opaque	53.0	3.60	2.40	4.00	2.70	0.60	0.20	bd	0.05	0.45	bd	23.0	10.0	bd	bd	bd	bd
P615 Colourless	55.0	4.00	2.50	4.00	1.80	0.60	bd	bd	0.20	1.50	bd	30.0	0.40	bd	bd	bd	bd
P615 Blue	51.5	3.30	3.20	3.90	2.90	0.45	0.20	bd	0.20	1.50	0.35	30.0	0.70	1.00	0.80	bd	bd
P615 Purple-brown	53.6	3.80	3.00	4.10	2.80	0.50	0.20	bd	0.15	0.55	bd	28.0	1.70	bd	bd	1.60	bd

\*bd, Below detection limit. Analysed but not detected: As, Bi, Ba and Zn.

1 opaque glaze to take the painted decoration (Tite 2009), but also to increase the viscosity of the  
2 opaque glaze, thus reducing the risk of the glaze flowing during firing and damage to the  
3 decoration.

#### 4 *Glaze colourants and pigments*

6 In what follows, colourants (i.e., elements dissolved in the form of ions colouring the transparent  
7 glassy phase of the glaze) and pigments (i.e., coloured crystalline inclusions suspended in the  
8 glassy phase) are discussed separately.

10 *Glass colourants* The green colour is associated with the cupric ions dissolved in a glaze and  
11 purple–brown with manganese ions.

12 The blue glazes were obtained by adding cobalt (CoO from 0.6% to 1.3%). Cobalt ions  
13 dissolved in glass have a high optical density (colouring efficiency) and their concentration in  
14 blue glassware (bottles, window glass etc.) rarely exceeds 0.15%. To colour thin glazes, large  
15 amounts were required. Until the industrial era, cobalt ores were used: distinctive associations of  
16 the different elements associated with cobalt, such as nickel, zinc, arsenic, bismuth and so on, can  
17 identify their origin, and in some cases the period of use. A chronology of the use of cobalt ore  
18 was first proposed by Gratuze *et al.* (1996) and revised by Biron (2004) and Zucchiatti *et al.*  
19 (2006) in their studies on Limoges painted enamels and the Della Robbia blue glazes,  
20 respectively.

21 Besides cobalt, the analyses of the blue glazes of both sites detected the presence of nickel  
22 (NiO 0.25–1.2%) and iron (especially high in the U609 and P304 glazes). No arsenic or bismuth  
23 were found (lower limit of detection of these oxides, about 0.3%). Following the observations of  
24 Zucchiatti *et al.* (2006), these blue glazes can be dated before about AD 1520. In fact, until this  
25 date, the cobalt blue glazes of the Della Robbia workshop contained significant amounts of nickel  
26 and iron and it was only later that arsenic and bismuth were also found in significant amounts.

28 *Pigments* Crystalline particles were used to colour glazes in white, yellow and orange. The  
29 following pigments (and their compositions) were observed:

- 30 • The white layer of sample U649 totally consists of tin oxide crystals (Fig. 7 (c)), 1–10 µm in  
31 size, much larger than the tin oxide crystals of the underlying opaque glaze (less than 1 µm).
- 32 • The yellow–orange pigments (samples P304, P615, U609 and U617; Fig. 7 (f)) are of the  
33 lead antimonate type (semi-quantitative analysis). The different hues were obtained with dif-  
34 ferent lead to antimony ratios and the introduction of some iron during the preparation of  
35 the pigment. This is confirmed by the analysis of glaze U617, where both orange-yellow and 1  
36 lemon yellow colours are present. The composition of the pigment particles differs both for 2  
37 the antimony (Sb<sub>2</sub>O<sub>3</sub> 32% in orange-yellow and 58% in lemon yellow) and lead (PbO 63% and  
38 35%, respectively) contents, as well as for the iron level (Fe<sub>2</sub>O<sub>3</sub> 5% in orange-yellow and  
39 2.5% in lemon yellow, respectively). Furthermore, small amounts of silica (SiO<sub>2</sub> 4%) were also  
40 detected in the lemon yellow pigments. The composition of the orange-yellow particles is  
41 consistent with the Pb<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub> lead antimonate, whereas that of the lemon yellow particles is  
42 consistent with the PbSb<sub>2</sub>O<sub>6</sub> antimonate.

43 The detection of traces of antimony in the transparent glaze over the yellow pigment layers as  
44 well as of important amounts of iron (Table 5, U617 over orange) supports the hypothesis of  
45 the migration of these elements from the pigment layer to the *coperta* during the firing of the  
46 glaze.

CONCLUSIONS

The main goal of the present study was a first scientific characterization of an important finding of maiolica from the Ducal Palace of Urbino. The study was performed on 10 samples by mineralogical–petrographic (OM, XRD) and quantitative chemical (ICP–MS/AES) analyses of the ceramic body. The glaze layers were investigated by SEM–EDS in polished cross-sections of three selected samples, with various colours representing the entire palette.

Similarly, nine samples found in Pesaro and preserved in the local museum were investigated, with the purpose of establishing a possible differentiation between the two findings.

The maiolica from Urbino consists of a ceramic body with a temper mainly formed by angular (to sub-angular and polycrystalline) quartz and small amounts of K-feldspar, muscovite/illite and pyroxene in a calcite-rich matrix coloured by dispersed hematite. From a chemical point of view, the body is characterized by a high CaO content, and moderately high MgO and Fe<sub>2</sub>O<sub>3</sub> levels. Similar results were also obtained for the ceramic body of the maiolica from Pesaro. The main differences are to be found in a slightly coarser grain size for the temper containing comparable quantities of angular and sub-angular quartz grains in a matrix containing less illite and calcite; this results in lower amounts of K, Ba and Sr, and a slightly higher Na content. Despite these differences, it is very likely that the clay used in both cases was of the illitic–calcareous type, and was most probably taken from the Pliocene deposits outcropping around the hills occupied by the town of Urbino, as well as over a large area of the province of Pesaro–Urbino; the lithological features of these sedimentary deposits are generally quite homogeneous in both the vertical and horizontal directions (Centamore and Micarelli 1991; Amadori *et al.* 2002). Similar conclusions may be obtained from a comparison with the published data relating to the late 16th to early 17th century maiolica attributed to Urbino (Tite 2009), thus indicating a continuity of use of the same clay deposits throughout the whole of the Renaissance period.

The glazes of the Urbino samples show a silica–lead–alkali type composition, with K prevailing over Na, and SnO<sub>2</sub> as an opacifier. Ground quartz and K-feldspar were found in different amounts in all the glazes and were probably added intentionally to the *marzacotto* in order to cover the ceramic body. In the blue glazes of both sites, cobalt and nickel were detected without arsenic and bismuth. This association indicates that these samples can be dated before about AD 1520 (Zucchiatti *et al.* 2006).

The analyses carried out on the Pesaro glazes did not allow any significant distinction to be found with respect to the Urbino group. Only minor differences in the average contents of sodium and calcium—slightly higher in the Pesaro sherds than in those from Urbino—were found. The features of the Urbino and Pesaro samples are typical of Italian Renaissance maiolica glazes and were also found in the mentioned analyses carried out on the late Renaissance maiolica from Urbino (Tite 2009). This accounts for the use of similar raw materials and production techniques for the maiolica of this area of the Marches.

As final conclusion, the data discussed above do not allow a definite difference to be established between the two sets of maiolica. In summary, on the basis of the chemical data, and as already suggested by Myers (1992), we cannot definitely exclude the possibility that the potting clay for both sets of objects was obtained from a single source, and then transported to two different maiolica production centres before the painting and glaze-firing stages. In view of the need to make further progress with this characterization study, more maiolica potsherds will be analysed, as well as clay samples from local (Urbino and Pesaro) known outcrops, in the hope that, in the meantime, kiln remains might be discovered amongst future archaeological findings.

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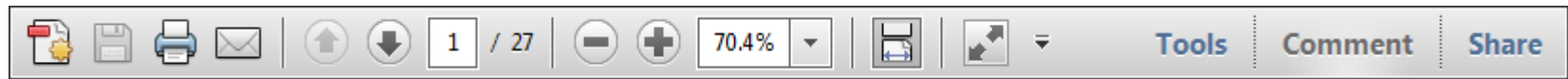
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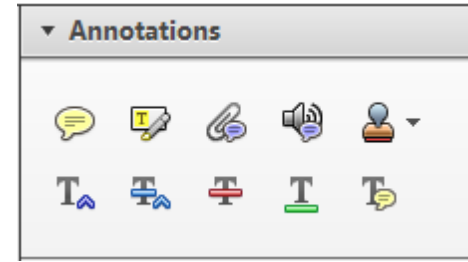
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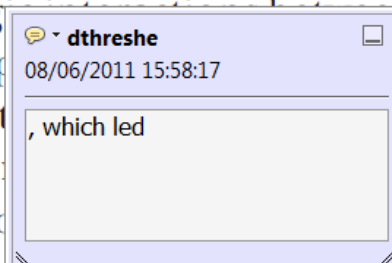


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there is no room for extra profits and the number of competitors are zero and the number of competitors (net) values are not determined by the number of firms. Blanchard and Kiyotaki (1987), in their paper on perfect competition in general equilibrium, show that the effects of aggregate demand and supply shocks in the classical framework assuming monopoly are not different from those in a perfectly competitive framework. An exogenous number of firms

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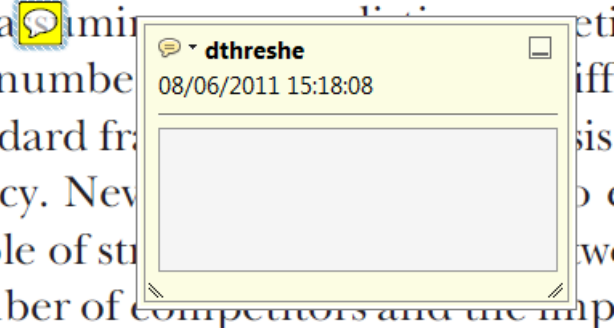


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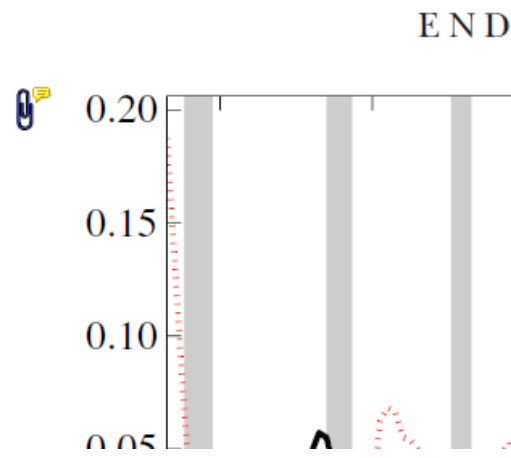
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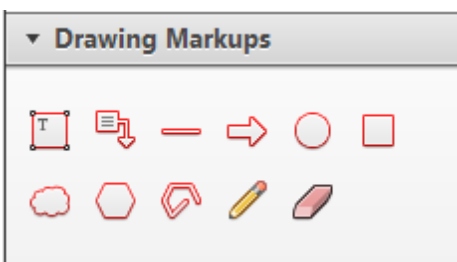


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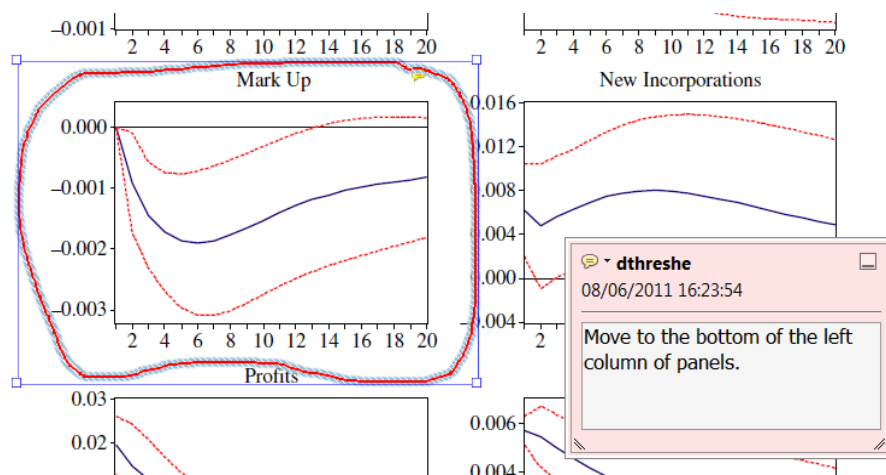


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