THE OLD POTTER'S ALMANACK

ITALIAN MAIOLICA

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Introduction

Italian maiolica is an earthenware ceramic coated with a white, opaque, lead-alkali glaze which was decorated using mineral pigments (Figures 1 and 2). The opacification was produced by the distribution within the glaze of small particles of tin oxide, typically less than 1 μm across, that result in the reflection and scattering of light (Vendrell *et al.* 2000).

Tin-opacified glazes were first produced in Abbasid Iraq in the 8th or 9th century AD, possibly in an attempt to imitate imported Chinese porcelain (Mason and Tite 1997; Wood *et al.* 2007). From Iraq,

the tin-opacified glaze technology was transferred to Fatimid Egypt during the 10th-11th centuries AD, and subsequently, from Egypt both eastwards to Syria and Iran, and westwards through north Africa to Spain. As a result of the Arab invasion of Sicily and parts of southern Italy, tin-opacified ceramics were both imported to Sicily, as well as being locally produced, during the 10th and early 11th centuries. However, during the subsequent Norman occupation, tin-opacified glazes disappeared and were effectively replaced by the use of a white slip under a lead glaze.

Figure 1. Maiolica albarello (1480-1500) – Montelupo. BM 1906.0418.1.

The tin-opacified glazes were then re-introduced into southern Italy and Sicily in the late 12th/early 13th century from north Africa or Egypt for the production of what is termed "Proto-maiolica". At much the same time, the tin-opacification technology was introduced into northern and central Italy, probably from Spain, for the production of what is here termed "Archaic maiolica" (Whitehouse 1978 and 1980). The range and quality of Italian maiolica progressively increased and by the end of the 15th century, a high level of artistic perfection had been achieved with the introduction of lusterware and *istoriato* plates and vessels which were decorated with

narrative and historical scenes (Figure 2). From Italy, tin-opacified glazed pottery spread northwards to France, the Netherlands, Germany and England, where it is referred to variously as faience, fayence and delftware.

Figure 2. Maiolica istoriato dish (c. 1530) – Urbino V&A 1748-1855.

Piccolpasso's treatise *"The Three Books of the Potter's Art"*

The technology of maiolica production in Italy in the 16th century AD is in general terms reasonably well understood, thanks to the treatise, "*The Three Books of the Potter's Art*", written by Cipriano Piccolpasso in *c.* 1557 AD (Lightbown and Caiger-Smith 2007). According to this treatise the clay body was biscuit-fired, probably to a temperature in the range from about 900-1000°C. A tin-opacified glaze was prepared by milling a mixture of *marzacotto* (i.e., a sintered mixture of sand, wine lees and sometimes, common salt) with lead and tin oxides, and sometimes, further sand. This mixture was applied to the biscuit-fired body. The decoration was then painted on the unfired powdery glaze surface, and a transparent glaze, referred to as *coperta*, was sometimes applied before firing the ceramic for a second time.

Although an extremely valuable source of information on Renaissance ceramic technology, it must be remembered that the Piccolpasso treatise was based on the observations of the technology as practised at one centre, Castel Durante, in the years

Vessel type	Provenance	Date	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO	TiO_2	FeO
Jug	Faenza	early15th	53.8	12.7	bd	2.7	2.2	22.0	na	6.6
Plate	Pesaro	mid 15th	55.0	13.6	2.5	0.9	3.7	18.5	0.5	5.3
Bowl	Deruta	late 15th	51.9	15.3	1.0	2.7	8.7	14.2	0.6	5.5
Bowl	Castel Durante	early16th	47.5	18.2	1.2	2.4	4.0	20.2	0.7	5.7
Bowl	Faenza	late 16th	55.8	15.7	1.2	2.7	4.1	14.2	0.7	5.6
Fluted bowl	Urbino	late 16th	48.0	13.1	0.9	1.9	4.1	25.1	0.5	6.3

Table 1. Chemical compositions of Italian maiolica bodies (analyses normalised to 100%; bd: below detection limit; na: not available).

before 1557, and that these observations were made by one person who was not himself a potter. Furthermore, there are the problems associated with the fact that potters are a secretive group (Piccolpasso's *Prologue for readers*), and with the difficulties of identifying the actual raw materials from the combination of their general description and, sometimes, the place name of their source.

Therefore, it is important to determine the extent to which the production technology described by Piccolpasso in *The Three Books of the Potter's Art* matches that inferred from the microstructural and compositional study of a range of Renaissance maiolica from Italy dating from the early 15th century through to the late 16th century (Tite 2009).

Reconstruction of the production technology

The principal technique used in the reconstruction of the production technology of Italian maiolica is the examination of polished cross-sections through the tin-opacified glazes and into the bodies of the ceramics in an analytical scanning electron microscope (SEM) (Kingery and Aronson 1990; Moroni and Conti 2006; Tite 2009). The SEM is operated in backscatter detection mode in which the different phases present can be distinguished on the basis of their atomic number contrast (e.g., quartz particles appear dark compared to the higher atomic number lead glazes and tin oxide particles). Typically, the bulk compositions of the glazes and bodies are determined by analysing areas up to about 0.3 mm x 0.3 mm using an energy dispersive spectrometer (EDS) attached to the SEM. These EDS analyses can be supplemented by the analysis of individual phases or homogeneous areas of glaze, such as the transparent *coperta*, using a wavelength dispersive spectrometer (WDS).

Bodies. Chemical analysis indicates that calcareous clays, with lime contents normally in the range 14-25 wt% CaO, were used in the production of the great majority of the Renaissance maiolica bodies (Table 1). As observed in the SEM, the maiolica bodies typically consist of abundant quartz and potassium feldspar particles set in a fine network of interconnecting relict clay and glass phases (Figure 3), an extent of vitrification that suggests a firing temperature in the range 850-1050°C (Maniatis and Tite 1981). The interaction between the body and the glaze is generally limited, with the glaze penetrating into the body to a depth of only about 20-30 μm.
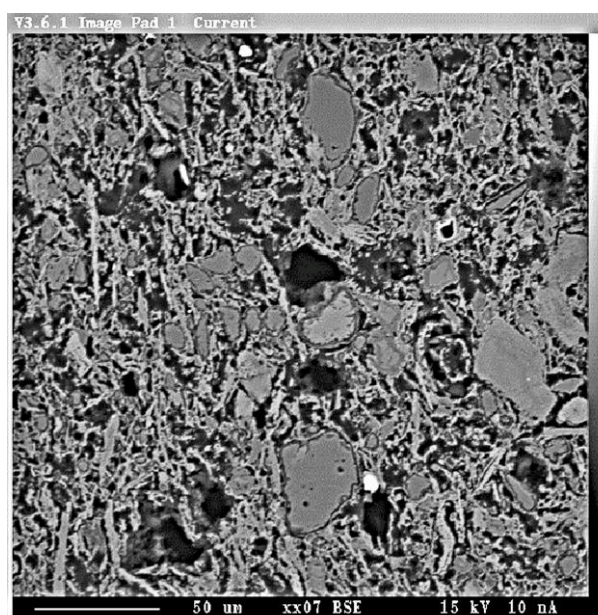

Figure 3. SEM photomicrograph of section through body of Renaissance maiolica vessel showing quartz and feldspar particles (darker grey) set in a network of interconnecting relict clay and glass phases.

In the context of Piccolpasso, the calcareous clay bodies are consistent with the inference from Piccolpasso (para. 3-4) that marly clays (i.e.,

"wherever the earth is white, or contains *genga*") were used. Similarly, the firing temperature range, estimated from the observed microstructure, is consistent with the use of up-draught kilns, as described by Piccolpasso (para. 91-95), for the biscuit firing of maiolica bodies. Further, the generally limited interaction between the body and the glaze reflects the use of separate biscuit and glaze firings.

Glazes. The microstructures of maiolica glazes, as seen in the SEM, indicate that there are two primary types of glaze. The first glaze type consists of a single opaque glaze layer containing fine tin oxide particles, ranging from individual particles typically less than about 1 μm across to clumps up to about 10 μm across (Figure 4). In addition, many of these glazes ontain varying amounts of angular quartz and potassium feldspar particles up to about 50 μm across. For this glaze type, when lead antimonate
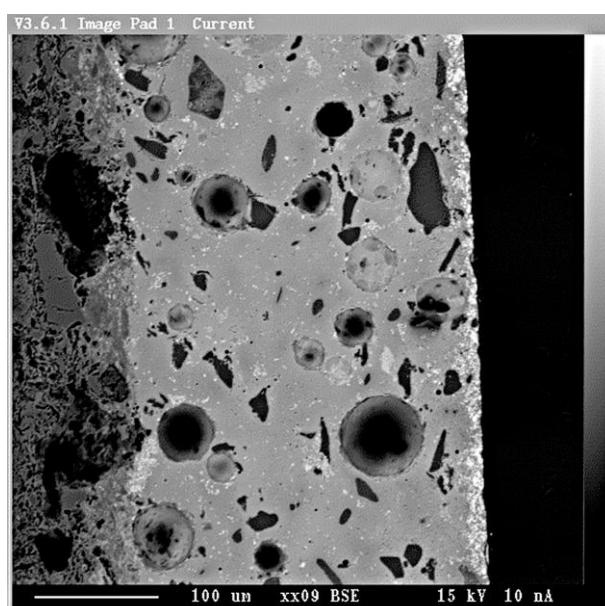

Figure 4. SEM photomicrograph of section through Renaissance maiolica glaze showing single glaze layer with a scatter of tin oxide particles (white) and quartz and feldspar particles (dark grey) distributed uniformly through the glaze together with a thin layer of lead antimonate particles (white) at the glaze surface.

particles associated with yellow decoration are included in the cross-section, they are present as a layer, up to about 50 μm thick, at the surface of the glaze. In contrast, the second glaze type consists of two layers. The inner opaque glaze layer again contains fine tin oxide particles, and angular quartz and potassium feldspar particles, whereas the outer transparent glaze layer (i.e., *coperta* layer), is more or

less clear of such particulate crystalline phases (Figure 5). For this glaze type, lead antimonate particles, when included in the cross-section, are located at the interface between the inner and outer glaze layers.
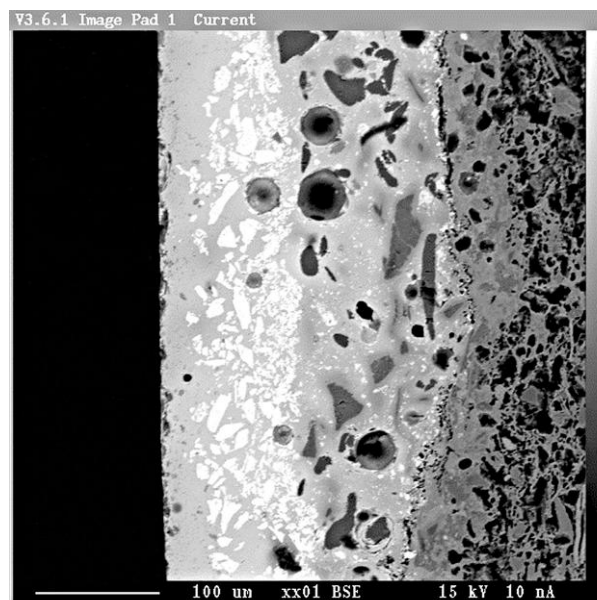

Figure 5. SEM photomicrograph of section through Renaissance maiolica glaze showing double glaze layer with inner glaze containing a scatter of tin oxide particles (white) and quartz and feldspar particles (dark grey), and outer glaze containing a well defined layer of lead antimonate particles (white) located at the interface between the two glaze layers.

Chemical analysis indicates that Renaissance maiolica glazes are consistently of the lead-alkali type with lead oxide contents in the range 13-35 wt% PbO and total alkali contents in the range 5-11 wt% ($Na_2O + K_2O$) (Table 2). The potash contents of these glazes are all greater than the soda contents, the K_2O/Na_2O ratios typically being in the range 1.5 - 6. In the case of the two-layer glaze type, the transparent outer glazes differ from the opaque inner glazes in generally containing lower silica (up to 13 wt% less SiO_2), higher lead oxide (up to 6 wt% more PbO) and higher total alkali (up to 4 wt% more ($Na_2O + K_2O$)). The tin contents of the opaque glazes are typically in the range 4-9 wt% SnO_2 with the great majority of the SnO_2/PbO ratios in the range 0.2-0.4.

In the context of Piccolpasso, the angular quartz and potassium feldspar particles observed in a high proportion of the glazes are almost certainly the result of the additional sand which Piccolpasso describes as sometimes being added to the glazing mixture of *marzacotto*, and lead and tin oxides, and

Vessel type	Provenance	Date (cent AD)	Glaze type	Glaze opacity	Glaze thickness (µm)	SiO2	PbO	SnO2	Na2O	K2O	CaO	MgO	Al2O3	FeO	MnO	CoO	SnO2/ PbO	K2O/ Na2O
Bowl	Florence	early 15th	Single	Opaque	150	45.1	34.4	5.5	0.8	4.6	4.2	0.7	3.3	1.2	bd	na	0.2	5.7
Jug	Faenza	mid 15th	Single	Opaque	50	53.4	20.0	4.7	2.2	8.4	2.7	3.7	2.4	2.2	bd	0.4	0.2	3.9
Bowl	Urbino	late16th	Single	Opaque	350	58.2	21.1	6.3	1.2	6.6	0.3	2.4	3.2	0.7	na	na	0.3	5.5
Jug	Siena	early 15th	Double	Opaque	200	53.4	27.6	5.1	1.2	5.3	3.6	0.4	2.5	0.6	na	na	0.2	4.4
				Transparent	200	49.5	34.1	0.6	0.8	7.5	4.0	0.5	1.9	0.6	0.1	bd	<0.05	9.1
Tile	Bologna	late 15th	Double	Opaque	200	63.0	17.8	5.8	2.1	4.2	2.0	0.1	4.2	0.6	0.2	na	0.3	2.0
				Transparent	100	50.3	24.2	0.3	3.8	6.4	2.7	0.5	4.8	6.3	bd	bd	<0.05	1.7
Plate	Faenza	early 16th	Double	Opaque	370	62.8	14.7	4.4	1.5	5.6	2.5	0.6	6.2	1.2	bd	0.5	0.3	3.7
				Transparent	230	59.6	15.4	2.8	2.0	6.1	1.7	0.6	6.1	2.8	bd	2.8	0.2	3.0

Table 2. Chemical compositions of Italian maiolica glazes (analyses normalised to 100%; bd: below detection limit; na: not available).

which underwent only limited dissolution during the second firing. The presence of both potash and soda in the glazes is similarly consistent with Piccolpasso's description (para. 62) of the use of wine lees, which are potassium-rich, and common salt in the production of the *marzacotto*. Further, the K_2O/Na_2O ratios estimated from representative recipes for *marzacotto* given by Piccolpasso are in the range 2-4, and therefore, match the measured ratios. The glaze compositions estimated from the recipes given by Piccolpasso indicate that, as observed, the transparent glazes are expected to have lower silica, and higher lead oxide and alkali contents than the opaque glazes. Finally, the SnO_2/PbO ratios estimated from Piccolpasso's recipes are in the range 0.15-0.5, and therefore, again match the measured ratios.

Pigments. The principal pigments used in the decoration of Renaissance maiolica are copper producing a green colour in a lead glaze, and cobalt producing a blue colour, both of which are present as ions in the glass phase. In contrast, lead antimonate, producing yellow and orange colours, is present as particles. The orange lead antimonate pigment differs from the yellow in being associated with significant amounts of iron oxide, which is probably both incorporated into the lead antimonate particles and dissolved in the surrounding glass phase.

Piccolpasso similarly lists a green pigment (para. 65) described as "burnt copper" and made from oxidised copper metal; a blue pigment (para. 67) described as a cobalt ore, *zaffre*, and obtained from the Erzgebirge region of Saxony by trade through Venice; and "light yellow" and "yellow" pigments. The "light yellow" and "yellow" pigments (para. 67 and 79-80), which correspond respectively to the yellow and orange pigments referred to above, are described as being

produced by prefiring mixtures of lead oxide, antimony oxide and wine lees, with iron scale being added to the mixture in the case of the "yellow" pigment, as observed for the equivalent orange pigment.

Reasons for the observed technological choices

The distinctive technological choices made in the production of Italian maiolica include the use of calcareous clays for the bodies, the use of lead-alkali glazes, the addition of further sand to the glazing mixture, and the application of a transparent *coperta* layer over the painted decoration.

Calcareous clay bodies. In addition to their ready availability throughout much of Italy, an important advantage of calcareous clays is that they fire to a pale buff colour even when they contain several percent of iron oxide (Molera *et al.* 1998). Consequently, the body colour is more readily concealed by a tin-opacified glaze than in the case of non-calcareous, red-firing clays. Second, calcareous clay bodies tend to have a higher thermal expansion coefficient (4.5-7.0 x 10^{-6}/°C) than that of comparable non-calcareous clays (2-3.5 x 10^{-6}/°C). Their thermal expansion coefficients, therefore, more closely match those of lead-alkali glazes (7-9 x 10^{-6}/°C), and consequently there will be less risk of glaze crazing during the cooling following the second firing (Tite *et al.* 1998: 246). A further advantage of calcareous clays is that, due to the formation of crystalline phases, their microstructures remain essentially unchanged over a 850-1050°C firing temperature range. Therefore, the control of the firing temperature needed to produce pottery of a consistent quality, and to avoid the distortion of the pottery resulting from overfiring, would have been less critical when calcareous clays were used. Finally,

as a result of the formation of crystalline phases, the shrinkage during firing of calcareous clays is significantly less than for non-calcareous clays (Tite 1970), and the resulting bodies have a greater rigidity and compressive strength than those produced from comparable non-calcareous clays.

Lead-alkali glazes. One significant advantage of lead-alkali glazes is that they absorb light in the blue region of the spectrum. Therefore, because the submicron sized tin oxide particles scatter light in the blue region of the spectrum, tin-opacified lead-alkali glazes appear whiter than both tin-opacified alkali glazes, which are slightly bluish, and tin-opacified high-lead glazes which, because of their greater absorption in the blue region, tend to appear cream.

Addition of further sand. The reason for the addition of further sand to the glazing mixture, resulting in the presence of angular quartz and feldspar particles in the opaque glaze layers, is not immediately obvious. Because the refractive indices of quartz and feldspars are comparable to that for the glaze, sand will not make a significant contribution to the opacity of the glaze when tin oxide, which has a much higher refractive index (about 2.0 as compared to 1.5-1.6 for the glaze), is also present. An alternative explanation is that, when sand is included in the glazing mixture, the unfired, opaque inner glaze is more robust and less powdery. Its surface is therefore better suited to taking the painted decoration, and also, the risk, discussed by Piccolpasso (para. 214), of the unfired, opaque inner glaze layer separating from the body when applying a *coperta* layer by dipping is reduced.

Application of coperta layer. An important advantage of applying a *coperta* layer over the decoration is that its higher lead oxide and alkali contents, as compared to the underlying opaque glaze, means that, during the second firing, it will have a lower viscosity and will therefore be more effective at filling the pores within any lead antimonate particulate pigment (Figure 5). Thus, the *coperta* layer will help in creating a bright smooth reflective surface, and in making the colours more luminous. In addition, the *coperta* layer will also provide a protective coating over the painted decoration and thus reduce wear, a factor that would have been particularly important in the case of maiolica floor tiles.

Conclusions

In summary, the microstructures and the body, glaze and pigment compositions for Italian maiolica, as determined by scientific examination in an analytical SEM, are fully consistent with the description of its production technology given by Piccolpasso in "*The Three Books of the Potter's Art*".

Further, the use of calcareous clay bodies and lead-alkali glazes, the addition of sand to the opaque glazes, and the final application of a transparent *coperta* glaze with a lower viscosity than the underlying opaque glaze can, in general, be explained in terms of ease of production and the quality of the final product.

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