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ORIGINAL ARTICLE

Technical changes in the glaze composition of tin-glazed sculptures by Benedetto Buglioni c. 1490–1510

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Abstract
During the 15th and into the mid-16th centuries, tin-glazed terracotta sculptures were celebrated for their luminous colours, perceived durability, and technical ingenuity of the novel medium. Although in high demand, the supply of these pieces was restricted because of the secrecy of the recipes used by the pioneers of the technique on the Italian peninsula, namely the Della Robbia family. As the Della Robbia workshop procedures did not come down to us in a written form, art historical scholarship has focused on retrieving the original recipes through scientific analyses of surviving pieces. Building on those investigations, this article addresses the technique of another master of tin-glazed terracotta sculpture, namely Benedetto Buglioni (1459/1460–1521). Buglioni likely experienced the Della Robbia production first hand as he trained in Andrea della Robbia's (1435–1525) workshop. He began his independent sculptural activity in the 1480s. For the present study, two of his figures, now in Polish collections, dated to the most prolific period of his artistic career, have been examined using X-ray fluorescence spectroscopy (XRF). The interpretation of the results is informed by previous examinations of the Della Robbia glazes, as well as by contemporary written sources, including an early 16th-century recipe book from Montelupo, Tuscany. The present study reconsiders the understanding of the Buglioni glazes as merely derivative and inferior to the surfaces of the

Della Robbia sculptures. The physical examination of Benedetto Buglioni's works reveals a high degree of experimentation in his approach to the medium of tin-glazed terracotta.

KEYWORDS
Benedetto Buglioni, body/glaze composition, Buglioni workshop, ceramic practice, Della Robbia, historic recipes, tin-glazed sculpture, XRF

INTRODUCTION

Studies of Renaissance glazed terracotta sculpture have focused on the analysis of clay bodies and glazes in the context of the celebrated Della Robbia family (Bouquillon et al., 2011; Dias et al., 2017; Gianoncelli et al., 2006; Hykin, 2016; Kupiec, 2016; Vaccari, 1996; Walker & Riccardelli, 2019). Within the framework of these studies, artworks attributed to the Buglioni workshop have been analysed; however, the focus of those examinations was on confirming the technical uniformity of the production process across almost a century of the development of the technique of tin-glazed sculpture in the context of Florentine production from c. 1430 to 1530 (Barbour & Olson, 2011; Zucchiatti & Bouquillon, 2011). Considerably lesser studied examples of sculptures from the Della Robbia workshop, which made use of the same technique but in the years of activity outside Tuscany, supported the data about the continuous use of the same recipes for artworks produced elsewhere (Amadori et al., 2013).

The Della Robbia artists did not share their secret recipes for making glazes with lesser known artists because their income depended on the technical ingenuity and on ways in which their product was distinctive from other works available at that time. However, despite their efforts to control the market, toward the end of the 15th century, their rivals, the Buglioni artists, also began to produce glazed terracotta sculptures (Tarchiani, 1934). In his *Life of Andrea del Verrocchio* (1435–1488), Giorgio Vasari included a story of a woman, from the house of Andrea della Robbia, who revealed the secret of the trade to the Buglioni workshop (Vasari 1568). The account is in all probability mythical, and the technical knowledge was likely gained gradually through direct observation, whereas the Buglioni worked as apprentices for the Della Robbia (Gentilini, 1992, p. 390).

The present study focuses on the analysis of the glazes in two artworks currently preserved in Polish collections, namely *Tondo with Christ the Redeemer*, now in the National Museum in Warsaw (Figure 1), and the *Virgin and Child*, now in the National Museum in Cracow, Czartoryski Collection (Figure 2). The study compared the elemental composition of the glazes of two artworks dated to the most prolific period of Benedetto Buglioni's career. The work seeks to reassess the view shared in art historical scholarship about the inferior and derivative quality of the Buglioni glazes.

For our survey, we chose to use X-ray fluorescence (XRF), exploiting a portable device as the artworks were not allowed to leave the museums nor was sampling allowed. Indeed, XRF is a well-established technique in the field of Cultural Heritage, as it allows to perform in situ non-destructive analyses and to obtain the elemental composition of the sample with fast measurements. This technique had already been used in published papers (Pappalardo et al., 2004; Zumbulyadis & Van Thienen, 2020) on similar materials, showing its great potential. In the present work, we coupled this technique with visible fluorescence induced by ultraviolet (UV) light and digital optical microscope (OM) images.

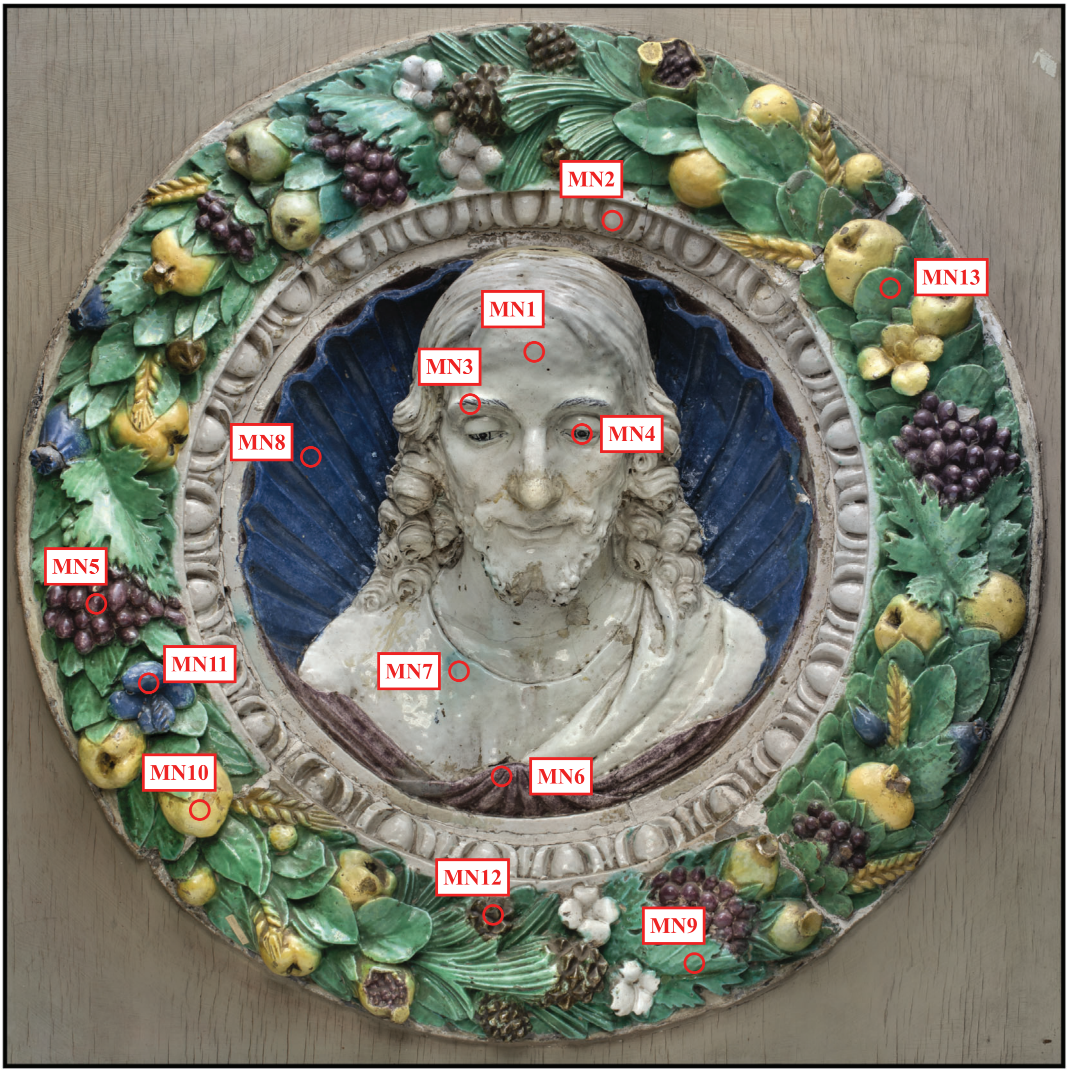

FIGURE 1 Benedetto Buglioni, *Tondo with Christ the Redeemer*, c. 1490, tin-glazed earthenware, diameter: 75 cm, depth: 11 cm, National Museum of Warsaw, inv. no. 77039 MNW (image with the marked points for XRF analysis).

MATERIALS AND METHODS

The two Benedetto Buglioni's terracotta sculptures

Both works considered in the present paper have been attributed on stylistic basis to Benedetto Buglioni (1459/1460–1521). The *Tondo with Christ the Redeemer* (d: 75 cm, depth: 11 cm) reveals clear affinities with the Florentine sculpture of the 1480s, reflecting the modelling tradition of Andrea del Verrocchio. The rings of curls around Christ's face could have been translated directly from a polychromed terracotta figure of the *Christ the Redeemer* by Verrocchio or his circle. A historical photo, reproduced in a journal in the 1920s shows the Warsaw tondo without the garland (Malaguzzi Valeri, 1922–1923), while another photograph preserved in the

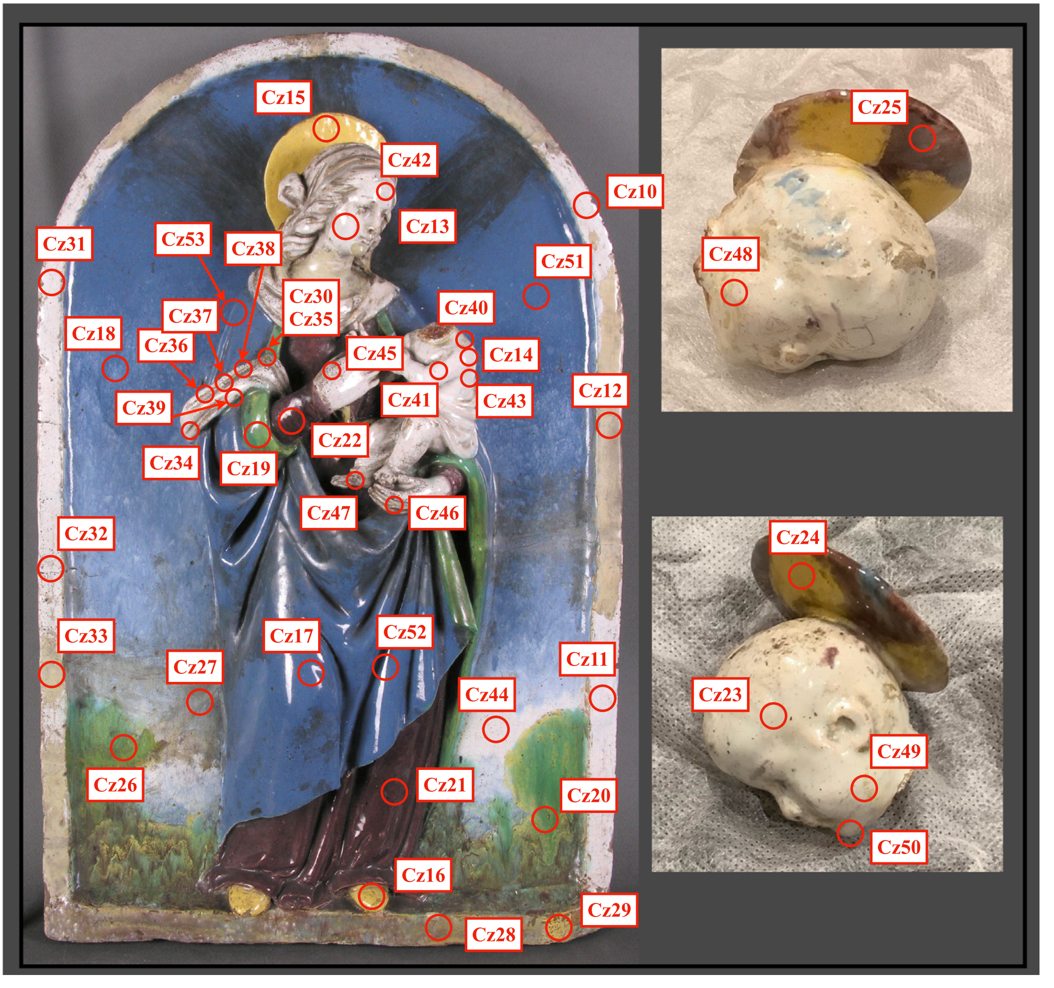

FIGURE 2 Benedetto Buglioni, *The Virgin and Child*, c. 1510, tin-glazed earthenware, h: 62 cm, w: 40 cm, depth: 9 cm, National Museum of Cracow, Czartoryski collection, inv. no. MNK XIII C 335 (image with the marked points for XRF analysis).

image collection of the Kunsthistorisches Institut in Florence shows the tondo without the garland with a caption "Ferrara, private collection. Andrea della Robbia". The photographs illustrate the early 20th-century state of the Warsaw tondo and suggest that the vegetal frame, with which it is currently preserved, is a later addition and therefore not commented on as original. The *Virgin and Child* relief is a small-scale devotional tabernacle (h: 62 cm, w: 40 cm, depth: 9 cm), a type of sculpture hugely popular in 15th- and 16th-century Italy. The relief is glazed throughout, including the background and the frame. The Virgin holds a nude Christ on her left arm, while her white shawl wraps around the lower part of his body, forming a kind of perizonium. She wears a mantle of blue with green lining and a maroon tunic. Her bright yellow shoes and the colour of her tunic are characteristic of Benedetto Buglioni's colour scheme in the early 1500s. In style it reflects Buglioni's fascination with slightly elongated proportions, as in his works for the Cathedral in Bolsena, Lazio region (Italy). The Cracow relief predates a similar example in the collection of the Cleveland Museum of Art (Marquand, 1921) with unglazed nudes and different proportions of the bodies.

The analytical protocol

The present study combines the traditional methods of art history and the scientific investigations using a fully non-destructive technique based mainly on X-ray fluorescence spectroscopy. The research relies on the object-based analysis of the two glazed terracotta sculptures and the technical and historical investigations into the processes of their making. This methodology benefits from the approach to Renaissance art that is informed by a series of technical analyses conducted in various international laboratories.

Visible fluorescence induced by UV light

Ultraviolet analysis of the whole surface of both objects was also conducted prior to the measurements in order to identify the non-original areas. This procedure, and the interpretation of obtained fluorescence, was made with the guidance of museum conservators.

X-ray fluorescence (XRF)

As mentioned in the introduction, due to the character of the analysed artworks, which are valuable objects housed in museum collections, the study had to be conducted in situ and with a fully non-destructive protocol. Therefore, the study of the chemical elements present in the glaze was done with a portable X-ray fluorescence (XRF) spectrometer, notwithstanding the limitation of the technique on light matrix materials and irregular surface. Indeed, previous works used XRF in several cases of glazed ceramic studies (Bajnóczi et al., 2015; Zumbulyadis & Van Thienen, 2020) also on the Della Robbia and the Buglioni artworks, in one case coupled with PIXE for the evaluation of both light matrix and trace medium-heavy elements (Pappalardo et al., 2004). In general, portable XRF spectrometers can detect elements from aluminium to uranium, allowing the analysis of a great variety of samples; it is also possible to perform quantitative analysis under special conditions, that is, if the sample is flat and optically smooth for the incoming radiation wavelength and homogeneous, whereas a variation of thickness can affect quantitative results. Samples related to the Cultural Heritage applications rarely satisfy these requirements, as they can seldom be considered homogeneous for the alteration processes they may have undergone or for their original structure, such as painted surfaces, gilded artifacts, or glazed ceramics, as in the present case.

The XRF measurements reported in the present paper were performed with a handheld Genius 7,000 (Jiangsu Skyray Instrument Co., Ltd.) spectrometer equipped with Ag anode microtube (operating at a maximum voltage of 40 kV and current of 100 μA) and a large silicon drift detector (SDD) with a resolution of about 139 eV at 5.9 keV and a Be window of 0.3 mil thickness. The incident radiation on the sample was collimated down to 4 mm in diameter. It was equipped with six different filters with automatic switching function to allow better excitation of both low and medium–high Z elements. For each considered point (detailed in the following sections) on the artworks, measurements were performed for 60 s at 38 kV and 50 μA and for further 60 s at 10 kV for a total measuring time of 120 s. We did not use the instrument algorithm for quantification of chemical elements but relied on the manual study of obtained spectra, exploiting intensity ratios for semi-quantitative evaluations, thus considering the specificity of the single analysed point. This choice results from the fact that, in the present case, as already mentioned, the quantitative evaluation of composition and of layer thickness is not immediate, as they both are unknown and depend on one another. As the glaze thickness typically is between 100 μm and 200 μm, we expect XRF spectra not to be influenced by the underlying ceramic bulk composition, but this aspect clearly depends on the exact thickness and composition of the investigated point glaze. On this base, we considered our spectra to be generated only from the glaze layer, with no influence from the clay below. Indeed, to have a reliable quantification on the chemical elements for layered samples, the use of specific set ups is required, such as Rutherford backscattering spectroscopy (RBS) (Pradell et al., 2007), or particle induced X-ray emission (PIXE) (Mandò, 2005), the use of confocal-XRF (Kanngießer et al., 2012), grazing emission-XRF (GE-XRF), and grazing incident-XRF (GI-XRF) or angle resolved-XRF (AR-XRF) (Baumann et al., 2021; Orsilli et al., 2023). None of these techniques was applicable to the present study, because working in museum collections and with a limited amount of time for the measurements, a fast investigation method was needed. Different methods of data elaboration have also been proposed for the analysis of layered samples using laboratory XRF set up, as the study of Kα/Kβ or Lα/Lβ ratios (Brocchieri et al., 2021) or the use of Monte Carlo simulations (Trojek, 2020), surely reliable if simple layers or mixtures are present. In our case, due to the significant amount of unknown variables, we decided against systematically applying such data elaboration methods. Therefore, following a procedure sometimes used for light matrix materials (Micheletti et al., 2020), and also for glazed ceramics (Zumbulyadis & Van Thienen, 2020) when working with portable XRF, the study does not include a quantitative analysis but relies on a semi-quantitative evaluation of significant element peaks, following a careful qualitative comparison of the spectra. All deductions and comparisons reported in the present paper consider the net peak X-ray areas of the XRF spectra, calculated by subtracting the background and fitting the spectra. The spectra were deconvoluted using the AXIL software suite (Vekemans et al., 1994) and the areas analysed with statistical tools developed for the purpose of the present study. Most of the analysis focused on the spectra acquired at 38 kV (40 kV nominal) voltage of the X-ray tube and used K-lines where possible. L-lines were used only when considering Pb. Even if only semi-quantitative analysis could be performed, making the comparison with literature data more difficult, it is surely a suitable approach for a qualitative overview and a comparison between different objects supposed to be from the same class (Micheletti et al., 2020; Zumbulyadis & Van Thienen, 2020). Repeatability is guaranteed by choosing flat areas and applying the measuring head directly on the object.

Digital optical microscope

Selected regions of the objects were inspected also by means of a portable optical digital microscope (OM) with polarised light, 1.3 Mpxls, and 50X enlargement (DinoLite AM4113ZT). These regions include all points analysed by XRF, prior to each measurement.

Choice of the investigated areas: The meeting point of the analytical protocol and historical-artistic information

The two objects have been examined under various lighting conditions (visual analysis using ambient light, fluorescence induced by UV light) and using the high-magnification microscope. Working closely with the museum conservators, this examination permitted the selection of the specific points for scientific measurements, in order to ensure that the study makes the best use of the resources available, time included.

In the following, the measured points on the *Tondo with Christ the Redeemer* will be indicated as MN (this reflects the present location of the object in the National Museum - Muzeum Narodowe - in Warsaw), whereas points of the *Virgin and Child* relief will be indicated as Cz (present location at the Czartoryski Collection, National Museum in Cracow), as reported in Figures 1 and 2. In both cases, XRF analyses were performed in situ in the respective museums. The expert conservators and curators from both institutions have guided the selection of the points from the original glazes, confirmed by the UV light. In Table 1, together with the elements detected by the X-ray fluorescence spectrometer, the description of the points and their colour is reported. The Renaissance palette of glazed terracotta figures was fairly restricted, and points were selected to cover all the colours present in the glazes of the two analysed works. However, the non-original points identified during the examination of the object under different lighting conditions have been excluded from the analysis.

Points on white glaze

In glazed terracotta sculptures lead is the main component of white glazes. From the 15th century with the influx of earthenware from the Islamic world, tin began to play the key role as the opacifier. In Iraq and Syria from the late seventh century tin oxide was added to transparent glazes to increase their opacity (Hess, 2004). Importantly, the Della Robbia's glazes contained almost three times more tin oxide than other glazed terracotta produced in various parts of Italian Peninsula at that time. As reported by Barbour and Olson, the Della Robbia glazes contained 20.3% versus 7.2% discovered in glazes from Casteldurante (Bouquillon et al., 2011). This ensured the high brilliance of white reliefs but also placed high tension on the surface, especially if the sculpture in its biscuit-fired state was not clean and dusted properly. Moreover, because of the high proportion of tin oxide, the Della Robbia's glazed sculptures had to be fired at a higher temperature than other glazed earthenware, as the reduced level of lead decreased the glaze's potential for melting (Hubbard & Moture, 2001). Based on this technical observation, in the present study we have decided to focus on the analysis of white, to conduct a semi-quantitative analysis, and to verify whether the relative ratios could provide information about the eventual change in the Buglioni's technique.

Points on coloured glaze

Purple and brown hues (usually manganese-based glaze), present in the Virgin's tunic, the Christ Child's halo, and the Christ the Redeemer's robes, were also examined; as described by Cipriano Piccolpasso in his 16th-century treatise on potter's art, manganese compounds of high quality and in considerable quantities were to be found in Tuscany and exported from the region across the peninsula in relation to the glass industry (Piccolpasso, 1980, vol. 1, c. 26r.). Copper green, after manganese purple/brown, was a colour traditionally widely used in ceramic glazes (Gelichi, 1992). As pointed out by Piccolpasso, copper green melts easily into a glaze; however, it had to be calcined in order to obtain the desired tone and ensure that the glaze is not too pale or too blackish. Because in the *Tondo with Christ the Redeemer* green is only present in the frame, which did not belong to the original work, we were not able to compare the approach to obtaining this hue within the Buglioni practice.

With time more colours were introduced, most notably blue from cobalt. The analysis of blue was of particular interest to our study, as the previous work on the Della Robbia glazes has provided ample comparative material, against which the chemical compounds of the investigated works in Polish collections could be seen.

Finally, we have selected points in sections with the yellow glaze, traditionally obtained from antimony. When attempting to create yellow decoration, the Buglioni had to take into account that both tin oxide and lead antimony are refractory, which could result in blistering of the glaze. Hence the need to add a sufficient amount of flux to ensure that the colours fuse properly without running or blistering (Kingery, 1993; Kingery & Aronson, 1990; Piccolpasso, 1980, vol. II, xix). Although absent in the original, central part of the Warsaw tondo, yellow has been used in many details of the Virgin and Child relief, including the Virgin's and Christ's haloes, her shoes and girdle, and in the background.

RESULTS

The results from analytical investigations have been cross-examined with the information from written sources, primarily contemporary artists' handbooks and recipe books, also keeping in mind that the study sought to confirm whether the glazes in these two artworks are sufficiently similar to be attributed to the same workshop. Subsequent aim was to reconstruct the specificities of Benedetto Buglioni's artistic technique and materials used in order to evaluate whether the differences in the glaze composition between the two works point to the revision of the working method.

The qualitative analysis obtained from the XRF spectra for the measured points both for the *Tondo with Christ the Redeemer* (MN) and for the *Virgin and Child* (Cz) is detailed in Table 1; elements characterising the colour of the glaze are highlighted in bold.

In Table 1 and in the following analysis and discussion, only regions of the two objects considered to be original and non-retouched are taken into account. Furthermore, points on areas that presented evident signs of damage to the glaze, in particular those on the frame of the *Virgin with Child*, were also not considered, because they have been partly abraded and retouched in several campaigns of conservation treatments, resulting in the high irregularity of the glaze-layer thickness. Hence, the points labelled MN2, Cz10, Cz11, Cz12, Cz32, Cz33, and Cz27 in Figure 1, as well as all those acquired on the frame of the *Tondo* in Figure 2 (MN5, MN9, MN10, MN11, MN12, MN13), which is not original, are not presented. For each measured point, an investigation by eye, with the optical microscope and with UV light, was conducted prior to selecting the area to analyse and acquiring the X-ray fluorescence spectra. The non-original areas of both objects were clearly identified (see UV images in Supplementary Materials Figures SM1 and SM2).

Glaze

The data allowed us to verify that the white glaze is characterised by the presence of Sn and Pb, coherently with the expected results. Nevertheless, there are clear differences in the relative amounts of Sn and Pb, with Sn/Pb ratios between the respective normalised areas varying from 4.8% to 10% for the white glaze. In Figure 3, the amount of Pb versus the amount of Sn, expressed as raw areas of the respective Kα and Lα peaks, are presented. Although the average Pb content is rather constant, the intensity of the Sn peaks has a greater variability and is on average higher for the white points in the *Tondo with Christ the Redeemer*, which predates the *Virgin and Child* by about 20 years.

Several of the white points analysed in the *Virgin with Child* (Cz34, Cz35, Cz36, Cz37, Cz38, Cz46, and Cz47) showed an interesting feature, because they are characterised by the presence in the spectra of Cu and Fe in slightly larger amounts and of a significant abundance of Zn. Indeed, an optical inspection both by eye and by optical microscope shows a much less smooth surface with metallic residues of a brass-like/goldish colour, which have corroded the smoothness of the glaze. It should be noted that no trace of Au nor Hg has been found in the data for the points in which the metallic residues are present, nor in any other of the points (see section Discussion for details). In Figure 4 microscope images corresponding to areas presenting the metallic inclusions (Cz35 and CZ45) and "clear" areas (Cz44 and Cz42) are shown as an example, whereas the corresponding spectra are reported in the Supplementary Material Figure SM3. Bivariate statistical analysis performed on the intensities of the Cu and Zn peaks

TABLE 1 Qualitative analysis of the XRF spectra. Major component xx, minor component x, and trace (x). Elements characterizing the pigment are in bold. With the exception of Pb, for which Lα was used, Kα lines were used for the qualitative amounts determination. AXIL was used to extract the areas from the spectra.

Point ID	Region	Color	Comment	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sr	Zr	Sn	Sb	Pb
MN1	White	White	Main body	x	(x)			x			x	x	x	x	Xx	(x)	Xx
MN3	White	White	Main body	x	(x)		(x)	x			x	x	x	x	Xx		Xx
Cz13	Cheek	White	Main body	x	**x**			x			x	**Xx**	x	Xx	Xx	(x)	Xx
Cz14	Baby's shoulder	White		x	(x)			x			x	x	x	x	Xx	(x)	Xx
Cz23	Baby's head	White		x	(x)			x			x	x	Xx	Xx	Xx	(x)	Xx
Cz30	Shawl	White	Region with gilding imitation	x	(x)			x			Xx	**Xx**	x	(x)	x	x	Xx
Cz31	Frame	White		x	x			x			x	x	x	x	x		Xx
Cz34	Scarf	White	Region with gilding imitation	x	x			x			x	x	x		x		x
Cz35	Scarf	White	Region with gilding imitation	x	x			x			x	Xx	x	x	x		x
Cz36	Scarf	White	Region with gilding imitation	x	x			x			x	x	x	x	x		x
Cz37	Scarf	White	Region with gilding imitation	x				x			x	x	x		x		x
Cz38	Scarf	White	Region with gilding imitation	x				x			x	x	x		x		x
Cz39	Scarf	White	Clear region	x				x			x	x	x		x		x
Cz40	Baby's scapole	White	Clear region	x				x			x	x	x		x		x
Cz41	Baby's arm	White	Clear region	x	x			x			x	x	x	x	x		x
Cz42	Virgin's forehead	White	Clear region	x				x			x	x	x		x		x
Cz43	Baby's back	White	Clear region	x				x			x	x	x		x		x
Cz44	Background	White	Clear region	x	x			x			x	x	x		x		x
Cz45	Virgin's right hand	White	Region with gilding imitation	x	x			x			x	Xx	x		x		x
Cz46	Virgin's left hand	White	Region with gilding imitation	x				x			x	x	x	x	x		x
Cz47	Baby's foot	White	Region with gilding imitation	x				x			x	x	x		x		x
Cz48	Baby's right cheek	White	Region with gilding imitation/paint	x				x			x	x	x	x	x		x
Cz49	Baby's left cheek	White	Region with gilding imitation/paint	x	x			x			x	x	x	x	x		x
Cz50	Baby's chin	White		x	x			x			x	x	x	x	x		x
MN7	Tunic	White/green	Main body	x	(x)		x	x			Xx	x	x	x	Xx	(x)	Xx
MN8	Shell background	Blue		x	(x)			Xx	**Xx**	Xx	x	x	x	Xx	Xx	(x)	x

(Continues)

TABLE 1 (Continued)

Point ID	Region	Color	Comment	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sr	Zr	Sn	Sb	Pb
Cz17	Cloak	Blue		x	(x)			Xx	**Xx**	Xx	x	x	x	Xx	Xx	x	Xx
Cz18	Sky	Blue		x	(x)			Xx	**Xx**	Xx	Xx	x	x	Xx	Xx	x	Xx
Cz51	Background	Blue		x	x			x	**x**	x	x	x	x	x	x		x
Cz52	Virgin's vest	Blue		x				x	**x**	x	x	x	x	x	x		x
Cz53	Virgin's vest	Blue		x			x	x	**x**	x	x	x	x	x	x		x
MN4	Eye	Purple		x	(x)		**x**	**x**		(x)	Xx	x	x	Xx	Xx	(x)	Xx
MN6	Drape	Purple		x	(x)		**Xx**	**x**			x	x	x	Xx	Xx	(x)	Xx
Cz25	Baby's aureole	Brown/purple		x	(x)		**Xx**	**Xx**			x	x	x	(x)	x	x	Xx
Cz21	Tunic	Brown		x	(x)		**Xx**	**Xx**			x	x	x	(x)	x	x	Xx
Cz22	Sleeve	Brown		x	(x)		**Xx**	**Xx**			x	x	x	Xx	x	x	x
Cz15	Aureole	Yellow		x	(x)			x			x	x	x	(x)	x	Xx	Xx
Cz16	Foot	Yellow		x	(x)			x			x	x	x		x	Xx	Xx
Cz24	Baby's aureole	Yellow		x	(x)		x	x			x	x	x	(x)	x	Xx	Xx
Cz19	Cloak	Green		x	(x)			Xx			**Xxx**	x	x	(x)	x	Xx	Xx
Cz20	Background	Green		x	(x)		(x)	Xx			**Xxx**	x	x	(x)	x	Xx	Xx
Cz26	Background	Green		Xx	**Xx**	x	(x)	x	x		**Xx**	Xxx	Xxx	Xx	x	Xx	x

Table 1 Qualitative analysis of the XRF spectra. The measured points for the *Tondo with Christ the Redeemer (MN)* and from the *Virgin and Child* (Cz) are listed with their ID according to the maps shown in Figures 1 and 2. The description of the region, colour, and comments are given. For each element, a qualitative description of its amount is marked with xx (major component), x (minor component), and (x) (trace amount). Elements characterizing the pigment are highlighted in bold. With the exception of Pb, for which Lα was used, Kα lines were used for the qualitative amounts determination.

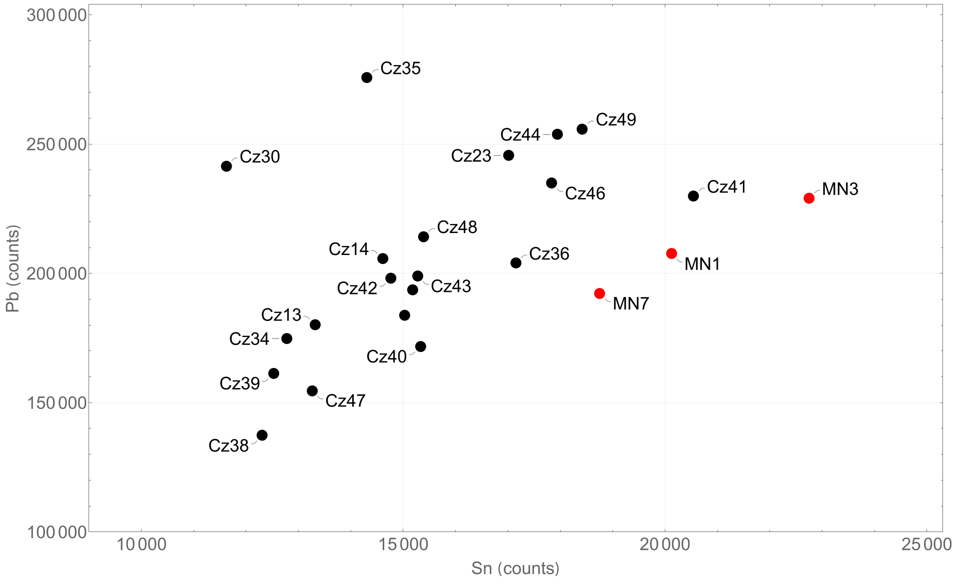

FIGURE 3 Pb versus Sn amounts (expressed as the raw area – background subtracted) of the respective Lα and Kα peaks for data obtained in this work.

for the white glaze points from both objects shows a clear separation in two groups with those stemming from the *Tondo* well embedded in the group without metallic inclusions from the *Virgin with Child*. In Figure 5 the dendrogram showing the hierarchical clustering for the Cu and Zn peak area obtained from XRF spectra is presented (Euclidean distance and complete linkage), see also Figure SM4 for a comparison of the spectra for the "clear" white areas on the two objects. On the other hand, Ti, Zr, and Sb, unless indicated as characterizing elements or recognized as companion elements to the metals in the gilding-imitation points, are present in trace and non-quantifiable amounts. Therefore, they can be considered as impurities in the raw material rather than an intentional addition to the recipe. One could use these traces of various metals to speculate on the origin of the raw materials, but such discussion goes beyond the scope of this paper.

Other colours

As a general consideration, in the original parts, chemical elements responsible for the various colours can be recognized, and namely Co and Ni for blue (Cz18 and MN8), Mn for brown and purple details (Cz21, Cz22, Cz25, and MN4), Pb/Sb for yellow (Cz16 and Cz24), and Cu for green (Cz19 and Cz20). These elements can be found in historic sources, which describe materials used by artists–practitioners, including Cipriano Piccolpasso's treatise on potter's art (Piccolpasso, 1980). It is worth noting that the spectra acquired for the blue regions in both objects show no presence of detectable amount of As, which is associated with cobalt in several cobalt minerals, supporting the pre-1520 assignment for both artefacts (Dias et al., 2020; Pappalardo et al., 2004; Zucchiatti et al., 2006). Moreover, there is a clear difference in the spectra acquired for the *Tondo with Christ the Redeemer* (for instance point MN8, sampled on the background shell, see Figure 1 and the *Virgin and Child* relief; for instance, points Cz17 and Cz18, sampled on the Virgin's tunic and the background, respectively, see Figure 2 and spectra in the Supplementary Material Figure SM5) as the spectra show that Co, the blue

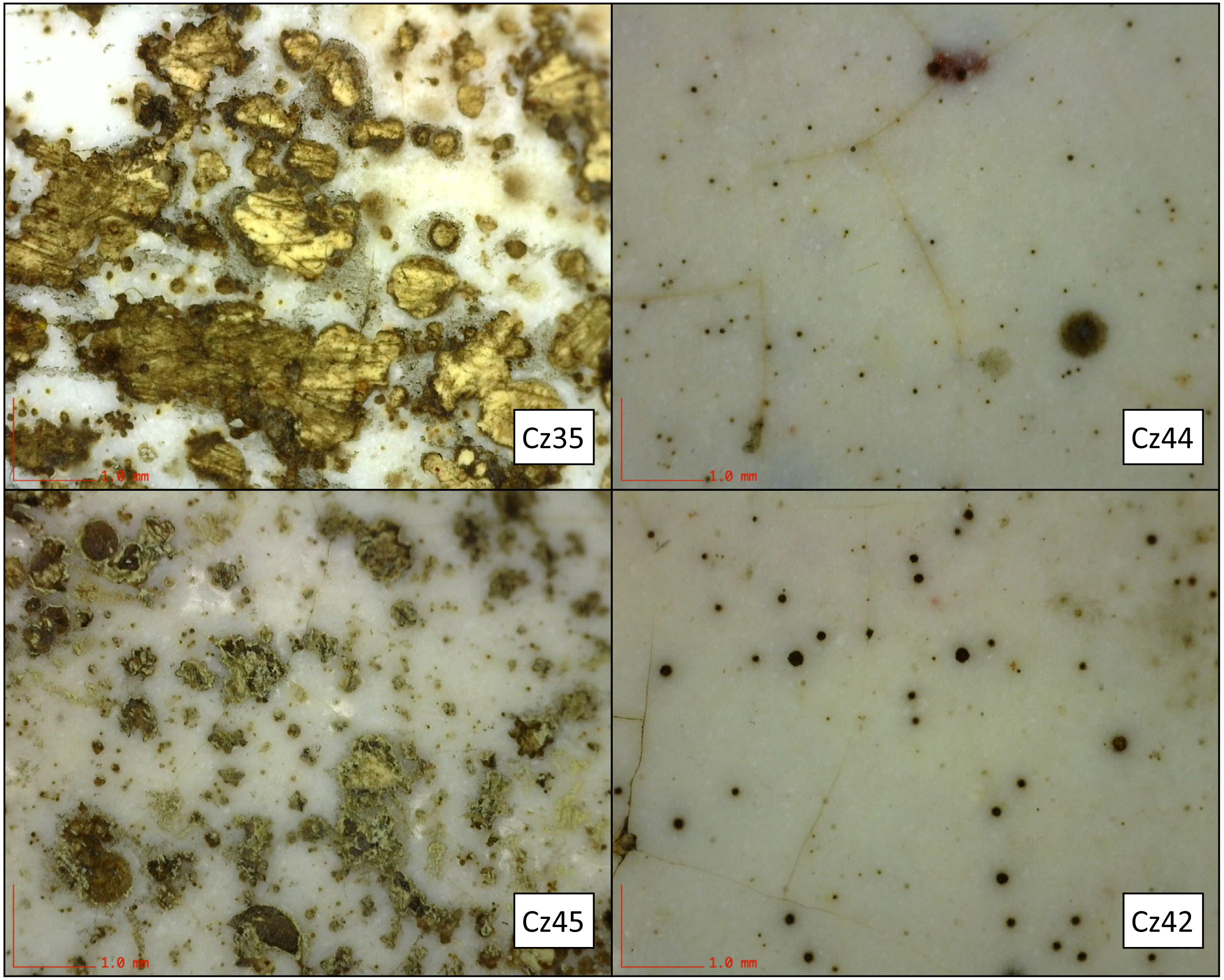

FIGURE 4 Microscope images (50X, polarised light) of selected points from the *Virgin and Child* relief, showcasing the regions with and without gilding imitation.

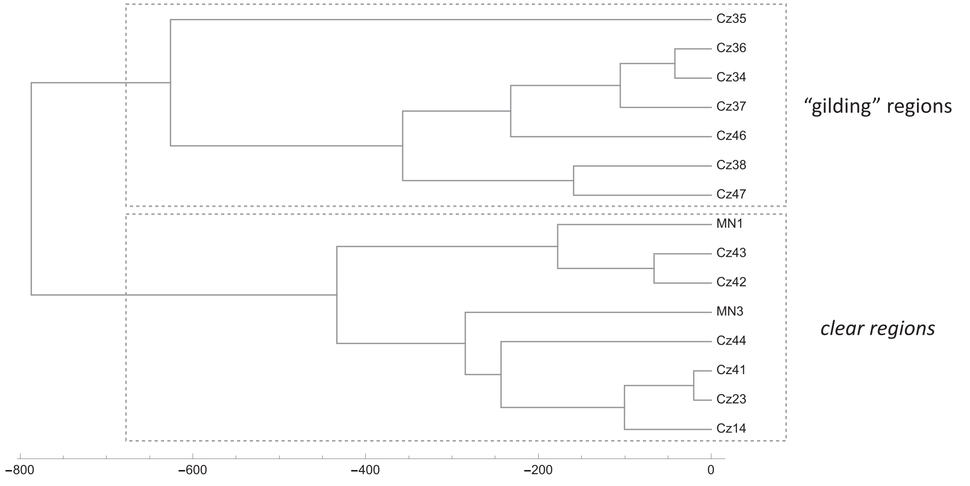

FIGURE 5 Dendrogram showing the hierarchical clustering for the Cu and Zn peak area obtained from XRF spectra (Euclidean distance, complete linkage) for the white glaze points. Only those points on original, not retouched nor damaged regions of the glaze, were considered in this analysis.

chromophore, and Ni, often correlated with cobalt, but with a great variability (Zucchiatti et al., 2006), are present in the same amount in the two artworks. This suggests the same source for raw material and allows us to speculate about the same workshop production. On the other hand, Fe and Cu are evidently much more abundant in the *Virgin and Child* relief, and Pb is considerably more abundant in the relief with respect to the *Tondo with Christ the Redeemer*. In the Supplementary material, OM images obtained on the original areas of the two artworks for the different colours are presented, see Supplementary Material Figure SM6.

DISCUSSION AND HISTORICAL-ARTISTIC IMPACT

The observable differences between the two analysed sculptures seem to point to the ambition of Benedetto Buglioni to experiment with the technique of tin-glazed earthenware. The slight change in the ratios of specific compounds of the glazes suggests a search for new solutions within the single workshop. When the results are compared with the studies of the Della Robbia works, it becomes apparent that the *Virgin and Child* relief differs significantly in the recipe in comparison to the studied artefacts from the more celebrated workshop.

The blue glaze in both works lacks arsenic, which appears in the post-1520 sculptures by the Della Robbia, and is related to the shift in the extraction method of cobalt ore (Zucchiatti et al., 2006). This strongly supports that their production to have taken place prior to 1520. On the other hand, we observe the addition of Cu and Fe to the blue pigment. Perhaps this has been done intentionally to yield different results and to increase the potential of glazes to maintain their vivid blue colour, and ensure smoothness. Piccolpasso discussed in his treatise that the so-called *zaffre*, which is an impure ore of cobalt, fuse very well when finely ground (Piccolpasso, 1980, vol. II, p. xix).

Another notable innovation in the technique of glazing within the Buglioni workshop is the way in which the artist modified the copper green. The artists from the Della Robbia family mixed yellow lead antimonates and copper antimonates to achieve a range of greens (Hykin, 2016, p. 136). However, as it is clear in Luca della Robbia's *Nativity with Gloria in Excelsis* c. 1465–70, now in the Museum of Fine Arts in Boston, for the interaction of the two colours Luca operated with discernible brushstrokes to achieve highlights in the hay under the Christ Child's body. Such strategy was described in Piccolpasso's treatise for "verdant meadows and certain bushes struck by sunlight" (Piccolpasso, 1980, vol. 1, c. 59r.). Benedetto Buglioni in the Cracow *Virgin and Child* introduced surfaces of superimposed layers of interacting colours (Cz20 and Cz26), applied in a highly impressionistic fashion, which seems to be his innovative solution. This method allowed the artist to achieve warmer tones and to introduce spatial effects in the lower area of the composition, thus enhancing the ephemeral and otherworldly quality of the depiction. Such layering of green with yellow becomes characteristic of the Buglioni glazes around 1500. Examples of this solution include the roof of the stable below the singing choir of angels in *The Nativity* from the Church of San Vivaldo in Montaione, Tuscany (its original location until 1882, since November 1957 the altarpiece has been on view in the Church, on loan from the Museum Nazionale del Bargello, inv. no. 56 R) (Paolozzi & Ciseri, 2012, pp. 134–135).

The considerably different ratio of Pb and Sn in the glaze as shown in the Figure 3 is another indicator of the divergence of the Buglioni recipe from the Della Robbia working method. This seems to confirm that Benedetto did not rely on a steady source of raw materials but rather tested different components for his glazes. The same was true of his experiments with the clay, which in some cases include calcium-rich marly clays and in others rely on iron-rich red-bodied clay (Bouquillon et al., 2011, p. 96–97).

Finally, the observation of the traces of secondary residues of "bronzine" (imitation of gold) on the shawl of the Virgin and in other areas including on the bodily parts, typically enhanced by gilding, suggests that Buglioni partook in a technical experimentation that would result in a reduced need of costly regilding of the surfaces of his works. To make the form more three-dimensional, in deeply undercut sections, he added volume to the specific sections. The second half of the 15th century and first decades of the 16th century were dedicated to the pursuit of the durable lustre in glazed terracotta sculptures and well as in tin-glazed ceramics (Sarnecka, 2023). Written accounts of Renaissance artist–practitioners from Tuscany and Umbria confirm the ambition to make ceramics seem like gold. In an attempt to retrieve the recipes for permanent gilding of tin-glazed earthenware, we are guided by the 16th-century technical handbooks, including the treatise by Cipriano Piccolpasso and a recently recovered treatise by an unknown potter from Montelupo transcribed by Dionigi di Francesco Marmi in the second half of the 17th century (Berti, 2005). If we are to trust Marmi in his estimate provided in the introduction to the volume, he put it to himself to transcribe a treatise, which was written 170 or 180 years before. This points to a continuity in ceramic practice and allows to date the original treatise to the early 16th century, or even late 15th century, as Marmi's manuscript was compiled between 1636 and 1674. In the recipe titled 'To make maiolica seem like gold', the artist–practitioner lists the following ingredients and quantities: 18 *grani* (a historic unit of measurement of mass calculated as an average weight of one grain of wheat) of cinnabar, 9 *grani* of copper, fine silver 6 oz and 3 *grani*, Armenian bole 4 oz and 24 *grani*. The recipe continues with the description of the procedure of calcinating silver, which should be pounded strongly with an anvil (*l'anchudine*), then put in an earthen pot, mixed with sulphur, and fired, so that sulphur would burn down the silver. The artist–practitioner concluded that if one wanted to make the substance finer, more silver should be used and the content of the Armenian bole had to be reduced. Benedetto Buglioni in attempting to achieve gold-like effect in this area diverged from such recipes, developing his own.

The corrugated surface of the glazes in the areas, in which the reflective particles are discernible, contrasts with the smooth and flawless glazing in other sections. This suggests that we are not faced with anomalies in glaze composition or errors in the application of the glazes and firing process but rather that a chemical reaction took place, which affected the glaze, which would have otherwise fired correctly. The discernible reflective particles do not have the elemental composition nor the surface homogeneity typical for the cold-gilding technique.

A recent study of Luca della Robbia's tomb of Bishop Benozzo Federighi (1453) reported a similarly corrugated surface in the glazes (Magrini et al., 2022), which was hypothesised to indicate "several firing campaigns" for the glaze. However, from the perspective of the present study, it seems more likely that the metal elements, which were meant to provide the durable gilding effect, were added to the surface before the second firing, and thus affected the ability of the white glaze to adhere properly to the clay body underneath. Indeed, what we observe in these areas resembles a microcrawling, insufficient coverage, of the glaze. Such microcrawling is observable in sculptures by the Della Robbia artists, including *The Virgin and Child* (c. 1450) from the Museo Capitolare of the Cathedral in Atri, Abruzzo. It remains to be verified whether in this work Luca similarly experimented with the metal particles, which could undergo the second firing and provide an alternative to the inherently less durable cold-gilding technique. If so, this could indicate that in the absence of reliable method of applying gilding, fired jointly with the glaze during the second firing, Benedetto Buglioni continued experiments within his independent workshop still in the early 16th century. At the same time, an attempt at a *luster* technique, understood as a method of the third firing at a lower temperature and in a reducing atmosphere, can be excluded by the fact that no surface transformation is detectible across the surrounding white glaze. The technique seems to partake of the *lustro al vernice* type of decoration explored by ceramicists in Faenza c. 1510, one of many instances where workshops working with tin-glazed earthenware in large-scale look to the workshop practices of artists–practitioners specializing in maiolica vessels (Sarnecka, 2021).

CONCLUSIONS

Due to historic vicissitudes the Warsaw *Tondo with Christ the Redeemer* and the Cracow *Virgin and Child* relief have been heavily restored in the past. The technical analysis confirmed several campaigns of restoration and the subsequent addition of the vegetal frame of the *Tondo*, which is materially distinct from the central, figurative part. At the same time, the technical analysis has confirmed that both works are genuine Renaissance pieces, which should be attributed to Benedetto Buglioni, the head of the workshop, which rivalled the celebrated Della Robbia production in the early 16th century.

The study has revealed several considerable divergences in the composition of the glazes with respect to contemporary Della Robbia works. Those included the addition of Cu and Fe to the blue pigment, the fact that Cu greens were modified with addition of Sb-based yellow, and the different ratio of Pb and Sn in the glaze.

The results from the investigation seem to indicate that although in the 1490s Benedetto Buglioni might have struggled to achieve the same results as the Della Robbia artists, toward the 1510s he moved beyond the faithful repetition of the formula toward the experimentation and development of his own approach to the making of tin-glazed terracotta figures. This hypothesis seems to be supported by the visible change in the quality of the glaze from lumpy and uneven surfaces of the *Tondo with Christ the Redeemer* from the National Museum in Warsaw dated to c. 1490, to merging and interactive effects of the glazes in the *Virgin and Child* from the Czartoryski Collection, Cracow dated to c. 1510. Benedetto Buglioni moved to Perugia in the late 1480s and must have established a kiln there, with several important works being commissioned in that city (Marquand, 1921). It is likely that the move away from the Florentine context and access to different raw materials could have provided a necessary stimulus for technical experimentation. Further research into Benedetto Buglioni's glazes is needed to verify this hypothesis. On the basis of the findings, the present study highlights the willingness of Benedetto Buglioni to diverge from what was considered a golden standard for making tin-glazed terracotta figures and experiment with the recipe on his own, in order to yield new results. In this narrative, rather than thinking about these artworks as poor executions of the

Della Robbia technique, we can think of them as bold test pieces, physical manifestations of the Renaissance artists readiness to make errors and following non-linear patterns of artmaking, willing to take step back to accomplish successful solutions.

AUTHOR CONTRIBUTIONS

Conceptualization and methodology: ZS, LB and CM; data collection: ZS, CM, AC, EM, MP, EKS, MW; data analysis: ZS, CM, LB; data processing tools: JT, LB, CM; writing: original draft preparation: ZS, CM, LB; writing: review and editing: ZS, CM, LB, MW; project administration: ZS. All authors have read and agreed to the published version of the manuscript.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in Yareta at https://yareta.unige.ch/home.

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REFERENCES

Amadori, M. L., Barcelli, S., Barcaioni, S., Bouquillon, A., Padeletti, G., & Pallante, P. (2013). The altarpieces of Della Robbia atelier in Marche region: Investigations on technology and provenance. *Applied Physics A*, *113*, 1129–1141.

Bajnóczi, B., May, Z., Ridovics, A., Szabó, M., Nagy, G., & Tóth, M. (2015). The tin content of the blue-glazed Hutterite and Haban ceramics — Implications for the production technology based on results of the handheld XRF and electron microprobe analyses. *Acta Ethnographica Hungarica*, *60*(2), 517–534.

Barbour, D., & Olson, R. (2011). New methods for studying serialization in the workshop of Andrea della Robbia: technical study and analysis. In A. Bouquillon, et al., (Eds.), *Della Robbia dieci anni di studi-dix ans d'études* (pp. 56–61). Genoa.

Baumann, J., Kayser, Y., & Kanngießer, B. (2021). Grazing emission X-ray fluorescence: Novel concepts and applications for Nano-analytics. *Physica Status Solidi B*, *258*(3), 2000471.

Berti, F. (2005). Segreti di fornace. *Dionigi Marmi*. Montelupo Fiorentino.

Bouquillon, A., Bormand, M., & Zucchiatti, A. (2011). *Della Robbia dieci anni di studi-dix ans d'etudes*. Genoa.

Brocchieri, J., Scialla, E., & Sabbarese, C. (2021). Estimation of Ag coating thickness by different methods using a handheld XRF instrument. *Nuclear Instruments and Methods in Physics Research, Section B*, *486*, 73–84.

Dias, M. I., Prudêncio, M. I., Kasztovszky, Z., Maróti, B., Harsányi, I., & Flor, P. (2017). Nuclear techniques applied to provenance and technological studies of renaissance majolica roundels from Portuguese museums attributed to della Robbia Italian workshop. *Journal of Radioanalytical and Nuclear Chemistry*, *312*, 205–219.

Dias, M. I., Rodrigues, A. L., Kovács, I., Zoltán Szőkefalvi-Nagy, M. I., Prudêncio, Z. K., Boglárka Maróti, R., Marques, P. F., & Cardoso, G. (2020). Chronological assessment of *della Robbia* sculptures by using PIXE, neutrons and luminescence techniques. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *477*, 77–79.

Gelichi, S. (1992). *La ceramica a Faenza nel Trecento. Il contesto della Cassa rurale ed artigiana*. Faenza.

Gentilini, G. (1992). *I Della Robbia. La scultura invetriata nel Rinascimento*. Florence.

Gianoncelli, A., Castaing, J., Bouquillon, A., Polvorinos, A., & Walter, P. (2006). Quantitative elemental analysis of Della Robbia glazes with a portable XRF spectrometer and its comparison to PIXE methods. *X-Ray Spectrometry*, *35*(6), 365–369.

Hess, C. (2004). *The Arts of Fire*. Los Angeles.

Hubbard, C., & Motture, P. (2001). The Making of Terracotta Sculptures: Techniques and Observations. In B. Boucher (Ed.), *Earth and Fire. Italian terracotta sculpture from Donatello to Canova* (pp. 82–95). New Haven.

Hykin, A. (2016). Materials and techniques. In M. Cambareri et al., (Eds.), *Della Robbia: Sculpting with Color in Renaissance Florence* (pp. 129–143), exh. cat., Boston.

Kanngießer, B., Malzer, W., Mantouvalou, I., Sokaras, D., & Karydas, A. G. (2012). A deep view in cultural heritage—Confocal micro X-ray spectroscopy for depth resolved elemental analysis. *Applied Physics a*, *106*(2), 325–338.

Kingery, D. (1993). Painterly maiolica of the Italian renaissance. *Technology and Culture*, *34*(1), 28–48.

Kingery, D., & Aronson, M. (1990). The Glazes of Luca della Robbia. *Faenza*, *76*, 221–225.

Kupiec, C. (2016). *The Materiality of Luca della Robbia's Glazed Terracotta Sculptures*. PhD Thesis. Rutgers University.

Magrini, D., Cantisani, E., Vettori, S., & Lund Rasmussen, K. (2022). Insights into Della Robbia's terracotta monument to cardinal Federighi: Raw materials and technologies. *Applied Sciences*, *12*(4304), 1–16.

Malaguzzi Valeri, F. (1922–1923). Sculture del Rinascimento a Bologna. *Dedalo*, *II*, 341–372.

Mandò, P. A. (2005). Nuclear Physics and archaeometry. *Nuclear Physics A*, *751*, 393–408.

Marquand, A. (1921). *Benedetto and Santi Buglioni*, Princeton.

Micheletti, F., Orsilli, J., Melada, J., Gargano, M., Ludwig, N., & Bonizzoni, L. (2020). The role of IRT in the Archaeometric study of ancient glass through XRF and FORS. *Microchemical Journal*, *153*, 104388.

Orsilli, J., Migliori, A., Padilla-Alvarez, P., Martini, M., & Galli, A. (2023). AR-XRF measurements and data treatment for the evaluation of gilding samples of cultural heritage. *Journal of Analytical Atomic Spectrometry*, *38*, 174–185.

Paolozzi, S. B., & Ciseri, I. (2012). *La raccolta delle Robbiane*. Florence.

Pappalardo, G., Costa, E., Marchetta, C., Pappalardo, L., Romano, F. P., Zucchiatti, A., Prati, P., Mandò, P. A., Migliori, A., Palombo, L., & Vaccari, M. G. (2004). Non-destructive characterization of Della Robbia sculptures at the bargello museum in Florence by the combined use of PIXE and XRF portable systems. *Journal of Cultural Heritage*, *5*, 183–189.

Piccolpasso, C. (1980). In R. Lightbown & A. Caiger-Smith (Eds.), *The Three Books of the Potter's Art* (Vol. 2) vols. London.

Pradell, T., Climent-Font, A., Molera, J., Zucchiatti, A., Ynsa, M. D., Roura, P., & Crespo, D. (2007). Metallic and non-metallic shine in luster: An elastic ion backscattering study. *Journal of Applied Physics*, *101*(10), 103518.

Sarnecka, Z., (2021). *The Allure of Glazed Terracotta in Renaissance Italy*. London and Turnhout.

Sarnecka, Z. (2023). Pursuit of a Durable Lustre: Gilding and third firing of glazed terracotta in Central Italy (c. 1480–1530). In P. Sénéchal, F. Carta, & C. Ambrosino (Eds.), *Sculptures polymatérielles du Moyen Âge et de la renaissance en Europe et dans le bassin méditerranéen (v. 1200–1500)* (pp. 89–96), Rome.

Tarchiani, N. (1934). Santi Buglioni e le botteghe rivali Dei Della Robbia. *Faenza*, *22*, 135–136.

Trojek, T. (2020). Iterative Monte Carlo procedure for quantitative X-ray fluorescence analysis of copper alloys with a covering layer. *Radiation Physics and Chemistry*, *167*, 108294.

Vaccari, M. G., 1996, *La scultura in terracotta: tecniche e conservazione*, Florence.

Vasari, G. (1568). In G. Milanesi (Ed.), *Le vite de' più eccellenti pittori, scultori ed architettori* (Vol. 9 vols, pp. 1878–1885). Florence, vol. 3, 376.

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.

Walker, W., & Riccardelli, C. (2019). Workshop practice revealed by two architectural reliefs by Andrea della Robbia. *Metropolitan Museum Journal*, *54*, 47–61.

Zucchiatti, A., & Bouquillon, A. (2011). Les glacures: Atout maitre des Della Robbia. In A. Bouquillon, Et al. (Eds.), *Della Robbia dieci anni di studi-dix ans d'etudes* (pp. 32–43). Gen.

Zucchiatti, A., Bouquillon, A., Katona, I., & D'Alessandro, A. (2006). The 'Della Robbia blue': A case study for the use of cobalt pigments in ceramics during the Italian renaissance. *Archaeometry*, *48*(1), 131–152.

Zumbulyadis, N., & Van Thienen, V. (2020). Changes in the body, glaze and enamel compositions of early Meissen porcelain, 1723–c. 1740. *Archaeometry*, *62*(1), 22–41.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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