



Visualizing and measuring gold leaf in fourteenth- and fifteenth-century Italian gold ground paintings using scanning macro X-ray fluorescence spectroscopy: a new tool for advancing art historical research

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Abstract

The size, shape, and application techniques of gold leaf in fourteenth- and fifteenth-century gold ground panel paintings attributed to artists working in Florence, Siena, and Fabriano was directly visualized using in situ scanning macro X-ray fluorescence spectroscopy (MA-XRF). The resulting gold (Au) La (9.712 keV) element distribution maps are of sufficient spatial resolution to enable an accurate and reproducible measurement of the shape and size of individual gold leaves. The resulting leaf measurements are discussed in the context of historical guild regulations, in particular, the 1403 reforms to the statutes of the Florentine Guild of Doctors and Apothecaries (Arte dei medici e speziale), which standardized the dimensions of gold leaf produced in Florence. The dimensions of the gold leaf from Florentine paintings created before and after the 1403 reforms were compared to each other as well as to gold ground paintings created in Siena and Fabriano. The results revealed the gold leaf squares in fourteenth-century Florentine and Sienese panels had side lengths averaging about 8 cm. In contrast, the gold leaf squares used in the fifteenth-century Florentine and Sienese paintings were smaller, with side lengths measuring about 7 cm. In addition, the degree of overlap between adjacent gold leaves was also measured. The amount of overlap was found to vary between artists, and the degree of overlap was consistent within the oeuvre of a specific artist. Taken together, these results suggest that the dimensions of the gold leaves found in panel paintings relate to the place of production on the Italian peninsula and the period in which they were created, while the degree of overlap relates to the individual hand of a gilder or artist/ workshop.

Keywords: MA-XRF imaging, Gold leaf, Gilding, Italian painting, Guilds, Giovanni di Paolo, Gentile da Fabriano, Fra Angelico, Masaccio, Taddeo Gaddi

Introduction

Gold leaf-small, thin, square sheets of gold-was a key component of ornately decorated panel paintings created throughout the Italian peninsula during the

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fourteenth- and fifteenth-centuries. Gilded backgrounds were composed of individual sheets of gold leaf laid down over an iron-rich clay adhesive layer (called bole), and burnished to achieve a smooth, mirror-like surface suggestive of solid gold [1]. Gold was prized for the embellishment of works of art for a variety of factors including its innate preciousness, related symbolic connotations of divinity, and aesthetic appeal [2]. Since gold was a precious commodity, the production of gold leaf was

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subject to strict guild regulations. In Florence, painters and other professionals associated with the craft of painting, including many gold beaters, belonged to the Guild of Doctors and Apothecaries (Arte dei medici e speziale). In 1403 this guild issued reforms to its existing statutes, which included new specifications and standardizations for the dimensions of fine gold (oro fine), part gold (oro di metà), and silver leaf (ariento battuto). The ordinance established that the costly oro fine was to be manufactured to a size between 1/8th and 1/9th of a Florentine braccio di panno, equivalent to squares with side lengths of about 7 cm in modern units. The less expensive oro di *metà* and *ariento battuta* were to be manufactured to a larger size, between 1/7th and 1/8th of a Florentine braccio di panno, corresponding to squares with side lengths measuring about 8 cm [3-5].

Despite the preponderance of gold leaf in paintings of this period, relatively little is known about the size, shape, and application patterns of individual gold leaves in works of art due to the difficulty in visualizing them using traditional broadband visible light-, infrared-, ultraviolet-, or even X-ray imaging techniques. In instances where the gold leaves are unusually thick, broadband X-radiography has been used to examine individual leaves [6], and a limited 'view' may also be possible with the naked eye in cases where the gold has been thinned as the result of surface abrasion or other damage [7, 8]. However, in the vast majority of cases, traditional imaging techniques do not provide for the direct visualization of gold leaf necessary to characterize any potential variation in the dimensions of the individual leaves.

The utility of scanning macro-X-ray fluorescence (MA-XRF) spectroscopy for the study of paintings and manuscript illuminations-primarily to characterize the distribution of elements from which pigments may be inferred-has been previously demonstrated with great success [9-11]. Importantly, the element distribution maps generated by this technique can also provide new information that results in abetter understanding of other aspects of an artist's technique. For example, scanning MA-XRF as well as other spatiallyresolved imaging spectroscopies has allowed for the visualization of preliminary or abandoned versions of compositions, revealed the sequence in which paint layers were applied, and even helped track changes that may have occurred over time [12-20]. In this work, the use of MA-XRF imaging spectroscopy to visualize individual gold leaves in Italian panel paintings was explored. It proved to have sufficient spatial resolution to enable the size of individual gold leaves to be measured with unprecedented accuracy. This new information allows researchers to better understand the place and manner by which these objects were created.

The current study was carried out on a group of thirteen Italian gold-ground panel paintings attributed to six artists working primarily in Florence and Siena (see Table 1 for complete object details). Eleven paintings date to the early fifteenth century and two were produced in the 1330s. The five panels attributed to the Sienese artist Giovanni di Paolo are thought to have once belonged to a single polyptych. Similarly, the two panels attributed to Fra Angelico likely originated from a single ensemble. MA-XRF scanning was carried out on each of the paintings, and the size of the individual gold leaf and overlaps between leaves in each object measured from the resulting gold (Au) L α element distribution maps. The results, contextualized within Italian guild regulations, provide an indication of the geographic and/or temporal origin of a painting and help elucidate the gilding technique of individual artists, providing new information regarding the painting technique of this time.

Experimental

Gentile da Fabriano's *Madonna and Child Enthroned*, in the Samuel H. Kress Collection at the National Gallery of Art (NGA), Washington DC, was studied at the NGA using a custom-built macro XRF imaging spectrometer [21]. The instrument consists of a 50 WRh X-ray tube with polycapillary focusing optics (XOS Labs, New Jersey) and an SDD detector with a 50 mm² active area (XGLabs S.r.l., Milan). The painting was moved on a motorized 2-D computer-controlled easel (SatScan System, LG Motion, UK) in front of the X-ray source and detector. The gold distribution map was obtained by integrating the area under the Au L α emission line (fitted to a Gaussian function) [22].

The remaining twelve panels were scanned at the Getty Conservation Institute (GCI) using a Bruker M6 Jetstream macro XRF spectrometer (Bruker Nano GmbH, Berlin). The M6 is outfitted with a 30 WRh X-ray tube with polycapillary focusing optics. The scanning parameters were selected individually for each object, determined both by the overall size of the scan and the level of detail that could be achieved in the time during which the painting was available for study. The gold element distribution maps were generated using the Bruker ESPRIT software.

For all thirteen scans, a spot size between 500 and 1000 μ m was employed, ensuring comparability of the data sets and providing sufficiently high spatial resolution to accurately measure the dimensions of the individual gold leaves. Specific instrumental acquisition parameters for each scan are provided in the appropriate figure captions.

The intensity of the Au L α signal is higher in those areas where, in some areas (see e.g., Figs. 4c, 5c) it can be seen with the naked eye that two gold leaves overlap. Similar areas of higher intensity, visible throughout all the maps,

Table 1 List of sc	anned objects and summary resu	ilts of leaf meas	urements						
Artist	Title, owner, accession no.	Date	Region	2	Mean vertical length (cm)	Mean horizontal length (cm)	Mean leaf length (cm)	Mean horizontal leaf overlaps (cm)	Mean vertical leaf overlaps (cm)
Simone Martini	St Luke J. Paul Getty Museum (82.PB.72)	1330 s	Siena	14	8.0±0.2	8.1 ± 0.2	8.1 土 0.2	0.5 土 0.1	0.5 ± 0.1
Taddeo Gaddi	Stigmatization of St Francis Harvard Art Museums (1929.234)	с. 1325-30	Florence	9	8.0±0.2	8.0±0.1	8.0±0.1	0.3 ± 0.1	0.3 ± 0.1
Gentile da Fabriano	Coronation of the Virgin J. Paul Getty Museum (77.PB.27)	с.1420	Fabriano	23	8.0±0.1	8.0±0.1	8.0±0.1	0.9±0.3	0.8 ± 0.4
	Nativity J. Paul Getty Museum (77.PB.27)	About 1420-22	Florence (?)	6	6.8±0.1	6.8±0.1	6.8±0.1	0.9±0.2	0.8±0.2
	Madonna and Child Enthroned National Gallery of Art (1939.1.255)	с. 1420	Florence	30	6.8±0.1	6.8±0.1	6.8±0.1	0.8±0.3	0.7 ± 0.2
Fra Angelico	St John the Baptist and St Dominic J. Paul Getty Museum (92.PB.111.2)	1420 s	Florence	Ś	6.9±0.1	6.9±0.1	6.9±0.1	0.3 ± 0.1	0.3 ± 0.1
Masaccio	St Francis and a Bishop Saint J. Paul Getty Museum (92.PB.111.1)	1420 s	Florence	Ś	7.0 土 0.1	6.9±0.1	6.9±0.1	0.3 ± 0.1	0.2 ± 0.1
	St Andrew J. Paul Getty Museum (79.PB.61)	1426	Florence	Ø	6.8±0.1	6.8±0.1	6.8±0.1	0.5 ± 0.2	0.4±0.2
Giovanni di Paolo	Branchini Madonna Norton Simon Museum (F.1978.01.P)	1427	Siena	33	6.8±0.1	6.8±0.1	6.8±0.1	0.5 ± 0.2	0.4±0.1
	Crucifixion Pinacoteca Nazionale di Siena (175)	1427	Siena	28	6.9±0.1	6.9±0.1	6.9±0.1	0.5 ± 0.2	0.4±0.2
	Presentation in the Temple Pinacoteca Nazionale di Siena (174)	1427	Siena	14	6.9±0.1	6.9±0.1	6.8±0.1	0.5 ± 0.2	0.4±0.2
	Adoration of the Magi Kröller-Müller Museum (607)	1427	Siena	11	6.8±0.1	6.9±0.1	6.9±0.1	0.5 ± 0.2	0.4±0.1
	Flight into Egypt Pinacoteca Nazionale di Siena (176)	1427	Siena	10	6.8±0.1	6.8±0.1	6.8±0.1	0.5 ± 0.2	0.4±0.2

even for areas where the gold is covered by paint, are therefore attributed to leaf overlap. Leaf measurements were carried out on the Au L α distribution maps using FIJI (ImageJ) [23]. While the maps show the use of whole (i.e., intact, with all four edges visible) leaf as well as leaf fragments, to establish the leaf dimensions, only whole leaves were considered.

Figure 1 illustrates how leaf measurements were made for gold leaf laid in a rectilinear grid (Fig. 1a, b) and an irregular pattern generally consisting of wedge-shaped overlaps where the gold leaf follows a curved edge (Fig. 1c, d). In a rectilinear pattern, the sides of an

individual square of gold leaf are designated 'top,' 'bottom,' 'right', and 'left' according to their relationship to the overall orientation of the object. In an irregular pattern, the term 'top' is used to designate the edge closest to the upper edge of the painting. For curved arches, for example as shown in the map data in Fig. 1c, this may mean that the 'top' of a leaf is at an angle with respect to the vertical axis of the painting. In Table 1, vertical length refers to the measurement between the 'top' and 'bottom' edges of leaf (irrespective of angle), and horizontal length refers to the measurement between the 'left' and 'right' edges of a leaf. The schematics in Fig. 1b, d show how the





leaf length (yellow arrows) were measured for each pattern; for each whole (i.e., intact) gold leaf, three replicate measurements of the leaf length were made along each of the two orthogonal directions.

For leaf overlap, the descriptors 'horizontal' and 'vertical' refer to the direction of the adjacent leaf that forms the overlap, with 'vertical' referring to displacement along the direction perpendicular to the top and bottom edges of the painting, and 'horizontal' referring to displacement perpendicular to the left and right sides of the painting. The schematics in Fig. 1b, d show how the horizontal and vertical leaf overlaps (black arrows) were calculated for both rectilinear and irregular patterns; three replicate measurements were made in both the 'vertical' and 'horizontal' orientations.

The number of individual leaves able to be measured (n) was restricted by the overall area of gilding present and the gilding technique and differs for each painting as noted in Table 1. The mean vertical and horizontal leaf lengths were calculated separately and compared to confirm that the leaves are square. The mean leaf length was then calculated by averaging the mean horizontal and mean vertical lengths.

Results

The results of the MA-XRF scans are shown in Figs. 2, 3, 4 and 5. XRF spectra (data not shown) from the gold leaf in each of the paintings showed it to be of sufficient purity to be classified as 'fine gold', (i.e., no detectable amounts of Ag or Cu was found in any of the gold leaf). The leaf lengths and overlaps for all thirteen paintings (arranged chronologically, and sub-grouped by artist) are summarized in Table 1. The majority of the paintings (ten of the thirteen) have a mean leaf length between 6.8 and 6.9 cm. The remaining three paintings -the early fourteenth-century panels St Luke by Simone Martini and The Stigmatization of St Francis by Taddeo Gaddi, and the early fifteenth-century panel Coronation of the Virgin by Gentile de Fabriano, have larger mean leaf lengths, measuring between 8.0 and 8.1 cm. The dimension of the leaf overlaps shows greater variation, which will be discussed below.

The relationship between gold leaf produced in Siena and Florence in the early fourteenth century is explored by comparing two paintings, scans of which are shown in Fig. 2:*The Stigmatization of St Francis* by Taddeo Gaddi (Fig. 2a, b), painted between 1325 and 1330 in Florence, and *St Luke*, painted around 1326 in Siena by Simone Martini (Fig. 2c, d). Although the *St Francis* and *St Luke* panels were painted in different regions—and therefore probably subject to their respective local guild regulations—the mean leaf lengths calculated from both paintings (8.0 ± 0.1 and 8.1 ± 0.2 cm, respectively) is essentially the same.



c Simone Martini, *St Luke*, 1330s, tempera and gold leaf on panel, 67.5 × 48.3 × 3.8 cm (J. Paul Getty Museum, 82.PB.72) visible light image; **d** Au Lα element map (instrumental settings: 50 kV, 600 µA, 530 µm spot size, 480 µm sampling, 18 ms/pixel dwell time). Note: Digital images courtesy of **a** Harvard Art Museums/Fogg Museum, Friends of the Fogg Art Museum Fund and **c** Getty Open Content Program

While the size of the gold leaf in these two panels was the same, the measured overlaps were different. The leaf overlaps in The Stigmatization of St Francis measured 0.3 ± 0.1 cm, while the leaf overlaps in the *St Luke* panel were about 60% larger, measuring 0.5 ± 0.1 cm. Small overlaps, like those employed in the St Francis panel, were more economical than large ones, since they allowed for coverage of a larger surface area with the same number of leaves; an important consideration when an artist used expensive fine gold leaf, especially on large paintings. Small overlaps also demonstrate the skill of the gilder of the St Francis panel, who deftly laid down each leaf with only a slight overlap, free of gaps. By contrast, the gilder of the St Luke panel adopted a different strategy employing larger leaf overlaps. This method would minimize the risk of gaps arising between the leaves, and likely required somewhat less time (or skill) to apply, but would require a larger amount of gold to cover the same surface area. The Au La map obtained from the St Luke







visible light image, detail; **b** Au Lα element map (instrumental settings: 50 kV, 600 μA, 530 μm spot size, 530 μm sampling, 6 ms/pixel dwell time); **c** Giovanni di Paolo, *Crucifixion*, 1427, tempera and gold leaf on panel, 73 × 52 cm (Pinocoteca Nazionale di Siena, 146) visible light image; **d** Au Lα element map (instrumental settings: 50 kV, 600 μA, 450 μm spot size, 460 μm sampling, 5 ms/pixel dwell time). Digital images courtesy of **a** Norton Simon Museum and **c** Pinacoteca Nazionale, Siena

panel also reveals more instances of small self-corrections in the gilding, known as *faulting* [24]. These corrections are visible as small, rectangular fragments, which were laid down by the gilder in order to cover small blemishes, such as cracks in the leaf, before burnishing. In contrast to the fourteenth-century objects discussed above, the dimensions of the gold leaf measured from paintings created in Florence and Siena during the 1420s were smaller, all consistently having mean leaf lengths measuring 6.8–6.9 cm (see Table 1). This value is in



precise alignment with the dictum of the 1403 Florentine guild statutes. For the four Florentine works—St John the Baptist and St Dominic (Fig. 3a), St Francis and a Bishop Saint (not shown), both by Fra Angelico, Masaccio's St Andrew (Fig. 3c), and Madonna and Child Enthroned by Gentile da Fabriano (Fig. 5c)-correspondence of the mean leaf lengths to the written stipulations of the statutes is perhaps not surprising as the statutes bound Florentine goldbeaters by law and under threat of a monetary penalty. However, it is interesting that the individual gold leaves used in the five panels by the Sienese artist Giovanni di Paolo (Fig. 4, all of which once belonged to a single altarpiece commissioned in 1427 for the Branchini family's private chapel in the Sienese church of San Domenico) also have the same mean leaf length. Additional data are needed to determine whether this attests to the influence of Florence as a center of gold production by the early-fifteenth century [5].

The leaf overlaps, however, showed greater variation. The horizontal and vertical leaf overlaps (0.5 ± 0.2 cm and 0.4 ± 0.2 cm, respectively) were consistent across all five panels by Giovanni di Paolo, but different from the

overlaps in the two panels by Fra Angelico, both of which measured only 0.3 ± 0.1 cm in both directions. This once again suggests that leaf overlaps can provide useful data pertaining to the manner in which the gilding was carried out, and as such, can serve as a figure of merit associated with the *hand* of a particular gilder or the technique of a particular workshop. However, it should be noted that this measurement alone cannot be used to identify the artist. For example, the leaf overlaps in Masaccio's St Andrew, are analogous to the overlaps in the five panels by Giovanni di Paolo. Similarly, the overlaps in both the Fra Angelico and Taddeo Gaddi panels are also the same within the margin of error. Nonetheless, an expanded data set of leaf overlaps might reveal characteristic trends in an artist's approach to gilding throughout his career, or between artists trained in the same workshop.

Discussion

No specific language stipulating leaf size in either Florence or Siena is known prior to the Florentine Guild of Doctors and Apothecaries statutes of 1403. However, during the first half of the fourteenth century, Siena and other Italian city states, such as Venice, dominated the gold industry throughout the Italian peninsula and, by the mid-fourteenth century, Sienese goldsmiths are documented as having emigrated to neighboring regions, including Florence, presumably bringing with them the established traditions of their native city [25]. While it is tempting to ascribe the leaf lengths taken from the earliest two paintings in the group, by Simone Martini and Taddeo Gaddi, to Sienese traditions, additional MA-XRF scans from securely attributed fourteenth-century Sienese and Florentine gold ground paintings is needed in order to assess the significance of these data.

By the 1420s, Florence had emerged as a leading center for goldsmithing [25]. In fact, surviving contracts from the early-fifteenth century drawn up between artists and patrons sometimes stipulate the use of Florentine gold leaf in commissions for paintings produced outside of Florence [5]. Such a stipulation from the Branchini patrons may account for the use of gold leaf which meets the requirements of the 1403 Florentine statute in the paintings created in 1427 in Siena by Giovanni di Paolo, an artist native to that city. Of course, this is a limited data set, and additional Sienese and Florentine paintings should be studied to better understand how these results fit into a larger context.

A test case for interrogating the hypothesis that the size of the gold leaf reflects the region in which a gilded panel was produced is the group of works in this study by the itinerant artist Gentile da Fabriano (Fig. 5). The three paintings are thought to have been produced within a 2-year time frame during which the artist moved from Brescia to Fabriano, and then to Florence. The leaf used in the Madonna and Child Enthroned, generally associated on stylistic grounds with the artist's early years in Florence, measured 6.8 ± 0.1 cm (Fig. 5a, b), clearly in accordance with the Florentine statutes. There has been historical debate as to whether the Coronation of the Virgin (Fig. 5c, d), thought to have been commissioned by a confraternity in Fabriano, was painted while Gentile was in Fabriano or in Florence [26]. The mean leaf length in the Coronation of the Virgin measured 8.0 ± 0.1 cm, larger than the Florentine statute for fine gold, suggesting a non-Florentine origin for the painting. Stylistically speaking, it is not clear whether the Nativity was painted in Florence or Brescia, but the calculated mean leaf length of 6.8 ± 0.1 cm (Fig. 5e, f) for the gold leaf used to decorate this panel gives weight to the argument for a Florentine origin.

Supporting the hypothesis that leaf overlap relates to the hand of the artist, the leaf overlaps were consistent across all three Gentile panels: between 0.8 and 0.9 cm in the horizontal direction and 0.7 and 0.8 cm in the vertical direction. The consistency of these overlaps, the largest of those measured in this study, is remarkable given that the overall size of the paintings was quite different (the *Madonna and Child Enthroned* is about 65% larger than the *Nativity*), and that the actual dimensions of the gold leaf used in the *Coronation of the Virgin* panel differed from the other two by about 1 cm. The observed variation in leaf dimension suggests Gentile used gold leaf produced in the region where he painted each panel, but the overlaps suggest his (or his workshop's) gilding technique remained consistent regardless of the source of his gold leaf.

Conclusions and future work

Scanning MA-XRF allows for the non-invasive visualization of gold leaf in paintings, not previously visible by other imaging techniques traditionally available to museum researchers. The resulting element distribution maps have high spatial resolution, which allows for the accurate measurement of the length of individual gold leaf squares, even when present under layers of paint. The leaf measurement method presented and discussed here is repeatable, reliable, and robust.

In summary, the results of leaf measurements on thirteen paintings by six different artists working in fourteenth- and early fifteenth-century Florence, Siena, and Fabriano suggest that the dimensions of an individual gold leaf relate to its geographic origin. Furthermore, the specificity of the 1403 Florentine guild statutes may also function as a useful chronological signpost. In contrast to overall dimension, the leaf overlaps relate to the technique in which the individual gold leaves were laid down onto the panel during gilding and, in general, leaf overlaps vary *between* different artists but are similar in works attributed to the *same* artist.

With a larger dataset, a careful analysis of both the leaf size and application technique has the potential to function as a powerful diagnostic tool for more securely attributing the geographic and/or temporal origin of unattributed gold ground panels, for example re-uniting disparate fragments from previously separated polyptychs, or attributing specific works to well-characterized artists' workshops. While the present study is limited in scope, it lays the groundwork for the analysis of additional paintings by this method. For example, the examination of works adorned using different types of metal leaf, including silver and tin, created from other regions outside Italy as well as in other media-including polychrome sculpture and illuminated manuscripts-may help to establish the examination of metal leaf and its application as a routine part of technical analysis of gilded objects.

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Authors' contributions

DKM, CSP, KT, JKD, KAD collected and processed the scanning macro X-ray fluorescence imaging data; DKM performed the leaf measurements; LL carried out archival research and translations of the Italian guild statutes; YS examined the J. Paul Getty Museum paintings. All authors were involved in drafting and editing the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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