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Does substrate colour affect the visual appearance of gilded medieval sculptures? Part II: SEM–EDX observations on gold leaf samples taken from medieval wooden sculptures

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Abstract

In the previous paper (Part I), the colorimetry and interferometric microscopy measurements on modern gold leaf models have revealed that the visual appearance of a gilded surface, both burnished and unburnished, depends strongly on the substrate type, surface roughness and texture, but not on the colour of the substrate. In this second part, we investigate the materials compositions and technical specifications of medieval gold leaf through combining literature sources and materials analysis such as scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM–EDX) on samples taken from gilded wooden sculptures. Our study shows that the late medieval gold leaf has a high purity of about 23.7 carat and has an average thickness of 160 nm (with a peak value of 138 nm), purer and thicker than the modern gold leaves studies in Part I. Supportive Rutherford backscattering spectrometry (RBS) measurements on gilded models confirms the accuracy and reliability of the SEM–EDX observations on the medieval gold leaf samples. We additionally present observations of a rarely recorded special variant of medieval gold leaf—“fine reinforced gold leaf”. Combined with the findings from Part I, we conclude that light penetrating the medieval gold leaf and reflected from the gilding substrate could not be a significant, or even perceptible contribution to the visual appearance of the gilding. We argue that the misconception surrounding the correlation between the substrate colour and the gilded surface appearance can be attributed to the historical development of gilding and polychromy technologies.

Keywords: Medieval, Gilding, Substrate, Gold leaf, Colour, Thickness, Purity, SEM–EDX, RBS

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Introduction

In the history of medieval gilding, a popular point of view states that the colour of the gilding substrate influences the visual perception of the gilded surface due to the ultra-thin gold leaf being not completely opaque [1–4]. This view has been circulated for centuries and often used to explain why particular substrate colours such as red, yellow and white have been frequently observed in medieval gilded artefacts [3, 5–7].

In the previous paper (Part I), we have investigated models that were made from modern gold leaves with traditional gilding techniques. Colorimetry measurements on such models show that there is no correlation between the substrate colour and the visual appearance of the gold leaf laid above. Indeed, the modern gold leaves were observed to be far too thick to allow any significant transparency to visible light. Instead, surface burnishing is the most critical factor in determining the colour appearance of a gold leaf through changing the roughness of its surface and thus the proportion of the specular and diffuse light reflections; and the quality of a surface burnishing is strongly dependent on the mechanical support provided by the substrate materials. In addition, the surface roughness and texture of the substrate were also shown to play supplementary roles in determining the appearance, especially for an unburnished gold leaf.

The current paper (Part II) focuses on investigating two technological parameters of medieval gold leaf, namely the gold purity and leaf thickness, which are critical factors for the colour perception of a gold leaf and important to determine whether the findings from Part I apply to the domain of medieval gold leaf. Information regarding these parameters is obtained through literature study in medieval gilding and materials analysis such as scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM–EDX) on samples taken from medieval gilded artefacts. Further literature study in the historical development of medieval polychromy is expected to show the motives for the creation and prevalence of the aforementioned view that the substrate colour influences the appearance of a gilded surface.

In order to assure the accuracy and reliability of SEM observations on the gold leaf samples, a novel sample preparation method through ultramicrotomy has been developed. As supportive data, Rutherford backscattering spectrometry (RBS) is applied to models made from modern gold leaves. The comparison between RBS and SEM investigations on modern gold leaf aims to verify the precision of the sample preparation and experimental methods.

Background

The historical manufacture of gold leaf, known as *goldbeating*, has not changed much since ancient times [8]. By hammering a lump of gold, a thin gold plate or ribbon is formed; the gold plate/ribbon is then cut into squares and placed within a stack of paper or parchment, and repeatedly beaten until it reaches the desired thickness [8]. In the medieval period, coins served as the most common material source for gold leaf [9–11]; especially from the mid thirteenth century, gold coins with stable, high purity such as *florins* (23.75–24 carat recorded in 1252) and *ducats* (23.75 carat recorded in 1284) became a reliable source for gold leaf [11]. Evidence of the use of such high-quality gold coins is traceable in some work contracts and guild regulations. For example, in the statutes of the goldsmiths' guild, the *Arte di Por Santa Maria*, of 1335, the gold used for artworks is required to be sourced exclusively from *florins* [12].

The leaf thickness is of great significance in gilding history and denotes the level of metallurgic and goldbeating technologies of the epochs. Nevertheless, the selection of gold leaf sometimes has to face a dilemma: on one hand using thin leaf is critical for artisans to keep a lower cost during the creation process of artworks; while on the other hand a moderate thickness provides mechanical stability, since very thin gold leaf can be easily torn during the burnishing process or worn out. Therefore, some medieval guild regulations and artists' treaties particularly defined a required leaf thickness by specifying a required number of gold leaves produced from each gold coin. For example, a Florentine guild statute fixes a rate of one *florin* to one hundred gold leaves [10]; Cennini also suggests 100–145 sheets of gold leaf from a single *ducat* [11]. In the latter case, combining the weight of *ducat* (ca. 3.5 g), its gold purity (23.75 carat) and the common sizes of gold leaf in the fourteenth century's Florence (6.8×6.8 cm and 8.2×8.2 cm [13]), the leaf thickness is calculated to be in the range of ca. 190–400 nm. Kubersky gives an even thinner and more specific number of 154 nm for the gold leaf of the sixteenth century based on Vasari's treaties [13]. The National Art Gallery of London [11] provides an average thickness of medieval gold leaf of around $2.69 \mu\text{m}$ based on the calculation with the given weight of the *florin* and the number of leaves per coin, which seems significantly thicker than the historical records, indicating the presence of diverse specifications for medieval gold leaf. Indeed, scientific analysis of artefacts has shown that the thickness of medieval gold leaf varies from 100 nm to a few microns [8, 14, 15]. It is interesting to note that while each of these estimates describes the produced gold leaf as having a very regular square or rectangular shape (in agreement with observations), there is no mention of the offcuts necessarily

produced from trimming the leaf edges and so the thickness estimates provided above should be considered as an upper bound.

A special variant of medieval gold leaf, called “*or fin renforcie*” (fine reinforced gold leaf), “*d’or fin doubles*” (double weight fine gold leaf) and “*or doubles renforciez*” (gold leaf, double reinforced), which was mentioned in records of the market price of artists’ supplies in Dijon in the turn of 1400 [16], deserves some attention. The two former types were double, and the latter was 1.5 times the price of a normal gold leaf, suggesting a respective leaf thickness of 2 and 1.5 times thicker than the standard. Indeed, the use of gold leaf with different thicknesses is recorded in medieval treatises, for example, Cennini suggests using thicker leaf (e.g. 100 or less sheets produced from one *ducat*) for flat backgrounds, as it is more suitable for burnishing, and thinner leaf (possibly 145 sheets per *ducat*) for mordant gilding and frame moulding [7]. Other medieval treatises such as *De diversis artibus* by Theophilus (twelfth century) and the Montpellier Treatise (fourteenth–fifteenth century) also mention that 2 or 3 layers of gold leaf can be applied through glair if desired [6].

In addition to the leaf thickness, the lateral size of the gold leaf is also an important technical specification of historical gold leaf. It is a critical factor for the traditional method of estimating or calculating the thickness of historical gold leaf, as discussed above with examples of Florentine gold leaf. However, literature records regarding the leaf size and format of medieval gold leaf present a great deal of variety. For example, gold leaf in northern European countries from 1390 till the Reformation is reported to be in either square or rectangular formats with one side of 80–93 mm [17], while other researchers state that gold leaf in northern Germany and Sweden has the sizes of 9.6, 7.2 and 6 cm square [15]. In southern European cities such as Florence, 6.8 × 6.8 and 8.2 × 8.2 cm are recorded for gold leaf in the fourteenth–sixteenth century [13], while in the painters’ statutes of the Florentine Guild of 1403, the size of gold leaf was fixed as one-ninth to one-eighth of a *braccio fiorentino* per side, corresponding to ca. 6.5–7.3 cm [11]. Therefore, the calculation or estimation of gold leaf thickness can be only performed based on reliable literature sources from specific regions and epochs.

Samples and methods

Samples and sample preparation

33 polychrome wooden sculptures, mainly dated in 1490–1525 and produced in southern Germany, eastern and central Switzerland, were first measured and selected through a Handheld X-ray fluorescence analyser (HHXRF) in the Swiss National Museum

(SNM)—Collection Centre. Details of the implementation of HHXRF on gilded artefacts are presented in our previous studies [18, 19]. A total of 34 gold leaf samples with a diameter of maximum 1 mm was taken mainly in the areas of saints’ golden gowns and gown bordures. The sample taking was preferably performed in positions invisible to viewers and difficult to access, in order to maintain the aesthetic integrity of the artefacts and to minimise the chance that the samples have been altered by previous restoration treatments. One example of a selected sculpture as well as its sample taking position is shown in Fig. 1. Detailed information regarding related objects and sample-taking positions are presented in Table 2.

Samples of modern gold leaf including *Spezial-Poliergold-Altgold-Dunkel* (from *Deffner & Johann*, Germany)



Fig. 1 Sculpture *Virgin and Child with St. Anna* (SNM, LM6982), dated early 16c. Sample was taken from the right-rear side of Anna's golden gown, next to an existing defect of the paint layers

and *Dukaten-Doppelgold* (from *Noris Blattgold*, Germany) were taken from the models investigated in Part I for use as controls in the measurements performed in this work. Procedures of the model production are presented in Part I.

Samples were embedded with epoxy resin Araldite 2020 and then cross-sectioned with a *Leica UC7* ultramicrotome at the Paul Scherrer Institute (PSI). A *DiATOME trimtool 45* diamond knife was used with a clearance angle of 6°. It is worthwhile to point out that producing sample cross-sections for the leaf thickness measurements through SEM requires a precise positioning of the sample during the embedding and cutting. An ideal circumstance is to cut the cross-section perpendicularly to the leaf surface. We have developed a reliable sample preparation method including sample embedding, trimming, cutting and coating, which is summarized and illustrated in Fig. 2. Note that the foil side of the sample needs to be placed face down during the embedding, since this side tends to have a flatter surface than the preparation layer side. Furthermore, the cutting direction should be along the foil, in order to avoid smearing of sample materials, especially the soft gold.

Analytical techniques and experimental conditions

A visual light microscope (VLM) *Leica DM4000M*, coupled with a *uEye UI144xSE-C* camera, was used to observe and image the stratigraphy of the sample cross-sections in the conservation laboratory of SNM, in both bright field (BF) and dark field (DF) modes. Through VLM observations, samples containing overlaid *Fassungs* (German term, refers to a set of polychrome layers applied on sculpture), which usually indicate the

presence of overpainting in later time, can be screened out from further SEM–EDX analysis.

The SEM–EDX measurements on sample cross-sections were implemented at the Paul Scherrer Institute (PSI, Switzerland) through a high-resolution *Hitachi Regulus 8230* SEM coupled with an *EDX X-Max detector*, using 5 kV voltage, 10 μA current and *Condenser Lens 1* of 2–6 [19]. Samples were coated with ca. 6.5 nm of chromium to increase the sample conductivity and reduce charging issues. A factory standard (5 kV set) was used for EDX quantification analysis. SEM observations on the gold leaf thickness were based on the backscattered electron (BSE) imaging on sample cross-sections.

RBS measurements on models were performed at the Swiss Federal Institute of Technology (ETH Zurich, Switzerland) laboratory for Ion Beam Physics, using both 2 MeV and 5 MeV 4He beams and a silicon PIN diode detector at 168°. The collected RBS data was analysed using simulations by the RUMP code [20].

Results and discussions

SEM–EDX and RBS measurements of modern gold leaf

Table 1 shows that the SEM–EDX observation on the gold (Au) content of modern gold leaf is 96.8±0.2% by weight (w%) for *Spezial-Poliergold* and 96.6±1.1 w% for *Dukaten-Doppelgold*, corresponding to the RBS data of 96.6±0.3 w% and 96.2±0.3 w% respectively. Compared to atomic ratios, weight ratios (w%) are preferably used for the quantification of the gold content of the medieval samples, since they can be easily transformed into carat, which is the most important and frequently used unit of gold purity in most literate records regarding medieval gilding leaves/foils. In the case of modern gold leaves

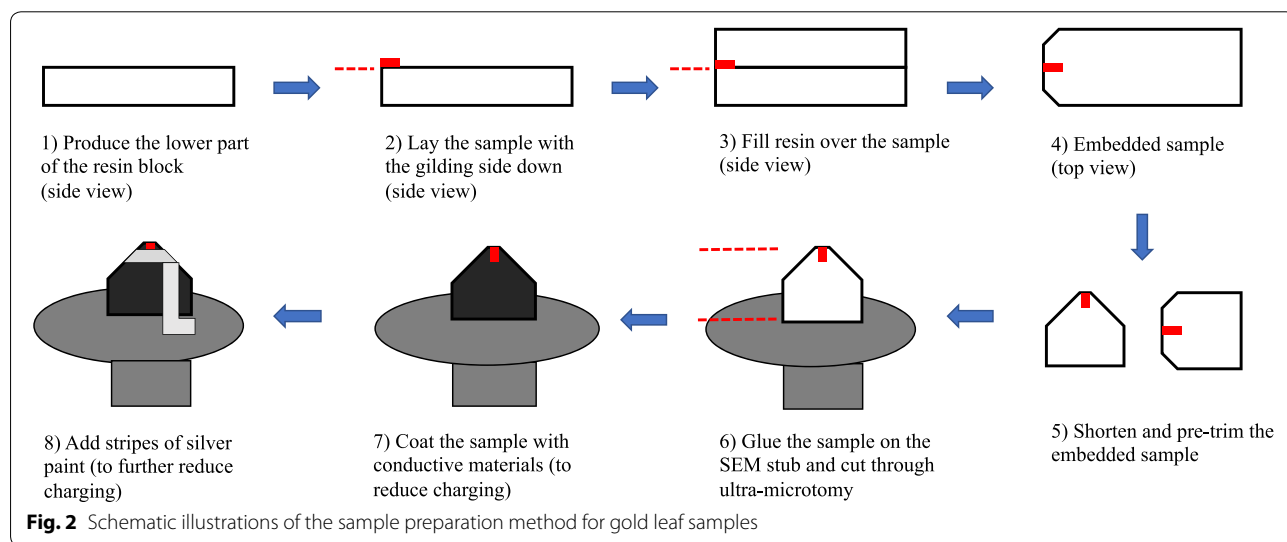


Table 1 SEM–EDX and RBS data of the modern gold leaves used in the models

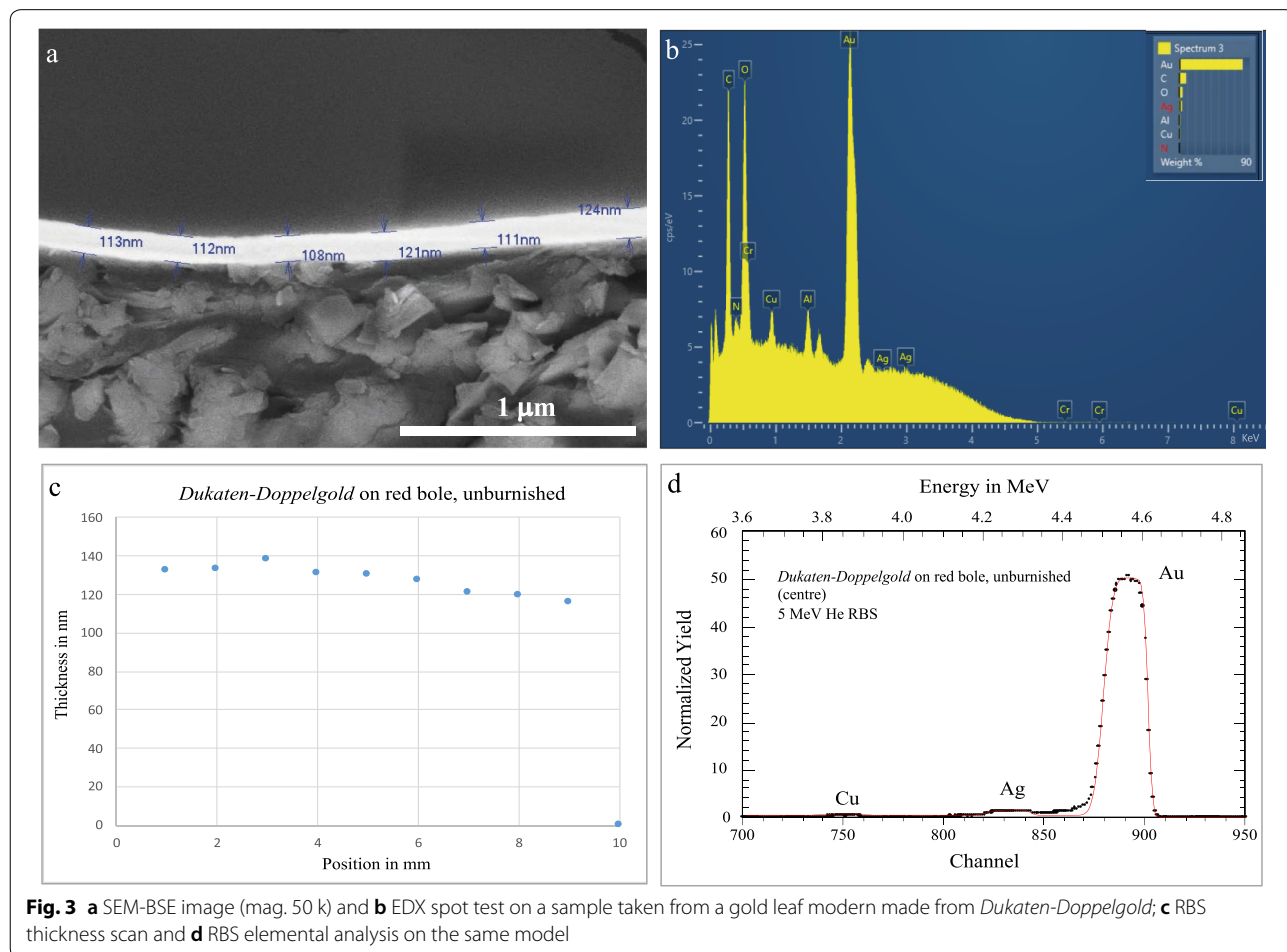
Gold leaf type	SEM–EDX				RBS			
	Cu content (w%)	Ag content (w%)	Au content (w%)	Thickness (nm)	Cu content (w%)	Ag content (w%)	Au content (w%)	Thickness (nm)
Spezial-Poliergold	1.1±0.3	2.1±0.4	96.8±0.2	96±9	0.8±0.1	2.6±0.2	96.6±0.3	92±7
Dukaten-Doppelgold	1.6±0.2	1.8±1.0	96.6±1.1	116±16	1.4±0.2	2.4±0.2	96.2±0.3	127±7

used in our study, their gold purity is about 23.1 to 23.2 carat.

SEM-BSE and RBS measurements further show that the *Poliergold* (96±9; 92±7 nm) appears slightly thinner than the *Doppelgold* (116±16 nm; 127±7 nm) by ca. 20–30 nm, but both of them are still within the published thickness range of 100–200 nm for modern gold leaf [21, 22]. The high consistency between SEM–EDX and RBS measurements of modern gold leaf samples proves that the samples were precisely prepared, which further

confirms the accuracy and reliability of the SEM–EDX observations on the medieval gold leaf samples.

Figure 3 presents one example of the SEM-BSE image (a) and a EDX spot test (a) on a sample taken from a small (ca. 10 × 10 mm), non-burnished gold leaf model made from *Dukaten-Doppelgold* (laid atop a red bole substrate), compared to the RBS measurements on the same model. Note that the RBS thickness measurement (Fig. 3c) was conducted in the thickness scan mode tracing a 2 meV beam (in a diameter of ca. 1 mm) along the middle line



of the model in steps of 1 mm; and its elemental analysis (Fig. 3d) was performed at the central position of the model with a 5 meV beam. Here, it is worth noting that no obvious thickness difference has been observed between the non-burnished and burnished states of gold leaf in both SEM and RBS measurements. Indeed, after the high pressure pressing and rolling during the manufacturing of gold leaf, a manual surface burnishing with agate tools should not generate sufficient pressure to significantly modify the leaf form. The same situation should also apply to the medieval gold leaf, which was produced through the *gold-beating* process [8].

SEM–EDX measurements of medieval gold leaf

In VLM observations on the sample stratigraphy, two of the 34 medieval gold leaf samples show an overlay of different *Fassungs*, indicating that they may not have been part of the original artefacts, and so were excluded from further analysis. Figure 4 shows an example of overlaid *Fassungs* in a sample stratigraphy (b), compared to a normal gold leaf sample (a). Therefore, a total of 32 samples were measured through SEM–EDX.

Table 2 presents details of SEM–EDX measurements on the 32 medieval gold leaf samples with respect to their gold content and leaf thickness. Note that 7 of the 32 samples contain multiple sub-layers. In 3 cases, the sub-layers can be clearly distinguished and hence the average thickness of the individual sub-layers are included in the summary of basic statistics of the leaf thickness and gold content in Table 3. In the remaining 4 multi-layered samples (marked with “*” in Table 2), the sub-layers are poorly defined and difficult to distinguish, and so these 4 samples were excluded from the statistics of leaf thickness, but still used for the statistics of gold content.

Table 3 exhibits the basic statistics of the leaf thickness and gold content of medieval gold leaf samples based on their SEM–EDX data presented in Table 2. Note that the

average (avg.), standard deviation (stdev.), median (med.), minimum (min.) and maximum (max.) values in the statistics are based on the averaged measurements of each sample.

Gold content

As shown in Table 3, the average gold purity of the medieval samples is around 23.70 carat, based on 342 measurements of 32 samples, which is close to the historical records of *florins* (23.75–24 carat) and *ducats* (23.75 carat). The main alloying elements observed in the sample leaves include copper (Cu) and silver (Ag), with an average content of 0.43 w% and 0.84 w% respectively. However, these are both unevenly distributed in the gold leaf, demonstrated by the relatively high standard deviations. Details regarding the Ag and Cu contents of each sample are presented in Table 2.

It is worth pointing out that 7 of the 32 samples show relatively lower gold quality of 22.02 to 23.26 carat (marked with “**” in Table 2), while the rest of the samples exhibit very high gold purity of 23.62 to 24 carat. We are not certain about the gold source for these 7 samples, which could be some other gold coins such as *Rhenish gold* with its early compositions. Evidence of using *Rhenish gold* for gold leaf can be found in some German work contracts of the early sixteenth century [15]. Compared to the *florin* and *ducat*, the quality of *Rhenish gold* was not stable, and its gold content sunk from 98% when it was first minted in 1354 to only 79% by 1419 [15].

Leaf thickness

Most of the medieval gold leaf samples (Fig. 5b–d) were observed to be slightly less even than the modern gold leaf (Fig. 5a); and their thickness varies significantly. The basic statistics in Table 3 show that the average thickness of medieval gold leaf is 162 ± 39 nm based on 2235 measurements on 28 gold leaf samples, with a median value

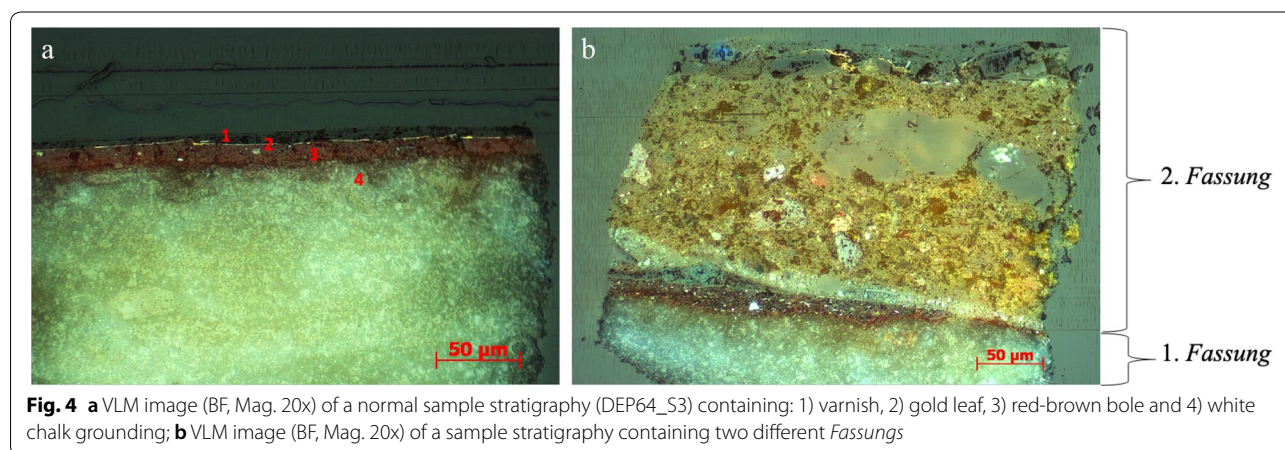


Table 2 (continued)

Object no	Inv. title	Object data	Production regions	Sample-taking area	Leaf thickness			Au content			Cu content			Ag content															
					Avg. (nm)	Stdev. (nm)	Med. (nm)	Min. (nm)	Max. (nm)	Avg. (w%)	Stdev. (w%)	Med. (w%)	Min. (w%)	Max. (w%)	Avg. (w%)	Stdev. (w%)	Med. (w%)	Min. (w%)	Max. (w%)										
LM18014	Descent from the Cross	1520	Eastern Switzerland	Gown	184	68	176	83	375	40	100.00	24.00	0.00	100.00	100.00	100.00	14	0.00	0.00	0.00	0.00	0.00	14						
LM18015*	Crucifixion	1520	Eastern Switzerland	Gown	364	83	357	159	598	79	99.66	23.92	1.09	100.00	96.55	100.00	10	0.00	0.00	0.00	0.00	0.00	0.00	10					
LM18016*	Resurrection of Jesus	1520	Eastern Switzerland	Gown	304	134	241	181	523	8	100.00	24.00	0.00	100.00	100.00	100.00	2	0.00	0.00	0.00	0.00	0.00	0.00	2					
LM20886	John the Baptist	1500	Southern Germany	Gown	155	62	143	52	368	153	99.95	23.99	0.17	100.00	99.46	100.00	10	0.05	0.17	0.00	0.00	0.00	0.00	0.00	10				
LM24174**	Half figure of a Holy Pope, possibly St. Paul	1500–1510	Southern Germany	Gown	150	55	141	67	317	78	91.77	22.02	2.71	91.50	88.36	97.08	7	2.39	0.32	2.38	1.87	2.92	7	5.84	2.93	5.99	0.00	9.13	7
LM5657	John the Baptist	1495	Southern Germany	Gown	113	25	108	58	177	55	98.71	23.69	1.25	99.32	96.60	99.50	8	0.51	0.24	0.55	0.00	0.74	8	0.78	1.45	0.00	0.00	3.40	8
LM6280	St. Lawrence	1500	Southern Germany	Gown	148	48	135	64	282	85	100.00	24.00	0.00	100	100.00	100.00	11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11	
LM6982	Virgin and Child with St. Anna	1500–1510	Southern Germany	Gown of Anna	139	59	134	55	291	55	99.14	23.79	0.27	99.02	98.91	100.00	15	0.86	0.27	0.98	0.00	1.09	15	0.00	0.00	0.00	0.00	0.00	15
LM7108	Mary with Child	1450	Southern Germany	Gown	127	43	127	50	214	55	100.00	24.00	0.00	100.00	100.00	100.00	8	0.00	0.00	0.00	0.00	0.00	8	0.00	0.00	0.00	0.00	8	
LM7202a (sub-layer)	Mary with Child, sur-rounded by two angels	1490–1500	Unknown	Gown	122	39	124	61	195	24	98.85	23.72	1.36	99.44	95.65	100.00	16	0.53	0.19	0.56	0.00	0.85	16	0.61	1.33	0.00	0.00	3.69	16
LM7202.b**	Virgin and Child with St. Anna	1520	Unknown	Gown	121	40	108	64	214	29	96.90	23.26	1.63	97.00	94.96	100.00	7	0.00	0.00	0.00	0.00	0.00	7	3.10	1.63	3.14	0.00	5.04	7
LM8139.2	Mourning John the Evangelist	1500–1510	Central Switzerland	Swit-Gown	160	49	152	60	327	77	99.23	23.82	0.48	99.06	98.71	100.00	16	0.77	0.48	0.94	0.00	1.29	16	0.00	0.00	0.00	0.00	0.00	16

Table 2 (continued)

Object no	Inv. title	Object data	Production regions	Sample- taking area	Leaf thickness			Au content			Cu content			Ag content															
					Avg. (nm)	Stdev. (nm)	Med. (nm)	Avg. (w%)	Stdev. (w%)	Med. (w%)	Min. (w%)	Max. (w%)	Counts	Avg. (w%)	Stdev. (w%)	Med. (w%)	Min. (w%)	Max. (w%)	Counts										
LM8554.1	Mary with Child (from a figure group "Mary with eight saints")	1510	Southern Germany	Gown	168	58	157	56	349	74	99.69	23.93	0.90	100.00	97.01	100.00	11	0.04	0.12	0.00	0.00	0.40	11	0.27	0.90	0.00	0.00	2.99	11
LM8554.3	St. Jerome	1510	Southern Germany	Gown	215	81	228	86	402	40	99.97	23.99	0.11	100.00	99.57	100.00	15	0.03	0.11	0.00	0.00	0.43	15	0.00	0.00	0.00	0.00	0.00	15
LM8658	Enthroned bishop, possibly St. Theodore	1500	Unknown	Gown hem	240	58	230	127	400	32	98.41	23.62	1.68	98.86	93.99	99.48	9	1.18	0.51	1.14	0.52	2.32	9	0.41	1.23	0.00	0.00	3.69	9
LM9282.2**	God the Father (from a figure group "Coronation of the Virgin")	1500	Southern Germany	Gown	196	46	203	92	305	95	96.21	23.09	2.68	96.30	92.85	99.02	14	1.24	0.17	1.22	0.98	1.61	14	2.55	2.66	2.28	0.00	5.82	14
LM9282.3**	Christ (from a figure group "Coronation of the Virgin")	1500	Southern Germany	Golden flakes on gown	168	55	166	55	360	80	96.07	23.06	2.11	95.01	2.11	98.92	9	1.27	0.15	1.31	0.15	1.45	9	2.66	2.02	3.66	0.00	4.69	9
LM9428**	Unknown bearded saint	Unknown	Unknown	Golden flakes on gown	159	50	162	48	279	86	94.99	22.80	2.83	93.09	90.13	98.96	17	1.98	1.01	1.96	0.00	4.45	17	3.03	2.73	3.94	0.00	7.54	17
LM9484*	Holly Kinship	1500	Southern Germany	Gown of Mary	388	124	404	144	730	93	100.00	24.00	0.00	100.00	100.00	100.00	11	0.00	0.00	0.00	0.00	0.00	11	0.00	0.00	0.00	0.00	0.00	11
LM9485	St. Dorothea	1490-1500	Unknown	Golden flakes on gown	238	75	217	111	467	118	100.00	24.00	0.00	100.00	100.00	100.00	6	0.00	0.00	0.00	0.00	0.00	6	0.00	0.00	0.00	0.00	0.00	6

*Gold leaf samples containing indistinct sub-layers

**Gold leaf samples showing relatively lower gold purity (22.02-23.26 carat)

Table 3 Statistics of SEM–EDX observations on the leaf thickness and gold content of medieval gold leaf samples

Measurement	Avg	Stdev	Med	Min	Max	Counts	Samples
Thickness	162 nm	39 nm	158 nm	103 nm	244 nm	2235	28
Cu content	0.43 w%	0.63 w%	0.07 w%	0.0 w%	2.39 w%	342	32
Ag content	0.84 w%	1.43 w%	0.13 w%	0.0 w%	5.84 w%	342	32
Au content	98.73 w%	1.93 w%	99.65 w%	91.77 w%	100 w%	342	32
	23.70 carat	0.46 carat	23.92 carat	22.02 carat	24 carat		

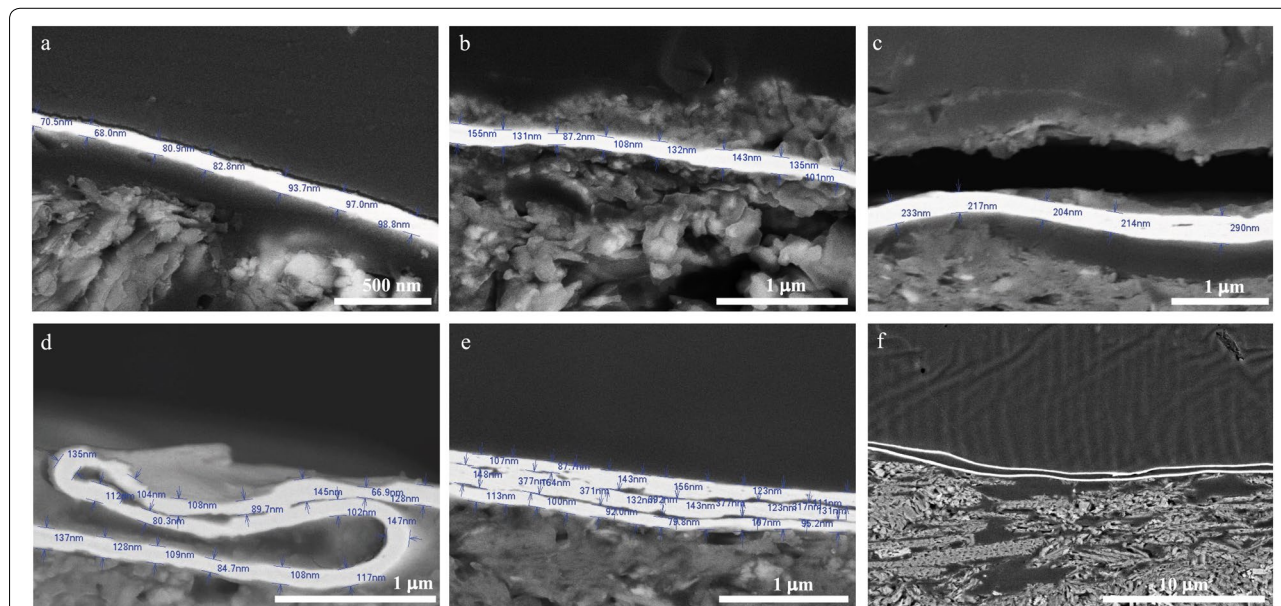


Fig. 5 Thickness measurements (indicated with blue numbers) for modern and medieval gold leaf samples based on SEM-BSE images: **a** modern gold leaf Spezial-Poliergold; **b, c** normal medieval gold leaves; **d** a folded normal medieval gold leaf; **e** a multi-layered medieval gold leaf; **f** two layers of modern gold leaf Dukaten-Doppelgold overlaid through a 1.5 w% water-based rabbit skin glue

of 158 nm, a minimum and a maximum value of 103 nm and 244 nm respectively. This observation is close to the literature record (possibly a calculated leaf thickness) based on Vasari’s treaties (154 nm for gold leaf of the sixteenth century) and ca. 1.4–1.7 times as thick as modern gold leaf that we have observed in *Spezial-Poliergold* (96 ± 9) and *Dukaten-Doppelgold* (116 ± 16).

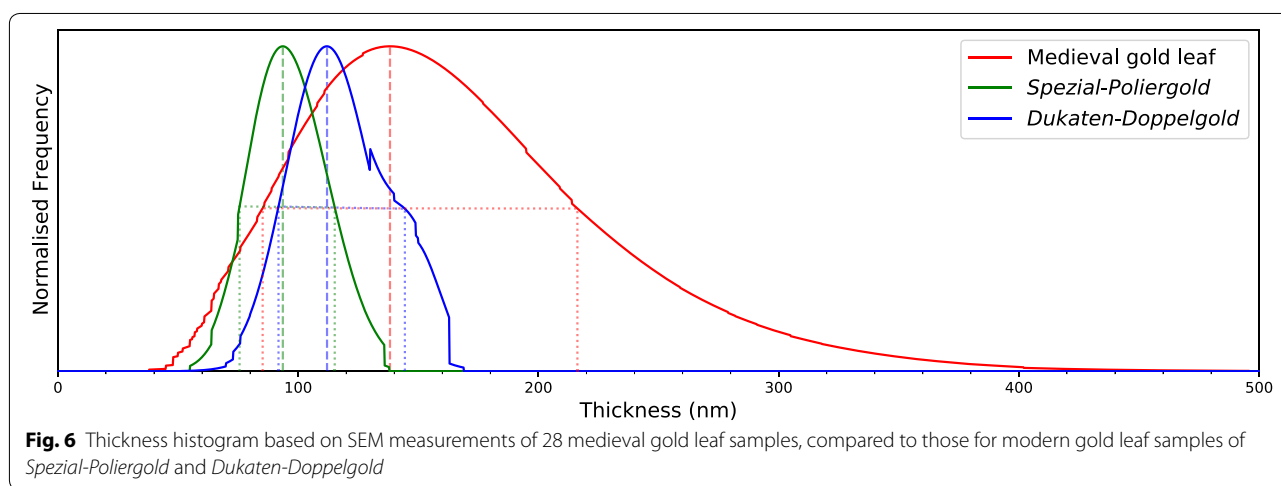
The seven sample gold leaves that contain multiple sub-layers (Fig. 5e) show an overall thickness of 388 ± 45 nm, ca. 2.5 times larger than the average thickness of normal gold leaves. Measurement data of these seven samples are presented in Table 4. Such thick, multi-layered gold leaf can be sometimes misidentified as a folded normal (i.e. single-layered) gold leaf (Fig. 5d), which usually occurs in wrinkled areas of a gilded surface. The observation of the multi-layered gold leaf reminds us of the special type of “fine reinforced gold leaf” recorded in artists’ supplies in Dijon in 1400. Since very little space is observed between these sub-layers, we believe that the artisans must have

combined a few thin gold foils in the later stages of beating, in order to ensure a desired final thickness relative to the normal gold leaf. This is different from Cennini’s suggestion of reducing the number of the gold leaves produced from one gold coin for greater leaf thickness, and also unlike Theophilus’s recipe of applying multiple layers of gold leaf with adhesive. SEM observations on a sample taken from a model applied with double layers of modern gold leaf (model produced in Part I) provide evidence supporting our hypothesis. Figure 5f shows that when adhesive (1.5 w% rabbit skin glue in this case) is used for laying one gold leaf above another, a relatively large space is present between these two leaves, even in a burnished state. Based on our experience in the production of models, overlaying gold leaves without adhesive is not practical, as the upper leaf does not adhere and is removed with the lightest touch.

More detailed information is presented in the thickness histogram in Fig. 6, which was constructed by summing

Table 4 SEM observations on leaf thickness of 7 medieval gold leaf samples containing multiple sub-layers

Object Inv. no	leaf structure	Measurements of the overall thickness (nm)					
		Avg	Stdev	Med	Min	Max	Counts
AG9061.2	3 distinct sub-layers	428	131	412	231	750	49
LM10419	2 distinct sub-layers	390	92	362	295	698	39
LM17796	Up to 2 indistinct sub-layers	402	118	395	160	667	78
LM18015	Up to 2 indistinct sub-layers	364	83	357	159	598	79
LM18016	Up to 3 indistinct sub-layers	304	134	241	181	523	8
LM7202.a	3 distinct sub-layers	439	160	385	217	862	45
LM9484	Up to 2 indistinct sub-layers	388	124	404	144	730	93



the set of clipped normal distributions corresponding to the average, standard deviation, minimum and maximum values calculated from the measurements on each medieval sample shown in Table 2 (four samples marked with “*” were excluded). The histogram of medieval gold leaf samples shows a half-peak range of 85–216 nm with the peak value of 138 nm, indicating a much broader thickness range compared to the modern samples of *Spezial-Poliergold* (76–115 nm with the peak at 94 nm) and *Dukaten-Doppelgold* (92–144 nm with the peak at 112 nm).

Further discussions

The SEM–EDX observations of the late medieval gold leaf samples are in high agreement with related literature records, often exhibiting greater leaf thickness and even higher gold purity than some modern gold leaves. Combined with the known optical properties of thin gold films excluding significant transparency in gold films thicker than 100 nm [23] and our findings through modern gold leaf models in Part I, our observations of medieval gold leaf samples indicate that no perceptible reflected light from the substrate could be able to penetrate through

the medieval gold leaf to the surface, except for through cracks or holes inside of the leaf. In Part I we determined that such crack and holes in the gilding typically do not make up a significant enough fraction of the surface area to make a perceptible difference to the colour. Therefore, we conclude that the substrate colour does not play any role in the visual appearance of late medieval artefacts gilded with gold leaf. However, why has this misconception been well accepted since at least the Middle Ages and circulated even till now? We believe that the main reason is likely related to the historical development of medieval polychromy. According to Brachert and Kobler [24], in the time period from the second half of the twelfth century till the early fourteenth century, white ground was generally used for glossy gilding in northern Europe, while the use of Armenian bole started in the South. During the trend of “Ideal polychromy” (translated from *Ideale Fassung* in German), which appeared in the first half of the fourteenth century, differentiated gold effects were preferred: for example, hair was always in matte gold, while gown could show a contrasted effect with glossy gold on white ground and matte gold on yellow substrate. By the end of the fourteenth century, gold

leaf was generally applied on a yellow, seldom white substrate, and red *Poliment* (German term, refers to fine clay bound with organic media and often mixed with pigments, similar to bole [26]) became popular since the middle of this century and dominant in later epochs [17, 24, 25]. Although the “yellow substrate” is not clearly specified by the authors, from its usage for matt gilding we believe that it refers to yellow mordant. Now we see a clear chronological sequence of using different substrates for gilding in the North of medieval Europe: white ground—mixture of white ground and yellow mordant—yellow mordant—red *Poliment*.

Since ground gilding can only offer a poor surface burnishing and mordant gilding is not burnishable, gold surfaces of North European sculptures in the time periods prior to the introduction of red bole/*Poliment*, must appear relatively matte and yellowish. Following the wide use of red bole, the quality of the surface burnishing was strongly enhanced, and the gold surface hence exhibited high metal gloss and more depth in its colour appearance, rendering a warmer and more saturated feeling to human eyes. From this perspective of working with a limited set of substrate materials, there is a clear correlation between the substrate colour and the gilding surface, and so it would be easy for medieval artisans to fall victim to the fallacy that the correlation implies causation. However, it is only a coincidence that the colour tone of these substrate materials correlates with the mechanical support and surface roughness properties that are the true cause of the mirror-like smooth surface of the gilding that provides the desired visual appearance. This was demonstrated in Part I with the use of a wider range of substrate material types and colour combinations than would have been available to artisans at the time that the substrate colour theory was being popularised. The occurrence of very fine gold leaf in the late Middle Ages could further strengthen people’s “faith” in using certain substrate colours for gilding, because they believed that the gold leaf was too “thin” to block the substrate colour.

Another contributing factor for artisans’ misconception could have been related to the parallel development of painting techniques in the late medieval period, especially the wide application of stand oil as a pigment binder for the late Gothic’s artworks [26]. Such heat-treated oil (e.g. linseed oil, walnut oil) can be dry within 24–48 h in the paint layers and is thus especially suitable for thin layers over a white grounding [26]. It was also commonly used for the half-transparent colour glazing or varnishes [10], due to its closer refractive index to many pigments for reduced light scattering, compared to water-based binding media [27]. For example, aluminium hydroxide was a common substrate for the organic lake pigments that were extensively used in coloured glaze; its

refractive index (ca. 1.5) is very close to that of linseed oil (1.48) and significantly larger than that of glue (ca. 1.35) [27]. Additionally, some mineral pigments and fillers such as ultramarine, smalt, chalk and gypsum also show similar refractive indices as oil (1.5, 1.49–1.52, 1.5–1.64, 1.53–1.62 vs. 1.48) [27]. The practical experience of dealing with oil containing binding media might have helped to build the fallacy in minds of the artisans that a thin gold leaf should behave similarly to the oil paint layers and also be unable to fully block the colour of an underlying layer (e.g. a red bole). The transfer of such ideas could occur especially easily in workshops where gilders and *Fassmaler* (German term, refers to painters working on sculptures) were working together, which was fairly common at that time.

Conclusions

This study refutes the long-accepted point of view in the history of medieval gilding that the substrate colour can influence the visual appearance of a gilded artefact due to the transparency of the ultra-thin gold leaf laid above. Our investigations combining literature sources and SEM–EDX measurements on samples taken from gilded artefacts show that the medieval gold leaf is of high gold purity of about 23.7 carat and around 160 nm thick (with a peak value of 138 nm), which is only about 1.4–1.7 times as thick as modern gold leaves, indicating a high technological level in the manufacturing of fine gilding materials in the late medieval period.

Since the medieval gold leaves are as pure and at least as thick as the modern gold leaves used in Part I, our previous findings must also be applicable to medieval gilding. Firstly, the gold leaf is too thick to transmit a perceptible amount of visible light reflected from the substrate, and secondly that the visual appearance of the gilded surface is dominated by the proportion of light in the specular and diffuse reflections, which is caused by the roughness of the gold surface and is, in turn, influenced by the roughness and mechanical support provided by the substrate. We argue that the fallacious substrate colour theory may have formed due to two factors: the limited set of material types and colours available at the time (together with their chronological introduction) that coincidentally correlated well with the smoothness of the gilded surfaces, and the analogy with the partial transparency of oil paint layers being used in the same workshops.

Abbreviations

Ag: Silver; Au: Gold; avg.: Average; BF: Bright field; BSE: Backscattered electron; Cu: Copper; DF: Dark field; ETH Zurich: Swiss Federal Institute of Technology, Zurich; HHXRF: Handheld X-ray fluorescence analyser; Inv. No.: Inventory number; max.: Maximum; med.: Median; min.: Minimum; RBS: Rutherford backscattering spectrometry; SEM–EDX: Scanning electron microscopy coupled

with energy dispersive X-ray analysis; SNM: Swiss National Museum; stdev.: Standard deviation; PSI: Paul Scherrer Institute; VLM: Visible light microscopy; w%: Percent by weight.

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Authors' contributions

QW designed the work, prepared sample cross-sections, performed SEM–EDX measurements, analysed and interpreted SEM data, and was a major contributor in writing the manuscript. MD performed the RBS experiments and analyzed the data. TL substantively revised the manuscript. KS substantively revised the manuscript. BW performed data visualization and substantively revised the manuscript. FN substantively revised the manuscript. DG designed the work. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analysed during this study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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