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Original article

Medieval nanotechnology: Thickness determination of Zwischgold samples



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ABSTRACT

A special gilding material called Zwischgold has been frequently observed in medieval gilded artefacts. As a bilayer metal leaf made from gold and silver, it exhibits similar but slightly paler golden colour tone compared to pure gold. Zwischgold surface can be darkened quickly due to the corrosion of its silver base. Despite its frequent mentions in medieval guild statutes, the production of Zwischgold and its important technological parameters have been under a veil of secrecy since the Middle Ages. Here, we examine the thicknesses and materials proportions of medieval Zwischgold, through high-resolution scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) on a large number of samples taken from late medieval gilded sculptures. We observe that medieval Zwischgold contains ultra-thin gold layers in a thickness range of ca. 20–50 nm, indicating the employment of high-precision technologies in manufacturing of delicate art materials in the late medieval period. It further clarifies some ambiguity in gilding history, regarding the colour appearance of medieval Zwischgold. As supportive data, Rutherford backscattering spectrometry (RBS) and scanning transmission electron microscopy (STEM) were applied, in order to confirm the precision and accuracy of the sample preparation and the SEM analysis.

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1. Introduction

A bi-layered metal leaf called *Zwischgold* (German, now a universal term) [1–4] or *part-gold* (English) [5–7] has been frequently observed in medieval gilded sculptures. It contains a gold layer on top and a silver layer underneath [1,5,7,8], in order to present an actual gold surface with lower cost [9–11]. Extant evidence shows that the application of Zwischgold in artworks started in the early 13th century [5,12]. Unlike the chemically stable gold leaf, this special gilding material tends to corrode quickly in air, causing surface

darkening [1,8,13]; its application was thus strictly controlled by medieval guilds [5,8]. Fig. 1 presents an example of a medieval artefact collected by the Swiss National Museum (SNM), in which Zwischgold was partly applied on the saint's hair, poleyn, stirrup and the horse saddle (outlined in green) [14]; the latter three are located on the less visible side and rear parts of the object, indicating that Zwischgold was intentionally used as an inferior substitute of gold leaf. Indeed, cost-saving is a commonly accepted reason for the use of Zwischgold [1,5,13,15].

Although the Zwischgold surface on the saint's hair now appears dark brown, indicating a strongly corroded state, it is expected to have been originally applied to the hair section due to its nuanced paleness (or brighter colour tone [4]) being closer to blonde than pure gold [14,16–18]. According to a popular theory that has been circulated for centuries, such a pale tonality of medieval Zwischgold is mainly attributed to the transparency of its gold layer that is too thin to fully block the light reflection from the underlying silver [16,17]. A modern understanding of light propagation through

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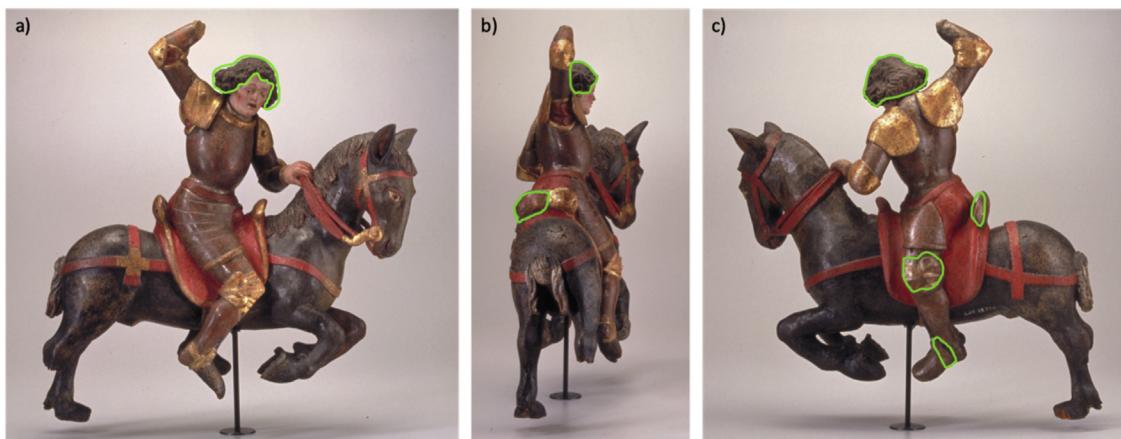


Fig. 1. Sculpture St. George on the horse (SNM, LM13716), dated 1500, viewed from (a) front, (b) side and (c) rear. Zwischgold application is indicated with green lines.

gold limits the thickness of the gold layer to a few tens of nanometers in order for such transparency to occur [19]. An alternative explanation is that the paleness is due to silver diffusing through the grain boundaries of the gold layer to form a thin surface layer of silver [20].

Despite its frequent mentions in guild statutes [5,8], details of the original forms, especially the leaf thickness of medieval Zwischgold, have not been discussed in early documentary sources. This knowledge gap has persisted in modern times, because the ultra-thin and strongly heterogeneous character of Zwischgold leaves, as well as its complex corrosion conditions [14,21], pose strong challenges to modern scientific analysis. In the current paper, we focus on investigating the technological parameters of medieval Zwischgold, including its gold layer thickness and the proportions of the silver and gold components, mainly through scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) on a large number of Zwischgold samples taken during a recently implemented object survey in the SNM [14,21]. The full leaf thickness of medieval Zwischgold can be further inferred based on the output of such SEM measurements. As important supportive data, Rutherford backscattering spectrometry (RBS) and scanning transmission electron microscopy (STEM) have been also applied to verify the precision of the sample preparation and to ensure the reliability of the SEM data.

2. Research aim

This study aims to provide high-confidence scientific details to fill a long-lasting knowledge gap of medieval Zwischgold regarding its technological parameters, and to clarify some ambiguity about its special colour tonality, which has long circulated in the research history of medieval gilding. With the output of this study, we expect to demonstrate a good understanding of the technological environments in the leaf-beating workshops of the late medieval period, and to further provide important references for research of other artefacts in the frame of Zwischgold.

3. Theory

In gilding history, thickness is a critical parameter for the metal leaf. It infers the technological level of the production of gilding materials in certain epochs and regions, and is especially of great significance to gilding leaves that contain layered structures, like Zwischgold. For example, our previous study shows that the modern Zwischgold (purchased from Noris Blattgold, Germany) has a leaf thickness of 500–700 nm, with a thin gold layer of around 100 nm [20]. Another earlier study (1959) even points out that the

gold layer of a modern Zwischgold leaf can be as thin as 30 nm [22], indicating a high technological level in the modern gold leaf industry. However, the full leaf thickness of medieval Zwischgold is not recorded in historical documents, and seldom discussed in modern scientific works (one of our recent studies demonstrates the measurements of an individual sample [21]). One likely reason could be that the complicated corrosion situations in individual Zwischgold artefacts, in which metallic silver (in the silver base) was fully or partly transformed into silver corrosion products and redistributed in the surroundings of the Zwischgold leaf [20,21], strongly limit the usefulness of direct observations of its leaf thickness.

Some researchers state assumptions that medieval Zwischgold should have a similar thickness as gold leaf [5,23] and thus be in a thickness range of 0.25–5 microns based on published data of gold leaf of that time [5]. However, we believe that a more precise and reliable estimation of the original leaf thickness of medieval Zwischgold could be achieved through quantifying the elemental constituents and then combining this result with the gold layer thickness measured. It is well known that gold is chemically inert and thus its observed layer thickness should be the same or at least very close to its original state. As for silver, although its chemical state and location can be altered by corrosion, its silver atoms should remain present in close vicinity to the gold layer and hence measurement of the silver/gold (Ag/Au) weight ratio should not be strongly affected. The original silver layer thickness and the total leaf thickness could then be reliably inferred from these parameters, together with the mass density ratio of silver and gold.

Despite the fact that historical records of the Ag/Au weight ratio involved in the Zwischgold production are very few and vary significantly, they still provide important references to our study. Within all medieval artists' treatises, only the 12th century's *De diversis artibus* suggests using 12 parts silver and 1 part gold (by weight) for producing metal strips (for wrapping silk threads) with a similar leaf structure as Zwischgold [24]. 650 years later, J.S. Halle records a more detailed recipe of 13 lots silver and 12 ducats for producing 2400 sheets of Zwischgold with a size of 2 square inches [25], corresponding to an Ag/Au weight ratio of ca. 4.5:1. Shortly after Halle, Lewis gives a similar ratio of 4:1 [26]. Based on Halle's descriptions, the gold and silver layer thicknesses are calculated to be ca. 0.35 μm and 2.94 μm respectively. However, material off-cuts from the Zwischgold production process are not mentioned in Halle's record; according to von Keess, off-cuts could be as high as three fourths of the initial input materials for the production of gold leaf [27]. Therefore, the actual gold and silver layer thicknesses could be much smaller than the above calculations. A smaller Ag/Au ratio of 2.17:1 deduced from von Keess's descriptions in the early 19th century seems more reliable, since it states that the gold leaf

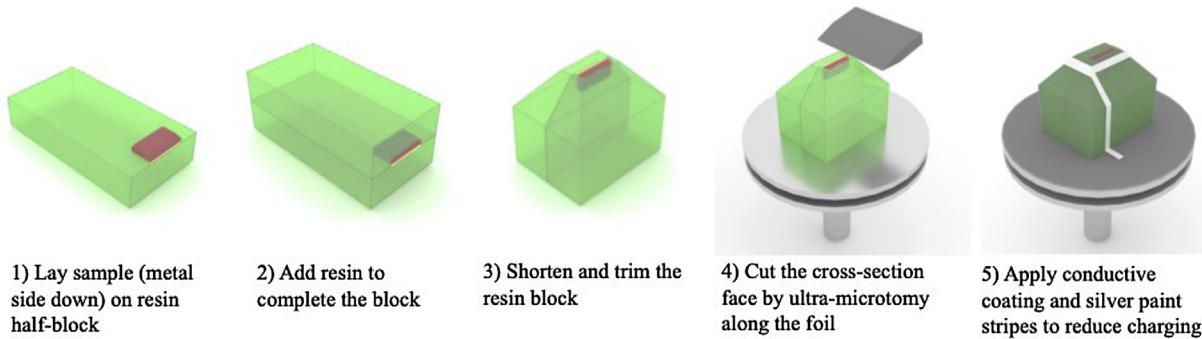


Fig. 2. 3D schematic illustrations for the sample preparation method. The metal leaf side of the sample is illustrated with the yellow line and the red layer represents the preparation layers; white lines in (5) refer to the silver paint stripes.

is already one fourth the thickness of the silver before they started to be beaten together [27]. From the known mass densities of bulk gold and silver, the aforementioned historical recipes indicate a wider Ag/Au layer thickness ratio range (4:1–20:1), which differs from our knowledge of modern Zwischgold (4:1–6:1) [20]. However, Herm has observed that medieval Zwischgold leaves have relatively higher proportions of gold compared to the modern reference sample (with one case that gold content is much higher than the silver content) [28], suggesting that the Ag/Au weight and thickness ratios of medieval Zwischgold were generally lower than those of modern Zwischgold (the Ag/Au weight ratio of modern Zwischgold is ca. 2.2:1–3.3:1, deduced from its thickness ratio).

In addition to the Au layer thickness and Ag/Au weight ratio, another factor, namely the Au and Ag purities, should not be omitted. The recent object survey in the SNM shows that all Zwischgold samples taken from the surveyed medieval sculptures contain only a small amount of copper (as an alloying metal in gold) with a Cu/Au weight ratio of less than 2% [21], not considering silver atoms diffused through and deposited in the gold grain boundaries [20]. Furthermore, no alloying metals were observed in either metallic silver or silver corrosion products in these Zwischgold samples [21], indicating the use of pure silver for medieval Zwischgold. Indeed, the discovery and fast development of silver mining started in Europe from the Middle Ages, and central Europe was famous for its silver deposits [29–31].

Compared to its leaf thickness and materials quality, the production procedures of Zwischgold seem clearer, although they are only briefly introduced in very few historical literatures. For example, in Halle's work of the 18th century, such procedures are so described that the gold was first beaten to the thickness of paper and then laid atop a silver leaf in a beater's parchment form, and beaten again until the leaves were doubled and cannot be separate; such semi-finished leaves were quartered and beaten again in other forms for a few iterations until the final product reached the desired thickness [25,29]. Meanwhile, the author points out that "it is difficult to reach the correct degree of paleness: if it is exceeded, the gold tonality is diminished and white spots [of silver] appear; if it is not attained, the costs of production exceed the worth of the metal leaf" [25,29]. Here, four hints are given by Halle's words, including (1) the pale tonality of Zwischgold was desired and intended to be obtained during the production; (2) the magnitude to which Zwischgold should be beaten is a highly skilled work; (3) the colour appearance of Zwischgold is strongly dependent on the thinness and evenness of its gold layer; (4) the materials cost in Zwischgold production needs to be strictly controlled. Such hints are of our strong interest and the way to verify them motivates this study.

4. Material and methods

4.1. Samples and sample preparation

A total of 75 Zwischgold samples were used for the SEM measurements in this study. These measurements were performed as part of the SNM object survey [14,21,32]. Information regarding the sample origins and sample taking areas is presented in [Supplementary Materials: S1](#). Measurement details for each individual sample are presented in [Table S1 in the Supplementary Materials](#).

The samples were embedded with epoxy resin Araldite 2020 and then cut with a *Leica UC7* ultra-microtome, using a *DiATOME trimtool 45* diamond knife and a clearance angle of 6°. Ultra-microtomy was chosen for preparing samples for the SEM measurements not only due to the similar flatness and smoothness of detail in its resulting cross-sections as those prepared with focused ion beam (FIB) [21], but also because of its additional advantages of high throughput and producing a large cross-section area. The latter is particularly helpful for the selection of observation sites for EDX analysis of the Ag/Au weight ratios of medieval Zwischgold samples (discussed in Section 5.2.2 and [Supplementary Materials: S3](#)). Nevertheless, FIB processed thin lamellae can provide very fine details of medieval Zwischgold and were thus used for the STEM-EDX analysis for certain samples.

It is worth noting that producing cross-sections for thickness measurements requires a precise positioning during the sample embedding and cutting [32]. Fig. 2 demonstrates the sample preparation process with 3D schematic illustrations. More details about the sample preparation and 2D schematic illustrations are presented in our recently published study regarding medieval gold leaf [32]. However, due to the complex situations (e.g., twisting, tilting, curving or overlapping) of historical Zwischgold leaves, ideal embedding and cross-sectioning are sometimes difficult to achieve, which might result in small geometrical errors in the thickness measurements.

In addition to the medieval samples, a couple of modern Zwischgold samples were also taken from self-made models [20,33]. The SEM data of these samples was compared to the RBS measurements on the models, in order to check the precision of the sample preparation.

Samples for transmission electron microscopy have been prepared by conventional FIB preparation using an *FEI Helios NanoLab 600*. To ensure minimal alteration of the Zwischgold layers during thinning with the ion beam, the primary energy of the ion beam was gradually decreased from 30 kV to 2 kV.

Table 1

SEM-BSE and RBS measurements on the gold and silver layer thicknesses of modern Zwischgold.

Analysis technique	Sample type	Au layer (nm)	Ag layer (nm)
SEM-BSE	Cross-section (uncorroded)	93 ± 19	480 ± 52
	Cross-section (3-year old)	87 ± 26	498 ± 59
RBS	Model (uncorroded)	95 ± 9	507 ± 62

4.2. Analytical techniques and experimental conditions

The stratigraphy of the sample cross-sections was observed and imaged with a visible light microscope (VLM) *Leica DM4000 M*, coupled with a *uEye UI144xSE-C* camera, in the SNM conservation laboratory. Both bright field (BF) and dark field (DF) modes were used.

The SEM-EDX measurements were implemented through an ultra-high resolution *Hitachi Regulus 8230* (cold field emission) SEM coupled with an EDX *Ultim Extreme Silicon Drift Detector* (with a detector area of 100 mm²) from *Oxford Instruments* at the Paul Scherrer Institute (PSI), under the experimental conditions of 5 kV voltage and 10 µA current. 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 thickness of the gold layer of Zwischgold were based on the backscattered electron (BSE) imaging, a technique sensitive to chemical composition, on sample cross-sections. More details and discussion regarding the SEM experimental settings can be found in [Supplementary Materials: S2](#).

STEM measurements were performed at the University of Siegen (Siegen, Germany). An *FEI Talos F200X* microscope, equipped with a *SuperX-detector*, was set to an acceleration voltage of 200 kV.

RBS measurements on models made from modern Zwischgold leaves were performed at the Swiss Federal Institute of Technology in Zurich (ETH Zurich, Switzerland), Laboratory for Ion Beam Physics, using a 2 MeV ⁴He beam and a silicon PIN diode detector at 168°. The collected RBS data was analysed using simulations by the RUMP code [34].

5. Results and discussion

5.1. SEM, RBS and STEM measurements on test samples

SEM-BSE imaging on modern Zwischgold samples and RBS measurements on models made from the same Zwischgold leaves exhibit a high degree of consistency in the layer thickness for gold and silver. [Table 1](#) shows that the average gold layer thickness of modern Zwischgold is around 100 nm and that of the silver base is in the range of 400–600 nm. Such consistency confirms that samples were prepared precisely, providing evidence for the reliability of the thickness measurements on medieval samples. [Fig. 3](#) presents the thickness measurements on an uncorroded Zwischgold sample based on the SEM-BSE image (a) and the data graph of an RBS measurement on a Zwischgold model (b).

However, medieval Zwischgold samples are observed to contain diverse leaf structures, corrosion states and surrounding materials, as we discuss in a complementary article [21]. For example, [Fig. 4](#) shows a comparison between the VLM and SEM observations on a sample taken from the hair of the same statue shown in [Fig. 1](#) and those on a modern sample taken from a 3 years old model. While the modern sample (d–f) exhibits a clear layered structure of gold and silver with only a few islands of corrosion products atop the gold, the medieval sample (a–c) shows a strongly corroded state with significant corrosion products around the gold layer; meanwhile the layer below the medieval leaf is composed of colourful mineral pigments. The complex situation of mediaeval

samples certainly increased the difficulty of the SEM measurements and thus observation on multiple sites of each sample is required for a representative characterisation.

Another important issue that needs to be clarified is the silver-gold diffusion. Silver has a slightly lower surface energy and so will tend to migrate to cover all gold surfaces that it comes into contact with [20]. This includes the grain boundaries inside the gold layer of Zwischgold, which are filled with silver atoms and then act as a conduit to transport silver across to then cover the upper surface. This grain boundary and surface diffusion is rapid, even at room temperature [35]. STEM-EDX analysis ([Fig. 5](#)) of a 600 years old sample, which was taken from one of the very few medieval Zwischgold artefacts that are still in a well-preserved condition (*Woman of the Apocalypse* [14,36]), shows distinct, thin channels of silver extending through the gold layer and also covering the upper surface. These structures demonstrate that the diffusing Ag atoms are limited to the grain boundaries and do not penetrate the crystal lattice of the gold. Therefore, Ag/Au grain-boundary diffusion cannot significantly change the form and size of the gold layer in Zwischgold leaves, nor its gold purity. EDX quantification shows that the gold layer of this sample contains less than 2 wt.% of Ag (some of which could be attributed to a few monolayers of silver forming on the front and rear faces of the section due to surface diffusion), indicating its materials source of high-quality gold.

The STEM-EDX analysis on one sample certainly does not indicate that all gold layers of the medieval Zwischgold samples are of very high quality, and the elemental composition of these gold layers should be obtained from direct measurements. However, due to a well-known issue of SEM that the penetration and scattering of the electron beam within the sample broaden the measurement spot to partly overlap the adjacent silver or silver corrosion layer, data obtained from SEM-EDX spot (or selected area) tests is not reliable and thus not utilised in the analysis. Instead, it is reasonable to assume that the same quality gold was used for both Zwischgold and gold leaves on the same artefacts; our study from the same SNM survey showed that medieval gold leaf contains an average gold content of ca. 98.73 wt.%, copper content of 0.43 wt.% and silver content of 0.84 wt.% [32]. Such elemental contents correspond to a mass density of 19.20 g/cm³ (calculation based on the mass density of bulk gold, copper, silver and their contents), very close to pure gold (19.32 g/cm³). In order to simplify calculations, we assume that the Zwischgold is composed of a pure gold layer over a pure silver layer.

5.2. SEM measurements on medieval samples

5.2.1. Gold layer thickness

During the thickness measurements on the gold layer of medieval Zwischgold samples, multiple observation sites with different magnifications were selected for each sample and the measurements were repeatedly performed on each site. A total of 3499 measurements have been accomplished across 75 samples.

Gold layers in these Zwischgold leaves display diverse and complex situations. [Fig. 6](#) exhibits some examples of such gold layers, with a reference sample of medieval gold leaf ([Fig. 6i](#)): [Fig. 6a–c](#) presents a common scenario in which the gold layer is above and/or below significant amounts of silver corrosion products; [Fig. 6d–f](#) shows some less common situations, including one Zwischgold leaf

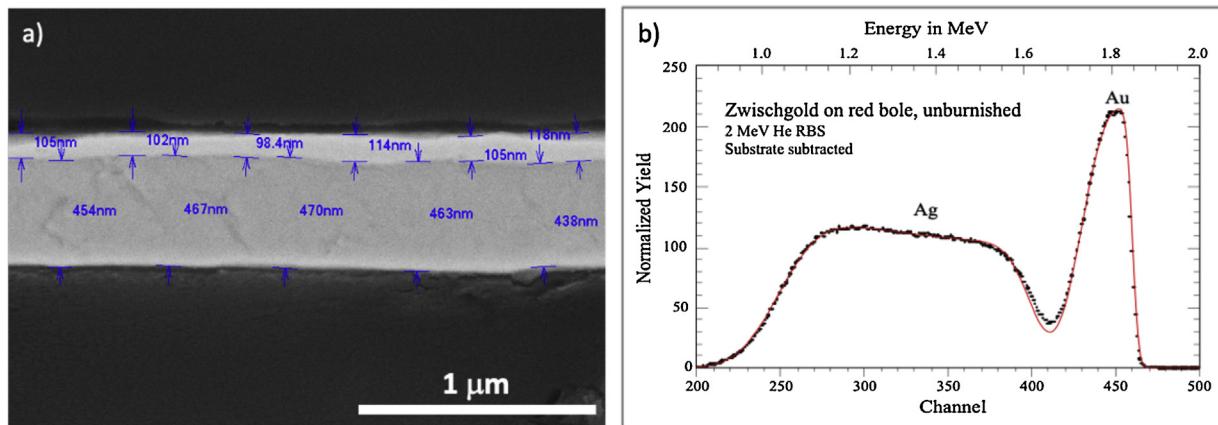


Fig. 3. Thickness measurements through (a) SEM-BSE imaging of an uncorroded Zwischgold sample and (b) through RBS on a model made from the same Zwischgold leaves.

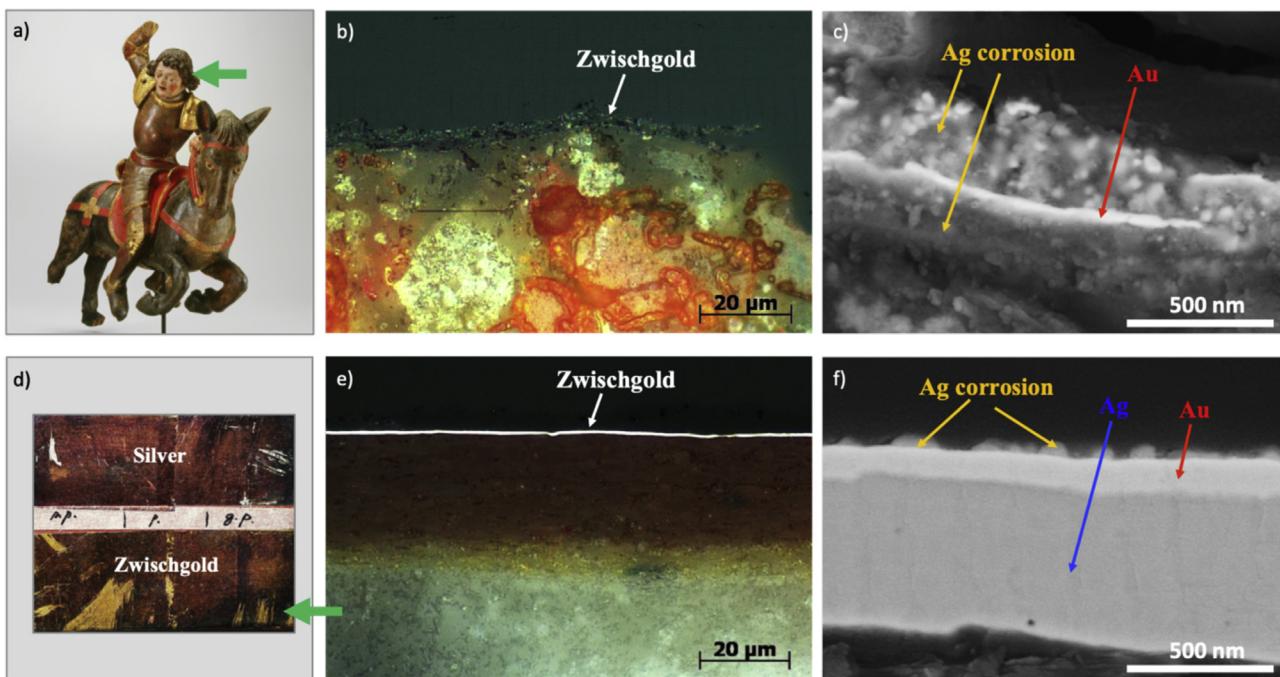


Fig. 4. VLM-BF (Mag. 50 \times) and SEM-BSE (Mag. 80k \times) images for: (a–c) a sample taken from the hair area of Sculpture St. George on the horse (SNM, LM13716), dated 1500; (d–f) a sample taken from a 3-year old silver/Zwischgold model. Sample-taking positions are indicated with green arrows.

containing two gold layers of different thicknesses (d), a discontinued gold layer in a folded leaf (e) and two gold layers having a corroded silver layer in between (f); Fig. 6g–h shows less or slightly corroded Zwischgold leaves, in which the silver base can be still observed below, atop or between gold layers.

It is surprising to observe that most of the medieval Zwischgold leaves contain ultrathin, namely “nanoscale” gold layers. Fig. 7 displays the set of gold layer thickness observations in terms of the simple average per sample (black bars) and a probability distribution (red line) that was constructed by interpreting the statistics for each sample (see Table S1 in the supplementary materials) as a normal distribution. The probability distribution of observed gold layer thicknesses peaks at 30.0 nm, matching the thinnest gold layer of modern Zwischgold published [22], and is skewed to the right (positive skew) with a half-peak range of 20.6 nm to 51.4 nm and a long tail corresponding to a few much thicker sections observed in the gold layers (up to 252 nm). Such observation indicates significant variations in the gold layer thickness in medieval Zwischgold, which very likely resulted from the use of handwork (e.g.,

hammering) during its production. No obvious correlation between the sample-taking position (i.e., Zwischgold applied areas) and gold layer thickness is observed.

It is worth noting that 10 samples that were taken from 8 objects exhibit an unusual type of Zwischgold, namely the “multi-layered Zwischgold”, which was first observed by Plahter in Ganthem Altar [37]. Such samples contain multiple gold and silver layers, as shown in Fig. 6h. A special sandwich-like structure is presented in Fig. 6f; it is mentioned (or rather prohibited) by the 1475 Montpellier guild ordinance for goldbeaters [5]. More information about multi-layered Zwischgold is included in our previous studies [14,21]. Note that the thickness measurements for such samples were performed on one gold layer; the same applied for the thickness measurements on the silver layer, if it is still available.

5.2.2. Silver/gold weight and thickness ratios

The Ag/Au weight ratio of the medieval Zwischgold samples were obtained through SEM-EDX quantification analysis of Ag and Au elements. These measurements were performed by map-

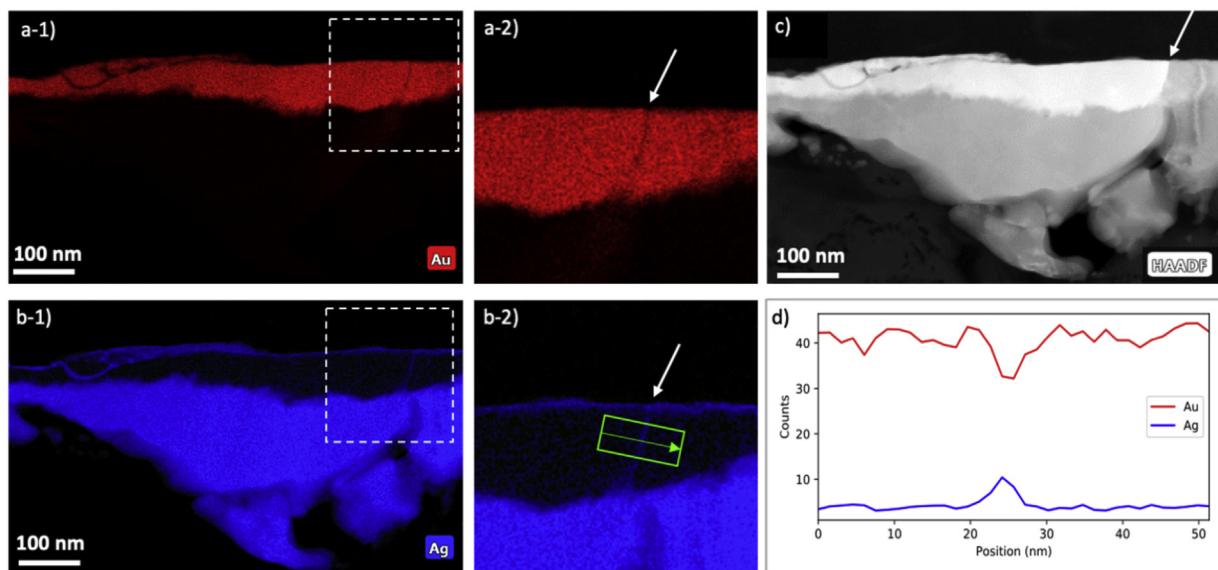


Fig. 5. STEM-EDX analysis on one site of a Zwischgold sample taken from a 600 years old artefact (SNM, LM16701.2), in which the grain boundary (pointed with a white arrow) of gold is filled with silver atoms: (a-1) & (a-2) Au elemental map; (b-1) & (b-2) Ag elemental map (all shown as intensity maps); (c) high-angle annular dark-field (HAADF) image; (d) EDX line profile across a gold layer grain boundary (along the green arrow).

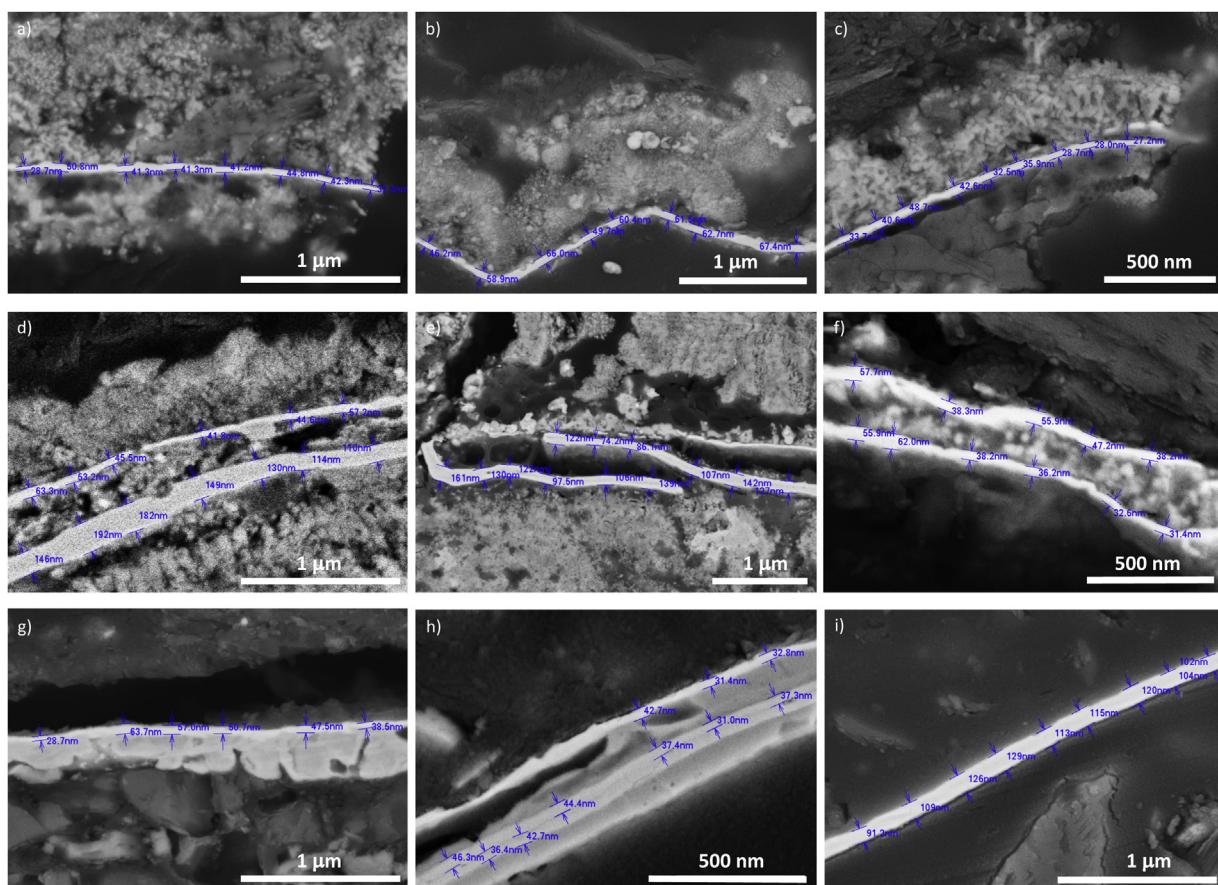


Fig. 6. Thickness measurements for the gold layers of medieval Zwischgold leaves with different structures (a–h) and for a reference sample of medieval gold leaf (i). Note that the lower gold line in (h) is actually composed of two gold layers.

ping areas wide enough to encompass all of the silver corrosion products around the Zwischgold leaf to ensure a full accounting of the materials present. Such averaging over large areas also sidesteps the spatial resolution issue, though one still has to be careful to avoid under-sampling (i.e., pixel size should not be lar-

ger than the sample-beam interaction volume). Site selection is also an important consideration, as some Zwischgold samples show strong heterogeneity and irregularity. [Fig. S1 in the Supplementary Materials](#) exhibits an ideal observation site (a) compared to some sites displaying irregular conditions (b–f). STEM-EDX analysis

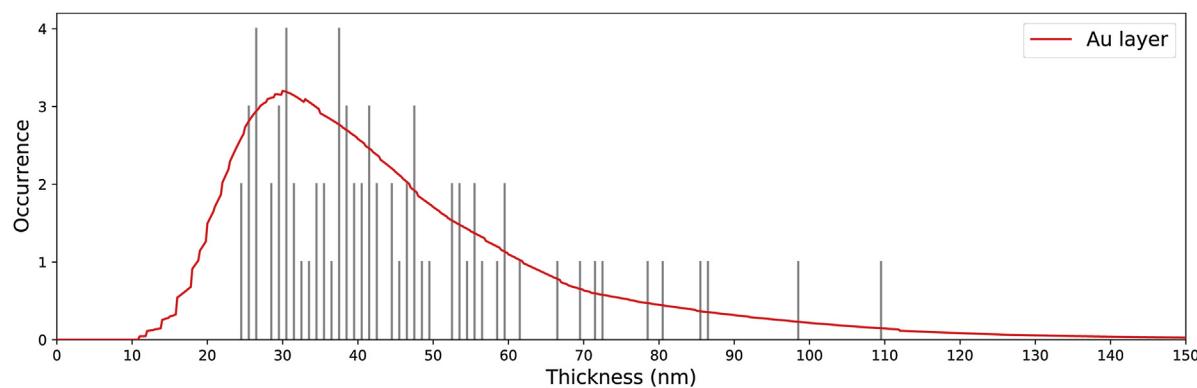


Fig. 7. Histogram of the measured Au layer thicknesses. Black bars show the simple occurrence of the average thickness of each sample (1 nm bins). The red curve uses the statistics of the observations to construct a continuous probability distribution.

in Fig. S2 in the Supplementary Materials demonstrates an unusual situation in which scraps of a broken Zwischgold leaf overlap a corroded Zwischgold leaf.

Fig. 8 shows that the Ag/Au weight ratio lies in a common range of 1:2–5:1, with the peak occurrence at 2:1. This ratio range appears much lower than historical records, e.g., 12:1 by Theophilus, but its upper threshold is closer to Halle's ratio of 4.5:1. For example, 5 of the 75 samples are observed to be in a similar range (4:1–5:1) suggested by Halle and only one sample is in the range suggested by the older Master Theophilus. Interestingly, the peak value (2:1) is close to von Keess's ratio of 2.17:1 and consistent with Herm's observations that medieval Zwischgold should have a lower Ag/Au weight ratio than that of the modern one (2.2:1–3.3:1). However, the actual Ag/Au weight ratio for medieval Zwischgold could possibly be higher than our observations, since some of the silver corrosion product could have been removed by conservation treatments such as wet cleaning in the past.

Combining the Ag/Au weight ratio and the mass density of the gold layer in the Zwischgold samples, the Ag/Au thickness ratio was calculated to be in a common range of 1:2–6:1, with the peak occurrence at 3:1 (Fig. 8).

5.2.3. Leaf thickness of medieval Zwischgold

The original, uncorroded silver layer and the overall leaf thickness of the Zwischgold samples were calculated based on the gold layer thickness and the Ag/Au thickness ratios. The distribution of calculated silver layer thicknesses shows a broader curve with a lumpier structure (local maxima occurring at 15.2, 66.6, 139.0 and 865.5 nm) than the gold layer thickness distribution, but still with positive skew and a long tail (dashed blue curve in Fig. 9). The silver layer distribution peaks at 66.6 nm with a half-peak range of 11.4 nm to 214.2 nm. The total leaf thickness distribution also shows a broad, positive skewed curve, with a peak at 125.0 nm and a half-peak range of 49.6 nm to 258.2 nm (dashed black curve in Fig. 9). The data therefore indicates that the average Zwischgold leaf is about 125 nm thick, with a 30 nm gold layer; and most Zwischgold observations should involve a total leaf thickness of 50–260 nm and a gold layer between 20 and 50 nm.

The calculated leaf thicknesses are far thinner than expected from previous literature [5,25] and less than half as thick as the modern Zwischgold leaf (500–700 nm) [20]. Luckily, 5 sample leaves still contain small sections that are only slightly corroded. The silver layer thickness and/or the leaf thickness of these sample sections were measured (Table 2) and then compared with the calculated ones. Additionally, a sample taken from a freshly made modern Zwischgold model (*T0*) and the 3 years old model (*T3y*) were also measured as reference, with a gold content of 96.07 wt.%.

obtained through RBS. Here, the mass density of pure gold is still applied in the thickness calculation of modern Zwischgold samples, in order to be consistent with the calculation of medieval samples. Fig. 10 exhibits three sites of one medieval sample (*LM16701.2.S2*) and one site of the modern sample *T0*, for the purpose of comparison.

Table 2 shows that the thicknesses calculated from the EDX measured Ag/Au ratio agree fairly well with the direct thickness measurements. Note that the precision quoted for each value is the standard deviation of the set of observations and indicates variability of the sample rather than measurement precision. The calculated thickness tends to be overestimated for the modern samples and slightly underestimated for the medieval samples. This trend in the measurement bias correlates with the smoothness of the cut surface of the samples (presented in Fig. S4 in the Supplementary Materials) and could be due to a few factors, e.g., shadowing of the X-ray signal by the sample topography due to the low elevation angle of the EDX detector of about 30°, or the less accurate EDX quantification under a low voltage [38] (see S2 in the Supplementary Materials for more information). Combined with sensitivity factors used by the EDX analysis software that appear to overestimate the presence of silver, these issues balance well for the medieval samples, while the EDX-derived thickness calculations for the much smoother modern samples remain overestimated. Since this study focuses on medieval Zwischgold samples where the EDX-derived thickness calculations already show good agreement with direct thickness measurements, we decided that no further calibration of the EDX measurements was required.

5.3. Further discussion

Zwischgold is well-known for its pale, blonde-like colour tonality compared to pure gold, which is the main reason for its frequent observations in hair and beard areas of medieval saint statues [14,39]. Although one of our previous studies has revealed that the pale tonality of modern Zwischgold is mainly attributed to the migration of silver atoms across the gold layer and depositing on the top surface [20], a well-accepted theory has been circulated for centuries that the paleness (or brightness) of the medieval Zwischgold is due to the transparency of its gold layer [16,17]. However, so far there is no strong scientific evidence supporting this theory.

According to the optical properties of gold, about 30% of the incident light ($\lambda = 492$ nm) can penetrate through a gold film of 30 nm thickness [19]. (A reproduced graph regarding the reflectivity and light transmission of thin gold films in terms of their thicknesses is presented in Fig. S5 in the Supplementary Materials.) Therefore, in the case of a medieval Zwischgold with a 30 nm thick gold layer,

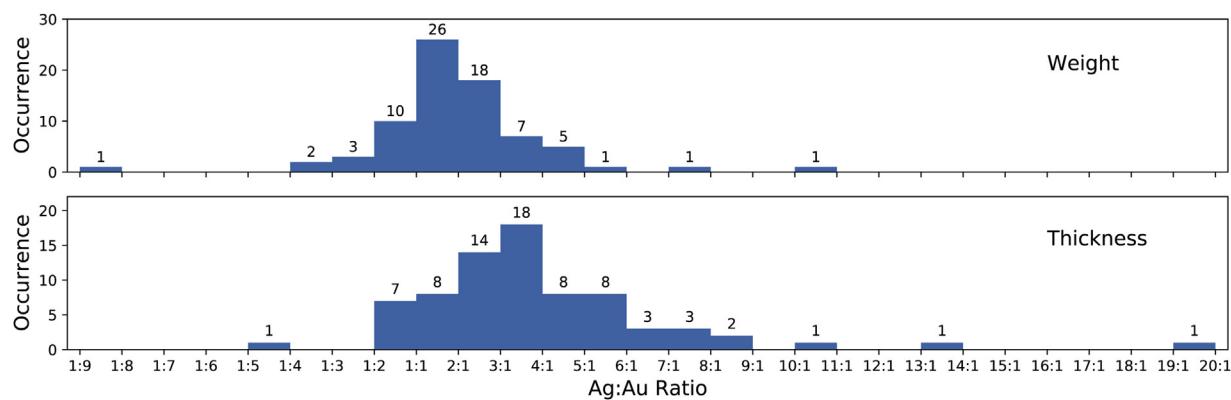


Fig. 8. Histograms of Ag/Au weight and thickness ratios of 75 medieval Zwischgold samples.

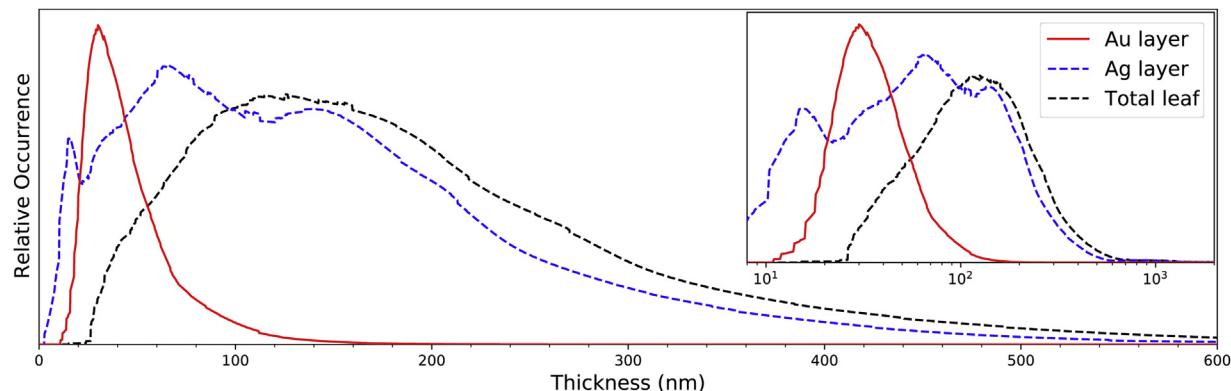


Fig. 9. Probability distributions of the measured Au layer thickness, calculated Ag layer and resulting leaf thickness of 75 medieval Zwischgold samples. The inset displays the same data on a logarithmic scale. Histograms combining curves and bar charts are presented in Fig. S3 in the Supplementary Materials.

Table 2

Comparison between directly measured and calculated layer thicknesses for 2 modern Zwischgold samples and the slightly corroded sample leaf sections of 5 medieval samples. Values in parentheses are derived from the mathematically complementary measurements.

Sample	Leaf type	Directly Measured data				Calculated data		
		Au thickness (nm)	Ag thickness (nm)	Leaf thickness (nm)	Ag/Au weight ratio	Ag/Au thickness ratio	Ag thickness (nm)	Leaf thickness (nm)
T0	Modern	93 ± 19	480 ± 52	(573 ± 71)	4.38	8.09	752 ± 154	845 ± 173
T3y	Modern	87 ± 26	498 ± 59	592 ± 85	4.85	8.96	779 ± 233	866 ± 259
LM10418_S1	Medieval	47 ± 15	(168 ± 35)	215 ± 20	1.83	3.37	158 ± 51	205 ± 66
LM10557_S1	Medieval	25 ± 5	172 ± 18	(197 ± 23)	3.66	6.74	169 ± 34	194 ± 39
LM16701_1_S2	Medieval	85 ± 40	448 ± 76	(533 ± 116)	2.50	4.60	391 ± 184	476 ± 224
LM16701_2_S2	Medieval	56 ± 26	251 ± 42	(307 ± 68)	2.28	4.20	235 ± 109	291 ± 135
LM6280_S1	Medieval	30 ± 6	(173 ± 36)	203 ± 30	2.65	4.88	146 ± 29	176 ± 35

30% of the incident light can transmit through the gold layer to reach the silver base and then only 9% of the light ($30\% \times 30\%$) can be reflected back (assuming the gold-silver interface is a perfect mirror) and escape the surface. In comparison, a 30 nm thick gold layer will reflect 30% of the incident light, more than three times the amount that would be observable after reflecting from the gold-silver interface. Since the common thickness range for the gold layer of medieval Zwischgold is ca. 20–50 nm, it is possible that a small amount of light could be reflected from silver to the surface through Zwischgold with the thinnest gold layer (20–30 nm), granting some credence to the theory that the paleness of Zwischgold is caused by the transparency of the gold layer. Furthermore, since the gold layer thickness inside of individual sample leaves varies significantly and some sections can reach a thickness of less than 20 nm, it is also possible that whitish spots could appear on the golden coloured leaves, as Halle noted 300 years ago.

6. Conclusions

This study provides the first body of knowledge from the materials aspect about important technological parameters of Zwischgold, including the gold layer thickness, silver/gold weight ratio as well as the inferred original full leaf thickness. The extremely thin gold layer is observed to be in a thickness range of 20–50 nm with a peak value of 30 nm, indicating a nanoscale level of precision in the manufacture of fine gilding materials for artworks in the late Middle Ages.

Although significant variations are observed in the obtained silver/gold weight ratio and thus the inferred leaf thickness of the medieval Zwischgold samples, which contain a common range of about 1:2–5:1 and 50–260 nm respectively, they are still of important reference values for understanding the materials used in the production of medieval Zwischgold. We believe that the artisans of that time already had a high degree of control over the mate-

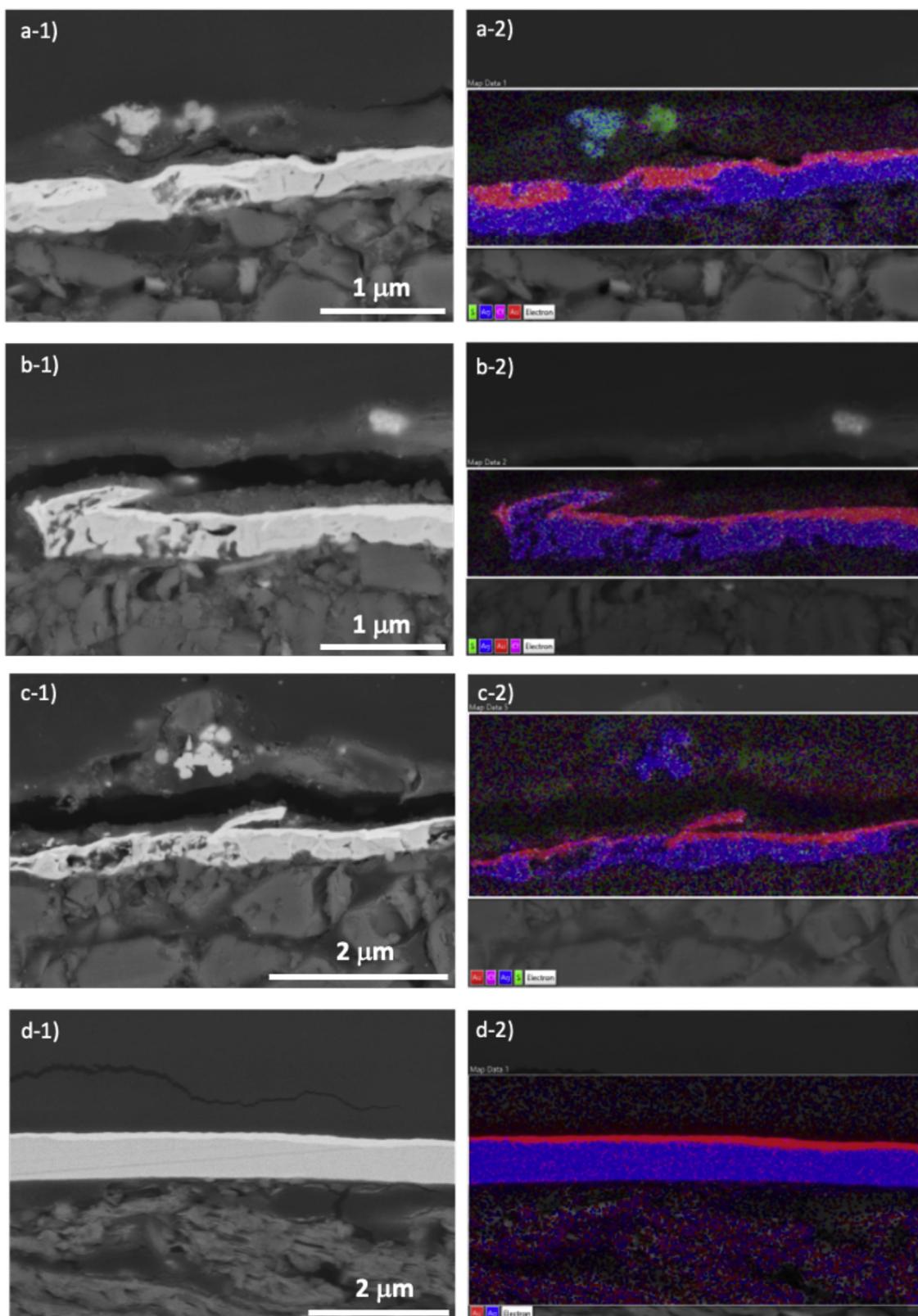


Fig. 10. SEM-BSE images and EDX-overlay images for selected sites of the medieval sample LM16701.2_S2 (a–c) and the uncorroded modern sample T0 (d). Colour labels: red for Au, blue for silver, magenta for Cl, green for S.

rials expense and a good balance between the product quality and labour cost. The fact that the peak occurrence of the leaf thickness of medieval Zwischgold samples (125 nm) is almost the same as that of the usual gold leaf of the same time and regions (138 nm [32]) fur-

ther explains why the market price of Zwischgold was much lower compared to the normal gold leaf, on top of the savings gained through maximising the proportion of silver, which was relatively inexpensive at the time. On the other hand, the production of such

thin Zwischgold leaves would have required higher-skilled workers and it is well-known that craftsmanship had gained great significance in the late medieval period, compared to the materials costs [40].

The output of this study also provides supporting scientific evidence for the long-lasting theory regarding the colour appearance of medieval Zwischgold. The special pale tonality of Zwischgold could be partly attributed to a small amount of light reflected from silver to the surface, although it only occurred when the thinnest gold layer was present. Future work could examine the interaction of visible light with nanoscale gold/silver leaves to determine the validity of the gold transparency theory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.culher.2021.01.010>.

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