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Technological study of the gilded *haft-rang* tiles of the Imamzadih Ismail mausoleum in Qazvin, Iran

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Abstract

Background: Gilding decorations on Islamic tiles have been previously studied either historically or technologically. The major emphasis in these studies has always been focused on the use of gold leaf on glazed tiles. The current research has been conducted by electron probe micro-analysis (EPMA), portable micro X-ray fluorescence (μ-XRF), scanning electron microscopy (SEM), optical microscopy and atomic force microscopy (AFM) to shed light on a less-known technique of gilding applied on the nineteenth century *haft rang* glazed tiles of the Imamzadih Ismail mausoleum in Qazvin, Iran.

Results: Our observations showed that the gilding decorations are performed on a blue alkali glaze. Plant ash was suggested to be the source of alkali and cobalt was identified as the colouring agent of the glaze. Moreover, trace amounts of arsenic in the composition of the blue glaze was interpreted to be associated with the colouring agent of the glaze; *i.e.*, cobalt. Furthermore, the gilding decorations were suggested to be achieved by firing gold powder on the pre-fired blue substrate glaze. AFM, SEM and optical microscopy proved that the gold flakes partially penetrated the pre-fired blue substrate glaze.

Conclusions: This paper established a local provenance for the colouring agent of the blue glaze used as a substrate of gilding decorations. In addition, our studies showed that the gilding decorations were achieved by firing gold powder on the pre-fired blue glaze of a nineteenth century Persian *haft rang* tile.

Background

The use of gold leaf on silica-based substrates may be dated back to the Roman period [1]. In the Islamic era, however, gilding on glassy substrates appears first on tableware in 12th century Persia [2] and shortly after on glassware under the Ayyubids and the Mamluks in Syria and Egypt during the 13th and 14th centuries [3].

Although the use of gold powder for gilding vitreous materials has been reported previously [3,4], technical literature about Islamic gilded tiles does not support this idea. In other words, the published data about gilding on the Islamic glazes are only limited to the use of gold leaf on glazes [2,5,6]. In addition, there is no general consensus about the technique of applying either gold leaf or powder on archaeological glazes. While the

use of an organic adhesive as mordant of gold leaf has already been reported [5,6], a firing process has also been suggested to be the reason of adhering gold leaf on a pre-fired glaze [2]. In support of the former idea, there is the Abu'l Qasim's treatise in which he describes how to fire gold leafs on a pre-fired glassy surface [7,8].

Here, in this paper, various analytical approaches are used to address technological features of a less-known technique of gilding applied on a glassy substrate found in the Imamzadih Ismail mausoleum of Qazvin, Iran, erected in the 19th century. To do so, tiny samples were removed from a gilded *haft rang* tile in the south-eastern portico of the mausoleum (for more details see the *Samples* sub-section in the *Methods* section) (Figure 1) and were studied by electron probe micro-analysis (EPMA), portable micro X-ray fluorescence (μ-XRF), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

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Chemistry Central

Figure 1 Detail of gilding decorations in a gilded *haft rang* tile at the Imamzadih Ismail mausoleum (the gilded line is pointed with a red arrow).

Results and discussion

Chemical composition of the substrate glaze

Under a closer look, it could be observed that the gold layer was placed on a blue glaze (Figure 1a), which was applied on a white glaze (Figure 2b). This stratigraphy demonstrates the usual structure of *haft rang* tiles [9]. The chemical composition of the white glaze (Table 1) showed that it was basically a lead-alkali tin-opacified glaze with a Pb/Sn ratio of 7.3, which is significantly higher than the Pb/Sn ratio reported for 17th century Persian *haft rang* tiles [9] and medieval Islamic glazes [10]. This value is also higher than the Pb/Sn ratio documented in medieval Persian treatises of glaze-making [7,11].

As far as the chemical composition of the blue glaze is concerned, it was an alkali glaze in which cobalt had yielded a dark blue colour (Table 1). On the other hand, 4.29 wt% and 0.37 wt% of potassium and magnesium respectively showed that the source of alkali in the blue glaze was most probably plant ash. Plant ash has been

reported to be the most common fluxing agent used in Persian archaeological vitreous materials [12,13]. More interestingly, the chemical composition of the blue glaze was interestingly associated with arsenic (Table 1). As it is generally well-known, the cobalt ores of Qamsar, near Kashsn in central Iran, have always been noted to be the source of supplying cobalt for achieving deep blue colours in glassy materials. These ores have been reported to be cobaltite ($CoAsS$) and erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$), which are As-bearing cobalt ores [7,14]. Thus, the detected arsenic in the composition of the blue glaze can be derived from these sources showing a Persian provenance for the blue colouring agent of the glaze. On the other hand, the absence of bismuth in the composition of the blue glaze can be considered as another evidence of the local provenance as bismuth is reported to be associated with the blue Co-bearing pigments found in Europe and India [15].

Another interesting point in the quantitative EPMA data is that the actual total of the quantified elements of the blue glaze does not sum up to 100 wt% and is significantly low (86.26 wt%) (Table 1). This could be related to the manufacturing process of the blue glaze. According to the descriptions provided by Rochechouart [16], Ali Mohamed [11], Olmer [17] and Schindler [18], 19th century Persian glaze-makers used to make a concentrated Co-bearing pigment from the cobalt ores of Qamsar by mixing and smelting the cobalt ores and borax. A tiny amount of this concentrated pigment was then added to an alkali frit to achieve a deep blue colour. Moreover, the analytical data provided on the raw materials used by Ali Mohamed (preserved at the Edinburg Museum of Science) confirm the presence of borax in the composition of Persian blue glazes in the 19th century [18]. However, as boron cannot be measured with EPMA due to its low atomic weight, this can provide an explanation for the loss of total amount of composing elements of the blue glaze. However, this hypothesis needs to be proved with more relevant analytical approaches. Due to the fact that the blue glaze was diffused in the white
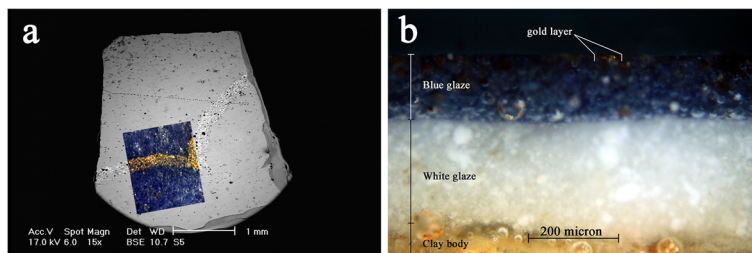

Figure 2 a) SEM back-scattered micrograph of the sample merged with the optical microscope image together with **b)** the cross section of the gilded area.

Table 1 The quantitative EPMA results on the blue and white glazes

Elements	Al	Si	K	Mg	Co	Na	Ca	Fe	Cu	Pb	As	Sn	Actual total (wt%)
Blue	2.81	63.99	4.29	0.37	0.51	9.43	1.84	1.95	0.04	0.95	0.06	0.02	86.26
White	1.57	48.86	3.05	1.79	nd[*]	7.91	4.03	0.58	0.07	20.86	nd	2.84	91.56

*nd: not detected.

glaze and its thickness was very small (Figure 2b), it was not practically possible to remove any sample from the blue glaze without contaminating the sample with the white substrate glaze. Thus, the most appropriate technique, which could quantitatively measure boron from one hand and, on the other hand, did not require removing the blue glaze, was laser ablation-induced coupled plasma mass spectrometry (LA-ICP-MS), which we did not have access to.

Gilding
Optical microscopy and back-scattered electron micrographs revealed that the gilded layer was achieved by applying gold flakes on the blue glaze (Figure 3). As it is evident in Figure 3b, multiple bubbles were evolved where the gold flakes were placed on showing a reaction happened when gold flakes were fired on the blue glaze. Moreover, AFM observations proved that the gold flakes were immersed in the blue substrate glaze (Figure 4). The roughness of the blue glaze was markedly changed where the gold flakes were used (with Z range, R_a and RMS values of 281.8, 75.4 and 95.7 nm respectively) confirming that the gold flakes were fired on the blue glaze.

The μ-XRF analysis showed that the golden layer was mainly composed of gold with which copper and silver were associated (Figure 5). Potassium, calcium, titanium, manganese, lead, cobalt and arsenic appeared in the μ-XRF analysis of the golden layer are most certainly derived from the blue substrate glaze. One should note that the copper content appeared in the composition of the golden layer can also be associated with the blue glaze (see Table 1). Based on the μ-XRF analysis, it could be hypothesised that the gold powder could not have been in a pure state and

that is why the gold was used as powder instead of gold leaf. In other words, the lower malleability of the alloyed gold mainly resulted from silver and copper [19] was the reason of its use as gold flakes.

Conclusion
Although previous studies on the Persian gilded vitreous materials had showed the use of gold leaf pasted on the glassy surface by an adhesive, the current study revealed, for the first time, the application of gold flakes on a 19th century Persian *haft rang* tile adhered by firing gold flakes on a blue glaze. Moreover, the blue substrate glaze was revealed to be an alkali glaze coloured by cobalt. Further, the colouring agent of the blue glaze was probably supplied from the Qamsar cobalt ores. These cobalt ores, which were either cobaltite or erythrite, are probably fused with borax to be used in the composition of the blue glaze. Moreover, the white glaze showed to be a lead-alkali glaze opacified with tin oxide with a relatively high ratio of Pb/Sn which is unusual in the context of Persian glaze technology.

Methods
Samples
AFM and μ-XRF were performed on a small sample which was delicately removed with scalpel from a well-preserved *haft rang* tile placed in the south-eastern portico of the mausoleum. SEM observations were performed on the gold coated sample in order to prevent charging effect. For observing the cross section of the sample under PLM, another tiny sample was mounted in a 1:1 mixture of Araldite AW 8545–1:Hardener HW 8545–1 and was cut and polished to
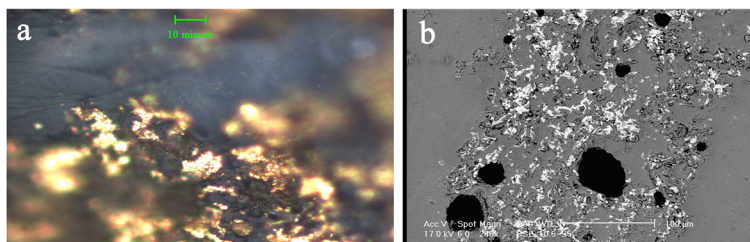

Figure 3 a) Optical microscope and **b)** back-scattered SEM image of the gildings.
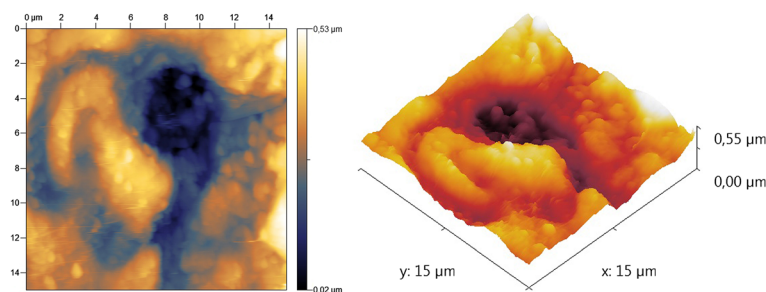
Figure 4 AFM images obtained from 15 × 15 μm surface area of the gildings.

be observed under the PLM. The same sample was then coated with carbon to be analysed by EPMA.

Optical microscopy

The optical microscopy was performed with an Alltion BK-POLT (China) polarised light microscope (PLM). A Canon EOS Kiss x4 digital camera was used to capture the photos under the plane light.

μ-XRF analysis

The portable XRF was an ARTAX™ 200 (Bruker AXS Microanalysis, Germany). Its X-ray tube was Mo placed at 6° involving a 100 μm beryllium window and a maximum voltage and current of 50 kV and 1000 μA respectively. The X-ray beam on the surface of the sample had 1 mm diameter and measurements were carried out in air for about 120 s.

SEM

Scanning electron microscopy images were obtained with a Philips XL30 electron microscope in secondary

and backscattered modes under about 10 mm of working distance and 17 kV as an accelerating voltage.

EPMA

Electron microprobe analysis was performed with a JXA-8230 field emission electron probe microanalyser in the wavelength-dispersive mode (WDS). The acceleration voltage, beam current and beam diameter were 15 kV, 5 nA and 10 μm respectively. On-peak counting times were 10 s and counting times on the background on both sides of the peak were 5 s. As standard for Si, Na and Al, we used well-characterised natural albite, galena for Pb, olivine for Fe and Mg, wollastonite for Ca and sanidine for K, plus pure metals of Co, Sn and Cu.

AFM

The topography of the gilded zone was studied by a Bruker-Nanos atomic force microscope (Germany). AFM images were obtained by measurement of the interaction forces between the tip and the sample surface. The experiments were performed in air at room temperature and AFM images were processed with Image Plus 2.9 software.
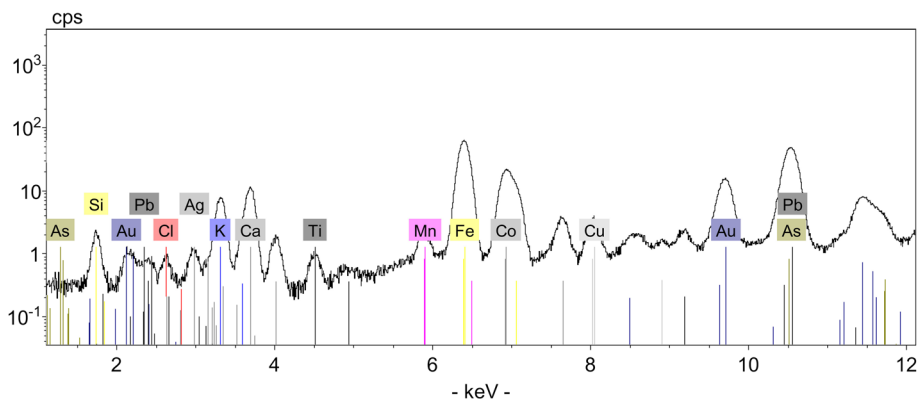

Figure 5 μ-XRF spectrum of the gilded zone.

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