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Multi-technique analysis of pigments on sandstone sculptures: Renaissance re-painting of a Roman relief

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Abstract

The Antonine Wall was commissioned by the Roman Emperor Antoninus Pius around 142 CE and stretches for c. 60 km across the central belt of Scotland, marking the Empire's most north-western frontier. This vanguard research reports on the materials referred to by Antiquarian sources as having been applied during the sixteenth century for the redecoration of an iconic Distance Sculpture that was once embedded into the mural barrier. Portable non-invasive technologies, including pXRF and in-situ microphotography were deployed. These techniques were further supplemented by micro-sampling for SEM/EDS, FTIR–ATR and microscopy of embedded cross-sections. The validity of applying these complementary techniques has been confirmed. They provide a comprehensive account of the polychromy present, including pigments that could have been applied during the Roman period and others that were only available from the fifteenth or sixteenth Centuries. The work has confirmed stratigraphic sequencing of the pigments which will, in due course, permit the digital reconstruction of how this Classical relief sculpture would have been adorned during the Renaissance.

Keywords: Roman sculpture, Sandstone sculpture, Polychromy, Microscopy, Microphotography, pXRF, FTIR–ATR, SEM/EDS, Renaissance, Antiquarian

Introducing an Antonine wall Roman distance sculpture (Hunterian Museum number: GLAHM.F1)

The Antonine Wall was commissioned by the Roman Emperor Antoninus Pius around 142 CE and stretches for c. 60 km across the central belt of Scotland. Constructed of turf, the Wall marked the Roman Empire's most north-western frontier [1–3]. A total of 21 sandstone relief sculptures have been recovered from south of the mural barrier [4]. These are inscribed with abbreviated Latin text recording measured sections of the frontier constructed by three Legions assigned to the task (*Legio II Augusta, Legio VI Victrix and Legio XX Valeria Victrix*).

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These Distance Sculptures are unique inscribed reliefs [5, 6] that were originally adorned in vibrant polychromy to reinforce decorative details and iconographic scenes [7]. One is thought to originate from east of Auchendavy fort [8] or the central sector of the Wall between Auchendavy and Twechar [9], hence its common nomenclature as the 'Auchendavy' sculpture (Fig. 1), but its provenance is unrecorded. This sculpture has a rich and diverse history [10], having been installed at various times into prominent positions at Dunnottar Castle, Aberdeenshire, by the Earls Marischal in the sixteenth Century. It remained visible there in 1642 [11–16] prior to being moved to the Marishal Museum in Aberdeen and its eventual donation by George Keith, the Tenth Earl Marischal [from 1712–78], to the Hunterian Museum in 1761 [9] where it was assigned museum number GLAHM.F1 [Roman Inscriptions of Britain [RIB] No. 2173] [17].

Fig. 1 Antonine Wall Distance Sculpture (Hunterian Museum No. GLAHM.F1)

Carved from buff sandstone that was probably quarried from the vicinity of the Wall, the sculpture comprises a central inscription panel framed with triple ribbed border, swirling ivy tendrils above and below and flanked on either side by elongated *peltae* depicting plumage of open-beaked griffins mounted with central rosettes. Two crampholes dovetailed at the top confirm it was originally embedded into a frame [18], probably also constructed of stone.

The inscription reads:

IMP CAESARI T AELIO HADRIANO ANTONINO AVG PIO P P VEXILLATIO LEG XX VAL VIC F PER MIL P III

(for the Emperor Caesar Titus Aelius Hadrianus Antoninus Augustus Pius, Father of his Country, a detachment of the Twentieth Valerian and Victorious Legion built this over a distance of 3000 units of measure).

A well-known Antiquarian [11] and Ambassador to Denmark for Queen Anne [16], George, the Fifth Earl Marischal (from 1581–1623) travelled extensively during a Renaissance period that prompted the rediscovery of Classical philosophy, literature and art [19]. This doubtless exposed him to Classical architecture and art so he would have been acutely aware of this inscription's cultural significance and motivated to erect it in a prestigious position at his ancestral stronghold on a majestic promontory off the north-east coast of Scotland.

Macdonald hypothesised the Distance Sculptures were likely to have originally been "brightly, if crudely, coloured… [though] no vestige of anything of the sort is visible on them now" [5]. Although he briefly refers to the gilding on inscribed letters not originating from this particular sculpture's creation in the second century, he does not draw out the vibrant polychromy that once adorned this relief and does not refer to it in his second edition [8]. This is despite Camden's [11] explicit mention of the sculpture being gilded under the direction of the Fifth Earl and Horsley [14] reporting the presence 'now' of black paint, suggesting a potential later episode of repainting some features by the early eighteenth century. Anderson [15] makes clear this painting was not the work of university staff upon its gifting to the University of Glasgow, while Gibb [20] confirms the paint was "very properly washed off" before traces were once more revealed during cleaning in 1976 [9].

These tantalising traces of polychromy permit a detailed exploration of at least one episode in the sculpture's itinerary. To identify, for the first time, the pigments used in past conservation treatments as well as their sequence and chronology of application we have undertaken multi-technique analyses, including *in-situ* non-invasive technologies supplemented by micro-sampling.

Methods

Non-invasive technologies, including portable X-ray Fluorescence (pXRF) and in situ microphotography were deployed for detailed surface examination and to analyse elemental and mineral compositions of surface pigments on each sculpted feature to determine whether historical accounts referencing their sixteenth Century application are verifiable. These techniques are supplemented by micro-sampling to provide invaluable information on chemical composition of the pigments and binders using Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS) and Fourier Transform Infrared spectroscopy with Attenuated Total Reflectance (FTIR–ATR) as well as, critically, microscopy of cross-sections to identify stratigraphic layers and determine whether later layers overlie and preserve original pigments applied in the Second Century by Roman artisans.

Portable X-Ray Flourescence (pXRF)

The pXRF instrument used was a Niton XL3t 900 SHE GOLDD Alloy Analyser, with a 50 kV Ag X-ray tube, 80 MHz real time digital signal processing and two processors for computation and data storage respectively; analyses were undertaken in the 'mining' calibration with resolution of *c*.165 eV at 35 keV which has been found most suitable for analysis of pigments. Analysis time was 80 s (with 30 and 30 s on the filters for light and low energy spectral lines respectively and 20 s on the filter for high energy spectral lines) and the area of analysis was 3 mm^2. Several of the thirty-six elements that the instrument can in principle detect in this mode were present below the limit of detection (LoD), and light elements with fluorescent peaks at low energies were poorly resolved at low concentrations.

A total of twenty-seven analysis spots were captured and composition tables comprising the full datasets are contained in Additional files 1 and 2: Appendix SI grouped according to sculpted features and the elements related to each feature are discussed in-text. Elemental concentrations are expressed in parts per million (ppm). Some elements, including Al, K, Ti, Cr, Zn, Rb, Sr and Zr have been excluded from the broader discussion on analysis as naturally occurring in the sandstone as confirmed with six background spots located on the sides and rear of the sculpture where pigments were not expected to have been applied, though it is possible that some of these may be present as trace elements of pigments. Some surface patination was visible in areas resulting from post-depositional processes, including episodic cleaning, weathering or atmospheric pollution. The remaining 18 elements provided a level of quantification at various spots in concentrations sufficiently above background levels to confidently infer the presence of pigments.

Microsamples

Microsamples were collected from 12 areas by scraping with a scalpel and sealing them in labelled glass vials (Additional file 3: Appendix SII). They were studied under a Leica M80 microscope with incident LED light and images were captured using integrated digital camera as well as a Leica Wild M420 fitted with LM digital SLR adapter connected to a Canon EOS. These were supplemented by *in-situ* images captured on a Dinolite Edge Digital Microscope for comparison. Some samples were then embedded in Technovit® 2000 LC, a fast light-curing methacrylate based resin, and hardened by UV light in the Technotray CU light curing device (Heraeus Kulzer GmbH, Wehrheim, Germany) then ground with a Beuhler Metaserve grinder before hand-polishing with Micro-Mesh polishing cloths.

Fourier Transform Infrared spectroscopy with Attenuated Total Reflectance (FTIR–ATR)

FTIR–ATR was carried out on microsamples, these were separate to the samples used for SEM/EDS and were not embedded in resin. The FTIR–ATR used was a Perkin Elmer Spectrum One FTIR–ATR Spectrometer with Spectrum software version 5.0.1 and fitted with a Universal ATR Sampling Accessory. The ATR crystal used was a diamond/thallium-bromoiodide (C/KRS-5) with a penetration depth up to 2 μm (FTIR–ATR is primarily a surface technique). 16 accumulations were used at a resolution of 8 cm^{-1}. Unless otherwise stated samples were placed on the ATR with the surface level facing downwards.

Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS)

A small number of embedded samples were selected for exploratory SEM/EDS analysis and a more comprehensive programme of work will commence soon to build on these preliminary results. Most of the samples were coated in gold for maximum conductivity, two containing visible gold gilding were carbon-coated. The samples were then secured with copper tape to fix samples in place and assist electron conduction. Sample characterisation was performed at ISAAC, University of Glasgow, and backscatter electron images obtained with Carl Zeiss EVO scanning electron microscope (SEM) at high vacuum conditions with an accelerating voltage of 15 kV. Mineral identification was performed with Oxford Instruments Aztec integrated EBSD/EDS system.

Mapping the monument's pigments

Initial pXRF analysis of this monumental inscription in 2013 [4] hinted at Sixteenth Century application of the visible pigments given their elemental composition, particularly the gilded frame and very high lead content on almost all painted features consistent with that period [21] as opposed to haematite or goethite [22] browns that were more common in the Roman artists' palette. That said, lead-based pigments were also commonly used by Roman artists so, given the intriguing trajectory of this sculpture and the absence of any similar studies of polychromy on sandstone statuary, it served as a unique platform to test the applicability of a comprehensive suite of non-destructive analytical techniques further supported by targeted invasive analyses for comparison and to establish a chronological framework for the pigment application.

All the painted areas displayed a cracked, resinous, waxy and degraded surface with visible pigments surviving only in some areas, largely due to episodic cleaning over the centuries. Systematic survey of the sculptural features provided the undernoted results.

Ivy tendril framing the top and bottom of the inscribed panel

The carved ivy tendrils framing the top and bottom of the inscription panel retain visible light brown pigment (Fig. 2A) overlying a clearly visible light pink layer (Fig. 2B). Microphotography and samples under microscope and in cross-section (Fig. 2B, C) confirm this pattern, with a clear definition between a base of heterogeneous pinkish pigment interspersed with numerous white inclusions of various size and occasional red inclusions. This is overlaid with an orangey-red

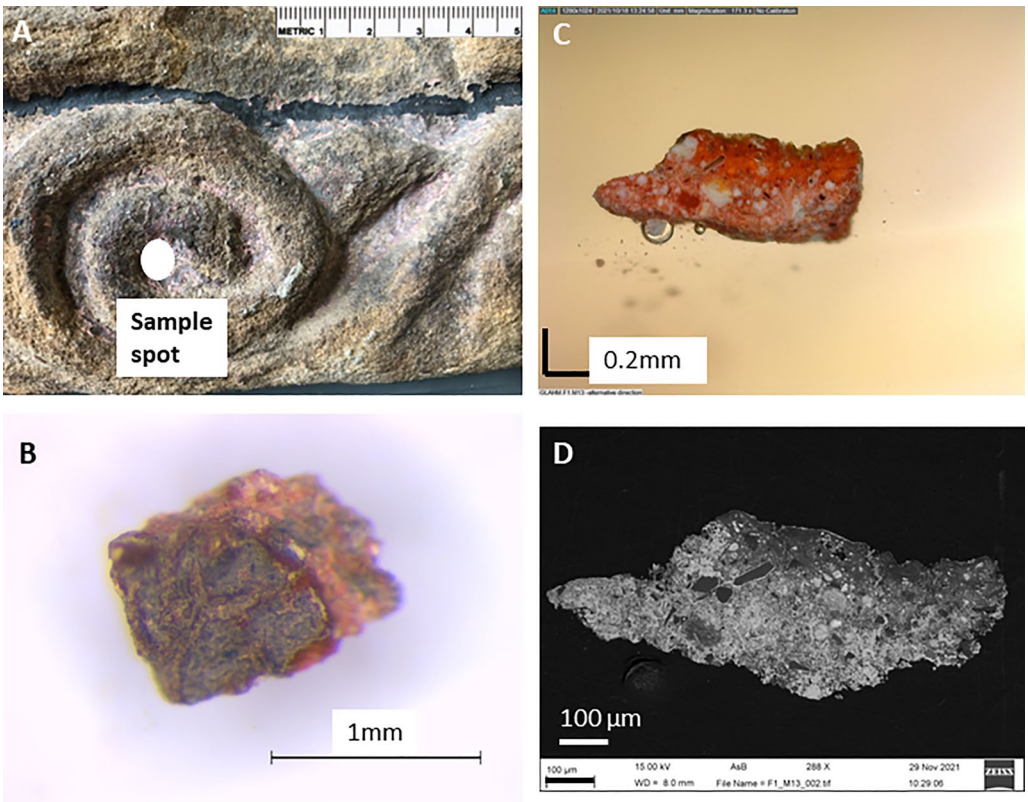

Fig. 2 Ivy tendril. **A** Detailed image; **B** Microsample; **C** LM image showing pinkish pigment in cross section; **D** SEM image (scale on images); **E** FTIR–ATR spectrum of organic resin; **F** FTIR–ATR spectra of quartz and lead sulphate

with occasional white inclusions, followed by a slightly darker red then brown top layer.

Deep, narrow, sculpted grooves made this feature challenging to target for pXRF and in situ microphotography, but elements detected on one analysis spot confirmed peaks of Fe and Cl at higher than background levels as well as traces of As and Pb. The high Cl may be explained by reported cleaning episodes or, perhaps, related to the use of a size [23] since EDS mapping detects this in the base layers of other features, discussed below. The Fe could indicate red ochre mixed with a lead-based pigment, white lead or lead sulphate, as confirmed with the white inclusions overlain with layers of red lead and possibly realgar, though lead and arsenic are linearly correlated with no evident addition of an As-rich material. Further analysis, including EDS mapping and others, will be carried out in a future programme of work to provide molecular information to clarify this. There is some debate surrounding the mixing of arsenic sulfide and lead-based pigments as the former can be unstable in alkaline conditions causing an adverse reaction with the copper and lead in lead-oxides [24]. But the presence of these mixtures applied with no evidence of negative impact on medieval wall paintings across Europe [25, 26], makes it perfectly plausible for arsenic and lead-based pigments to have been used together here, but in layers rather than mixing on the palette as confirmed in cross-section.

The SEM image (Fig. 2D) confirms this stratigraphy more clearly and FTIR–ATR spectrum indicates the presence of an organic material (Fig. 2E). From the shape and position of the bands it is most likely to be a resin. The bands at 2926 and 2853 cm^{-1} are associated with the aliphatic hydrocarbon chains but are less sharp than those longer chains found in oils and waxes. The carbonyl absorbance at around 1700 cm^{-1} further confirms this as this is associated with the carbonyl acid. The spectrum is shown beside a shellac standard spectrum to highlight the likelihood of the presence of a resin. It is not possible to determine if the resin is shellac or a tree resin from its spectra. To determine this gas chromatography mass spectrometry would be required.

From this spectrum (Fig. 2F) the presence of inorganic materials can also be deduced. The spectrum shows the

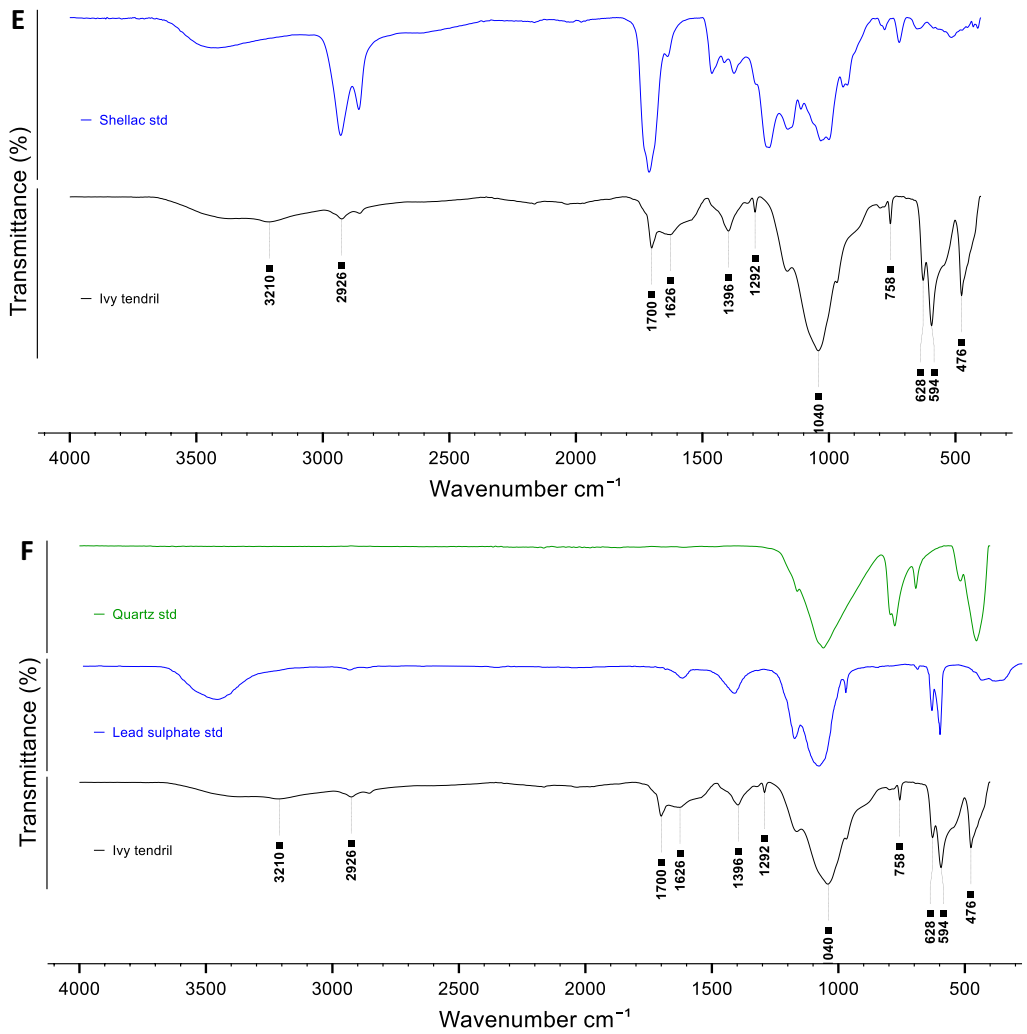

Fig. 2 continued

likelihood of the presence of lead sulphate and quartz due to the strong wide absorbance at 1040 cm^{-1}. The presence of a shoulder around 1060–1070 cm^{-1} and sharp shoulders either side of it at 1173 and 971 cm^{-1}; bands at around 1400 and 1626 cm^{-1} and the sharp bands at 698 and 594 $cm^{-1}$are indicative of lead sulphate.

The presence of lead sulphate as a ground layer is reported as rare and is usually thought to be due to degradation of other pigments and a comprehensive review has found it to be present in a number of works crossing the prehistoric to Medieval periods [27]. It was identified in a study of the Room of the Beds in the Royal Bath of Comares of the Alhambra monument in the Iberian peninsula redecorated during the Renaissance period and the intentional presence of lead sulphate cannot be fully disregarded [28]. From the analysis reported here, it is not possible to state that its presence was intentional or unintentional, nor whether it derives from a degraded lead white in a sulphate-rich gypsum substrate [27] originating from an original Roman layer. The absence of evidence for green or blue pigments on a feature depicting foliage is intriguing.

Griffin peltae

The zoomorphic shapes of griffins flanking the central inscription panel retain visible dark greyish/black pigment, predominantly in the grooves where past cleaning episodes failed to reach. Microsamples were taken from a groove in the plumage and eye pupil for analysis.

Griffin plumage

Some slight cracking is visible on the surface of the plumage sample (Fig. 3A, B and D), but less so than other

pigmented areas and in cross-section (Fig. 3C) it appears very resinous with sporadic black and white inclusions overlying a distinct orange-red layer. The pXRF results reveal a low peak of Pb with traces of As which might be suggestive of a realgar or realgar mix base layer along with a resinous pigment mixed with some black and red lead could explain the thin red base layer, while the Cl peak could derive from soap during episodic cleaning. This could be clarified through SEM/EDS mapping. Trace levels of P were picked up by pXRF; however, phosphate was not detected with FTIR–ATR. This discounts the presence of Ivory or Bone black in the surface layer which provided a deep warmer black than other carbon-based black pigments [29, 30]. Taken together with the C evident on black inclusions in this layer of the griffin eye (below), then, this is most likely a carbon-based black.

The FTIR–ATR of this sample shows the presence of lead sulphate and a resinous material which explains the visibly resinous appearance of this sample, and a hint of proteinaceous material, probably a binder. As with the ivy tendril, above, the presence of an organic material has been detected. Given the position and shape of the prominent absorbance bands 2920, 2852 and 1710 cm^{-1} this is likely to be a resin (Fig. 3E).

Again, the spectrum (Fig. 3F) shows the likelihood of the presence of lead sulphate and quartz due to the strong wide absorbance at 1040 cm^{-1}. The presence of a shoulder around 1060–1070 cm^{-1} and also sharp shoulders either side of it at 1173 and 971 cm^{-1}; bands at around 1400 and 1626 cm^{-1} and the sharp bands at 698 and 594 $cm^{-1}$are indicative of lead sulphate.

Griffin eye

Close inspection of the griffin eye (Fig. 4A) reveals white painted directly over the resinous layer with black inclusions that covers the griffin plumage. This defines eye whites (sclera) that were then topped with a surface layer

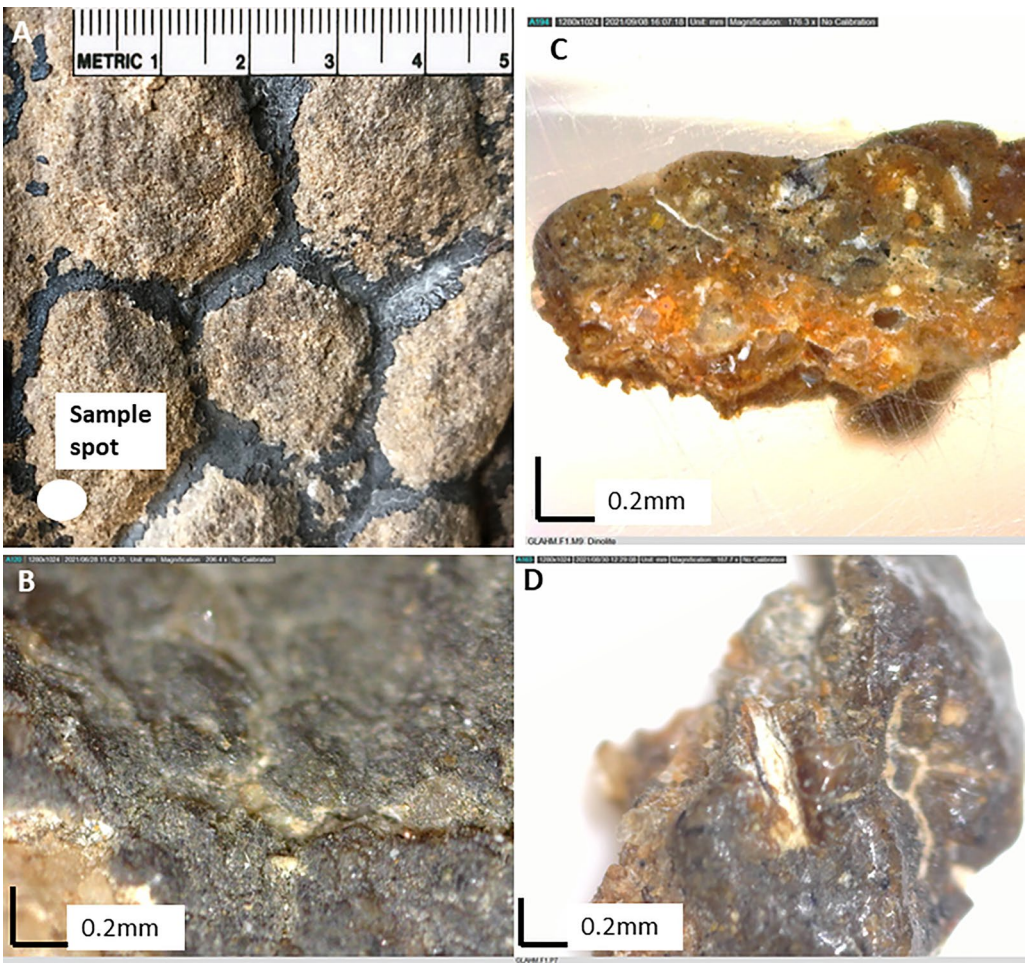

Fig. 3 Griffin peltae plumage. **A** Detailed image; **B** In situ microphotograph; **C** LM image showing pigment and resinous layers in cross section; **D** Microsample (scale on images); **E** FTIR–ATR spectrum of organic resin; **F** FTIR–ATR spectra of quartz and lead sulphate

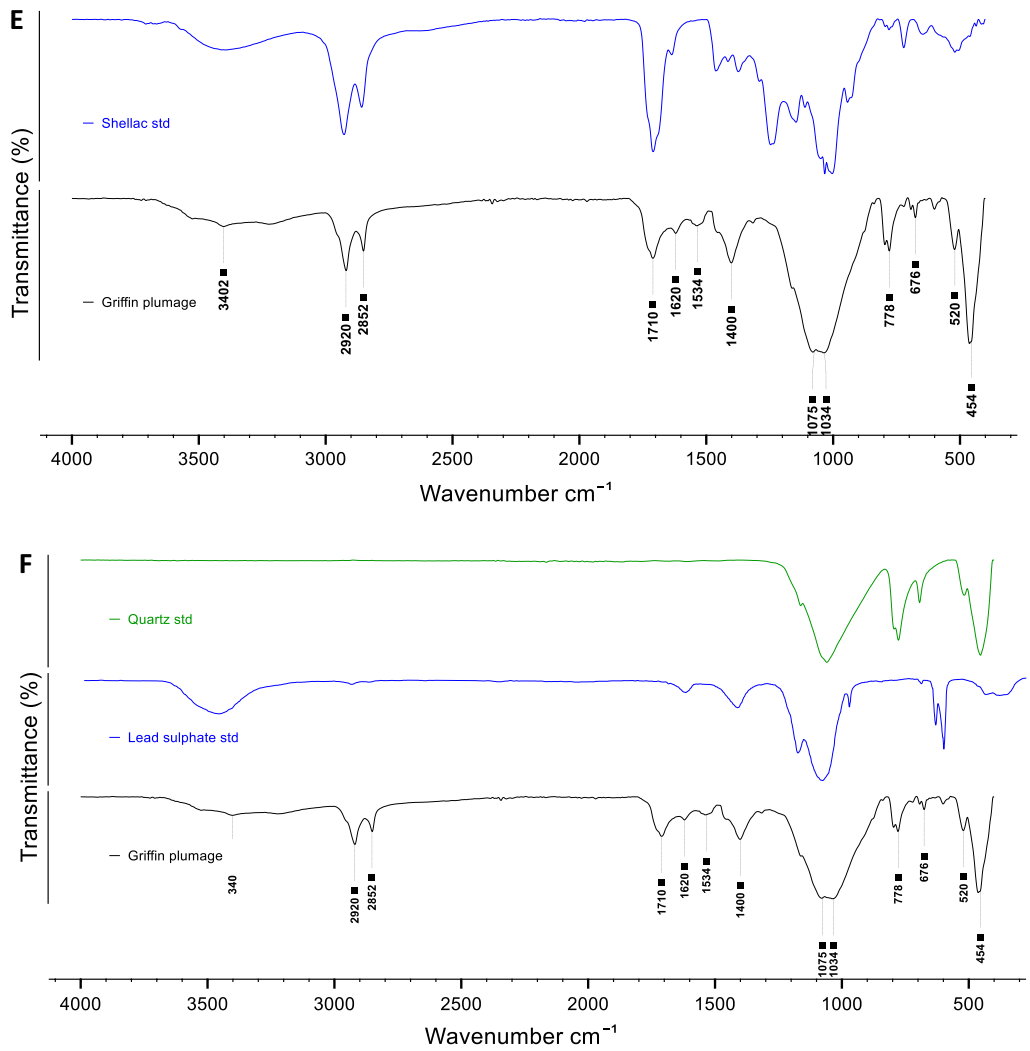

Fig. 3 continued

of shiny black pigment forming a circular pupil in the centre. Visible traces of white pigment are also extant on the crest of the right griffin's head plumage, suggesting all four griffin-heads were very likely crowned with white. This stratigraphy is confirmed in cross-section (Fig. 4B) of the microsample (Fig. 4C) and in situ (Fig. 4D) with crisp and very clearly defined layers of a thin orange-red base covered by the resinous layer then an additional thick band of white with a final black surface layer comprised of heterogeneous black angular inclusions. Ultra Violet (UV) light microscopy showed the white to be comprised of heterogeneous white and cream inclusions (no image included).

The pXRF results detect much higher levels of Pb than the groove sample, confirming the presence of a lead-based pigment to define the eye whites. Intriguingly, high levels of Sn and traces of Cu are also present at this feature indicating the possible presence of a copper and tin-based pigment, perhaps to create a shiny metallic surface for the pupil or eye white but this cannot be confirmed here. The absorbance bands 2920, 2852 and 1710 cm^{-1} are most likely to be associated with an organic resin as noted in the ivy tendril and griffin plumage. The spectrum is shown in comparison to shellac, although it should be made clear that from the FTIR–ATR it is not possible to determine the specific resin (Fig. 5G).

In this sample the presence of calcium carbonate is clearly seen in the large broad band at 1392 and the bands at 872 and 710 cm^{-1} (Fig. 5H).

High levels of Cl (Fig. 4viii) are also detected here with pXRF and confirmed by EDS mapping in the base layer where Na (Fig. 4ix) is detected in the same context which may indicate a size.

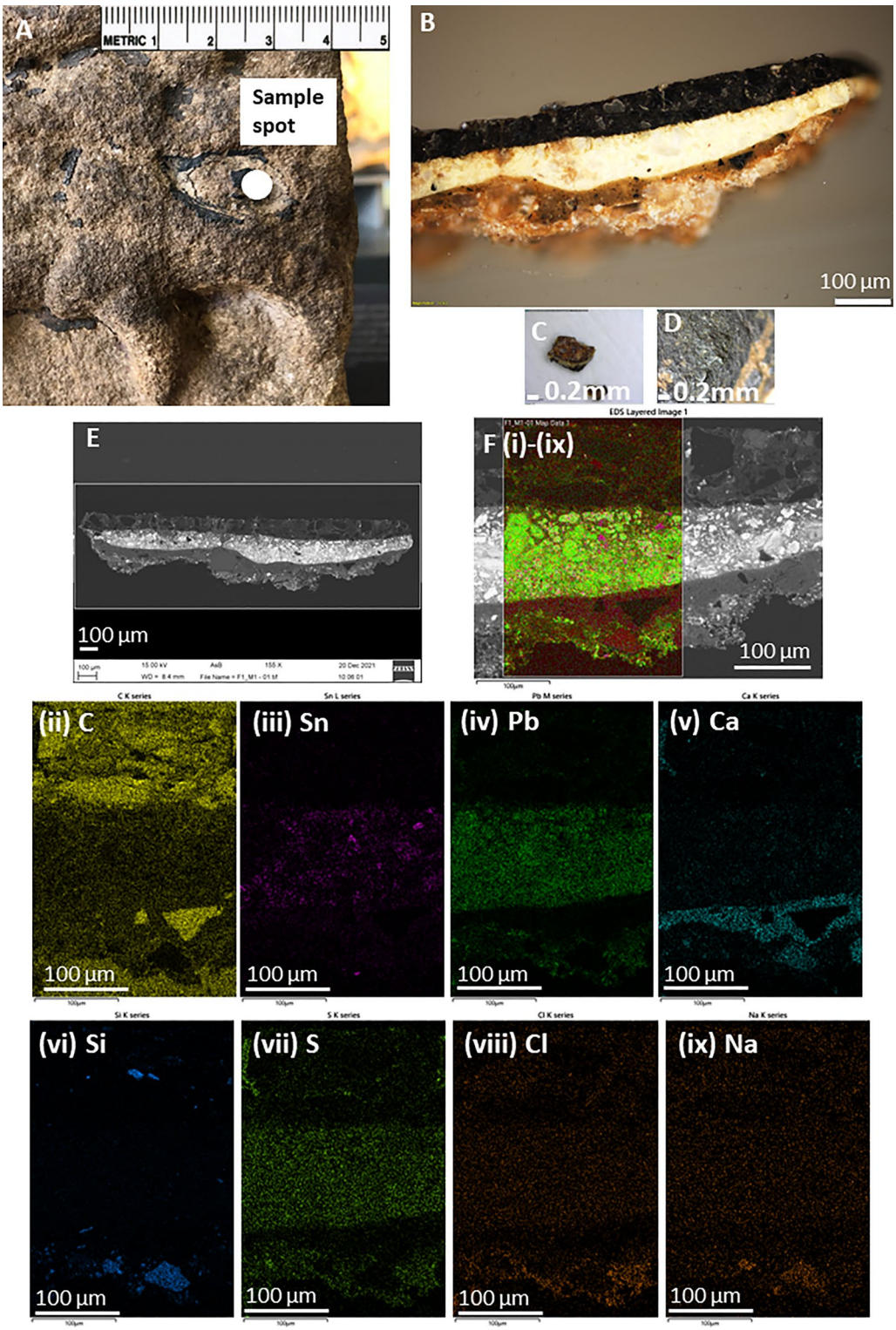

Fig. 4 Griffin eye. **A** Detailed image; **B** LM image showing clear stratigraphic sequence of pigments in cross section; **C** Microsample; **D** In situ microphotograph; **E** SEM image; **F** (i–ix) EDS Mapping (scale on images); **H** FTIR–ATR spectra of calcium carbonate

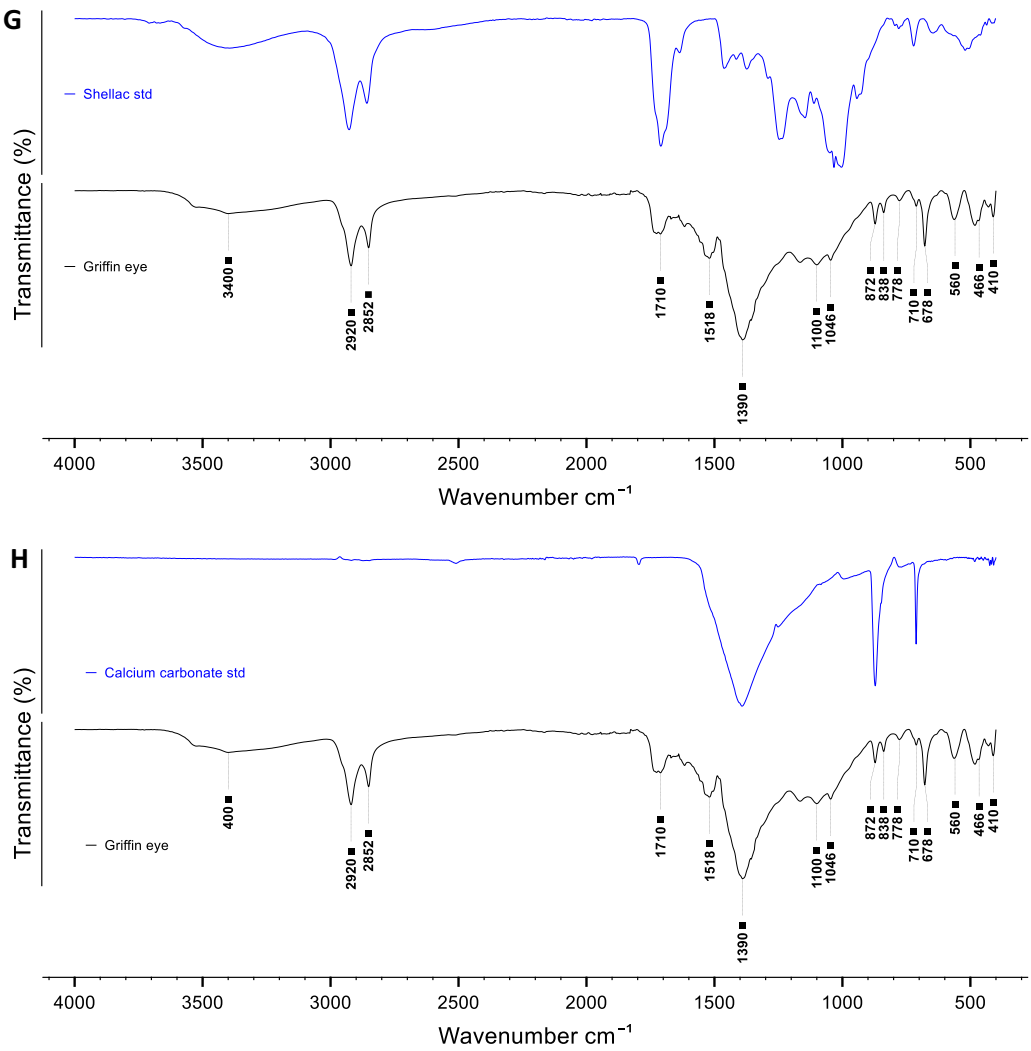

Fig. 4 continued

SEM imaging (Fig. 4E) confirms the heterogeneous character of inclusions in each layer. EDS mapping (Fig. 4i–ix) detects C in the top layer (Fig. 4ii), confirming a carbon-based black pigment. EDS further validates the presence of a lead pigment with a strong signal for Pb (Fig. 4iv) in both the white band immediately below the black as well as in the base layer interspersed by a calcium-rich layer (Fig. 4v) with carbon black inclusions similar to the griffin groove sample. This appears to confirm the presence of a lead pigment depicting the griffin's eye white and a thin base layer of red lead, possibly mixed with realgar which would explain the pXRF detection of As. Sn (Fig. 4iii) and S (Fig. 4vii) are also present in the white layer, the latter may suggest a lead sulphate ($PbSO_4$) or sulphate products from degradation. Sn is present uniquely in this white layer, distinguishing it chemically, and visibly, from the red lead base. A feasible deduction would be that some lead tin yellow may have been mixed in with this to achieve a desired colour for the eye white. The Cu detected by pXRF suggests a copper-based pigment mixed into one of the layers in this feature, most likely the surface or eye white. Ca is restricted to the layer immediately underlying the lead sulphate, identifying the location of the calcium carbonate sandwiched between the red lead possibly mixed with a realgar base layer and the white above.

Griffin rosette

No significant pXRF results were detected in the rosette centre. Conversely, the pXRF results for the petal of the central rosette contain only trace levels of Pb with high levels of Fe, S and Mg, indicating this decorative feature

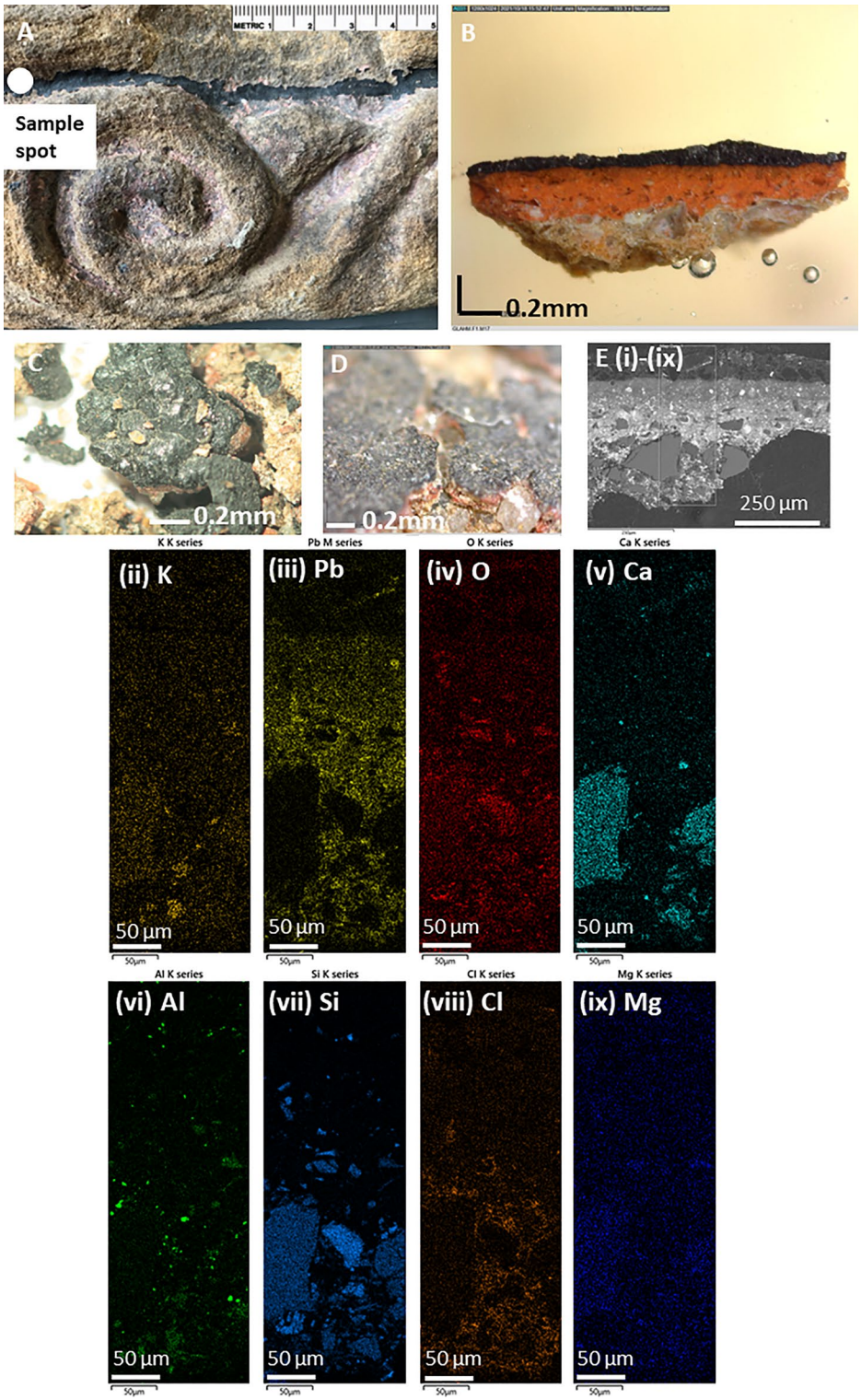

Fig. 5 Inscription panel frame—grey/black exterior. **A** Detailed image; **B** LM image showing clear stratigraphic sequence of pigments in cross section; **C** Microsamples; **D** In situ microphotograph; **E** (i–ix) EDS Mapping (scale on images); **F** FTIR–ATR spectrum of organic resin; **G** FTIR–ATR spectra of quartz and lead sulphate

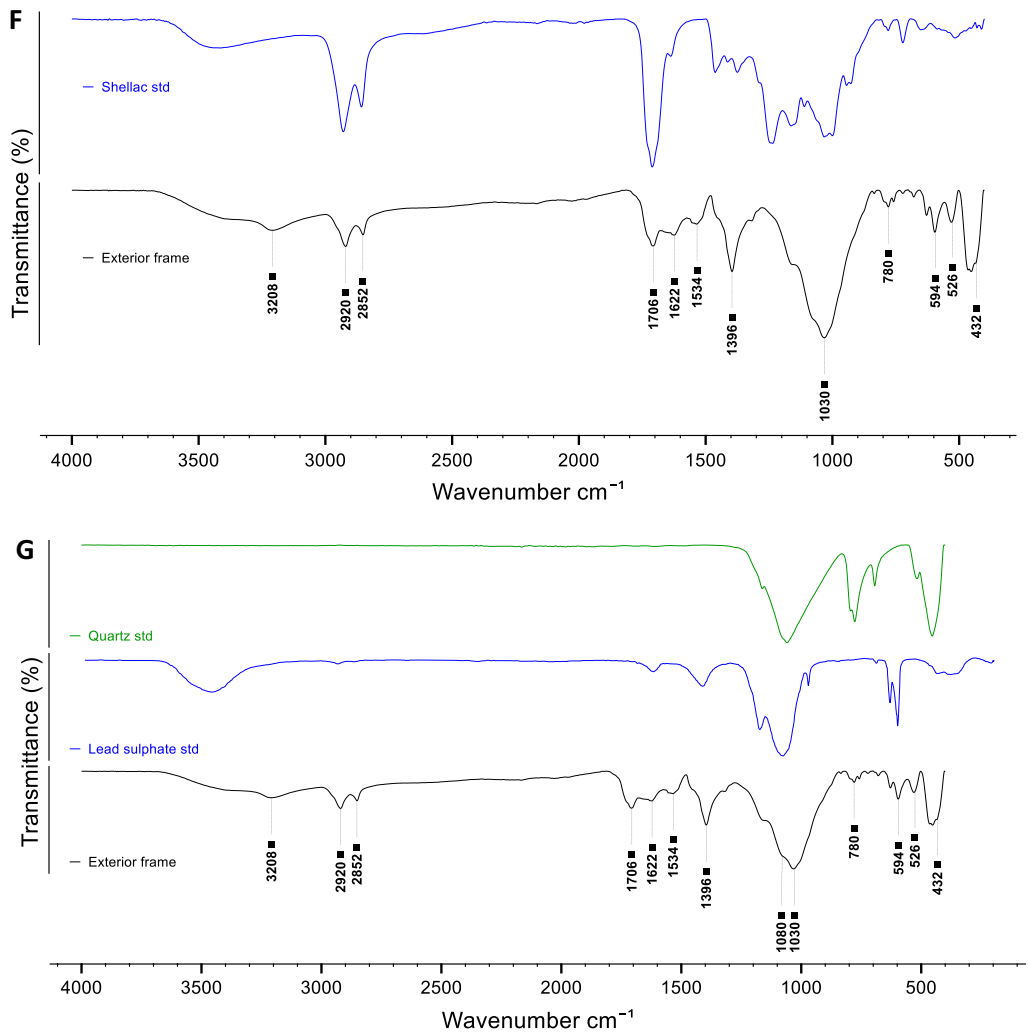

Fig. 5 continued

was depicted in a different pigment, possibly red ochre. That said, these elements could derive from soil particles and/or sulphation and the Pb traces may indicate an original lead pigment. No microsamples or in situ microphotography images were taken of this feature since no pigment traces were visible.

Inscription panel frame

The inscription panel is set within a triple-ribbed carved frame that retains visible traces of a mid-brown pigment overlain with gold gilding (Fig. 6) and flanked by informal borders in grey/black pigment around the exterior (Fig. 5) and very shiny black pigment in the interior (Fig. 6A, top left). Each of these painted features are dealt with in detail below.

Exterior frame

The inscription panel frame is bordered around the exterior by a grey/black pigment (Fig. 5A). In cross-section (Fig. 5B) this comprises three distinctive layers: a very bright orange-red sandwiched between a black surface and a whitish/pink base with large crystalline inclusions. Visual inspection of the cross-section, microsample (Fig. 5C) and in situ (Fig. 5D) appears to confirm the central orange-red underlying the black surface to be the same pigment as on the exterior of the griffins (Additional file 3: Appendix II, pXRF13), confirming a layer of red was painted across the entire area up to the carved frame then overlaid with a band of black on the exterior of the carved frame, perhaps to highlight the gilded area, and in some places this has extended onto the high

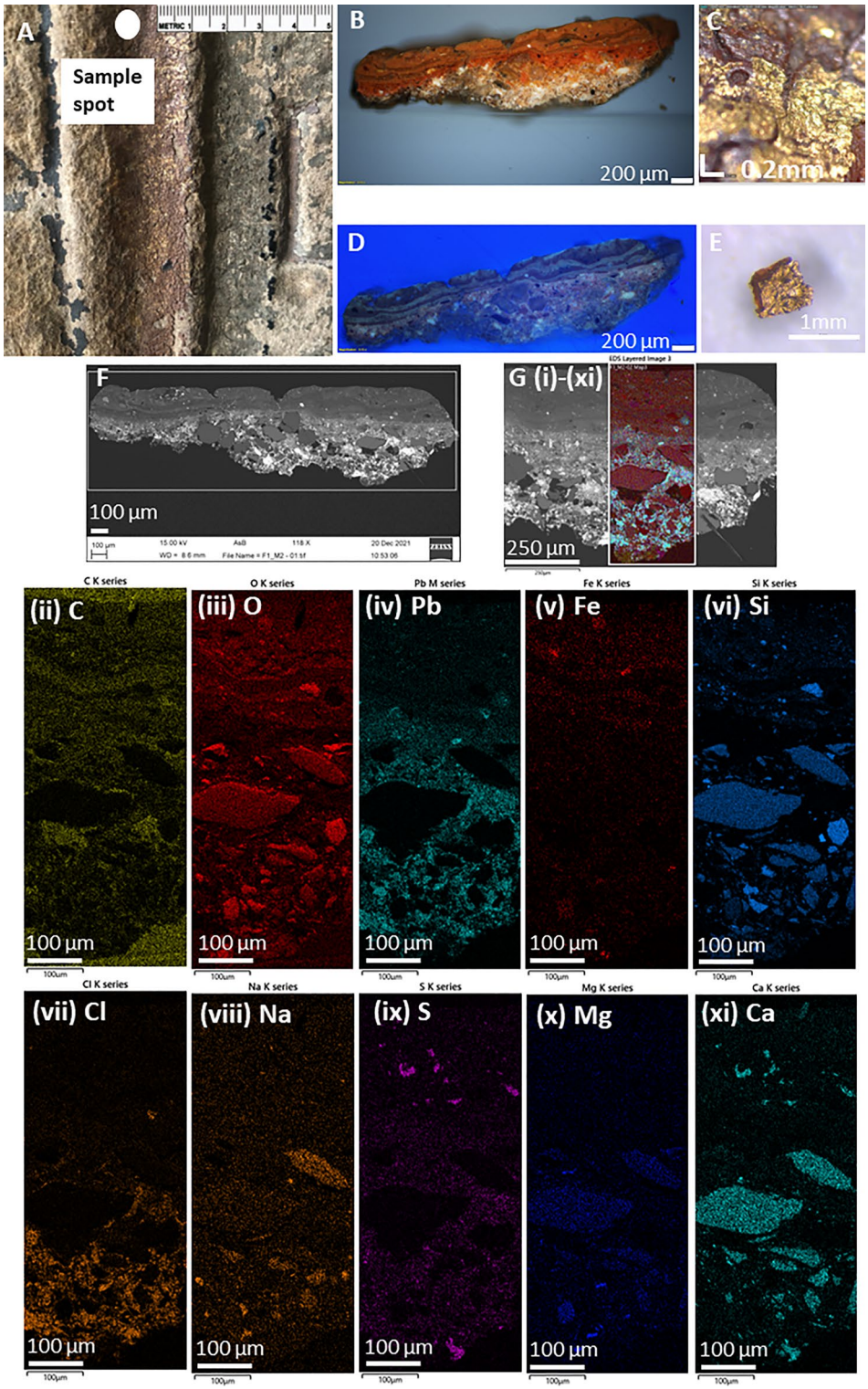

Fig. 6 Inscription panel gilded frame. **A** Detailed image; **B** LM image showing complex pigment and resinous layers in cross section; **C** In situ microphotograph; **D** UV Cross section; **E** Microsample; **F** SEM image; **G** (i–xi) EDS Mapping (scale on images); **H** FTIR–ATR spectrum of organic resin; **I** FTIR–ATR spectra of quartz and lead sulphate

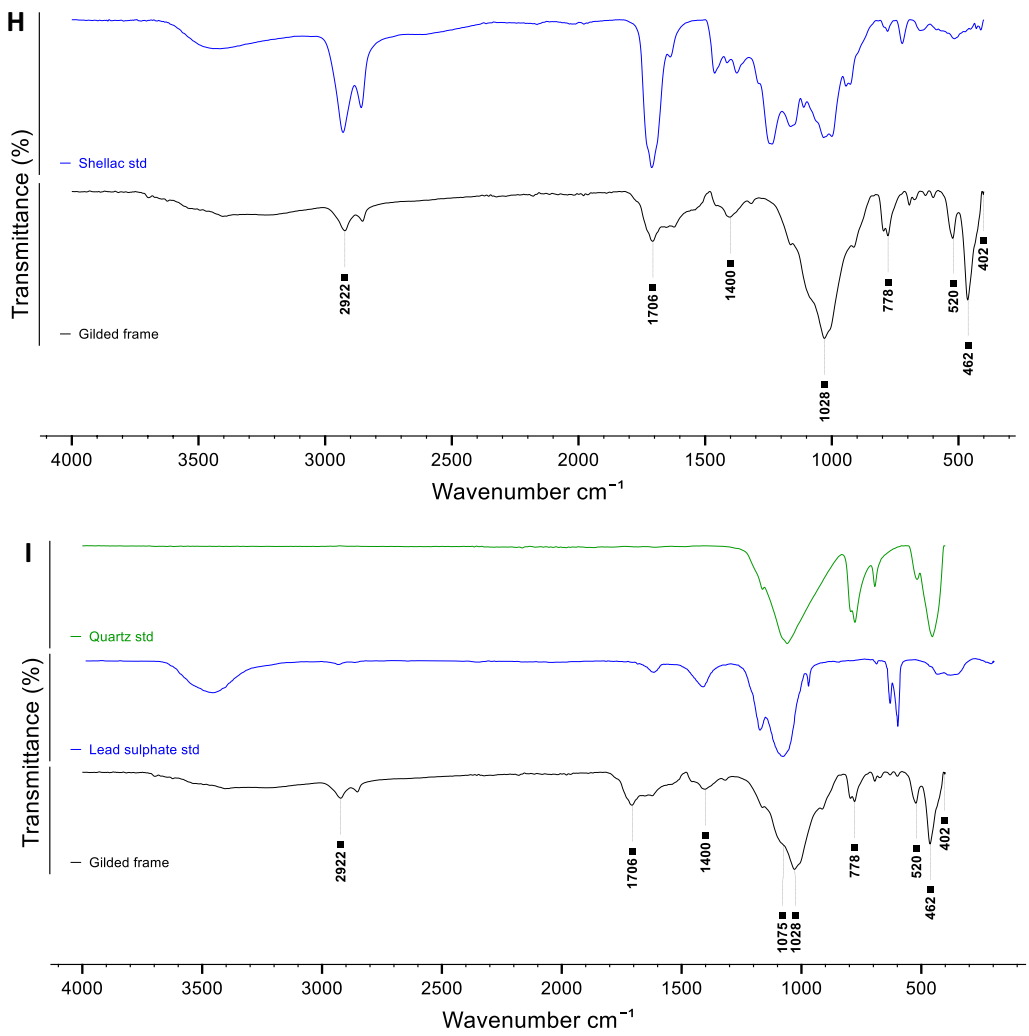

Fig. 6 continued

carved area of the frame. Again, pXRF results confirm a Pb-based pigment with traces of As. One sample from this area (17.4) records high levels of P, Fe, Au which suggest this reading was taken from an area contaminated by an underlying Fe-rich bole with glue applied to the gilded frame (see below).

SEM imaging (Fig. 5E) shows the heterogeneous character of these layers and EDS mapping (Fig. 5Ei–ix) combined with targeted spot analyses confirm Pb (Fig. 5iii) dominates the base layer with frequent Ca (Fig. 5v) and Si (Fig. 5vii) inclusions, suggesting the mixing of lead sulphate and red lead. The presence of As and Pb detected by pXRF and the vibrancy of the red layer as well as EDS mapping of O (Fig. 5iv) strongly suggests the mixing of red lead and realgar also evidenced on other features.

The absorbance bands 2920, 2852 and 1710 cm^{-1} are most likely to be associated with an organic resin as noted in in the ivy tendril, griffin plumage and griffin eye are also seen here (Fig. 5F).

The spectrum (Fig. 5G) shows the likelihood of the presence of lead sulphate and quartz due to the strong wide absorbance at 1040 cm^{-1}. The presence of a shoulder around 1060–1070 cm^{-1} and sharp shoulders either side of it at 1173 and 971 cm^{-1}; bands at around 1400 and 1626 cm^{-1} and the sharp bands at 698 and 594 cm^{-1}are indicative of lead sulphate. Si–O-Si bands at around 1060, 780 and 450 cm^{-1} and correspond to quartz.

Taken together, cross section and SEM images suggest the black surface pigment is likely carbon-based, similar to the griffin eye pupil. Traces of P in one sample

could point to a bone/ivory black, but that analysis spot is anomalous with the other samples from this feature and may be a contaminant from the gilded frame which contains similar elements. The FTIR–ATR results do not detect P-containing compounds which renders the possibility of bone/ivory black unlikely. EDS spectra on samples from this surface layer detect Pb (Fig. 5iii) and traces of Na, Mg (Fig. 5ix), Cl (Fig. 5viii) and Al (Fig. 5vi) and Ca (Fig. 5v) in the base layer which, combined with the Pb here, suggest the mixing of red lead and/or lead sulphate and calcium carbonate as calcium was detected by the EDS.

Gilded frame

The carved frame is finished with a layer of gold gild (Fig. 6A) over mid-brown that is visible in microsample (Fig. 6E) and in situ (Fig. 6C). In cross-section (Fig. 6B) at least 9 stratigraphic layers of pigments are discernible, including a white base layer, then a yellowish layer with abundant crystalline inclusions that may constitute seepage or contamination from the ground white followed by an orange-red layer characteristically similar to that evident on other features then three layers of a resinous orange with occasional black inclusions interspersed by light resinous brownish layer then a final very thin surface of gold gild.

In common with the gilded letters, discussed below, pXRF results from this area show the broadest range of elements from any of the sculpted features, including Ba, As, Au, Pb, W, Fe, P and Cl. One spot contained additional traces of Bi, Cu, Ni, Co, Mn, Cl and Mg with lower than ground level of Si and Ca (the latter common to almost all pXRF results), which correlates to the readings for the inscription background, below, suggesting cross contamination from the panel pigment in at least some parts of the frame.

The organic bands and shape point to the presence of a resin. Again, from the FTIR–ATR (Fig. 6H) it is not possible to identify the specific resin. Despite the presence of gold on the sample there was no indication of proteinaceous glue however gas chromatography with mass spectrometry would perhaps have indicated its presence or otherwise.

As in previous samples, the presence of lead sulphate, which may be a degradation product of lead white, and quartz can be seen in the gilded frame sample (Fig. 6I).

Since W is detected at significantly high levels only where gilding visibly survives, this element is likely connected to the gold gilding. Bismuth has been identified under metal leaf in a study of the use of powdered bismuth in Late Gothic painting and sculpture polychromy [31]. This is a complex sample that perhaps indicates more graphically than all others the extensive expertise of the artist deploying these pigments and surface treatments. In cross section, it is evident that every layer was carefully and skilfully applied then left to dry before application of the next, this is most clear in the UV image (Fig. 6D) which shows no seepage between levels.

All layers are clearly discernible in the SEM image (Fig. 6F) which depicts many large inclusions in the base layer of glassy structure. EDS mapping (Fig. 6Gi–xi) confirms Ca (Fig. 6xi) mixed with Pb (Fig. 6iv) in the base layer, suggesting the presence of a lead sulphate which may be a degradation product of lead white likely mixed with calcium carbonate detected in FTIR–ATR. Some mixing of orpiment may explain the yellowish hue just above here, though the EDS mapping did not stretch to mapping As in this sample to corroborate the source of the As detected with pXRF. This yellow hue might derive from yellow ochre in a size layer underlying the bole [23]. A compilation of yellow ochre, linseed oil, varnish and minium (red lead) are recorded as a mordant for matte gilding during the seventeenth century [32] and complex recipes for gilding preparatory layers of orpiment with other arsenic sulphides are known from fifteenth–sixteenth century German sources, including orpiment, chalk vermillion and hematite [33] or orpiment, red lead and gum [34].

Occasional traces of Fe are present in the base layer and also in the orange-red layers above, most prominently on the penultimate layer, the latter could then be a bole, comprised predominantly of clay with naturally occurring iron oxides to which red pigments are added since metal leaf is generally not burnished over oil or resin-based layers which can tear delicate gilding due to their sticky texture [35]. In northern Europe during the thirteenth century a smoothed white ground of chalk or gypsum mixed with animal-skin glue was commonly overlain with a carefully prepared poliment (polisher) which was moistened with water before gilding [35]. Bole was used as poliment throughout Europe from the mid-thirteenth century, particularly from the fifteenth century, and the red colour resulted in a warm tone of the gold gilding applied above [36]. White mordant comprised of lead white mixed with other additions is also known from German-speaking countries during the fifteenth–eighteenth centuries, confirmed in a fifteenth century manuscript *Cod. Pal. Germ. 558* [37], but this is currently only known to have been applied below white metal leaf [23]. This tradition of layering later became common during the seventeenth Century when Rembrandt and other artists built up multiple layers commencing with orange-red ochre in oil as a primer interspersed with thin resinous layers which effectively sealed in those below, preserving

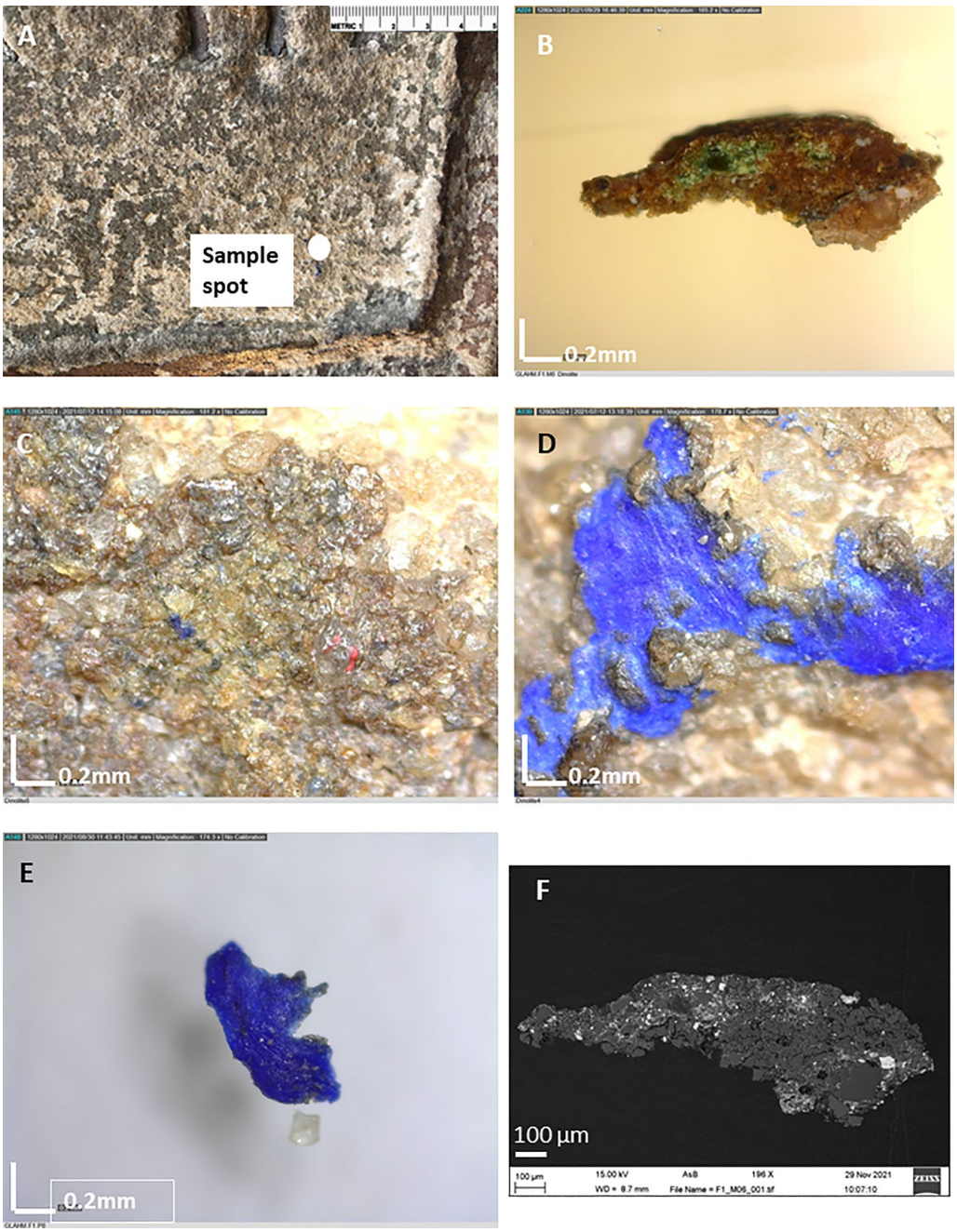

Fig. 7 Inscription panel background. **A** Detailed image; **B** LM image showing clear stratigraphic sequence of pigments in cross section; **C** In situ microphotograph; **D** In situ microphotograph of blue splash; **E** Microsample; **F** SEM Image (scale on images); **G** FTIR–ATR spectra of smalt and beeswax; **H** FTIR–ATR spectra of quartz, lead sulphate and smalt

the vibrancy of their colour [38]. There is no evidence for glaze layers above gilded surfaces common to paintings from this period, but the concentration of Cl (Fig. 6vii) and Na (Fig. 6viii) in the base layer is strongly suggestive of a size [23]. Further research is necessary to validate this hypothesis.

Informal black border inside panel frame

The black informal border depicting the interior of the carved gilded frame (see Fig. 6A, top left) has been applied directly over the smalt covering the inscription panel. This pigment differs markedly from all others on the sculpture. The substance is highly shiny and the

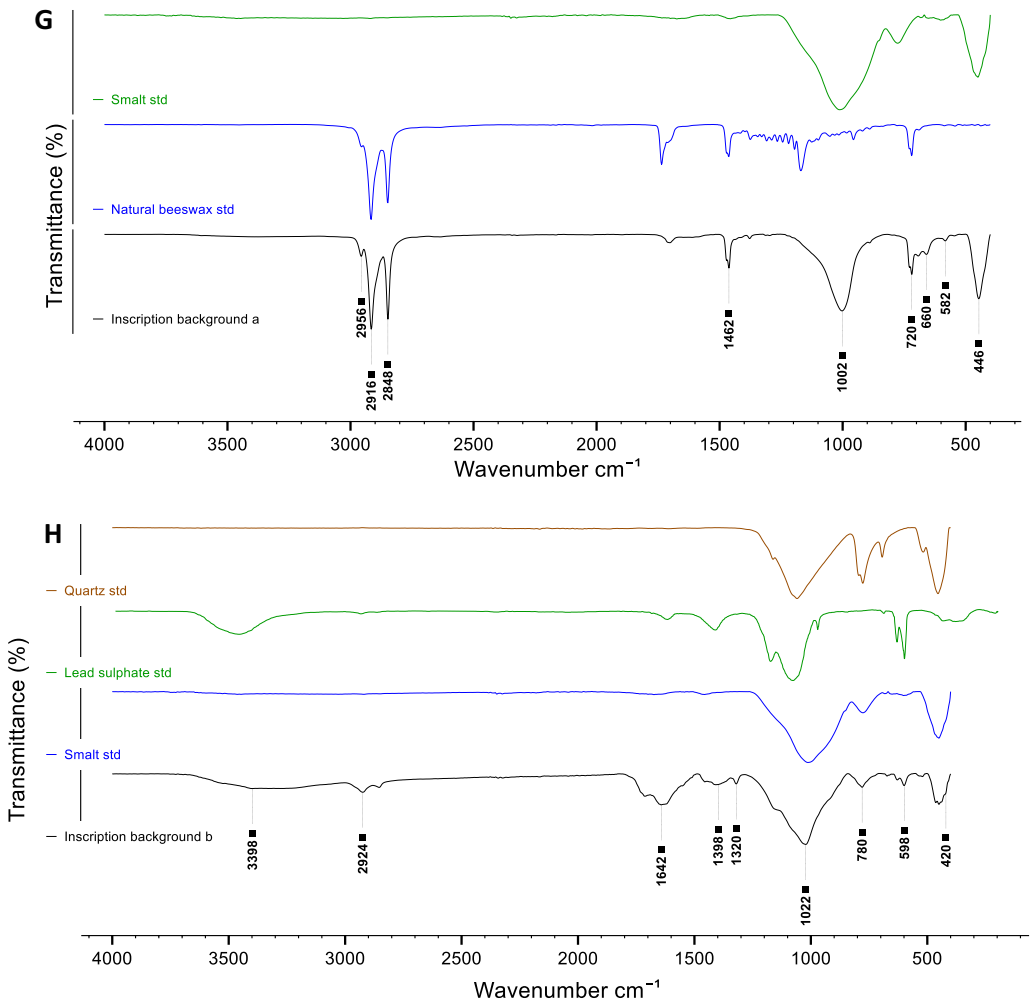

Fig. 7 continued

extraction of microsamples was challenging due to its sticky pitch-like character. As and Pb detected here by pXRF likely derive from the layers underlying the black (see inscription background, below) which is probably carbon based and therefore not detectable with pXRF. Natural wax is the only material detected by FTIR–ATR on this sample (Additional file 4: Appendix SIII with detailed band absorbance information).

Inscription background

Close inspection reveals a heavily cracked and degraded surface layer across the inscription panel (Fig. 7A) that has survived fragmentarily, perhaps accelerated through successive cleaning episodes [9]. The colour appears greyish-brown and the surface is less shiny than other surface features. This layer appears to have been applied to the entire internal panel in advance of the application of pigments and gilding on the inscribed letters, see below. Critically, a small splash of barely visible, but very vibrant, blue is evident in the bottom right section of the panel (Fig. 7D) which demands more detailed interrogation and a separate microsample of this blue was taken for FTIR–ATR analysis (Fig. 7E). Stratigraphically, this blue splash blends into the top-most layer of pigment here and microscopic *in-situ* inspection of various points across the panel using a DinoLite microscope (Fig. 7C) confirms a pigment with heterogeneous matrix dominated by brownish crystalline grains interspersed by small flecks of blue and red.

As with the other pigments present, pXRF confirms Pb is the dominant element with peaks of As, Cu, Ni and Co also detected along with a low reading of Ca, in common with other analysis spots, and traces of Bi. The presence of these elements combined with the tantalising traces of visible blue identify the presence of smalt [39]. Commonly used from the late fifteenth—early eighteenth

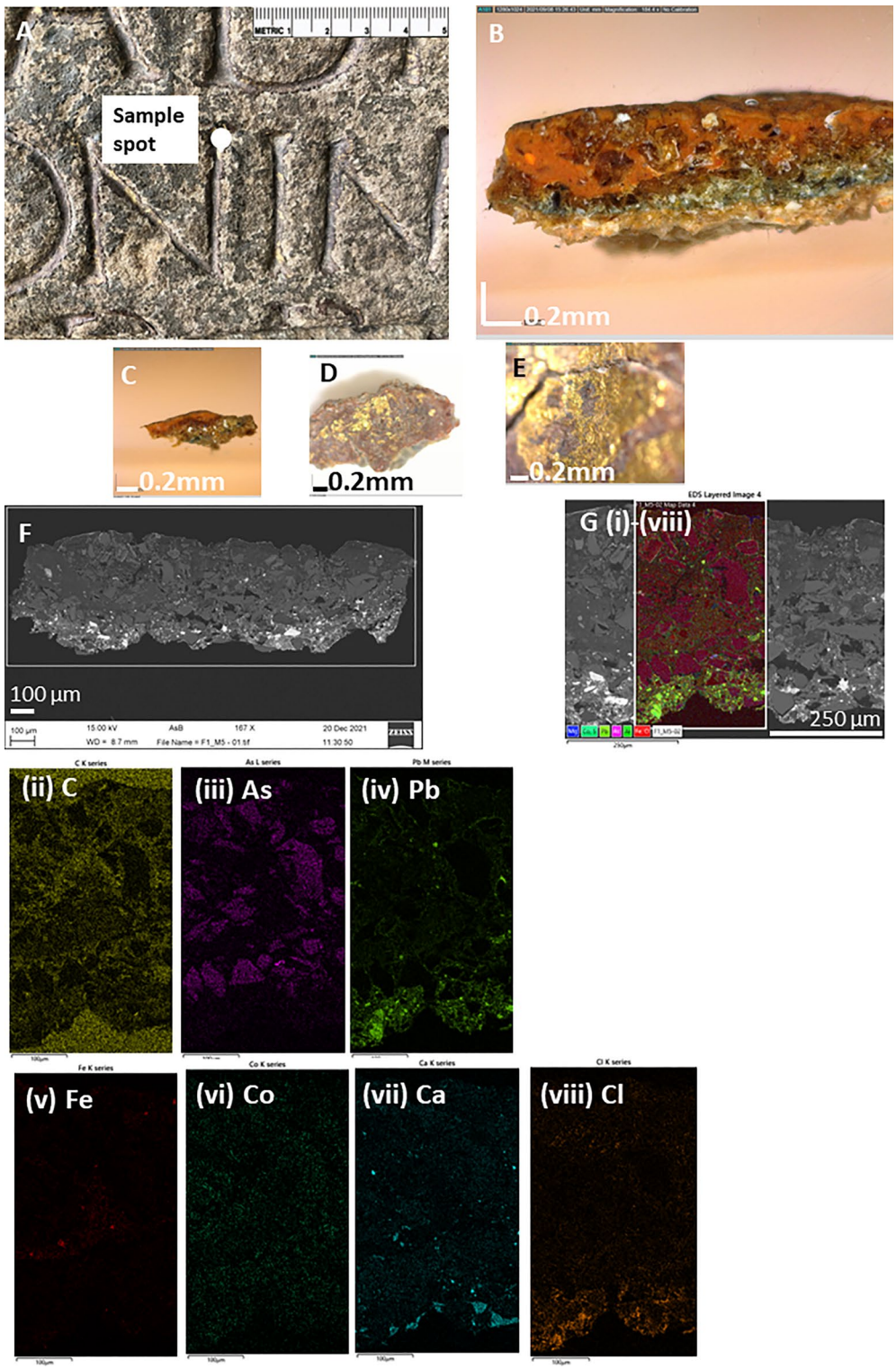

Fig. 8 Gilded letters. **A** Detailed image; **B**, **C** LM image showing clear stratigraphic sequence in cross section; **D** Microsample; **E** In situ microphotograph; **F** SEM image; **G** (i–viii) EDS Mapping (scale on images); H) FTIR–ATR spectra of wax and smalt

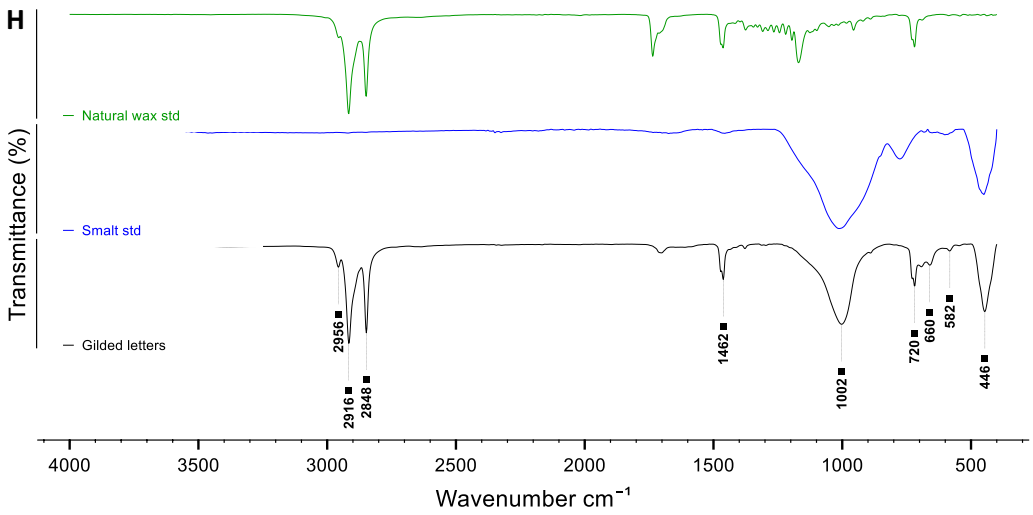

Fig. 8 continued

Centuries, smalt is a vibrant blue derived from a potash silicate glass coloured with cobalt and often substituted for more expensive pigments [40]. Due to its siccative [41] and refractive properties which could result in the migration of cobalt ions and leaching of potassium from potash glass flux used in its manufacture the colour was unstable and could discolour to brownish grey [40–44]. This could explain the grey-brown colour of the inscription panel and cracked surface from shrinkage in a dry museum environment [39].

In cross-section (Fig. 7B) three distinct layers are defined, including a blueish/green surface pigment, a brownish central layer constructed of heterogenous inclusions and a pinkish base layer with large inclusions. The SEM image confirms this stratigraphy more clearly. These suggest a surface layer of smalt overlying a possible red lead and/or orpiment/realgar.

Two micro samples were taken from the panel background. A sample was taken from the visible blue area (Fig. 7E) and here the presence of smalt can clearly be seen due to the characteristic broad peak at 1002 cm $^{-1}$ (Fig. 7G). In previous samples it was difficult to determine its presence due to interferences from quartz which also contains the Si–O–Si grouping. These species partly undergo condensation reactions creating more bridging Si–O–Si. As a result, in the FTIR–ATR spectra the Si–O–Si stretching appears to become more intense and to shift to higher wavenumber [39]. Beeswax is also detected in this sample due to the strong aliphatic absorbance between in the area 2956–2848; around 1710; 1642 and 720 cm^{-1}.

Calcium carbonate was not detected, though this was a deliberately surface sample which did not encompass lower layers). Beeswax has been recorded in the seventeenth century mixed with smalt to create a high gloss surface to the panel to imitate the more expensive lapis lazuli [45]. The FTIR–ATR of the second sample (Fig. 7H) showed its composition to be very much like that of the ivy tendril and griffin plumage samples. Here it is difficult to determine the presence of smalt as lead sulphate and quartz are both present. The spectrum shows the likelihood of the presence of lead sulphate and quartz due to the strong wide absorbance at 1040 cm^{-1}. The presence of a shoulder around 1060–1070 cm^{-1} and also sharp shoulders either side of it at 1173 and 971 cm^{-1}; bands at around 1400 and 1626 cm^{-1} and the sharp bands at 698 and 594 cm^{-1} are indicative of lead sulphate.

Inscribed letters

The letters are painted with a reddish pigment with waxy appearance then overlain with gold gilding (Fig. 8A, D and E). As with all other painted areas, a high Pb reading is present in the pXRF results along with high Au, Fe, Mn, P and Cl with lower levels of Si in areas with visible gilding. Au is not detected in the analysis spots where gilding is not visible and Ba, Bi and P are lower than the gilded areas with Ca and Pb detected at lower levels than the background sandstone. In common with the panel background and frame, peaks of As, Cu, Ni and Co are detectable along with a low reading of Ca. Together, this suggests a layer of smalt was applied to the entire panel and frame (or at least some parts of the frame) including the inscribed letters, before the letters were overlaid with an iron-rich pigment, possibly ochre.

In this sample the presence of smalt and a natural beeswax are clearly seen. Beeswax detected in this sample due

Table 1 Results of pXRF analysis on GLAHM.F1 (displayed as ppm)

Sample	Location	Ba	Sn	Bi	As	Au	Pb	W	Cu	Ni	Co
PXRFback1	Background—left side below centre pelta	298	< LOD	< LOD	< LOD	< LOD	52	< LOD	< LOD	< LOD	< LOD
PXRFback2	Background—left side middle bottom griffin	244	< LOD	< LOD	< LOD	< LOD	58	< LOD	< LOD	< LOD	< LOD
PXRFback3	Background—right side back at exposed crack	274	< LOD	< LOD	< LOD	< LOD	39	< LOD	< LOD	< LOD	< LOD
PXRFback4	Background—right side bottom next to circular feature	338	< LOD	< LOD	256	< LOD	1753	< LOD	< LOD	< LOD	< LOD
PXRFback5	Background—left exposed cracked surface at edge bottom griffin	181	< LOD	< LOD	144	< LOD	1858	< LOD	< LOD	< LOD	< LOD
17.1	Background right side edge—bottom close to griffin head	499	< LOD	< LOD	11	< LOD	55	< LOD	< LOD	< LOD	< LOD
MEAN		316			112		997				
STD DEV		97			94		1033				
PXRF1	Grey/black next to exterior frame	< LOD	< LOD	< LOD	115	< LOD	1479	< LOD	< LOD	< LOD	< LOD
PXRF2	Gold on brown in frame	1531	928	440	17,594	4530	145,735	5442	779	519	1314
PXRF3	Gold at top middle N of ANTONINO	600	346	571	14,871	1692	72,886	2428	2098	867	3118
PXRF4	Panel background above E of CAESARI	503	154	213	6892	< LOD	35,119	< LOD	2455	735	3996
PXRF5	Bottom inner frame mid brown	354	75	< LOD	1991	< LOD	23,995	< LOD	91	< LOD	< LOD
PXRF6	Black/grey on right of frame	435	100	< LOD	2799	< LOD	26,613	382	209	< LOD	< LOD
PXRF7	Black in interior frame—informal border	409	109	< LOD	3114	< LOD	25,007	< LOD	447	< LOD	< LOD
PXRF8	Gold at top middle N of ANTONINO	1017	585	1167	20,057	1099	82,120	950	3759	1371	4109
PXRF9	Bottom artillery ball (double circle)	242	< LOD	< LOD	63	< LOD	496	< LOD	< LOD	< LOD	< LOD
PXRF10	Middle artillery ball circle in AVG	< LOD	< LOD	< LOD	< LOD	< LOD	594	< LOD	< LOD	< LOD	< LOD
PXRF11	Black—right bottom griffin eye	567	6230	< LOD	8782	< LOD	76,671	< LOD	948	< LOD	< LOD
PXRF12	Greyish/black right bottom griffin in grooves	304	112	< LOD	2189	< LOD	23,919	< LOD	120	< LOD	< LOD
PXRF13	Mid-brown—spot on background to right bottom griffin	392	156	< LOD	5450	< LOD	43,355	< LOD	< LOD	< LOD	< LOD
Noa 11	Artillery? Hole	< LOD	< LOD	< LOD	< LOD	< LOD	573	< LOD	< LOD	< LOD	< LOD
Noa 13	Left petal of flower in left griffin	260	< LOD	< LOD	86	< LOD	2799	< LOD	< LOD	< LOD	< LOD
Noa 14	Centre of flower in left griffin	194	< LOD	< LOD	< LOD	< LOD	1540	< LOD	< LOD	< LOD	< LOD
Noa 15	Bottom right ivy tendril swirl	< LOD	< LOD	< LOD	881	< LOD	7162	190	< LOD	< LOD	< LOD
17.2	Right of bottom right griffin	397	< LOD	< LOD	98	< LOD	2414	< LOD	34	< LOD	< LOD
17.3	Right of top right griffin	297	48	< LOD	53	< LOD	1748	< LOD	< LOD	< LOD	< LOD
17.5	Left edge of frame—dark brown	894	223	< LOD	4105	< LOD	29,198	544	459	< LOD	< LOD
17.6	Left inside frame with light brown	606	738	< LOD	11,517	502	48,579	1128	135	174	< LOD
17.7	Top frame with visible gold (above P of IMP)	2389	548	< LOD	10,083	3925	41,493	2278	114	111	< LOD
17.8	Second N in ANTONINUS gold at top	2282	612	412	20,795	3968	60,104	2215	2594	799	2375
17.9	Second A in CAESAR mid-brown	461	448	145	13,199	< LOD	45,115	565	1001	615	2051

Table 1 (continued)

Sample	Location	Ba	Sn	Bi	As	Au	Pb	W	Cu	Ni	Co
17.10	Flaking light brown above M of IMP	354	< LOD	< LOD	103	< LOD	3130	< LOD	73	< LOD	< LOD
17.11	Mid brown inside frame—background to whole inscription panel	3341	1973	1182	29,501	< LOD	80,739	680	7355	2462	10,604
17.12	Dark brown spot next to S in CAESARI	1111	3899	796	34,134	< LOD	73,013	792	13,621	1635	5153
17.13	Mid brown under cross bar of H in HADRIANO	2289	518	192	13,488	< LOD	45,653	561	2307	1040	4855
17.14	Top above a dk border	1548	314	< LOD	5642	872	48,778	< LOD	356	98	< LOD

Sample	Location	Fe	Mn	Ca	Al	P	Si	Cl	S	Mg	Notes
PXRFback1	Background—left side below centre pelta	2317	< LOD	34,003	12,832	< LOD	287,459	1170	38,312	< LOD	> si; < fe, ca, s
PXRFback2	Background—left side middle bottom griffin	6008	< LOD	38,918	15,807	315	236,424	4456	31,785	< LOD	> si; < fe, ca, s; trace cl
PXRFback3	Background—right side back at exposed crack	1763	< LOD	90,088	< LOD	< LOD	51,412	531	51,833	< LOD	> ca, s; < si
PXRFback4	Background—right side bottom next to circular feature	4780	< LOD	53,305	15,553	423	219,226	2630	66,329	< LOD	> si, s; < fe, ca
PXRFback5	Background—left exposed cracked surface at edge bottom griffin	7989	< LOD	21,918	22,501	1062	339,596	3752	28,504	< LOD	> si; < fe, s; trace ca, cl
17.1	Background right side edge—bottom close to griffin head	2373	149	44,244	11,433	< LOD	214,610	1150	101,403		
MEAN		< LOD		47,647	16,673	600	226,823	2508	43,353		
STD DEV		4230		26,256	4112	404	108,758	1663	15,649		
PXRF1	Grey/black next to exterior frame	2110	< LOD	6394	14,071	578	250,180	3183	8197	< LOD	**Significant LOW CA and S**
PXRF2	Gold on brown in frame	4969	514	9710	19,788	18,563	64,043	16,836	55,834	22,337	Highest pb; > as, au, w, fe, cl, p, mg; < ba, bi, cu, ni, co, mn; **LOW ca, si**
PXRF3	Gold at top middle N of ANTONINO	25,314	407	15,682	15,059	13,873	95,325	12,445	35,899	14,471	> pb, as, au, cu, ni, co, fe, p, cl; < bi, w, mn, mg; **LOW ca, si;** trace ba
PXRF4	Panel background above E of CAESARI	38,104	< LOD	11,260	10,018	1113	200,719	6535	30,164	< LOD	> pb cu, ni, co; < as, bi; **LOW ca**; trace ba
PXRF5	Bottom inner frame mid brown	5337	< LOD	12,014	15,905	574	287,509	3031	18,399	< LOD	> pb,fe; **LOW ca, s**
PXRF6	Black/grey on right of frame	11,483	< LOD	30,134	5338	682	149,750	4921	17,252	< LOD	> pb; **LOW s**; trace w
PXRF7	Black in interior frame—informal border	4002	271	10,808	17,125	965	228,652	6486	29,440	< LOD	> pb; **LOW ca**
PXRF8	Gold at top middle N of ANTONINO	5564	423	11,637	16,938	16,200	65,479	14,155	50,276	< LOD	> pb, fe, as, au, bi, cu, ni, co, p, cl; < ba, mn; **LOW ca, si**
PXRF9	Bottom artillery ball (double circle)	37,199	< LOD	4368	16,386	693	317,009	1959	3401	8193	> mg; **LOW ca, s**
PXRF10	Middle artillery ball circle in AVG	8306	< LOD	5972	17,915	< LOD	320,499	1504	4596	< LOD	**LOW ca, s**

Table 1 (continued)

Sample	Location	Fe	Mn	Ca	Al	P	Si	Cl	S	Mg	Notes
PXRF11	Black—right bottom griffin eye	7705	600	52,969	11,469	925	39,634	16,949	61,808	< LOD	> pb, sn, as, cl; < cu, mn; **LOW si**
PXRF12	Greyish/black right bottom griffin in grooves	2505	187	81,744	6951	1257	107,692	10,153	30,416	< LOD	> pb, cl; **LOW al**
PXRF13	Mid-brown—spot on background to right bottom griffin	4601	516	10,187	9214	1464	99,277	15,001	52,637	< LOD	> pb, as, cl; **LOW ca**
Noa 11	Artillery? Hole	5217	< LOD	6652	10,979	< LOD	189,811	1805	5774	< LOD	**LOW ca, s;** trace pb, fe
Noa 13	Left petal of flower in left griffin	6592	< LOD	13,397	28,214	963	319,553	4962	13,719	10,493	> fe, mg; **LOW ca, s;** trace pb
Noa 14	Centre of flower in left griffin	17,583	< LOD	6018	26,451	617	321,632	4784	10,185	< LOD	**LOW ca, s;** trace pb, fe
Noa 15	Bottom right ivy tendril swirl	5393	< LOD	15,856	13,950	952	215,786	10,064	43,168	< LOD	
17.2	Right of bottom right griffin	10,422	198	13,655	9200	< LOD	286,323	3722	31,773		
17.3	Right of top right griffin	3880	196	13,328	9587	< LOD	263,306	3805	26,356		
17.5	Left edge of frame—dark brown	4729	137	6254	< LOD	< LOD	126,747	5239	37,971		> pb; **LOW ca,** trace w
17.6	Left inside frame with light brown	3227	406	9397	3572	4116	68,290	9041	21,381		> bi, as, au, pb, w, fe, p; **LOW ca & al**
17.7	Top frame with visible gold (above P of IMP)	15,321	301	8377	9412	17,711	93,910	7139	32,620		> ba, as, au, pb, w, fe, p; **LOW ca & al**
17.8	Second N in ANTONINUS gold at top	14,910	417	13,484	12,433	22,017	87,589	10,428	34,226		> ba, bi, as, au, pb, w, cu, co, fe, mn, p; **LOW ca**
17.9	Second A in CAESAR mid-brown	28,331	332	13,637	5150	1912	70,274	8945	24,430		> as, pb, cu, co, fe; **LOW ca & al**
17.10	Flaking light brown above M of IMP	16,548	151	4741	17,836	< LOD	316,177	4656	17,152		**LOW ca**
17.11	Mid brown inside frame—background to whole inscription panel	1287	533	10,095	< LOD	< LOD	86,007	10,191	25,272		> ba, sn, bi, as, pb, cu, ni, co, fe, mn; **LOW ca**
17.12	Dark brown spot next to S in CAESARI	10,316	558	14,425	< LOD	< LOD	49,104	14,910	30,723		> ba, sn, bi, as, pb, cu, ni, co, mn; **LOW ca**
17.13	Mid brown under cross bar of H in HADRIANO	6224	377	9628	4205	< LOD	138,542	8459	22,788		> ba, as, pb, cu, ni, co; **LOW ca & al**
17.14	Top above a dk border	6454 15,119	311	11,395	10,031	13,406	114,559	10,500	30,716		> ba, au, pb, fe; **LOW ca**

Table 2 Palette of Pigments on GLAHM.F1

Pigment	Chemical formula	Feature	Colour
Lead sulphate	$PbSO_4$	Ivy tendril Griffin Groove? Griffin eye External border of carved inscription frame Carved inscription frame Letters	
Lead tin yellow	Pb_2SnO_4	Griffin eye white (sclera)	
Red lead	Dilead(II) lead(IV) oxide: Pb_3O_4	Ivy tendril Griffin groove Griffin eye Flat area beside griffin External border of carved inscription frame Carved inscription frame Inscription panel background Letters	
Realgar?	Arsenic(II) sulfide, As_4S_4	Ivy tendril? Griffin groove Griffin eye Flat area beside griffin External border of carved inscription frame Carved inscription frame Inscription background Letters	
Red ochre	Iron(III) oxide chromophore (Fe_2O_3 + clay + silica)	Ivy tendril Griffin rosette petal Carved inscription frame Letters	
Carbon black	Carbon	Griffin eye (pupil) Griffin groove External border of carved inscription frame Carved inscription frame	
Smalt	Cobalt(II) silicate $CoO.nSiO_2$	Carved inscription frame Inscription panel background Letters	
Gold gilding	Au	Carved inscription frame Letters	
Orpiment	Arsenic(III) sulfide, As_2S_3	Carved inscription frame Inscription background? Letters	

(Colour swatches obtained from https://colourlex.com/)

to the strong aliphatic absorbance between in the area 2956–2848; around 1710; 1642 and 720 cm^{-1}. The presence of smalt can clearly be seen due to the characteristic broad peak at 1002 cm^{-1}.

As with the gilded frame, a yellow-ish hue is definable in the base layer with abundant glassy inclusions in cross section (Fig. 8B and C). This is followed by a thick blue layer of smalt, a brown/red layer, an orangey-red layer with multiple inclusions of various size and colour, including dark red, golden yellow, orangey-red and black, then a gilded surface. SEM imaging (Fig. 8F) confirms this stratigraphy and EDS mapping (Fig. 8Gi–viii) clearly detects C (Fig. 8ii) throughout the sample, with As (Fig. 8iii) identified in all but the base layer, confirming the presence of orpiment or realgar. The yellowish layer immediately above the blue is most likely orpiment with realgar in the reddish layer and Fe (Fig. 8v) and Pb (Fig. 8iv) above confirming a penultimate bole layer consisting of iron oxides mixed with realgar and red lead immediately below the surface gilding. Pb is also

Table 3 Stratigraphic Sequences on Polychromy on GLAHM.F1

Feature	Visible colour/s	XRF elements	FTIR–ATR results	Pigments present	Cross section stratigraphy (top to base)
Ivy tendril	Light brown	As, Pb, Fe, Cl Low Ca,	Calcium carbonate, lead sulphate	Realgar?, red lead, lead sulphate, red ochre, calcium carbonate	1. Realgar? 2. Red lead 3. Lead sulphate, calcium carbonate and red ochre*
Griffin groove	Grey-black	As, Pb, Cl Low Al	Lead sulphate, resin, proteinaceous material (binder?)	Carbon black, realgar?, red lead, lead sulphate?	1. Carbon black and resin* 2. Realgar? and red lead and/or lead sulphate*
Griffin eye pupil	Black overlying white	Sn, As, Pb, Cu, Mn, Cl Low Si	Calcium carbonate, organic material (resin/oil?)	Carbon black, lead sulphate, lead tin yellow, red lead, realgar?, Red lead, calcium carbonate	1. Carbon black 2. Lead sulphate and lead tin yellow* 3. Carbon black, resin/oil and calcium carbonate* 4. Realgar? and red lead and/or lead sulphate*
Rosette petal in griffin	No colour visible	Fe, Cl, Mg Trace Pb Low, Ca, S	No micro sample	Red ochre	No micro sample
Flat area beside griffin	Medium brown	As, Pb, Mn Low Ca	No micro sample	Realgar?, Red lead	1. Realgar? and Red Lead * (based on external border of frame)
External border of carved inscription frame	Grey-black	Pb Trace As Low Ca, Al, S	Calcium Carbonate, Lead Sulphate, Proteinaceous material (binder?)	Carbon black, realgar?, Red lead, lead sulphate, calcium carbonate	1. Carbon black 2. Red lead and realgar?* 3. Red lead and/or Lead Sulphate and Calcium Carbonate*
Carved inscription frame	Medium brown overlain with gold	Ba, As, Au, Pb, W, Fe, P Traces Sn Low Ca (one analysis spot has additional Bi, Cu, Ni, Co, Mn, Cl, Mg and low Si, Ca)	Lead Sulphate, Resin, Calcium Carbonate, Organic binder (hint)	Gold gild, Red ochre, carbon black, resin, realgar?, Red lead, lead sulphate, calcium carbonate Orpiment?	1. Gold Gilding 2. bole with Red Ochre and Carbon Black * 3. resin 4. same as 2 5. same as 3 6. same as 2 7. Realgar? and red lead * 8. Lead sulphate and orpiment? * 9. Lead sulphate and calcium carbonate *
Internal border of carved inscription frame	Black	As, Pb, Cu Low Ca	Natural Wax	Carbon black	1. Carbon Black and Wax *
Inscription panel background	Grey-brown	Ba, Sn, Bi, As, Pb, Cu, Ni, Co, Mn Low Ca, Al	Smalt, Beeswax Blue spot – Beeswax, Smalt	Wax Smalt Red lead Orpiment	1. Smalt and wax* 2. Red lead 3. Orpiment?

Table 3 (continued)

Feature	Visible colour/s	XRF elements	FTIR–ATR results	Pigments present	Cross section stratigraphy (top to base)
Letter (N of ANTONINO and A of CAESAR)	Medium brown overlain with gold	Ba, Bi, As, Au, Pb, W, Cu, Ni, Co, Fe, Mn, P, Cl Low Ca, Al, Si, Mg Traces Sn	Smalt, calcium carbonate, wax or resin, proteinaceous material (binder/bole?)	Gold gild, realgar?, Red lead, red ochre, smalt, lead sulphate, calcium carbonate, resin/wax (hint)	1. Gold gild 2. Realgar?, Red lead and red ochre * 3. Realgar 4. Orpiment 5. Smalt and wax * 6. Lead sulphate and calcium carbonate (red lead?)* Resin hint (layer uncertain)

* Indicates mixing of more than one pigment in a layer

dominant in the base layer along with Ca (Fig. 8vii) which suggests a preparatory layer of lead sulphate and calcium carbonate possibly mixed with some red lead given the EDS mapping of O here.

'Pockmark' indentations

The readings from circular gouges referred to by Keppie [9] as 'pockmarks' in the stone closely mirror those of the ground sandstone along with extremely lowered readings of calcium, chlorine and sulphur with elevated magnesium in one reading. This, combined with their obliterating of underlying features, including parts of the upper panel frame and letters, as well as the absence of any evidence for pigments, confirm this damage must have occurred after the final episode of painting, perhaps during a siege of Dunnottar by Cromwell in 1651–2 [10].

Results

The results are reported as found with little or no speculation. These have established the elemental composition of surface treatments defined by pXRF (Table 1), drawn out a palette of the pigments present (Table 2) and identified complexities in their mixtures, stratigraphic layering and application (Table 3) that have hitherto been unexplored for repainted Classical statuary [10], with the exception of a marble relief from Bursa, Turkey, repainted centuries later in the nineteenth century [46]. The palette comprises white, reds, black, blue, yellow and gold which, perhaps unsurprisingly, reflects contemporary tastes for colours applied to architectural features, statuary [47] and framed paintings [36, 48] combined with the antiquarian penchant for the collection and display of Classical sculpture [49, 50]. This has facilitated an authentic digital reconstruction of the sculpture from the Renaissance period in full polychromy for publication in a future article [10].

Conclusion

This vanguard research has successfully deployed a suite of analytical techniques to fingerprint surface treatments applied to a unique Classical relief sculpture repainted during the Scottish Renaissance. Given the innovative context of this work, comparative research is limited, but we have effectively stripped back multiple layers to ascertain, with confidence, the stratigraphic sequencing of pigment application and, critically, the timeframe for this episode in the sculpture's trajectory. This validates accounts of antiquarian writers who attribute the visible polychromy to the 16th C under the direction of George Keith, the Fifth Earl Marischal.

The combination of mixing in pigments with siccative properties with other pigments to maximise the impact of each painted feature and allow for the rapid drying of each layer before the application of subsequent layers [38, 47] align with contemporary practice of a highly skilled artist who doubtless was commissioned to undertake the painting. A resin has been clearly detected in the letters, hints of this are also present in other samples. Further detailed analysis would be required to fully identify the type of resin present.

Yet, there remains much to be revealed about this unique monument that invites us to delve deeper and peel back additional layers, including the complexities and diversity evident in base layers of some features that may be associated with original pigments applied in Antiquity. Aside from the smalt and lead sulphate detected on various features and the lead tin yellow present in the griffin eye, the other pigments identified could equally date from the Roman era. Indeed, the lead sulphate detected in six out of nine samples could very well originate from a degraded lead white in a sulphate-rich gypsum substrate [27] originating from a Roman application. This and other aspects, including the potential presence of metal soaps, will be fully explored through a comprehensive programme of SEM–EDS of samples from all features and other analysis using cutting-edge materials science techniques.

Abbreviations

LM: Light microscopy; FTIR–ATR: Fourier transform infrared spectroscopy with attenuated total reflection; pXRF: Portable X-ray fluorescence; SEM/EDS: Scanning electron microscopy/ energy-dispersive X-ray spectroscopy; UV: Ultra-violet.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-022-00790-7.

Additional file 1: Appendix SI. pXRF Analysis Spots.

Additional file 2: Appendix SI. pXRF results.

Additional file 3: Appendix SII. Microsample Locations of GLAHM.F1.

Additional file 4: Appendix SIII. FTIR.

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Author contributions

The concept for this research derived from LC. LC undertook exploratory pXRF and the historical/archaeological research relating to the sculpture and samples. LC extracted and embedded the samples for cross section analysis and for SEM/EDS analysis and undertook microscopy and microphotography of the samples. LC and MS jointly undertook the pXRF and FTIR–ATR data capture and analysis of the pXRF and SEM/EDS results. MS undertook FTIR–ATR analysis. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
The authors declare that they have no competing interests.

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