Establishing a multi-dimensional methodology to analyse pigments on sandstone sculptures: Exploratory investigations of an Antonine Wall Distance Sculpture

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Research Article

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Abstract

The Antonine Wall was commissioned by the Roman Emperor Antoninus Pius around 142 CE and stretches for c. 37 miles across the central belt of Scotland, marking the Empire's most north-western frontier. This vanguard research reports on the materials used during the 16th century in the redecoration of an iconic Distance Sculpture that was once embedded into the frontier.

Portable non-invasive technologies, including pXRF and in-situ microphotography were deployed. These techniques are supplemented by micro-sampling for SEM/EDS, FTIR-ATR and microscopy of cross-sections.

Introducing An Antonine Wall Roman Distance Sculpture (Hunterian Museum No. Glahm.f1)

The Antonine Wall was commissioned by the Roman Emperor Antoninus Pius around 142 CE and stretches for c. 37 miles 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*).

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 16th Century. It remained visible there in 1642 (11–16) prior to its 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).

Carved from buff sandstone probably 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)

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 hypothesises 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 2nd century, he does not draw out the vibrant polychromy that once adorned this relief and fails to 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 18th century. Anderson (15) makes clear the 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 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

Portable non-invasive technologies, including portable X-Ray Flourescence (pXRF) and *in situ* microphotography were deployed to analyse elemental and mineral compositions of surface pigments on each sculpted feature to validate or refute historical accounts referencing their 16th Century application. These techniques are supplemented by micro-sampling to provide invaluable information on chemical composition of the pigments and binders using SEM/EDS (Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy) and FTIR-ATR (Fourier Transform Infrared spectroscopy with Attenuated Total Reflectance) as well as, critically, microscopy of cross-sections to identify stratigraphic layers and determine whether later layers overlie and preserve original pigments applied during the 2nd Century CE by Roman artisans.

pXRF

The pXRF instrument used was a Niton XL3t 900 SHE GOLDD Alloy Analyser, with a 50kV Ag X-ray tube, 80MHz 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 seconds (with 30 and 30 seconds on the filters for light and low energy spectral lines respectively and 20 seconds on the filter for high energy spectral lines) and the area of analysis was 3mm^2. Several of the thirty-six elements that the instrument can in principle detect in this mode were concentrated below the limit of detection (LoD) or light elements with fluorescent peaks at low levels poorly resolved at low concentration. Analysis taken in 2013 in the 'TestAllGeo' calibration in the 'soils and minerals' mode (labelled soil in the database) for 60 seconds with an analysis area of c. 5mm^2 spot also were incorporated to augment the dataset.

A total of twenty-seven analysis spots were captured and composition tables comprising the full datasets are contained in Appendix I 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 Zr, Sr, Rb, Zn, Cr, Ti, K and Al, 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. 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 identify the presence of pigments.

Microsamples

Microsamples were collected from 12 areas by scraping with a scalpel and sealing them in labelled glass vials (Appendix II). 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. The 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.

FTIR-ATR

Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR) was carried out using Perkin Elmer Spectrum One FTIR 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 (Appendix III).

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. These 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 16th 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 more common in the Roman artists' palette. 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 supported by targeted invasive analyses for comparison.

All the painted areas displayed a cracked, resinous, waxy and degraded surface with visible pigments surviving only in some areas, largely resulting from 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 overlying a clearly visible light pink layer (Fig. 2). Microphotography and samples under microscope and in cross-section 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 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 a size (23) since EDS mapping detects this in the base layers of other features, while the Fe could indicate red ochre on the base layer mixed with white lead (Pb) or lead

sulphate as confirmed with the white inclusions overlain with layers of red lead and realgar, as opposed to the alternative arsenic-containing pigment – yellow orpiment. 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 being applied with no evidence of negative impact on medieval wall paintings across Europe refutes that hypothesis (25, 26). More recent experimental work combining orpiment with lead-based pigments and oil as well as egg and gum binders resulted in only very minor alteration, even in humid environments, making it perfectly plausible arsenic and lead-based pigments were used together here, but in layers rather than mixing on the palette as confirmed in cross-section. The SEM image confirms this stratigraphy more clearly and FTIR results confirm the presence of a calcium carbonate and lead sulphate ground layer.

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. 3), but less so than other pigmented areas and in cross-section 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 could suggest a realgar or realgar mix base layer along with a resinous pigment mixed with same black and red lead could explain the thin red base layer, while the Cl peak could derive from soap during episodic cleaning. Trace elements of P picked up by pXRF are not detected on FTIR which discounts the presence of Ivory or Bone black in the surface layer which provided a deep warmer black than carbon-based black pigments (27, 28). Taken together with the C evident on black inclusions in this layer of the griffin eye (below), this is most likely carbon-based, e.g. Lamp Black.

The FTIR of this sample shows the presence of both lead sulphate and a resinous/wax varnish which explains the resinous appearance of this sample, and a hint of proteinaceous material, probably a binider. Smalt is also detected here.

Griffin Eye

Close inspection of the griffin eye reveals white painted directly over the resinous layer with black inclusions that covers the griffin plumage. This has defined eye whites that were then topped with a surface layer of shiny black pigment forming a circular pupil in the centre (Fig. 4). Visible traces of white

pigment are also extant on the crest of the right griffin's head plumage, suggesting all 4 griffin-heads were very likely crowned with white. This stratigraphy is confirmed in cross-section 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.

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 FTIR spectrum of this sample does not definitively detect lead sulphate or lead white (lead carbonate), probably due to the position of the sample and the instrument focus on the lowest layer. FTIR does detect an organic material, likely to be an oil and/or resin, as well as calcium carbonate which exhibits a broad band around 1392 cm^{-1} but additionally an overtone at 872 and around 712 cm^{-1} which are visible on the spectrum. High levels of Cl are also detected here with pXRF and confirmed by EDS mapping in the base layer where Na is detected in the same context which may indicate a size.

SEM imaging confirms the heterogeneous character of inclusions in each layer. EDS detects C in the top black layer, confirming a carbon-based pigment, likely lamp or vine black. EDS further validates the presence of a lead pigment with a strong signal for Pb in both the white band immediately below the black as well as in the base layer interspersed by a calcium-rich layer 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 and S are also present in the white layer, the latter indicating a lead sulphate ($PbSO_4$). 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 confirms a copper-based pigment mixed into one of the layers in this feature, most likely the surface or eye white, but this is unverifiable here. 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 realgar base layer and the white above.

Griffin Rosette

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 was depicted in a different colour, most likely red ochre. 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 and flanked by informal borders in grey/black pigment around the exterior (Fig. 5) and very shiny black pigment in the interior (Fig. 6, 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. 5). In cross-section 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 appears to confirm the central orange-red to be the same pigment on the exterior of the griffins (pXRF13), confirming a layer of red was painted across the 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 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 surface treatments applied to the gilded frame.

SEM imaging shows the heterogeneous character of these layers and EDS mapping combined with targeted spot analyses confirm Pb dominates the base layer with frequent Ca and Si 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 strongly suggests the mixing of red lead and realgar also evidenced on other features.

FTIR results show the presence of calcium carbonate and smalt that has been degraded, as well as lead sulphate and a proteinaceous signal that is indicative of a binder. Taken together, cross section and SEM images suggest the black surface pigment is likely carbon-based similar to the griffin eye pupil, likely lamp black. 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 results do not detect P which renders the possibility of bone/ivory black unlikely. EDS spectra on samples from this surface layer detect Pb and traces of Na, Mg, Cl and Al and Ca in the base layer which, combined with the Pb here, suggest the mixing of red lead and/or lead sulphate and calcium carbonate.

Gilded frame

In cross-section at least 9 stratigraphic layers of pigments are discernible on the gilded frame (Fig. 6), including a white base layer, then a yellowish layer with abundant crystalline inclusions that may constitute seepage or contamination from the base 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. FTIR detects calcium carbonate and lead sulphate as well as hints of an organic binder, the source of which is indeterminate, and quartz or talc.

The presence of Au is as expected given extant surface gilding and W could derive from the yellowish base layer, perhaps as a reflective surface for the uppermost gilding through the subsequent red layers that appear to comprise of realgar and ochre as well as red lead as indicated by the high readings of Pb. However, since W is detected at significantly high levels only where gilding visibly survives this element is likely connected to the gold gilding. 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 which shows no seepage between levels.

All layers are clearly definable in the SEM image which depicts many large inclusions in the base layer of glassy structure. EDS mapping confirms Ca mixed with Pb in the base layer, suggesting the presence of a lead white/lead sulphate mixed with calcium carbonate detected in FTIR. 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 17th century (29) and complex recipes for gilding preparatory layers of orpiment with other arsenic sulphides are known from 15th -16th century German sources, including orpiment, chalk vermillion and hematite (30) or orpiment, red lead and gum (31).

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 (32). In northern Europe during the 13th 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 (32). Bole was used as poliment throughout Europe from the mid-13th century, particularly from the 15th century, and the red colour resulted in a warm tone of the gold gilding applied above (33). White mordant comprised of lead white mixed with other additions is also known from German-speaking countries during the 15th -18th centuries, confirmed in a 15th century manuscript *Cod.*

Pal. Germ. 558 (34), but this is currently only known to have been applied below white metal leaf (23). This tradition of layering later became common during the 17th C 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 the vibrancy of their colour (35). There is no evidence for glaze layers above gilded surfaces common to paintings from this period, but the concentration of Cl and Na 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. 6, 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 extraction of microsamples was challenging due to its sticky pitch-like character. As, Pb and Cu detected here by pXRF likely derive from the smalt-based layers immediately 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 on this sample.

Inscription background

Close inspection reveals a heavily cracked and degraded surface layer across the inscription panel (Fig. 7) 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 which demands more detailed interrogation. Stratigraphically, this blue splash blends into the top-most layer of pigment here and microscopic *in-situ* inspection of various points across the background using a DinoLite microscope confirms a pigment with heterogeneous matrix dominated by brownish crystalline structures 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 (36). Commonly used from the late 15th - early 18th Centuries, smalt is a vibrant blue derived from a potash silicate glass coloured with cobalt and often substituted for more expensive pigments (37). Due to its siccative (38) 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 (37, 39–41). This could explain the grey-brown colour of the inscription panel and cracked surface from shrinkage in a dry museum environment (36).

In cross-section 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. It has not been possible to definitively fingerprint each layer present though it is reasonable to confirm a surface layer of smalt overlying a possible red lead and/or orpiment/realgar.

Two samples were taken from the panel background are, on one the FTIR results confirm presence of smalt and a natural wax is also hinted at, as is calcium carbonate which may derive from a preparatory ground layer. The other sample was taken from the visible blue area and FTIR confirms the presence of a wax, calcium carbonate was not detected, though this was a deliberately surface sample which did not encompass lower layers. These species partly undergo condensation reactions creating more bridging Si–O–Si. As a result, in the FTIR spectra the Si–O–Si stretching appears to become more intense and to shift to higher wavenumber (36). Beeswax has been recorded in the 17th century mixed with smalt to create a high gloss surface to the panel to imitate the more expensive lapis lazuli (42).

Inscribed letters

The letters are painted with a reddish pigment with waxy appearance then overlain with gold gilding (Fig. 8). 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. FTIR confirms the presence of smalt and a hint of proteinaceous material, probably a bole preparatory layer for the gilding, as well as calcium carbonate. There are hints on the spectrum of resin, possibly shellac.

As with the gilded frame, a yellow-ish hue is definable in the base layer with abundant glassy inclusions in cross section (Fig. 8). 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 confirms this stratigraphy and EDS mapping clearly detects C throughout the sample, with As 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 and Pb above confirming a penultimate bole layer consisting of iron oxides mixed with realgar and red lead immediately below the surface gilding. Pb is also dominant in the base layer along with Ca which suggests a preparatory layer of lead sulphate and calcium carbonate mix.

‘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).

Concluding Remarks

This vanguard research has successfully deployed a suite of analytical techniques to fingerprint surface treatments applied to a unique Classical 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 results are reported as found with little or no speculation. These have drawn out a palette of the pigments present (Table 1) and identified complexities in their mixtures, stratigraphic layering and application (Table 2) 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 19th century (43). The palette comprises white, reds, black, blue, yellow and gold which, perhaps unsurprisingly, reflects contemporary tastes for colours applied to architectural features, statuary (44) and framed paintings (33, 45) combined with the antiquarian penchant for the collection and display of Classical sculpture (46). This has facilitated an authentic digital reconstruction of the sculpture in full polychromy for publication in a future article (10).

Table 2

Stratigraphic Sequences on Polychromy on GLAHM.F1

Feature	Visible Colour/s	XRF Elements	FTIR	Pigments Present	Cross Section Stratigraphy (top to base)
Ivy tendril	Light creamy-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 & Red Ochre *
Griffin groove	Grey-black	As, Pb, Cl Low Al	Lead Sulphate, Smalt, Wax or Resin, Proteinaceous material (binder?)	Realgar, Red Lead, Carbon Black	1 Carbon Black & Resin/Wax* 2 Realgar & Red Lead 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 & Lead Tin Yellow* 3 Carbon Black, Resin/Oil & Calcium Carbonate* 4 Realgar & Red Lead OR Lead Sulphate*
Flower petal in griffin	No colour visible	Fe, Cl, Mg Trace Pb Low, Ca, S	No micro sample	Red Ochre	No micro sample
Centre of flower in griffin	No colour visible	Trace Pb Low Ca, S	No micro sample	None identified	No micro sample
Flat area beside griffin	Medium brown	As, Pb, Mn Low Ca	No micro sample	Realgar, Red Lead	1 Realgar & 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, Smalt (degraded), Proteinaceous material (binder?)	Carbon Black, Realgar, Red Lead, Lead Sulphate, Calcium Carbonate	1 Carbon Black 2 Realgar & Red Lead * 3 Smalt, Red Lead and/or Lead Sulphate & 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)	Calcium Carbonate, Lead Sulphate, Resin Organic binder (hint)	Gold gild, Red Ochre, Carbon Black, Resin/ Wax, Realgar, Red Lead, Lead Sulphate, Calcium Carbonate, Orpiment?	1 Gold Gilding 2 bole with Red Ochre & Carbon Black * 3 resin or wax 4 same as 2 5 same as 3 6 same as 2 7 Realgar & Red Lead * 8 Lead Sulphate & Orpiment? * 9 Lead Sulphate & Calcium Carbonate? *
Internal border of carved inscription frame	Black	As, Pb, Cu Low Ca	Natural Wax	Carbon Black, Smalt, Wax	1 Carbon Black & Wax * 2 Smalt & Wax *
Inscription panel background	Grey-brown	Ba, Sn, Bi, As, Pb, Cu, Ni, Co, Mn Low Ca, Al	Smalt, Wax or Resin, Calcium Carbonate (hint). Blue spot – Wax, Smalt	Wax Smalt Red Lead	1 Smalt & Wax* 2 Red Lead

				Orpiment	3 Orpiment? & Calcium Carbonate *
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?)	Gold gild, Realgar, Red Lead, Red Ochre, Smalt, Lead Sulphate, Calcium Carbonate, Resin/wax (hint)	1 Gold Gild 2 Realgar, Red Lead & Red Ochre * 3 Realgar 4 Orpiment 5 Smalt 6 Lead Sulphate & Calcium Carbonate* Resin/wax? (layer uncertain)

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 (47, 38) 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 letter, 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 more layers, including the complexities and diversity evident in base layers of some features that may be associated with original pigments applied in Antiquity. 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

Al - aluminium

As - arsenic

Ca - calcium

Cl^{-1} - chloride

Cr - chromium

Cu - copper

K - potassium

Rb - rubidium

S - sulphur

Sn - tin

Sr - strontium

Ti - titanium

Zn - zinc

Zr - zirconium

$CaCO_2$ - calcium carbonate

$PbSO_4$ - lead sulphate

Declarations

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

Competing Interests

The authors declare that they have no competing interests.

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Authors' Contributions

The concept for this research derived from LC's work. LC undertook exploratory pXRF and the historical/archaeological research relating to the sculpture and samples; extracting and embedding the samples for cross section and SEM/EDS analysis; microscopy and microphotography. 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.

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Table

Table 1 is available in the Supplementary Files section

Figures

Figure 1

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

Figure 2

Ivy tendril. A) Detailed image; B) Microsample; C) LM cross section; D) SEM image (scale on images)

Figure 3

Griffin peltae plumage. A) Detailed image; B) In situ microphotograph; C) LM cross section; D) Microsample (scale on images)

Figure 4

Griffin eye. A) Detailed image; B) In situ microphotograph; C) Microsample; D) LM cross section; E) SEM image; F) EDS Mapping (scale on images)

Figure 5

Inscription panel frame – grey/black exterior. A) Detailed image; B) Microsamples; C) In situ microphotograph; D) LM cross section; E) SEM image and EDS Mapping (scale on images)

Figure 6

Inscription panel frame – gilded frame. A) Detailed image; B) In situ microphotograph; C) Microsample; D) LM cross section; E) UV Cross section; F) SEM image; G) EDS Mapping (scale on images)

Figure 7

Inscription panel background. A) Detailed image; B) In situ microphotograph; C) In situ microphotograph of blue splash; D) LM cross section; E) Microsample; F) SEM Image (scale on images)

Figure 8

Gilded letters. A) Microsample; B) In situ microphotograph; C) and D) LM cross sections; E) SEM Image; F) EDS Mapping (scale on images)

Supplementary Files

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- AppendixIpXRFanalysisspots.docx
- AppendixIpXRFresults.xlsx
- AppendixIIMicrosamplelocations.docx
- AppendixIIIFTIR.docx
- Table1.docx