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ASSESSMENT OF GEORGE STUBBS' PORTRAIT OF JOSEPH BANKS

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Abstract

By the mid-1760s, George Stubbs had matured as a master of human and animal painting. One example is his large oil-on-canvas portrait of the great botanist Joseph Banks on his inheritance. Electron microscopy with atomic scatter was carried out on a sample of paint and varnish from the edge. This demonstrated iron, calcium, carbon and oxygen ratios such that Stubbs must have used Black Ivory and Burnt Sienna color pigments in a nine-to-one ratio for his dark brown background. The absence of wax globules substantiates the received wisdom of Stubbs commencing its addition from 1767 and matches the date of the portrait being shortly after Banks' 1764 inheritance. Stubbs was observed to have used evenly plasticized linseed varnish without lead drying agent or markedly carbonized burning. This was of high quality compared to a varnish applied on relining decades later. The same appearance implied pure linseed in Stubbs' oil paint ground. Stubbs' skill in art materials to a clear scientific degree reflects his academic ability as an anatomical scientist. These are inexpensive, new findings on Stubbs' painting and varnish technique, with the potential to help conservators and researchers working on other important canvases by the great artist.

Keywords: *George Stubbs; Joseph Banks; Electron microscopy; Atomic scatter; Black Ivory; Burnt Sienna; Linseed oil varnish; Brush technique*

Introduction

Joseph Banks had his portrait painted by George Stubbs (Fig. 1), depicting his 1764 inheritance [1]. It is oil on canvas and signed. Stubbs' full-size portraits of people from the late 1750s and early 1760s represent his artistic maturation but have been repeatedly overlooked and are sometimes unsigned. Surprisingly, for such beautiful and important works, they usually lack published technical investigation for comparative identification, restoration, or research. There has been more attention to Stubbs' horse paintings and their materials. Stubbs's human portraits must have been more numerous than appreciated in his artistic career before his great equestrian painting popularity, termed the 'lacuna years' by *Anthony Mould* [2].

Later, Stubbs evidently put wax in his paint from around 1767 and altered his drying oil from 1783 [3]. This was substantiated by the analysis of ten of Stubbs later paintings by The National Gallery, London [4]. In Stubbs' *Hambletonian, Rubbing Down*, of 1800, investigation implied modified drying oil technique well into his late phase [5].

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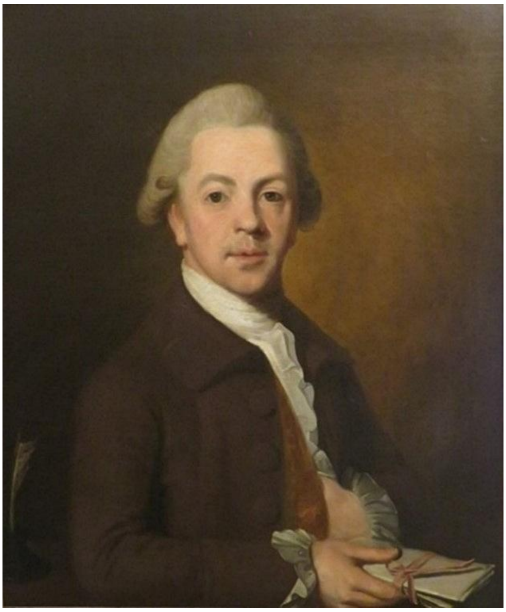

Fig. 1. Joseph Banks on his inheritance by George Stubbs

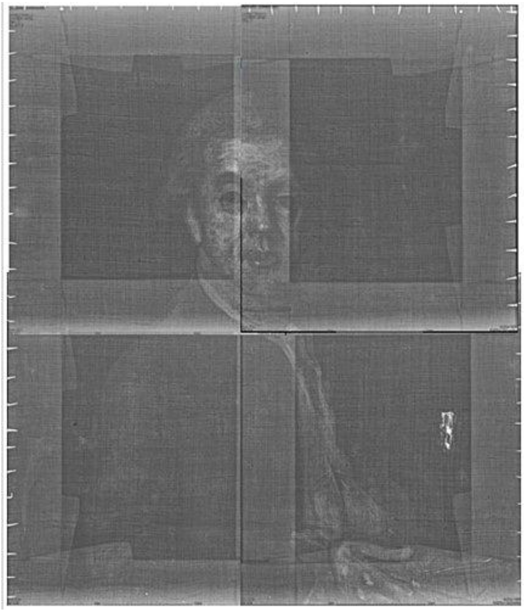

Fig. 2. X-ray of the portrait

Previous X-ray of the index painting had revealed an underlying sketch with the characteristic radio-opacity of white lead paint (Fig. 2). This is published here in full for the first time. Stubbs had not just laid out planning lines, proving originality, but he sketched remarkable anatomical details, like one of his dissections, especially in some of the facial musculature. This was discussed from a medical and psychological perspective in an earlier paper [1]. Stubbs used white lead sketching of the figure throughout the canvas. Radio-opaque bone glue showed up in a historic repair, bottom right. The painting was relined, recoated with varnish and reframed, probably in Banks' lifetime during the Regency period. This was inferred by the complex, personalized botanical and nautical frame iconography referring to Captain Cook's first voyage after Banks' inheritance, which funded his exploration. That was also consistent with a period of the painting being stored, suffering some plaster loss to the top of the frame and requiring patching, quite possibly following the death of Banks' mother, Sarah, who, by all evidence, appears to have had the picture for most of Banks' life.

The study aimed to ascertain the structure and composition of Stubbs' characteristic dark brown portrait background color for the first time from micrographic and atomic pigment characteristics, along with a search for potentially datable, visible globular wax content known from previous research. The secondary aim was to investigate characteristics of Stubbs' and the restoration varnish. Linseed oil was used in the main for oil ground in paint and in varnish in England at the time and had long been predominant in northern Europe [6, 7]. Poppy and walnut oils were generally used earlier [8] and their use lasted longer in southern Europe, after proliferating in the Renaissance, with some application for specific colors [9]. Due to pronounced yet variable oxidation on drying, linseed oil's atomic composition in art analysis can be misleading, and triglyceride molecules alter to different compounds chromatographically. Besides atomic analysis, we anticipated from the start that electron micrographs of varnish were important. Also, explorative, non-hypothesized observation sought potential visual and chemical factors for unforeseen lessons and future comparisons with this rare, signed portrait.

Materials and Methods

The painting on its antique stretcher was removed from the frame. A 1×3mm paint and varnish sample was taken in the UK from the edge of Stubbs' characteristic portrait dark brown background, from the top left, sourcing an area usually invisible behind the frame rebate. This size was planned to be appropriate for scanning electron microscope micrographs and X-ray emission scatter atomic profiling. The sample was stored and transported in a boxed, jiffy-bagged, tight-lidded, new, clean petri dish. The investigation was done at Khon Kaen University, Thailand, by the research collaborators of the education project, Baan Dong Bang Museum (BDBEC), which owns the painting, though it remains in the UK. The sample was subdivided into four pieces in the laboratory to increase areas of analysis. It was not fixed in the matrix but adhered to copper tape on mount block discs.

A TESCAN Mira 3rd generation field emission scanning electron microscope (SEM) [10] was used. This image characterizes the surface of an object by beaming electrons, resulting in a 3D micrograph image. Built-in Energy Dispersive X-Ray Spectroscopy (EDS) additionally analyzes the chemical components of surface materials, defining proportions of atomic elements from detecting the emitted X-ray scatter pattern after electron impact and displacement, so-called atomic scatter.

A comprehensive visual survey and electron micrography of the surface images at different magnifications were carried out with thorough, careful, thoughtful inspection and running discussion, making concurrent written laboratory notes. We found that this attitude to observation boosted enthusiasm and helped notice more findings. The block was then removed from the drawer with the samples remaining adhered and not moved. Gold was applied by spraying onto the samples on their original copper tape in a vacuum chamber for electron-induced x-ray scatter of regions of interest (ROIs). This allowed further electron micrographs with 5, 10 and 15KeV beam energy in resolution scan mode for the defined fields. These regions generated atomic scatter graph peaks, relating to inner K, central L and outer M electron shells of the atoms. These shells are the electron orbital layers from where an electron is scattered with X-ray emission on impact from the incoming primary electron beam. Surface detection mode is indicated as SE on the electron micrograph data bars, with collected image data and regions of interest comprising an image-specific micron scale, magnification (Mag), beam current (BC), field of view (FoV) and working distance (WD).

The contingent percentage composition tables comprised the atomic element or elements detected from scatter, the percentage of specific element atoms amongst all atoms detected and the percentage of weight of each element in the sampled area. Whilst pie charts were also generated, they only duplicate the other data in a different graphic form, so these are omitted from publication. Atomic proportions derived from the scatter were compared with known coeval pigment mineral atomic ratios for identification. The whole process of sampling and microscopy of the index portrait was photographed for verifiability (Fig. 3). The research group wanted not only to demonstrate but also exemplify pictorial recordings of the process, especially with such a rare painting.

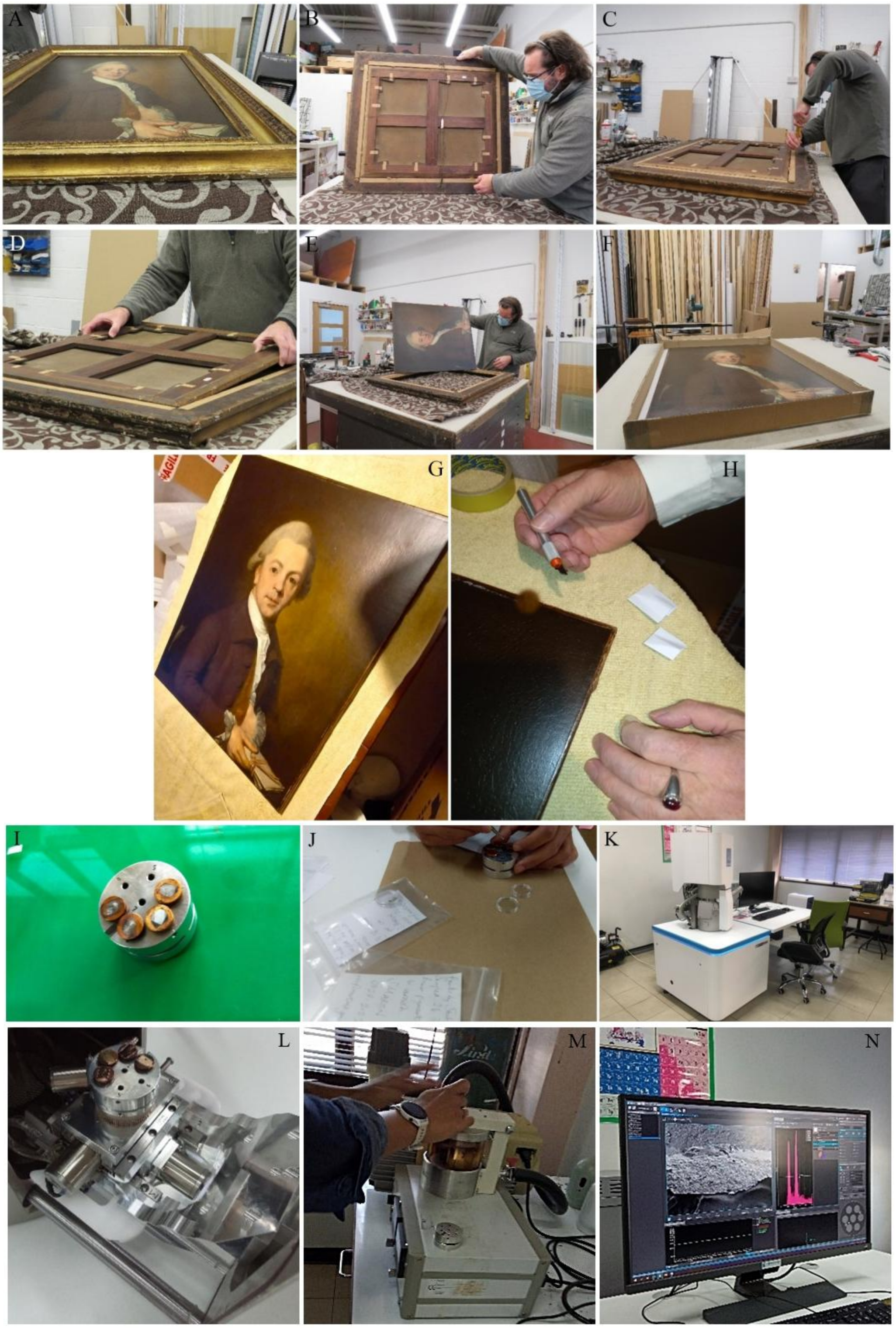

Fig. 3. Method process. A-H: sampling behind rebate. I-N: TESCAN Mira 3 SEM-EDS, Khon Kaen University

Results and Discussions

Whole section

A representative whole sample section is shown in figure 4. This illustrates the conservation varnish topcoat surface, with a right-angled planar loss fractured off top left, revealing the original varnish coat's outer surface underneath. Both varnish coats are colorized here post hoc as linseed oil for illustrative purposes. The dark brown background paint matrix forms the undersurface, also with illustrative post-hoc colorization. Any coloring of SEM has a degree of subjectivity, as electrons and X-rays, not light, are emitted. Here the colors are selected from the varnish on the edge of the original painting and from the dark brown background. This whole cross-sectional sample illustrated is 1mm across and variably 200-300 microns thick. The complete varnish layers are c. 50 microns in depth and the paint is c. 120-250 microns in depth. The large, lower right indentation reflects a single, spun and woven canvas thread impression in the paint of about 800 microns across, as opposed to a much smaller individual flax fiber width.

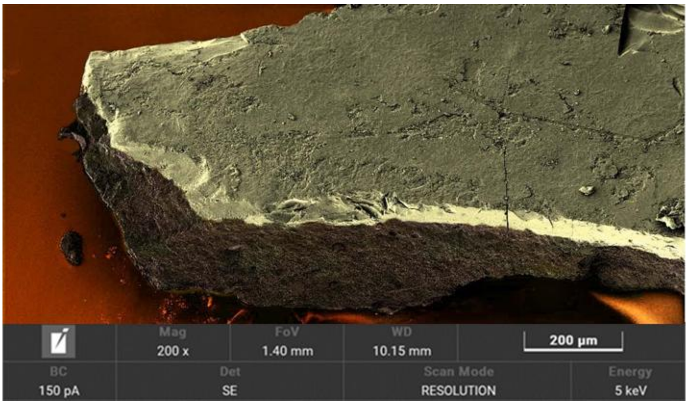

Fig. 4. Section of whole sample showing varnish and paint ground in electron micrograph

Varnish

The top layer of conservation varnish had extensively powdered into yellow dust on sampling to the naked eye. Micrographs of its deepest levels on top of the original varnish had almost pure carbon scatter patches, especially in over twenty multiple, highly cracked, darker image zones, too numerous to warrant every image. Three examples are illustrated (Fig. 5). These were all clearly embedded flush within the surface, some being interspersed. They were not scattered like superficial dirt contaminants, as might be seen with atmospheric chimney soot particles.

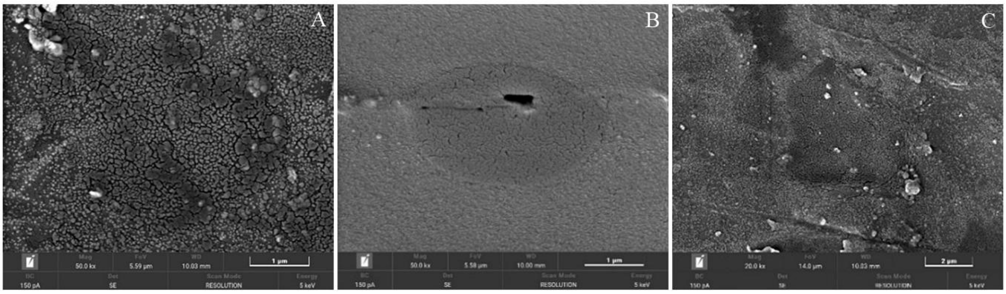

Fig. 5. Electron micrographs of cracked restoration varnish surface, incorporating carbonized burnt patches

The deepest level of conservation varnish and its interface with the original varnish underneath showed visible, scattered globules of around 50 nanometer diameters (Fig. 6A). The globules cast shadows. One image appeared to show these globules on the interface of restoration varnish on top of brush stroke indentations in the original varnish (Fig. 6B). Varnish with extensive fine cracking is shown across the bottom of the electron micrograph (Fig. 6C), with pure carbon and visible globules adhered to the ripple-fractured surface of the deeper original varnish in the top of the image. Here again, the globules were visible in the deepest part of the conservation layer, on top of the original varnish and had apparently failed to plasticize. A central line in this image appeared to demonstrate the full thickness of restoration varnish.

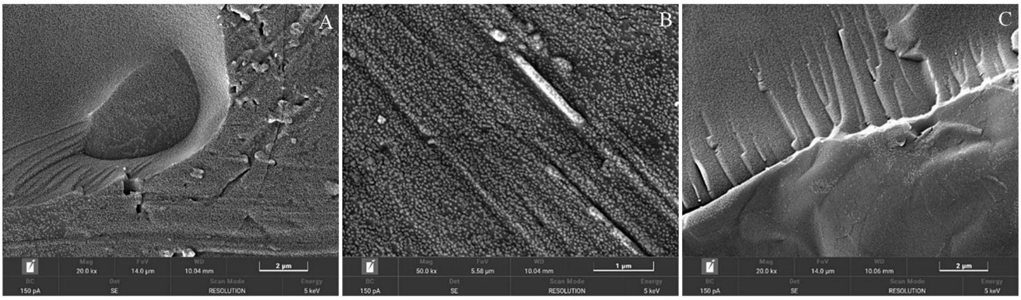

Fig. 6. Electron micrographs from the interface of the original and restoration varnish

There was no atomic lead on or in any varnish images, neither particulate nor on whole field scatter analysis, with regions of interest drawn as widely as possible. The restoration varnish's deep remaining surface, despite the multiple dark areas of very high carbon peaks, had C to O in a circa 6 to 1 ratio on wide-field analysis after subtracting trace calcium carbonate proportionally (Fig. 7 and Table 1).

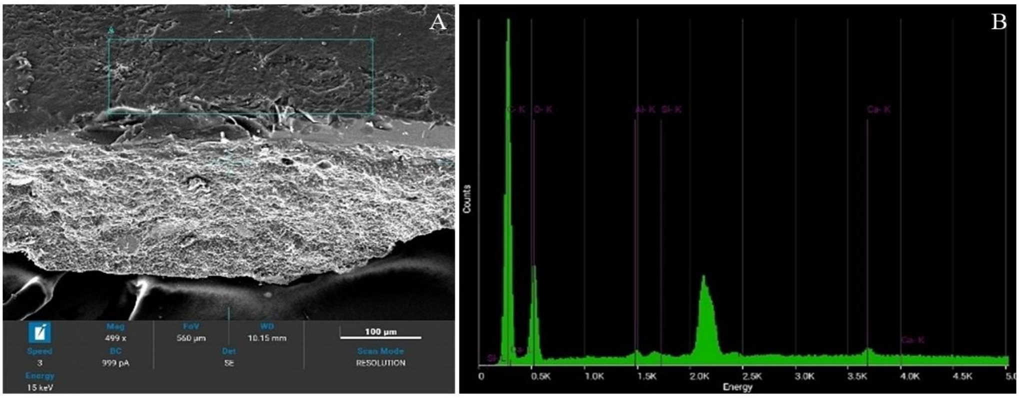

Fig. 7. Electron micrograph of restoration varnish surface ROI and associated atomic scatter plot

Table 1. Atomic composition and weight percentages of elements in restoration varnish surface ROI from Figure 7

Element	Atomic (%)	Weight (%)
Carbon	78.25	69.53
Oxygen	19.02	22.51
Calcium	2.59	7.67
Aluminum	0.08	0.16
Silicon	0.07	0.14

As linseed oil dries and polymerizes in air at room temperature, it oxidizes, distorting the original carbon to oxygen ratio in the direction of more oxygen to less carbon [11, 12]. It may be that the principal component triglyceride linolenate, usually comprising over half of linseed oil molecules, oxidizes in particular, but the process is not completely understood. This sample was clearly super-oxygenated from original C:O ratios in Linseed's five lipid components, given in Table 2.

Table 2. Carbon:Oxygen ratios of linseed oil triglyceride components before oxygenation on drying

Linseed Oil Triglycerides in descending order of % component	Formula	Carbon:Oxygen ratio
Linolenate	$C_{18}H_{36}O_2$	9:1
Oleate	$C_{18}H_{33}O_2$	4.5:1
Linoleate	$C_{18}H_{31}O_2$	9:1
Stearate	$C_{18}H_{36}O_2$	9:1
Palmitate	$C_{16}H_{32}O_2$	8:1

While the approximate C:O 6:1 ratio detected is closest to oleate, it is only a small component of linseed oil and it does not explain the high oxygen proportion. Interestingly, this oxygenation effect on the C:O ratio is more than compensated for by higher carbon in the pure carbon patches. Calcium on surface varnish was probably from frame plaster.

One sample edge (Fig. 8A) had a fragment of canvas cellulose fiber on varnish. The 1-micron-wide branching appears to be flax, rather than 10-micron-wide, smoother-stranded, transverse-rippled and much less ramiform linen [13], revealing eighteenth-century canvas technology immediately behind the paint. This was substantiated by two other fragments from areas on the edge of the sample adhered to varnish, apparently incorporating original and restoration canvas areas. One (Fig. 8B) again showed 1 micron-wide branching flax fibers on varnish. Another (Fig. 8C) revealed 10-micron-wide, apparent linen fibers with fluting, in fragments of poorer quality varnish, from the conservation relining canvas [14, 15]. Figure 9 shows a discernible portion of intact restoration varnish, colorized as linseed pale yellow.

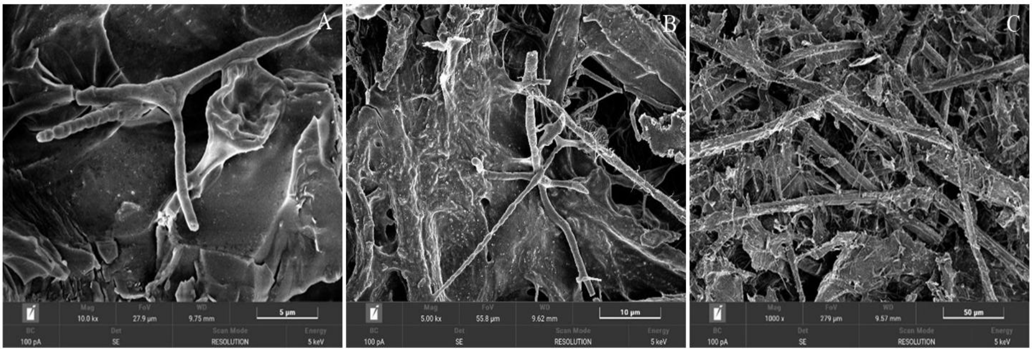

Fig. 8. Flax (A, B) and linen (C) fibres in plasticised linseed oil varnish

The deeper, original varnish of Stubbs was well-preserved, with consistent plasticization, rippled edge fracturing from the sample cut and a general absence of globules. Interestingly, this layer also showed obvious brush hair stroke evidence applied at 90 degrees and built up in layers. The uppermost stroke from the bottom right up to the center left in figure 9 might represent the larger part of a single hair width.

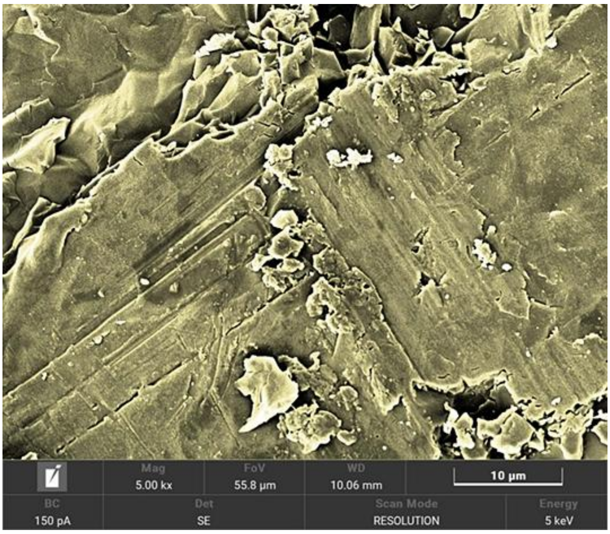

Fig. 9. Original varnish surface showing layering and 90-degree brush strokes with hair and particle streak impressions

One image of the homogeneous original varnish showed two fracture planes parallel to the paint and canvas as lines of holes apparent tangentially to the sharp laboratory cut, which implies that Stubbs painted three coats of varnish (Fig. 10). The first two varnish coat depths were around 10 microns, with a final topcoat of around 20 microns. A thicker final application could be allowed longer to dry exposed to the air.

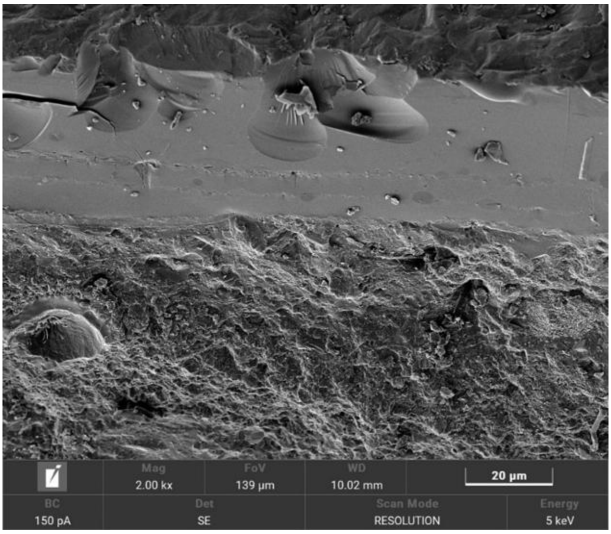

Fig. 10. Triple-layered original varnish, the outer most being double thickness for slow drying

Paint Ground

Paint ground showed many ROI's of high carbon and calcium carbonate component peaks on atomic scatter analysis in the expected chemical formula ratio of $CaCO_3$ with considerable additional carbon. Individual particles included a non-embedded varnish fragment of linseed oil appearance, as polymerized varnish resembling broken plastic, presumably from the surface varnished on sample cutting. This appears in figure 11 lower right. There were large quantities of chaotically strewn, flat, square crystals with rhomboid corners, which were calcium, carbon and oxygen in a calcium carbonate ratio, with some lamellar aggregate swirls. This is explained as the product of dental mineral from heat-denatured ivory, making black pigment. Ivory collagen fibers burn, forming black carbon in the calcium carbonate matrix. Some of these were stacked in rings (Fig. 12).

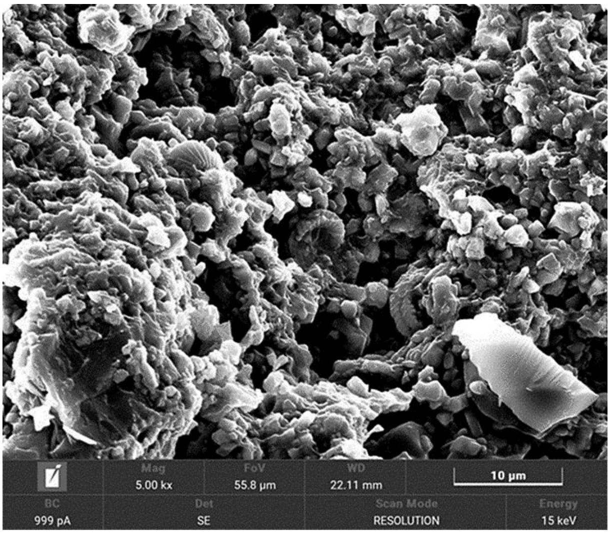

Fig. 11. Paint ground of calcite crystals, some in rings, with plasticized stray surface varnish fragment lower right

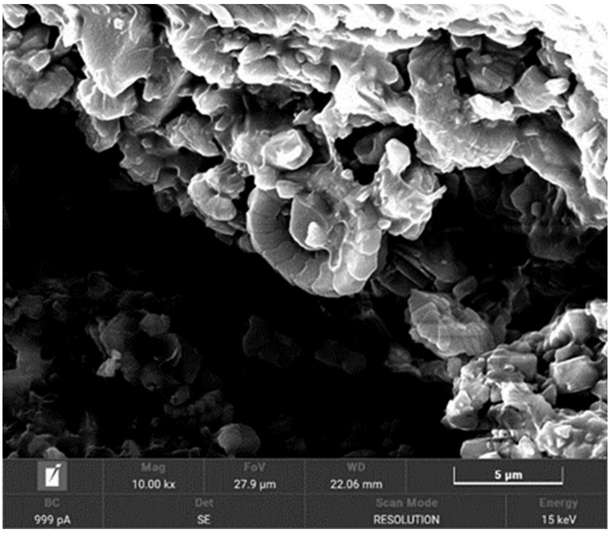

Fig. 12. Ring of calcite crystals in paint ground

They too were calcium carbonate on element proportion analysis, so, given the flattened appearance with rhomboid corners, these are calcite crystals (Fig. 13 and Table 3).

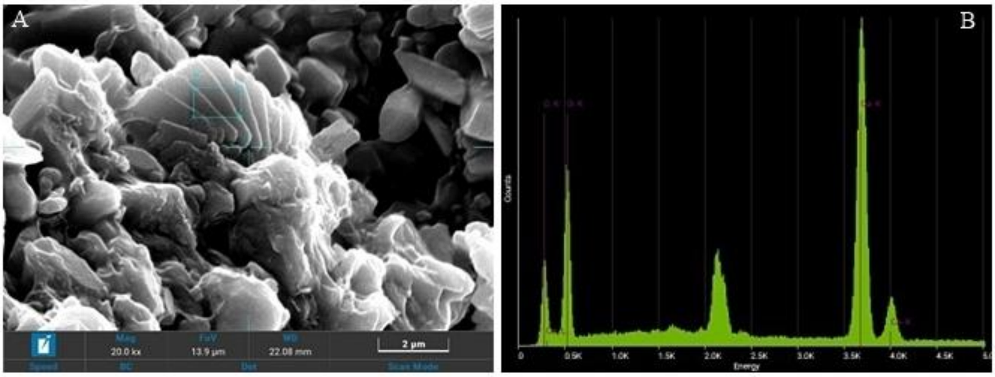

Fig. 13. Electron micrograph of stacked rhomboid calcite crystals ROI and associated atomic scatter plot

Table 3. Atomic composition and weight percentages of elements in calcite crystals from ROI in Figure 13

Element	Atomic (%)	Weight (%)
Oxygen	46.58	35.98
Carbon	29.04	16.84
Calcium	24.38	47.18

The homogeneous matrix had high carbon atomic scatter throughout, consistent with burnt collagen. Several oval calcium carbonate bodies had varied spicules and some clear lacunae (Fig. 14).

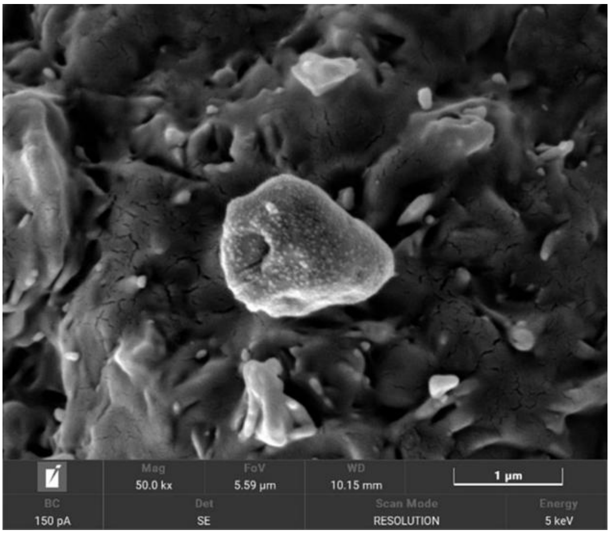

Fig. 14. Electron micrograph of lacunated calcium carbonate particle

One globule had lost all tubules but retained an ovoid shell shape with an internal tetrahedral spike appearance. It was calcium carbonate on scatter, besides ground soil trace elements (Fig. 15 and Table 4).

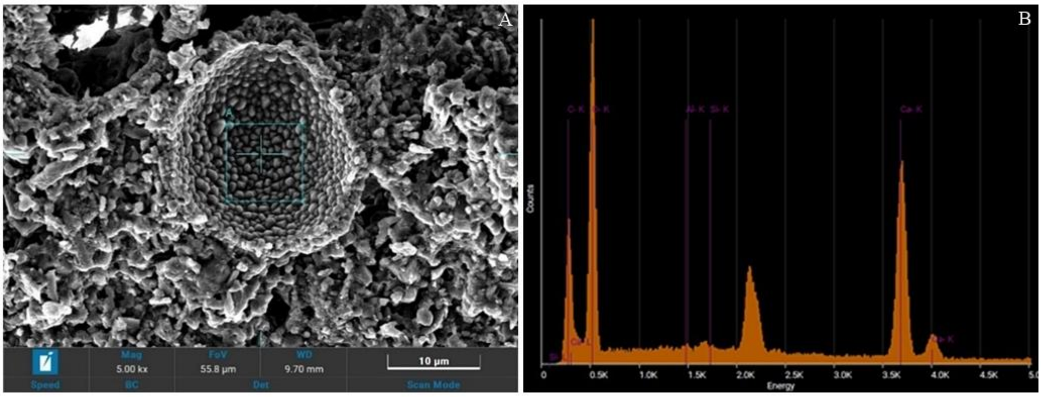

Fig. 15. Electron micrograph of ovoid calcium carbonate formation ROI and associated atomic scatter plot

Table 4. Atomic composition and weight percentages of elements in ovoid calcium carbonate ROI from Figure 15

Element	Atomic (%)	Weight (%)
Oxygen	44.68	33.48
Carbon	28.09	15.80
Calcium	26.57	49.87
Silicon	0.43	0.57
Aluminum	0.22	0.28

A similar globule with partial spicules arising from a globule was seen in isolation in the paint matrix (Fig. 16).

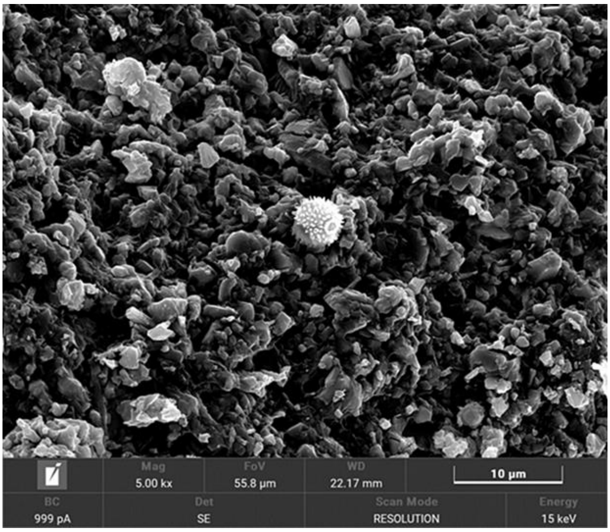

Fig. 16. Calcium carbonate particle in globular spicule-tubule formation of dentine

It was 5-micron diameter and also demonstrated calcium carbonate proportions with some soil trace elements (Fig. 17 and Table 5).

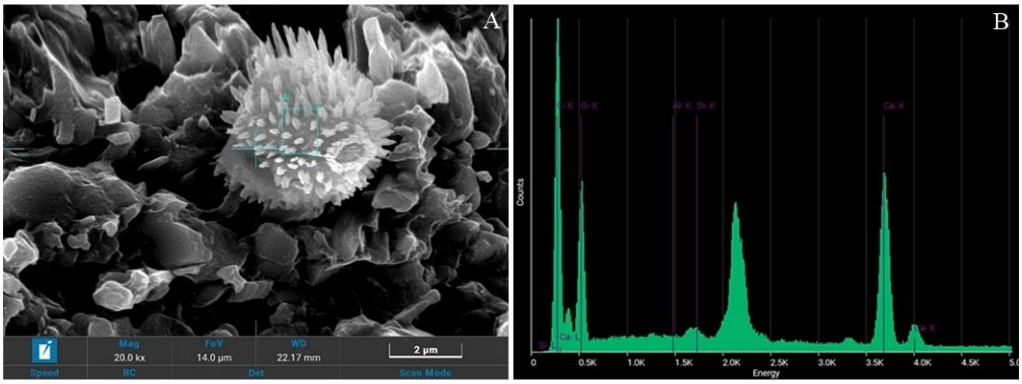

Fig. 17. Electron micrographic ROI of apparent dentine particle and associated atomic scatter plot

Table 5. Atomic composition and weight percentages of elements in dentine ROI from Figure 17

Element	Atomic (%)	Weight (%)
Carbon	65.64	50.96
Oxygen	25.44	26.31
Calcium	8.43	21.85
Silicon	0.38	0.69
Aluminum	0.11	0.19

A single, isolated cubic crystalline particle was observed amongst smaller calcite crystals, below an area of embedded plasticized linseed. The particle contained the only lead detected anywhere, with some calcium carbonate and, proportionally from atomic percentage, much additional carbon (Fig. 18 and Table 6).

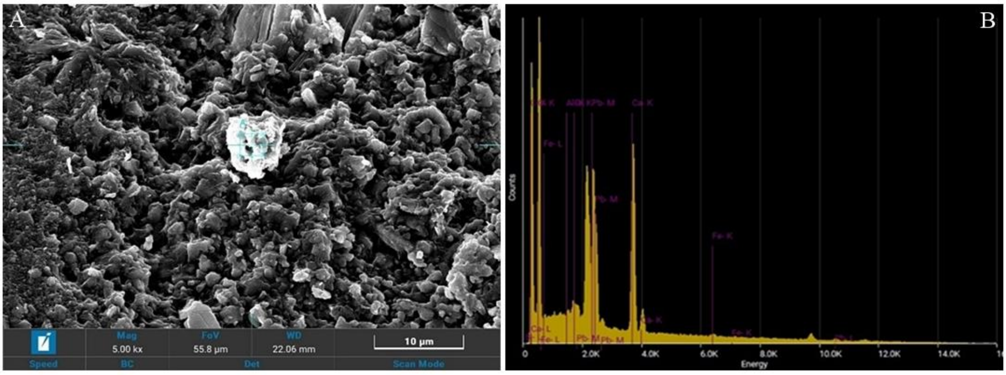

Fig. 18. Electron micrographic with ROI of lead particle and associated atomic scatter plot

Table 6. Atomic composition and weight percentages of elements in lead compound particle ROI from Figure 18

Element	Atomic (%)	Weight (%)
Carbon	57.13	25.53
Oxygen	27.54	16.39
Calcium	7.80	11.63
Lead	5.62	43.35
Iron	1.08	2.25
Silicon	0.45	0.47
Aluminum	0.37	0.37

This was the only fragment with this appearance showing any lead on scatter and the only lead detected anywhere in the wide field ROI in all of the paint or varnish. White lead is a lead carbonate complex of $2PbCO_3 \cdot Pb(OH)_2$. The image of the particle partly resembles the aggregated cubic crystals of galena, which is lead sulphide, but no sulphur was detected in this particle or anywhere else.

A wide-field study at different magnifications found no other lead particles or lead scatter signal at all in any paint or varnish.

When a large area ROI of paint ground bordering the original varnish, cut at an oblique angle to the varnish surface, was analyzed for scatter, iron was detected, demonstrating a ratio of around one to nine with calcium (Fig. 19 and Table 7).

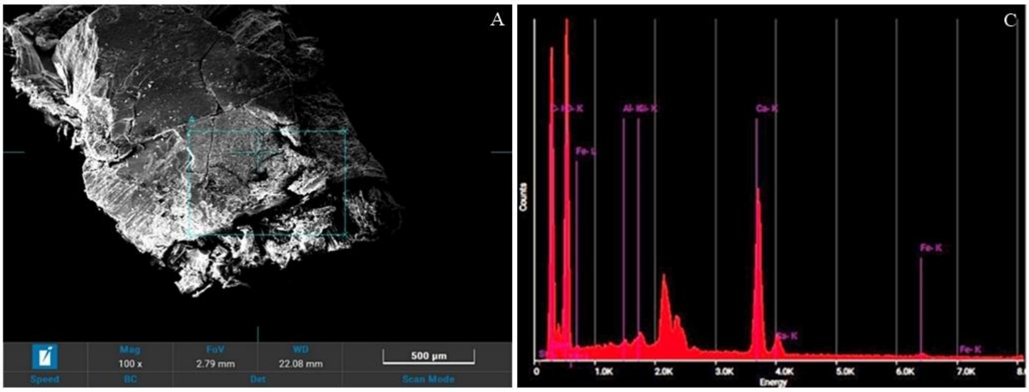

Fig. 19. Electron micrograph with wide field ROI of iron-bearing paint ground and associated atomic scatter plot

Table 7. Atomic composition and weight percentages of elements in paint ground wide field ROI from Figure 19

Element	Atomic (%)	Weight (%)
Carbon	56.74	43.27
Oxygen	35.10	35.66
Calcium	6.72	17.10
Iron	0.80	2.84
Silicon	0.43	0.77
Aluminum	0.21	0.36

Other non-pigment soil elements found in this wide field sample included nitrogen, silicon and aluminum. The atomic percentages, in paint and varnish, are consistent with ratios for Ca (6.7) C (6.7) O (20) in Calcium carbonate ($CaCO_3$) of Burnt Ivory, with extra carbon and oxygen from oil and collagen.

No wax globules were observed anywhere in the entire paint section surfaces at the 5–10-micron level of resolution on surveying the complete field areas. [7] Interestingly, there was also some friability of 70 x 30-micron fragments of the brown paint ground onto the copper tape, as seen at the bottom of the electron micrograph in figure 4.

The apparent oil in the paint base was wedged between pigment particles in layered sheets, identical in plasticization, scatter and fracture patterns to Stubbs' original surface varnish. These were occasionally seen in varying sizes of piled laminae or planar sheets embedded in the pigment, as observed around the lead particle in figure 18. Though not necessary with this picture, such polymerized triglyceride binding material, in its visible area ratio to pigment ground area, can be important in attribution or authenticity research in attempting to characterize an artist's mixing formula. Here the pigment to ground area ratio is around 1:12. With such an image, analysis of scatter for every square micron in multiple wide fields is possible. Researchers have recently proven the worth of this ratio application in comparative authentication and identification [14-16]. It warrants more investigation.

Paint and canvas

Stubbs' brown background pigments in wide field matched the iron of Burnt Sienna and carbon-calcium carbonate of Black Ivory, in an approximate 1 part Burnt Sienna to 9 parts Black Ivory mix. The atomic elements and proportion ratios observed did not match the chemical formulae proportions of any other contemporaneous pigment minerals. The traces of silicon, nitrogen and aluminum are typical soil elements as accompaniments of ground-derived Burnt Sienna's iron-rich mineral. They are not key constituents in any coeval pigments. Silicon does, however, bind into some natural plant oils. Nitrogen could have accompanied canvas cellulose, though it per se is a complex carbohydrate, unlikely to be in the central paint ground. It was clearly present at the edge. Egg white albumen in paint ground stiffening is another possible source of nitrogen, though hard to explain in these trace quantities.

From the micrographs, the original canvas was flax and the later restoration lining was linen. The original canvas being flax fits the date of the painting. Linen typifies a later Regency restoration date, consistent with Banks' old age, having perhaps acquired the painting after some time in storage following the death of his mother and hence the need for restoration linen relining.

The non-crystalline, spicule-lacunar ovoid particles of calcium carbonate can only have been mortar-ground and burnt ivory in Black Ivory color, around 4-5 microns across, preserving some of the original anatomy of the dentine and not completely destroyed on burning. In general, though, complete carbonization and calcite crystallization were seen throughout almost all of the paint ground matrix. The dental fragments could be original particle sizes from mortar grinding or reduced cores after burning. The odontoblast tubules and intertubule dentine spicule remnants, normally rich in collagen, were striking in some of these scattered anatomical particles.

The globule, which had lost all tubules but retained its ovoid shape with the internal tetrahedral spike appearance, appears to represent a combination of incomplete collagen burning and calcium carbonate spicule deformation, but not true tetrahedral crystals, as that would not be characteristic calcite crystal morphology. Modern preparations of Black Ivory contain Bone Black and Prussian Blue, inconsistent with the historic pigment having any dental microanatomy. Diesbach had already discovered Prussian Blue in the first decade of the eighteenth century, but none of its constituent cobalt was found in this sample. Additionally, modern bone is excluded, as it has calcium hydroxyapatite containing phosphate. No phosphorus was detected in these samples.

The annular morphology of multiple calcite crystals begs the question of ground ivory cores shaping the ring formation. This appearance still has identification potential and conservation planning implications for material choice [17, 18]. Understanding dynamic chemistry over time within art materials is important but seldom addressed [19]. The recent findings of possible iron and fatty acid interactions in historic paint are a helpful example, though [20]. Dynamic calcite formation over time at some point in the art material process needs more research.

The high-carbon paint matrix overall fits linseed in paint ground and burnt collagen from ivory.

No chromium was found, but as an early nineteenth-century choice for potential yellow in lighter brown, it was not expected with the date of this painting.

The single lead-containing particle may have come from the palette from the time of Stubbs' underlying white lead planning sketch found radiographically. It would not have colored the general background. It appears to be stray material, especially as iron contaminant was with it, also potentially from Burnt Sienna on the palette. No lead was seen in particles or revealed atomically on wide-field scanning in the varnish. This excludes leaded drying oil at the time of this painting.

We had considered mercury-based Vermilion as a possibility in the brown background mix. It was in use well before Stubbs' time, but no mercury was found. Did he know it was toxic and avoid it, or was it just too much of a bright red color for neutral dark brown? Stubbs certainly had the medical ability to work out mercury toxicity. Mercury was used historically in tanning, which surrounded Stubbs' father's profession as a leather finisher.

The uniform plasticization of apparent linseed in the paint ground may have been assisted by its storage in a small conical tin, wedged into a palette hole [21], though there is no direct evidence for Stubbs using that technique and no tin was detected, which might have occurred as a sparse contaminant.

The appearance in these images of linseed oil in paint and as varnish, besides the appearance of particulate lead, burnt ivory anatomical fragments, calcium carbonate crystals and canvas fibers, may assist other investigators.

Inspection of potential wax globules

The only distinctly demarcated areas showing high carbon were in calcium carbonate crystals, denatured ivory globules, plasticized linseed, or obvious burnt restoration varnish. Diffuse, very high carbon within the amorphous general paint ground was explained by burnt ivory collagen. No other observable areas of distinct morphology showed any different appearance or yielded high carbon scatter. Stearate can retain a 10-micron diameter globular appearance in paint ground [22]. Stubbs had not apparently added wax or lipid beyond visible linseed inclusions for paint ground, matching the varnish appearance. The absence of any visible wax globules fits Stubbs' pre-1767 techniques, after which he added waxes. They can potentially enhance paint shine and elasticity. Banks inherited in 1764, so the apparent finding of no positive evidence for wax substantiates both dates being close together. It also fits Stubbs' phase preceding leaded drying oil.

The observed friability of some of Stubbs' paint ground crumbling onto the microscope blocks could have been one of several reasons for his later use of wax. Other reasons were later use of different media, including enamels, with painting on wood and ceramics. Though the index painting has no losses, it is possible that its craquelure, amongst other relatively early Stubbs pictures, could have been perceived by Stubbs early on in this and other works as being related to excess fragility and therefore something to improve in later works of his, with wax addition for enhanced adhesion and elastic flexibility. Patchy visible linseed as seen in the paint ground also explains friability.

In conservation, knowledge of the presence of wax, where an artist is known to use it in certain periods, is crucial. Inappropriate choice of organic solvents dissolving wax or ammonia-dissolving linseed can be disastrous [23].

Varnish

Stubbs applied his original varnish in 90-degree strokes. At 10 microns across, the smallest groove marks likely arose from abrading particles between the brush hairs and surface, as they are too small for hair widths. The wider strokes at 20-micron width or more probably represent whole brush hair indentations. Sable hairs, from sable marten outer coat guard hairs, are 30-45mm long and 60-176 microns in diameter [24]. Sable underfur can be as small as 12 microns in width and springy at the tip of the tail, making it a hair of choice by artists [25]. Hog hair from a pig's back is 18-49 microns in diameter [26].

This hair width evidence fits Stubbs using a stiffer hog hair brush to apply the varnish. The imaging reveals obvious triple coat application, with a double-depth final coat. He must have used a high-quality, well-prepared, slow-drying linseed varnish. Pure linseed oil naturally dries in air as a smooth, homogeneous plastic polymer of oleate, linoleate, linolenate, stearate and palmitate, hence the observation of plastic-like fracture ripples, both in the paint ground and varnish. Varnishing was not done with beeswax, so the same micrographic appearances in varnish and paint ground have to be linseed oil. The earlier renaissance alternative of walnut oil had faded out by then, even in southern Europe.

The poorer quality, part-unplasticized Regency restoration varnish was very friable to the naked eye and obviously part-burned to excess carbon from overheating in visible patches. This was apparent in small and wide fields. In comparison, Stubbs was expertly choosing and applying plastic technology in his carefully heated varnish, albeit without knowing the microscopy and molecular chemistry. There was no visual or scatter evidence at all that his own original varnish was overheated and burnt extensively into carbon. He used a slow-drying method, requiring patience on the part of the artist and sitter, who had to wait longer for the commission to be completed.

The findings emphasize the importance of flax in eighteenth-century art materials, generating linseed oil for painting ground and varnish, besides flax fibers for canvas. Understanding the precise nature of materials in canvas needs more research and has implications for conservation, where purism in originality might repeat a problem such as craquelure, or modern alternatives might be unacceptably artificial. In a painting with multiple canvas materials, SEM might inform a happy compromise [27].

Stubbs as artist and scientist

Stubbs' technical varnish quality was commensurate with his scientific ability as a professorial-level anatomist. His depth of knowledge and sharpness of scientific writing are borne out breathtakingly when you read Stubbs' anatomical writing today [28].

These findings shed some light on Stubbs as a scientific artist. Stubbs' colleague and biographer, Ozias Humphry [29], made it clear that Stubbs experimented in color and material techniques, selling his first enamel picture in 1769. Stubbs treasured independence and gave a lot of his colleagues a wide berth [30], though his artistic work amidst serious materials science mirrored that of his friend Josiah Wedgwood. The microtechnology of his materials, unknown to Stubbs, of course, is remarkable and poignantly makes for beautiful imagery in its own right, deep within its visible beauty. The findings in this particular portrait are science, within a portrait of Banks, the great scientist, by Stubbs, the great scientist and great artist.

Conclusions

Iron, calcium, carbon and oxygen results with particle microscopy indicate that Stubbs used Black Ivory and Burnt Sienna color pigments in an apparent nine-to-one ratio for his dark brown background. The absence of wax globules substantiates the existing view that Stubbs added wax from 1767, which fits the date of the portrait shortly after Banks' 1764 inheritance. Stubbs used evenly-plasticizing linseed varnish without lead drying agent or markedly-carbonized burning. His varnish was of high quality compared with that applied on relining decades later. The same appearance implied pure linseed in Stubbs' oil paint ground. Stubbs' skill in art materials science reflects his academic ability as an anatomical scientist. These are new findings on Stubbs' painting and varnish technique, with inexpensive potential to help conservators and researchers study and preserve other important paintings by the great artist.

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