Rembrandt's *Aristotle with a Bust of Homer* revisited: technical examination and new insights

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ABSTRACT Rembrandt's *Aristotle with a Bust of Homer* was examined and analysed to investigate the origin of a disfiguring hazy bloom, most visible in the dark paint passages that had been developing in the painting for decades. By combining the results of macro X-ray fluorescence imaging and the re-examination of photographic documentation, X-radiographs, autoradiographs and cross-section paint samples taken in earlier studies, the deterioration is attributed to the degradation of abundant smalt present throughout the paint structure. The observation that deterioration products were already present in the paint samples removed in 1980 is of critical interest in assessing the condition of the painting and how it evolved over time.

Figure 1 Rembrandt, *Aristotle with a Bust of Homer*, 144 ×136 cm, oil on canvas, signed and dated 'Rembrandt. f. 1653.' Purchase, special contributions and funds given or bequeathed by friends of the Museum, 1961. The Metropolitan Museum of Art, New York, 61.198.

Introduction

On 19 November 1961, the director of the Metropolitan Museum of Art (MMA), New York, James Rorimer, signalled his final bid with the blink of his right eye to win Rembrandt's *Aristotle with a Bust of Homer* for the museum (Fig. 1). More than 2000 people attended the auction that evening at Park-Bernet Galleries on Madison Avenue and the staggering sum paid generated much publicity and excitement. The MMA experienced record-breaking attendance when, shortly after the sale on 24 November, the painting went on view in the Great Hall, receiving over 120,000 visitors in two days.[1] *Aristotle with a Bust of Homer* is the only painting by Rembrandt in the collection acquired by purchase and is still today considered one of the museum's most significant holdings.

This well-documented painting was commissioned by the Sicilian nobleman Don Antonio Ruffo and delivered to him in the summer of 1654.[2] The seven pages of references in Walter Liedtke's catalogue of Dutch paintings is an indication of its historical significance.[3] Since entering the collection, the painting has been subject to technical investigations by curators, conservators and scientists from within and outside the MMA. It has been cleaned and restored twice,[4] was included in the groundbreaking 1982 autoradiography study of Rembrandt's work,[5] and featured prominently in the museum's 1992 exhibition *Rembrandt/Not Rembrandt.*[6]

The present study was initiated in response to changes in appearance that had been observed on the surface of the painting for decades. In the course of the investigation, photographic documentation was studied and the X-radiographs, autoradiographs and cross-sections of paint samples were re-examined with the aim of characterising possible deterioration and assessing the extent to which physical changes may have affected the visual impact of the painting.

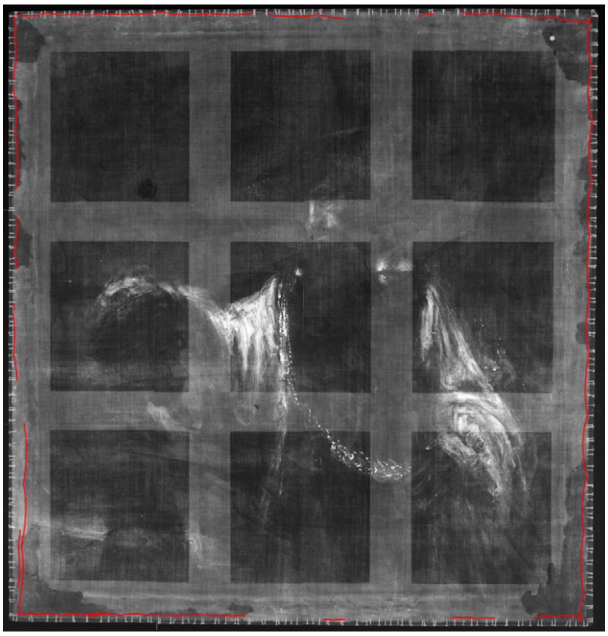

Figure 2 Rembrandt, *Aristotle with a Bust of Homer*: X-radiograph. The red line indicates the cusping of the fabric support. © The Department of Paintings Conservation, The Metropolitan Museum of Art, New York.

Results and discussion

Rembrandt painted *Aristotle* on a canvas support which currently measures 144 × 136 cm. In the past questions were raised as to whether the painting retained the original dimensions, based primarily on interpretations of historical inventories in which the dimensions are listed in *palmi*, an Italian measurement of uncertain proportions.[7] The presence of a selvedge along the left edge of the support confirms that the width is completely original.[8] Examination of an X-radiograph of the whole painting, recorded in 2006, reveals that cusping is present along the entire perimeter. In the X-radiograph, the fabric of the original support is obscured to a degree by the fabric of an early lining which was attached with a lead-containing adhesive.[9] Portions of this adhesive were partially removed in a subsequent relining, accounting for the dark, less radio-opaque patches along the perimeter. The fabric weave of the original support and that of the lining support are clearly distinguishable. In Figure 2, the cusping of the original support is indicated on a digital image after close scrutiny of the actual X-radiographic plates. The technical evidence strongly suggests that the painting is very close to its original dimensions and, at the most, may have been reduced by only a small amount at the bottom of the composition since the cusping is only slight along the bottom edge.

Examination of photographic documentation of the conservation treatments that were carried out after the painting entered the collection, as well as photographs taken over the years by MMA photographers, was crucial to this study. In 1963, just two years after it was acquired, the painting was cleaned by Hubert von Sonnenburg.[10] By 1980, a hazy bloom had developed which interfered with its appearance, prompting another cleaning that was carried out by John Brealey.[11] A comparison of before and after treatment photographs demonstrates that the bloom was no longer apparent after the painting had been cleaned and given a fresh coat of varnish (Fig. 3). By 1995, however, only 15 years after its last restoration, the haze-like bloom had returned, appearing as a distinct shape emerging in the background at the right just above Aristotle's elbow.

One suggestion for the origin of the surface bloom in *Aristotle* made soon after it was observed was the possible deterioration of smalt in the paint layer.[12] Smalt is a blue pigment composed of potassium silicate glass coloured by cobalt ions. Smalt pigment found in paintings dating from the sixteenth to the eighteenth century typically contains significant

Figure 3 Rembrandt, *Aristotle with a Bust of Homer*: (*left*) before and (*right*) after cleaning, 1980.

Figure 4 Rembrandt, *Aristotle with a Bust of Homer*: condition record, 2014 (*left*), and seventh autoradiograph (*right*) revealing the distribution of arsenic from smalt. The red arrows point to features discussed in the text. © The Department of Paintings Conservation, The Metropolitan Museum of Art, New York.

amounts of other elements such as arsenic, iron, nickel and bismuth.[13] Examination of one of the autoradiographs from the 1982 study, the seventh in a series of nine (Fig. 4), revealed the distribution of arsenic in the painting, which was interpreted as being due to the presence of smalt in the painting.[14] The distinct shape created by the distribution of this element corresponded precisely with the shape that was observed developing as a haze on the surface of the painting. As Rembrandt evolved his composition, he tried out various features and made a number of changes. The shape revealed in the seventh autoradiograph was just one indication of various ideas abandoned by the artist as the composition evolved.[15]

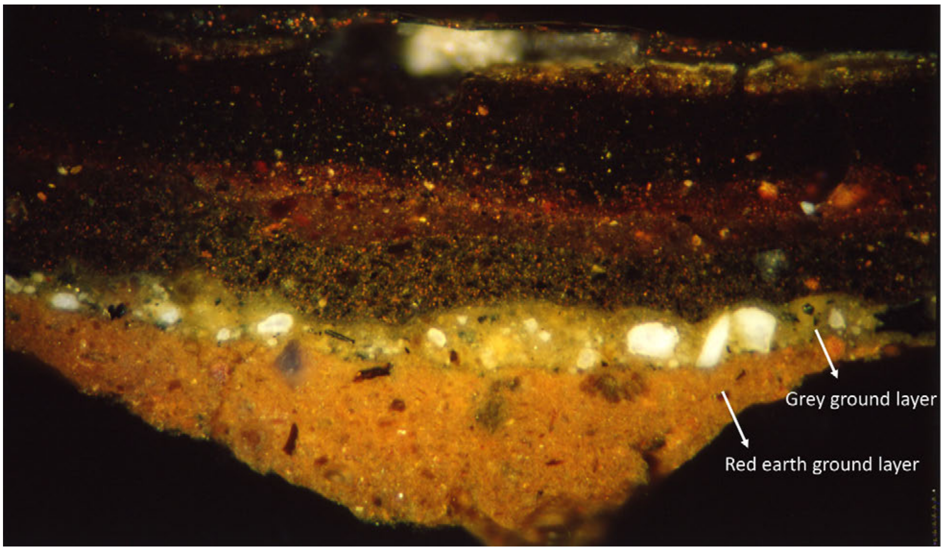

Figure 5 Rembrandt, *Aristotle with a Bust of Homer*: photomicrograph of a sample removed from the tablecloth in the lower left of the painting, mounted as a cross-section revealing the double layer structure of the ground preparation. In this ground, the first (orange-red) layer is composed of red earth, and the second (grey) layer contains lead white, a little chalk, bone black, brown and yellow ochre, umber (EDX, Raman spectroscopy). Original magnification ×250. © The Department of Paintings Conservation, The Metropolitan Museum of Art, New York.

We have interpreted this correspondence as critical evidence that points to the likely deterioration of smalt in the underlayers.

Rembrandt's prolific use of smalt was noted in the 1982 autoradiography study.[16] Our records on file in the MMA Department of Paintings Conservation include a report by Joyce Plesters, formerly Principal Scientific Officer at the National Gallery in London, who had been invited by John Brealey to examine and sample the painting after he had cleaned it in 1980.[17] Plesters, working with Ashok Roy, former director of Collections and head of the Scientific Department at the National Gallery, who had carried out microscopy and spectrographic analyses of the samples, reported a remarkable abundance of smalt in many places, in quantities not observed in any previous investigation. The possibility of carrying out the present study was facilitated by Roy, who generously agreed to lend 11 cross-sections from the Plesters and Roy investigation that were on file in the National Gallery scientific archives. Re-examining these cross-sections was most valuable since it avoided the need for further sampling. There were two further samples from *Aristotle* in the archives of the Paintings Conservation Department at the MMA, one of which is discussed below.

A sample removed from the lower right of the red tablecloth, mounted and prepared as a cross-section, revealed a double ground preparation (Fig. 5).[18] The first layer of this ground, which was applied directly onto the canvas support, is orange-red and composed mainly of a red earth. The second thinner grey layer contains lead white, a little chalk, bone black and some earth pigments. This double ground is characteristic of those reported in many paintings by Rembrandt.[19] All the pigments – identified in this study by Raman spectroscopy and scanning electron microscopy coupled with elemental analysis using energy dispersive X-ray spectrometry (SEM–EDX) on the cross-sections[20] – are consistent with pigments that have been reported widely in the literature in other works by Rembrandt. His unique and complex layering of combinations of opaque and translucent pigments included red and yellow lakes, carbon-based black, iron-containing earths, vermilion and frequently copious quantities of smalt. Rembrandt exploited the optical properties of these pigments when building up his paint layers in order to achieve rich translucent effects.[21]

Rembrandt's abundant use of both red and yellow lake is apparent in all the samples analysed for this study. High performance liquid chromatography (HPLC) analysis carried out on a sample removed from the lower left of the tablecloth in *Aristotle* identified a dye derived from cochineal in the red lake.[22] SEM–EDX determined that the substrate in

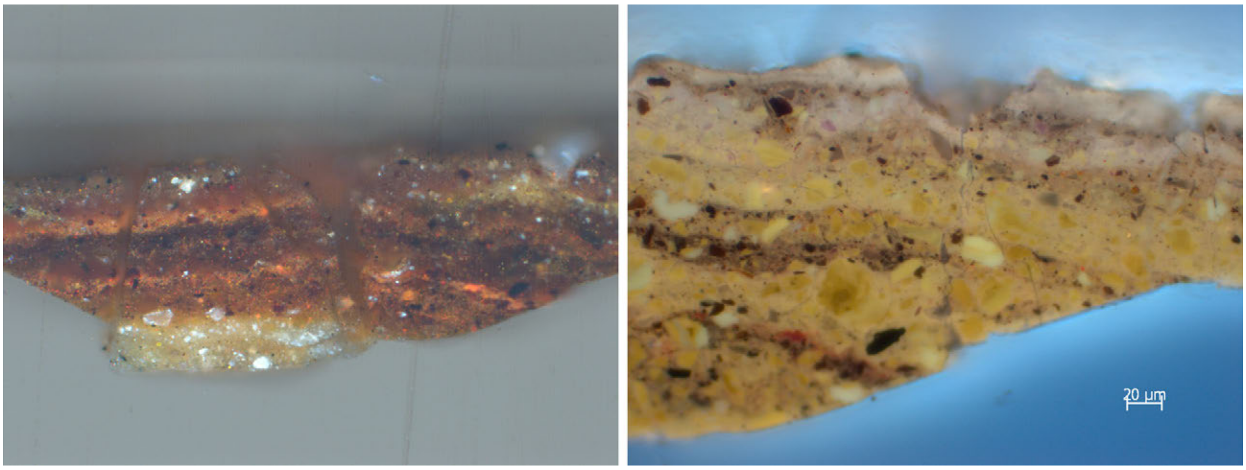

Figure 6 Rembrandt, *Aristotle with a Bust of Homer*: photomicrographs of sample 15 removed from Aristotle's hat, mounted as a cross-section, in visible (*left*) and UV (*right*) illumination. The photomicrograph on the left displays a complex layering of translucent and opaque pigments including a yellow lake, a cochineal lake, a red iron earth, a carbon-based black, lead white and smalt (EDX, Raman spectroscopy). In the photomicrograph on the right, the yellow lake particles fluoresce bright yellow. Original magnifications ×200 and ×400, respectively. © The Department of Paintings Conservation, The Metropolitan Museum of Art, New York.

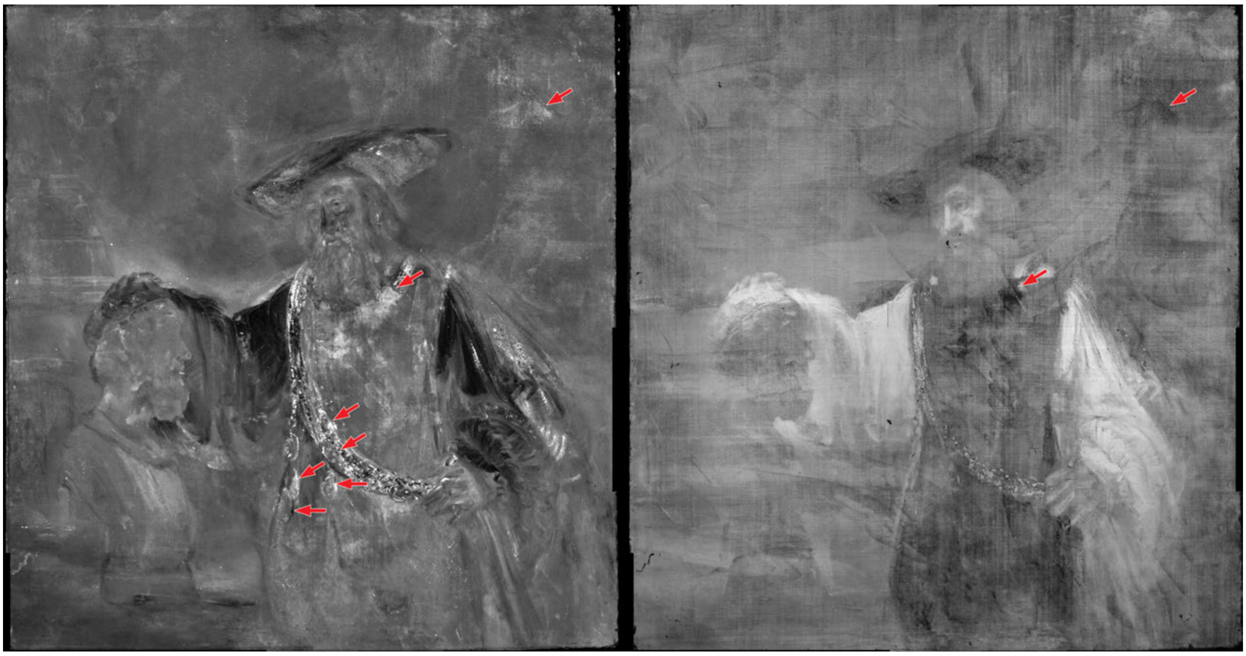

Figure 7 Rembrandt, *Aristotle with a Bust of Homer*: iron distribution map (*left*) and lead distribution map (*right*), both acquired by XRF imaging. The red arrows point to an area where the iron in the ground preparation is more visible due to thinner areas of application of the lead-containing layer on top, and to changes in the positions of the gold chain and medals. © The Department of Scientific Research, The Metropolitan Museum of Art, New York.

this red lake contains aluminium.[23] When some of the cross-sections were viewed under illumination in ultraviolet light, spectacular large particles that fluoresced bright yellow were observed (Fig. 6). SEM–EDX analysis showed that the components of these particles appear to be mainly organic and that significant amounts of aluminium are present, indicating strongly that these are a yellow lake pigment and that an aluminium compound forms the substrate. Two samples removed as scrapings – one from the red tablecloth containing particles of what appeared to be a yellow lake, and one from Aristotle's apron skirt just below the bottom edge of the picture and possibly containing an orange-yellow lake – were analysed in 1995 by Jo Kirby at the National Gallery, London, using HPLC, but

Figure 8 Rembrandt, *Aristotle with a Bust of Homer*: eighth autoradiograph showing the distribution of phosphorus from the bone black pigment (*left*) and calcium distribution map acquired by XRF imaging (*right*). © The Department of Scientific Research, The Metropolitan Museum of Art, New York.

the precise identity of these yellow lake pigments remained elusive.[24] The firm identification of yellow lakes in paint cross-sections is also difficult. A laser ablation Raman technique has been used to confirm red anthraquinone lakes [25] but to date the technique has been unsuccessful with regard to the identification of yellow lakes localised in paint cross-sections.

X-ray fluorescence (XRF) mapping or imaging, developed at the University of Antwerp and the Delft University of Technology,[26] is a powerful technique that complemented other technical analyses we carried out to find answers to the questions raised during this study. While the X-radiograph revealed the artist's characteristic sweeping spatula marks resulting from the use of this tool to apply the second grey ground, a lead distribution map acquired by XRF mapping[27] provided a more detailed image of this upper ground layer (Fig. 7). In the iron distribution map of the lower ground application, light passages register in locations where the lead-containing second layer in the ground is thinly applied or missing. XRF imaging reveals these features in the ground preparation as complementary images. It is also apparent that multiple changes were made to the positions of the gold chain and medals, which are revealed as a result of the iron content of the yellow earth pigments used to paint these objects.

It is well known that Rembrandt made frequent changes to his compositions during the painting process. In the case of *Aristotle*, some of these design transformations were revealed by the 1982 autoradiography study.[28] When the full sequence of autoradiographs was considered, various stages in the modification of Aristotle's costume were noted, but the exact evolution in design proved too complicated to determine with the available data. The eighth autoradiograph, which reveals the presence of phosphorus in the bone black pigment, clearly shows an early idea for a dark tunic with close-fitting sleeves that extends to the bottom edge of the picture plane (Fig. 8). The presence and distribution of bone black can also be evaluated from the distribution of calcium in the corresponding XRF map. In the case of *Aristotle*, this distribution map provides a more readable image of some of the changes to the costume, including a shorter divided tunic and a much clearer image of the hat (Fig. 8). Because calcium is an element that emits radiation of relatively low energy, the XRF distribution map will only record the presence of bone black when used by the artist in the upper layers.[29] Since we were concerned with questions of condition, particularly in relation to the complex paint layer structure observed in the cross-sections in addition to the elemental distribution maps, the cross-sections from

Figure 9 Rembrandt, *Aristotle with a Bust of Homer*: photograph taken in 2014 (*left*), and distribution map for cobalt from the pigment smalt, acquired by XRF imaging (*right*). The red arrows point to the location of the area of hazy bloom developing on the surface of the painting. © The Department of Paintings Conservation, The Metropolitan Museum of Art, New York.

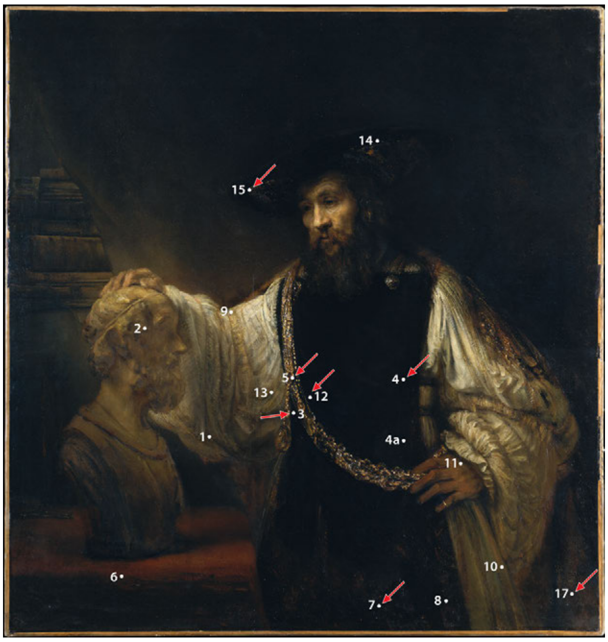

Figure 10 Rembrandt, *Aristotle with a Bust of Homer*: the locations of the 17 samples removed during the Plesters study in 1980. The red arrows point to the seven samples analysed for the present study.

these areas were scrutinised in order to investigate further the speculative assessments developed during earlier investigations with regard to artist changes.[30] The location of the bone black pigment in the layer structure was confirmed by Raman spectroscopy and SEM–EDX analysis of these cross-sections, which helped to confirm that the final length of the tunic extended to the bottom of the composition and that Rembrandt originally intended the finished colour of both the hat and the tunic to be black.

In the cobalt distribution map (Fig. 9), which records the presence of smalt, the short divided tunic revealed in the calcium distribution map is even more sharply defined. For the purpose of this study, the cobalt map is perhaps the most valuable new image. The passages rich in cobalt and the shape defined in the background at the right should be noted in particular. When viewing the painting in its present condition, the hazy bloom can just be seen across the whole surface, but the very specific faint shape that is developing in the background to the right on the surface of the painting corresponds precisely to the shape displayed in the cobalt distribution map.

Six of the 17 cross-sections from the study by Plesters, which were removed from points now shown to contain cobalt by XRF imaging, were selected for analysis by SEM–EDX and Raman spectroscopy (Fig. 10). The results demonstrated that the layers rich in smalt are lower down in the paint stratigraphy. Analysis of sample 7 (Fig. 11) from the lower area of the tunic showed that the top layer contains mainly bone black together with some red iron oxide

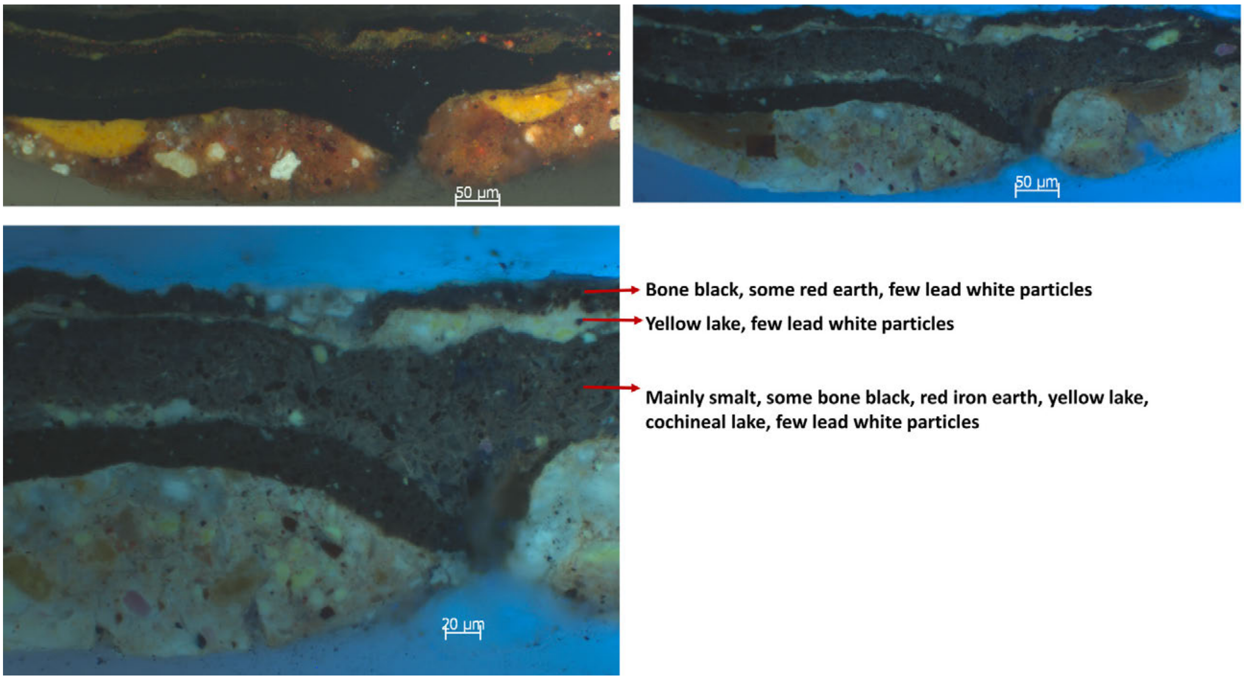

Figure 11 Rembrandt, *Aristotle with a Bust of Homer*: photomicrographs of sample 7, removed from the lower area of Aristotle's tunic, mounted as a cross-section. Photographed in visible light (top left, original magnification ×200) and UV light (original magnifications: top right ×200 and bottom ×400). © The Department of Paintings Conservation, The Metropolitan Museum of Art, New York.

earth and a few particles of lead white. Below is a layer containing a yellow lake with a few particles of lead white under which is a relatively thick layer, rich in smalt, which also contains a cochineal-based lake, a red iron oxide earth, yellow lake and carbon-based black. This mixture of pigments suggests that the colour was intended to be dark and translucent but, despite the abundance of smalt, it was certainly not meant to be blue. In all the samples with paint layers containing large quantities of smalt, similar pigment mixtures were observed. It seems likely that the smalt was added in this case for translucency, in combination with red, yellow and black, to achieve a deep rich brown.

Supporting this conclusion is the SEM–EDX analysis of the paint cross-sections which confirmed that the cobalt oxide (CoO) content of the smalt used by Rembrandt in *Aristotle* was between 2 and 3 percent by weight, indicating a pale smalt. In the seventeenth century, many grades of smalt were available that varied in colour depending on their particle size and cobalt content, ranging from barely coloured to brilliant blue.[31] In this case, Rembrandt used a smalt pigment with a barely perceptible blue colour, so any speculation of colour change due to degradation and subsequent discoloration of brighter blue smalt is untenable. In addition, the presence of an uppermost paint layer containing primarily bone black confirms that the tunic was intended to be a deep black and, as mentioned above, originally extended to the lower edge of the picture plane.

Analysis and SEM imaging of a sample removed from a smalt-rich area in the lower right of the painting has contributed to an understanding of the degradation phenomena that are taking place in the painting. This sample contains some relatively large smalt particles allowing detailed elemental analysis by EDX. The SEM images of sample 17 (Fig. 12) revealed that the potassium content in some smalt particles decreases from the core to the periphery, indicating that potassium has leached out of the particles while their cobalt content has remained approximately constant.

The process of smalt deterioration has been studied by numerous researchers in different institutions.[32] Results from these studies have shown that the decrease in alkali content within the smalt particles as a result of leaching of potassium induces a change in the coordination geometry of the cobalt ions from tetrahedral to octahedral, leading to the loss of the blue colour in the pigment, and that at the same time important structural modifications

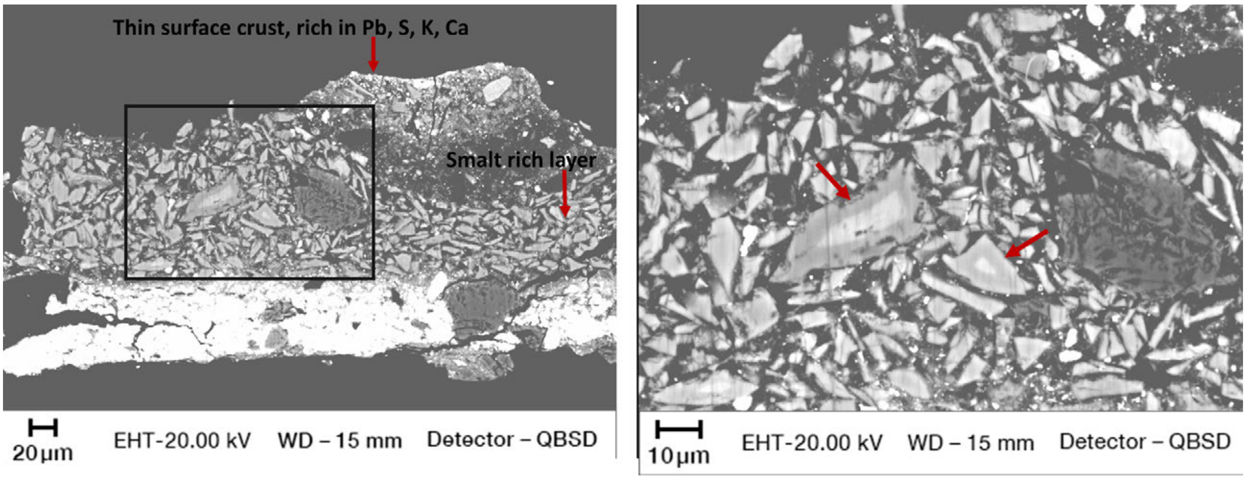

Figure 12 Rembrandt, *Aristotle with a Bust of Homer*: backscattered electron SEM images of sample 17, removed from Aristotle in the background, lower right, mounted as a cross-section. The image on the right was taken in the area indicated by a rectangle in the image on the left. The red arrows in the image on the right point to large smalt particles where potassium is preserved in the core (brighter areas) and has leached from the perimeter. Original magnifications ×800 and ×2000, respectively. © The Department of Scientific Research, The Metropolitan Museum of Art, New York.

occur in the smalt silicate network. It has also been proposed that these reactions are responsible for changes in the physical properties of the paint films and for the darkening of the oil medium. It has been shown that potassium that has leached from the particles reacts with free fatty acids in the oil binding medium to form potassium soaps, and that migration processes also take place that result in the formation of salt crusts on the surfaces of paintings. In addition, the composition of these crusts may be modified further by reaction with environmental contaminants.

A very thin layer observed at the top of sample 17 (Fig. 12) was found by SEM–EDX to be composed of lead, sulfur, potassium and calcium. The molecular composition of this surface layer was below the detection limit of *in situ* Raman spectroscopy; a synchrotron radiation (SR)-based technique is required to identify fully the materials present.[33] However, from the results of the SEM–EDX analysis, it is possible to propose that this surface crust probably contains a complex compound, or a mixture of compounds, involving sulfate, lead, potassium and calcium ions. It seems likely that the cause of the recurrent hazy bloom is the continuous formation of these products. Our observation that these degradation products were already present in the paint samples removed in 1980 is of critical interest in assessing the condition of the picture and how that may evolve over time.

Conclusions

The significant benefits of gaining new information from existing technical documents, cross-sections and non-invasive analyses provided by XRF imaging should not be underestimated. As with all investigations, although some questions are answered, more are raised. Analysis by a SR-based technique of the sample cross-sections taken in the past from the affected paint passages is necessary to understand the phenomenon more fully. It is hoped that insights gained from this new investigation will contribute to finding the best possible solution for the preservation and presentation of such an important and popular work by Rembrandt in the Metropolitan Museum of Art's collection.

Acknowledgements

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8. We wish to acknowledge Petria Noble's contribution to this observation which was made in 2006 when the painting was examined in connection with research being carried out on Rembrandt's *Homer*, inv. no. 584, Mauritshuis, The Hague.
9. The lead-containing adhesive and open-weave relining fabric visible in the X-radiograph of *Aristotle* is similar to the structure revealed in the X-radiograph of Rembrandt's *Homer* (inv. no. 584, Mauritshuis, The Hague). Petria Noble carried out a technical examination of *Homer* in 2001–2006 in which she identified the relining adhesive as red lead and speculated that this lining may have been attached in Italy after the paintings were damaged in the 1783 earthquake.
10. Hubert von Sonnenburg was a conservator in the Department of Paintings Conservation at The Metropolitan Museum of Art, New York, from 1959 to 1972 and again from 1989 to 2004.
11. John Brealey was a conservator in the Department of Paintings Conservation at The Metropolitan Museum of Art, New York from 1975 to 1989.
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17. Unpublished report in the National Gallery Scientific Department files by Joyce Plesters, dated 9 October 1998. Ashok Roy prepared and examined the cross-sections and carried out the analyses described in this report.
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27. The XRF instrument used consists of a measuring head that is moved across the painting surface by means of a motorised X-Y stage with a maximum travel range of 80 × 60 cm. The measuring head includes a 30 W Rh-target micro-focus X-ray tube and a silicon drift detector (SDD) to collect the fluorescence signal. The X-ray source was operated at 50 kV and 500 mA, and the resulting beam focused by means of a polycapillary optic. The A Z motor allowed the spot size to be optimised to the step size by varying the distance between the painting and the measuring head. The overall painting was scanned at 150 msec/pixel with a 1 mm step size. Smaller areas including the head of Aristotle and the lower part of the tunic were also analysed with 800 and 750 μm step sizes respectively, and at 300 msec/pixel. The spectra were processed through dynamic analysis employing a combination of Pymca and Datamuncher software as described by Alfeld, M. and Janssens K. (2015), 'Strategies for processing mega-pixel X-ray fluorescence hyperspectral data: a case study on a version of Caravaggio's painting *Supper at Emmaus*', *Journal of Analytical Atomic Spectrometry* 30: 777.
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