ART MATTERS

New Insights into Rembrandt's Susanna

Changes of format — smalt discoloration — identification of vivianite — fading of yellow and red lakes — lead white paint

Petria Noble and Annelies van Loon

1 Introduction

Biblical and mythological nudes form a recurring theme in Rembrandt's oeuvre.[1] In Rembrandt's second painting of a full-length female nude, depicting the biblical Susanna (Daniel 13:19–23), signed and dated 163[6], in the collection of the Mauritshuis,[2] we see a brightly-lit Susanna who has just undressed to take a bath (fig. 1). Startled by two men hiding in the bushes (their heads can just be made out) she desperately tries to cover her nakedness.[3] In her anguish she looks towards us, as though we too were spying on this intimate scene.

The recent varnish removal in 2002 allowed a close examination of the painting, which, together with chemical analytical research, provides a better understanding of the pictures original appearance. This article reports on analyses that have been carried out regarding changes that have taken place to the format of the panel — the added strip and the overpainted corners — as well as changes in colour due to the degradation of paint layers. In addition other aspects of the painting technique have been investigated where possible.

fig. 1 Rembrandt, *Susanna*, 1636, oil on panel, 47.4 x 38.6 cm, Mauritshuis, inv. 147, after treatment.

The dimensions of the panel depicting *Susanna* were originally slightly different. That a strip of oak measuring 4.6 cm wide at the top and 4.1 cm at the bottom was added to the right side of the panel sometime before 1758 is known, because in that year the picture was auctioned in Antwerp with its present dimensions, as part of the collection of P. J. Sneijers.[4] That the addition is later, has so far as we know, never been doubted; stylistically the manner of painting on the addition differs from that of the original panel, the handling totally lacking the contrasts between smooth and pastose, translucent and opaque, so characteristic of Rembrandt's surfaces. Furthermore the paint has a gritty texture that is foreign to the paint elsewhere in the painting. The join, which passes through the signature and up just to the right of the nose of the far right head, is clearly visible to the naked eye. Probably to facilitate adhesion of the oak strip, it seems that the right edge of the original single member panel was also slightly trimmed. The reason for this was probably woodworm damage, for we see on the back, along the join, that the panel is riddled with tiny wormholes. As Broos points out, evidence of the reduction of the original panel is provided by the signature at the lower right where the original letters 'andt' disappeared. This part of the signature was subsequently supplemented on the added strip with 'ant' followed by an extra 'f.' (fig. 2). This change is odd because, as pointed out by the Rembrandt Research Project (RRP), the 'd' is missing from Rembrandt and the 'f', of fecit [made it], already precedes the date 'f 1636' on the line below.[5] While the 'f 163' is original, the last '6' was added on the new strip, the paint of which extends a millimetre or so over the original panel, obscuring the remains of the underlying original final digit. Though difficult to discern, parts of a curve from either a 6 or an 8 can be made out beneath the overpaint. Although this might cast doubt on whether the picture is indeed from 1636, the picture certainly existed in 1636 because Rembrandt's pupil Willem de Poorter (1608–after 1649) made a drawing after the painting which is signed and dated 1636.[6]

There is also something odd about the upper corners of the panel, for in raking light raised paint corresponding to rounded corners can be discerned. From the near infrared image [7] (fig. 3) it is clear that Rembrandt first filled in the corners with a loosely brushed-out black paint to give the scene an arch-shaped format. This black layer is also visible with the stereomicroscope along the upper left edge of the picture where here and there it is exposed. It is also evidenced in cross-section

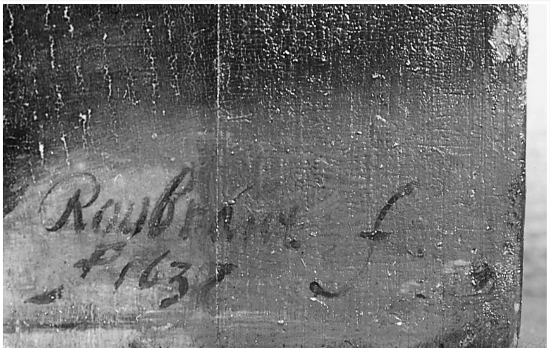

fig. 2 Detail of signature, lower right, Rembr[ant f.] / f 163[6].

(fig. 4). While Rembrandt's intention must have been to conceal these corners from sight with a rectangular frame with corner spandrels,[8] at some point the corners of the painting were filled in, but before the present study it was not known whether Rembrandt or a later artist did this. More than a century ago C. Hofstede de Groot observed that the painting may originally have had rounded corners,[9] but it is only more recently that this suggestion has been revived.[10] Certainly van Thiel, in his entry, is correct in observing that the overpainting must have occurred some considerable time after the paint had hardened since the arch is visible in the surface relief in raking light. He also suggests, quite logically, that the change could have been made at the time of the addition of the strip. Changes to the dimensions of pictures, often drastic, frequently occurred, usually because of damage,[11] though sometimes simply to fit another frame or an interior.[12] That the overpainted corners had gone undetected for so long is no doubt due to the condition of the picture before the removal of varnish in 2002.[13] Covered in several layers of discoloured brown varnish, the overpainted corners were almost impossible to discern.[14] Detection was made even more difficult since the paint from the addition overlaps the upper right corner of the original part of the panel by a few centimetres. Furthermore age cracks that formed in this continuous paint layer extend across the join.

Using microscopic and chemical analyses of paint samples from the strip and the corners on the original panel, this paper aims to show that the changes in format, the addition of the strip and the filling-in of the corners took place at the same time (see following sections on *Preparatory layers* and *Overpaint in upper right corner*).

fig. 3 Overall near IR image (compilation of 6x4 images).

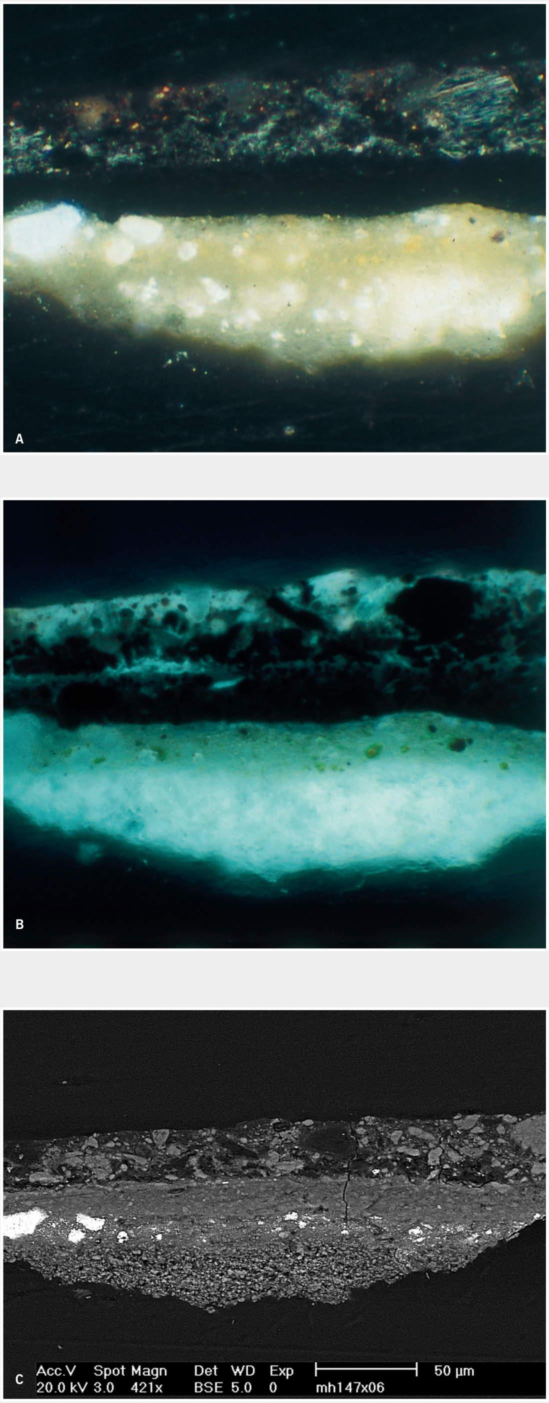

fig. 4 Cross-section from top edge of original panel showing Rembrandt's ground layers, the black spandrel layer and dark overpaint. Normal light (A), UV (B) and SEM image (C).

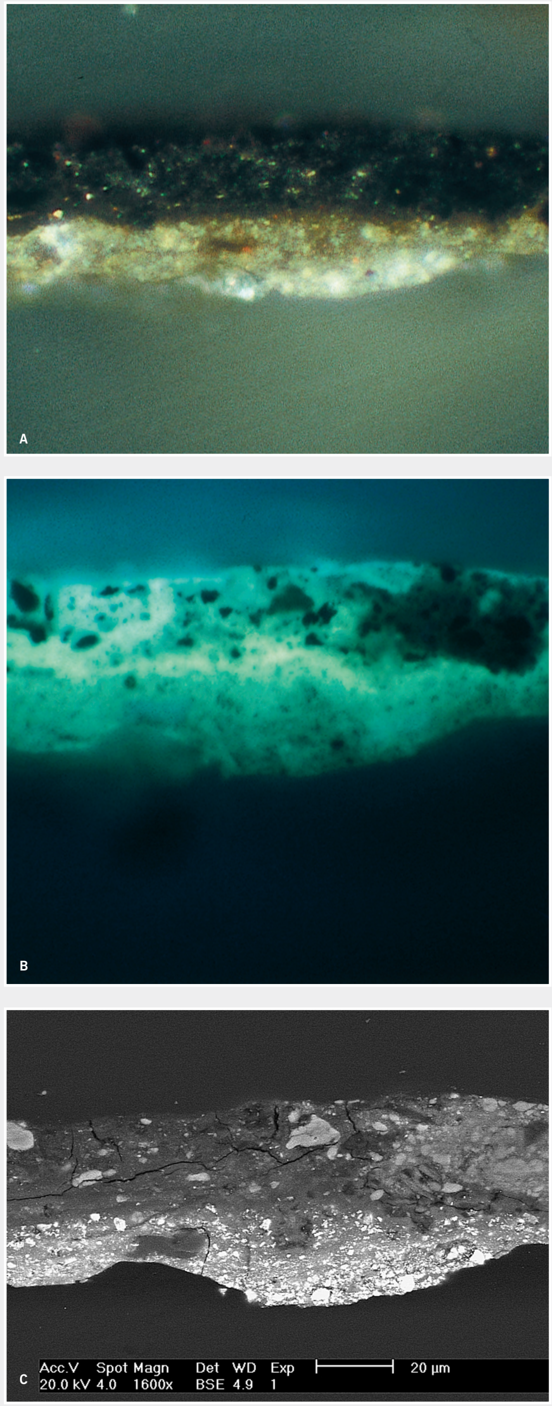

fig. 5 Cross-section from top edge of added strip showing ground and dark paint layer on addition. Normal light (A), UV (B) and SEM image (C).

2 Investigations of the original panel and the later additions

The analytical approach involved embedding several minuscule paint samples as cross-sections for comparison of the paint layer build-up and for material analysis using Optical Microscopy[15] and Scanning Electron Microscopy with Energy Dispersive X-Ray micro-analysis (SEM-EDX).[16] Loose sample material was collected for binding medium analysis with Direct Temperature resolved Mass Spectrometry (DTMS).[17] Additional sample material from the lead white paint was analysed with X-Ray Powder Diffraction (XRD) and Lead Isotope analysis, and the red lakes were characterised with High-Performance Liquid Chromatography (HPLC).[18]

- *Preparatory layers*

The preparatory layers of the original panel (including the spandrels) are typical for Rembrandt's panel paintings: a whitish chalk ground, covered by a beige-coloured imprimatura (fig.4) containing mainly lead white (EDX: Pb) and chalk (EDX: Ca), with additions of brown umber (EDX: Fe, Mn, Si, Na, Mg, Al), red earth (EDX: Fe, Al, Si) and some silica particles (EDX: Si, O). DTMS analysis provided evidence of the use of a linseed oil medium in the imprimatura (P/S = 1.7).[19] While the ground and imprimatura layers of the original panel are commonly found in Dutch paintings of the seventeenth century, the single dark grey ground on the addition, is unusual (fig. 5). The significance of the absence of the lower chalk layer is hard to assess, as so little is known about seventeenth and eighteenth century panel additions. The use of a dark ground only became popular in the Netherlands towards the end of the seventeenth century, but an addition may not necessarily reflect normal priming practice. Consisting of a mixture of coarse and fine lead white and chalk with fine black (probably lamp black) and very fine red earth pigment (EDX: Al, Si, Fe, K, Mg) in a binding medium-rich matrix of linseed oil (P/S = 1.4) with the addition of a little pine resin[20], this ground has not been encountered in any of Rembrandt's studio, or followers' paintings.[21] The addition of pine resin, not usually found in seventeenth century ground layers, explains why exposed areas were somewhat sensitive to organic solvents (iso-propanol mixtures were used during cleaning). Interestingly, the addition of diterpenoid resin has been found in several pictures of the eighteenth and nineteenth centuries.[22] This ground was applied after the strip was added — as here and there it overlaps the original panel by a few millimetres; in the upper right corner, however, it

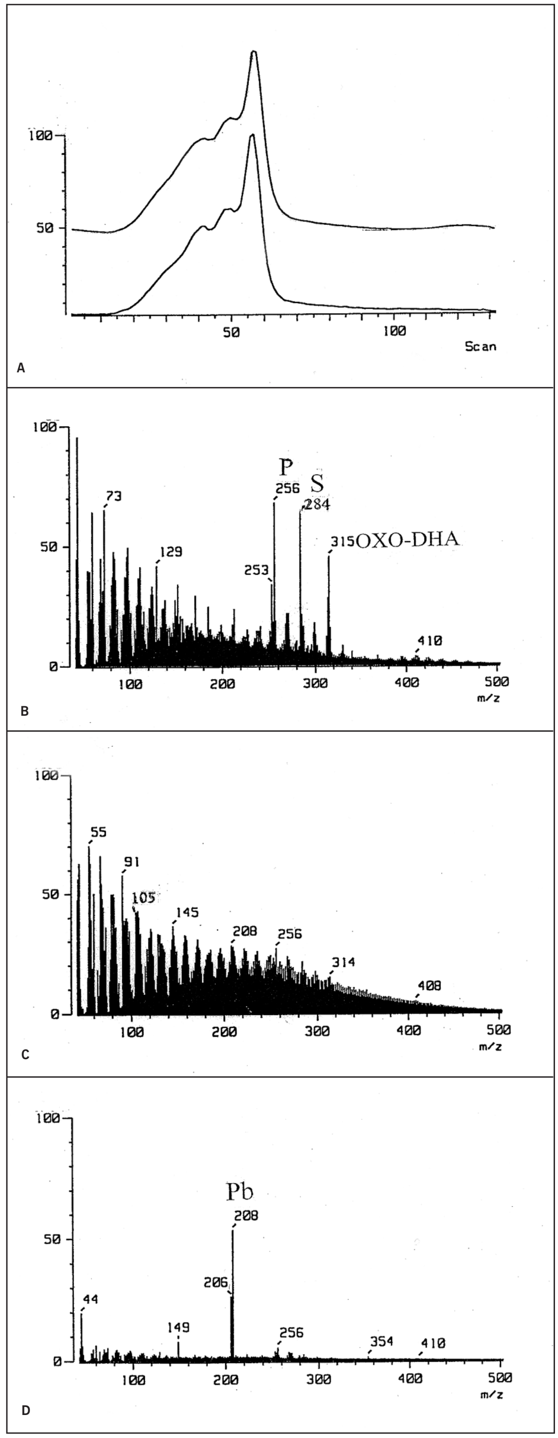

fig. 6 DTMS: total ion current (TIC) diagrams of brown overpaint on the original and brown paint from the addition are identical (A); summed mass spectra of the volatile region (scans 20, 53) (B); the polymer region (scans 52, 62) (C); and the iorganic fraction (scans 63, 88) (D).

extends a few centimetres over the original paint. Paint cross-sections from this area show a grey layer directly on top of Rembrandt's black paint of the spandrel, which appears to be identical to the grey ground on the addition. With high resolution imaging and elemental analyses with SEM-EDX of these layers, it could be established that they have an identical layer morphology, whereby the pigment composition and distribution are the same.

- *Overpaint in upper right corner*

After varnish removal, it was clear that the gritty dark brown background paint in the top right corner on the addition extended over the original panel up to and around the tree, where part of the branch was also added. Although it had been established that the grey layer below on the original panel was identical to the ground layer on the addition, which in itself is proof that this brown paint must also be later, analysis of this layer was also carried out in the hope that it would provide more information about the date of these changes. Cross-sections from both the brown background in the upper right corner of the original panel, and from the brown background in the addition show identical brown top layers that consist of strikingly coarse black particles with a little bright red (figs. 4–5). Analysis with SEM-EDX of these layers in the two cross-sections confirmed these observations (figs. 4c and 5c). In both samples the black pigment was identified as bone black (EDX: Ca, P, (Mg)).[23] Binding medium analyses with DTMS gave an exactly identical composition for the binding medium of the corner paint and that on the addition (fig. 6).[24] Both EDX and DTMS spectra gave evidence of the presence of lead in the dark-brown background paint.[25] In back scatter SEM images, tiny bright white dots in the otherwise dark matrix of the organic binding medium are interpreted as lead drier which the artist must have added, either to the oil binding medium or by mixing directly into the black paint.[26] This would have enhanced the drying of the paint since such black pigments, in addition to absorbing a considerable amount of oil due to their porous structure, are known anti-oxidants which retard the drying of oil films.[27] This role of lead was confirmed by DTMS by the absence of an event associated with the carbonate in lead white. The DTMS spectra also indicate a substantial amount of pine resin present in the linseed oil medium.[28] This also may explain the sensitivity of the paint to polar organic solvents during cleaning, and for the strong UV-fluorescence of the binding medium matrix around the dark bone black particles, though the presence of lead soaps can also contribute to this.[29]

The analysis convincingly shows that the overpaint on the right spandrel, consisting of bone black in oil/resin medium with lead drier, is identical to the dark paint on the addition. Although this indicates these changes were made at the same time, it is hard to judge when this occurred, since their composition is not specific to any one period. Clearly the addition of pine resin places it outside Rembrandt's studio.[30]

- *Smalt and smalt discoloration*

Smalt, a blue pigment made of ground potassium silicate glass, was available in different grades from pale grey to deep blue — the colour dependent on the cobalt content and particle size.[31] It was one of the most popular blue pigments in Europe in the seventeenth century and was widely produced in Holland, Flanders and Germany.[32] Rembrandt made great use of smalt in a variety of ways : as a blue pigment, alone and in mixtures, as a bulking agent to give volume and texture, and as a drier.[33] In *Susanna* it is found in many areas of the painting: in the sky and the hills of the upper left background, in the foliage at the lower left, in the hair and in the intermediate undermodelling layer which is for the most part covered by the final paint layers (figs. 8, 10, 13).

Smalt-containing paints often appear degraded and greyed — what is usually referred to as 'blanched'.[34] Although previous research has shown that greyed and blanched paint layers in Rembrandt can be associated with the use of smalt, in these cases, as far as we know, it has not been established whether the colourless particles were intended or are the result of discoloration.[35] This has sometimes led to the assumption that pale varieties were most often used by Rembrandt. Recent research by Boon et al.[36] and Burnstock[37] has made it possible to distinguish analytically between smalt that has discoloured and smalt that was originally pale in colour. In this painting the degradation is probably most disturbing in the sky, where the thicker ridges of the single layer of smalt paint have become an opaque grey and the thinner areas a translucent brown (fig. 7). In the thin areas it is thought that the smalt must be almost completely colourless, allowing the underlying panel and imprimatura to play a role in the brownish appearance. While smalt is the main component in the sky with the addition of a little bone black, and in some places also a trace amount of lead white, in the upper left corner the grey paint there, in addition to smalt, also contains lead white (EDX: Pb), bone black (EDX: Ca, P) and red and yellow earth pigments (EDX: Al, Si, Fe).

Table 1	Semi-quantative SEM-EDX analyses showing the elemental composition of the smalt particles in each layer. The Si : K ratios are indicative for the degree of discolouration and the Si : Co ratios for the colour intensity.					
Cross-section	Sample area	Layer description	Composition [1] smalt	Si:K ratio [2] Discoloured particles	Si:K ratio Non-coloured particles	Si:Co ratio [2]
01	Overpaint in left spandrel — blanched and discoloured sky (surface layer)	Smalt, also little lead white, bone black and red and yellow earths	Si, K, Co, Fe, As, (Na), (Al), (Bi), (Ca), (Ni)	50 : 1	4 : 1	10 : 1
02 (fig. 8)	Upper left – blanched and discoloured sky (surface layer)	Discoloured smalt with small additions of bone black and very fine red	Si, K, Co, Fe, As, Al, (Na), (Bi), (Ca), (Ni)	45 : 1	4 : 1	17: 1
16	Upper left – non-blanched sky (surface layer)	Discoloured smalt, bone black, trace amt. lead white	Si, K, Co, Fe, As, Al, (Na), (Bi), (Ca), (Ni)	50 : 1		16 : 1
07 (fig. 10)	Blanched foliage (intermediate layer)	Smalt, quartz, vivianite, chalk (yellow lake substrate), plus small amts. bone black, earth pigments, vermilion and red lake.	Si, K, Co, Fe, As, Al, Bi), (Ca), (Ni)	45 : 1		17 : 1
	Reddish brown undermodelling layer	Smalt, quartz, chalk, earth pigments, red lake, bone black and a little lead white.	Si, K, Co, Fe, As, Al, (Bi), (Ca), (Ni)	60 : 1		16 : 1
13	Reddish brown undermodelling layer (left uncovered)	Smalt, quartz, chalk, earth pigments, red lake, vermilion, bone black and a little lead white.	Si, K, Co, Fe, As, Al, (Bi), (Ca), (Ni)	75 : 1		17 : 1

1. __ = main element, ( ) = less than 1%.
2. Si : K and Si : Co ratios are in weight percent. The ratios are calculated from the peak intensities corrected for matrix effects by the ZAF method. All samples except the blanched foliage layer were measured from at least three spots on the same day under the same conditions to allow for comparison.

These pigments were probably added in order to match the colour to the adjacent original paint. Applied evenly, directly over Rembrandt's black paint of the spandrel, this is thought to be overpaint. Here too it is degraded, but it has become an even grey, lacking the discontinuous transparent / opaque passages of Rembrandt's paint lower down.

Blanched paint and coarse cracking is also evident in the thickly applied greyish foliage on the lower left, where it is part of a more complex mixture containing vivianite and possibly chalk (interpreted as the support of a yellow lake) modified with some bone black and red pigments (fig. 9–10). Here the smalt was probably mainly used to give body to the thick foliage under-layer for the vivianite and a yellow lake glaze that was applied on top (see sections 2.4 and 2.5). In turn these foliage layers were applied over a thick undermodelling layer in which a lot of smalt also features. This undermodelling, a heterogeneous reddish brown layer, the colour of which varies slightly depending on area, contains in addition to smalt, quartz (EDX: Si, O), chalk (EDX: Ca), earth pigments (EDX: Fe, Si, Al), red lake (Al, K, S), bone black (Ca, P) and a little lead white (EDX: Pb). Here it would be logical to think that the smalt was not used for its blue colour but for its bulking and drying properties. This layer, which was used to develop the composition by indicating the light and dark contrasts, is visible in the extreme lower left foreground where it was deliberately left uncovered, and also where it has become exposed by tiny losses in the surface paint.

The research by Boon et al. has established that the degradation of smalt is the result of potassium being leached out of the glass by interaction with the oil medium, being replaced by hydrogen-bearing species, the cobalt(II) ions changing from a tetrahedral co-ordination that is blue to an octahedral co-ordination state that is a weak pink colour.[38] A shift in alkalinity takes place whereby the basicity of glass is lowered below a critical level for colour maintenance. Since we know that various grades of smalt ranging from deep blue to pale grey were manufactured, the question is whether the greyish sky that we now see is the result of the discoloration of smalt, or whether the artist deliberately chose a pale colourless variety. As the picture is now essentially a monochrome painting, this question has important consequences for understanding the original appearance of the picture. Also — in terms of Rembrandt's working practise — is the smalt used in the final paint layers different from that used in the undermodelling layer? Is it possible to differentiate between the type of smalt used in the paint on top of the left spandrel and that in Rembrandt's paint? And finally, what are the factors that contribute to the discoloration/degradation of these smalt paints?

fig. 7 Detail upper left corner showing overpainted spandrel and Rembrandt's sky: the thick ridges are blanched and the thin areas have become transparent.

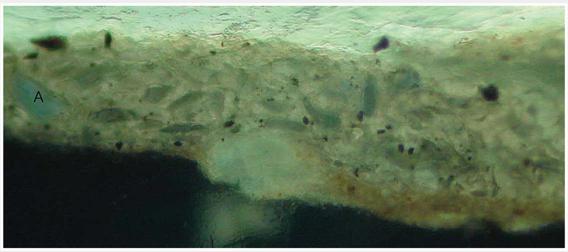

fig. 8 Cross-section 02 (see Table 1) of Rembrandt's blanched sky (UV illumination). The large smalt particle at the extreme left is still blue while the smaller particles have turned grey. The layer below is the beige imprimatura (second ground layer). The lower chalk ground is not present in this sample.

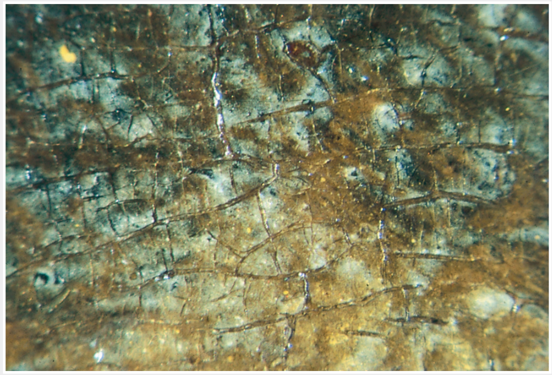

fig. 9 (upper right)
Detail of greyish green foliage at lower left showing blanching and coarse cracking.

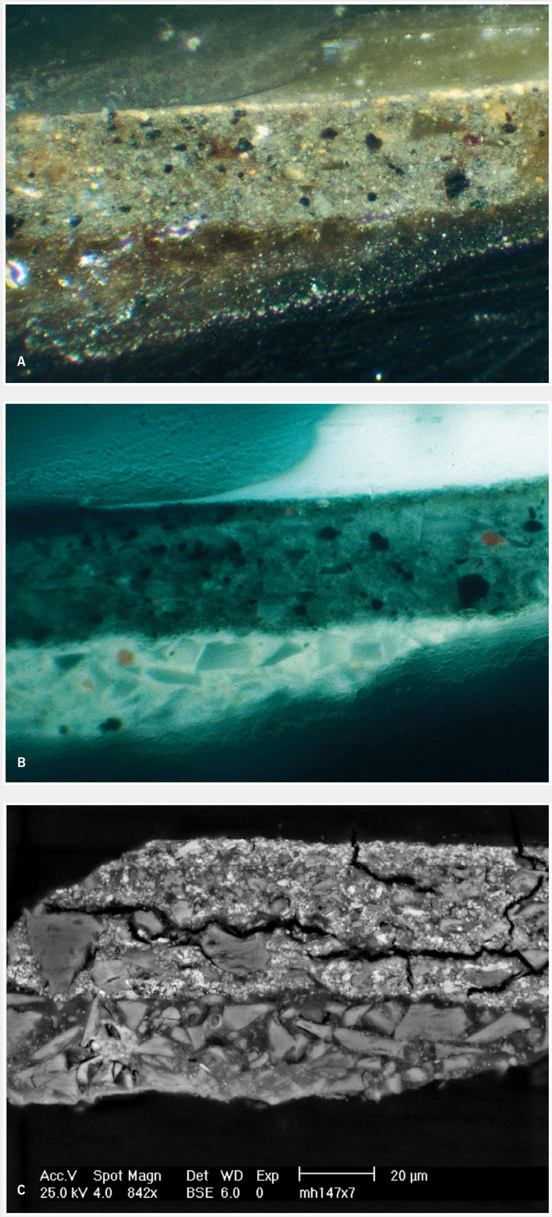

fig. 10
Cross-section 07 (see Table 1) from greyish green foliage. On top of a thick warm undermodelling containing a lot of smalt the foliage was applied in one thick layer containing the blue earth pigment vivianite and chalk (from a yellow lake), as well as a little smalt, earth pigments, quartz, bone black, red lake and a tiny bit of vermilion. This was modified with a thin glaze layer (now faded and cracked) rich in vivianite and chalk. The chalk is interpreted as the substrate of a faded yellow lake. Ground layers missing from sample. Normal light (A), UV (B) and SEM image (C).

To answer these questions, the different smalt compositions were analysed with SEM–EDX; the results are presented in Table 1. It has been established that, by looking at the proportion of silica (Si) to potassium (K) and silica to cobalt (Co), we can in fact differentiate between various qualities of smalt and between degraded and well-preserved smalt,[39] the Si:Co ratio determining the intensity of the colour and the Si:K ratio the degree of discoloration. In well-preserved smalt, regardless of colour, the proportion of Si to K is in the order of 3:1 or 2:1.[40] From Table 1 we can conclude that the proportion of Si to K in the smalt particles is more in the order of 50:1, indicating that the smalt-containing paint must have discoloured. In a cross-section from Rembrandt's sky in the upper left, a large smalt particle with a blue core can be seen with a discoloured rim (fig. 8). Measurements in the colourless rim show a dramatic drop in potassium content compared to the preserved blue core. Since the majority of the smalt particles are small and colourless, showing the same diminished potassium levels, we can conclude that they have all discoloured, implying that Rembrandt's sky was originally blue. The presence of a little bone black and hardly any lead white must mean that a darkish blue was originally intended here. There is indeed some variation between the smalt in the overpaint that covers the left spandrel and Rembrandt's smalt used elsewhere in the painting. Analyses of smalt particles in the overpaint show a higher cobalt content and a lower percentage of aluminium pointing to a differently manufactured smalt.
Comparison of the Si and Co ratios show no difference between the smalt used in the upper paint layers and the smalt used in the undermodelling paint, indicating that a lesser quality smalt was not used for areas that were to be covered up, as might have been expected.

It has also been shown that the stability of smalt depends on its composition, which can vary. Smalt is composed mainly of silica (Si) dioxide, along with variable amounts of oxides of potassium (K), cobalt (Co), iron (Fe), nickel (Ni) and arsenic (As) depending on the geological source of the cobalt ore.[41] Barium (Ba), calcium (Ca), sodium (Na), magnesium (Mg), copper (Cu), aluminium (Al), bismuth (Bi) and manganese (Mn) can also be present, depending on the composition of the raw glass, or other additives possibly used in the manufacturing process. From the glass degradation literature we have learned that high alkali/low lime glass compositions are generally considered unstable.[42] Certainly high amounts of K, very little Ca and no Mg were detected (Table 1). The high K and the lack of glass network stabilising components can be held responsible for the severe discoloration; not only in *Susanna*, but also in seventeenth century smalt paints in general.
The role of other pigments present, or not present, in the smalt paint layer was also considered. The stabilising influence of (sufficient) chalk (calcium carbonate) or lead white is mentioned several times in the literature.[43] While only a trace amount of lead white and no chalk was found in the degraded smalt sky, suggesting that insufficient pH buffering could play a role in its degradation, in the intermediate foliage layer the chalk, presumed to be present from the yellow lake, was obviously insufficient to protect against loss of colour, since the smalt there shows the same diminished potassium levels as the smalt in the sky.

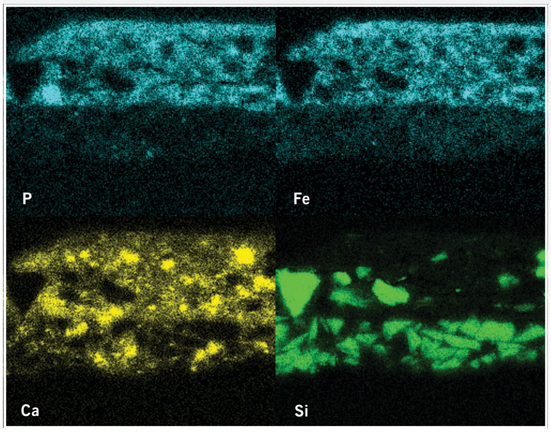

fig. 12 Elemental maps showing showing distribution and intensity of Ca, Si, P and Fe in cross-section 07 (see Table 1) of greyish green foliage. The P and the Fe associated with the vivianite show overlap. See fig. 10c for corresponding SEM image

The role of the binding medium, which was found to be linseed oil (P/S ratios = 1.5 to 2)[44], was also considered. In the back scatter SEM images of Rembrandt's smalt paint in the sky, tiny discrete highly scattering particles are observed in the binding medium between the large smalt pigment particles. These lead-containing particles are considered to be from a lead drier that was added to the oil to aid in the homogeneous drying of the layer.[45] It has been suggested that the addition of lead drier improves the drying properties of a smalt layer and that without lead the smalt layer would preferentially dry at the surface.[46] The strong UV-fluorescence of the matrix around the smalt particles is thought to be due to the saponification of the lead drier in the oil, since DTMS-gave no indication for the addition of other components such as resin, protein, or gum which might be held responsible.[47] Whether the relatively small contribution

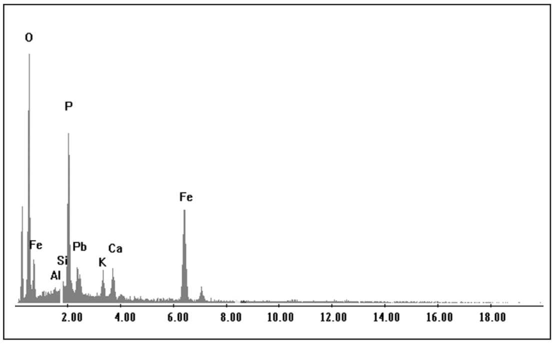

fig. 11 EDX spectrum of vivianite particle in foliage layer of cross-section 07 (see Table 1) from greyish green foliage.

of lead (from the drier) in the binding medium also has an enhanced effect on the discoloration process is still under investigation. Boon et al. discuss the oil binding medium's role as ion exchanger with the potassium ions in the smalt.[48] In this sense a low level of available lead ions would probably be insufficient to inhibit the leaching of potassium, the aged oil thus acting as a trap for the potassium leached from the smalt.[49]

The changes that occur in the binding medium also seem to play a part in the greyed/blanched appearance of the smalt paint. The interaction of moisture with the oil binding medium and the smalt is thought to accelerate/enhance not only the discoloration[50], but also the physical degradation of the paint layer, causing cracks and voids that scatter light. The observation that the varnish layer covering the discoloured smalt paint had also become degraded, appearing whitish and spotty, is thought to be due to the interaction of potassium ions with atmospheric water either close to or at the varnish interface. The poor connection between varnish and paint would increase the degree of light scattering. The possible contribution of vivianite and yellow lake to the degradation and blanched appearance of the foliage will be discussed at the end of the following two sections.

• *The use of vivianite in the foliage*

Never before identified in Rembrandt's paintings, the identification of the greyish blue earth pigment vivianite [51] in the grey green foliage represents a new discovery (fig.9). Until recently vivianite has mainly been mainly associated with medieval wall paintings and polychromy in Germany and England from 1065–1370, and in Baroque and Rococo Austrian and German painting and polychromy from 1698–1780.[52] Its use in Dutch seventeenth century easel paintings was first reported by Marika Spring in blue and mixed green areas of eight landscape paintings by Aelbert Cuyp, the earliest dating from 1640–41.[53] Recently other examples have emerged, indicating that vivianite, or blue ochre/earth as it was probably known, was more commonly used in Dutch seventeenth century painting than had previously been thought.[54] Documentary sources mention various synonyms that might have been used for vivianite: 'blue ashes', 'blew clay earth', 'terra de Harlem' or 'Harlems Oltramarin.'[55] Its use in the seventeenth century is certainly not surprising; it could be found in peat bog iron ores and sedimentary deposits in the Netherlands, Germany and Flanders.[56]

In *Susanna* it is present in substantial amounts in both the thick intermediate foliage layer and in the thin glaze that covers it (fig.10). The intermediate foliage layer comprises a complex mixture of pigments; in addition to vivianite and chalk (yellow lake), the layer contains smalt, quartz, and small amounts of earth pigments, bone black, red lake and vermilion. In this mixture the very small (1–2 μm), and sometimes larger (up to 10 μm) angular greyish particles of vivianite are not easy to see, and consequently may often have been overlooked. They only became apparent after numerous particles in the cross-section were analysed with SEM–EDX demonstrating the exclusive presence of the elements iron (Fe) and phosphorus (P) (fig.11).[57] EDX mapping was also carried out in order to assess the elemental distribution and amounts present (fig.12). From the EDX mapping it also became clear that there is a discrete thin top layer containing vivianite and chalk (from yellow lake), but with relatively less chalk compared with the layer below, which can be interpreted as a greenish glaze that has faded.

Vivianite is a naturally occurring crystalline mineral — a hydrated iron phosphate ($Fe_3(PO_4)_2\_8H_2O$) which, depending on the environment in which it was formed, is a translucent greenish blue or greyish / blackish blue. In general the more finely ground the vivianite the bluer the colour, due to increased surface area for oxidation to take place.[58] In its natural unoxidized state vivianite is a colourless/whitish grey but turns blue when exposed to air,[59] the blue colour resulting from ferrous (Fe^{2+})– ferric (Fe^{3+}) interaction (Intervalence Charge Transfer (IVCT)) under the absorption of light.[60] According to Richter the greyish/blackish variety is the result of being formed in more organic, phosphate-rich peat-bog ores and clay deposits. A special feature of this variety is its colour transformation upon exposure to air.[61] The colour deepens with increased exposure to air and in its fully oxidised state becomes brown/yellow/orange.[62] Alteration of vivianite to a yellow colour has been observed in medieval wall painting.[63] How stable it is in the long term is as yet unclear, but certainly one would not expect the oxidation process to stop completely once it is incorporated into paint.[64] It would also not be unusual to find a degradation gradient in the paint layer where the vivianite is more oxidised towards the surface than deeper down in the layer. Although the mineral does not seem to be especially stable, it is unclear whether it might have played a role in the degraded appearance of the greyish foliage, especially since other heavily cracked and blanched areas, such as Susanna's hair, do not contain vivianite. In these areas it is thought that the presence of a faded yellow lake might explain their greyish/blanched appearance.

- *'Schiet-yellow', evidence of a faded yellow lake*

Indeed, the abundance of chalk in the foliage layer suggested that a yellow lake had been used in combination with blue vivianite in the greenish foliage (fig. 9–10).[65] According to historical sources organic yellows became more common in the seventeenth century in the making of mixed greens.[66] Rembrandt appears to have consistently used yellow lakes. The fact that they are not so frequently identified[67] must be due to their deterioration, which makes them difficult to detect visually, especially in mixtures with other pigments; but also because of the breakdown of the organic colouring matter, which often cannot even be identified by chemical analysis. A degraded yellow lake was also suspected to be the cause of the greyed and blanched paint of Susanna's hair, particularly the hair that falls through her fingers, though close study also revealed grey areas along the curve of her back that prior to the present treatment had been concealed with brown overpaint. A paint cross-section confirmed the presence of a yellowish layer consisting of large light yellow amorphously shaped particles, with the addition of a little smalt and a tiny amount of yellow earth (fig. 13). EDX analyses of the yellowish particles in the cross-section revealed the exclusive presence of calcium (from the substrate) and carbon (from the organic dyestuff component), which together can be interpreted as a (now faded) yellow lake.[68] The back scatter SEM image also suggests that this layer was further modified with a thin pure yellow lake glaze (fig. 13c).

Chalk based yellow lakes, or *pinks* as they were known in the seventeenth century, became increasingly common, despite the fact that they were known to suffer severe light-induced fading.[69] The reason for their instability seems to be that they are not true lakes prepared by precipitation methods, but are adsorbed onto a calcium salt substrate. This type of complexation makes these colours even more vulnerable to light-induced fading.[70] However, it is considered that the blanched and greyed appearance of the hair and the aforementioned foliage is not due only to the loss of the organic colouring material from the greyish chalk substrate. As has been noted by many researchers in the past, the physical break down of a paint film, leading to cracks and voids in the surface that scatter light, also contributes to a blanched appearance. In *Susanna* evidence for this is seen in the light-microscope and back scatter images where, in samples from both hair and foliage, the paint surfaces are broken up and full of micro-cracks. It is plausible to think that the absorption of moisture by these chalk-rich layers, possibly introduced through conservation treatments or high relative humidity from past display/storage conditions, is sufficient to have caused this disruption of the paint film.[71]

- *Fading of red lakes*

Rembrandt typically uses red lake in combination with other pigments rather than as a traditional glaze. In Susanna red lake is present in many mixtures in various areas: in the flesh paint, in the undermodelling layer, in the warm dark brown mixtures with black depicting the tree and background foliage and the darkest shadows of the figure, as well as being mixed with a touch of vermillion and lead white in the red cloak.[72] Although the red lake of the cloak has largely maintained its bright crimson tone with touches of orangey vermilion and pink (where vermilion and lead white were mixed with the red lake) some deterioration is evidenced by a slight greyness in the darkest passages which to some extent flattens the modelling (fig. 14).[73] By comparison, the smoothly applied dull reddish brown of the drapery on the addition seems to have suffered extreme darkening. This is evident along the edge of the picture where it is much redder as a result being protected by the frame rebate.

Paint cross-sections from the original panel and from the addition show large differences in the build up, pigment morphology and distribution. In the sample from the shadow area on the original panel, we see typically a multi-layered build-up (fig. 15). Over the thick reddish brown undermodelling layer, which in this area contains a good deal of red lake, three red lake layers have been applied. The first is a thin pure lake layer,

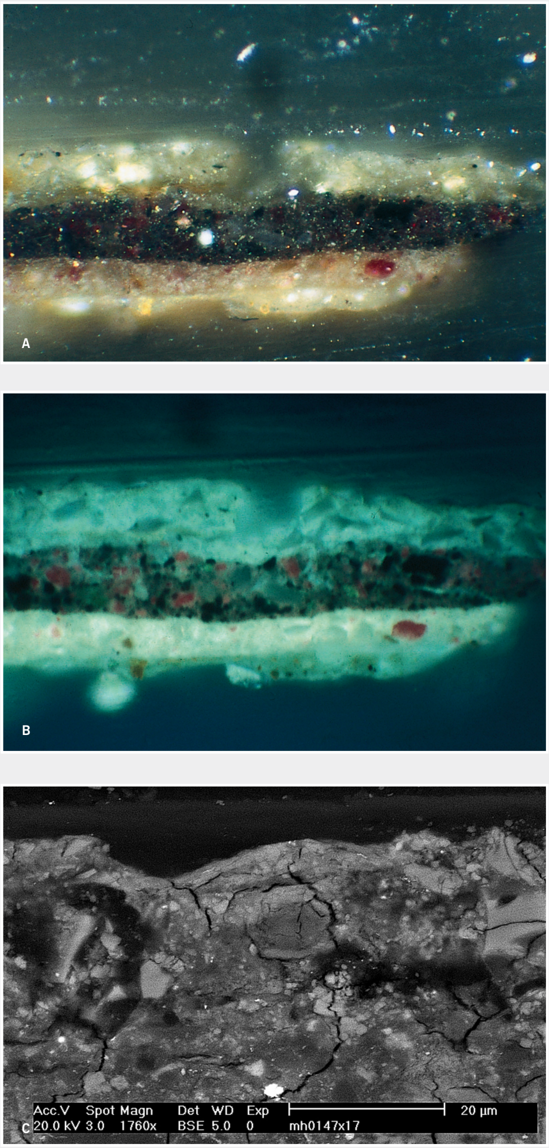

fig. 13 Cross-section from Susanna's hair showing the faded yellow lake top layer. Here the surface is physically broken up. Normal light (A), UV (B) and SEM image showing a detail of the top layer (C).

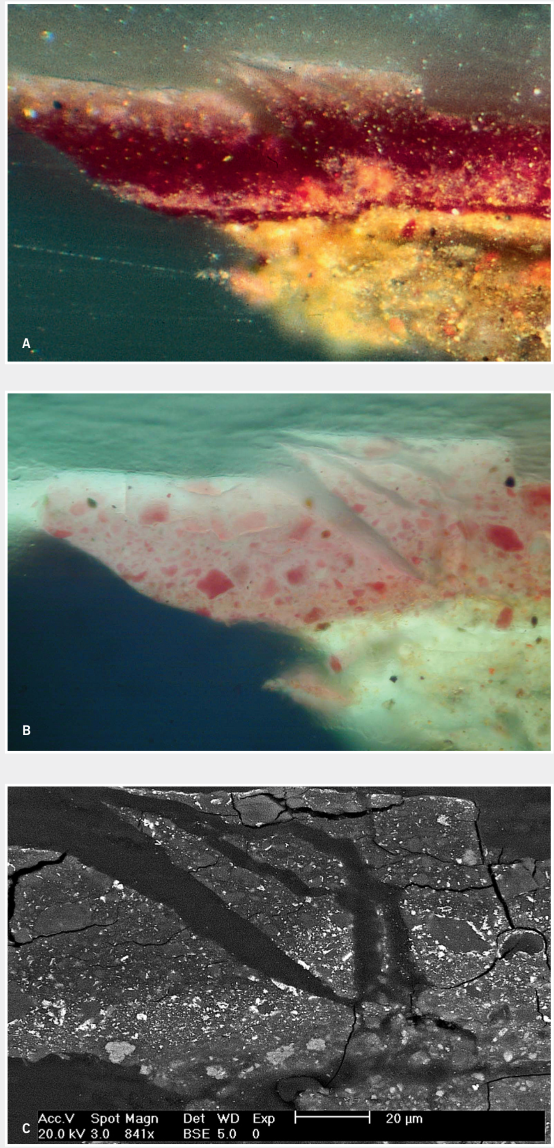

fig. 15 Cross-section from red cloak on original panel showing a multi-layered build up: on top of an initial brown sketch a thick warm undermodelling containing a complex mixture of pigments was applied. This was followed by three red lake layers: a thin layer of pure red lake, then a red lake layer containing fine lead white, and a final layer that also contains a trace amount of vermilion. Fading of the top layer has occurred. Normal light (A), UV (B) and SEM image showing a detail of the top layer (C).

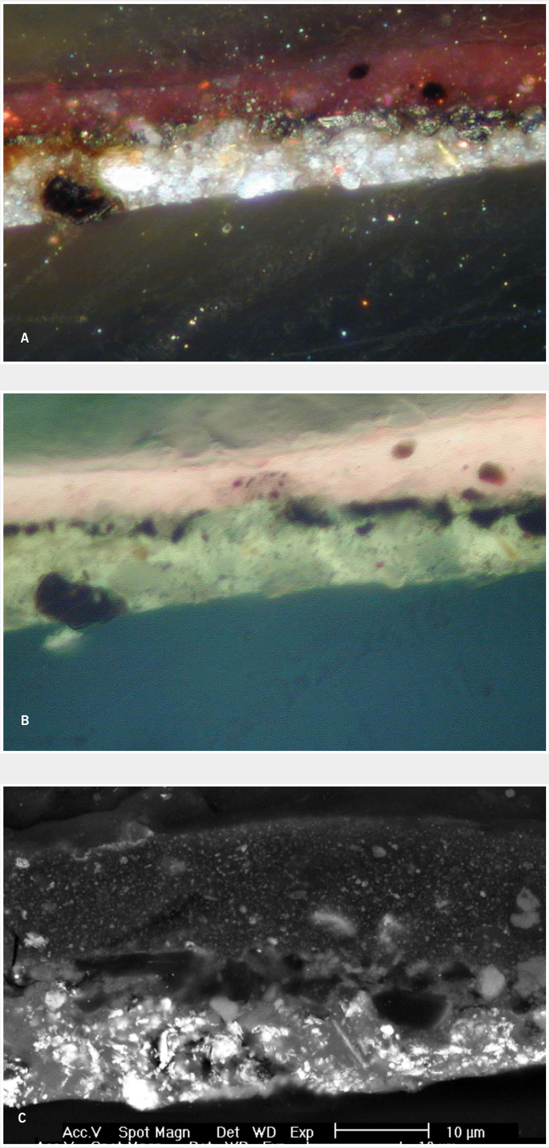

fig. 16 Cross-section from red cloak on addition showing ground, a dark underpaint and a single smooth extremely homogenous red lake layer that also contains a little bone black and vermilion. Normal light (A), UV (B) and SEM image (C).

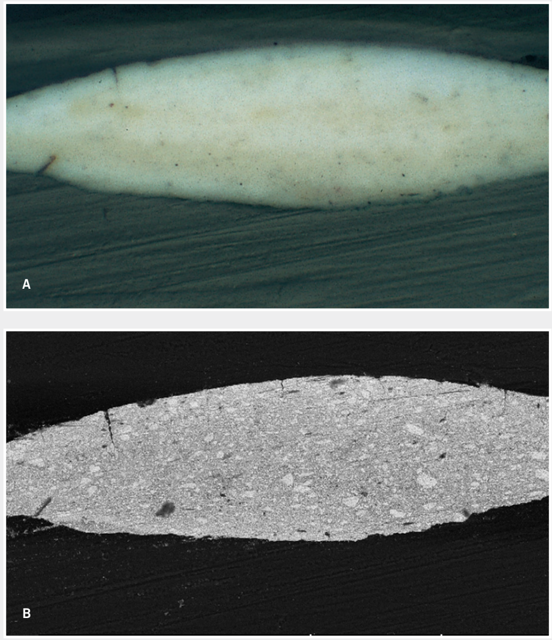

fig. 17 Cross-section from Rembrandt's white drapery on original showing a thick compact, pure lead white ground. Ground layers missing from sample. Normal light (A) and SEM image (B).

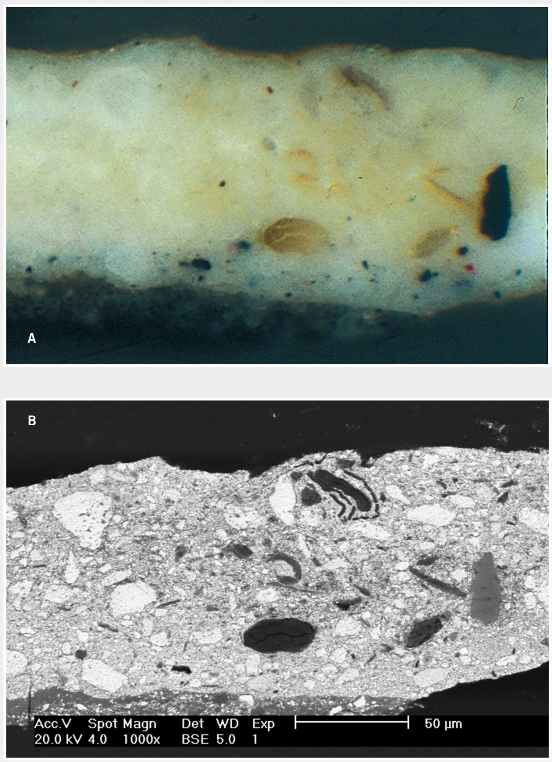

fig. 18
Cross-section from white drapery on addition showing a less compact lead white layer. Here the lead white particles are much coarser, and a small amount of red and yellow earths, bone black, charcoal black and minium have been added.Normal light (A) and SEM image (B).

probably used for an initial sketch, followed by a thicker layer consisting of large globular particles of red lake (up to 20 μm) and very fine lead white, modified by the top layer that also contains a very small amount of vermilion. Fading is seen at the surface of the uppermost red layer, while in the bottom of the layer and in the layer below, the brilliant colour survives. By comparison, in a cross-section of a sample from along the right edge of the addition, where it has not discoloured, we see a single homogenous layer of extremely fine red lake particles (about 1 μm) mixed with tiny amounts of bone black and vermilion (fig. 16). Only in the back scatter SEM image can the fine splintery red lake particles (a result of being finely ground) be distinguished (fig. 16c).

The organic dyestuffs in both red lakes were identified by Wouters as containing carminic acid, the main component of insect red dyes.[74/75] Unfortunately it was not possible to quantify other components so as to identify the exact species of cochineal in these samples, but considering historical and geographical context both samples are likely to be Mexican cochineal (Dactylopius coccus). In the seventeenth and eighteenth centuries Mexican Cochineal was a widely used source for the preparation of red glazes.[76] The substrate, the material onto which the organic dyestuff was usually precipitated by the addition of an alkali, was found to be aluminium-based. Aluminium hydroxide is the most commonly found substrate in red lakes. Analyses with SEM-EDX of Rembrandt's red lake layers indicate the presence of the elements Al, S, K and Ca. The Ca suggests that a calcium salt, such as calcium carbonate or calcium sulphate, was added in addition to a potassium salt, where the excess would act as an extender.[77] The substrate on the addition appears to be similar, as suggested by the detection of the elements Al, S and K as well as a little Ca; here, however, the calcium could come from the bone black in this layer. We can therefore conclude that, although the red lakes on the original and on the added strip are chemically very similar, they look different and are used in very different ways.

- *Pastose lead white paint*

The lead white passages of the original part of the painting were also compared with that of the addition. In contrast to the degraded and discoloured sky and foliage, the lead white areas on the original part, namely the flesh paint and Susanna's white shirt, are in almost perfect condition. Here Rembrandt has maximised the good standing properties of lead white, building up the short buttery paint into almost a sculptured mass. In contrast, the paint on the addition is smooth, as well as being warmer and greyer (fig. 14).

Samples from both areas were embedded as cross sections to compare the build up and composition of the layers (figs. 17–18). An electron back scattered SEM image of a cross-section from a white highlight of the shirt in the original part of the panel shows a thick, compact, pure lead white layer showing coarse and fine particles (fig. 17b). Here the lead white has not been adulterated with chalk (*lootwit*), the cheaper quality of lead white available in the seventeenth century, but instead the pure *schulpwit* has been used.[78] Only a few very minor contaminations of red lake and bone black (from the palette or surrounding paint) could be identified. Since Groen established that the particle size distribution of lead white is what largely determines the rheology of the paint, the combination of coarse with very fine particles observed here must be held responsible to a large extent for the good standing qualities of the impasto in this painting.[79] DTMS analysis indicated the binding medium is linseed oil (P/S = 2) with a low oil content, corresponding with the dense appearance in the SEM image. There was also no indication for the addition of protein.[80]

The back scatter SEM image of the white paint from the added strip gives a rather different picture (fig. 18b). In contrast, here the lead white is less compact, less finely ground, containing much coarser lead white particles than Rembrandt's paint. But here too it is not adulterated with chalk, though additional pigments were found to have been added (a little yellow and red earth pigment (EDX: Si, Al, Fe), bone black (EDX: Ca, P, Mg), charcoal and minium (EDX: Pb)). The DTMS analysis shows it is linseed oil (P/S = 2) with a higher organic content than that of the original.[81] The mineral composition of lead whites can sometimes vary, but XRD analyses gave the same composition in both cases.[82/83]

With the idea that origin determination could provide essential information about the date of the addition, minute samples of lead white, from the drapery on the original panel and from where it was extended onto the strip, were subjected to lead isotope analysis.[84] The element lead (Pb) occurs in nature as a combination of four stable isotopes ^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb, and, depending on the geological conditions in which lead ore is formed, these isotopes occur in different concentrations. Thus the ratio of these lead isotopes can be

Table 2	Lead isotope ratios				
Lead isotope ratios	$Pb_{208/206}$	$Pb_{207/206}$	$Pb_{206/204}$	$Pb_{207/204}$	$Pb_{208/204}$
Lead white from drapery on original	2.08034	0.84636	18.4750	15.6365	38.4342
Lead white from drapery on addition	2.08235	0.84702	18.4441	15.6225	38.4071

indicative for its origin, enabling us to discover where the lead ore was mined (presuming there is only one source of lead in the samples). Samples from the original part of the picture and that of the strip show ratios that correlate with isotopic data of known lead ores mined in England in the seventeenth century (see Table 2).[85] While both samples have related isotopic compositions, they are not identical (fig. 19), meaning that both lead samples stem from England but not from the same mine.[86] Since at that time lead ore mining was limited to a few places, the present data suggests that the lead from the lead white on the strip has a seventeenth century origin, since in the eighteenth century the possible ratios vary more due to mines opening up throughout Europe. Of course, it is still possible that the strip was added in the eighteenth century using a lead white made in the seventeenth century.

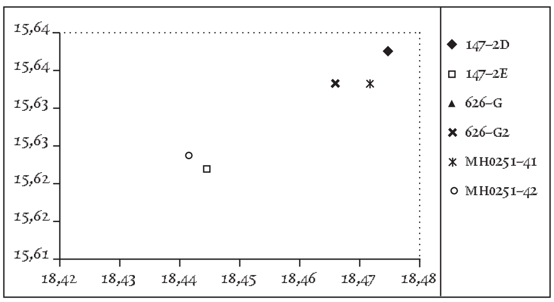

fig. 19 Ratios of lead isotopes 207Pb/204Pb plotted against 206Pb/204Pb. Rembrandt's lead white from *Susanna* is sample 147-2D and the lead white from the addition, 147-2E. Samples 626-G and 626-G2 are lead white from a Rembrandt studio painting, from c.1630 and samples 251-41 and 251-42 from a Rubens' painting from the 1620s.

3. Original dimensions — a reconstruction

Although we could establish that the picture originally had an arched-top composition, the question as to the panel's original dimensions remains unanswered. While the left edge is intact, since here the ground goes over the edge, and possibly the bottom edge as well, we now know that the top edge was trimmed, though probably not by more than 1 cm if we presume that the arch was originally complete.[87] But how wide was the panel originally? How much disappeared at the right before the new piece was added? If we can assume that the arch was in the middle of the panel we can deduce that about 1 to 2 cm have been trimmed from the right side. This agrees with the difference in the depth of bevelling between the left and right edges observable on the back of the panel. At the right (as seen from the back) the irregular bevelling ranges between 2 and 4.5 cm, while at the left, where the original panel was reduced, the bevelling is only about 1.5 cm at the deepest point. As the addition is about 4 cm wide, this means that the painting is now at least two centimetres wider than it originally was.

Since Rembrandt would have bought his panels from a joiner who probably had a large range of standard sizes, it is not surprising that the proposed original dimensions of approximately 48 x 36 cm, as well as the present dimensions of 47.4 x 38.6 cm, fit into a group of standard-size panels identified as *groot stooters*.[88/89] Van de Wetering proposes that small variations probably existed within each group of standard sizes, which could have been dealt with by adapting the width of the rebates of the corresponding standard-sized frames with strips of wood.[90] Research into original proportions by Bruyn (1979), Miedema (1981)[91] as well as observations by Martin Bijl, however, suggest that specific height:width ratios were in use in the seventeenth century, which would make it possible, if one dimension were known, to exactly calculate the other. As at the present time there seems to be no consensus as to which height:width ratio was in use — if indeed one was — it is not possible to calculate dimensions. The fact that panels shrink slightly in one direction (across the grain) and hardly at all in the other must also be taken into account.[92] The proposed original dimensions of 48 x 36 cm for *Susanna* are based on physical evidence in the panel itself and fall into the height:width ratio of 4/3 (1.33 : 1).

A logical subsequent step in the treatment of the picture would be to make a new frame for the painting that would cover two centimetres of the addition and the upper corners, returning it more closely to its original format. For the time being, this change is merely being simulated on the computer, as part of the decision making process (fig. 20).

fig. 14 Detail of red cloak and white drapery, showing original and later additions.

fig. 20 Computer reconstruction showing painting with its proposed original format in an arched-top frame.

4. Conclusion

Analyses have been clearly able to establish that when the addition was made to the right side the upper corners were also filled in. This is demonstrated by the fact that the brown paint in the upper right corner of the original panel is chemically identical with the brown paint on the addition. It is also significant that the underlying grey paint in the upper right corner of the original part of the panel is also both optically and chemically identical with the ground layer on the added strip. In the upper left corner, comparison of the paint covering the black spandrel with that of the original sky revealed a different pigment composition and distribution. While this in itself is not proof that the upper left corner was overpainted it is reasonable to assume that this corner was filled in at the same time as the upper right. Exactly when the addition of the strip and the overpainting of the corners took place, we cannot say. The addition of pine resin in the ground and the brown paint on the addition tend to point to the eighteenth century. This is also suggested by the strikingly coarse texture of the brown paint. We know it must have taken place before 1758; but nothing is known about earlier restorations, which might have provided clues as to when this occurred. The reason for the addition was almost certainly the woodworm damage that had occurred along the right edge of the panel. Why the corners were also overpainted may have been simply because it was easier to disguise the join if the same paint extended over the upper right corner of the original panel.

Chemical analyses established that Rembrandt's smalt was originally bluer, from which we can conclude that the sky was originally blue-grey and not the present brown-grey. The degradation observed in Rembrandt's sky was found to be a result of the use of an unstable smalt and its combination with Rembrandt's choice of pigments. The fact that degraded smalt paints occur in many artists' work of the seventeenth century seems to suggest that unstable varieties were manufactured, from which — depending on the amount of buffering conferred by the paint mixture — potassium leached out over time into the surrounding paint medium. The discovery of the use of the greyish-blue earth pigment vivianite in the mixed green grey of the foliage is significant because not only has this pigment never before been identified in pictures by Rembrandt, it is the earliest use of vivianite in seventeenth century easel painting. As it could also be established that this blue was mixed with a chalk-based yellow lake that has largely faded indicates the foliage was originally greener. A degraded yellow lake was also demonstrated in the badly cracked and greyed hair of the figure of Susanna, which must once have appeared golden. In these areas, the deterioration is due to the physical breakdown of the paint in combination with loss of the organic colouring matter. Although there is no doubt that discoloration has occurred, it is still likely that originally these colours were rather subdued. In the sky there is only a trace of lead white and very little bone black; therefore, while it was originally blue, it was certainly intended to be dark. Similarly in the foliage, the choice of greyish vivianite was a conscious one, so the desired effect must have been a dull green. Regardless of how subtle these colours might once have been, colour changes have important consequences for understanding the original appearance of the picture. Certainly stronger colours would have provided greater contrast with the upper right background and foreground, areas which because of their stable pigment composition must always have been monochromatic.[93] Perhaps we can now better understand Sir Joshua Reynolds' reaction when he saw the picture in The Hague in 1781, when he spoke of: [...] 'the colouring and effect, in which it must be acknowledged he [Rembrandt] has attained the highest degree of excellence'.[94]

Acknowledgements
The authors wish to thank the following for their assistance: Jaap Boon for interpretation of DTMS data; Peter Hallebeek for the XRD measurements; Jerre v/d Horst for DTMS measurements; Giuseppino Fortunato for Lead Isotope analysis and interpretation; Jørgen Wadum for the computer simulation and Jan Wouters for HPLC measurements. The research is part of the Open Laboratory agreement between the FOM Institute for Atomic and Molecular Physics (FOM–AMOLF, Amsterdam) and the Royal Picture Gallery Maurithuis (The Hague) taking place under the umbrella of the MOLMAP project in the De Mayerne program of the Dutch Foundation for Scientific Research (NWO, The Hague).

Additional photo credit
Fig.19 Graph courtesy of G. Fortunato (EMPA) 2004.

Notes

1 Rembrandt's other full-length female nudes include *Andromeda*, c. 1630 (Mauritshuis), *Danae*, c. 1636/1643 (Hermitage), *Susanna and the Two Elders*, 1637/1647 (Gemäldegalerie Berlin), *Bathsheba Reading King David's Letter*, 1654 (Musée du Louvre).

2 Since 1815 as part of the Royal Collection in The Hague, see B. Broos, *Intimacies and Intrigues History Paintings in the Mauritshuis*, (The Hague, 1993), 262.

3 In the past the picture has been interpreted as a *Bathsheba*, see A.B. de Vries et al., *Rembrandt in het Mauritshuis*, (Alphen a/d Rijn, 1978), 126–130 and J. Bruyn et al., *A Corpus of Rembrandt Paintings*, vol. 3, (Dordrecht/ Boston/London, 1989), 200, where they describe the presence of the second male figure, whose head can just barely be distinguished in the bushes a little to the left of the other figure.

4 In the sale catalogue of 23 May 1758 described as: '...hoog 18 duym, breed15 [46.8 x 39 cm]', Bruyn et al. 1989, 201, and Broos 1993, 267.

5 Broos 1993, 262. Also E. Runia, P. Noble and J. Wadum, 'Twee naakten van Rembrandt gerestaureerd en onderzocht', *Mauritshuis in Focus*, 16, 1 (2003), 15–19. The RRP also states that the signature was painted by two different hands, 'the letters *Rembr* and *f 163*, are convincing in their shaping, and can thus be looked on as the remains of an authentic signature', Bruyn et al. 1989, 199.

6 Bruyn et al. 1989, 200. Also Broos 1993, 262.

7 Documented by Annelies van Loon with the Artist camera (Art Innovation, Hengelo) mounted with a CCD progressive scan image sensor (1360 x 1036 pixels) and a Schneider Kreuznach Xenoplan 1.4/23 mm CCTV-lens in N12 with a long wave pass filter 1000 nm. The images were captured with Artist Software (release 1.2) and stitched with PanaVue ImageAssembler.

8 In the Noordeinde Palace inventory of 20 March 1668 the frames of the seven arched-top paintings in the Passion series (1632–46) are described: 'Seven stucken schilderije bij Rembrandt gemaeckt, alle met swarte lijsten, boven ovaelsgewijse ende rontom vergulde feuillages' in Ch. Brown et al., *Rembrandt the Master & his workshop*, ed. S. Salvesen, [exh. cat., Rijksmuseum] (Amsterdam, 1991-1992), 156, see also 227 which shows Rembrandt's drawing, *Portrait of a Man in a Armchair*, c. 1634 where an arched-top frame has also been included. Rembrandt seems to have been predisposed to arched-top frames (or formats), which must have served to strengthen the *trompe l'oeil* effect making paintings appear as if they were viewed from an open window. Also E. van de Wetering, *The Painter at Work*, (Amsterdam, 1997) 78, figs. 107 and 108.

9 'Le tableau semble être paint pour un cadre cintre' in A. Bredius, C. Hofstede de Groot, *Musée Royal de Tableaux Mauritshuis à La Haye: Catalogue raisonné des tableaux et sculptures*, [coll. catalogue] (The Hague, 1895), 334, no. 147 and 'Das Bild scheint für einen oben Rahmen gemalt zu sein' in C. Hofstede de Groot, *Beschreibendes und kritsches Verzeichnis der Werke der hervorragendsten Holländisches Maler des XVII. Jahrhunderts*, vol. 6, (Erlingen/Paris, 1915), 37, no.57.

10 Brown et al. 1991–2, 196. In the technical examination of the picture in the Mauritshuis in the 1970s, the rounding off of the corners is mentioned, but no difference was detected, De Vries et al. 1978, 130. The RRP also detected no difference, Bruyn et al. 1989, 199, 201, though they state the picture initially had unpainted spandrels.

11 Several of Rembrandt's important paintings have been cut down: *The Anatomy Lesson of Dr Johannes Deyman*, 1656, (Amsterdams Historisch Museum) and *Homer*, 1667, (Mauritshuis) as a result of fire damage, and *The Nightwatch* (Rijksmuseum Amsterdam) when it was moved from its original location to the Amsterdam Town hall in 1715. A. K. Wheelock. Jr., 'The Art Historian in the Laboratory: Examinations into the History, Preservation, and Techniques of 17th Century Dutch Painting', in *The Age of Rembrandt. Studies in Seventeenth-century Dutch Painting. Papers in Art History from the Pennsylvania State University*, vol. 3, R. E. Fleischer, S. Scott Munshower eds., (The Pennsylvania State University, 1988), 215.

12 A change in format to Rembrandt's *Simeon's song of praise*, (Mauritshuis) was carefully documented when it became part of an interior scheme in Palace Het Loo in 1733. According to the inventory of all the royal possessions made in 1757/1763, the corners of the Rembrandt were trimmed and an arched top was added in 1733 by the painter/ restorer Philip van Dijk in order to hang in the painting cabinet there as a pendant to the arched-top Gerard Dou, *Young Mother*, (Mauritshuis) forming a sort of triptych with Cornelis van Poelenburch, *The Annunciation of the Shepherds*, (Gray, Musée Baron Martin), which hung in the middle. P. van der Ploeg , C. Vermeeren, *Princely Patrons: The Collection of Frederick Henry of Orange and Amalia of Solms in The Hague*, M. Enklaar ed., [exh. cat. Mauritshuis] (The Hague, 1998), 191.

13 The treatment, along with the present research was carried out by Petria Noble in the Conservation Studio of the Maurithuis in 2002. The research was carried out in collaboration with FOM Institute AMOLF, Amsterdam, as part of the 'Open-laboratory' collaboration.

14 'Schoongemaakt en oude vernislaag verwijderd', the picture was previously cleaned in 1948 by

the restorer J. C. Traas.
15 Microscopy was carried out by Petria Noble using a Nikon Optiphot-2 microscope with normal light provided by a 100W Halogen projection lamp. An Osram Mercury Short Arc HBO 103 W/2 lamp and Nikon filter V-2A (excitation 380–425 nm, emission > 430 nm) were used for fluorescence microscopy.
16 SEM–EDX analysis was carried out by Annelies van Loon and Petria Noble, FOM Institute AMOLF, Amsterdam, using a FEI XL30 SFEG high vacuum electron microscope and EDAX detector. This technique supplies information on the particle size, shape and distribution, and on the elementary composition of the paint materials. The back scatter (BSE) images show the contrast in composition between the light and heavy elements. Besides the highly informative back scatter images, information on the elemental composition is obtained by EDX spot analysis and elemental mapping.
17 Binding medium analysis by DTMS was carried out by Jerre v/d Horst, Annelies van Loon and Jaap J. Boon, FOM Institute AMOLF, Amsterdam, using a JEOL JMS-SX/SX102A 4 sector double focusing mass spectrometer. DTMS is an effective technique for characterising the organic components in tiny and complex paint samples. The sample is applied on a filament probe that is inserted directly into the ion source and heated. The temperature is linearly increased from room temperature to approximately 800°C in two minutes. This results in volatilisation of weakly bound and low molecular weight desorbing compounds at a low temperature and subsequent pyrolysis of polymeric material at higher temperatures. The compounds released from the filament are ionised under electron ionisation (EI) conditions and subsequently mass analysed.
18 Peter Hallebeek, Netherlands Institute for Cultural Heritage (ICN), Amsterdam, carried out the XRD analysis of the lead white samples using Debye-Scherrer powder diffraction. Lead Isotope analysis was performed by Giuseppino Fortunato, Swiss Federal Laboratories for Materials Testing and Research (EMPA), St. Gall, 2003–2004. The organic colorants in the red lake pigments were analysed with HPLC by Jan Wouters, Royal Institute for Cultural Heritage (IRPA/KIK), Brussels, 2003.
19 See also note 17. In the desorption part of the total mass spectrum, which is the low-temperature region, a high content of fatty acids was observed with characteristic peaks at m/z 256 and 284 of palmitic acid (C16) and stearic acid (C18) respectively. In the pyrolysis part of the total mass spectrum, which is the higher temperature region, the characteristic pattern of the pyrolysis products of the oil paint network was present. The ratio of the molecular ions of the palmitic to stearic acids (P/S) is considered to be a relatively stable feature and thus can be used to identify the type of drying oil: linseed oil (P/S=1.6), walnut oil (P/S=2.5) or poppy oil (P/S>3). See J. S. Mills, R. White, *The Organic Chemistry of Museum Objects*, 2nd ed., (London, 1994), 171.
20 See also note 19. In addition, the spectrum shows traces of oxidized abietic acids, dehydroabietic acid (DHA: m/z 239, 287, 300) and oxidised dehydroabietic acid (OXO–DHA: m/z 253, 314, 315 and 330), diterpenoid acids characteristic of pine resin. See research results by K. J. van den Berg et al., 'Mass spectrometric methodology for the analysis of highly oxidized diterpenoid acids in Old Master paintings', *Journal of Mass Spectrometry*, 35 (2000), 512–533.
21 Personal communication Karin Groen, Netherlands Institute for Cultural Heritage (ICN), 2003.
22 Pine resin is, however, listed in a recipe for a ground in Armenini's *On the true precepts of the art of painting* of about 1609 (Italian). With thanks to Maartje Witlox, *De Mayerne* project 'Historically Accurate oil paint Reconstructions', 2004. For mention of diterpenoid resin in the grounds of 18th and 19th century paintings, see K. Groen, M. de Keijzer and E. Baadsgaard, 'Examination of the Painting Technique of Nine Dutch Pictures of the First Half of the 18th century', Preprints *ICOM-CC 11th Triennial Meeting Edinburgh*, J. Bridgland et al. eds., vol. 1, (London, 1996), 360–366, particularly 362.
23 Made of charred bones, bone black is composed mainly of calcium phosphates and contains only 10% carbon as the black colouring substance. Its mineral content helps distinguish bone black from other carbon blacks with EDX.
24 The TIC diagrams show a summation of all mass spectra from the components that have evaporated from the filament at different temperatures over time. See also note 17.
25 The DTMS spectra show lead isotope mass peaks at m/z 206, 207 and 208.
26 Lead drier was also found in a bone black layer from the cloak in *A young Monk (Titus)*, 1660 (Rijksmuseum Amsterdam), K. Groen, 'Investigation of the Use of the Binding Medium by Rembrandt', *Zeitschrift für Kunsttechnologie und Konservierung*, 11 (1997), 2, 219. See also the paintings in the Oranjezaal (Royal Palace Huis ten Bosch) from about the same period see A. van Loon, J. J. Boon, 'Characterization of the Deterioration of Bone Black in the 17th Century Oranjezaal Paintings using electron-microscopic and micro-spectroscopic imaging techniques', Forthcoming publication in *Spectrochimica Acta B* ICXOM XVII special issue (2004).
27 See H.F. Mark et al., *Encyclopaedia of polymer science and engineering*, (New York, 1990) and J. Winter, 'The characterization of pigments based on carbon', *Studies in Conservation*, 28 (1983), 49–66.
28 See note 20. The addition of a substantial quantity of pine resin to the oil medium is in not normally encountered in Rembrandt. However, several painters in his circle occasionally appear to have added small amounts of pine resin to the oil medium. See R. White, J. Kirby, 'Rembrandt and his Circle: Seventeenth-Century Dutch Paint Media Re-examined', *National Gallery Technical Bulletin*, 15 (1994), 71–74.
29 The UV-fluorescence can also be due to the presence of lead carboxylates (soaps), see for example P. Noble et al., 'Dissolution, aggregation and protrusion, Lead soap formation in 17th century grounds and paint layers', *ArtMatters. Netherlands Technical Studies in Art*, 1 (Zwolle, 2002), 46–61.
30 White and Kirby 1994.
31 The mineral cobalt ore was roasted to produce cobalt oxide, which was then melted together with quartz and potash, or added to molten glass. It was then poured into cold water and the resulting particles were ground in water mills. B. Muhlethaler and J. Thissen, 'Smalt', in *Artists Pigments, A handbook of their history and characteristics*, vol. 2, A. Roy ed., (Washington, 1993), 113–130.
32 R. Harley, *Artists' Pigments c. 1600–1835, A Study in English Documentary Sources*, 2nd ed. (London, 1982), especially 197.
33 Rembrandt's varied use of smalt is discussed in D. Bomford et al., *Art in the Making. Rembrandt*, [exh. cat. National Gallery, London] (London, 1988), 25 and Groen 1997, 218.
34 Blanching is a general term referring to a light scattering effect occurring in paint and/or varnish layers from different causes such as fading, migration, residues, abrasion, leaching, cracking.
35 Colourless smalt associated with degraded layers in paintings by Rembrandt was found in *The Denial* (1660) and *the Staalmeesters* (1662) (Rijksmuseum, Amsterdam), Groen 1997, 218. Blanched/discoloured smalt is referred to in the lining of the cloak in Rembrandt's *Man in Armour/Alexander the Great, 1655/1659* (Kelvingrove Museum, Glasgow), Ch. Brown, A. Roy, 'Rembrandt's Alexander the Great', *The Burlington Magazine*, 134 (1992), 294. Smalt was also found in discoloured greyish blue sky in *Portrait of Frederik Rihel on Horseback*, 1663 (National Gallery London), Bomford et al. 1988, 25. Degraded smalt-containing paint was also observed in the purplish red beret of Rembrandt's *Tronie of a man with a feathered beret*, c. 1635, (Mauritshuis). Also Van de Wetering 1997, 258 suggests the almost white sky in *Baptism of the Eunuch* (Catharijne Convent, Utrecht) from 1626 could be the result of discoloured smalt. The degradation of smalt layers has, in fact, been observed in numerous paintings by many different artists, see for instance, Muhlethaler and Thissen 1993, 116.
36 J. J. Boon et al., 'Imaging Microspectroscopic, Secondary Ion Mass Spectrometric and Electron Microscopic Studies on Discoloured and Partially Discoloured Smalt in Cross-Sections of 16th Century Paintings', *Chimia*, 55 (2001) no. 11, 952–960.
37 A. Burnstock et al.,

'Morphology of the Blue Artist's Pigment Smalt using Scanning Electron Microscopy', *Proceedings on Art 2002 – Conference on Non-Destructive Testing and Micro-analysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage*, (Antwerp, 2002).

38 Boon et al. 2001, 952–960.

39 A. Burnstock, 'Characterising degraded smalt by particle morphology and elemental analysis', Lecture given at the *Smalt Symposium* held in the Catharijne Convent Utrecht, 30 May 2002.

40 Burnstock et al. 2002 and Boon et al. 2001.

41 According to Muhlethaler and Thissen 1993, 113–115 the principle cobalt ores used in the manufacture of smalt in the 17th century were smaltite ($[Co.Ni]As_{3-2}$), erythrite ($[Co.Ni]_3[AsO_4]_2.8H_2O$) and cobaltite ($(Co,Fe)AsS$).

42 Addition of K_2O lowers the melting point, whereas CaO serves for higher water insolubility. Aluminium oxide is mentioned as a glass network former. See C. Neelmeijer, M. Mäder, 'Endangered Glass Objects identified by Ion Beam Analysis', in *Proceedings on Art 2002 — Conference on Non-Destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage*, (Antwerp, 2002). See also J. L. Ryan et al., 'Glass Deterioration in the Museum Environment: A Study of the Mechanisms of Decay using Secondary Ion Mass Spectrometry', in *Preprints to ICOM-CC 11th Triennial Meeting Edinburgh*, J. Bridgland et al. eds., vol. 2 (London, 1996), 839–844.

43 Burnstock et al. 2002 discusses the possible retarding effect of calcium on the degradation of smalt in oil. She gives four examples where smalt is well preserved and where the presence of natural chalk was detected.

44 See note 20 for details.

45 The use of a lead siccative was also found in the oil binding media in (degraded) smalt layers in *The Staalmeesters*, *The Denial*, and *The Jewish Bride* (Rijksmuseum Amsterdam) and *Esther before Haman* (Bucharest), Groen 1997, 219.

46 Groen 1997, 219. See also E. —im—nková, 'The influence of cobalt blue pigments on the drying of linseed oil', *Studies in Conservation*, 30 (1985), 161–166.

47 See note 28.

48 Boon et al. 2001.

49 Personal communication, Jaap Boon, FOM Institute AMOLF, Amsterdam 2004.

50 The enhanced effect of moisture on the ageing of oil paint (hydrolysis) and on its ion-exchange properties is explained by Boon et al. 2001. Furthermore, a direct interaction of moisture with the smalt particles can be expected as well, in which mobile alkali (potassium) ions are leached out and replaced by water molecules.

51 The mineral was named after the 19th century English mineralogist J.G. Vivian.

52 M. Richter, 'The Use of Vivianite in Baroque and Rococo Polychromy and Painting', in *Historical Polychromy, Polychrome Sculpture in Germany and Japan*, M. Kühlenthal, S. Miura eds., (Munich, 2004), 205–208.

53 M. Spring, 'Pigments and Color Change in the Paintings of Aelbert Cuyp', in *Aelbert Cuyp*, A. K. Wheelock Jr. ed., [exh. cat., National Gallery of Art et al.] (Washington, 2001), 65–73.

54 In the *Oranjezaal* (Royal Palace Huis ten Bosch) vivianite has been identified by Annelies van Loon in blue draperies and foliage areas in paintings executed between 1648–1652 by Theodorus van Thulden, Salamon de Bray and Pieter de Grebber, *Comparative studies of the paintings in the Oranjezaal*, Forthcoming publication. Spring has recently identified vivianite in two paintings by Carel Fabritius in The National Gallery London, *A View of Delft with a Musical Instrument Sellers's Stall*, 1652 and *Self Portrait*, 1654, Forthcoming publication [exh. cat. Mauritshuis] (The Hague, 2004).

55 In De Mayerne Manuscript (1620) mention is made of *cendre dázur* (blue ashes), Richard Symonds (1650s) mentions *Harlems Oltramarin* and Samuel van Hoogstraten (1678) lists *English, German and Haarlem ashes*, though whether these names actually refer to vivianite is unclear, see Spring 2001, 66, 67, 70, 71. Also Harley 1982 59–60. Beurs mentions *Duitsche* and *Engelsche as*, W. Beurs, *De Grote Waereld in 't kleen geschildert...*, (Amsterdam, 1692), 6; for eighteenth and nineteenth century documentary sources see Richter 2004, 205.

56 There was an active peat industry in the Netherlands, see for instance, Spring 2001, note 47.

57 Identifying the pigment with polarised light microscopy (PLM) is not so straightforward as the pigment has different optical and pleochroic properties depending on the form it is in. P. & A. Mactaggart, *A Pigment Microscopist's Notebook*, 7th rev. ed. (1998), 8. T. L. Watson, 'The color change in vivianite and its effect on the optical properties', *The American Minerologist*, vol. 3 (8) (1918), 159–161.

58 D. Hanzel et al. 'Mössbauer effect study of the oxidation of vivianite', *Solid State Communications*, 76, No. 3 (1990), 309.

59 Two oxidation processes can take place: oxidation by oxygen diffusing into the vivianite from outside and auto-oxidation by decomposition of bound water. Hanzel et al. 1990, 307–310. The last reaction will occur at higher temperatures (between 65–315 °C), but the first one at room temperature when the mineral is exposed to air, the iron oxidising from the Fe^{2+} to the Fe^{3+} oxidation state ($4Fe_3^{II}(PO_4)_2$_ $8H_2O + 3O_2$_ $4Fe_3^{III}(PO_4)_2(OH)_3 + 26H_2O$).

60 In the case of a partly oxidized vivianite, with Fe^{2+} and Fe^{3+} in adjacent cation sites, under the stimulation of light the following reaction can occur: Fe^{2+} (in site 1) + Fe^{3+} (in site 2) goes to Fe^{3+} (in site 1) + Fe^{2+} (in site 2). See http://minerals.gps.caltech.edu/COLOR—Causes/IVCT/Index.htm (09/02/2004). See also K. Nassau, *The Physics and Chemistry of Color, The Fifteen Causes of Color*, (New York, 1983), 140–151.

61 Richter 2004, 204, note 6, 209. He has suggested that the bluer more crystalline variety was used in German examples and that the greyish translucent variety thus far identified in Dutch seventeenth century pictures possibly reflects the peat bog source of the mineral deposits found in The Netherlands. Personal communication, 2004.

62 Nassau 1983, 145; G. P. Nembrini et al., 'A Mössbauer and chemical study of the formation of vivianite in sediments of Lago Maggiore (Italy)', *Geochimica et Cosmochimica Acta*, 47 (1983), 1459–1464.

63 H. C. Howard, 'Techniques of the Romanesque and Gothic Wall Paintings in the Holy Sepulchre Chapel, Winchester Cathedral', in *Historical Painting Techniques, Materials, and Studio Practice*, Preprints of a symposium University of Leiden, The Netherlands, A. Wallert . E. Hermens, M. Peek eds., (Getty Conservation Institute, 1995), 91–104. Richter 2004, 210 mentions a greatly altered vivianite-containing layer in the Gothic wall painting of Urschallung in Bavaria, dated 1370.

64 Although not within the scope of this study the colour of vivianite as a function of its oxidation state could be carried out directly on paint cross-sections with micro-XANES (microscopic X-ray Absorption Near Edge Structure spectroscopy).

65 As was reported by Spring in foliage areas in numerous pictures by Aelbert Cuyp, Spring 2001, 65, 66.

66 J. Kirby, D. Saunders, 'Sixteenth- to eighteenth-century green colours in landscape and flower paintings: composition and deterioration', in *Painting Techniques, History, Materials and Studio Practice*, Preprints to the IIC Dublin Conference, A. Roy et al. eds., (London, 1998), 155–156.

67 Yellow lakes have been identified in numerous pictures from The National Gallery London: *Sakia van Uylenburch in Arcadian Costume*, 1635; *Belshazzar's Feast*, 1636-8; *The Woman taken in Adultery*, 1644, *Portrait of Frederik Rihel on Horseback*, 1663; Bomford et al. 1988, 63-65 and 78-79, 91, 139. A yellow lake was also found in a mixture with a cochineal based red lake in the cloak from Rembrandt's *'Tronie' of a man with a feathered beret* (Mauritshuis) (HPLC analyses: Netherlands Institute for Cultural Heritage (ICN) 2000).

68 The identification of the source of the colouring matter was not successful with HPLC, Jan Wouters 2003, which was not surprising since it is often difficult to identify due to the severe breakdown of the organic component. In this case (and probably more often) evidence of a yellow lake is provided by the visualisation of a yellowish layer in cross-section combined with detection of large amounts of calcium (from the substrate) throughout the layer.

69 In the documentary sources mention is made of the impermanence of these pinks. See Jo Kirby and David Saunders 1998, 156. Also E. Hermens, A. Wallert, 'The Pekstock Papers, Lake Pigments, Prisons and Paint-Mills', in *Looking through Paintings* , E. Hermens ed., (Baarn/London, 1998), 269-294.

70 Hermens and Wallert 1998, 289. The instability of these chalk-based yellow lakes is confirmed by reconstructions carried out by Saunders and Kirby, see D. Saunders, J. Kirby, 'Light-induced Colour Changes in Red and Yellow Lake Pigments', *National Gallery Technical Bulletin*, 15 (1994), 79–97.

71 For the contribution of chalk in blanched mixed green paint layers see: K. Groen, 'Scannning Electron microscopy as an aid in the study of blanching', *Hamilton Kerr Institute Bulletin*, 1, (Cambridge, 1988), 48–65; Kirby and Saunders 1998, 158; B. Epley, 'Jan Both's Italian Landscape Materials, techniques and treatment', *Hamilton Kerr Institute Bulletin*, 3 (Cambridge, 2000), 131 and Spring 2001, 68.

72 For Rembrandt's use of red lakes see for example, Van de Wetering 1997, 240, 256, 259; Groen 1997, 220-222; Bomford et al. 1988, 24.

73 See Saunders and Kirby 1994, for discussion of possible mechanisms involved in the degradation of lake pigments.

74 Red lakes based on cochineal have been identified in several paintings, for instance, Bomford et al. 1988, 24. See also note 67.

75 HPLC analyses by Wouters 2003. See also J. Wouters, A. Verhecken, 'The Coccid insect dyes: HPLC and Computerised Diode-Array Analysis of Dyed yarns', *Studies in Conservation* 34 (1989) 183-188. And J. Wouters, 'Notes on the Biology, History, Geography and Analysis of Insect Red Dyes and Pigments', in *Historical Polychromy, Polychrome Sculpture in Germany and Japan*, M. Kühlenthal, S. Miura eds., (München, 2004), 380-392.

76 In the Northern Netherlands European cochineal was introduced at the end of the sixteenth century, but in the seventeenth was more and more replaced by Mexican cochineal. See also J. H. Hofenk de Graaff et al., *The Colourful Past: The Origins, chemistry and identification of natural dyestuffs*, (Riggisberg, 2004). Also Wouters 2004.

77 As described by Saunders and Kirby 1994, 83. See also Hermens and Wallert 1998 for discussion of red lakes.

78 Van de Graaf, Het *De Mayerne Manuscript als bron voor de schildertechniek van de Barok*, (Mijdrecht, 1958), 33-35. Despite the various and confusing nomenclature, two main types of lead white are distinguished: the cheap quality lead white consisting of an admixture of lead white and another material such as chalk, and pure lead white. The lesser quality adulterated lead white(s) were referred to as *lootwit*, *céruse*, *blanc espagne* or *Spanish white* to name a few. Pure lead white was known by various names, including: *schelp-* or *schulpwit*, *blanc du plomb*, *blanc du plomb en écailles* and *céruse pure*. T. Goedings, K. Groen, 'Dutch Pigment Terminology I: A Seventeenth-century explanation of the word "Schulpwit" ', *The Hamilton Kerr Institute Bulletin*, 2 (Cambridge, 1994), 85-87.

79 Groen 1997, 207–227, particularly 215–218.

80 See note 19.

81 That it is medium richer is seen by the larger peak area of the network fraction and the higher content of free fatty acids (palmitic C16, stearic C18 acid and C14, C20, C22, C24 and C26 fatty acids) than Rembrandt's paint.

82 Both samples show 90% basic lead carbonate ($Pb_3(CO_3)_2(OH)_2$ hydrocerussite), 5% lead carbonate ($PbCO_3$ cerussite) and 5% lead oxide carbonate hydroxide ($Pb_{10}(CO_3)_6(OH)_6O$ plumbonacrite). The last compound, plumbonacrite has been interpreted as an intermediate stage in the production of lead towards lead carbonate when metallic lead is exposed to acetic acid vapours, as in the traditional Dutch stack process. The composition of 30 historic and modern lead white samples determined using XRD show similar results: 85–95% hydrocerussite, 5–15% cerussite and 5–15% plumbonacrite. Peter Hallebeek, Netherlands Institute for Cultural Heritage (ICN), 2003. With thanks to Leslie Carlyle, *De Mayerne* project 'Historically Accurate Oil Paint Reconstructions', 2004.

83 See also X-ray diffraction analysis carried out on nine lead white samples, K. Groen, 1997, 209–211.

84 Analyses for isotope determination were carried out by Giuseppino Fortunato at the *Swiss Federal Laboratories for Materials Testing and Research* (EMPA), St. Gall, 2003-2004 using multi collector inductive coupled plasma mass spectrometry (MC–ICP–MS). These analyses were carried out as part of the ongoing *Lead Isotope Project* set up by Daniel Fabian, Giuseppino Fortunato and Axel Ritter to investigate the origin of lead ores in Rubens and Van Dyck and other seventeenth century artists of the Northern and Southern Schools.

85 Personal communication, Giuseppino Fortunato, EMPA, 2003.

86 Isotopic analyses by Wallert of other 'Dutch' lead whites in three seventeenth century paintings painted between 1650 and 1675 in The Netherlands found lead originating from deposits in Avon and Derbyshire, see A. Wallert, 'Questions and Answers. The Technical examination of polychrome Terra-cotta sculptures by Johan Georg van der Schardt', *ArtMatters. Netherlands Technical Studies in Art*, 1 (Zwolle, 2002), 32–45, especially 40, 42, 43 and fig. 13.

87 Bruyn et al. 1989, 198. The RRP stated the bottom edge was trimmed, however, after present cleaning it was possible to see that there are numerous areas along this edge that are still intact. Water damage may have caused localised loss of the paint and ground along this edge.

88 Van de Wetering lists three pictures from the Leiden period having roughly the same dimensions: *Old man Asleep* (Turin), *Self-Portrait* (Japan MOA Museum) and *St Paul* (Nuremberg). Van de Wetering, 1997, 13.

89 Bruyn identified the group of standard size panels of c.55 x 40 cm as *groot stooters*, the name deriving from coins in use at the time. In reality the *stooter* coin was the equivalent of 2.5 stuivers [there were 20 stuivers in 1 gulden]. A panel with a *groot stooter* format cost 3 stuivers since a *klein stooter* kost 2.5 stuivers. See J. Bruyn, 'Een onderzoek naar 17de-eeuwse schilderformaten, voornamelijk in Noord Nederland', *Oud Holland*, 93 (1979), 97, 107, 109.

90 Van de Wetering 1997, 13 and 293 (note 5).

91 Bruyn found proportions ranging between 1.33:1 and 1.22:1 for *groot stooters* used by Rembrandt in the Leiden period, Bruyn, 1979, 108, 109; Miedema proposes for panels of a standing format a height:width ratio of 6/5 (1.2:1) or 5/4 (1.25:1), H. Miedema, 'Verder onderzoek naar zeventiende-eeuwse schilderijformaten in Noord-Nederland', *Oud Holland*, 95 (1981), 31–47.

92 Martin Bijl, previous Chief Restorer of the Rijksmuseum Amsterdam, suggests possible height:width ratios of either 1.4:1 or 1.414:1 (involving the square root of two) may have been in use. Personal communication, June 2003.

93 These areas are composed of varying amounts of brown and yellow earth pigments, lead white and black.

94 Bruyn et al. 1989, 200–201.