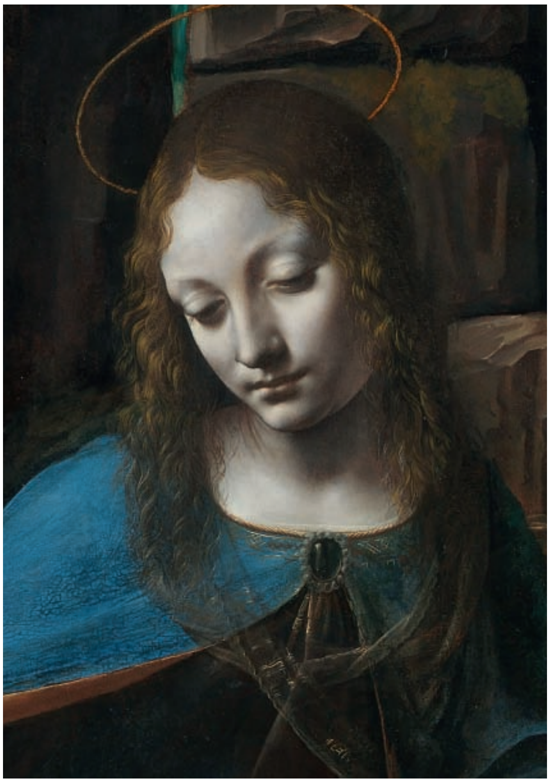
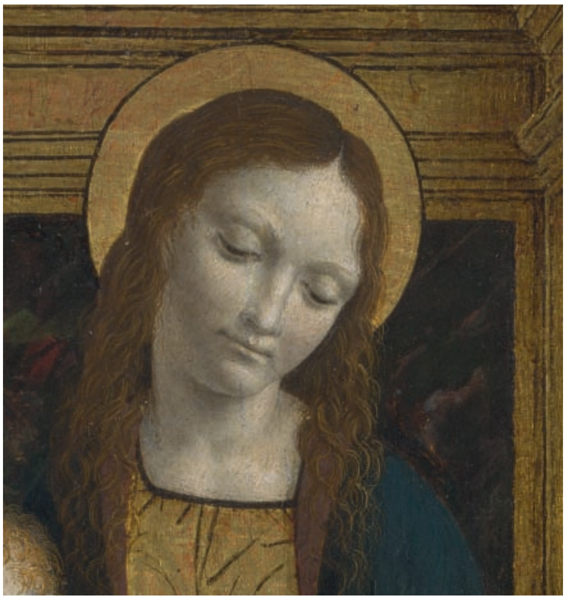
National Gallery Technical Bulletin

VOLUME 32 *Leonardo da Vinci: Pupil, Painter and Master*





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FRONT COVER
Leonardo da Vinci, *The Virgin of the Rocks* (NG 1093), *c.*1491/2–9 and 1506–8 (detail).

TITLE PAGE
Top left: Andrea del Verrocchio, *The Virgin and Child with Two Angels* (NG 2508), *c.*1467–9 (detail).
Bottom left: Master of the Pala Sforzesca, *The Virgin and Child with Four Saints and Twelve Devotees* (NG 4444), probably *c.*1490–5 (detail).
Right: Leonardo da Vinci, *The Virgin of the Rocks* (NG 1093), *c.*1491/2–9 and 1506–8 (detail).

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Leonardo da Vinci's *Virgin of the Rocks*: Treatment, Technique and Display

LARRY KEITH, ASHOK ROY, RACHEL MORRISON AND PETER SCHADE

Although the restoration of the National Gallery's *Virgin of the Rocks* (FIG. 1) was begun in November 2008, the origins of the project lie in the examination, cleaning and restoration, started almost fifteen years earlier, of a group of paintings from within the Gallery's collection made by Leonardo's Milanese associates and assistants. The initial results of this work were published several years ago, and have been an essential preliminary study for the subsequent exploration of Leonardo's artistic intent and painterly techniques, which has in turn informed the physical restoration of *The Virgin of the Rocks*.[1] The practical intent of this restoration is primarily aesthetic, firmly directed toward our visual experience of the picture, but it also provides an example of the Gallery's interdisciplinary approach to such an undertaking. Wherever possible, major restorations are intended as the hub of a wide range of research activity that sees curators, scientists and restorers working together – increasingly alongside colleagues from other institutions. Our work on *The Virgin of the Rocks* should be understood within such a context.[2]

The Virgin of the Rocks was first commissioned by the Confraternity of the Immaculate Conception at San Francesco Grande in April 1483, probably not long after Leonardo had first arrived in Milan. The commission was given to Leonardo and the brothers Ambrogio and Evangelista de Predis, local artists with established reputations there. It included panel paintings of the Virgin and two groups of musician angels, all of which were to be set into a carved altarpiece incorporating sculpture made between 1480 and 1482 by Giacomo del Maino. The central painting was almost certainly finished by the mid-1480s, and is now nearly universally agreed to be the painting known as *The Virgin of the Rocks* which is now in the Louvre (FIG. 2). Having finished it, it appears that the partners felt that the agreed fee was lower than the painting's true worth, and it seems to have been sold (in around 1491) to an unknown third party. At about this time a replacement version appears to have been started – the painting now in the National Gallery that came from San Francesco Grande. Although it was probably installed in the chapel by 1503, this second version was itself the subject of another dispute about payment and lack of completion in 1506, no doubt resulting in large part from Leonardo's absence in Florence between 1501 and 1506. After his return to Milan in 1506 the project seems to have been restarted, with the painting finally being considered finished enough for the artists to receive final payment in 1508.[3]

The Virgin of the Rocks remained in Milan until 1780, when it was purchased and brought to England by Gavin Hamilton (1723–98). It passed through two more British collections until the National Gallery bought it from the Earl of Suffolk in 1880.[4] The picture was painted on a four-member poplar panel that was thinned and cradled by William Morrill shortly after acquisition (FIG. 3). Despite this treatment the panel, though rendered more fragile, has remained stable, and the application of the cradle has not caused any subsequent structural problems, particularly since the introduction of air conditioning.[5] There may have been some thinning of the varnish at about this time – there are references to some removal of varnish in connection with treating it for fogging or bloom – but a more comprehensive cleaning and restoration was undertaken by Helmut Ruhemann in 1948–9. Ruhemann left on the edges of the painting three small dark-brown squares of the varnish that he otherwise removed, allowing analysis by gas-chromatography linked to mass-spectrometry (GC–MS) in the Gallery's Scientific Department. This varnish was found to contain mastic, some dammar, a substantial amount of fir balsam and heat-bodied linseed oil (FIG. 4). This complicated mixture of materials may indicate that more than one layer of varnish had been present. However, the detection of the oleoresin fir balsam strongly suggests that the varnish was applied in a nineteenth-century restoration before the painting entered the National Gallery Collection.[6] Both the composition and the degree of discoloration of the squares left by Ruhemann suggest that any cleaning which occurred around the time of the 1880 acquisition must have left substantial amounts of older varnish on the surface.

FIG. 1 Leonardo da Vinci, *The Virgin of the Rocks* (NG 1093), *c*.1491/2–9 and 1506–8. Oil on poplar, thinned and cradled, 189.5 × 120 cm. After cleaning and restoration.

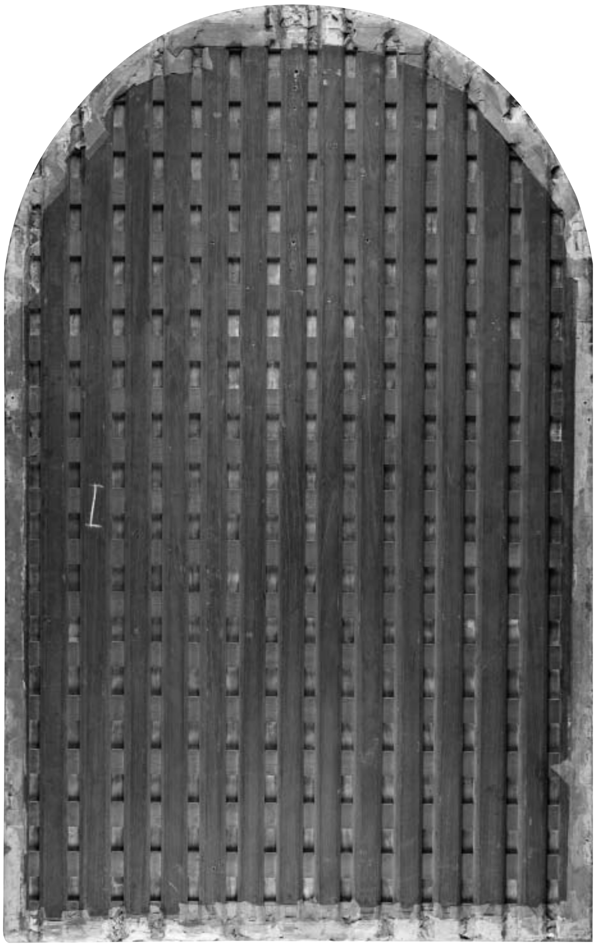

FIG. 2 Leonardo da Vinci, *The Virgin of the Rocks*, 1483–*c*.1485. Oil on wood, transferred to canvas, 199 × 122 cm. Paris, Musée du Louvre, inv. no. 777.

FIG. 3 NG 1093, showing cradle applied to the panel reverse.

FIG. 4 NG 1093, detail of the foot of Saint John the Baptist, showing a small square of old varnish left untouched during the 1948–9 restoration (removed 2009).

Ruhemann's restoration of the picture included a method of varnishing that aged quickly and badly. The panel presents a particularly difficult surface to varnish, as it combines extensive dark passages and notable variation between smooth, cracked and wrinkled surface textures – much of which has resulted from problems associated with the initial drying of the paint. The most effective varnish applications for saturating the smooth dark passages also draw unwanted attention to the areas with more disrupted surfaces, while less glossy varnish applications which seek to reduce this effect usually compromise the saturation of the darker tones. Ruhemann's choice of mastic resin in turpentine with a significant addition of linseed oil, all of which are described in his reports and confirmed by recent GC–MS analysis, unwittingly resulted in both rapid yellowing and considerable desaturation, while the microcrystalline wax layer he subsequently applied to that varnish additionally ensured the speedy accumulation of surface dirt. The resulting degradation of the surface layer seriously compromised the viewer's ability to appreciate fully Leonardo's manipulation of the range of tonal modelling from light to dark, which is perhaps the single most distinctive quality of his painting of this period. This obstacle to the proper reading of the picture was the reason for its recent treatment (FIG. 5).

Before beginning the treatment itself, the painting was extensively documented with non-invasive methods, including infrared reflectography (IRR) and X-radiography, in order to achieve as thorough an understanding as possible of the picture's condition before the beginning of the treatment itself (FIGS 7 and 8). Moreover, Ruhemann's recording of his restoration was, for its day, unusually thorough, including an extensive record of high-quality large format black and white photography of the painting after he had finished its cleaning, giving a wealth of information on its condition. The original 1948 black and white negatives, most of which were taken in 12×8 inch format, have been digitally scanned, allowing the retrieval of far more information from the whole tonal range than would be discernable from any given print (FIG. 6). More recently, the 2005 infrared reflectography investigation, which is noted later in this article, gave a more precise record of the picture's condition.[7] Recent developments in the digitisation of the X-radiographic plates also allowed a clearer image of the ground and paint films by reducing the visual impact of the wooden cradle on its reverse (FIGS 9 and 10).

The cleaning of the painting began in November 2008, and was finished by May of the following year. While the image which emerged during cleaning was indeed appreciably less yellow, the most important gains came not from the shifts in colour relationships, but instead from the significantly improved saturation of the darker tones – thereby re-establishing the full range of

FIG. 5 NG 1093, in-situ in the Gallery, before restoration. The cloudiness apparent in the upper part of the painting is the result of degraded varnish layers.

tonal modelling, the depicted volumes, and the intended spatial relationships, to the extent that this is still possible. Ruhemann's degraded varnish was soluble in mixtures of isopropyl alcohol in white spirit (ranging from *c*.28% to 35%), sometimes with a little xylene. All of the solvent mixtures that were used left a very thin layer of old varnish over the majority of the picture. This is discernibly fluorescent in ultraviolet (UV) light. A greater amount of old varnish was retained over the gilding of cross and haloes; on the former because the yellowed varnish effectively simulated the warm glazes which were initially applied to the tin-leaf of the cross, and on the latter because the subsequent shell and powder gold restorations of the more conventionally mordant-gilded haloes were bound up in later varnishes. The painting was photographed after each day that significant cleaning was undertaken, providing a comprehensive record of its progression. The intent of the cleaning was to effect the desired aesthetic improvement through the reduction of the old varnish, not simply to remove it, and in the main a very thin remnant of that layer – visible in UV fluorescence images taken during and after the cleaning of the panel – remains on the picture (FIG. 11).

The restoration allowed a campaign of precise and comprehensive sampling, following the logical investigative sequence from the earlier non-destructive investigations. There were few technical issues around identification of overpaints, for example – in part due to the thoroughness of Ruhemann's cleaning and also because of the clarity of his documentation – but the additional campaign of sampling and analysis did allow a better understanding of the picture's inconsistent level of finish, which in turn informed the approach to its restoration. Cross-sections taken from the crudely blocked-in areas of blue paint at the upper right of the sky confirmed, for example, that the top layer of ultramarine with a little white was applied directly onto an underlayer of lead white and azurite. Both layers are entirely consistent in their use of contemporary materials and it

FIG. 6 NG 1093, large format black and white photograph from the 1948 restoration, detail showing the angel, taken after cleaning, before restoration.

FIG. 7 NG 1093, X-radiograph, with the effect of the applied cradle reduced by digital manipulation.

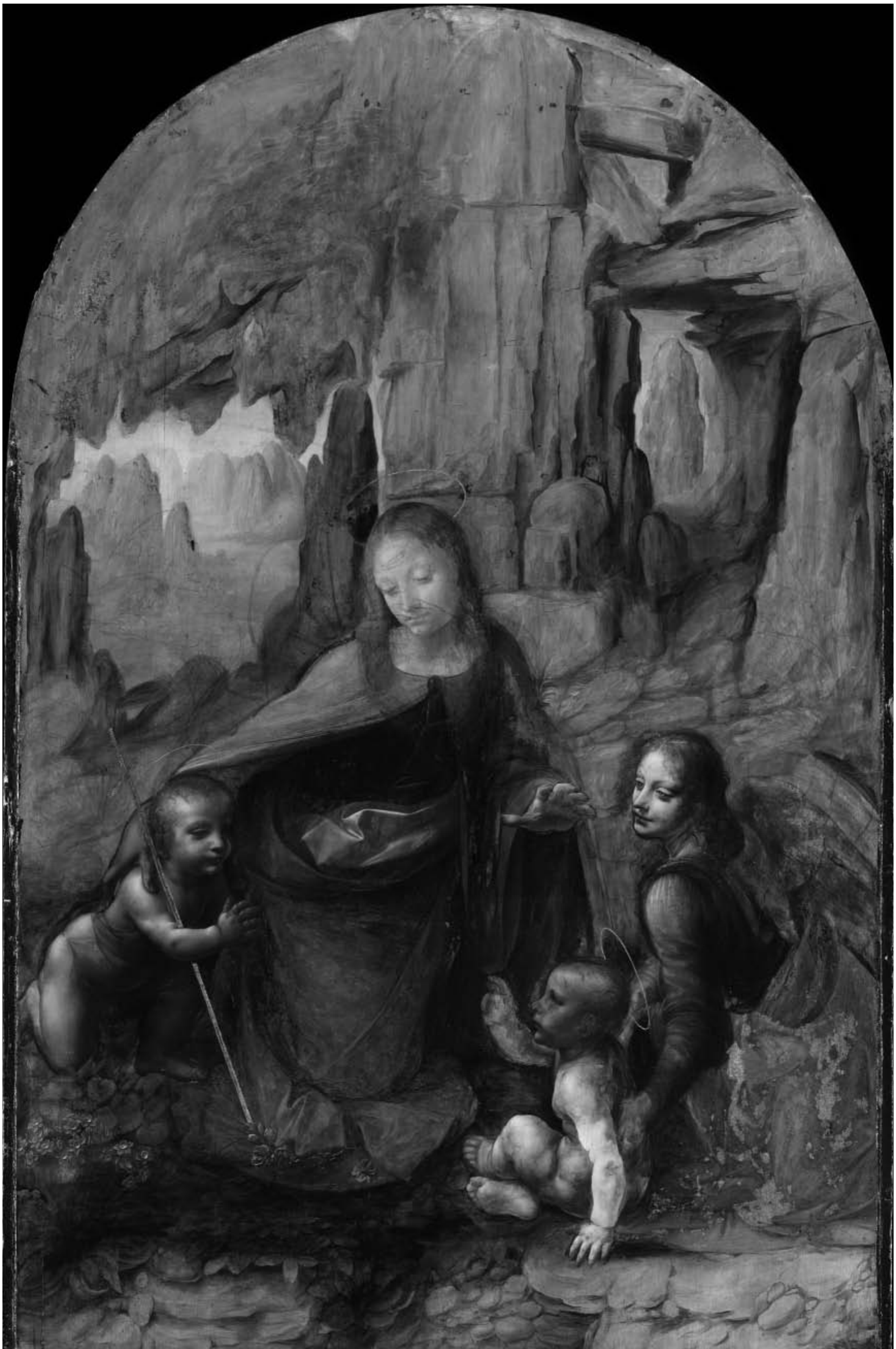

FIG. 8 NG 1093, infrared reflectogram.

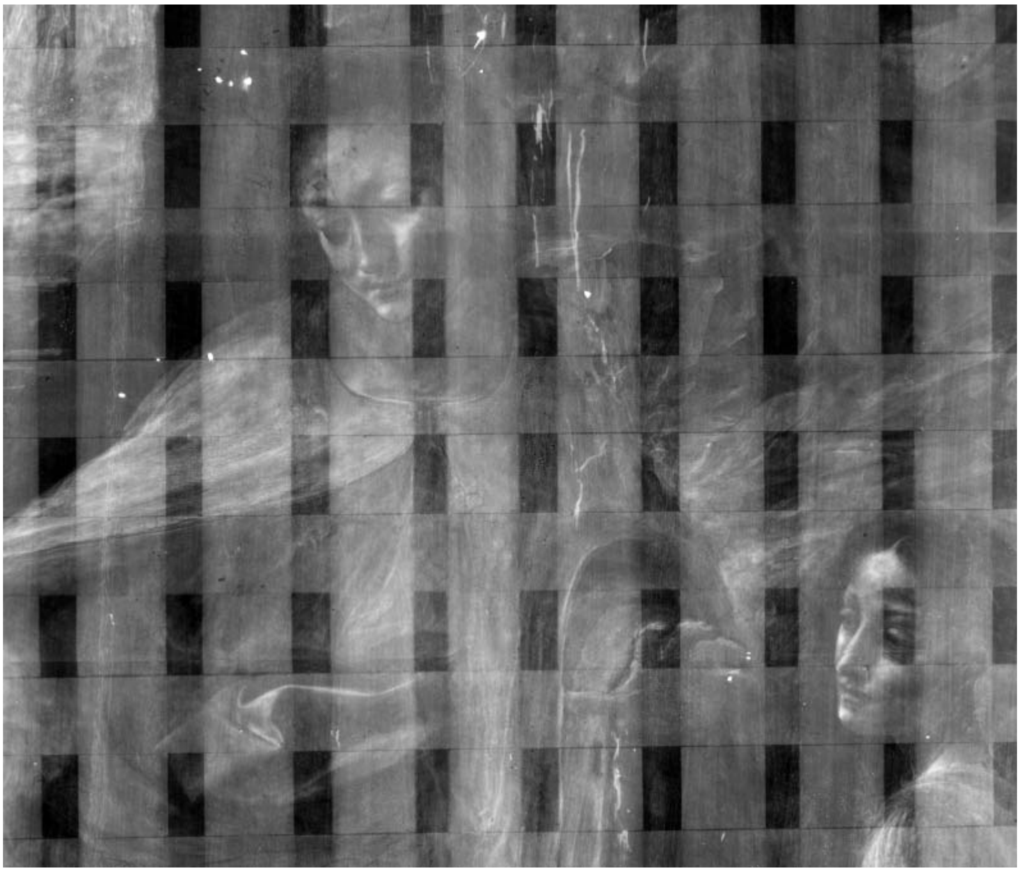

FIG. 9 NG 1093, X-radiograph detail. The cradle applied to the panel reverse is strongly evident, making it more difficult to see the paint layers.

FIG. 10 NG 1093, X-radiograph detail showing the same area as FIG. 9, with the cradle interference digitally suppressed.

was established that there is no evidence of intermediary varnish layers between the two blue paints (FIGS 12 and 13). Its rather crude appearance, therefore, could not be explained as the consequence of an early restoration. Instead it became more likely that the upper layer was applied rather casually *in situ* during the final campaign of work between 1506 and 1508. Indeed it is evident, along the top arched edge of the panel, that this paint was applied after the picture had been fitted into a frame, presumably the original framing assembly.

Similarly, the smear of brown paint applied over the completed folds of the Virgin's blue mantle around and below the Baptist's left foot was found to be entirely consistent in composition with brown paint associated with Leonardo's adjustment of the contours of the Virgin's left shoulder, and can therefore be considered another relatively incomplete area of the picture (FIGS 14, 15, 16 and 17). This analytical confirmation that such roughly worked areas were never resolved by the artist, and do not derive from the picture's subsequent restoration history, accords with the lengthy and complex documentary record of the original commission, and is an essential factor in decision-making about its attribution and, of course, its restoration.

FIG. 11 NG 1093, ultraviolet photograph taken during cleaning, showing strongly fluorescent, uncleaned area at lower right and thinned varnish elsewhere.

FIG. 12 NG 1093, detail showing the crudely applied ultramarine, blocked into the openings in the rocky landscape on the right, laid over an underpaint of lead white and azurite. The two paints have different media, although no intermediary dirt or varnish layers are discernible.

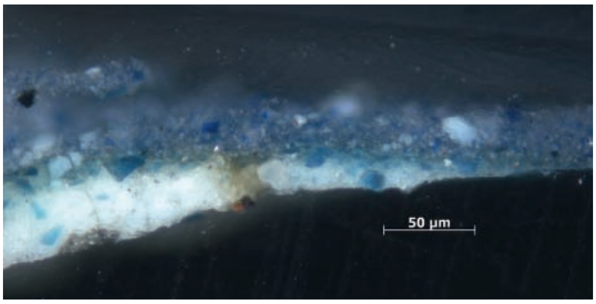

FIG. 13 NG 1093, paint cross-section from the sky seen through the aperture in the grotto, upper right. The lower layer consists of natural azurite with white and there is a second layer containing natural ultramarine with a little white. The ultramarine is slightly blanched. There is no discontinuity between layers, indicating roughly contemporaneous application.

FIG. 14 NG 1093, detail showing brown paint applied over the blue drapery as an unresolved change in relationship between drapery, foot and landscape.

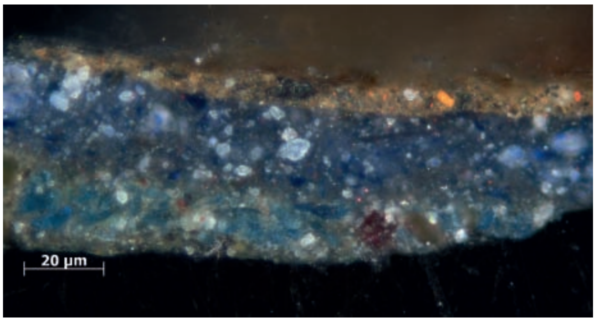

FIG. 15 NG 1093, Paint cross-section from brown foreground just below the Baptist's proper left foot (shown in FIG. 14). The brown paint represents an adjustment made to this area of the painting, since a small section of the Virgin's completed blue cloak lies beneath. The latter consists of a layer containing natural azurite and an upper layer of natural ultramarine, now rather blanched. The pigment constitution of the brown paint is similar to that for certain parts of the rocky grotto, including the area to the left of the Virgin's arm where the background paint has been applied on top of the Virgin's drapery (see also FIG. 17).

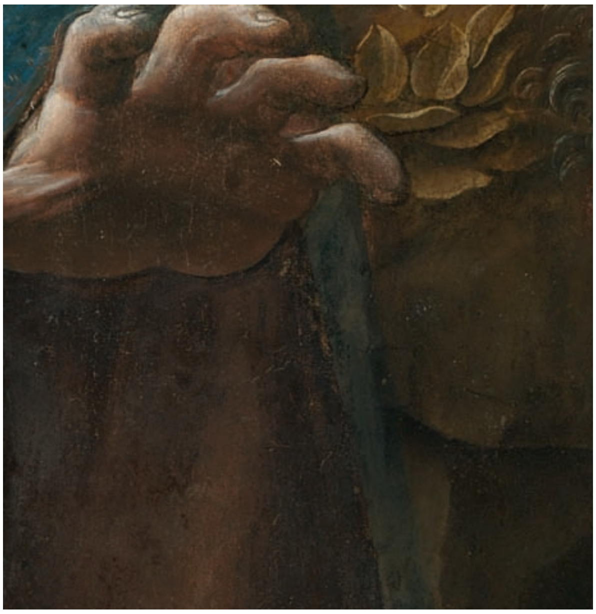

FIG. 16 NG 1093, detail showing brown paint applied over blue drapery to change the figure's silhouette.

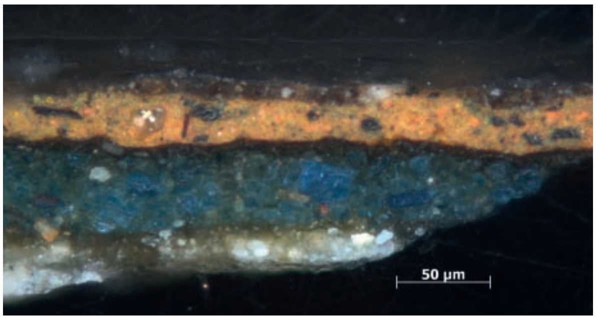

FIG. 17 NG 1093, paint cross-section from the rocks in background, close to the Virgin's proper left upper arm. The brown paint of the rocks passes over a layer of azurite, with dark modelling at the surface, representing a pentimento of the fabric of the cloak.

FIG. 18 NG 1093, detail taken after the 2009 cleaning, before restoration, showing the retention of a stable 1948 restoration underpaint in the damage above Saint John the Baptist's eye.

Just as the degree to which the varnish was reduced during the cleaning was guided by the desired aesthetic result, the retouching was carried out with the goal of achieving maximum legibility of the painting – but only in so far as its inherent condition and uneven execution would allow. Discrete losses were retouched with deceptive intent, sometimes incorporating the unaltered tempera underpaints applied by Ruhemann in 1949. Because Ruhemann's retouchings were achieved for the most part by the application of resinous glazes over more opaque underpaints carried out in egg tempera or watercolour, his underpainting has generally retained its colour well. Consequently, where such underpainting was strictly confined within losses, it was sometimes retained for the current restoration, serving as a basis for new retouching work. Such an approach can be seen in the damaged area over the eye of Saint John the Baptist (FIG. 18). In other parts, such as the extensive damage of the angel's drapery, it was felt that a closer optical match to the surrounding original could be only be made by redoing the underlayers completely, building up from the brown-red undermodelling through to the altered appearance of the upper ultramarine pigments (FIG. 19). Drying cracks were either toned or matched to surrounding paint where it was felt that the visual distraction of the pattern they created across modelled forms was detrimental to the viewer's understanding of the painting. While tiny, pinpoint losses and abrasion in the darker areas were carefully retouched, particularly in the foreground – which was very effective in allowing the existing modelling to function better – no attempt was made to correct any inherent defect in the ultramarine pigment of the drapery of the angel or the Virgin. Instead the visual impact of the drying cracks was selectively reduced with the aim of enhancing the appreciation of the surviving modelling.[8]

Both the historical and the technical research associated with the restoration reinforced the visual evidence of a picture that was notably uneven in its level of completion, and also not entirely consistent in its paint handling. The implications of these features are essential to the understanding of the picture's authorship, and are explored at length elsewhere; as far as the restoration is concerned, it was essential to be aware of these aspects, and to seek to avoid any imposition of a misleading stylistic homogeneity or harmonious level of finish falsely achieved through modern retouching. The wider purpose of that retouching was therefore to do no more than allow the viewer to appreciate as fully as possible the qualities of the painterly effects that had always been there, including the more idiosyncratic aspects of its uneven execution – and thereby in some measure to enable the continuing process of forming new critical judgements.[9]

Leonardo's painting technique for *The Virgin of the Rocks*

The London *Virgin of the Rocks* (NG 1093) has a long history of technical study and, as we have seen, an even longer history of archival documentation (largely photographic) at the National Gallery. Larry Keith has noted the importance of the photographic survey of the picture undertaken in conjunction with its earlier conservation

FIG. 19 NG 1093, detail taken after the 2009 cleaning, before restoration, showing the losses in the angel's drapery which reveal the remains of the reddish-brown underlayer.

treatment by Helmut Ruhemann in 1948–9, at which time some micro-chemical analysis of repaints and cleaning swabs was undertaken by Joyce Plesters.[10] The first attempts to understand the nature of the original materials of the picture were also made by Plesters, though rather later, in 1965, when she took three paint samples – from the Virgin's blue cloak, its yellow lining and the blue sky – to study as cross-sections. The results were not formally published except in a brief internal report to the Honorary Scientific Advisory Committee of the Gallery (HSAC).[11] No further detailed analysis was undertaken until April 1995, when twelve further samples were taken by Ashok Roy from the extreme edges of the composition while the picture was unframed in the studio for detailed surface examination and a routine assessment of its condition. No infrared examination was undertaken at this point. At this time, four further samples were analysed by GC–MS by Raymond White, giving the first indication that one of the paint binders employed was heat-bodied walnut oil. These results and some preliminary observations on the layer structure of the picture were reported to the HSAC and the media results were subsequently published in the *Technical Bulletin*.[12] However, as indicated below, new organic analyses carried out by Rachel Morrison in support of the 2008–9 conservation treatment have shown a more complicated range of materials than those identified in 1995.

Perhaps the most significant discovery made this century regarding *The Virgin of the Rocks* comes as a result of examination of the picture in infrared light and concerns Leonardo's comprehensive recasting of its design during the course of execution. It revealed an earlier underdrawn design for a quite different composition, apparently depicting the Virgin adoring the Christ Child. Leonardo abandoned this design, and then partially suppressed it so as to compose the present surface design of *The Virgin of the Rocks* in a second fully reworked underdrawing. This radical change of direction for the picture was first revealed in studies made by Rachel Billinge in January 2004 with the Gallery's infrared vidicon camera, at the suggestion of the picture's curator, Luke Syson. A full IRR mosaic was constructed from the digitised vidicon images, enabling Leonardo's underdrawings and complex revisions to be seen for the first time. The opportunity arose in 2005 to acquire an improved high-resolution infrared composite image using digital scanning technology with help offered by leaders in digital infrared image capture at two collaborating Italian institutes, both based in Florence, with which the National Gallery Scientific Department had a formal partnership under the European Commission-sponsored EU-ARTECH project.[13] These were the Istituto Nazionale di Ottica Applicata (INOA; now CNR-INO) and the Opificio delle Pietre Dure (OPD). Colleagues from these institutions came to London in March of that year with a portable digital infrared scanner, and the high-resolution image was subsequently published with a full interpretation of the resulting images of the underdrawings.[14] In conjunction with this examination, two new microsamples for cross-sections were taken from the background composition towards the left edge, at points where the two separate underdrawings coincide, to determine whether their location within the layer structure could be ascertained (see FIG. 20).

Some of the results of sampling and analysis have been the subject of a preliminary report.[15] During the course of treatment, as pre-existing damages to the paint layers were revealed by cleaning, it became possible to remove, without harm to the picture, a new series of microsamples to mount as cross-sections, and on which to perform analysis, the results of which are summarised on the following pages.

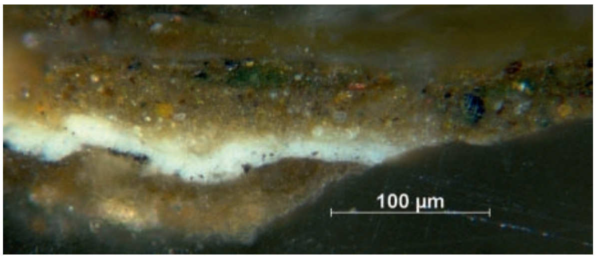

FIG. 20 NG 1093, paint cross-section from the thinly painted brownish-green foliage behind Saint John the Baptist, left. Black particles of a fragmentary layer of the first underdrawn design are visible between a discoloured gesso ground and the very light grey first *imprimitura*. The second underdrawn design at this point is represented by a layer of fluidly applied dark brown paint containing a mixture of pigments. A thin final layer of greenish brown is present at the surface.

Panel, gesso and primings; the underdrawing layers

The panel support for *The Virgin of the Rocks* had long been presumed to be of poplar wood, in spite of the consistent use also of walnut for Lombard panels of the late fifteenth and early sixteenth centuries (see the article on 'Painting Practice in Milan in the 1490s' in this *Bulletin*, pp. 78–112). The use of poplar has now been confirmed from a thin transverse section of the wood grain taken for examination under the microscope from the arched upper profile of the panel. The relatively large size of the panel (189.5 × 120 cm) in this case may have precluded the use of walnut. While possible on this scale, the use of walnut was likely to have been prohibitively expensive for such an imposing altarpiece assemblage, which, apart from its large painted panels, also included carved and gilded wood and sections of polychromed sculpture. The poplar panel of Leonardo's *Virgin of the Rocks,* of course, occupied the central position in this altarpiece.[16]

The wood panel was first given a gesso and glue ground in the conventional manner. Evidence from cross-sections shows that the first drawn design – representing, it is interpreted, the Virgin in a pose of adoration – was executed by Leonardo in a fluid, brownish-black medium, probably some form of paint containing solid pigment, directly onto the gesso ground (FIG. 21).[17] This design was then partially concealed with the light grey oil-based priming (*imprimitura*) containing lead white and a little carbon black. A second layer of priming was brushed on top, probably somewhat later; this contained varying amounts of lead white and a proportion of lead-tin yellow. It is very probably this layer that registers in the X-radiograph as bearing the impression of palm and fingerprints from manipulation during application. The palm-prints have not so far been tied to an individual. The precise function of the second, faintly greyish-cream coloured priming is difficult to ascertain: it appears to be present beneath the larger part of the whole composition, except at the very edges, and it seems likely that it was applied to suppress more fully the image of the first underdrawn design at the point that Leonardo decided to recast the composition in the way we now see. The first, lower, underdrawing would have remained visible through the thin veil of the initial greyish *imprimitura*; this was a standard method of partially concealing an underdrawing so that its outlines and shading could be followed in the painting stage, but would not be visible in the finished picture.[18] Thus the application of a second greyish-cream coloured priming was probably intended to eliminate all traces of the first underdrawing, and to provide a suitable surface, and base colour, for the final composition. The relative translucency of this second *imprimitura* layer, which is now visible in some cross-sections, may be accounted for by the formation of lead soap inclusions, which have been identified by Fourier transform infrared (FTIR) microscopy. When applied, this layer was probably more opaque, only becoming gradually more transparent as the lead soaps formed (FIG. 22).[19]

The second underdrawing layer is different in character and more regular than the initial drawn design, which is in general more broadly brushed. In cross-section at least, the second drawing layer merges seamlessly into areas of elaborate wash-like monochrome underpaint of a type used elsewhere by Leonardo as his next phase in the process of painting.[20] These dark yellow, brown and blackish-brown underpaints, which contain a translucent dark brown of the Cassel earth type,[21] other earth pigments and black, seem to be relatively rich in medium, and their presence probably accounts for some of the drying defects noted in the overlying, more colourful paint layers. Some evidence for this is provided in certain cross-sections, which show these underlayers as reticulated or in places 'drawn up' into the paint layer immediately above, as though only partially dried when painted over (FIG. 23).[22]

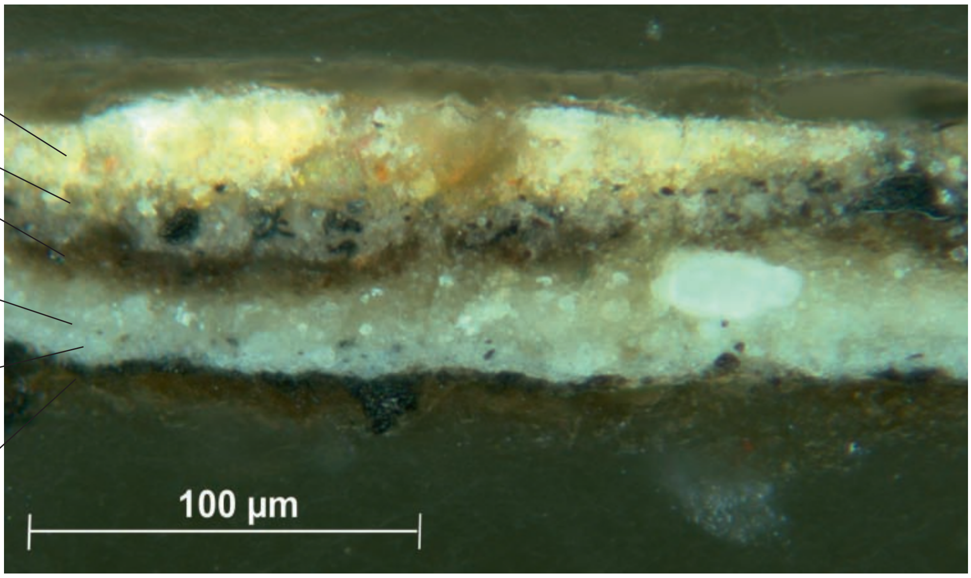

FIG. 21 NG 1093, detail of paint cross-section taken from the yellow lining of the Virgin's mantle. This sample contains thin layers which relate to both schemes of underdrawing.

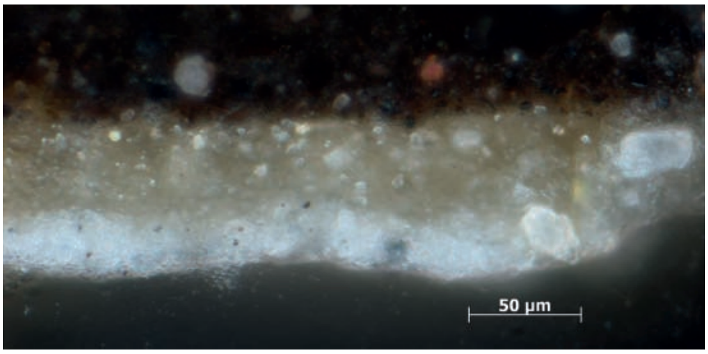

FIG. 22 NG 1093, detail of paint cross-section from dark translucent brown of rocks, upper left, showing the two superimposed *imprimitura* layers. The lower layer is faintly grey, while the second layer is both more translucent and slightly warmer and yellower in tone.

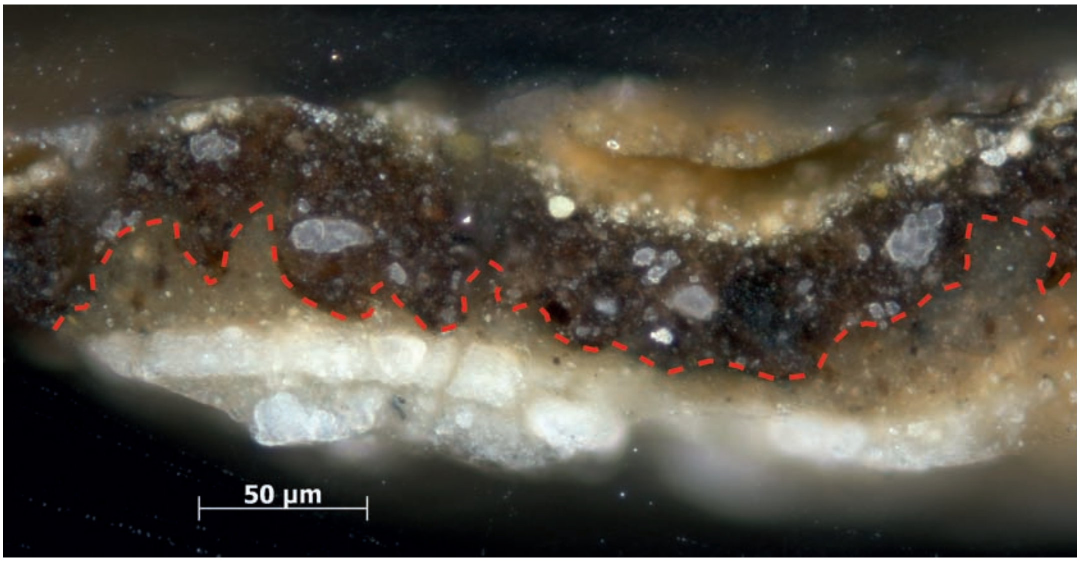

FIG. 23 NG 1093, detail of a paint cross-section taken from the foliage at the top centre of the painting, showing the underlayer being 'drawn-up' into the paint layers above. The dotted red line indicates the uneven interface between the underlayer and the subsequent brown paint.

Background grotto: foliage

The rocky grotto is executed quite simply, with paints containing earth pigments, black and some verdigris, worked over the monochrome underpaint described above. Where the rocks are warmer in tone, the paint mixture is dominated by Cassel earth, with smaller quantities of red and yellow earth pigments and a little black.[23] The foliage of the large plant clinging to the rocky crevice above the Virgin's head is depicted in a mixture of translucent brown paint formed of black, yellow and brown ochre with a little white; there is a thin scumble of lead-tin yellow to create the relatively lighter, denser edges of the individual ovate leaves (see FIG. 23).

Foreground: foliage

The foreground rocky setting is more thinly painted than the geological features of the grotto behind. It is laid in, as elsewhere, in a mid-brown translucent layer with brownish-black and black pigment constituting the upper layer.[24] The foliage of the two larger plants, to the left in the foreground, is more appreciably green in tone than that of the background plants, and contains a mixture of verdigris, yellow earth and charcoal black pigment, with upper layers containing either a greater proportion of black or yellow earth according to the final tonality depicted (FIG. 24). The greenest parts contain some azurite in addition.

Draperies

The combination of the Virgin's blue drapery and its gold-coloured lining is the central focus of colour for the composition. Both these parts were begun with relatively dark grey underpaints containing charcoal, modelled in density according to the intended final tonality of the finished section of drapery. The blues have a second thick underpaint layer of natural azurite over the grey; the final layer consists of varying thicknesses of natural ultramarine-containing paint, with or without some white. From cross-sections it appears that in certain parts of the blue drapery a second dark modelling layer is present over the azurite applied before the ultramarine final paint. The ultramarine has blanched rather patchily so that the light and shade values no longer read as they were first created (FIG. 25). This is less disturbing in the upper half of the Virgin's robe, where the ultramarine is applied more thickly. In the lower, more shadowed part of the robe, the ultramarine seems to have been applied only as an extremely thin glaze, which is now very broken up. Although some bright blue particles are still visible in cross-section, the majority of the layer has a cloudy, whitish appearance, and on the surface of the painting the greenish-blue tonality of the underlying azurite paint has become more visible. It seems that in this case, blanching of the ultramarine-containing paint has occurred to some degree, even in those parts of the drapery which were covered during the course of painting as Leonardo made late adjustments to the composition. An area of brownish foreground beneath the Baptist's proper right foot was painted directly over a small finished section of the Virgin's blue drapery, in which the ultramarine layer has an overall cloudy appearance in cross-section (see FIG. 15).[25] Elsewhere, for example in the rocky mid-ground below the Virgin's right shoulder, the

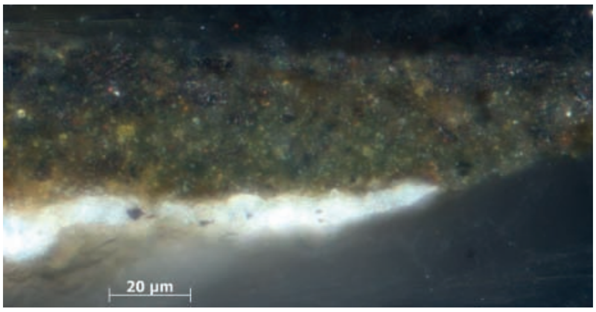

FIG. 24 NG 1093, paint cross-section of dark green foliage of clump of narcissus, lower left, showing Leonardo's use of verdigris, yellow earth and charcoal black. There is a 'scumble' of black pigment at the surface to darken the tone.

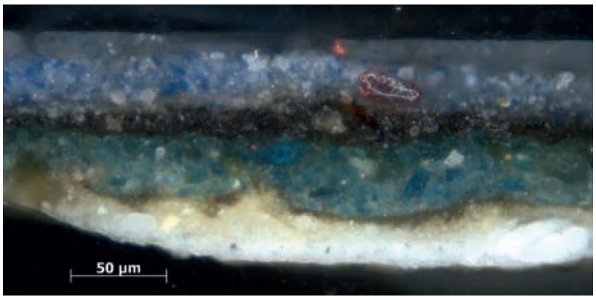

FIG. 25 NG 1093, paint cross-section from the Virgin's blue cloak, near neckline, right, showing the extent of ultramarine blanching in the surface layer. There is also a dark-coloured undermodelling layer at this point, on top of the azurite underpaint, although this is not present in the cloak throughout its extent. It is this dark layer that can be seen at the surface in cracks and fissures in the grey-blue uppermost paint layer. The double *imprimitura* is visible beneath the layer of azurite.

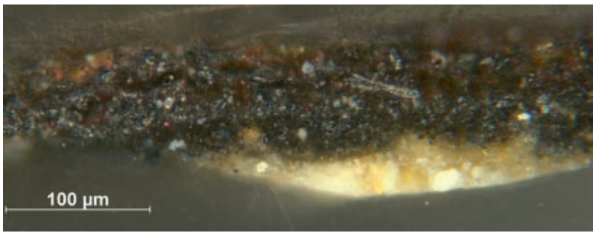

FIG. 26 NG 1093, paint cross-section from the Virgin's deep plum-coloured underdress, centre, consisting of one (or possibly two) underlayers comprising charcoal black pigment, red lake pigment and minor quantities of azurite. The surface layer is similar in constitution, but contains a greater proportion of red lake (see also FIG. 27).

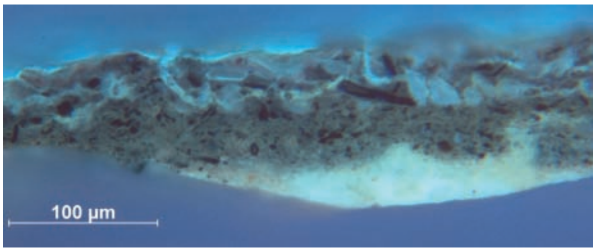

FIG. 27 NG 1093, paint cross-section as in FIG. 26, photographed digitally in ultraviolet light. The large rounded or oval bluish-white fluorescing inclusions in the upper part of the paint structure represent grains of the starch 'extender' incorporated with the red lake pigment.

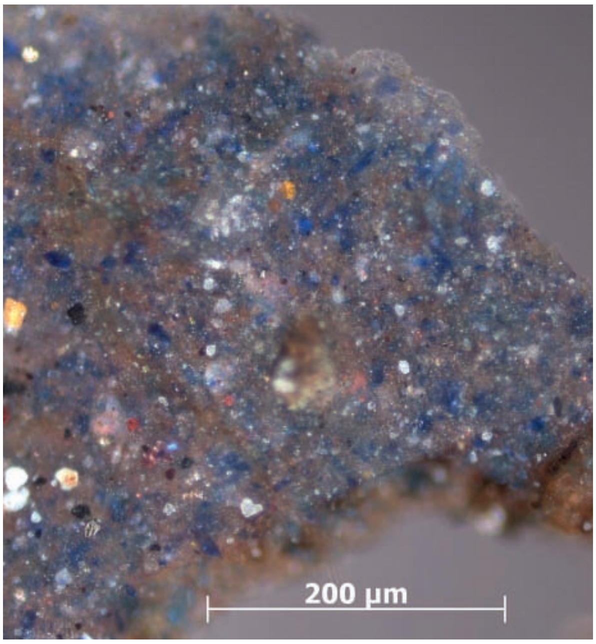

FIG. 28 NG 1093, the top surface of an unmounted microsample from the angel's billowing faintly mauvish grey-blue drapery, right-hand side, showing a surface 'scumble' of natural ultramarine combined with some mineral azurite over an underpaint consisting of red lake, black pigment and a little azurite.

brown paint of the rocks was drawn over the drapery before the final ultramarine layer was applied, and passes over a layer composed only of azurite.

The golden yellow lining of the drapery is painted in a single layer over a grey underpaint (see FIG. 21). It consists principally of lead-tin yellow with white and some golden ochre. There are also particles of red lead (lead tetroxide) in the yellow paint layer, but these may have formed by chemical interactions in the paint layer rather than arising as a deliberate addition.[26]

The Virgin's underdress is now strikingly dark, perhaps very much murkier than originally painted. As elsewhere in the figure of the Virgin, there is an under-modelled grey paint layer, in this case containing black, a little lead white and chalk, and some azurite, before the final applications of a very deep plum-coloured layer containing charcoal black and a red lake pigment (FIG. 26). Ultraviolet fluorescence microscopy has shown large fluorescent rounded or oval particles (some about 20–30 microns across), which have been identified by FTIR-microscopy as starch; the starch was evidently an addition to the red lake pigment, probably as an extender (FIG. 27).

The kneeling angel's billowing drapery at the right consists of glazes and scumbles of natural ultramarine with azurite over a layer of black with red lake; this lower layer is notably similar in constitution to the original dark plum colour of the Virgin's underdress (FIG. 28). Attenuated total reflectance Fourier transform infrared imaging (ATR–FTIR) analysis was performed directly on a cross-section from the angel's drapery, confirming the identification of the oval particles in this sample as starch; presumably the same type of lake, extended with starch, has been used in both the Virgin's and the angel's draperies.[27] The duller yellow of the lining of the angel's cloak is based on yellow earth pigments combined with some black.[28] Again this paint was laid over a plum-coloured layer of red lake and black as beneath the greyish blue sections of the drapery.

Flesh paint

The manner of execution of Leonardo's flesh paints has been the subject of intense interest, involving particularly the speculation that, while the underpaints may be relatively straightforward, both in layer structure and pigment constitution, the final blending of light and shade – the creation of Leonardo's subtle *sfumato* transitions – was accomplished with many superimposed, particularly fine, translucent layers. However, the London *Virgin of the Rocks* does not bear out this theory of Leonardo's presumed practice. In the areas studied in cross-section (the Baptist's proper right foot in shadow, his heel and the Christ Child's illuminated thigh and an adjacent shadow value), the paint layer structure consists of just two layers of quite similar opaque flesh paint, largely white pigment with very small quantities of vermilion, red lake and black pigment, laid over the generally applied monochromatic understructure of the composition (FIG. 29).[29] Some of the final modelling effects in the flesh were accomplished in the opaque underlayers, since the underpaint for the Christ Child's thigh, where it is cast into shadow, is somewhat darker and warmer in tone than that for the adjacent highlit portion, and contains a proportion of very fine brownish earth. The final shadow value was laid on in a single thin layer of partially translucent paint consisting of charcoal black, very fine brown ochre and a little orange-toned earth pigment (FIG. 30). The transition from shadow to highlight was therefore achieved rather simply – by thinning and blending the surface shadow paint layer most carefully, reducing its visual impact by degrees, as the lower, lighter layer was allowed to dominate the appearance of the surface. Both UV-fluorescence microscopy and high-power microscopy with the oil-immersion objective indicated only minor quantities of red lake pigment in the flesh paints examined, with no clear evidence of extensive fading.[30] We conclude, therefore, that the rather marmoreal whitish and greyish brown cast of the flesh paints is much as Leonardo had intended, particularly since some black pigment has also been incorporated into the flesh paint (see FIG. 29).

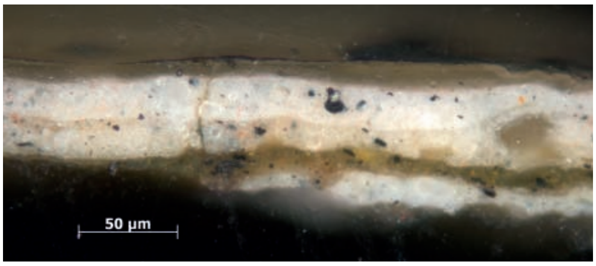

FIG. 29 NG 1093, paint cross-section of relative highlight on the Baptist's heel, extreme left edge, showing a two-layered system with a light-coloured surface paint incorporating minor amounts of vermilion, black pigment and red lake. The greenish-brown translucent layer beneath consists both of the 'second' underdrawing and the 'monochrome' fluid paint used to elaborate the second, final, composition.

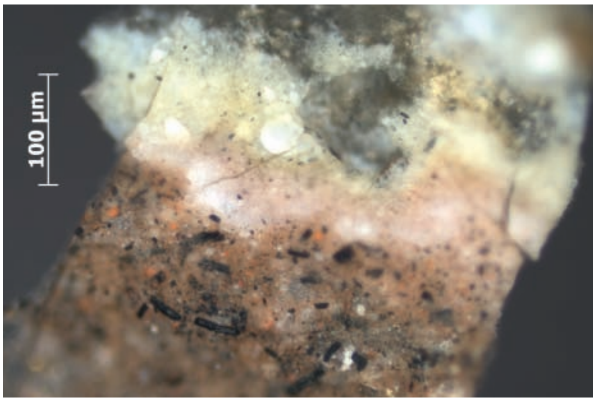

FIG. 30 NG 1093, the top surface of an unmounted microsample from the translucent dark brown shadow of the Christ Child's groin, showing a mixture of charcoal, fine-grained brown ochre and orange-coloured earth modifying a pale pink flesh underpaint. This surface film represents Leonardo's *sfumato* effect in the flesh tones and here consists of a single, blended layer. The yellowish section of the upper part of the image is the surface of the second *imprimitura* layer exposed beneath the flesh paint in this unmounted fragment.

Final gilded details

There is a notable difference in the use of gilding between the London picture and the earlier Paris version: the infant Baptist is holding a gilded cross, and the Virgin, the Christ Child and the Baptist are depicted with plain gilded oval haloes. There is a three-dimensional quality to these features, and they were presumably included to pick up reflected candlelight in the original setting for the altarpiece. The raised nature of the Baptist's cross is particularly striking, and it has been shown by analysis with energy-dispersive X-ray analysis (EDX) to comprise a fairly thick layer of metallic tin (now darkened and degraded) on top of which gold leaf was applied. Since this cross has incised outlines which appear to lie beneath the surface (although it is not clear at precisely which stage of the evolution of the composition the incisions were made) it seems likely that the cross was an original feature of the composition. There is no definitive evidence either way for the haloes, and these seem to be in a form of mordant gilding over the final paint layers. The use of gilded tin as a decorative device goes back to the early fourteenth century at least, and there are cases of its use in sixteenth-century Northern Italian painting.[31]

Medium analysis

The progress of the conservation treatment also allowed for a more thorough analysis of the binding medium of various passages of the painting than had been possible during the preliminary examination in 1995. As already mentioned, Raymond White's initial findings had suggested the use of a walnut oil binding medium, but the more recent results show that in fact both walnut oil and linseed oil were employed.[32] At present it has not been possible to find a distinct pattern in the distribution of these materials, although some interesting points can be made.

Both the azurite-containing underpaint of the sky and the ultramarine layer applied to the sky seen through the aperture in the grotto were painted using walnut oil which had undergone some degree of heating to 'body' or thicken it before use. Nonetheless, these layers represent distinct stages in the painting of the sky, since the upper ultramarine layer was applied after the rocky grotto was 'completed' and goes over the edge of its brown paint in places. Interestingly, the more crudely worked areas of ultramarine paint on the right hand side of the picture, mentioned earlier in this article, were found to have a different binding medium, with heat-bodied linseed oil being used instead.

It is not possible, however, to use these variations in the binding medium of different passages as a guide to the internal chronology of the painting, or as an indication of different hands at work. Heat-bodied linseed oil was used as the medium for some of the underpainting layers in the draperies, identified in samples from both the grey undermodelling layer of the Virgin's tunic and the red lake-containing underlayer below the angel's blue robe. Moreover, heat-bodied linseed oil was found in the dark grey paint of the angel's oversleeve, while conversely the yellow lining of the cloak seems to be bound in heat-bodied walnut oil.

But we cannot conclude that linseed oil was routinely chosen for all the lower paint layers; in fact, quite the contrary. The uppermost *imprimitura*, containing the lead-tin yellow and a high degree of lead soaps, was bound in walnut oil. GC–MS analysis also suggested that, unlike the oil used for the main paint layers, in this case the oil had not been heat-bodied.[33] This would have dried more slowly than the heat-bodied linseed oil used elsewhere on the painting and is therefore an unusual choice for an *imprimitura* layer.

The dark brown, thinly applied, paint of the rocks in the foreground was executed in heat-bodied walnut oil, giving a similar result to that obtained in 1995 for the brown paint from the rocks on the upper right edge of the picture. However, a further sample of paint from the rocks on the left hand side of the picture, where there are very pronounced drying cracks, gave GC–MS results suggestive of heat-bodied linseed oil. A related cross-section shows that here the brown paint was applied in several layers, and perhaps we can imagine that the uppermost layer was finished in a linseed oil medium only after the rocks in the other parts of the picture had been completed. In any case, it does not appear that the use of a particularly unusual medium is the cause of the drying cracks in this passage. Rather, this is the result of building up several layers with poorly drying pigments, and perhaps inadequate drying times between applications.

Only one sample of flesh paint was obtained for medium analysis, taken from the foot of Saint John the Baptist on the extreme left edge of the painting. GC–MS suggested the use of walnut oil for the flesh paint, giving a ratio of palmitic and stearic fatty acid methyl esters considerably higher than that expected for linseed oil.[34]

The medium analysis results obtained from a sample of the ultramarine paint of the Virgin's mantle present some problems of interpretation. GC–MS analysis indicated a reduced proportion of the di-acid methyl azelate, compared to that expected for a drying oil. However, results of this type have often been seen for paint samples containing ultramarine, even when the binding medium is clearly a drying oil.[35] In this case the paint texture of the blue robe, and the formation of drying cracks and wrinkles in this passage, strongly suggest an oil medium. However, in addition, protein-like bands were visible in some FTIR spectra, and the possibility that a proteinaceous component is also present within the sample must be considered.[36] Nonetheless, the interpretation of the FTIR spectra is complicated by the presence of calcium oxalate, characterised by a small sharp band at ~1324 cm^{-1}, and also giving rise to a broad band in the region of ~1640 cm^{-1}. This latter band could be misinterpreted as an amide band, making the identification of protein by FTIR more challenging.[37] In any case, no protein analysis has been undertaken, and therefore no firm conclusions can be drawn about the binding medium of this passage on the basis of FTIR analysis, but on balance it seems most likely that the Virgin's blue robe is painted in an oil medium.

Reframing Leonardo's *Virgin of the Rocks*

Like many of the National Gallery's large altarpiece paintings, Leonardo's *Virgin of the Rocks* was, until recently, framed in a nineteenth-century evocation of a sixteenth-century Italian tabernacle frame (FIG. 31). However, such frames are not exact copies of originals, and framers were often blithely oblivious to available models. In the case of the frame formerly adorning Leonardo's picture, the ornament (and the distinctive skull capitals) derive from a doorway at San Giobbe in Venice.

The restoration of the painting did not initially include any plan of reframing. The Gallery's current framing policy is, whenever possible, to try to find visually compatible frames of the same period and place as the paintings, but large frames dating back to *c.*1500 are very rare indeed, and finding an appropriate frame for *The Virgin of the Rocks* was thought to be an unlikely prospect. However, the opportunity to attempt this kind of reframing arose when elements from an original early sixteenth-century tabernacle frame appeared at a general antiques auction in Italy in March 2009 (FIG. 32). The

FIG. 31 NG 1093, shown in its previous frame, before restoration.

Gallery successfully acquired the parts, including two pilasters and a cornice section. The pieces are of an *all'antica* design of a kind found throughout Italy between about 1480 and 1510, and hence were perfectly suitable to use as the principal elements of a newly assembled frame for the picture.

Leonardo's *Virgin of the Rocks* was first commissioned to be placed within a large altarpiece already designed and executed by the workshop of Giacomo del Maino. The workshop's surviving *Altar of the Immaculate Conception* (FIG. 33) in Ponte in Valtellina in Lombardy, made shortly after 1495, has parts that are similar to the design of our newly acquired pieces, and this was used as a guide for the plausible recreation of the new frame's missing elements, including its base, spandrels and the inner edges (FIG. 34).

The carpentry and carving work was carried out by Peter Schade in the National Gallery framing workshop. The original frame elements, like most Italian sixteenth-century gilded woodwork, are made from poplar, and therefore European poplar was also used for all the reconstructed decorative elements. Both original and new parts were assembled on a backframe made from Canadian pine. The ornament on the pilasters and the frieze of the original parts is not carved wood, but instead has been modelled in a thick paste made from rabbit skin glue, gesso powder, paper pulp and linseed oil; the same technique was used for the recreated ornament on the base (FIG. 35).

The experienced specialist gilder Adriano Lorenzelli worked together with the National Gallery's Isabella Kocum on the gilding and finishing of the new parts.

FIG. 32 Frame fragments purchased as the basis for the new frame for NG 1093.

FIG. 33 Giacomo del Maino and workshop, *Altar of the Immaculate Conception*, after 1495. Polychrome and gilded wood. San Maurizio, Ponte in Valtellina.

FIG. 34 Detail of the altar in FIG. 33, showing some of the motifs used by del Maino which were incorporated into the new frame for NG 1093.

FIG. 35 Gessoing of newly constructed frame components.

FIG. 36 NG 1093, shown in the newly constructed frame, after restoration.

The surface of the original pieces was in very good condition, and only a few significant losses were replaced; all the newly created pieces were toned to match the general wear and patination of the original elements.

Even though we cannot replicate the full splendour of Maino's elaborate multi-tiered construction, the new frame is intended to evoke something of the flavour of that original setting. The richness of the frame's decoration has, if anything, underscored Leonardo's mastery of his deliberately limited palette, and thereby enhanced our appreciation of his handling of light, tone and space. The level of the inner edge of the frame is only slightly in front of the surface of the painting, which allows Leonardo's composition to exert much of its full force without the distractions of the elaborate framing and surrounding accompaniments of carving, gilding and painted panels (FIG. 36).

At the same time the London *Virgin of the Rocks* has been made much more visible by its new treatment after 60 years of a developing miasma in the varnish. The visual gain that removal of this distorting varnish has achieved has been revelatory, and the painting can now be judged once more for its power, beauty and magical impact.

Acknowledgements

The authors are extremely grateful to Cecilia Frosinini of the Opificio delle Pietre Dure in Florence for her most perceptive comments and suggestions on this article. At the Gallery, we would like to express our thanks to Luke Syson for reading the manuscript and recommending many improvements, and to Marika Spring for EDX analytical work and for literature suggestions.

This article is available for download at:
http://www.nationalgallery.org.uk/technical-bulletin/keith_roy_morrison_schade2011

Notes

1 L. Keith and A. Roy, 'Giampietrino, Boltraffio and the influence of Leonardo', *National Gallery Technical Bulletin*, 17, 1996, pp. 4–19.

2 Luke Syson, Curator of Italian paintings before 1500, has been instrumental to both the conception and development of this project and his input throughout has been extremely valuable.

3 L. Keith, 'In Pursuit of Perfection: Leonardo's Painting Technique' in L. Syson et al., *Leonardo da Vinci: Painter at the Court of Milan*, exh. cat., National Gallery, London 2011, pp. 54–77.

4 Information relating to the acquisition of *The Virgin of the Rocks* is contained in the National Gallery Archive. The records also contain a letter, NG68/3/15, from Layard to Burton, 3 September 1880, which gives the noted connoisseur Giovanni Morelli's views about the painting.

5 The National Gallery conservation records contain information pertaining to the earlier study of the cradle, which was initially identified in 1949 as being constructed from cedar. Subsequent investigation revealed the wood to be mahogany.

6 Varnishes of similar composition have been found on other paintings in the National Gallery collection, but in most cases they can be related to conservation treatments carried out prior to acquisition of the picture. See L. Keith, A. Roy and R. Morrison, 'Leonardo da Vinci's *Virgin of the Rocks*: technique and the context of restoration', in *Studying Old Master Paintings, Technology and Practice, The National Gallery Technical Bulletin 30th Anniversary Conference Postprints*, M. Spring (ed.), with H. Howard, J. Kirby, J. Padfield, D. Peggie, A. Roy and A. Stephenson-Wright, Archetype Publications in association with the National Gallery, London 2011, pp. 72–9. See also R. White and J. Kirby, 'A Survey of Nineteenth- and early Twentieth-Century Varnish Compositions found on a Selection of Paintings in the National Gallery Collection', *National Gallery Technical Bulletin*, 22, 2001, pp. 64–84.

7 The IRR revealed an extensive underdrawing of an abandoned composition of an Adoring Virgin, which proved fundamental in establishing the likely chronology and dating of the NG picture. See L. Syson and R. Billinge, 'Leonardo da Vinci's use of underdrawing in the *Virgin of the Rocks* in the National Gallery and in *St Jerome* in the Vatican', *The Burlington Magazine*, CXLVII, 1228, July 2005, pp. 450–63.

8 Retouching carried out with Gamblin Conservation Colors, proprietary restoration paints made using Laropal A–81 resin. See http://www.conservationcolors.com/papers.html for more information on their composition, manufacture and testing. The picture was varnished with dammar resin, brushed before restoration with a 30% solution (w:w) in Fluka white spirit, and sprayed with a 25% w:w solution after the completion of the retouching. The varnish was applied with the intention of achieving the fullest possible saturation of the darker colours with the least amount of material – resulting in a surface which also clearly reveals the various surface textures within the paint itself. This is preferable to the suppression of the saturation which would inevitably result from the attempt to create a more uniform and matte surface; any visual distraction now caused by the apparent variations of surface gloss is easily avoided by small changes in the angle of viewing by the spectator, which are naturally made when viewing such a work.

9 See Syson et al. 2011 (cited in note 3), pp. 54–77, for the history of the range of views on the picture – including that of its present curator, Luke Syson, who believes the picture to be entirely from the hand of Leonardo.

10 Extensive manuscript notes on these largely microscopical and microchemical analyses are kept in the Scientific Department files for the picture; they are undated, but must have been compiled in 1948. The microchemical procedures are those published in J. Plesters, 'Cross-sections and Chemical Analysis of Paint Samples', *Studies in Conservation*, II, 1956, pp. 110–57.

11 See 'Report by the Senior Experimental Officer' [J. Plesters] to the Honorary Scientific Advisory Committee, 2 October 1969, National

Gallery Archive, unpublished. These notes deal particularly with the detection of lead-tin yellow ('type I') by X-ray diffraction analysis in Renaissance paintings, including Leonardo's *Virgin of the Rocks*.

12 R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 17, 1996, pp. 96–7.

13 The infrared scanner employed is described in L. Pezzati, M. Materazzi and P. Poggi, 'Infrared Reflectography and the INOA High Resolution Scanner', in C.B. Strehlke and C. Frosinini (eds), *The Panel Paintings of Masolino and Masaccio. The Role of Technique*, Milan 2002, p. 267. The IR scanning work in London was undertaken by C. Frosinini and R. Bellucci (of the OPD, Florence) and L. Pezzati and P. Poggi (of the INO-CNR, Florence) and attended by R. Billinge, A. Roy and L. Keith from the National Gallery.

14 Syson and Billinge 2005 (cited in note 7). See also R. Bellucci, C. Frosinini, B.G. Brunetti, L. Pezzati and P. Poggi, 'La Vergine delle Rocce di Leonardo: soprese nell' *underdrawing* della versione di Londra', *Kermes*, 60, 2005, pp. 39–53.

15 Keith, Roy and Morrison 2011 (cited in note 6).

16 See Syson et al. 2011 (cited in note 3), pp. 54–77.

17 Scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM–EDX) performed on this cross-section detected iron-containing particles, located in the lowest drawing layer.

18 P. Riitano and C. Seccaroni, 'Attorno all'imprimitura', in M. Ciatti, C. Frosinini, A. Natali and P. Riitano (eds), *Raffaello: la rivelazione del colore. Il Restauro della* Madonna del Cardellino *della Galleria degli Uffizi*, Florence 2008, pp. 95–103.

19 FTIR microscopy identified lead soap agglomerations containing lead palmitate and lead stearate within samples of the lead-tin yellow-containing *imprimitura* layer. Some lead azelate was also detected, which appeared to be more dispersed. See also C. Higgitt, M. Spring and D. Saunders, 'Pigment-medium Interactions in Oil Paint Films containing Red Lead or Lead-tin Yellow', *National Gallery Technical Bulletin*, 24, 2003, pp. 75–95.

20 See Syson et al. 2011 (cited in note 3), pp.54–77.

21 The translucent brown pigment particles detected in a number of paint layers contain a proportion of iron (by EDX analysis) and probably also a certain amount of organic matter. This type of pigment came to be called, among other names, Cassel (Kassel) or Cologne (Cullen) earth by the seventeenth century, and may be best described as the material identified in the Armenini Treatise (1586) as '*terra d'ombra*' (umber), a translucent brown earth pigment recommended for shadowing flesh paints. See E. Olszewski (ed.), translation of G.B. Armenini, *On the True Precepts of the art of Painting* [*De' veri precetti della pittura*], New York 1977, pp. 178–9. [Mrs] M. P. Merrifield states that the possibly equivalent term '*terra di Colognia*' was not used in Italian treatises until the seventeenth century, see Mrs Merrifield, *Original Treatises [o]n the arts of Painting*, Vol. I, 1849, p. cxxxiv. The Milanese painter, Giovan Paolo Lomazzo, also mentions the use of '*terra d'ombra*' or '*terra di campana*' for creating the shadows of the flesh. See G.P. Lomazzo, *Tratto dell'Arte de la Pittura*, Milan 1584, Libro Terzo, Capit. IV, p.191.

22 A notably indistinct and indefinite interface is observable under the microscope in samples in many places on the picture where the extensive monochrome underlayers are in contact with the overlying design layers. It seems likely that the underlying monochrome design was probably rather rich in paint medium in order that it could be brushed in broadly as a rapidly applied fluid layer. This has led to drying defects in the paint layer system as a whole. The nature of the paint boundary at these points can be seen in cross-section more clearly by UV-fluorescence microscopy.

23 SEM–EDX analysis of a scraping from the brown background rocks identified various types of silicates, including some which contain mixtures of silicon, aluminium, potassium and magnesium in addition to iron, and might suggest a green earth-type composition.

24 EDX analysis showed the presence of earth pigments. Various silicates and a proportion of dolomite (mineral calcium magnesium carbonate) and calcite were identified as mineral constituents of one or other natural earth pigment employed. In addition significant amounts of copper were also detected, suggesting the presence of some verdigris.

25 The blanching of ultramarine appears to be an intrinsic phenomenon associated with the pigment since it has occurred to some degree even where the ultramarine has been covered by subsequent paint layers. Nonetheless, it often appears more pronounced at the surface and environmental factors may play a significant role. It is known that ultramarine is sensitive to acidic conditions and that discoloration of the blue particles can take place on exposure to acid through the disruption of the aluminosilicate framework and the release of the $S_3^{\cdot -}$ chromophore. This has sometimes been suggested in the literature as a possible mechanism for the degradation of ultramarine, but the blanching of ultramarine paint on easel paintings, where many of the blue particles retain their colour and the surrounding matrix has become cloudy and white-looking, is likely to be a more complicated phenomenon related to changes in the binding medium. For a discussion of the effects of acidic conditions on ultramarine see M. Wyld, J. Mills and J. Plesters, 'Some observations on blanching (with special reference to the paintings of Claude)', *National Gallery Technical Bulletin*, 4, 1980, pp. 49–63, esp. p 62; E. Del Federico, W. Shöfberger, J. Schelvis, S. Kapetanaki, L. Tyne and A. Jerschow, 'Insight into framework destruction in ultramarine pigments', *Inorganic Chemistry*, 45, 2006, pp. 1270–6; J. Plesters, 'Ultramarine Blue, Natural and Artificial' in *Artists' Pigments. A Handbook of Their History and Characteristics*, Vol. 2, A. Roy (ed), National Gallery of Art, Washington and Oxford University Press, New York and Oxford, 1993, p. 45 and p. 58.

26 J.J. Boon, J. van de Weerd, K. Keune, P. Noble and J. Wadum, 'Mechanical and Chemical Changes in Old Master Paintings: dissolution, metal soap formation and remineralization processes in lead ground/intermediate paint layers of 17th-century paintings', *Preprints of ICOM–CC 13th Triennial Meeting, Rio de Janeiro*, London 2002, pp. 401–6. See also Higgitt, Spring and Saunders, 2003 (cited in note 19).

27 See Keith, Roy and Morrison, 2011 (cited in note 6), pp. 76–7.

28 EDX performed on a sample from the duller yellow lining of the Angel's cloak identified a few particles of lead-tin yellow as well as the yellow earth pigment. In addition, some particles of dolomite (see note 24), silicates and copper-containing particles were identified.

29 It was noted by FTIR-microscopy that the lead white present in the flesh paint, as elsewhere on the painting, for example in the pale blue sky, was composed principally of cerussite ($PbCO_3$), neutral lead carbonate. Cerussite is often detected in conjunction with the more common basic lead carbonate or hydrocerussite ($2PbCO_3 \cdot Pb(OH)_2$), but to find it on its own or with very little hydrocerussite present is unusual, although this has previously been reported for a priming layer of one of the panels in Grünewald's Isenheim Altarpiece. See E. Welcomme, P. Walter, P. Bleuet, J.L. Hodeau, E. Dooryhee, P. Martinetto and M. Menu, 'Classification of lead white pigments using synchrotron radiation micro X-ray diffraction', *Applied Physics A*, 89, 2007, pp. 825–32. At present it is difficult to assess the significance of this observation, but it has been suggested that differences in lead white composition may reflect the different grades of lead white production. See B. Berrie and L. Matthew, 'Lead white from Venice: a whiter shade of pale?', in M. Spring et al. 2011 (cited in note 6), pp. 295–301.

30 The red lake pigment used in the flesh paint is composed of small pale pink particles that are just visible in ordinary light in cross-section; they are more evident under UV illumination. This lake would appear to be of a different composition from that used in the draperies and does not seem to be extended with starch in the same way. UV-microscopy suggests some degree of fading, the full extent of which is difficult to judge. However, there is little difference between the upper portion of the paint layer and that further below the surface, as sometimes occurs in faded paints.

31 See, for example, gilded tin linear decoration on draperies in two associated panels by Gaudenzio Ferrari: *Christ rising from the*

Tomb (NG 1465) and *St Andrew* (?) (NG 3925), both 1530–4. Communicated by M. Spring.

32 The recent GC–MS analysis was performed using an Agilent Technologies 7890A gas chromatograph coupled to a 5975C quadrupole mass spectrometer. Derivatisation was carried out using *m*-(trifluoromethyl)phenyltrimethylammonium hydroxide (TMTFTH). Fatty acid ratios were used to gain an indication of the type of oil employed in the binding medium of the paint.

33 A sample of the *imprimitura* from a loss in the angel's drapery (P/S 2.5, A/P 1.7, A/Sub 7.2) gave a much higher ratio of the di-acid methyl esters azelate and suberate, which can be used as an indication of the degree of pre-polymerisation, than expected for a heat-bodied oil. An additional sample of the *imprimitura* was taken from an area of worn paint on Christ's arm (P/S 2.7, A/P 1.6, A/Sub 4.0) and was also found by GC–MS analysis to contain walnut oil, but here the ratios of the di-acids gave an intermediate result, suggesting there may have been some heat-bodying of the oil in that particular sample. However, a portion of the thin and abraded overlying flesh paint may have contributed to the ratio of the di-acids in this case.

34 Although GC–MS analysis of a sample of flesh paint indicated a ratio of palmitic and stearic fatty acids consistent with the use of walnut oil, the level of the di-acid methyl ester azelate, which is often taken to be an indication of a drying oil, was significantly reduced (P/S 2.4, A/P 0.6, A/Sub 3.3). FTIR microscopy indicated the presence of lead soaps of both palmitic and stearic acid and a cross-section from a similar area shows large lead soap agglomerates within the layers of flesh paint. The formation of soap agglomerates can alter the relative amounts of fatty acids detected by GC–MS and this is probably the explanation for the results obtained from this sample. No proteinaceous components were detected by FTIR microscopy, and there is no evidence to suggest that the binding medium of the flesh paint is anything more complicated than walnut oil. See Higgitt, Spring and Saunders 2003 (cited in note 19) p. 82.

35 Other examples of ultramarine-containing paint analysed by GC–MS in the National Gallery Scientific Department have often given similar results, with a lowered ratio of azelate to palmitate. For example, a sample of ultramarine-containing paint from the sky of Guido Reni's *The Adoration of the Shepherds* (NG 6270) gave an A/P ratio of 0.4.

36 It has been suggested that a proteinaceous component such as egg may have been added to the binding medium of blue passages of paint in Leonardo's *The Madonna with the Carnation (Die Madonna mit der Nelke*). See J. Koller and U. Baumer, '"Er [...] erprobtedie seltsamsten methoden, um öle zum malen [...] zu finden.", Leonardos rolle in der frühen italienischen ölemalerei', in C. Syre, J. Schmidt and H. Stege (eds), *Leonardo da Vinci, Die Madonna mit der Nelke*, Alte Pinakothek and Schirmer/Mosel, Munich 2006, pp. 155–74.

37 C. Higgitt and R. White, 'Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries', *National Gallery Technical Bulletin*, 26, 2005, pp. 89–104; esp. pp. 93–4. Various sources for the formation of calcium oxalate have been suggested in the literature, and in this case it is likely to be a deterioration product resulting from the biological activity of micro-organisms, which may bring about the deterioration of the binding medium. For a discussion of the formation of calcium oxalate crusts, see F. Cariati, L. Rampazzi, L. Toniolo and A. Pozzi, 'Calcium oxalate films on stone surfaces: experimental assessment of the chemical formation', *Studies in Conservation*, 45, 2000, pp. 180–8. It is worth noting that oxalate crusts are more often observed on paint films containing certain pigments; particularly red lakes, ultramarine, smalt and copper greens. For further discussion of the relative reactivity of paint films containing different pigments, see A. Zoppi, C. Lofrumento, N.F.C. Mendes and E.M. Castellucci, 'Metal oxalates in paints: a Raman investigation on the relative reactivities of different pigments to oxalic acid solutions', *Analytical and Bioanalytical Chemistry*, 397, 2010, pp. 841–9. The presence of a proteinaceous material may increase the likelihood of calcium oxalate formation, but in turn the processes involved could also be responsible for the occurrence of small amounts of protein, detected by FTIR microscopy. It is not clear if there may be some relationship between the blanching of ultramarine-containing paint and the formation of oxalate crusts, and these processes are presently not well understood.