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Front cover: Giampietrino, *Salome*; detail of Plate 1, page 4.

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**Plate 1** Botticelli, *Four Scenes from the Early Life of Saint Zenobius* (NG 3918), *c.*1500. Poplar, 66.5 × 149.8 cm.

**Plate 2** Botticelli, *Three Miracles of Saint Zenobius* (NG 3919), *c.*1500. Poplar, 65 × 140.3 cm.

# The Materials of a Group of Late Fifteenth-century Florentine Panel Paintings

JILL DUNKERTON AND ASHOK ROY

## Introduction

In the past few years six panels all painted in the last quarter of the fifteenth century by Florentine artists have undergone cleaning and restoration in the Conservation Department of the National Gallery, these treatments providing an opportunity to take paint samples for the identification of materials. A seventh panel, *The Virgin and Child with Saint John and Angels* ('*The Manchester Madonna*') by Michelangelo, was examined in connection with the exhibition *Making and Meaning: The Young Michelangelo* (1994/5) and, although it may not have been painted in Florence, it is included in this survey for reasons given below.

As the Table of Results (pp. 24–7) shows, most of the materials are common to all the paintings and differences in their use are generally slight. This should not be surprising, for the artists can be shown to have been linked by more than their city of origin and training.

The two panels by Botticelli, *Four Scenes from the Early Life of Saint Zenobius* and *Three Miracles of Saint Zenobius* (Plates 1 and 2), are from a series of four *spalliere* which have always been accepted as late works. It has been suggested recently that they were painted for the marriage of a member of the Girolami family who claimed descent from the saint's father, and more specifically for the marriage of Zanobi Girolami in 1500[1] – although a narrative in which the first episode shows Zenobius rejecting his prospective bride might seem rather inappropriate for the occasion. In addition, there are some notable differences between the last panel in the sequence, now in Dresden, and the other three.[2] While there can be no doubt that the Dresden picture is from the same series, the figure scale tends to be larger and the range of colours more limited. Furthermore there is no trace of the shell gold which embellishes costumes and architectural detail in the preceding scenes.

*The Virgin and Child with Saint John* (Plate 3) by Filippino Lippi is a relatively early work, probably dating from the late 1470s, and therefore painted not long after the period when Filippino had been closely associated with Botticelli. Indeed, it came into the Collection in 1894 as a Botticelli.[3]

*The Virgin and Child with an Angel* (Plate 4) has been catalogued until recently as by a follower of Botticelli and thought by some to be an early work by him, an attribution based on its similarities with a more widely accepted painting in Naples.[4] Both these pictures are derived from a painting by Filippo Lippi in Florence (Uffizi). On grounds of quality and certain technical features – including a degree of hesitancy, if not incompetence – the National Gallery panel seems unlikely to be associated with Botticelli and it has now reverted to an earlier, more approximate attribution as by an Imitator of Filippo Lippi.[5] It was not necessarily painted in Filippo's lifetime and is quite likely to be close in date to Filippino's little panel.

The attributions of the two arch-topped panels from the Ghirlandaio workshop have also been adjusted. Following cleaning it has become apparent that the *The Virgin and Child* (Plate 5), previously catalogued as 'Studio of Domenico Ghirlandaio', is a beautiful and characteristic work of about 1480 by Domenico himself (as had already been suspected by some scholars).[6] *The Virgin and Child with Saint John* (Plate 6) is now given to Domenico's brother and

**Plate 3** (*left*) Filippino Lippi, *The Virgin and Child with Saint John* (NG 1412), late 1470s. Poplar, 59.1 × 43.8 cm.

**Plate 4** (*below left*) Imitator of Fra Filippo Lippi, *The Virgin and Child with an Angel* (NG 589), *c.*1480. Poplar, 69.9 × 48.3 cm.

business partner, David, a painter whose output has only recently been established with any certainty.[7] The view of Rome in the background suggests that it is likely to have been painted after 1482 when the Ghirlandaio brothers returned from working alongside Botticelli in the Sistine Chapel. Botticelli and Domenico were near contemporaries and are also thought to have been associated with the large and busy workshop of Verrocchio at about the same time.

In its turn Domenico's workshop became the training ground for a significant proportion of the next generation of artists, including, most famously, the young Michelangelo. There is a possibility that the '*Manchester Madonna*' (Plate 7) was begun in Rome in 1497, but an earlier date cannot be excluded.[8] In technique the panel emerges as entirely within the tradition of the Ghirlandaio workshop.

This technical tradition, which is also that of Botticelli and Filippino Lippi (at least in the earlier part of his career), is relatively conservative. Although, as the Table of Results shows, some oil was used for specific colours, the panels were executed with what was still in its essentials an egg-tempera technique, retaining the characteristic light and brilliant tonality, and often making extensive use of gilded decoration. They seem to have rejected – perhaps quite consciously – the more innovative and experimental development of the properties of the oil medium as exploited by, for example, the Pollaiuoli brothers, Leonardo da Vinci and even the more conservative artist Perugino. In panels such as those for the Certosa di Pavia,[9] Perugino made use of glazes in a manner approaching that of Netherlandish painters to achieve both depth of tone and optical complexity.

**Plate 5** Domenico Ghirlandaio, *The Virgin and Child* (NG 3937), *c.*1480. Poplar, 92.3 × 58 cm (including modern addition at the top of the arch).

**Plate 6** David Ghirlandaio, *The Virgin and Child with Saint John* (NG 2502), 1480s. Poplar, 78.8 × 46.5 cm.

**Plate 7** (*right*) Michelangelo, *The Virgin and Child with Saint John and Angels* ('*The Manchester Madonna*') (NG 809), perhaps 1497. Poplar, 104.5 × 77 cm.

# Table of Results

| ARTIST/PAINTING | Botticelli, *Four Scenes from the Early Life of Saint Zenobius* (NG 3918) | Botticelli, *Three Miracles of Saint Zenobius* (NG 3919) | Filippino Lippi, *The Virgin and Child with Saint John* (NG 1412) |
|---|---|---|---|
| SUPPORT | Poplar, presumed | Poplar, presumed | Poplar, identified[1] |
| GROUND[3] | Gesso | Gesso | Gesso |
| UNDERDRAWING | Particles of **vegetable black**[4] visible in some cross-sections. Fine brush drawing to delineate contours and folds visible in infra-red. Architectural elements incised. | Particles of **vegetable black** visible in some cross-sections. Fine brush drawing to delineate contours and folds visible in infra-red. Architectural elements incised. | Some broad lines of brush drawing visible in infra-red. Parapet incised. |
| BLUE | Sleeve of Zenobius rejecting his bride: **azurite** and **lead white**, traces of **natural ultramarine** in shadow.<br>Sky: **azurite** and **lead white** in **egg**.[6] | Blue areas not sampled for pigments.<br>**Azurite** found in purple mixture.<br>Sky, medium: **egg**.[6]<br>Blue tunic of man in central group, medium: **egg**.[6] | Virgin's mantle: mid-tone, **natural ultramarine** and **lead white**, probably in **egg**,[6] over **lead white** local *imprimitura*; shadow, as above but with additional **natural ultramarine** glaze in **linseed oil**.[6]<br>Sky: **azurite** and **lead white** in **egg**.[6] |
| GREEN | Dark green carpet: **artificial malachite**[7] in **egg**, with some **walnut oil**.[6]<br>Green and yellow *cangiante* robe of the rejected bride: mid-tone, **artificial malachite** and **lead-tin yellow**.[8] | Dark green sleeve of beggar, far right: **artificial malachite** and **lead-tin yellow**. | Lining of Virgin's mantle: **artificial malachite** in **egg**[6] over **lead white** local *imprimitura*. Sample for medium analysis also included a **copper green** glaze in **linseed oil**.[6]<br>Foliage between Saint John and the Virgin: **artificial malachite** over black underpaint.[9]<br>Tree on top of grass, right edge: **azurite** over **artificial malachite** and **lead-tin yellow**. |
| RED, PINK AND RED-BROWN | Opaque red draperies: **vermilion**.<br>Pink-brown floor, right-hand episode: **vermilion** and **lead white**.<br>Red-brown urn at baptism of Zenobius: **vermilion**, **vegetable black** and **lead white**, modelled with **vermilion** and **vegetable black**. | Opaque reds not sampled.<br>Pink of cope of Zenobius, left-hand episode: **red lake** in **egg** with a little **oil**.[6] | Pink of Saint John's drapery: **red lake**, dyestuff identified as **lac**,[12] in **walnut oil**.[6] |

| | Imitator of Fra Filippo Lippi, *The Virgin and Child with an Angel* (NG 589) | Domenico Ghirlandaio, *The Virgin and Child* (NG 3937) | David Ghirlandaio, *The Virgin and Child with Saint John* (NG 2502) | Michelangelo, *The Virgin and Child with Saint John and Angels* ('*The Manchester Madonna*') (NG 809) |
|---|---|---|---|---|
| | Poplar, presumed | Poplar, presumed | Poplar, presumed | Poplar, identified[2] |
| | Gesso | Gesso | Gesso | Gesso |
| | Particles of **vegetable black** visible in some cross-sections. Broad lines of brush drawing visible in infra-red. Architectural elements incised. | Particles of **vegetable black** visible in some cross-sections. Brush drawing to delineate contours and folds visible in infra-red.[5] Arch incised. | Particles of **vegetable black** visible in some cross-sections. Fine brush drawing and some broader lines of wash to indicate contours and folds visible in infra-red.[5] Lines of **red lake** visible in damaged areas of Virgin's mantle. Arch incised. | Brush drawing with **vegetable black** in an aqueous medium (**egg**?) to indicate contours and folds visible in unpainted areas and in infra-red.[5] |
| | Virgin's mantle: two layers of **natural ultramarine** and **lead white** in **egg**[6] over **lead white** local *imprimitura*. | Virgin's mantle: highlight, **azurite** and **lead white**; shadow, **azurite** in **walnut oil**.[6]<br>Sky: **natural ultramarine** and **lead white**. | Virgin's mantle: **natural ultramarine** and **lead white** in **egg**.[6]<br>Sky: **natural ultramarine** and **lead white**. | Sky: **azurite** and **lead white** in **egg**.[6] |
| | Lining of Virgin's mantle: **artificial malachite** and **lead-tin yellow**, traces of discoloured '**copper resinate**' type glaze, over **lead white** local *imprimitura*.<br>Grass to left of angel's waist: **artificial malachite** and **lead-tin yellow** over layer of **lead white** to cover *pentimento*.[10]<br>Grass in distant landscape: **artificial malachite**. | Lining of Virgin's mantle: mid-tone, **artificial malachite**; shadow, **artificial malachite** with discoloured '**copper resinate**' type glaze.<br>Dark green lattice pattern on textile: medium, **walnut oil**.[6]<br>Grass in landscape on right: **artificial malachite** and **lead-tin yellow**.<br>Tree on right: **artificial malachite, azurite** and **natural malachite** with a discoloured '**copper resinate**' type glaze. | Lining of Virgin's mantle: **natural malachite** (**rosasite**).[11]<br>Brown-green of grass on left: **artificial malachite, lead-tin yellow** and **yellow earth** over **natural malachite** (**rosasite**) and **artificial malachite**.<br>Tree on left: **artificial malachite** (discoloured) and a little **natural ultramarine** with a discoloured '**copper resinate**' type glaze in **linseed oil**.[6] | Lining of Virgin's mantle: **natural malachite**.<br>Grass in foreground: **natural malachite**, sometimes with some **lead-tin yellow**, in **egg** with a little **oil**.[6]<br>Pale green of *cangiante* sash of angel on far right: **natural malachite** and **lead white**. |
| | Book, lower right: **vermilion**.<br>Virgin's dress: **red lake** in **egg**[6] over **lead white** local *imprimitura*. | Virgin's dress: **red lake**, identified as **lac** with a little **kermes**[12] mixed with **lead white** in the highlights.<br>Shadowed area of red stripe on textile: **vermilion** glazed with **red lake** in **egg** (probably in the underlayer) and **walnut oil** (in the glaze).[6] | Virgin's dress: **red lake**, identified as **kermes** with a little **lac**.[12]<br>Saint John's red drapery: **red lake** over **red lake** and **lead white**.<br>Red area of carpet: **vermilion** in **egg** glazed with **red lake**, dyestuff identified as lac,[12] in **linseed oil**.[6] | Virgin's dress and tunic of angel on far right: **red lake** dyestuff identified as **lac** possibly with a little **kermes**,[12] in **egg** and **walnut oil**.[6]<br>Red of *cangiante* sash of angel on far right: **vermilion**.<br>Red shadows of *cangiante* tunic of angel second from right: **vermilion**. |

| ARTIST/PAINTING | Botticelli (NG 3918) | Botticelli (NG 3919) | Filippino Lippi (NG 1412) |
|---|---|---|---|
| YELLOW AND YELLOW-BROWN | Green and yellow *cangiante* robe of the rejected bride: highlight, **lead-tin yellow**[8] and **yellow earth.** | Cloak of blind beggar on right: highlight, **lead-tin yellow** over **lead-tin yellow** and **yellow earth**; shadow, **lead-tin yellow, yellow earth, lead white** and a little **vermilion.**<br>Green mixtures contain **lead-tin yellow.** | Green mixtures contain **lead-tin yellow.** |
| BLACK, GREY, PURPLE AND PURPLE-GREY | Lilac drapery of woman, far left: **natural ultramarine, red lake** and **lead white.**<br>Purple-grey pilaster: **vegetable black, vermilion** and **lead white.** | Purple robe of figure running down steps: **azurite, red lake** and **lead white** with (in the shadows) a glaze of **red lake, vermilion** and **vegetable black.**<br>Shoe of acolyte to left of Zenobius in central episode: **vegetable black** over **lead white,** black and a little **red earth.**<br>Shoe of youth having devil driven out, on left: **vegetable black, lead white** and a little **red earth.** | Christ Child's mauve drapery: three layers of **azurite, red lake** and **lead white** (the **red lake** has faded in the upper layer). |
| FLESH | Translucent brown shadow of forearm of Saint Sophia: **yellow earth,**[15] **vegetable black** and **lead white.**<br>Underpaint: **lead white.** | Not sampled. | Saint John's upper arm, junction between highlight and shadow: **lead white** with a little **vermilion** over a translucent brown consisting of **yellow earth,**[15] **vegetable black** and **lead white.**<br>Underpaint: **green earth** and **lead white.** |
| GILDING | **Shell gold.**<br>Sample from hem of lilac drapery of woman, far left. | **Shell gold** – not sampled. | **Mordant gilding** – not sampled. |

**Notes to the Table of Results**

1. The wood of the panel was misidentified in 1917 as American basswood or butternut and the picture designated a forgery. The wood was correctly identified in 1935. See p. 30, note 1 (Davies p. 288).
2. Identified by Joyce Plesters.
3. The gesso grounds have been examined by X-ray diffraction analysis; in general a mixture of gypsum and anhydrite is found. Because of the inhomogeneity of the grounds, the proportions vary.
4. Microscopically these black pigments are carbonised plant materials, but do not exhibit the particle character of wood charcoal.
5. For infra-red images, see p. 30, note 6.
6. For fuller media results for NG 3918, 3919, 3937, 2502 and 809, see R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 16, 1995, pp. 86-7; for NG 1412, see pp. 96–7 of this *Bulletin*; and for NG 589 see J. Mills and R. White, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 12, 1988, pp. 78–9.
7. Artificial malachite ($CuCO_3.Cu(OH)_2$) is distinguished from its natural counterpart by a distinctly globular particle form, variable particle size and the occurrence of fused spherulites. For fuller details see p. 31, notes 14–16.
8. Lead-tin yellow identified microscopically and by EDX (Pb, Sn). In two cases (yellow samples from NG 3937 and 2502), the 'type I' form of lead-tin yellow was confirmed by XRD. EDX results for the remainder suggest 'type I' in all cases.
9. This is a traditional method for constructing dark foliage and landscape greens in tempera paintings.

| Imitator of Fra Filippo Lippi (NG 589) | Domenico Ghirlandaio (NG 3937) | David Ghirlandaio (NG 2502) | Michelangelo (NG 809) |
|---|---|---|---|
| Green mixtures contain **lead-tin yellow**. | Cushion: highlight, **lead-tin yellow**; shadow, **yellow** and **red earths** and a little **vermilion** in **egg**.[6]<br>Green mixtures contain **lead-tin yellow**. | Yellow-brown of Saint John's cross: **lead-tin yellow, yellow earth** and a little **vegetable black**.<br>Green mixtures contain **lead-tin yellow**. | *Cangiante* tunic of angel second from right: highlight, **lead-tin yellow**; midtone and underlayer, **yellow earth**. Green mixtures contain **lead-tin yellow**. |
| Angel's purple tunic: **azurite, red lake** and **lead white** in several layers over **lead white** local *imprimitura*.<br>Pale purple-grey of table, right foreground: **azurite, red lake** and **lead white**.<br>Pink-grey of distant mountains: **vegetable black, vermilion** and/or **red earth** and **lead white**.<br>Warm grey of architecture: **lead white**, finely ground **vegetable black** and a little **yellow earth** in **egg**.[6] | Purple-grey of stone of arch: mid-tone, **lamp-black**(?),[13] **red lake** and **lead white**; shadow, as mid-tone but with glaze of **charcoal black**,[14] **red lake** and **azurite**. | Purple-grey of stone of arch: highlight, **natural ultramarine, red lake** and **lead white** over **natural ultramarine, red lake** and **vegetable black**; shadow, **natural ultramarine, red lake** and **vegetable black**. | Black undermodelling of Virgin's mantle: **vegetable black** in **egg**.[6]<br>Purple-grey of angel's wing and area between heads of angels on right: **vegetable black, red lake** and **lead white**. |
| Highlights of Christ Child's foot and thigh: **lead white** with a little **vermilion**.<br>Shadow of foot: **vermilion, lead white** and **vegetable black**.<br>Underpaint: **yellow earth, vegetable black** and **lead white** (*verdaccio*) over **lead white** local *imprimitura*. | Virgin's forehead, junction between highlight and shadow: **lead white** with a little **vermilion** over a translucent brown.[16]<br>Highlight on Virgin's collarbone: **lead white** with a little **vermilion**.<br>Christ Child's right hand, medium: **egg**.[6]<br>Underpaint: **green earth** and **lead white**. | Highlight on top of Christ's foot: **lead white**.<br>Virgin's cheek: **lead white** over **lead white** with a little **vermilion**.<br>Saint John's left arm, medium: **egg**.[6]<br>Underpaint: **green earth** and **lead white**. | Christ's forearm, mid-tone: **lead white** with a little **vermilion** and **red earth**, followed by a thin layer of translucent brown.<br>Underpaint: **green earth** and **lead white**. |
| **Mordant gilding.**<br>Mordant from neckline of Virgin's dress: **vegetable black, vermilion** and **red earth**. | **Mordant gilding.**<br>Mordant from neckline of Virgin's dress: **brown earth** and **lead white** with a high proportion of medium. | **Mordant gilding.**<br>Mordant from Saint John's drapery: **brown earth** and **lead white** with a high proportion of medium. | Not present. |

10. Cross-sections from NG 589 (for example Plate 9) often show many paint layers which result both from *pentimenti* and adjustments to outlines; intermediate layers of lead white are used in areas where the design has been modified.
11. Rosasite is a rare mineral closely related to malachite, in which a proportion of the copper atoms are replaced by zinc ($(Cu,Zn)CO_3.Cu(OH)_2$). For fuller details see text and p. 31, note 17.
12. For fuller results of HPLC analysis of red lakes, see pp. 68-70 of this *Bulletin*. In two cases (NG 3937 and 2502) the lake substrates were examined by EDX; strong peaks for aluminium and calcium were recorded.
13. Lampblack suspected from the very fine, even, rounded grains.
14. Typical angular and splintered wood charcoal fragments.
15. The yellow components of these brown flesh tones appear to be translucent forms of earth pigment; a proportion of yellow lake pigment, however, cannot be excluded.
16. The underlayer here is so thin (*c.* 2μ) that the individual components cannot be discerned even at high magnification under the microscope; however, the appearance both on the painting and in cross-section suggests the same constitution noted for NG 3918 and 1412.

## Commentary on results

The most immediately striking feature of the Table of Results is the consistent occurrence of the same materials throughout the paintings surveyed and also how limited these materials are in range, even allowing for the relatively restricted palette available in the fifteenth century.[10] Apart from the inevitable uses of lead white and carbon blacks, the same few pigments appear repeatedly, both on their own and as components of very similar mixtures. The two blue pigments, ultramarine and azurite, seem to be used interchangeably on both skies and draperies so that in Botticelli's panels we find azurite skies and draperies (ultramarine is reserved for the deepest shadows and for some of the purple mixtures),[11] and in the Madonnas of David Ghirlandaio and the Imitator of Filippo Lippi, ultramarine was used for all blue areas. Filippino combines an azurite sky with an ultramarine drapery; the converse is found on Domenico's panel. Michelangelo's intentions for the unfinished mantle of the Virgin in the *'Manchester Madonna'* are not known of course, but the pattern set by the paintings discussed here suggests that the black underpainting could have been completed either with ultramarine or azurite.

Only two types of red pigment appear: the opaque red, vermilion, and red lakes. In all cases where analysis has been possible, the dyestuffs have been found to derive principally from lac, with the exception of David Ghirlandaio's panel where the Virgin's dress was found to contain a kermes lake. The glaze on the carpet, however, was lac. As kermes was considerably more expensive than lac, in this instance there may have been a deliberate distinction between the two dyestuffs. On the other hand, in the paintings by Domenico Ghirlandaio and Michelangelo analysis suggests that there may be small amounts of kermes with the lac lake (see pp. 68–70 of this *Bulletin*). Since the dyestuffs are similar in appearance and colour, both as dry powders and when used as a paint, and the addition of kermes would not significantly modify the colour of the lac, here it seems more likely that the combination was accidental.

The lead-tin yellow (artificial lead-tin oxide) which appears in all these paintings was a standard material, but by this time only the 'type I' was used,[12] in contrast to the regular appearance of the 'type II' pigment (Cennino's *giallorino*), based on glass manufacture, found widely in Florentine altarpieces of the fourteenth century.[13]

With the exception of the specific role of green earth, the only green pigment to occur is malachite. In fifteenth-century Italian painting, malachite for greens, in one form or another, became a standard part of the palette and is widely used for draperies, landscape and foliage, replacing the mixtures for green that had been the principal method in the trecento. By the sixteenth century, with the dominance of oil medium, verdigris was preferred. The lack of alternatives to make satisfactory greens in tempera – verdigris works rather poorly in egg and the type of *terra verde* available at this period was too weak in colour for most purposes other than for underpainting flesh – presumably encouraged the use of malachite, which functions reliably well in egg. Particularly evident is an artificial form of the pigment (Plates 8 and 9), characterised by a distinctive spherulitic particle morphology[14] that arises from preparation by precipitation from soluble copper salts in an aqueous solution using calcium carbonate (chalk).[15] Artificial malachite of this type is not confined to Florentine paintings. It has been detected in a number of panel paintings of the fifteenth century, including those by Sienese, Venetian and Ferrarese painters, for example Sassetta, Bellini, Cosimo Tura and Cossa, but it is wholly typical of the workshops that owe their technical traditions to Florence, going back at least as far as Uccello.[16] Ground mineral malachite, as a dry pigment, was probably indistinguishable from the artificial equivalent, unless the natural material was coarsely ground and of a notably strong colour, as used for the lining of the Virgin's cloak (Plate 10) in the *'Manchester Madonna'*.

The identification in the lining of the Virgin's mantle (Plate 11) of David Ghirlandaio's *Virgin and Child with Saint John* of the rare copper- and zinc-containing analogue of malachite, known as rosasite,[17] is an unusual occurrence, but it is unlikely that this rare material was recognised as anything other than malachite, perhaps of a particularly favourable tone, and it is significant that artificial malachite occurs also in the same

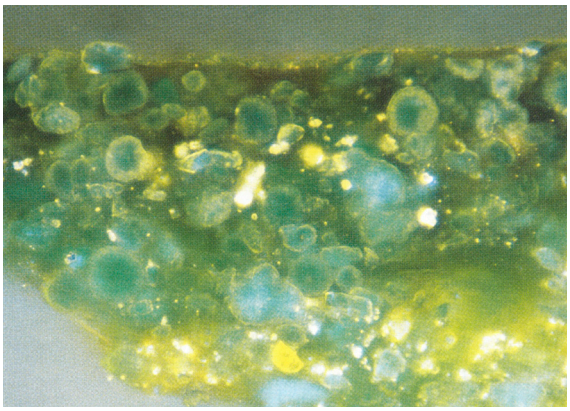

**Plate 8** Filippino Lippi, *The Virgin and Child with Saint John* (NG 1412). Cross-section from the mid-green lining of the Virgin's mantle showing the characteristic spherulitic particle form of artificial malachite. Original magnification 600 ×; actual magnification 500 ×.

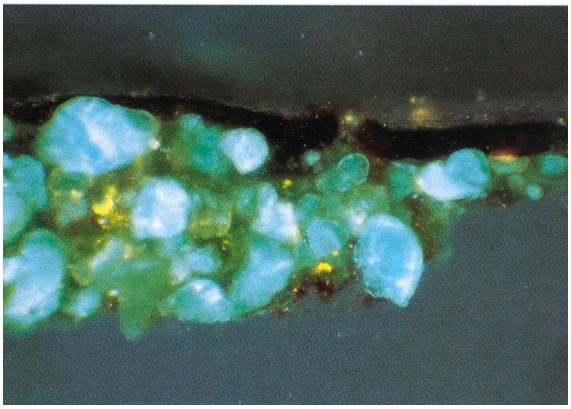

**Plate 10** Michelangelo, *The Virgin and Child with Saint John and Angels* ('*The Manchester Madonna*') (NG 809). Cross-section from a point where the hem of the robe of the angel on the far right overlaps the green of the grass, showing a thin layer of red lake over coarsely ground particles of natural (mineral) malachite. Original magnification 275 ×; actual magnification 240 ×.

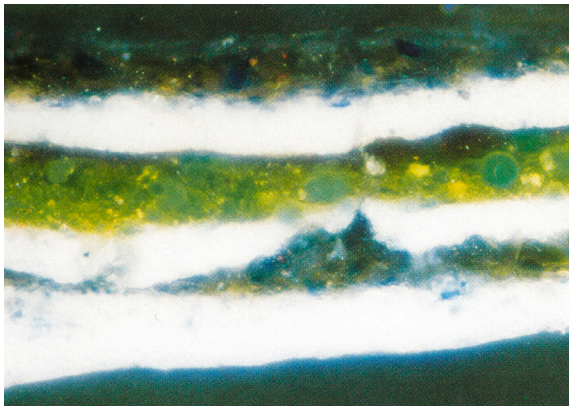

**Plate 9** Imitator of Fra Filippo Lippi, *The Virgin and Child with Saint John* (NG 589). Cross-section from blue-green of Virgin's cloak, between Saint John's legs showing an intermediate paint layer (pentimento) composed of artificial (spherulitic) malachite. The surface paint is natural ultramarine and the complex layer structure arises from a series of original modifications to the design made in the course of execution. Intermediate stages were obliterated with layers of lead white. Original magnification 390 ×; actual magnification 310 ×.

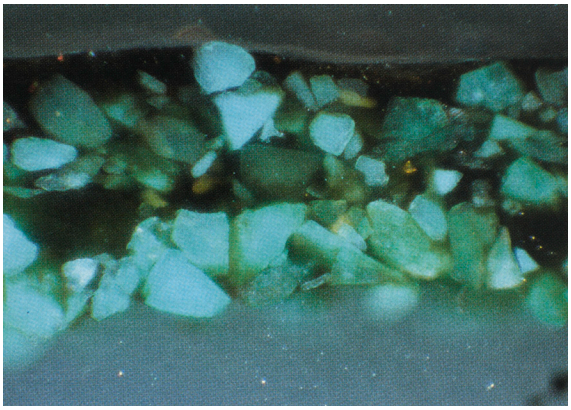

**Plate 11** David Ghirlandaio, *The Virgin and Child with Saint John* (NG 2502). Cross-section from lining of the Virgin's dark green mantle painted in natural (mineral) malachite containing substituted zinc (rosasite). Original magnification 240 ×; actual magnification 220 ×.

picture in the background landscape. It is possible that this group of green pigments was regarded by the suppliers and users as interchangeable materials.

The suppliers of these varieties of malachite, and of the other pigments, were most probably the Gesuati friars of San Giusto alle Mure. Botticelli, Ghirlandaio and Michelangelo are among the many Florentine artists documented as having obtained pigments from them, while there is indirect evidence to suggest that Filippino was also a customer (as was his father).[18]

A similar consistent pattern appears in the choice of media. In all the paintings the lighter colours, including the skies, the flesh painting and areas of yellow and white,[19] are in pure egg tempera. With the exception of the painter of the *Virgin and Child with an Angel* (Plate 4) who seems to have used egg throughout (at

least in the colours sampled), all the artists employed some drying oil for darker and more transparent shades of red, green and blue. It is not always easy to determine by analysis whether the oil and egg have been used in distinct layers or whether the oil has been incorporated into the egg to make an enriched tempera or *tempera grassa*. However, examples of the former would seem to include the final ultramarine glaze on the blue mantle in Filippino's Virgin and the azurite blue mantle of the Virgin in the panel by Domenico Ghirlandaio, where the pigment has been applied entirely in walnut oil. Several of the paintings include 'copper resinate'-type glazes containing oil, but in the case of the dark greens in the two Botticelli panels and in the '*Manchester Madonna*' the oil seems to have been added to the egg in small quantities. Analysis suggests that *tempera grassa* is also the medium for the red lakes in these three paintings. The rich red glazes on the textiles draped over the parapets in the two panels by the Ghirlandaio brothers are both based on oil, and also the pink of Saint John's drapery in Filippino's panel. Filippino was later to make increasing use of the oil medium in his paintings.[20]

The composition of the flesh tones in the paintings we have surveyed is directly comparable since all the samples are from the flesh of women and young children (the inclusion of older male figures might have increased the variety). In every case the highlights consist of lead white lightly pigmented with vermilion.[21] The appearance of the thin and delicate touches of translucent brown used to model the midtones and shadows on most of the panels is very similar, both in surface appearance and in cross-sections. Where the layer is sufficiently substantial for the components to be recognised under the microscope, it can be seen to contain yellow earth, vegetable black and lead white, a traditional mixture for flesh painting called *verdaccio* by Cennino. The only painting with a slightly different composition to the darker flesh tones is that now attributed to an Imitator of Filippo Lippi in which a mixture of vermilion, vegetable black and lead white is used. In this work the cooler effects were obtained by the use of a *verdaccio* mixture as an underpainting for the flesh areas. The flesh tones in the panels by Botticelli are applied over a layer of pure lead white. All the others are underpainted with green earth and lead white. The survival of this highly traditional technique through to the last years of the fifteenth century is particularly associated with the Ghirlandaio workshop.[22] Filippino, for example, seems to have abandoned it by about 1480, soon after the probable date of execution of his National Gallery panel.

The technique of mordant gilding is equally traditional. Only in the panels by Botticelli is there any shell (powdered) gold, but he often used mordant gilding as well.[23] The mordants employed by the two Ghirlandaio brothers, not unexpectedly, are identical in constitution, and similar coloured mordants can be seen on many products of their workshop. The mordant in the panel given to an Imitator of Filippo Lippi is more unusual and again suggests a slight separation between this painting and the rest of the group in this survey. However, it is only in such small details that the materials found can begin to indicate differences between the various workshops, let alone between individual painters.

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**Notes and references**

1. E. Callman, 'Botticelli's "Life of Saint Zenobius"', *The Art Bulletin*, LXVI, 1984, pp. 492–5. For other suggestions as to their original location see M. Davies, *The Earlier Italian Schools*, National Gallery Catalogues, London 1961, reprinted 1986, p. 109.
2. For large colour reproductions of the panels in Dresden and New York (the latter is the least well-preserved of the four), see R. Lightbown, *Sandro Botticelli: Life and Work*, London 1989, plates 111 and 112.
3. Davies, cited in note 1, p. 288.
4. Davies, cited in note 1, pp. 113–14.
5. It entered the Collection in 1857 as a work by Filippo Lippi.
6. For a fuller discussion of this painting with a note on its cleaning, see M. Hirst and J. Dunkerton, *Making and Meaning: The Young Michelangelo*, London 1994, pp. 86ff and p. 128, note 9.

7. See Hirst and Dunkerton, cited in note 6, pp. 86ff and p. 128, notes 8 and 10.
8. Hirst and Dunkerton, cited in note 6, pp. 37ff and pp. 83ff.
9. For the technique of these panels see D. Bomford, J. Brough and A. Roy, 'Three Panels from Perugino's Certosa di Pavia Altarpiece', *National Gallery Technical Bulletin*, 4, 1980, pp. 3–31. An account of the treatment (with some observations on the technique) of another panel in the Collection given to Perugino has also been published (D. Bomford, 'Perugino's "Virgin and Child with Saint John"', *National Gallery Technical Bulletin*, 1, 1977, pp. 29–34). However, the attribution of this panel to Perugino is now doubted, partly because of the removal during cleaning of a spurious inscription from the Virgin's mantle, but principally because of contradictions between the style which would appear to be late, perhaps around or after 1500, and the technique which is conservative and quite unlike that of Perugino's works of the 1490s. Indeed the technique is directly comparable with that of the panels studied in this survey and includes the use of natural malachite.
10. For the range of pigments available in the fourteenth and fifteenth centuries, see D. Bomford, J. Dunkerton, D. Gordon and A. Roy, *Art in the Making: Italian Painting Before 1400*, London 1989, pp. 30–43, and J. Dunkerton, S. Foister, D. Gordon and N. Penny, *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, London 1991, pp. 182–7.
11. Botticelli frequently used ultramarine on other works. For a comparative survey of the technique of several paintings, mainly in Florence, see M. Ciatti (ed.), *'L'Incoronazione della Vergine' del Botticelli: restauro e ricerche*, Florence 1990, pp. 81–109. A study of the technique of *The Adoration of the Kings* (NG 592), usually taken to be an early work by Botticelli, was published in 1955 (see H. Ruhemann, 'Technical analysis of an early painting by Botticelli', *Studies in Conservation*, II, 1955, pp. 17–40). A few cross-sections were prepared but the study is based principally on an examination made using a stereo binocular microscope, supported by photographic techniques. The observations (which are not entirely consistent with the evidence of the samples as presented) need to be confirmed by more up-to-date methods of examination and analysis.
12. Lead-tin yellow 'type I' appears to have been a product of Northern Europe, specifically Germany, as one early name – *giallo tedesco* – implies, although the technology of manufacture was almost certainly adopted in Italy. See H. Kühn, 'Lead-Tin Yellow' in *Artists' Pigments. A Handbook of Their History and Characteristics*, Vol.2, rev. and ed. by A. Roy, Washington D.C. 1993, pp. 86–9 and 99–110; also, E. Martin and A.R. Duval, 'Les deux variétés de jaune de plomb et d'étain: étude chronologique', *Studies in Conservation*, 35, 1990, pp. 117–36.
13. See D. Bomford et al, cited in note 10, pp. 37–9.
14. See R.J. Gettens and E.W. FitzHugh, 'Malachite and Green Verditer' in A. Roy, 1994, cited in note 12, pp. 194–5, particularly Figs. 12, 13, 14 and 15C. EDX spot analysis on individual pigment particles yield strong peaks for copper and little else.
15. P. Mactaggart and A. Mactaggart, 'Refiners' verditer', *Studies in Conservation*, 25, 1980, pp. 38–40.
16. Artificial malachite is present in foliage and landscape of Uccello's *Battle of San Romano* (NG 583) probably from the 1450s. It may also occur on an earlier panel, in foreground paint of Masaccio's *Saints Jerome and John the Baptist* (NG 5962) of the late 1420s.
17. Another occurrence is reported in E. Martin and M. Eveno, 'Contribution to the study of old green copper pigments in easel paintings', *3rd International Conference on Non-Destructive Testing, Microanalytical Methods and Environment Evaluation for Study and Conservation of Works of Art*, Viterbo 1992, pp. 781–91.
18. P. Bensi, 'Gli arnesi dell'arte. I Gesuati di San Giusto alle Mura e la pittura del rinascimento a Firenze', *Studi di Storia delle arti*, III, 1980, pp. 33–47.
19. Samples of white or cream-coloured paint not included in the Table were taken from NG 3918, 3919 and 589. All were egg. For references see Notes to Table (note 6).
20. Results have been published showing walnut and linseed oils, with some egg in lighter colours and in underpaints, in two panels in the Collection which were then catalogued as by Filippino (NG 4094 and 4095; see J. Mills and R. White, 'Organic Analysis in the Arts: Some Further Paint Medium Analyses', *National Gallery Technical Bulletin*, 2, 1978, pp. 74–5). Although they are now assigned to a Follower of Filippino, possibly the Master of Tavernelle who may be a painter called Niccolò Cartoni (see E. Fahy, *Some Followers of Domenico Ghirlandaio*, New York and London 1976, p. 201), this use of media probably reflects Filippino's later workshop practice.
21. The layers of pure lead white which occur in the samples of flesh paint from the panel by David Ghirlandaio are a consequence of his application of the tempera with very precise and distinctly separated brushstrokes. The pinker tones are of the same composition as on the other paintings.
22. See Hirst and Dunkerton, cited in note 6, pp. 96–7.
23. See Ciatti, cited in note 11, p. 103 for a useful table of Botticelli's gilding methods.