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'Black Earths': A Study of Unusual Black and Dark Grey Pigments used by Artists in the Sixteenth Century

MARIKA SPRING, RACHEL GROUT AND RAYMOND WHITE

In his *Lives of the Artists*, Vasari describes 'an astounding piece of painting' by Sebastiano del Piombo, a portrait of Pietro Aretino in which there may be seen 'five or six different kinds of black in the clothes that he is wearing – velvet, satin, ormuzine, damask, and cloth – and, over and above those blacks, a beard of the deepest black'.[1] Several different black pigments would have been available to painters in the sixteenth century to achieve this kind of effect. Those most commonly mentioned in treatises of the period on painting materials are charcoal black, bone or ivory black, lamp black, fruit-stone black and black earth.[2] The numerous references to black in Vasari's writing make it clear that artists were well aware of the differing hues and working properties of these blacks, and that they chose which pigment to use accordingly. Bone black gives a deep saturated warm black paint, charcoal black is bluer in tone, while lamp black has less body and can have a slightly greasy quality.[3] The nature of these carbon black pigments is well understood, because their preparation is discussed in detail in early treatises.[4]

Black earth, in contrast, is not a single pigment but a class of pigments, which could include a number of different black minerals. Comparatively little is known about which minerals were actually used as black pigments. In treatises on painting technique, the terms black earth, black chalk and black stone tend to be used interchangeably, whether discussing black pigments or drawing materials. Sometimes good sources are mentioned, or shreds of information about their properties are given, which could provide some clue as to their exact nature and composition. A soft black stone from Piedmont is described as being suitable for drawing by Cennino Cennini, and may also have been used as a pigment.[5] Vasari mentions black chalk from the hills of France,[6] and Antonio Filarete mentions a black earth from Germany which was suitable for use in fresco in his *Trattato dell'Architettura* (*c*.1461–4).[7] Much later, in the eighteenth century, the Spanish painter Palomino wrote that black earth 'is very beautiful for all lights and all shadows, and especially if it is the one from Venice, which comes in little balls'.[8] A *terra nera di campana* (black earth of bells) is mentioned by Vasari, Armenini, Lomazzo, Borghini and Baldinucci. Vasari describes it as a pigment suitable for priming mixtures, and states that it has siccative properties in oil.[9] Borghini gives the most complete description, describing it as a crust that forms on the moulds in which bells and artillery have been cast, but he does not indicate what the composition of this crust might be.[10] Lomazzo also refers to *nero di scaglia*, which he says is a black earth.[11] Merrifield translates the word *scaglia* as 'scales' in her translation of the Marciana manuscript, where *scaglia di ferro*, used for colouring window glass, is described as 'those scales which fall from the iron when it is beaten'.[12] These last two are clearly not natural materials, and the fact that they are called black earths suggests that the term was being used in a broader sense to mean a pigment with soft, friable 'earth-like' properties.

In the current technical literature, black earth is generally assumed to be a black shale or chalk (the colour arising from incorporated carbon).[13] A coarse black silicate-containing pigment found in a painting in the National Gallery by Hendrik Terbrugghen may well be a black earth of this type.[14] During recent technical examination of sixteenth-century Italian paintings in the National Gallery, black pigments with the microscopic appearance of a crushed mineral were observed in many samples.[15] A number of these have been analysed in detail, using energy dispersive X-ray analysis (EDX) in the scanning electron microscope (SEM) and, in those cases where it was suspected the black might be predominantly organic in nature, pyrolysis–gas-chromatography–mass-spectrometry (Py–GC–MS). A few examples from seventeenth-century Italian paintings have also been included in the study.

From these analyses, several pigments were identified which were likely to have been termed black earth by artists, but which are not black shale. Some selected results, listed in the Table, will be discussed in this paper. Two of the most interesting black minerals identified were black coal and pyrolusite (natural black manganese dioxide). Black coal has not, to our knowledge, previously been confirmed and characterised in paintings; the history of its use has so far been based solely on references to coal as a pigment in historical treatises.[16] A few scattered examples of the use of natural pyrolusite in paintings have been published but have received little attention.[17] As a result, the generally held belief that black manganese dioxide was only used as a pigment in oil paint in the nineteenth century, in a synthetic form, is often repeated in the literature.[18] The occurrences of pyrolusite added here seem to suggest that it was relatively common in sixteenth- and seventeenth-century paintings. The 'black' or dark grey minerals stibnite (antimony trisulphide) and bismuth were also found in a few paintings, as well as tin-rich (grey) bronze powder and black lead sulphide (see Table). Since the number of published occurrences is small,[19] the examples added here usefully contribute to our knowledge of where, when and how these pigments were used.

Sulphur-rich coal-type black

In a surprising number of the paintings in this study, a black pigment was found in which sulphur is the main element detectable by EDX analysis.[20] The particle characteristics suggest a crushed rock or mineral, as does the detection by EDX, in most cases, of variable (but small) amounts of calcium, silicon, aluminium and potassium as impurities associated with the pigment. The pigment appears to be organic in nature, but harder and less soluble than the black organic pigments asphalt and bitumen; the particles in the paint layers have clean hard edges and there is no sign of solubility in the oil medium. Certain types of common coal can be sulphur-rich, and the initial analyses seemed to suggest that this is what was used in these paintings.[21] In some samples the rock has occasionally cleaved in such a way that the particle shape could be mistaken for charcoal, but there is none of the woody cell structure seen within particles of charcoal (PLATE 1). Larger particles of the pigment are a rich intense black, while smaller thinner particles have a slightly brownish hue. This can be seen very clearly in the biscuit-coloured priming on *The Birth of Jupiter* by Giulio Romano and his workshop (NG 624, PLATE 2; see also pp. 38–49).

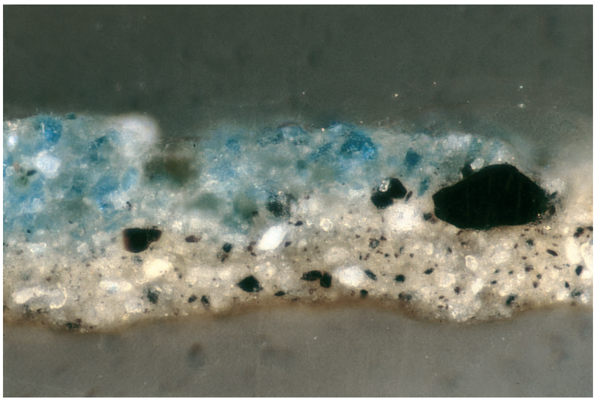

PLATE 2 Giulio Romano, *The Birth of Jupiter* (NG 624). Cross-section of a paint sample from the greenish blue of the distant hills on the left. The priming contains a large black coal particle together with some that are thinner and brownish in colour. Original magnification 500×; actual magnification 440×.

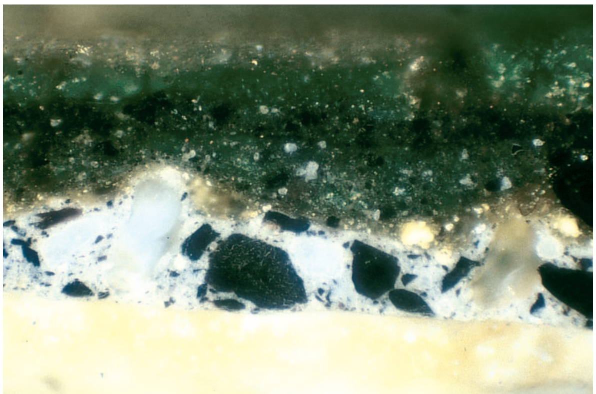

PLATE 1 Dosso Dossi, *A Man embracing a Woman* (NG 1234). Cross-section of a paint sample from the dark green of the woman's sleeve. The black pigment in the grey priming is coal. Original magnification 500×; actual magnification 440×.

Coal is a carbonaceous organic sedimentary rock, formed from the partial decomposition and metamorphosis of tree-like ferns, woody land-based plants and trees, formed millions of years ago. The plant material (composed predominantly of cellulose and lignin) would initially have degraded by oxidation and biological activity in aerobic conditions. The aerobic stage of the transformation of the biomass would cause a substantial elimination of the cellulosic components and transformation of the phenolic-based lignin polymer. Coal is formed in swamp-like wetland environments where immersion of the plant material and accumulation of the plant debris result in a decrease in the oxygen supply so that anaerobic organisms continue the degradation. Some of the anaerobic bacteria use sulphate salts in the environment as a source of

PLATE 3 Lorenzo Costa, *Portrait of Battista Fiera* (NG 2083), *c*.1507–8. Panel, 51.4 × 38.7 cm.

oxygen, employing it for redox reactions that produce sulphides and organic thio-compounds. This accounts for the pronounced sulphur levels in many lower rank coals. Anaerobic degradation is far less efficiently destructive of the organic biomass than degradation by aerobic organisms, so that the biomass is not completely destroyed but is altered, with loss of functional groups, fragmentation, loss of side chains and a relative increase in carbon content. As the deposits become buried more deeply, the effects of increasing temperature and pressure cause further alteration. The many different plant species from which coal can originate and the varying geological conditions endured during its formation are factors that influence the degradation process, leading to variation in the chemical composition of the resulting coal. One way in which different types of coal are classified is by their degree of 'coalification', which broadly corresponds to their geological age. The initial step in the coalification process is the formation of lignite (via peat), which is then transformed to brown coal (a low-grade coal), followed by bituminous coal and finally anthracite, which has a relatively high carbon content.[22]

Analysis of coals is a challenge, because their chemistry is complex and varies considerably. In addition, in most of the small paint samples examined here where coal appeared to be present, it was only a minor component of the pigment mixture. In three paintings, however, a black pigment of this description formed the main constituent of the paint, and was present in sufficient quantity to allow further investigation by Py–GC–MS to analyse the organic components of the pigment.

The results of Py–GC–MS carried out on the black pigment in a sample from the black background of *The Portrait of Battista Fiera* by Lorenzo Costa (NG 2083, PLATE 3) showed strong evidence for the presence of organic compounds that would point to the use of a coal-type material (rather than an asphaltic or bituminous rock). The liberated simple phenolics, alkylbenzenes and polynuclear aromatics seen in the chromatogram derive from fragmentation of partially functionalised aromatic macromolecular structures. These structures are generated from the original lignin by a combination of the early biological activity and the subsequent geological environment.[23] The high proportion of aromatic hydrocarbon species detected, and the presence of phenolic fragments, support a coal source and distinguish the pigment from other similar, but softer, materials such as bitumen and asphalt.[24] In addition, triterpanes and modified (partially aromatised) triterpane components are present. These include constituents such as fernane, indicating that the coal was formed from primitive fern-like plants, bacteriohopanoids from the accumulated remnants of bacteria, and other components indicative of a higher plant input, as would be expected for a geologically modified coal-type material.[25]

Py–GC–MS analysis of a sample from the black preparatory layer on Tintoretto's *Christ washing his Disciples' Feet* (NG 1130) suggested that the black pigment in this painting was similar in composition to that in the painting by Costa. The other painting in which a sulphur-rich black pigment was analysed in this way, Giampietrino's *Salome* (NG 3930), gave different results. Components that suggest a retinite-type material, derived from geologically modified diterpenoid resins, were detected. Modified diterpenoid resins are also found in softwood pitch, but pitch typically contains residual resin acids and other components (retene, hydroretene and norabietatrienes). These are not present in the Giampietrino sample and it is therefore not a pitch. Some retinite-like components were also found in the Costa and Tintoretto samples, but in the case of the Giampietrino sample no lignin-derived phenolics were detected, and thus a resinous source is probable. A more detailed description of the Py–GC–MS analyses can be found in the Appendix.

Retinite can be similar in appearance to true coal, particularly if it has undergone geological modification at relatively high temperatures (greater than 150°C), and can be found in low-grade coal deposits.[26] In common with coal, it is a relatively translucent brownish black, harder than asphalt and bitumen, and can also be burnt as a fuel. Artists would not have been able to distinguish between them. The Py–GC–MS results on these three paintings suggest that, while the black pigment is not identical in composition in each case, it does derive from geologically modified organic material. Even in the painting by Giampietrino where the pigment is chemically somewhat different, it could originate from a coal deposit. The chemical differences are not surprising, given the variation in the conditions under which coal forms, and in the plant material from which it originates. It seems reasonable therefore to designate the sulphur-rich organic black pigment with similar optical and physical properties in the other paintings listed in the Table as a coal-type black.

References to the use of coal as a black pigment in Northern seventeenth-century painting treatises are well known. Theodore de Mayerne, for example, mentions *charbon de pierre* and *charbon de terre d'Escosse*, both common coal, and it also appears under the names of *sea coal* and *smythe coal* (forge coal) in several English treatises of the period.[27] The earliest reference seems to be in *The Arte of Limning* by Nicolas Hilliard dating from the beginning of the seventeenth century.[28] Edward Norgate stated that 'sea cole makes a Red Blacke', which is consistent with the warm black appearance of the coal that has been identified in paintings; in a second version of his treatise he even lists it among the brown pigments.[29] Several writers recommend its use for shadows, particularly in flesh paint.[30] The sea coal that was collected from shallow deposits on the coast was probably a low-grade coal, which would be likely to have a high sulphur content; it was therefore probably similar to the coal pigment identified in paintings in this study.[31] As noted earlier, none of the names of black pigments referred to in sixteenth-century Italian painting treatises can be specifically identified with common coal. Biringuccio confirms that it was available in Italy during this period, however, describing its use as a fuel in his *Pirotechnia*, first published in 1540 in Venice.[32] It is perhaps not surprising then to find a

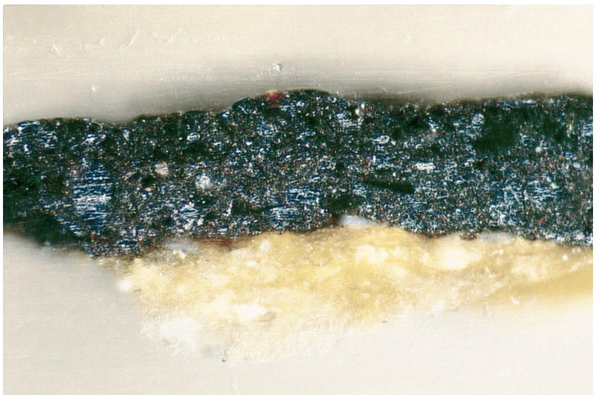

PLATE 4 Lorenzo Costa, *A Concert* (NG 2486). Cross-section from the black background. The paint layer contains mostly coal with a little verdigris and silicaceous material. Original magnification 250×; actual magnification 220×.

large number of occurrences of a sulphur-rich organic black pigment (assumed to be coal) among the paintings analysed here, suggesting that it was already a common black pigment in Italy during the sixteenth century. Coal black was also found in two paintings by Guercino in this study (see Table), indicating that it was also used as a pigment in the seventeenth century in Italy. While there do not appear to be any specific references to its use as an artist's pigment in Italian painting treatises at this time, the French painter Pierre Lebrun does mention that the Italians were using coal as a black pigment for external painting.[33]

Although one might expect coal to be a poor drying pigment in oil, because other organic black pigments, such as asphalt, bitumen and pitch, are known to be problematic in this respect, this is an assumption not borne out in the examples found in this study. Verdigris was often mixed with the other black pigments available in the sixteenth century to aid drying, and has been found here mixed with coal in the black backgrounds of Lorenzo Costa's *Concert* (NG 2486, PLATE 4), Alvise Vivarini's *Portrait of a Man* (NG 2672) and Giampietrino's *Salome* (NG 3930). However, in the black background of Costa's *Portrait of Battista Fiera* (NG 2083) coal has been used without the addition of driers, yet does not appear to have caused any serious paint defects. The black paint does contain a significant amount of chalk, probably naturally associated with the black coal, but this would not act as a siccative for oil. Examination of the black background of this painting at close hand shows evidence of a fine drying craquelure, although this is not severe enough to be visible in gallery conditions.

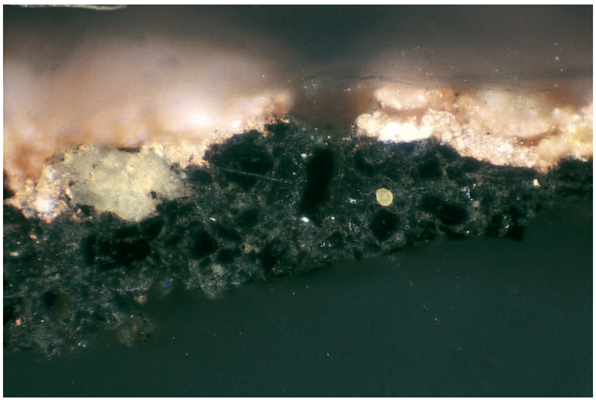

PLATE 5 Jacopo Bassano, *The Purification of the Temple* (NG 228). Cross-section from the orange-pink highlight on the tunic of the man in the left corner. The thick black priming is composed almost entirely of coal. Original magnification 250×; actual magnification 220×.

Further evidence that the drying properties of coal were satisfactory is provided by two paintings where it is used as the major ingredient in black priming layers, *Christ washing his Disciples' Feet* (NG 1130) by Tintoretto and *The Purification of the Temple* by Jacopo Bassano (NG 228, PLATE 5). The priming layer would be the very worst place to employ a pigment if it were poorly drying, as it would almost certainly lead to serious defects in the paint layers above. However, in neither of these works does the state of the surface paint suggest that these black primings were problematic, even though the coal is not mixed with additional driers and is applied fairly thickly in Bassano's *Purification of the Temple*.

In most of the examples listed in the Table black coal has been found in pigment mixtures. Where it is mixed only with lead white, as in the priming of Romanino's polyptych of *The Nativity with Saints* (NG 297), the coal has imparted a distinctive warm brownish-grey colour to the layer. This is visible where the priming has been left exposed at the edge of one of the panels. The same is true of the priming of *The Birth of Jupiter* (NG 624) by Giulio Romano and his workshop, where the coal, again mixed only with lead white, is largely responsible for the warm biscuit colour (PLATE 2). In several paintings examined here, coal constitutes a minor component of the paint layers, added simply to deepen the local colour (see Table). Raphael appears to have exploited the warm, semi-transparent qualities of coal by employing it as an ingredient in some of the dark, saturated shadows in *The Ansidei Madonna* (NG 1171), notably the deep purplish shadow beneath the Virgin's canopy and the darkest shadows of Saint John's red drapery. Other applications include Perugino's use of coal black for the warm greenish grey of Saint Francis's habit in *The Virgin and Child with Saints Jerome and Francis* (NG 1075), where it is mixed with lead white and a little ochre. The character of coal is perhaps most clearly displayed where it is used almost pure in the black backgrounds of the four paintings mentioned above. Employed in this way, the pigment is ideal for depicting the warm, penetrating darkness that lies behind the figures.

Pyrolusite (manganese black, natural manganese dioxide)

Pyrolusite is a soft black earthy manganese dioxide mineral. Its occurrence as a pigment in three sixteenth-century paintings, Correggio's *Allegory of Virtue* (Paris, Louvre) and two paintings by Perugino in the National Gallery of Umbria (Perugia) has been reported by Seccaroni.[34] Seven further occurrences on sixteenth-century paintings in the National Gallery are added here (see Table). In a number of paintings by Moretto and Moroni (who trained in Moretto's studio), pyrolusite was identified in the reddish-brown ground layers, mixed with red and yellow earth pigments. Only manganese could be detected in the pigment particles by EDX analysis, and it is therefore distinct from dark brown umber, where manganese is always associated with iron. In cross-sections the pigment is slightly more opaque and cooler in tone than the coal pigment described above, and is quite unlike the more transparent brown umber (PLATE 6). Larger particles appear soft, earthy and crumbly.

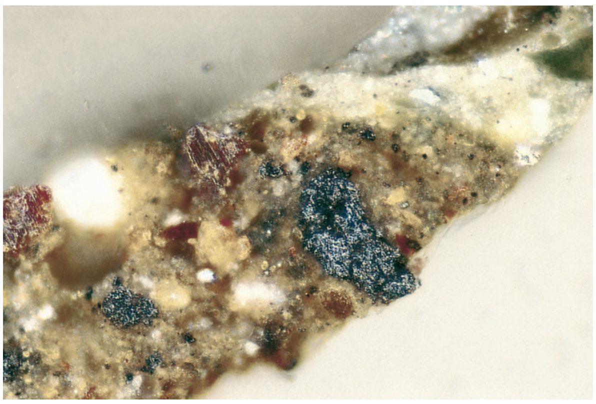

PLATE 6 Giovanni Battista Moroni, *Portrait of a Man* (NG 3129). Cross-section showing coarse particles of manganese black pigment in the brown priming. Original magnification 460×, actual magnification 400×.

The greenish-grey background of Moroni's *Portrait of a Man* (NG 3129) was also found to contain pyrolusite, mixed with lead white and a small amount of green earth. In Titian's *Virgin and Child with Saint John the Baptist and a Female Saint* (NG 635) it has been mixed with lead white for the grey underpaint beneath the orange shawl of the female saint (probably Saint Catherine).

In these paintings pyrolusite has been found only in pigment mixtures, and it has been suggested that if used alone its fast drying properties might cause problems.[35] However, this was not evident when painting out pyrolusite alone, bound in linseed oil, on a test panel, which in fact produced a rich glossy black paint with good working properties.[36] Many of Moroni's portraits depict the sitters in a range of black fabrics, and it may be that for some of these pyrolusite was used unmixed, but it was not possible to sample the draperies in these paintings. Hence, our understanding of Moroni's use of black pigments is at present incomplete.

The use of pyrolusite as a pigment is not confined to sixteenth-century paintings from Northern Italy; it has also been identified on the seventeenth-century *Portrait of a Man* in the National Gallery catalogued as 'After Guercino' (NG 5537), on *Saint John in the Wilderness* (NG 69) attributed to Pier Francesco Mola, and on *A Boy with a Bird* (NG 933) which is currently catalogued as 'After Titian' (see Table).[37] The *Boy with a Bird*, probably painted in the seventeenth century, contains pyrolusite associated with a small amount of barium, and is therefore slightly different from that in the *Virgin and Child* discussed above that is securely attributed to Titian.[38] Pyrolusite has also been reported on Dutch seventeenth-century paintings by Cuyp and Verspronck, although in the context of a general study of the painters' technique and hence with little discussion.[39] It is well known that manganese accelerates the drying of oil, so the 'black chalk that dries easily' mentioned by Theodore de Mayerne in the seventeenth century may well have been pyrolusite.[40]

There are deposits of black pyrolusite mineral in several parts of Italy; these were known already in Renaissance times, as they are listed by Biringuccio. He states that it is found 'on the shore at Salo', which is on Lake Garda only 25 km from Brescia where Moroni and Moretto were working. He also mentions that pyrolusite was being imported from Germany, and it must have been easily available because it was widely used in other branches of the arts such as glassmaking and ceramics.[41] As Seccaroni has discussed, pyrolusite was also used as a pigment in early civilisations. It has been found in the prehistoric cave paintings at Lascaux, France,[42] on wall paintings in Cyprus of the Roman period, and on Greek paintings of the bronze age.[43] A synthetic form of manganese dioxide, known as manganese black, was patented as a pigment by Rowan in England in 1871, and it has been stated in the past that the natural form has not been much used in oil painting.[44] However, the occurrences on sixteenth- and seventeenth-century paintings from both Italy and Holland discussed here tend to suggest that pyrolusite was much more widely used as a pigment in oil paintings than is generally recognised.

Stibnite (antimonite, antimony trisulphide)

Stibnite, or antimonite as it is sometimes called, is a naturally occurring mineral, the most abundant ore of antimony. Biringuccio's account of the ore notes: 'The ore of antimony is found in mountains just like other metallic ores and it is mined by various operations. The ore that I know is found in Italy in various places. From Germany they bring to Venice some of the smelted kind in cakes for the use of those masters who make bells.'[45] The smelted ore is likely to have been the partially oxidised sulphide.[46] He goes on to say that 'it serves to make yellow colours for painting earthenware vases and for tinting enamels, glasses and other similar works...'.[47] It was also used for making an alloy for casting type, for parting silver from gold, for making mirrors and for medicinal purposes.[48]

The numerous uses of stibnite in the field of the arts listed by Biringuccio, and the fact that mineral stibnite from a deposit in Germany was traded through Venice, suggests that it would not have been difficult for artists to obtain. Stibnite has been found as a pigment in the polychromy of German gothic sculpture, and also in much later polychromy dating from the seventeenth century on the exterior of the town hall in Duderstadt.[49] It was not commonly used as a pigment on easel paintings, however, and very few instances have been published. It was first reported as a grey pigment in easel paintings in 1991 by Ferretti et al., on three works by Correggio.[50] Several other occurrences have since been published, on other paintings by Correggio, two paintings by Fra Bartolommeo and a *Deposition* begun by Filippino Lippi and finished by Perugino.[51] Three paintings in the National Gallery have been found to contain stibnite (see Table).

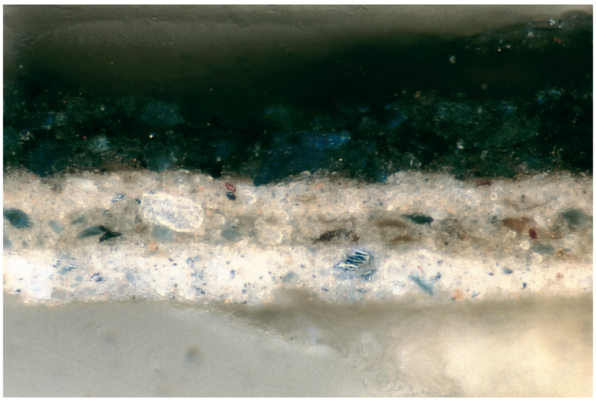

PLATE 7 Correggio, *The Madonna of the Basket* (NG 23). Cross-section of a paint sample from blue drapery at the left edge of the painting, showing stibnite particles in both the priming and undermodelling. Original magnification 500×; actual magnification 440×.

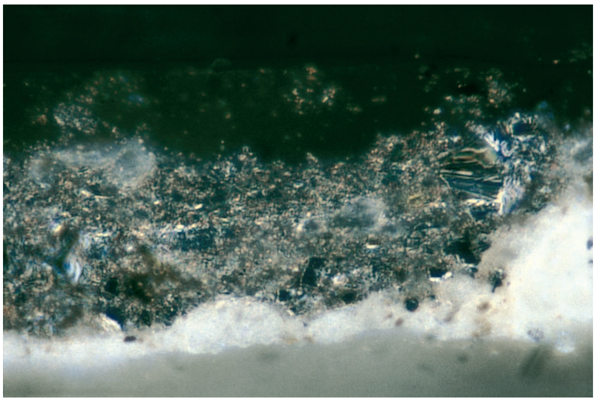

PLATE 9 Francesco Bonsignori, *The Virgin and Child with Four Saints* (NG 3091). Cross-section of a paint sample from the grey stibnite-containing shadow of the right-hand saint's white tunic. Original magnification 900×; actual magnification 790×.

They fit well into the pattern of occurrences discovered so far, since they were painted in Northern Italy in the first few decades of the sixteenth century. Correggio's *Madonna of the Basket* (NG 23), where stibnite has been used in the pinkish-grey priming layer, dates from around 1526 and was probably painted in Parma. The light purplish-grey mixture used for a sketchy undermodelling also contains some stibnite, mixed with lead white and a little azurite and red earth (PLATE 7).[52] In Francesco Bonsignori's *Virgin and Child with Four Saints* (NG 3091, PLATE 8), probably painted in Mantua in the first decade of the sixteenth century, stibnite is used as a dark grey pigment in the shadows of the white drapery of the unidentified saint holding a palm (PLATE 9), and in the grey beard of the elderly saint. Lorenzo Costa's *Adoration of the Shepherds* (NG 3105) is thought to date from around 1499, at which time the artist was working in Bologna.[53] Here Costa used stibnite for the mid-grey draperies of the lowest tier of angels (PLATE 10). In the detail of the infrared photograph of this painting illustrated in FIG. 1, the shadows and the dark grey borders of the draperies (also painted with stibnite) have almost completely disappeared. Unusually for a black pigment, it is remarkably transparent to infrared light. This property was also clearly demonstrated by infrared reflectography of a test panel painted with stibnite in linseed oil.

Mineral specimens of stibnite often consist of needle-shaped crystals with a metallic lustre. This metallic lustre was exploited in German polychrome sculpture such as the Franziskaner-Altar in Rothenburg by Tilman Riemenschneider, where

PLATE 8 Francesco Bonsignori, *The Virgin and Child with Four Saints* (NG 3091), *c.*1490–1510. Canvas, 48.3 × 106.7 cm.

PLATE 10 Lorenzo Costa, *The Adoration of the Shepherds* (NG 3105). Detail of the group of angels in the lower right corner. Their cool grey draperies contain stibnite mixed with lead white.

FIG. 1 Lorenzo Costa, *The Adoration of the Shepherds* (NG 3105). Detail of the infrared photograph.

coarsely ground stibnite was used to give texture and sparkle to areas depicting the ground in the landscape.[54] In polished cross-sections of samples from the paintings in this study, the pigment also has a characteristic silvery metallic appearance. It was not chosen to create a metallic effect, however, as it has been ground to a fine grey powder; the lustre is visible only under the microscope. Its appeal over a conventional carbon black (which was presumably cheaper) may have been the subtle clean cool grey colour obtained when it is mixed with lead white, and that when unmixed it is a dark grey rather than a true black.

Bismuth

The use of a bismuth-containing grey pigment was first reported in several paintings by Fra Bartolommeo.[55] It has similar properties to stibnite – in cross-sections under the microscope it has the appearance of shiny metallic particles – but with a distinctive pinkish or reddish tinge. The reddish tinge of the pigment is evident in the pale purplish-grey colour of the architecture on Raphael's large altarpiece of *The Madonna and Child with Saints John the Baptist and Nicholas of Bari (The Ansidei Madonna)* (NG 1171), where it is mixed with lead white (PLATES 11 and 12). It was established by spot EDX analysis on a paint cross-section in the scanning electron microscope that the pigment in this painting contains the element bismuth. Both bismuth metal and bismuth trisulphide (bismuthinite mineral) have a metallic lustre when viewed under the microscope, and distinguishing between them by EDX analysis is not straightforward, as the Bi M_{α} peak in the spectrum is close to the S K_{α} peak and they are not well resolved. However, X-ray diffraction, and matching of the EDX spectrum to constructed spectra of bismuth metal and bismuth trisulphide, show that in the painting by Raphael, at least, the pigment is bismuth metal.[56] Bismuth metal

PLATE 11 Raphael, *The Madonna and Child with Saints John the Baptist and Nicholas of Bari (The Ansidei Madonna)* (NG 1171), 1505. Panel, 209.6 × 148.6 cm.

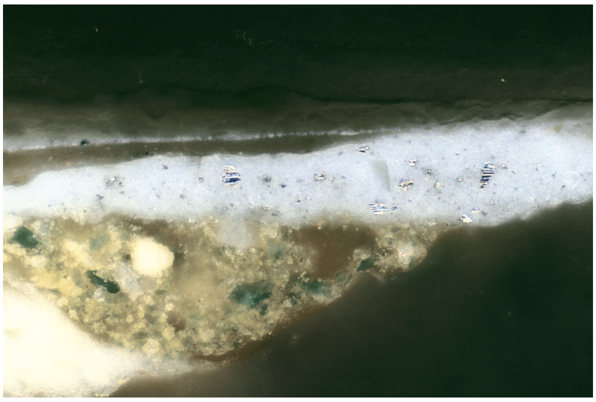

PLATE 12 Raphael, *The Madonna and Child with Saints John the Baptist and Nicholas of Bari (The Ansidei Madonna)* (NG 1171). Cross-section from the grey stone arch where it extends over the landscape paint. The grey paint layer contains lead white, bismuth and some colourless silicaceous particles. Original magnification 500×; actual magnification 440×.

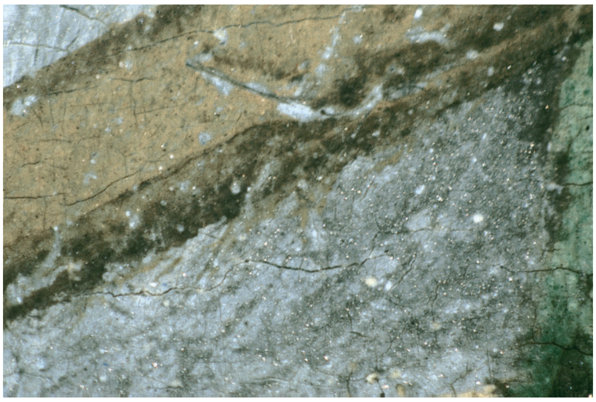

PLATE 14 Raphael, *The Procession to Calvary* (NG 2919). Macro photograph of the grey horse's under-belly, showing the sparkly grey paint surface. Original magnification 20×; actual magnification 17×.

is, in any case, the most abundant ore of bismuth.[57] The mines at Schneeberg in Saxony were probably the main source in the sixteenth century. Mining of bismuth began in Schneeberg around the middle of the fifteenth century, which can probably be taken as a boundary for the earliest possible use of the pigment.[58]

When the surface of Raphael's *Procession to Calvary* (NG 2919) was examined under the stereomicroscope, a silvery grey pigment with a metallic

PLATE 13 Raphael, *The Procession to Calvary* (NG 2919). Detail of the grey horse.

FIG. 2 Raphael *The Procession to Calvary* (NG 2919). Detail of the infrared reflectogram mosaic showing the grey horse.

PLATE 15 Attributed to Francesco Granacci, *Portrait of a Man in Armour* (NG 895), *c.* 1510. Panel, 70.5 × 51.5 cm.

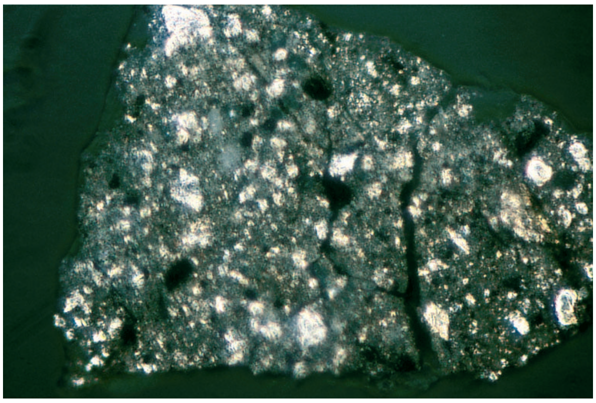

PLATE 16 Attributed to Francesco Granacci, *Portrait of a Man in Armour* (NG 895). Surface of an unmounted paint sample from the man's silvery-grey armour. The coarse, reflective bismuth-containing particles are visible, but the overall colour of the sample is affected by the presence of a yellowed varnish. Original magnification 400×; actual magnification 350×.

lustre was seen in the paint of the grey horse (PLATES 13 and 14) and the grey hose of Simon of Cyrene. The horse has a clean grey colour, and the paint has rather poor covering power. Raphael has exploited this property by applying it thinly in areas of highlight, allowing the off-white priming to show through. Since it was not possible to take samples from these areas of the painting, no further analysis has been carried out, but the pigment has a pinkish tint that suggests it is bismuth rather than stibnite. Even more compelling evidence is provided by the infrared reflectogram, in which the shadows of the horse and of Simon's legs appear a deep black, despite the fact that in normal light they are a relatively light grey (FIG. 2). This is very characteristic of bismuth, as was confirmed by infrared reflectography of a test panel on which bismuth ground in linseed oil had been painted. This contrasts conveniently with the properties of stibnite which, as mentioned above, is surprisingly transparent to infrared light. The same bismuth-containing pigment was used for the armour in the *Portrait of a Man in Armour* attributed to Granacci (NG 895, PLATES 15 and 16). As in the painting by Raphael, the properties of bismuth have resulted in an unusual effect where the dark grey half shadows of the armour (painted in bismuth) are darker in the infrared reflectogram than the deepest black shadows, which contain a carbon black. In this painting bismuth has also been mixed with red earth for the brown paint of the architecture behind the figure.

The main use of bismuth in the sixteenth century appears to have been in alloys for type metal.[59] In Germany, bismuth metal was used to imitate metal leaf on decorated wooden boxes, but perhaps the use most closely related to the field of painting was in manuscripts. Numerous German documentary sources of the fourteenth and fifteenth centuries have recipes for inks made from bismuth, to imitate silver, and an example of its use in a fifteenth-century German bible has been published.[60] Some bismuth was also found mixed with red earth and red lake in the mordant layer beneath God the Father's gilded halo on the *Coronation of the Virgin* (NG 263) by the Master of Cappenberg. The Master of Cappenberg was probably in fact Jan Bagaert, who was working in Westphalia at the beginning of the sixteenth century (see Table).[61] The use of bismuth does not, therefore, seem to be entirely confined to Italian paintings.

Tin-rich bronze powder in Perugino's *Archangel Michael*

A sample from the brownish-grey paint of the armour of Perugino's *Archangel Michael* (NG 288.2, PLATE 17) contains some particles that are microscopically very similar in appearance to the

PLATE 17 Pietro Perugino, *The Archangel Michael* (NG 288.2), *c.*1496–1500. Panel, 114 × 56 cm.

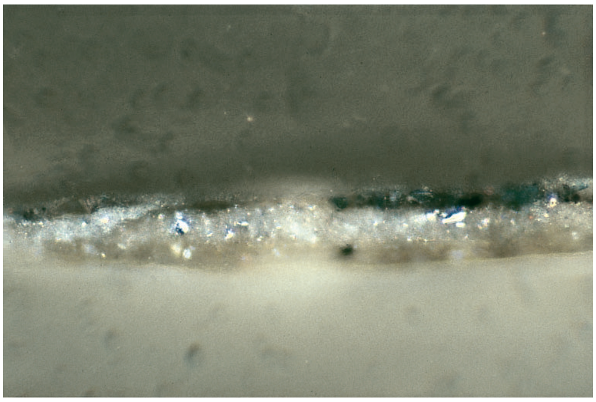

PLATE 18 Pietro Perugino, *The Archangel Michael* (NG 288.2). Cross-section of a blue-grey paint sample from Saint Michael's armour, showing the presence of a grey metallic pigment which contains copper and tin. Original magnification 500×; actual magnification 440×.

stibnite and bismuth pigments, and were initially mistaken for one of these (PLATE 18). However, copper in combination with tin was detected in the particles by spot EDX analysis. Their metallic lustre suggests that they are finely ground particles of a copper-tin alloy, which is, of course, bronze. The proportion of tin to copper is high – quantitative EDX analysis on several particles in the cross-section gives an average ratio of roughly one part tin to two parts copper by weight – which is consistent with the fact that the particles have the appearance of a white metal. Bronze is more usually a yellow metal and typically contains around 10–15% tin. A high-tin bronze with about 25% tin content by weight, which may well have been white or grey in colour, was used for bells and for mirrors in the sixteenth century, according to Biringuccio.[62]

Interestingly, Seccaroni has also reported finding copper in combination with tin in some areas of paint on two paintings in the Accademia Gallery in Florence; the *Pala di Vallombrosa* painted by Perugino in 1500 (in very dark blue paint), and the *Deposition from the Cross* begun by Filippino Lippi but finished by Perugino (in bluish-grey paint).[63] The *Archangel Michael* in the National Gallery, which is part of a polyptych painted for the Certosa di Pavia, was probably painted in the last year of the fifteenth century.[64] Seccaroni's analyses on the Accademia Gallery paintings were carried out by X-ray fluorescence (XRF), a non-destructive technique which allows the elements in the paint to be detected, but does not give information on the characteristics of the pigment particles, the pigment mixtures or the layer structure. However, the constant ratio of copper to tin Seccaroni detected in the blue areas on the *Deposition* by Perugino and Lippi suggests that the copper and tin are combined in the same particles, and that the pigment in this painting is similar to that observed in the samples from Perugino's *Archangel Michael*.[65]

Seccaroni puts forward several possibilities for the identity of this pigment, with reference to pigment recipes of the period for tin white and for artificial blue pigments which contain tin oxide, as well as copper or its compounds, as an ingredient. His hypotheses can be re-examined in the light of the additional information obtained from the samples from the National Gallery painting. The

PLATE 19 Lorenzo Costa with Gianfrancesco Maineri, *The Virgin and Child Enthroned between a Soldier Saint and Saint John the Baptist* (NG 1119). Detail of the soldier saint.

possibility that tin white has been used can be excluded, since the copper and tin are located in the same particles. He also suggests that copper stannate ($CuSnO_3.nH_2O$) might be a possible product of the recipes for artificial blues, but this is clearly not present in the National Gallery painting since the copper-tin particles are metallic in appearance. Moreover, the treatises indicate that the blue pigment made with these recipes is as good as ultramarine and better than azurite, but in the National Gallery painting, the paint of the Archangel Michael's armour is bluish grey and is certainly not comparable in colour to ultramarine.[66]

In the National Gallery painting, the metallic grey copper-tin particles in the bluish-grey paint are mixed with a small amount of blue copper carbonate, which could suggest that an artificial blue has been made from powdered bronze rather than pure copper, with the metallic particles being residual unreacted bronze. However, the grey underpaint in Saint Michael's armour contains far more bronze powder than blue copper carbonate, and ordinary natural mineral azurite has been used for the bluer areas, while the copper-tin metallic particles are in areas that are more grey than blue. In another panel of Perugino's Certosa di Pavia altarpiece, *The Archangel Raphael with Tobias* (NG 288.3), the same grey metallic pigment was found in the pale grey underpaint of Raphael's blue robe, where it was mixed only with lead white. The powdered tin-rich bronze, which is grey in colour, has therefore been used as pigment in its own right, in the same way as the grey metal bismuth.[67]

Galena (black lead sulphide)

The large altarpiece *The Virgin and Child Enthroned between a Soldier Saint and Saint John the Baptist* (NG 1119) is thought to have been painted mainly by Gianfrancesco Maineri in Ferrara, but finished and altered by Lorenzo Costa.[68] The armour of the soldier saint in this altarpiece has a blue cast, which is rather similar to Saint Michael's armour in the painting by Perugino (PLATE 19). Comparison of paint samples from the armour in these two paintings shows that they are

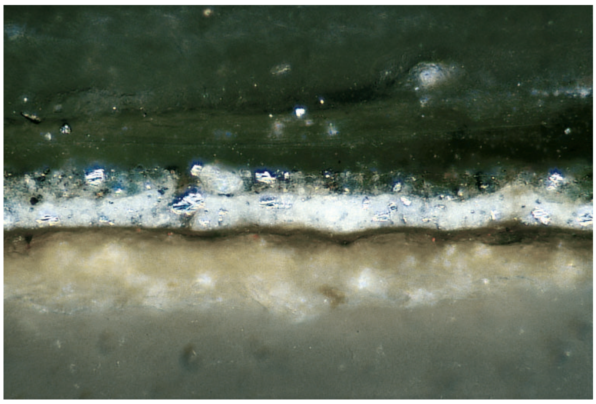

PLATE 20 Lorenzo Costa with Gianfrancesco Maineri, *The Virgin and Child Enthroned between a Soldier Saint and Saint John the Baptist* (NG 1119). Cross-section from a grey-blue shadow on the soldier's armour. The grey underlayer contains galena mixed with lead white, and the grey-blue glazed shadow contains azurite and galena. Original magnification 500×; actual magnification 440×.

PLATE 21 Lorenzo Costa with Gianfrancesco Maineri, *The Virgin and Child Enthroned between a Soldier Saint and Saint John the Baptist* (NG 1119). Detail of the soldier's cool grey sword.

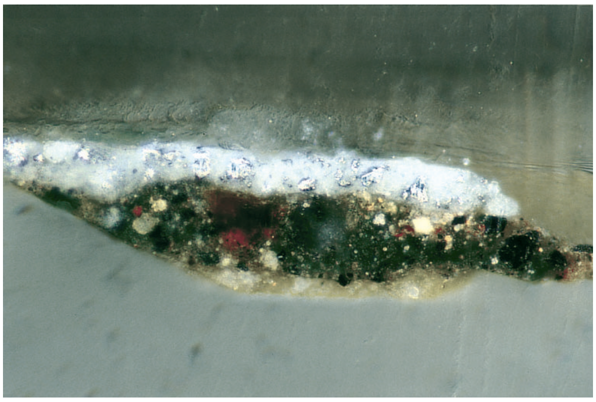

PLATE 22 Lorenzo Costa with Gianfrancesco Maineri, *The Virgin and Child Enthroned between a Soldier Saint and Saint John the Baptist* (NG 1119). Cross-section from the soldier's sword. The grey upper layer contains lead white and coarsely ground galena. The mixed brown paint layer underneath, corresponding to the wooden part of the Virgin's pedestal, contains particles of coal black. Original magnification 500×; actual magnification 440×.

painted in a very similar technique. The upper blue-grey layer visible in the cross-sections is based on azurite, mixed with a pigment that has a metallic lustre under the microscope. The grey underpaint also contains this lustrous pigment, mixed only with lead white (PLATE 20). Although it is similar in microscopic appearance to the copper-tin particles in the samples from the painting by Perugino, analysis identified the pigment as lead sulphide.[69] The occurrence of a different pigment with similar properties in this blue armour lends weight to the argument that in the paintings by Perugino discussed above a grey tin-rich bronze powder deliberately mixed with azurite was used, rather than a copper-tin blue.

As with stibnite and bismuth, the metallic appearance of the pigment in cross-sections does not correspond with the dark grey colour observed when viewing the surface with the naked eye. The true colour is best seen in the paint of the soldier saint's sword, where it is mixed only with lead white (PLATES 21 and 22). It may be either the natural mineral (galena) or the synthetic lead sulphide described in the sixteenth century by Agricola in *De Re Metallica*, his treatise on metallurgy.[70] Both were used as a flux, for ceramics and glassmaking, and for parting gold from copper.[71] The properties of galena place it in the same category as stibnite, bismuth and tin-rich bronze, since it is a grey pigment rather than a true black. The Latin names used by Agricola also illustrate the close relationship between galena and bismuth; he calls galena *plumbum nigrum* and bismuth *plumbum cinereum*.[72] Two later instances of the use of galena as a pigment in exterior polychromy have been published. It was used in the paint on a tower which is part of the castle at Jever, Friesland (dating from 1730), and for the polychromy on figures on the outside of the town hall at Duderstadt, which dates from the seventeenth century.[73]

Discussion and conclusions

This survey of black pigments has covered a relatively limited number of sixteenth-century Italian paintings and is therefore far from comprehensive. It seems very likely that with further work, some other black minerals will be found to have been used as pigments. For example, preliminary EDX analysis of a black pigment in *The Sons of Boreas pursuing the Harpies* (NG 5467) by Paolo Fiammingo, suggests that it is an iron phosphate.[74] It would be interesting to investigate whether this has been used more extensively in oil paintings. Black iron oxide has been reported in a sixteenth-century Italian wall painting and black iron sulphide in a fifteenth-century German manuscript.[75] Small amounts of black iron sulphide have been detected in three oil paintings in the National Gallery: *Saint John the Evangelist on Patmos* (NG 6264) by Velázquez, Parmigianino's *Mystic Marriage of Saint Catherine* (NG 6427) and *A Bearded Man holding a Lamp* (NG 5537) after Guercino. In each case the iron sulphide was found in the ground layers mixed with red and yellow iron oxides and silica, where it is very likely that it is simply a natural mineral impurity associated with the iron oxide pigments.[76] It seems possible, however, that black iron oxide, and iron sulphide as a pigment in its own right, may be found in future examinations of oil paintings.

Some conclusions can be drawn from the occurrences of black mineral pigments identified in this study. The pattern that has emerged so far is that a coal-type black was perhaps as common as the other carbon blacks, given the number of occurrences found from analysis of a relatively small group of paintings. The earliest occurrence in the Table dates from the last years of the fifteenth century, and a preliminary look at some blacks in seventeenth-century paintings has shown that it was still being used in Italy at this time. It seems likely that if black pigments were analysed more frequently black coal would also be identified in Dutch and English seventeenth-century paintings, since there are references to coal in Northern European documentary sources.

Pyrolusite, while apparently used less frequently than coal, cannot be considered rare as a pigment. All four of the paintings by Moretto in the National Gallery that have been sampled have been found to contain pyrolusite. These were painted in Brescia between 1526 and about 1555, and the painting by Titian in which pyrolusite has been used dates from around 1530–5. Although these were all painted in Northern Italy, the occurrence in paintings by Perugino and Correggio reported by Seccaroni, and in seventeenth-century Dutch and Italian paintings, show that its use was not restricted to a limited geographical area or time.

Stibnite and bismuth seem to have been much less frequently used than coal and pyrolusite. They might more accurately be described as dark greys rather than blacks, and are natural minerals. It is unlikely that the tin-rich bronze powder observed in the painting by Perugino is a natural pigment, but it has been included in this study of black earth pigments because microscopically it could easily be mistaken for stibnite or bismuth and because it was almost certainly also used as a dark grey pigment. In any case, as discussed above, some of the 'black earths' described in treatises, were probably not natural minerals. The occurrences of stibnite and bismuth reported here add to the list of artists known to have used them, and also reinforce the impression that they were only used in easel paintings during the first few decades of the sixteenth century. Lead sulphide (galena), reported here for the first time in an easel painting, has similar properties to stibnite and bismuth, and was found on a painting that also dates from the beginning of the sixteenth century. The artists who have been found to use these pigments are not an entirely random group. There are perhaps some geographical connections. Among the artists who used bismuth, Granacci and Fra Bartolommeo were both working in Florence. The two paintings by Raphael containing bismuth were painted in Perugia around 1505, but it is possible that Raphael had already visited Florence. The city of Mantua could be a link between the artists using stibnite. Lorenzo Costa was established as court painter to the Gonzaga at Mantua by 1507. Correggio's early training is thought to have taken place at Mantua, and Bonsignori was also active at the Gonzaga court from about 1490.[77] The mobility of artists at this time should not be underestimated however. A more convincing pattern may become apparent once more occurrences have been found.

The question of why artists chose to use these unusual pigments is intriguing, and is probably related to their differing working properties and hue, as was made clear in our experiments painting them out (bound in linseed oil) on a test panel.[78] Both stibnite and bismuth were indeed dark grey rather than black when used alone. They have a tendency to sink, and require a high proportion of oil to make a workable paint, in the same way as the other natural minerals that were painted out. What is not obvious is why artists started to use these pigments at the beginning of the sixteenth century. These materials were all more commonly used in other branches of the arts, and were perhaps also sold by the *speziali* from whom artists usually obtained their pigments.[79] Some of these artists may have obtained their pigments from the same source – Perugino and Granacci, for example, are both known to have bought pigments from the Gesuati in Florence.[80] Biringuccio used the general term 'marcasite' for all sulphide minerals with a metallic lustre and also for bismuth metal, as no distinction was made between it and bismuth sulphide at this time. Although Biringuccio and Agricola had some understanding of the different types of marcasite, it seems likely that artists did not know which type they were using, but simply bought it as a dark grey pigment.[81] These pigments with a metallic appearance were used for painting armour in three of the paintings, even though their lustre is only visible under the microscope. However, a dark grey rather than a black pigment would be ideal for depicting a metallic reflective surface where even the deepest shadows are not true black.

The paintings in this study illustrate that artists were indeed using a wide range of black pigments in the sixteenth century. Raphael used both bismuth and coal in different areas of the same painting; bismuth where a cool grey was required, and coal black for deeper shadows and in mixtures, while in paintings by Perugino coal, pyrolusite, stibnite, and tin-rich bronze powder have been discovered, sometimes in the same painting.[82] Lorenzo Costa also used both stibnite and coal, and coal and galena were used in the painting by Gianfrancesco Maineri that Costa is believed to have finished (PLATE 22). Raffaello Borghini, in his *Il Riposo* of 1584, lists nine black pigments and states that 'some of the listed pigments are more black and some are less black'.[83] The way individual black pigments have been used in the paintings examined in this study suggests too that artists were aware of the distinctive yet subtle differences between them.

Acknowledgements

We are grateful to Ashok Roy and Jilleen Nadolny for allowing us to use the results of their EDX analysis on samples from three of the paintings in this study. Thanks are also due to Rachel Billinge, for infrared reflectography, and to Ad Stijnman (ICN, Amsterdam, The Netherlands) for useful discussions on the use of bronze powder for works on paper.

Notes and references

1 G. Vasari, *Le Vite de'più eccellenti pittori, scultori ed architettori*, Florence 1966–87, ed. R. Bettarini, Vol.V, 'Vita di Sebastiano Viniziano, frate del Piombo e Pittore', pp. 94–5. 'Ritrasse ancora in questo medesimo tempo messer Pietro Aretino, e lo fece sì fatto, che, oltre al somigliarlo, è pittura stupendissima per vedervisi la differenza di cinque o sei sorti di neri che egli ha addosso, velluto, raso, ermisino, damasco e panno, et una barba nerissima sopra quei neri, sfilata tanto bene, che più non può essere il vivo e naturale.' The portrait described still survives in the Palazzo Comunale in Arezzo (reproduced in Michael Hirst, *Sebastiano del Piombo*, Oxford 1981, plate 119) but is in poor condition.

2 G.B. Armenini, *De' Veri Precetti della Pittura*, 1586, ed. M. Gorreri, Turin 1988, p. 192. Black earth (*negro di terra*), willow charcoal, peachstone black and lamp black are recommended as pigments for painting. G.P. Lomazzo, *Trattato dell'arte de la pittura*, Milan 1584, p. 191, lists ivory black, almond-shell black, lamp black, and black earth. R. Borghini, *Il Riposo*, Florence 1584, pp. 206–7, lists ivory black, peachstone and almond-shell black, lamp black and black earth.

3 J.A. van de Graaf, *Het De Mayerne manuscript als bron voor de schildertechniek van de barok*, Utrecht 1958, p. 142. De Mayerne mentions the blue-black colour of charcoal. Armenini (cited in note 2) refers to lamp black lacking body, Book II, chapter IX, p. 142. R.D. Harley, *Artists' Pigments c.1600–1835*, second edn, London 1982, p. 160, discusses the greasy qualities of lamp black.

4 Cennino d'Andrea Cennini, *The Craftsman's Handbook, 'Il Libro dell'Arte'*, trans. D.V. Thompson, New York 1960, pp. 19–23. Cennini describes the preparation of charcoal black and lamp black. N. Hilliard, *The Arte of Limning*, *c.*1600, eds R.K.R. Thornton and T.G.S. Cain, Northumberland 1981, pp. 90–1. Hilliard gives detailed instructions on how to make ivory black.

5 Cennini, cited in note 4, pp. 20 and 22.

6 Vasari, cited in note 1, p. 118.

7 Antonio Averlino Filarete's *Trattato dell'Architettura*, *c.*1461–4, German edn, *Tractat Über die Baukunst nebst seinen buchern von der Zeichenkunst und den bauten der Medici*, trans. W. von Oettingen, Vienna 1890, pp. 638–9. Under the heading 'Farben fur Malerei al fresco' Filarete states 'auch ein Schwarz wird gefunden, das aus Deutschland kommt und eine Erde is'.

8 Z. Veliz, *Artists' Techniques in Golden Age Spain, Six Treatises in Translation*, New York 1986, p. 179.

9 Vasari, cited in note 1, Vol. I, p. 134: 'Ma conviene far prima una mestica di colori seccativi, come biacca, giallolino, terre da campane…' Armenini, cited in note 2, p. 129. Lomazzo, cited in note 2, p. 191.

10 Borghini, cited in note 2, pp. 206–7: '…nero di terra di campana, cioè quella scorza della forma con cui si gittano le campane, e l'Artiglieria, e questo s'adopra à olio.' Baldinucci almost repeats this in his *Vocabulario del Disegno*, Milan 1800, Vol.1, p. 364: 'Nero di terra di campana. Una sorta di color nero fatto d'una certa scorza della forma, con cui si gettano le campane e artiglierie.'

11 Lomazzo, cited in note 2, p. 191: 'il nero di scaglia detto terra nera'.

12 Merrifield, *Original Treatises, dating from the XIIth to XVIIIth Centuries on the Arts of Painting*, London 1849, p. 614. The Marciana manuscript is thought to be Venetian and to date from the sixteenth century. Other types of scales such as copper scales are mentioned by Agricola: G. Agricola, *De Re Metallica*, 1556, trans. H.C. Hoover and L.H. Hoover, New York 1950, p. 221. In this edition it is suggested that copper scales are cupric oxide and iron scales are partly iron oxide.

13 J. Winter, 'The Characterization of Pigments Based on Carbon', *Studies in Conservation,* 28, 1983, pp. 49–66. A black earth from Verona which is a carbonaceous clay is mentioned in P. Scarzella and P. Natale, *Terre Coloranti Naturali e Tinte a Base di Terre,* Turin 1989, Seconda Parte, *Catalogo*, 1.2. *Terre Veronesi* (no pagination).

14 The first red-brown ground layer on Terbrugghen's *Jacob reproaching Laban* (NG 4164) contains a relatively translucent coarse black pigment in which the principal component detected by EDX analysis was silicon. The EDX analysis was carried out by Ashok Roy. A black chalk from France supplied by Kremer Pigmente was found to be very similar in composition, as was a black chalk from a nineteenth-century paint box in the Victoria and Albert Museum formerly belonging to the English nineteenth-century painter William Etty.

15 The results of pigment analysis presented here are drawn from technical examination of Italian sixteenth-century paintings in the National Gallery carried out for a programme of revision of the scholarly schools catalogues, as well as from samples taken for a study of the preparatory layers in paintings of this period. The latter was published in J. Dunkerton and M. Spring, 'The development of painting on coloured surfaces in sixteenth-century Italy', *Painting Techniques. History, Materials and Studio Practice, Contributions to the IIC Dublin Congress, 7–11 September 1998,* eds A. Roy and P. Smith, London 1998, pp. 120–30. Some of the analyses of blacks were published here first. The paintings by Raphael discussed in this paper were examined for a forthcoming exhibition.

16 Harley, cited in note 3, pp. 156–7. Harley states that common coal is mentioned in a number of early seventeenth-century sources, indicating its use in oil and watercolour at this time, but that it was hardly used before or after this period.

17 A number of occurrences of pyrolusite in seventeenth-century Dutch

paintings have been published, but little discussed. See M. Spring, 'Pigments and Color Change in the Paintings of Aelbert Cuyp', *Aelbert Cuyp*, ed. A. K. Wheelock Jr., Washington 2001, pp. 64–73; E. Hendriks, 'Johannes Cornelisz. Verspronck. The technique of a seventeenth century Haarlem Portraitist', *Looking through Paintings,* Leids Kunsthistorisch Jaarboek XI, eds E. Hermens, A. Ouwerkerk and N. Costaras, London and Baarn 1998, pp. 227–68. A more extensive discussion appears in C. Seccaroni, 'Some rarely documented pigments. Hypotesis [sic] and working observations on analyses made on Three Temperas by Correggio', *Kermes*, 34, January–April 1999, pp. 41–59. In this article, three occurrences on sixteenth-century paintings are published.

18 K. Wehlte, *Werkstoffe und Techniken der Malerei*, Ravensburg 1967, p. 170. H. Kühn, H. Roosen-Runge, R.E. Straub and M. Koller, *Reclams Handbuch der künstlerischen Techniken, Band 1, Farbmittel, Buchmalerei, Tafel- und Leiwandmalerei*, Stuttgart 1984, p. 42.

19 Seccaroni, cited in note 17.

20 The EDX detector used for the analyses in this paper does not detect elements lower in atomic number than 12, that is sodium. Also, the S K_α peak in the EDX spectrum overlaps the Pb M_α peak, so that it can be difficult to identify a sulphur-containing black when mixed with lead white.

21 The sulphur content of different types of coal is discussed in P. Brimblecombe, *The Big Smoke, A History of Air Pollution in London since Medieval Times*, Cambridge 1987, p. 66. The sulphur content of some coals can be as much as 12%.

22 J.G. Speight, *The Chemistry and Technology of Coal*, New York 1994, pp. 3–39 and 94–112.

23 S. Watts, A.M. Pollard and G.A. Wolff, 'Kimmeridge Jet – A Potential New Source for British Jet', *Archaeometry*, 39, 1, 1997, pp. 125–43.

24 R. White, 'Brown and Black Organic Glazes, Pigments and Paints, *National Gallery Technical Bulletin*, 10, 1986, pp. 58–71.

25 J.M. Hunt, *Petroleum Geochemistry and Geology*, 2nd edn, New York 1996, p. 89. G. Ourisson, P. Albrecht and M. Rohmer, 'The Microbial Origin of Fossil Fuels', *Scientific American*, 251, no.2, 1984, pp. 34–41.

26 J.C. Crelling, 'The Petrology of Resinite in American Coals', *Amber, Resinite, and Fossil Resins*, eds K.B. Anderson and J.C. Crelling, Washington 1995, pp. 218–33.

27 Van de Graaf, cited in note 3, pp. 148 and 151. Harley, cited in note 3, refers to five English seventeenth-century treatises that mention coal as a pigment, see p. 157. See also C. L. Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, New York 1960, Vol. 1, p. 467, for references to coal in van Mander and MS Harley 6376. A Spanish seventeenth-century treatise on painting by Hidalgo mentions *carbon de piedra molida*, which is probably coal. See Veliz, cited in note 8, p. 136 and n. 9.

28 Hilliard, cited in note 4, p. 99.

29 Eastlake, cited in note 27, p. 467. The quote is from MS 6376, which is a variant of the first version of Norgate's treatise (for the history of this manuscript see J. Kirby, 'The Painter's Trade in the Seventeenth Century: Theory and Practice', *National Gallery Technical Bulletin*, 20, 1999, p. 42, n. 38). *Seacole* is listed with the brown pigments in the second version of Edward Norgate's *Miniatura or the Art of Limning,* eds J. M. Muller and J. Murrell, New Haven and London 1997, p. 59. However, in a variant list from a copy of Norgate's first treatise (National Library of Wales 21753 B, 91) it is listed with the black pigments, see eds Muller and Murrell, cited above, p. 254.

30 Hilliard, cited in note 4, p. 99, when discussing how to depict pearls, recommends applying 'a small shadow of seacoal undermost of all'. De Mayerne in van de Graaf, cited in note 3, p. 148, suggests coal for rendering the shadows of flesh, as does Henrie Peacham: H. Peacham, *Graphice or The Most Ancient and Excellent Art of Drawing and Limning*, London 1612, p. 95.

31 Hilliard, cited in note 4, indicates that sea coal had a high sulphur content, 'the culers them sellues may not endure some ayers, especially in the sulfirous ayre of seacole', p. 74. Brimblecombe, cited in note 21, discusses the foul, sulphurous fumes produced by burning medieval sea coal, pp. 7–9.

32 Vannoccio Biringuccio, *Pirotechnia*, originally printed in Venice in 1540, trans. C. Stanley Smith and M. Teach Gnudi, Cambridge, Mass, 1959, p. 174. Deposits of coal in Italy, in Liguria, Lipari and Sicily, are mentioned by Theophrastus. His discussion is discussed and quoted in a note in Hoover and Hoover's translation of Agricola, cited in note 12, pp. 34–5. Liguria and Lipari are rich in lignite, a low-grade coal. See Scarzella and Natale, cited in note 13, Seconda Parte, *Catalogo*, 2, 'Terre Piemontesi, Terre coloranti delle principali località di cave piemontesi, descritte nel 1835 da V. BARELLI, 2.1.1, Terre di Vicoforte, Barelli', confirms the existence of a black earth pigment: 'lignite so widely dispersed in this soil decomposes so as to turn into earthy lignite and this is used like its predecessor for painting.'

33 Merrifield, cited in note 12. See the *Brussels manuscript*, 'Recueuil des essaies des merveilles de la peinture' by Pierre Lebrun, painter, 1635, p. 813: 'Les Italiens se servent de noir de charbon de terre pour travailler hors d'oeuvres, comme estant un noir qui resiste plus longtemps à l'injure du temps que pas ung autre.'

34 Seccaroni, cited in note 17.

35 Seccaroni, cited in note 17.

36 Natural mineral pyrolusite from India was used for the test samples.

37 For the history of NG 5537 see M. Levey, *National Gallery Catalogues: The 17th and 18th century Italian Schools*, London 1971, pp. 144–5; for the history of NG 69 see pp. 161–2. For the history of NG 933 see C. Gould, *National Gallery Catalogues: The Sixteenth-century Italian Schools*, revised edn London 1975, pp. 298–9.

38 J. Vouvé, J. Brunet and F. Vouvé, 'De l'usage des mineraux de manganese par les artistes de la grotte prehistorique de Lascaux, Sud-ouest de la France', *Studies in Conservation*, 37, 1992, pp. 185–92. Minerals containing barium in combination with manganese, such as psilomelane, are often found with pyrolusite.

39 Spring 2001 and Hendriks 1998, both cited in note 17.

40 Van de Graaf, cited in note 3, p. 142, 'black (c)halke qui facilement se seiche'. It is well known that manganese accelerates the drying of oil. See J.S. Mills and R. White, *The Organic Chemistry of Museum Objects*, second edn, Oxford 1994, p. 38.

41 Biringuccio, cited in note 32, p. 113.

42 Vouvé et al., cited in note 38.

43 I. Kakoulli, 'Roman Wall Painting in Cyprus: A Scientific Investigation of their Technology', *Roman Wall Painting. Materials, Techniques, Analysis and Conservation, Proceedings of the International Workshop on Roman Wall Painting, Fribourg March 1996*, Fribourg 1997, eds H. Béarat, M. Fuchs, M. Maggetti, D. Paunier, pp. 131–41. S. Profi, B. Perdikatsis, S.E. Filippakis, 'X-ray analysis of Greek Bronze Age pigments from Thera (Santorino)', *Studies in Conservation*, 22, 1977, pp. 107–15.

44 R. Mayer, *The Artist's Handbook of Materials and Techniques*, revised and updated edn, New York 1982, pp. 40 and 55.

45 Biringuccio, cited in note 32, p. 92. Biringuccio is quite specific about where the ore can be found – he mentions several mines in central Italy near Siena (which in fact is where he came from) and also the Maremma, near the west coast. There are also small deposits in the mountains north of Milan.

46 Agricola, cited in note 12, p. 110.

47 Biringuccio, cited in note 32, p. 92.

48 E.L. Richter, 'Seltene Pigmente im Mittelaltar', *Zeitschrift für Kunsttechnologie und Konservierung*, 2/1988, Heft 1, pp. 171–6.

49 For German gothic sculpture see Richter, cited in note 48, and C. Böke, 'Ein neuer Beleg zu Antimonglanz', *Restauro*, 100, 6, 1994, pp. 402–3. For seventeenth-century polychromy see W. Fünders, 'Aktuelle Befunde zur Verwendung "vergessener" Pigmente in niedersächsischen Raumfassungen', *Restaurierung von Kulturdenkmalen: Beispiele aus der niedersächsischen Denkmalpflege*, 1989, pp. 44–8.

50 M. Ferretti, G. Guidi, P. Moioli, R. Scafè and C. Seccaroni, 'The presence of antimony in some grey colours of three paintings by Correggio', *Studies in Conservation*, 36, 1991, pp. 235–9.

51 Seccaroni, cited in note 17. The paintings by Correggio in which stibnite was found, discussed in this article, date between *c.*1517 and 1531. The two paintings by Fra Bartolommeo are from the first decade of the sixteenth century, and *The Deposition* begun by Filippino Lippi was finished by Perugino around 1507.

52 An undermodelling with this pigment composition was seen in all four of the cross-sections from this painting.

53 Gould, cited in note 37, p. 75.

54 Richter, cited in note 48.

55 P. Moioli, R. Scafè and C. Seccaroni, 'Appendice I, Analisi di fluorescenza X su sei dipinti di Fra' Bartolomeo', and G. Lanterna and M. Matteini, 'Appendice II, Analisi SEM/EDS di un campione di film pittorico (sez. n. 5312 – s. 744.3 – Fra' Bartolomeo, pala Pitti)', *L'Età di Savonarola, Fra' Bartolomeo e la Scuola di San Marco*, ed. Serena Padovani with Magnolia Scuderi and Giovanna Damiani, Venice 1996, pp. 314–18. See also E. Buzzegoli, D. Kunzelman, C. Giovannini, G. Lanterna, F. Petrone, A. Ramat, O. Sartiani, P. Moioli, and C. Seccaroni, 'The use of dark pigments in Fra' Bartolomeo's paintings', *Art et Chimie, la couleur. Actes du Congrés,* Paris 2000, pp. 203–8.

56 An Oxford Instruments INCA system was used for the EDX analysis, with a GEM detector which has a resolution of 125eV. Thanks are due to Simon Burgess for assisting us with the analysis. The conventional Si(Li) detector in use at the National Gallery has a resolution of about 155eV. The X-ray diffraction pattern was in agreement with JCPDS file no. 5–519.

57 C.S. Hurlbut Jr, *Dana's Manual of Mineralogy*, 18th edn, New York and London 1971, pp. 233–4.

58 Katharina Mayr, 'Wismutmalerei', *Restauratorenblätte*, 7, 1984, pp. 153–71, states that mining of bismuth in Schneeberg began in 1460.

59 J.R. Partington, *A History of Chemistry*, Vol. 2, p. 59. Mathesius (1571) states that the metal was used in Milan work called counterfey and for metal type.

60 R. Gold, 'Reconstruction and Analysis of Bismuth Painting', *Painted Wood: History and Conservation*, Proceedings of a symposium in Williamsburg, Virginia, November 1994, eds V. Dorge and F.C. Howlett, Los Angeles 1998, pp. 166–78.

61 M. Levey, *National Gallery Catalogues: The German School*, London 1959, pp. 66–70.

62 Biringuccio, cited in note 32, p. 210, 'Those who want it to make bells put twenty-three, twenty-four, twenty-five, and twenty-six, (pounds of tin with every hundred pounds of copper) depending on the tone.' Biringuccio states that bell metal was traditionally also used for casting metal mirrors, but that 'nowadays most of the masters who make them take three parts of tin and one of copper', p. 388.

63 Seccaroni, cited in note 17.

64 M. Davies, *National Gallery Catalogues: The Earlier Italian Schools*, London 1951, rev. edn 1961, pp. 403–7.

65 Seccaroni, cited in note 17.

66 Seccaroni, cited in note 17.

67 The history of the use of bronze powder (which was not always true bronze) for writing inks and printing is discussed in C.W. Gerhardt, 'Das Drucken mit metallpigmenten in Geschichte und Gegenwart', *Polygraph*, 1982, pp. 1121–41. Milling of gold, silver, brass and copper to make a powder to use for illuminating manuscripts is described in Theophilus, *On Divers Arts*, trans. J.G. Hawthorne and C. Stanley-Smith, New York 1979, pp. 34–5. This work is thought to have been written in the twelfth century. It seems likely that bronze powder was also used.

68 Gould, cited in note 37, pp. 47–50. It has been proposed that Maineri started the painting, and that it was probably he who painted the armour of the soldier saint. Costa is thought to have altered the soldier's head and right hand.

69 Identified by X-ray diffraction, in agreement with JCPDS file no. 5–592.

70 Agricola, cited in note 12, mentions artificial lead sulphide prepared from metallic lead and sulphur to be used as a flux, p. 237.

71 Agricola, cited in note 12, pp. 462–4.

72 Agricola, cited in note 12, p. 110.

73 Fünders, cited in note 49. On the town hall in Duderstadt, galena was used for the cuirass of the figures of Commerce and Justice. Interestingly, stibnite was used for the cuirass of the figure of War on the same building.

74 *The Sons of Boreas pursuing the Harpies* is thought to date from between 1581 and 1596. Fe and P were detected in a black pigment in the priming layer by spot EDX analysis in the SEM on a paint cross-section.

75 The use of pyrite as a black pigment (iron sulphide) has been reported in the Bylant-Stundenbuch, dated 1475. See D. Oltrogge and O. Hahn, 'Über die Verwendung mineralischer Pigmente in der mittelalterlichen Buchmalerei', *Aufschluss*, 50 (6), 1999, pp. 383–90. A black iron oxide has been reported in wall paintings dating from *c.*1500 attributed to the circle of Pintoricchio. See *Materiali e Tecniche nella pittura Murale del Quattrocento*, Vol. 2, Parte II, Inchiesta sui dipinti murali del XV secolo in Italia sotto il profilo delle indagini conoscitive in occasione di restauri (1975–2000), Schede analitiche, coordinated by C. Seccaroni, Rome 2001, p. 330.

76 The pyrite in these paintings was identified by spot EDX analysis on cross-sections in the SEM.

77 Gould, cited in note 37, and Davies, cited in note 64.

78 Stibnite, bismuth, pyrite, pyrolusite, graphite and black shale as well as several types of carbon black were ground with linseed oil. Three patches were painted out on a panel for each pigment: a pale grey, a mid grey (both mixed with lead white) and the black or dark grey pigment alone. The pyrolusite was from a mineral sample from India, the others were supplied by Kremer Pigmente.

79 For a discussion of where artists obtained their pigments see L.C. Matthew, 'Vendecolori a Venezia: The Reconstruction of a Profession', *The Burlington Magazine*, CXLIV, November 2002, pp. 680–6.

80 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*, 1980, pp. 33–47.

81 Biringuccio, cited in note 32, pp. 92–3. Potters would almost certainly have known about the different types of sulphide as they were used to produce different colours in glazes.

82 Seccaroni, cited in note 17.

83 Borghini, cited in note 2.

TABLE 1 Summary of EDX analysis

Sulphur-rich organic black: coal

Lorenzo COSTA, *A Concert* (NG 2486), *c.*1485–95, panel, Bologna.
Black background; S-rich black mixed with a little verdigris and silicaceous extender. Some Ca and a little red iron oxide in the matrix around the sulphurous black particles. Also a minor ingredient in other areas of the painting.

Alvise VIVARINI, *Portrait of a Man* (NG 2672), 1497, panel, Venice.
Black background; S-rich black mixed with a little verdigris (with a large amount of chalk and tiny amounts of red iron oxide, K and Si).

Lorenzo COSTA with Gianfrancesco MAINERI, *The Virgin and Child Enthroned between a Soldier Saint and Saint John the Baptist (La Pala Strozzi)* (NG 1119), probably 1499, panel, Ferrara.
S-rich black in the dark, transparent brown paint of the wooden parts of the pedestal.

RAPHAEL, *The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (The Ansidei Madonna)* (NG 1171), 1505, panel, Perugia.
S-rich black in some of the darker paint mixtures, including the deep purplish shadow beneath the canopy of the Virgin's throne and the deepest shadows of Saint John's red drapery.

Lorenzo COSTA, *Portrait of Battista Fiera* (NG 2083), *c.*1507–8, panel, Mantua.
Black background; S-rich black with chalk.

Pietro PERUGINO, *The Virgin and Child with Saints Jerome and Francis* (NG 1075), *c.*1507–15, panel, Perugia.
Saint Francis's warm greenish-grey habit; S-rich black, lead white and a little ochre.

GIAMPIETRINO, *Salome* (NG 3930), probably *c.*1510–30, panel, Milan.
Black background; S-rich black with small amounts of Ca, Si, K and Fe and a little verdigris.

DOSSO Dossi, *A Man embracing a Woman* NG 1234), probably *c.*1524, panel, Ferrara.
Dark grey priming layer; S-rich black (with a little K, Ca and Si), lead white.

Gerolamo ROMANINO, *The Nativity with Saints* (polyptych) (NG 297.1–5), probably 1525, panel, Brescia.
S-rich black in the donkey-brown priming and a minor ingredient of Joseph's orange cloak.

PARMIGIANINO, *The Mystic Marriage of Saint Catherine* (NG 6427), *c.*1527–31, panel, Bologna.
Brownish-grey priming; S-rich black, lead white, silicaceous particles.

Workshop of GIULIO Romano, *The Birth of Jupiter* (NG 624), probably 1530–9, panel, Mantua.
Warm biscuit coloured priming layer; S-rich black and lead white.

Workshop of GIULIO Romano, *The Nurture of Jupiter* (Royal Collection), 1530s, panel, Mantua.
Warm biscuit-coloured priming layer; S-rich black and lead white.

DOSSO Dossi, *The Adoration of the Kings* (NG 3924), probably 1530–42, panel, Ferrara.
Large particles of S-rich black pigment in the priming and as an ingredient of some paint layers.

Jacopo TINTORETTO, *Christ washing his Disciples' Feet* (NG 1130), *c.*1556, canvas, Venice.
Black priming; S-rich black, with some silicaceous particles.

Jacopo BASSANO, *The Purification of the Temple* (NG 228), *c.*1580, canvas, Bassano.
Black priming; S-rich black, a little yellow earth, some K and Si, all possibly associated with the black pigment.

GUERCINO, *The Incredulity of Saint Thomas* (NG 3216), 1621, canvas, Cento.
A S-rich black pigment was identified in a thin brown underpaint from Christ's blue shawl.

GUERCINO, *La Vestizione di S. Guglielmo d'Aquitania* (Pinacoteca, Bologna).
A few particles of a S-rich black pigment were identified in a blue paint layer.

Manganese black

TITIAN, *The Virgin and Child with Saint John the Baptist and a Female Saint* (NG 635), probably 1530–5, canvas, Venice.
Grey underlayer beneath the female saint's orange shawl.

MORETTO da Brescia, *The Madonna and Child with Saints Hippolytus and Catherine of Alexandria* (NG 1165), *c.*1538–40, canvas, Brescia.
A coarse black containing Mn only in the brown priming.

MORETTO da Brescia, *The Madonna and Child with Saint Bernardino and other Saints* (NG 625), *c.*1540–54, canvas, Brescia.
A coarse black containing Mn only in the brown priming

MORETTO da Brescia, *Portrait of a Man at Prayer* (NG 3095), *c.*1545, canvas, Brescia.
A coarse black containing Mn only in the reddish-brown priming

Giovanni Battista MORONI, *Portrait of a Gentleman* (*Il Cavaliere dal Piede Ferito*) (NG 1022), probably *c.*1555–60, canvas, Brescia.
A coarse black containing Mn only in the brown priming

Giovanni Battista MORONI, *Portrait of a Lady* (*La Dama in Rosso*) (NG 1023), probably *c.*1555–60, canvas, Brescia.
A coarse black containing Mn only in the brown priming.

Giovanni Battista MORONI, *Portrait of a Gentleman* (NG 1316), *c.*1555–60, canvas, Bergamo(?).
A coarse black containing Mn only in the brown priming.

Giovanni Battista MORONI, *Portrait of a Man* (NG 3129), probably *c.*1560–5, canvas, Bergamo.
A coarse black containing Mn only in the brown priming. Also found in the greenish-grey background paint.

After TITIAN, *Boy with a Bird* (NG 933), probably 17th century, canvas.
Manganese black was identified in a paint layer beneath the dark sky, which may belong to an earlier composition. A very small amount of Ba was detected in the Mn-rich black particles.

After GUERCINO, *A Bearded Man holding a Lamp* (NG 5537), 1617–64.
A coarse black containing Mn only in the brown ground.

Pier Francesco MOLA, *Saint John the Baptist preaching in the Wilderness* (NG 69), *c.*1640, canvas.
A coarse black containing Mn only in the red-brown ground layer.

Stibnite

Lorenzo COSTA, *The Adoration of the Shepherds* (NG 3105), *c.*1499, panel, Bologna.
Stibnite is mixed with lead white in the cool grey drapery of the lowest tier of angels along the edge of the painting and used almost pure for the dark grey edging of the drapery.

Francesco BONSIGNORI, *The Virgin and Child with Four Saints* (NG 3091), *c.*1500, canva, Mantua.
Stibnite was found in the grey beard of the elderly saint and in the grey shadows of the white robe of the saint holding a palm.

CORREGGIO, *The Madonna of the Basket* (NG 23), *c.*1524, panel, Parma.
Stibnite was identified in the pinkish-grey priming and the greyish-pink undermodelling, mixed with lead white and a little bright red earth.

Bismuth

RAPHAEL, *The Procession to Calvary* (NG 2919), *c.*1502–5, panel, Perugia.
A silvery-grey pigment, most likely bismuth, is visible under the stereomicroscope in the grey horse and the grey hose of Simon of Cyrene.

RAPHAEL, *The Madonna and Child with Saints John the Baptist and Nicholas of Bari (The Ansidei Madonna)* (NG 1171), 1505, panel, Perugia.
Bismuth was used for the grey stone arch that frames the figure group, mixed with lead white and a little silicaceous material.

Attributed to Francesco GRANACCI, *Portrait of a Man in Armour* (NG 895), *c.*1510, panel, Florence.
Stibnite is the main pigment used for the grey armour, mixed with a little azurite, lead white and another black pigment. It is also used as a minor ingredient in the dark, chocolate-brown wall colour, behind the man's right elbow.

MASTER of CAPPENBERG (Jan Bagaert?), *The Coronation of the Virgin* (NG 263), *c.*1520, panel.
Stibnite is mixed with red earth and red lake for the mordant beneath God the Father's gilded halo.

Tin-rich bronze powder

Pietro PERUGINO, *The Archangel Michael* (NG 288.2), *c.*1496–1500, panel.
Silvery-grey pigment containing only Cu and Sn in the grey paint of Michael's armour and chainmail. The grey layer is thinly glazed with azurite.

Galena (black lead sulphide)

Lorenzo COSTA with Gianfrancesco MAINERI, *The Virgin and Child Enthroned between a Soldier Saint and Saint John the Baptist* (NG 1119), probably 1499, panel, Ferrara.
Coarse lead sulphide with lead white for the cool grey paint of the soldier's sword and for the grey underlayer of the soldier's armour. Also mixed with azurite in upper blue-grey modelling strokes on the soldier's armour.

Appendix: Py–GC–MS analysis of samples of the sulphur-rich organic black pigment

The samples used had previously been treated with TMTFTH to extract the paint binding medium. The remnants of the samples after this treatment were centrifuged and briefly washed with benzene/methanol (9:2). The solid residues were transferred to a quartz pyrolysis capillary for pyrolysis in a SGE Pyroprobe furnace-type on-column pyrolysis unit. Pyrolysis was carried out at 450°C in a helium carrier and the products were flushed onto a 30 metre long SGE BP5-0.5 quartz column (0.32mm internal diameter) in a Hewlett Packard 5890 Series II gas chromatograph, temperature programmed: 70°C (1 min.) × 10°C min^{-1} to 300°C (55 min.), linked to a Micromass Trio 2000 gas chromatograph–mass spectrometer. Mass spectra were collected at 70 eV, source temperature: 210°C, scanned at 1 cycle sec^{-1}, mass range 45–620 Da. The total ion chromatograms were recorded and the relevant sections are displayed in FIGS 3a, b and c.

In the sample of black background paint from Lorenzo Costa's *Portrait of Battista Fiera* (NG 2083) and Jacopo Tintoretto's *Christ washing his Disciples' Feet* (NG 1130), the overall range of liberated component types is similar, although there are quantitative differences (FIGS 3b and c). For the sample of black pigment from Giampietrino's *Salome* (NG 3930), the spectrum of liberated components is restricted essentially to smaller aromatic hydrocarbon ring systems, without any evidence of phenolic fragments (FIG. 3a). This sample appears to match more closely the characteristics of a defunctionalised and aromaticised retinite derived from purely resinous material. No furan-based fragments, resulting from cellulosics or heated cellulosics, were found in any of the samples and no still-extant diterpenoid or triterpenoid resin acids were detected at any stage of the analysis to suggest the possibility of wood or resin pitch. Indeed the intractability of the samples would speak against this – the organic components of the pigment could not be extracted by treatment with TMTFTH.

On the other hand, the Costa and Tintoretto samples exhibit a much broader range of liberated chemical types, which include simple phenolic fragments, alkyl-benzenes, and polynuclear aromatic hydrocarbons. These groups of compounds can be related to the sheets of aromatic ring structures that are typical of coal, with some hydroxyl functions attached that result from the geological transformation of originally lignin-based material from trees or their 'woody' predecessors, such as plants of the tree fern type. The absence of syringyl, sinapyl, coniferyl and cinnamyl entities precludes the likelihood of a lignin content of any significance remaining, as might be the case for peats and low-rank lignitic coals. The presence of triterpanes, some of which show the characteristics of extended hopane- and moretane-based homologues, underlines the activity of a seething, bacteria-rich, reducing environment that participates in the metamorphosis of the lignins.

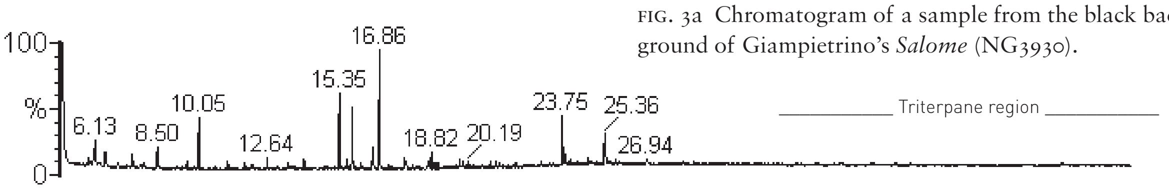

FIG. 3a Chromatogram of a sample from the black background of Giampietrino's *Salome* (NG3930).

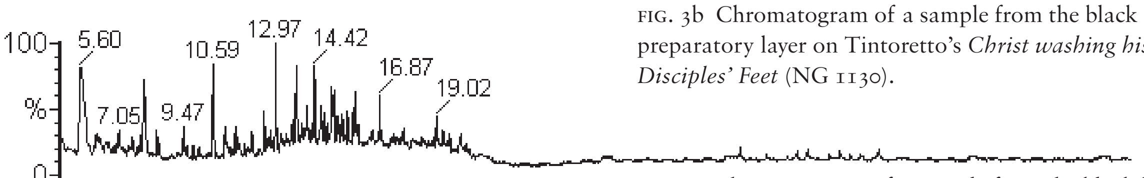

FIG. 3b Chromatogram of a sample from the black preparatory layer on Tintoretto's *Christ washing his Disciples' Feet* (NG 1130).

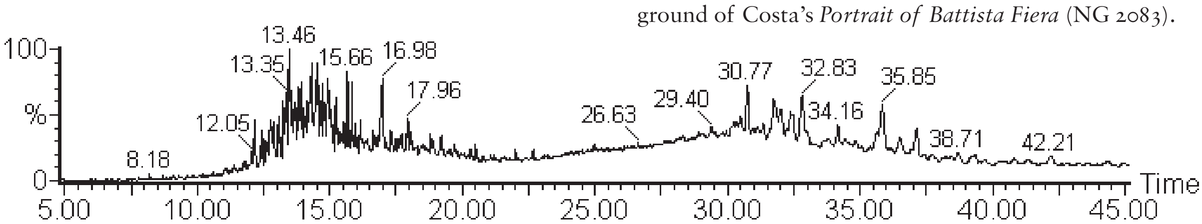

FIG. 3c Chromatogram of a sample from the black background of Costa's *Portrait of Battista Fiera* (NG 2083).