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FRONT COVER
Rubens, *The Judgement of Paris* (NG 194), detail of plate 1, page 4.

TITLE PAGE
Joachim Beuckelaer, *The Four Elements: Air* (NG 6587), detail of serving girl.

The Technology of Red Lake Pigment Manufacture: Study of the Dyestuff Substrate

JO KIRBY, MARIKA SPRING AND CATHERINE HIGGITT

If recipes for the red lake pigments used in western European easel painting from the twelfth century or earlier until the end of the eighteenth century are examined, it is clear that, apart from the dyestuff, by far the most common ingredient was alum, generally potash alum, potassium aluminium sulphate, $AlK(SO_4)_2 \cdot 12H_2O$. The use of alum as a mordant in textile dyeing is well known; in the case of lake pigments, it was used as a reagent to form a substrate for the dyestuff, to make a pigment. The reaction between this and an alkali forms a type of hydrated alumina which precipitates together with the dyestuff, in solution with one or other of the reagents. The alkali was commonly lye prepared from wood ash, but it could equally well be made from lime, or varieties of calcium carbonate, such as chalk, marble dust, egg shells or cuttlefish bone could have been used. These last are more usually found in recipes for yellow lake pigments, but also occur in recipes for red or rose-pink lake pigments from brazilwood, *Caesalpinia* spp.[1]

The analysis of red lake pigments has lagged behind that of other pigments used in easel painting. For many years examination of the dyestuff component was generally unfeasible as the size of sample required for spectroscopic or chromatographic analysis was unacceptably large. As these methods became more sophisticated and the sample size could be reduced, examination of the dyestuff extracted from paint samples became possible following methods similar to those already used for textile dyestuff samples.[2] Until recently, surprisingly little interest has been shown in examination of the substrate, in spite of the fact that it influences the colour, transparency and working properties of the pigment, as well as its permanence.[3] It is usually assumed that in a painting dating from before the nineteenth century the substrate is hydrated alumina. Before suitable instrumental methods of analysis were available, only the presence of aluminium could be detected, paradoxically often by means of a microchemical test using a dyestuff such as morin or alizarin as reagents.[4] The nature of the aluminium compound present could not be determined.

The use of energy dispersive X-ray microanalysis in the scanning electron microscope (SEM–EDX) has made the examination of lake substrates much easier, but at the same time has shown that, while aluminium is indeed often the major component detected, the elemental composition of the pigment is more complicated than might be expected. Small, but significant, amounts of other elements, such as sulphur, phosphorus, silicon, magnesium, potassium and calcium, are often also present, and these are not due to interference from other pigments. In some paintings the red lake pigment particles contain relatively little aluminium and the major element detected by EDX is sulphur. The evidence of the recipes suggests that the presence of a significant proportion of calcium as well as aluminium might be expected in some brazilwood lakes, or in certain eighteenth-century cochineal pigments, since calcium-containing materials are listed as ingredients.[5] The variation in the elements detected by EDX, and the presence of elements other than aluminium, may be explained by the way in which the pigment was made. The sources of the dyestuff, the alkali, the alum – even the recipe itself and the vessels used – all may affect the composition.

In order to investigate how these factors affect the composition of the red lake pigment, an analysis was made of the dyestuffs and other raw materials used to make the pigments, and of a range of lake pigments made in the laboratory following historical recipes, as well as of lake pigments in samples taken from paintings during routine cataloguing work or conservation treatment. The methods used for investigation of inorganic constituents were SEM–EDX and Fourier transform infrared microscopy (FTIR) and spectroscopy. High-performance liquid chromatography (HPLC) was used to analyse the dyestuffs; the medium and other organic constituents of the paint samples were identified by gas chromatography–mass spectrometry (GC–MS) and FTIR. In certain cases microchemical tests were used. Wherever possible, the paint samples chosen for analysis contained layers consisting only or mainly of red lake, to minimise interference from other pigments. Occasionally more than one red lake pigment was present in the sample, often in different layers and sometimes with different substrates. The results are summarised in Table 1 (see p. 86).

The contribution made by natural dyestuffs

In *The Virgin and Child with a Pomegranate* (NG 2906), from the workshop of Botticelli and painted around 1480–1500, an intense cherry-red lake pigment has been used in the Virgin's red dress (PLATE 1). It contains the dyestuff extracted from the kermes insect, *Kermes vermilio* Planchon. In the EDX spectrum of the red lake, the largest peak is from aluminium (Al). The FTIR spectrum shows that the substrate is essentially hydrated alumina; it shows a feature at 600 cm^{-1} characteristic of Al–O lattice vibrations, and other bands (broad *c.*3400 and *c.*1650cm^{-1}), from coordinated water.[6] However, small peaks for sulphur (S), phosphorus (P), silicon (Si), calcium (Ca) and potassium (K) can also be seen in the EDX spectrum (FIG. 1), and within the lake glaze are small regions containing less Al and rather more Ca, P and S, suggesting that small amounts of calcium phosphate and sulphate are present.

PLATE 1 Workshop of Sandro Botticelli, *The Virgin and Child with a Pomegranate* (NG 2906), *c.*1480–1500. Panel, 67.9 × 52.7 cm.

As the Table shows, elements other than aluminium are frequently detected in lake pigments, even if only in small amounts. Although they could derive from the alkali or alum used, EDX analysis of the scale insects and plant material from which dyestuffs were extracted shows that they all contain these elements, in varying amounts. To explore the contribution of the dyestuff raw material to lake pigments, specimens of each dyestuff from several different sources, together with pigments prepared from them where available, were examined: kermes, *Kermes vermilio* Planchon (five sources); Polish and Armenian (or Ararat) cochineals, *Porphyrophora polonica* L. and *P. hameli* Brandt (one each); the Mexican cochineal insect, *Dactylopius coccus* Costa (six sources); lac, *Kerria lacca* Kerr, as sticklac, the form in which it was imported into Europe before the eighteenth century (three sources); and madder root, *Rubia tinctorum* L. (four sources). In the case of brazilwood, the evaporated aqueous extract from the Old World variety sappanwood, *Caesalpinia sappan* L., was examined as it was difficult to detect anything in the wood itself.

A similar range of elements was detected in both the plant and insect specimens: S, P, Si, Ca and K, as seen in the painting from the workshop of Botticelli, and also chlorine (Cl), magnesium (Mg), sodium (Na) and copper (Cu). The presence of these elements is not surprising since all living things require a range of minerals to sustain life, usually in very small amounts. In the samples of madder root needle-shaped silicates of sodium, magnesium and aluminium could be observed, which probably derive from aluminosilicates in the soil and, in two specimens, calcium-containing crystals were found: madder will grow in calcium-rich soils and, indeed, it has been observed that the colour of textile dyeings obtained is redder if the plant has been grown on calcareous soils.[7] Madder also prefers a moist soil, rich in organic matter, with a reasonable phosphorus content.[8]

The same elements were present in the scale insects, the most significant being P, S, K and Cl, followed by Mg. It is notable that a larger amount of these elements was detected in the New World cochineal insects, which are also the richest in dyestuff, containing at least 10% – and potentially as much as 19% – by weight.[9] All the insects were markedly richer than the plant sources in phospho-

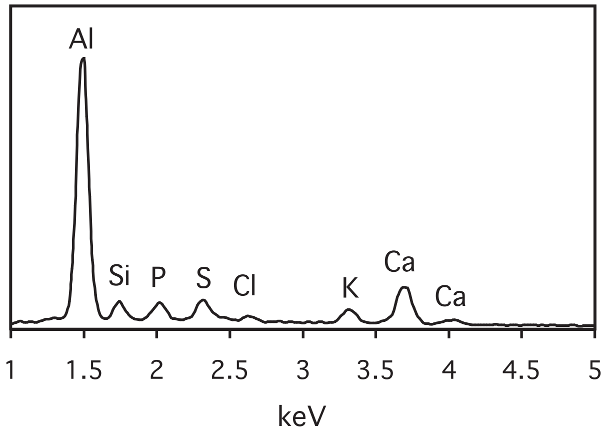

FIG. 1 Workshop of Sandro Botticelli, NG 2906. EDX spectrum of a sample of the red lake pigment from the Virgin's dress.

rus, an element involved in metabolic processes fundamental to the life of all animals. Scale insects feed on plant sap, the adults remaining attached, immobile, to the plant host and it may be that, like other phytophagous insects, they require a relatively large amount of potassium, but little sodium: in general very little sodium was detected. Other elements likely to be necessary for life include the magnesium and copper detected in all the insects; possibly also manganese and zinc, although these were not found.[10] Mg was sometimes detected in combination with P (specimens of kermes and cochineal), or with Si (cochineal). Particles containing K and P (perhaps potassium phosphate) were frequently found. Ca was only detected in small amounts, sometimes (in the bodies of the cochineal and kermes insects) as discrete particles in combination with P (so presumably calcium phosphate) or occasionally S (presumably calcium sulphate).

There was some difference between the relative quantity of elements detected within the dyestuff-rich bodies of the insects, and in the waxy surface coating they secrete. In most soft scale insects this coating consists largely of waxy, lipid material, and may be quite substantial in those that are immobile in the adult stage of their life cycle: in the case of the lac insect it is very massive indeed and is the source of shellac resin.[11] As it is secreted by the insect the coating is likely to include excess elements excreted in order to maintain the insect's physiological equilibrium; in general EDX analysis of the white coatings showed higher levels of calcium salts and silicates than the bodies of the insects. It is also possible that elements could be introduced by surface treatments or spraying, or from the environment in which the animal lives. Armenian cochineal, which has a pronounced white waxy coating, spends its adult life just below the soil surface, attached to the roots of a grass growing in saline marshes; it is therefore no surprise to find sodium and chlorine in the coating.

Examination of lakes prepared from the dyestuff raw materials discussed above showed that some of the elements detected in the insects are also present in the pigments. Hydrated alumina substrates prepared in a way that is analogous to the method used for the pigments, but without dyestuff, contained none of the additional elements with the exception of sulphur: this is discussed below. A reference lake made directly from kermes insects, following a seventeenth-century Italian recipe,[12] was found to contain a significant amount of P (the peak height in the EDX spectrum is about one-third that of the principal, Al, peak), in addition to trace amounts of S, Ca, Mg and Cu. The only possible source of the phosphorus was the insect and these particular specimens were relatively phosphorus-rich. Apart from aluminium and sulphur (discussed below), the element most frequently detected in the laboratory lake pigments was phosphorus, most conspicuously in the lakes from insect sources. When the dyestuff is not obtained directly from the insect, the phosphorus is present at much lower levels. In a kermes lake prepared by extracting the colorant from silk according to a fifteenth-century Italian recipe, using potassium carbonate solution and precipitating with potash alum,[13] only a little P, S, Si, Ca and Cu (the elements present in the insect source) were detected in addition to Al. Other elements detected in the insect, including K, Na, Mg and Cl, presumably remained in solution or were washed away and were thus not incorporated into either the dyed textile or the lake pigment derived from it.

A very similar pattern of elements is quite often found in lake pigments from fifteenth- and sixteenth-century paintings, such as the *Virgin and Child with a Pomegranate* lake pigment described above, and a similar kermes lake in Francesco Bissolo's *Virgin and Child with Saints Michael and Veronica and Two Donors* (NG 3083), dating from 1500–25 (PLATE 2). In a cross-section from Saint Veronica's red cloak in the latter painting (PLATE 3), much aluminium was detected in the red lake particles, together with some S, K, Ca, P and Si. In addition, tiny particles of calcium phosphate (Ca, P) were identified within the cherry-red lake particles (FIGS 2 and 3). Similar particles were seen in the red lake glaze in the Botticelli workshop painting. It is, of course, possible that a little ground bone was added to the lake by design or by chance, but one would then expect the particles to be larger and more irregularly sized: these particles are extremely small. Also, in several of the dyestuff raw materials that were analysed, small particles of calcium phosphate were found, so it is likely that the calcium phosphate in the paint samples originates from the dyestuff source.

Since the same series of elements was seen in all the raw dyestuffs, EDX analysis does not provide precise information on the origin of the dyestuff. However, where a lake pigment is particularly rich in phosphorus it is likely to contain an insect dyestuff. One such lake is that used in the uppermost glaze layer of the kneeling king's red brocade cloak in Veronese's *Adoration of the Kings* (NG 268), painted in 1573. The dyestuff in this case has been identified as perhaps having been extracted from Polish cochineal.[14] A significant amount of phosphorous was also seen in several of the kermes red lake pigments in the paintings in the Table, for example that used for the Virgin's dress in Marco Marziale's *Virgin and Child with Saints* (NG 804, 1507), and in Matteo di Giovanni's *Saint Sebastian* (NG 1461, probably 1480–95).

PLATE 2 Francesco Bissolo, *The Virgin and Child with Saints Michael and Veronica and Two Donors* (NG 3083), 1500–25, panel, 62.2 × 84.1 cm. Detail showing Saint Veronica.

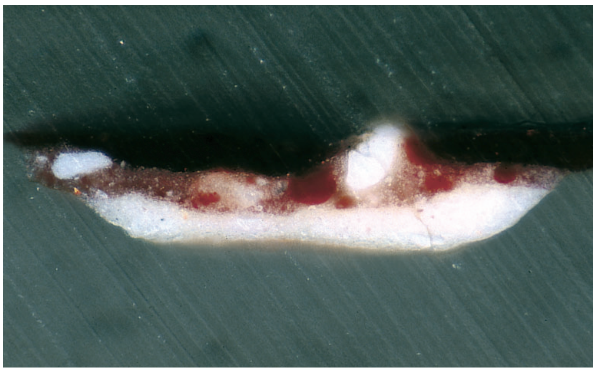

PLATE 3 Francesco Bissolo, NG 3083. Cross-section of Saint Veronica's red cloak, showing round cherry-red particles of lake mixed with lead white in the underpaint and a homogeneous deep red glaze. Original magnification 320×, actual magnification 280×.

Influence of the method of dyestuff extraction

The low dyestuff content of the raw materials means that a large number of insects or mass of root or wood is required when making lake pigments, in order to obtain a sufficient strength of colour. It is thus not surprising that constituents other than the dyestuff itself are present in the pigment at detectable levels. In practice this is influenced by whether the dye is extracted directly from the raw material or not. The evidence from documentary sources suggests that from the fourteenth to the seventeenth centuries, for lakes prepared from kermes, the various cochineals, and probably madder, the dye was generally extracted from shearings of textile dyed with these colorants. This practice may even have continued later: some late eighteenth-century recipes still refer to dyestuff extracted from rags, although by this time recipes using cochineal and madder directly are found. Clearly, if the source of the colorant is dyed textile, rather than the raw material itself, elements that are present in large quantities in the insect or plant may not appear in the final pigment, or, like phosphorus, may appear in very much reduced quantity, depending upon their solubility and whether or not they become attached to the textile. Much of the material detected in the cochineal and kermes insects would thus remain behind in the dyebath with the

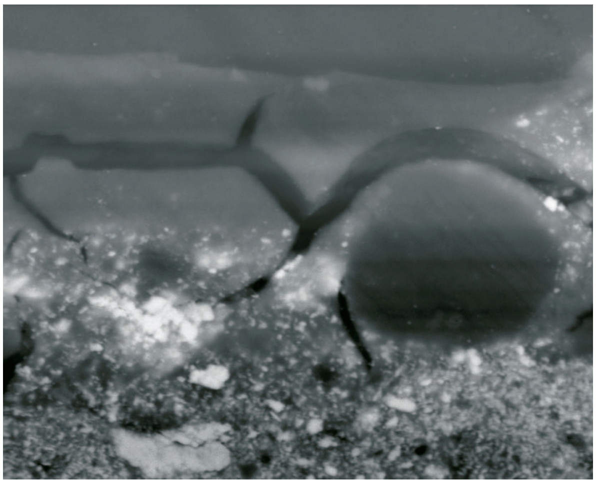

FIG. 2 Francesco Bissolo, NG 3083. Back-scattered image of the cross-section in PLATE 3. Within the large round red lake particle and the red glaze at the top of the cross-section are small, lighter grey particles of calcium phosphate.

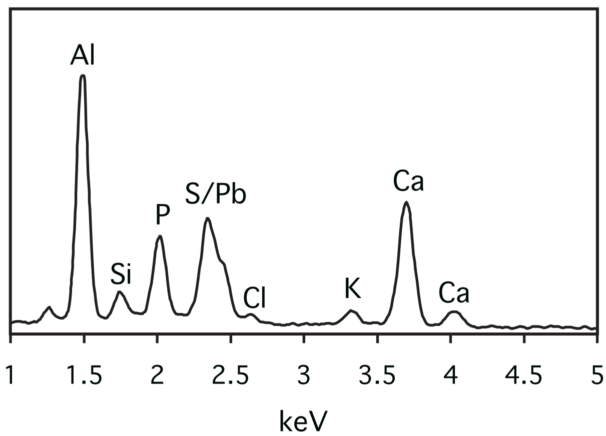

FIG. 3 Francesco Bissolo, NG 3083. Spot EDX spectrum on a small particle inside a large red lake particle (see FIG. 2). The calcium and phosphorus peaks in the spectrum are larger than in spectra from elsewhere in the lake particle, showing that the small particle is calcium phosphate.

chitin and other insect matter. The evidence of the documentary sources suggests, however, that lac (in the form of pieces of sticklac) and brazilwood are most likely to have been used directly as sources of dyestuff and in this case it is more likely that constituents present in the raw material will be found in the lake pigment.[15]

Direct extraction from the raw material

Sticklac consists of the hard brownish substance (mostly shellac resin) secreted by and completely enclosing the lac insects. In most recipes for lac lake pigments the entire raw material was ground and extracted with alkali; alum was then added to precipitate the lake. Constituents of both the dyestuff and shellac may therefore appear in the pigment. The elements detected in sticklac by EDX are similar to those in kermes and cochineal: P, K, Mg and S, with traces of Si, Cl, Al and Cu. EDX analysis of a lac lake made according to a fifteenth-century German recipe confirmed that these elements become incorporated into the pigment.[16] This can be compared with the results obtained from a sample of lac lake pigment used in the red false enamel decoration on the *Westminster Retable* (London, Westminster Abbey), painted in about 1260–80, where rather large amounts of P, S, K and Ca were detected by EDX in addition to Al (see Table 1 and FIG. 4).[17]

Alkaline extraction of sticklac brings into solution not only the water-soluble dyestuff components, the laccaic acids, but also the alkali-soluble hydroxyanthraquinones, including erythrolaccin, and also the shellac resin itself. Erythrolaccin is detected during analysis of the dyestuff by HPLC with diode-array detection, because it has a characteristic spectrum in the UV-visible region. It has been identified in the laboratory-prepared lac lake described above and in others prepared similarly, and also in samples from paintings, including the *Westminster Retable* and *The Story of Papirius* (NG 1430), painted by the Sienese painter Domenico Beccafumi in about 1540–50.[18] It is undetectable in lakes prepared by aqueous extraction of the dyestuff; its presence is therefore an indication of alkaline extraction. With FTIR microscopy and GC–MS analysis, shellac resin constituents in lac lakes, which are another indicator of alkaline extraction can be detected, as long as other constituents from the binding medium do not interfere.[19] Shellac constituents have been detected by these methods in the sample from the *Westminster Retable*, and in Philippe de Champaigne's *Cardinal de Richelieu* (NG 1449, 1633–40), among others (see Table 1). In fact, alkaline extraction of the dyestuff appears to have been the usual method used to manufacture lac lakes, since shellac constituents or erythrolaccin have been detected in almost every sample of lac lake that was examined, from paintings dating from the thirteenth to the seventeenth centuries.

Brazilwood lakes were also prepared by direct extraction of the dyestuff from the wood following a variety of recipes. Often calcium carbonate (commonly chalk) was an ingredient, thus in these cases calcium-containing salts would be present in

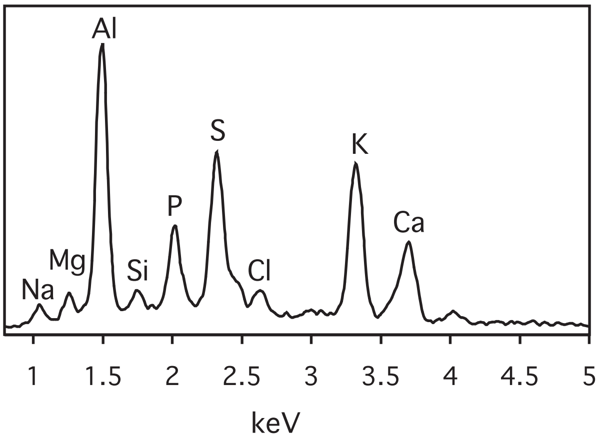

FIG. 4 English School, *The Westminster Retable* (London, Westminster Abbey), *c.*1270. EDX spectrum of the lac lake pigment used in the false enamel decoration. As well as the high proportion of potassium and sulphur relative to aluminium, other elements that derive from the insect used to prepare the pigment, such as phosphorus, magnesium, sodium, silicon and chlorine are present in significantly high quantity.

the substrate. The dyestuff is found in the wood in the form of brazilin, a homoisoflavonoid (rather than a neoflavonoid as usually stated), which is very easily oxidised to brazilein, particularly in slightly alkaline solutions (brazilin is apparently stabilised in slightly acidic solutions).[20] Depending on the acidity or alkalinity of the reagents used, colours varying from yellowish to purple can easily be produced, explaining the wide range of recipes available for brazilwood inks and pigments. However, it has become clear that because of the dye's tendency to turn brown in alkaline solutions when left to stand, some pigments made by the addition of alum to an alkaline brazilwood dyestuff solution tend to be a brownish crimson colour.

PLATE 4 Pietro da Cortona, *Saint Cecilia* (NG 5284), 1620–5. Canvas, 143.5 × 108.9 cm.

Alkalinity may affect the permanence, as well as the original colour, of the pigment. A brazilwood pigment prepared in the laboratory according to a nineteenth-century recipe in which the amount of alkali (sodium carbonate in this case) recommended was in excess of that needed,[21] and where it was not removed by washing, was found to be so fugitive that it turned an unpleasant yellowish brown colour even when kept in the dark. FTIR examination of the lake showed that the substrate is a basic sodium aluminium carbonate (dawsonite $NaAl(CO_3)(OH)_2$). The brazilwood lake used in the underpaint of the canopy in Raphael's *Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari* (*The Ansidei Madonna*) (NG 1171, 1505), and therefore also protected from light, now appears yellowish and must have degraded. The substrate of the pigment contains aluminium, calcium and sulphur, suggesting the use of a calcium-containing (and possibly alkaline) ingredient.[22] In Pietro da Cortona's *Saint Cecilia* (NG 5284, 1620–5) a brazilwood lake was used in the paint of the brocade dress. Here the substrate contains aluminium and sulphur but no calcium, and is better preserved (see PLATES 4–6).

Extraction of dyestuff from shearings of dyed wool

The Trinity with Christ Crucified, attributed to the Austrian School (NG 3662), dates from around 1410 (PLATE 7). The thick red paint used for the drapery of the central figure of God the Father and in several other areas has a distinctive lumpy texture, and is poorly covering, due to the use of a transparent madder lake pigment of large particle size (PLATE 8). Examination of the pigment substrate by EDX analysis showed that it was surprisingly rich in sulphur with relatively little aluminium (FIG. 5); in most particles the sulphur peak was larger than the aluminium peak. The irregular shape of the particles is clearly visible in the SEM back-scattered image: some have a rather distinctive ragged edge and are surrounded by a lighter halo (FIGS 6 and 7).

When the paint was analysed using FTIR microscopy, focusing on individual red lake particles, protein was detected within the pigment; this was confirmed with a positive ninhydrin test.[23] The paint medium, however, was identified by GC–MS as linseed oil.

In some lake pigment recipes in which the dyestuff is extracted from textile material, the alkali used is described as strong enough to dissolve a feather; it would therefore be capable of dissolving a proteinaceous fibre such as wool. Lake pigments were prepared in this way, following a fifteenth-century German recipe, using potassium carbonate or potassium hydroxide solutions of different strengths to extract the dyestuff from wool dyed with madder.[24] A series of pigments of good red colour were obtained, with dissolution of the wool to varying degrees. Examination of the resulting pigments by EDX and FTIR revealed that the more intense the treatment, the greater the amount of dissolution of the wool, and the more sulphur was present in the lake pigment. Wool protein is characterised by a relatively high sulphur content, about 3–4% of the dry weight, largely derived from the amino acid cystine, which contains a disulphide bond.[25] Alkaline extraction of dyestuff from dyed wool waste is accompanied by an unpleasant sulphurous odour as cleavage of the disulphide bond takes place.[26] It was also found that the proportions of the madder dyestuff constituents present differed: lakes prepared by gentler alkaline treatments contained more pseudopurpurin, while those prepared under more forceful conditions contained more alizarin and purpurin. The extreme variability of the dyestuff content of fifteenth- to seventeenth-century madder lakes has been noted by several authors; this is one possible explanation.[27]

It seems likely that the pigment in the Austrian School painting was made by a similar method. This would explain its high sulphur and protein content: wool is rich in sulphur, and FTIR analysis showed that it is not present as sulphate, but is probably present as organic sulphur derived from the wool. The madder dyestuff in the lake pigment had an unusually high alizarin content (HPLC); only a trace of pseudopurpurin and purpurin, which are fluorescent components of madder, could be detected. In the cross-section, some orange fluorescence that is typical of madder can be seen under ultraviolet light, but this is variable, and some of the madder lake particles do not fluoresce (PLATE 9).

The high sulphur content relative to aluminium, the rather large particle size, a distinctive irregular shape and sensitivity to the electron beam during EDX analysis seem to be characteristic of this kind of lake. A similar madder lake pigment is present in the lower of two layers of red lake paint used for the Virgin's red drapery in *The Virgin and Child* (*The Madonna with the Iris*), attributed to the workshop of Albrecht Dürer (NG 5592, 1500–10). Again, the sulphur peak seen by EDX analysis is larger than the aluminium peak; protein was detected by FTIR microscopy and a ninhydrin test was positive. In this case, a microchemical test for organic sulphur was also positive.[28] Similar high sulphur, protein-containing lake pigments have been identified in *Saints Matthew, Catherine of Alexandria and John the Evangelist* by Stephan Lochner (NG 705,

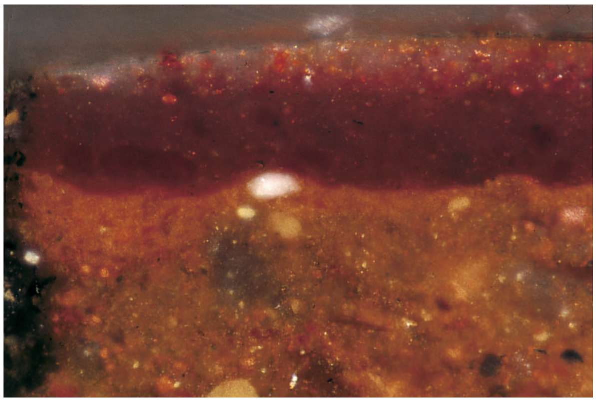

PLATE 5 Pietro da Cortona, NG 5284. Cross-section from Saint Cecilia's red dress. The red-lake containing paint lies on an orange underpaint consisting mainly of earth pigments. The red paint contains a mixture of brazilwood and cochineal lake pigments. Original magnification 360×, actual magnification 315×.

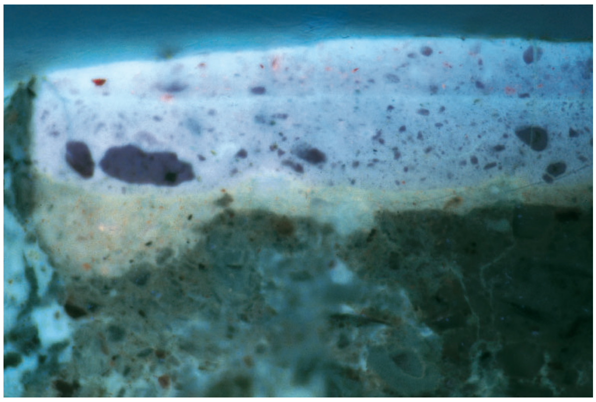

PLATE 6 Pietro da Cortona, NG 5284. Cross-section in PLATE 5 under ultraviolet light. The layer structure is more easily visible than under normal light, so that two red lake-containing layers can be seen. The lake pigments do not fluoresce but appear a dull greyish purple. Original magnification 360×, actual magnification 315×.

PLATE 7 Austrian School, *The Trinity with Christ Crucified* (NG 3662), *c*.1410. Panel, 118.1 × 114.9 cm.

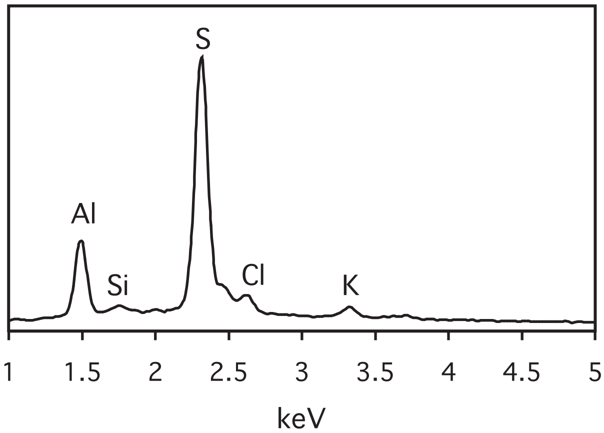

FIG. 5 Austrian School, NG 3662. Spot EDX spectrum of a madder lake particle. The peak for aluminium is relatively small; sulphur is the major element detected. Small amounts of silicon, chlorine and potassium are also present.

c.1450), *Christ crowned with Thorns* attributed to the workshop of Dirk Bouts (NG 712, *c*.1470–5), Gerard David's *Virgin and Child with Saints and a Donor* (NG 1432, probably 1510) and other paintings including one by the Italian artist Garofalo, *The Virgin and Child with Saints Dominic and Catherine of Siena* (NG 3102, probably 1500–5, see Table 1). It is interesting that quite frequently the sulphur-rich protein-containing red lakes have been found to contain madder dyestuff: alkaline extraction from dyed wool may have been the principal method for madder lake preparation.

Extraction of dyestuff from shearings of dyed silk

Silk, like wool, is a protein fibre, but with a different morphology. Only a trace of sulphur can be detected in silk thread by EDX analysis. Silk takes up less dye than wool and the dye is easier to remove by treatment with alkali; indeed, this process was used to re-dye silk fabric.[29] In raw silk, as obtained from the cocoon, the fibroin threads are bound together by hydrophilic sericin proteins, which make up some 25% of the weight of the silk. However, as sericin reduces the lustre of the silk and makes it difficult to dye, it is usually removed before dyeing by boiling the silk with soap (degumming). To restore some of the weight lost, the silk was weighted by treating it with a solution of oak galls, or some other source of gallotannins. Traces of ellagic acid, a component of oak galls, were detected by HPLC in a number of paintings (see Table 1), suggesting extraction of the dyestuff from weighted silk.[30] Many examples were kermes lake pigments; kermes and the different varieties of cochineal were most commonly used to dye silk. Although silk protein is attacked by alkali, the dyestuff is so easy to remove that probably little protein is dissolved during extraction, and none was detected in these lake pigments.

The kermes lake in the upper layer of glaze on Christ's robe in *Christ Crowned with Thorns*, a painting produced in the workshop of Dirk Bouts, contains some ellagic acid, suggesting extraction from dyed silk. A significant amount of sulphur was detected within the lake particles by EDX analysis, which could be interpreted as evidence for dissolution of the silk fibres. However, FTIR analysis showed that the sulphur was present as sulphate and not as organic sulphur and that the pigment did not contain protein.

Influence of the recipe and the method of substrate manufacture

The principal ingredients in the preparation of the hydrated alumina-type lake substrates are an alkali and an aluminium salt, which is usually potash alum (potassium aluminium sulphate). The alkali, or lye, was commonly prepared from wood or other plant ash extracted with water.[31] Depending on the plant source, the resulting alkali consisted essentially of a solution of potassium or sodium carbonate, with a certain amount of other water-

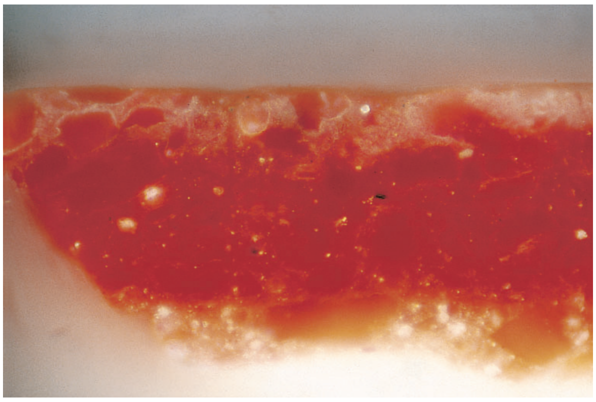

PLATE 8 Austrian School, NG 3662. Cross-section of the red paint of God the Father's robe. The paint contains large irregularly shaped particles of red lake, mixed with a small amount of lead white. The surface of the paint is deteriorated. Original magnification 380×; actual magnification 330×.

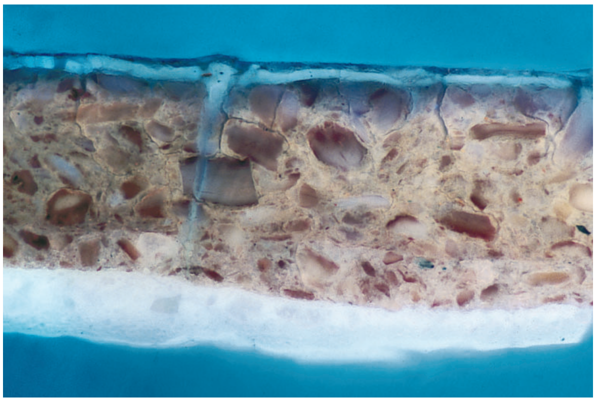

PLATE 9 Austrian School, NG 3662. Cross-section in PLATE 8 under ultraviolet light (after regrinding). Original magnification 380×; actual magnification 330×.

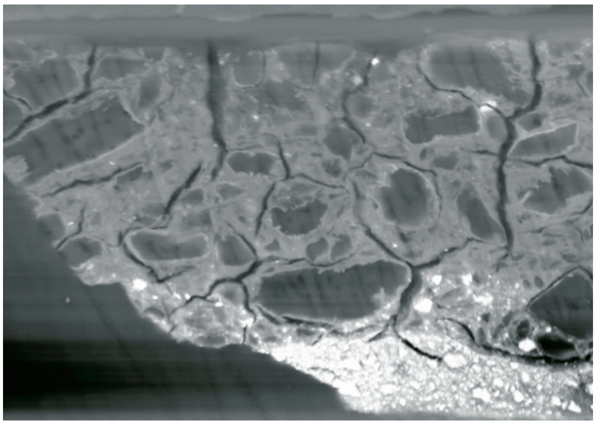

FIG. 6 Austrian School, NG 3662. Back-scattered image in the SEM of the cross-section in PLATE 8. The red lake pigment appears dark grey. The large particle size and irregular shape are typical of a protein-containing red lake pigment.

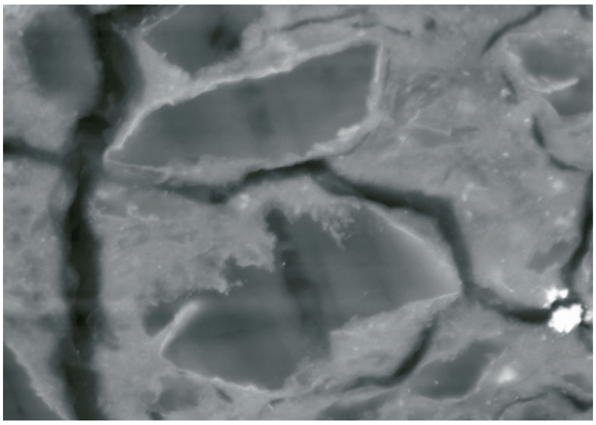

FIG. 7 Austrian School, NG 3662. Back-scattered image of two red lake particles at the right of FIG. 6. The edges of the particles are not well defined, but instead are ragged, as is typical of a protein-containing red lake pigment.

soluble salts. Other possible sources of alkali included stale urine (containing ammonia), wine lees (argol or cream of tartar, the potassium salt of (+)-2,3-dihydroxybutanedioic acid) calcined to give potassium carbonate, and lime water prepared from quick lime (CaO). These sources might be mixed: urine might be used to prepare an alkali from plant ashes; or a plant ash solution might be left to stand over quick lime, resulting in a much stronger and purer product, potassium or sodium hydroxide.

Samples of alkali made in the laboratory from the ashes of mixed hardwoods (predominantly English oak), were found to contain largely potassium, a very little sulphur, chlorine, sodium and aluminium and sometimes traces of manganese and silicon.[32] When these alkalis were used to prepare lake pigments, elements from the plant ash were not detected in the substrates. However, the use of a calcium-containing alkali, or possibly even hard water, could result in the presence of a small amount of calcium in, or associated with, the substrate, probably largely in the form of calcium sulphate. Examples of paintings where some calcium sulphate has been detected, clearly associated with the lake pigment particles, include the Austrian School *Trinity with Christ Crucified*, Stephan Lochner's *Saints Matthew, Catherine of Alexandria and John the Evangelist*, referred to above, and *The Story of Patient Griselda, Part III* (NG 914), painted by the so-called Master of the Story of Griselda around 1493–1500. In all these cases, only a small amount of the calcium salt is present, usually in the matrix around the red lake particles, rather than within the particles themselves, but the fact that it is also found in northern European paintings, in which calcium sulphate is otherwise a rather uncommon constituent, is further evidence that the lake pigment, and more specifically the alkali used during its manufacture, is the probable source. Where much higher levels of calcium are found in a red lake, it is likely to be a result of the deliberate use of a calcium-containing salt such as chalk to make the pigment, as is most commonly found in recipes for brazilwood lakes, discussed above.

Potash alum (the common source of aluminium in lakes) is a member of what is perhaps the best known series of double salts, $M^{I}M^{III}(SO_4)_2 \cdot 12H_2O$ ($M^{I} = K^+$, Na^+ or NH_4^+, etc; $M^{III} = Al^{3+}$, Fe^{3+} or Cr^{3+}, etc.). The alum industry is ancient; the principal mineral deposits are referred to by writers such as Dioscorides and Pliny.[33] The main mineral sources include alunite, $KAl_3(SO_4)_2(OH)_6$, which is formed from potassium-rich feldspars by the action of sulphate-rich waters. Large deposits were found at Phocœa in the eastern Mediterranean; from the 1460s those at Tolfa in Italy were also exploited. Another important, widely occurring source is alum shale, a mixture of pyrite (FeS_2), aluminium silicates and bituminous matter. Alunite mineral was roasted, then exposed to the air and moisture (weathered) until it became powdery, after which it was treated with hot water. The solution was decanted off and the potash alum was allowed to crystallise.[34] Alum shale was treated similarly by roasting and/or weathering. The addition of water dissolved out sulphuric acid, formed by oxidation of the pyrite; the reaction of this with the clay produced aluminium sulphate in solution. Iron and calcium salts would separate out on standing; the aluminium sulphate solution was then decanted off and the addition of, for example, urine or a potassium salt in solution produced ammonium or potash alum.[35] As alum was made by crystallisation from solution, it was a relatively pure product.

The lake pigment substrate is produced by the reaction between an alkali and alum, and is loosely described as hydrated alumina, but in practice is difficult to characterise, partly because it is amorphous and highly variable.[36] It does not correspond to any of the various crystalline aluminium (oxy)hydroxides or anhydrous oxides, many of which are known mineral species such as γ-$Al(OH)_3$ ($\equiv Al_2O_3 \cdot 3H_2O$, gibbsite), or γ-$AlO \cdot OH$ ($\equiv Al_2O_3 \cdot H_2O$, boehmite).[37] EDX and FTIR examination of the substrates of the laboratory-prepared lakes and of the lake pigments in paintings revealed that essentially they fall into two groups. The first, typified by the pigments seen in the Botticelli workshop *Virgin and Child with a Pomegranate* and Bissolo's *Virgin and Child with Saints Michael and Veronica and Two Donors*, contains principally aluminium and oxygen and is best described as amorphous hydrated alumina.[38] Using FTIR, broad bands linked to vibrations of the Al–O crystal lattice may be observed below 950 cm^{-1}. Vibrations due to coordinated water occur as broad bands at *c.*1650 and 3400 cm^{-1}.[39] The second group contains a significant amount of sulphur in addition. FTIR reveals clearly that the sulphur is present as sulphate (bands characteristic of S–O vibrations at 1125 and 985 cm^{-1}), not as proteinaceous sulphur derived from wool.[40] This type of substrate has been quite commonly found in nineteenth-century lake samples, but rather less so in earlier paintings.

The exact nature of the substrate produced will depend on factors such as the pH; the temperature of the reaction; the concentration of the reagents; the speed of their addition; how rapidly precipitation takes place; and the order of addition of the reagents. The most significant factor in determining which of the two varieties of hydrated alumina substrate described above is produced appears to be the last. Even into the eighteenth century, the sequence suggested in the recipes for lake pigments is the extraction of the dyestuff from its source – textile shearings or raw material – using alkali, followed by the addition of alum to precipitate the pigment. When a substrate was made in this way following a typical fifteenth-century recipe, but omitting the dyestuff, examination by EDX and FTIR revealed the presence of aluminium and Al–O bands and it was essentially similar to the substrates of many of the lakes listed in the Table (see FIG. 8). Hydrated alumina is gelatinous and highly absorbent when first precipitated, thus if precipitation is rapid, a certain amount of carbonate from the alkali may be brought down as well.[41]

By contrast, a substrate made by the reverse sequence, adding alkali to an alum solution (which would have contained the dyestuff), following a nineteenth-century recipe,[42] was found to contain sulphur (by EDX) and S–O bands (by FTIR), of similar size to the Al–O bands. It was therefore similar to the second type of alumina substrate observed in the nineteenth-century paint samples and to the light alumina hydrate described in paint technology literature.[43] In this case, sulphate anions have become incorporated into the substrate as it precipitated. Very few earlier pigment recipes for red lakes are of this type, apart from a few for brazilwood lakes: the brazilwood lake used by Pietro da Cortona discussed above, which contains a marked amount of sulphate, may be an example. The other anion that was commonly found to have been incorporated into the substrate in the lake pigments from paintings and those prepared in the laboratory was phosphate (probably from the dyestuff source). If phosphate is present in significant quantity, the sulphate band visible in the infrared spectrum can be shifted to *c.*1080 cm^{-1}.[44]

Potash alum itself is occasionally found in the lake pigment substrate, as particles in which potassium, aluminium and sulphur are combined. This is probably left over from the reaction forming the pigment. In many cases the alum was added to the alkaline dyestuff solution in crystalline form, rather than in solution, and perhaps until the reaction stopped, rather than as a weighed quantity. An example of this is *The Adoration of the Kings* attributed to the workshop of Giovanni Bellini (NG 3098, *c.*1475–80). EDX analysis of the red lake used for the cloak of the kneeling King showed that the main component was aluminium, but within the layer were small particles, lighter grey in the back-scattered image, which contain potassium, aluminium and sulphur, and are likely to be residual alum. In other particles potassium and sulphur were detected, perhaps potassium sulphate, which would normally be removed if the red lake pigment was thoroughly washed.

It is rare to find potash alum present in sufficient amounts for it to be described as the substrate. One example is the red lake pigment used in the shadows of the red curtain in the background of Garofalo's *Virgin and Child with Saints Dominic and Catherine of Siena* (PLATE 10). The paint sample contains both kermes and madder lakes, distinguishable by the characteristic orange fluorescence of the madder dyestuff. The madder lake particles were found to contain a significant amount of potash alum; potassium, sulphur and aluminium were detected by EDX (FIG. 9).[45] The particles also have all the characteristics of a pigment in which the dyestuff was extracted by alkaline treatment from wool, appearing large and irregular in shape in the back-scattered image, with a surrounding lighter halo and ragged edges (FIG. 10), as discussed above. The most likely explanation again lies in the type of recipe followed, where alum crystals are ground with the sticky protein-containing mass produced by boiling red textile shearings in alkali. Under these circumstances, it would be very easy to add too much alum, and inadequate washing of the pigment could result in alum remaining in the product.

Conclusions

The substrates identified in the red lake pigments used in paintings before the late eighteenth century or thereabouts are essentially amorphous hydrated alumina, sometimes including other anions, but other elements may be present in significant quantity. If sulphate anions are incorporated into the red lake pigment, this suggests that, in the recipe used, the dyestuff and alum were mixed first and the alkali was then added, a method commonly followed in the nineteenth century. The dyestuff raw materials may contribute a range of elements, including sulphur, phosphorus, silicon, calcium, potassium, chlorine, magnesium, sodium and copper. Marked amounts of phosphorus were found in the scale insect raw materials – lac, kermes and the Old and New World cochineals – and this study suggests that if significant amounts of phosphorus are present in the substrate of a lake pigment, then the dyestuff is probably from an insect source. The detection of phosphorus in lake samples by EDX therefore need not indicate that a proteinaceous binder such as casein or egg yolk has been used.[46]

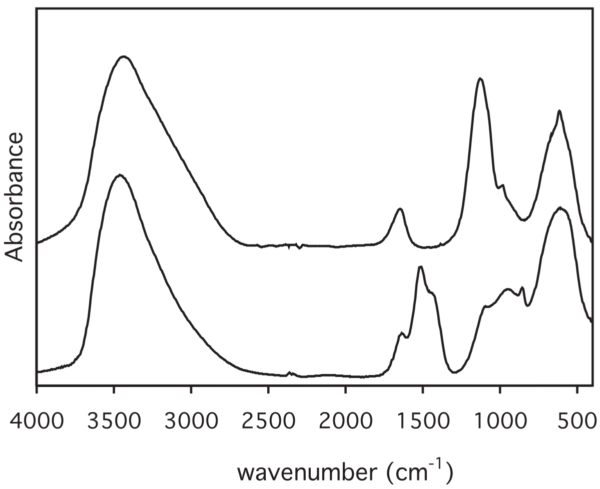

FIG. 8 IR spectra (4000–400 cm^{-1}) of hydrated alumina lake substrates prepared without dyestuff: (i) addition of potassium aluminium sulphate to a solution of potassium carbonate (substrate contains some carbonate), lower trace; (ii) addition of sodium carbonate to a solution of aluminium sulphate (substrate contains some sulphate), upper trace.

The presence of lake pigments for which the source of the dyestuff is dyed wool is particularly significant when proteinaceous textile matter dissolved by the alkali is present in large quantity in the lake pigment, as this can produce anomalous results during analysis of the paint medium. Detection of protein in the lake pigment in the Austrian School *Trinity with Christ Crucified* might be taken as an indication that the binding medium was proteinaceous, whereas in fact GC–MS showed that linseed oil had been used. This method of lake pigment production also explains the fact that the substrate contains a great deal of sulphur (derived from wool protein), but very little aluminium: the red proteinaceous matter coagulates in the alkaline solution in which the textile matter was boiled, particularly on cooling, and quite little alum may be added. Where dyed silk textile was the dyestuff source, there is no evidence so far that silk protein appears in lake pigment substrates, probably because the dyestuff is so easily removed. The ellagic acid detected in a number of red lakes from paintings is one indication that the colorant was extracted from weighted dyed silk;[47] in fact, until well into the seventeenth century, probably most kermes and cochineal lakes were made this way.

It is interesting how frequently two lakes were used in separate layers to paint a passage of red in a painting: often a madder lake below and a scale insect (kermes or cochineal) lake above. In one or two cases a brazilwood lake has been identified in the lower layer. Often the two lakes have been found to have different substrates: a conventional hydrated alumina substrate for the scale insect dyestuff;

PLATE 10 Garofalo, *The Virgin and Child with Saints Dominic and Catherine of Siena* (NG 3102), probably 1500–5. Panel, 46.3 × 34.8 cm.

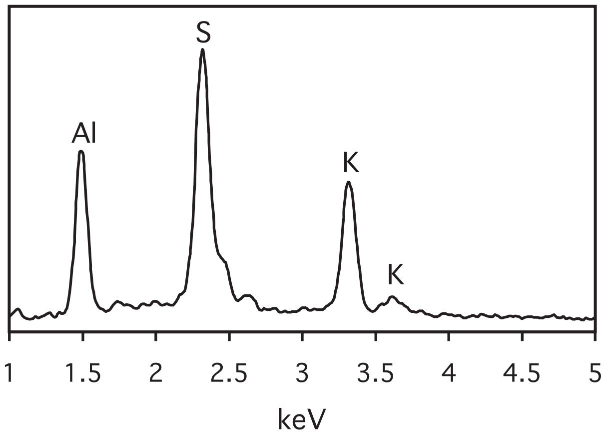

FIG. 9 Garofalo, NG 3102. Spot EDX spectrum of the red lake particle in FIG. 10. Sulphur is the major peak in the spectrum, as is characteristic of a protein-containing red lake. Potassium is also present in significant quantity suggesting that some residual potash alum is present.

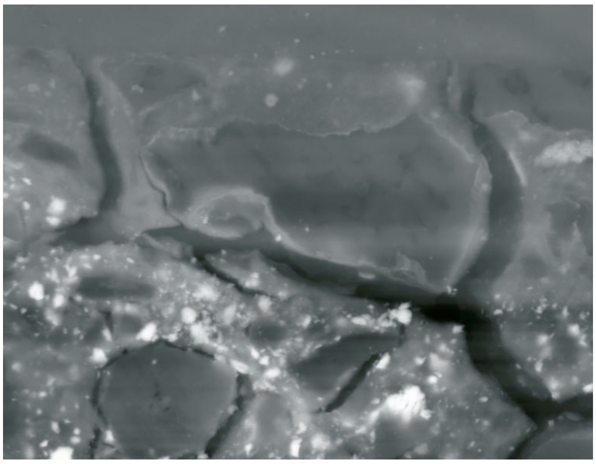

FIG. 10 Garofalo, NG 3102. Back-scattered image in the SEM of a red lake particle in a cross-section from the red curtain around the throne. The particle is large and has an irregular shape, as is typical of protein-containing red lake pigments.

something different for the madder lake. In many cases the madder dyestuff has been found to derive from dyed wool (resulting in proteinaceous sulphur in the substrate). If this was the common method for madder lake preparation, it may provide a partial explanation for the mysterious absence of recipes for them. The effect of this method of preparation on the proportions of the madder dyestuff anthraquinones present in the pigment is also significant as the colour, and perhaps also the permanence, of the pigment may have been affected. The reasons for the use of two pigments may have been economic or aesthetic; the scale insect pigments are purplish crimson in hue, and were probably quite expensive. The madder lakes are usually a more orange red, and possibly less expensive. Brazilwood lakes are a slightly crimson red, but the impermanence of the dyestuff was well known so it is no surprise to find the pigment used in an underlayer.

Only in the eighteenth century is there any indication of an extender being added to the pigment, quite separate to the substrate. In Giovanni Antonio Pellegrini's *Rebecca at the Well* (NG 6332), painted around 1708–13, and Canaletto's *Regatta on the Grand Canal* (NG 4454), of about 1740, starch grains are clearly visible, mixed with the red lake pigments (see Table 1). It is noticeable that in both cases the dyestuff present is cochineal, which can give a very intense colour. The use of starch (that is, flour) as an extender would maintain the pigment's translucency without making it lighter in colour.

The close links between the pigment-making and dyeing technologies are clearly demonstrated by the use of textile shearings as a source of dyestuff. However, developments in the use of different mordants for textile dyeing, notably the use of tin salts with cochineal dyestuff to give scarlet, discovered by the Dutchman Cornelius Drebbel (1572–1633), were not taken up by the pigment makers until much later. At the very end of the eighteenth century, or beginning of the nineteenth, recipes for tin-containing cochineal pigments appear and these pigments became very widely used. Recipes also appear in which a hydrated alumina substrate was prepared and then added to the dyestuff solution. By this time the principles underlying dyeing and pigment making were becoming better understood, and in the nineteenth century developments in organic chemistry and in pigment technology led to a more varied range of organic pigments becoming available.

Notes and references

1 See, for example, M.P. Merrifield, *Original Treatises dating from the XIIth to XVIIIth Centuries on the Arts of Painting*, 2 vols, London 1849 (reprinted New York, 1967), Vol. I, *Experimenta de coloribus*, compiled by Jehan Alcherius, Manuscripts of Jehan le Begue, no. 299, pp. 282–5; also nos 304, pp. 292–3, and 334, pp. 310–11; Alessio Piemontese, *The Secretes of the Reverende Maister Alexis of Piedmont* ... tr. (from French) by W. Warde, London 1558, ff. 91v.–92 r. (Vol. 1 of four bound together; the translation of Alessio's *Secreti*, Book 1).

2 The methods of analysis are summarised in J. Kirby and R. White, 'The Identification of Red Lake Pigment Dyestuffs and a Discussion of their Use', *National Gallery Technical Bulletin*, 17, 1996, pp. 56–80. See also the section on the identification of natural dyestuffs in J.H. Hofenk de Graaff, *The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuffs*, Riggisberg and London 2004, pp. 19–41, contributed in part by W.G.Th. Roelofs and M.R. van Bommel; also J. Wouters, 'High performance liquid chromatography of anthraquinones: analysis of plant and insect extracts and dyed textiles', *Studies in Conservation*, 30, 1985, pp. 119–28; J. Wouters and A. Verhecken, 'The scale insect

dyes (*Homoptera: Coccoidea*). Species recognition by HPLC and diode-array analysis of the dyestuffs', *Annales de la Société Entomologique de France*, (N.S.) 25, 4, 1989, pp. 393–410.

3 Methods for identification of substrates, including microchemical tests, are given in H. Schweppe and H. Roosen-Runge, 'Carmine – Cochineal Carmine and Kermes Carmine', *Artists' Pigments: A Handbook of their History and Characteristics*, Vol. 1, ed. R.L. Feller, Washington and Cambridge 1986, pp. 255–83, esp. p. 275; H. Schweppe and J. Winter, 'Madder and Alizarin', *Artists' Pigments: A Handbook of their History and Characteristics*, Vol. 3, ed. E. West FitzHugh, Washington and Oxford 1997, pp. 109–42, esp. pp. 131–4. For examples of analytical results from paintings see A. Wallert, '"Cimatura de grana": Identification of Natural Organic Colorants and Binding Media in Mediaeval Manuscript Illumination', *Zeitschrift für Kunsttechnologie und Konservierung*, 5, 1, 1991, pp. 74–83; G. McKim-Smith, G. Andersen-Bergdoll and R. Newman, *Examining Velázquez*, New Haven and London 1988, pp. 85–6, 118, 124–6; J. Dunkerton, N. Penny and M. Spring, 'The Technique of Garofalo's Paintings at the National Gallery', *National Gallery Technical Bulletin*, 23, 2002, pp. 20–41; M. Clarke, P. Fredrickx, L. Speleers, I. Vanden Berghe and J. Wouters, 'Comparative studies of seventeenth-century Netherlandish red lake glazes in the Oranjezaal, Palace Huis ten Bosch', *Dyes in History and Archaeology*, 22, in course of publication.

4 F. Feigl and V. Anger, *Spot Tests in Inorganic Analysis*, 6th English edn, Amsterdam 1972, pp. 95–104.

5 See, for example, *A Compendium of Colors and other Materials used in the Arts dependant on Design*, London 1797, p. 59.

6 FTIR analysis was generally carried out on samples placed in a diamond micro compression cell using an IR microscope fitted with a MCT-A detector, giving a working range of 4000–650 cm^{-1}: above the region of M–O lattice vibrations, unfortunately. However, if there was sufficient sample micro KBr disks (2–3 mm diameter) were prepared and used with a beam condenser in the main IR bench; this has a DTGS detector with a working range of 4000–400 cm^{-1}.

7 D. Cardon, *Le monde des teintures naturelles*, Paris 2003, p. 102.

8 S. Başlar and H.H. Mert, 'Studies on the Ecology of *Crozophora tinctoria* L. and *Rubia tinctorum* L. in Western Anatolia', *Turkish Journal of Botany*, 23, 1999, pp. 33–44.

9 N.M. Barcenas and G. Aquino, 'In Vitro Culture of *Dactylopius coccus* Costa (Homoptera: Dactylopidae): Potential Production of the Natural Dye Carminic Acid', *In Vitro Cellular and Developmental Biology*, 33, 1997, p. 21A (abstract of Symposium paper).

10 J.L. Nation, *Insect Physiology and Biochemistry*, Boca Raton 2002, pp. 75–6, 89–92, 101–14. Hardening of an insect cuticle is not due to mineralisation and generally only small amounts of minerals are incorporated into the cuticle itself. In species of fly where this has been investigated the mineral ions present are calcium, phosphorus and magnesium.

11 Y. Tamaki, 'Chemistry of the test cover', in Y. Ben-Dov and C.J. Hodgson (eds), *Soft Scale Insects: Their Biology, Natural Enemies and Control*, Amsterdam 1997, pp. 55–72; J.S. Mills and R. White, *The Organic Chemistry of Museum Objects*, 2nd edn, London 1994, pp. 115–18.

12 Merrifield 1849 (cited in note 1), Vol. II, *Ricette per far ogni sorte di colore* (the Paduan Manuscript), no. 116, pp. 702–3.

13 Merrifield 1849 (cited in note 1), Vol. II, *Segreti per colori* (the Bolognese Manuscript), no.110, pp. 432–5. The silk was dyed according to a recipe in G. Rosetti, *The Plictho of Gioanventura Rosetti* (Venice 1548), tr. S.M. Edelstein and H.C. Borghetty, Cambridge (Mass.) 1969, pp. 44–5 and 134–7, 52–3 and 144–5.

14 N. Penny, A. Roy and M. Spring, 'Veronese's Paintings in the National Gallery, Technique and Materials: Part II', *National Gallery Technical Bulletin*, 17, 1996, pp. 32–55, esp. p. 49; Kirby and White 1996 (cited in note 2), p. 71. The structure of the sample was complicated, with several layers containing lake. It is also possible that the dyestuff was extracted from New World cochineal with the addition of a little kermes, and/or that the dyestuff content is different in the different layers. It is extremely difficult to distinguish between the different cochineals when only tiny quantities of dyestuff are available and the possibility of mixtures cannot be ruled out.

15 J. Kirby, 'Some Aspects of Medieval and Renaissance Lake Pigment Technology', *Dyes in History and Archaeology*, 21, in course of publication. For eighteenth-century lakes from textiles see, for example, *A Compendium of Colors* 1797 (cited in note 5), p. 59.

16 E. Berger, *Quellen und Technik der Fresko-, Oel und Tempera-Malerei des Mittelalters*, Munich 1897, pp. 143–76, esp. pp. 160–1; *The Strasburg Manuscript: a Medieval Painter's Handbook*, tr. V. and R. Borradaile, London 1966, pp. 34–5. The pigment was made using potassium carbonate solution and potash alum.

17 Kirby, in course of publication (cited in note 15).

18 Kirby, in course of publication (cited in note 15). The reaction between erythrolaccin and alkali (giving a purple solution) was used to distinguish commercial shellacs from other resins: see H. Vollmann, 'Identification of shellac', *Journal of the Oil and Colour Chemists' Association*, 40, 1957, pp. 175–82.

19 Shellac resin constituents give rise to characteristic infrared bands at 1735 and 1715 cm^{-1} (ester and acid carbonyl bands) and 1240 cm^{-1} (ester C–O band). In oxidised shellac-containing samples characteristic, but unidentified, components with ions at m/z 308 and 276 are seen in the mass spectrum, see Mills and White 1994 (cited in note 11), pp. 180–3. C.L. Higgitt and J. Kirby, in preparation for publication; see also Kirby, in course of publication (cited in note 15).

20 W. Nowik, 'The Possibility of Differentiation and Identification of Red and Blue "Soluble" Dyewoods: Determination of Species used in Dyeing and Chemistry of their Dyestuffs', *Dyes in History and Archaeology*, 16/17, 2001, pp. 129–44, esp. pp. 131–4.

21 P.F. Tingry, *The Painter's and Colourman's Complete Guide ...* , 3rd edn, London 1830, pp. 121–2.

22 A. Roy, M. Spring and C. Plazzotta, 'Raphael's Early Work in the National Gallery: Paintings before Rome', *National Gallery Technical Bulletin*, 25, 2004, pp. 4–35, esp. p. 22 and note 53, p. 35.

23 F. Feigl, *Spot Tests in Organic Analysis*, 5th English edn, Amsterdam 1956, pp. 282–4.

24 E.E. Ploss, *Ein Buch von Alten Farben: Technologie der Textilfarben im Mittelalter mit einem Ausblick auf die festen Farben*, Heidelberg and Berlin 1962: the Nuremburg Kunstbuch, no. li, pp. 113–14; Kirby, in course of publication (cited in note 15).

25 H. Höcker, 'Fibre Morphology', in *Wool: Science and Technology*, ed. W.S. Simpson and G.H. Crawshaw, Cambridge and Boca Raton 2002, pp. 60–79, esp. pp. 60–9; *Fibres, Films, Plastics and Rubbers: A Handbook of Common Polymers*, ed. W.J. Roff and J.R. Scott, London 1971, p. 205. Wool contains only a trace of phosphorus.

26 W.S. Simpson, 'Wool Chemistry' in *Wool: Science and Technology* 2002 (cited in note 25), pp. 131–59, esp. pp. 135–9, 142–3.

27 Kirby, in course of publication (cited in note 15); Hofenk de Graaff 2004 (cited in note 2), pp. 127–9.

28 Feigl and Anger 1972 (cited in note 4), pp. 462–7: test by pyrolysis with calcium oxalate, pp. 465–6.

29 Wool contains α-keratins – protein molecules in an α-helix conformation, in a complex mixture with proteins of irregular structure – whereas silk is composed of β-keratins; that is, protein molecules partially in a β-pleated sheet conformation. It is in the less crystalline, more random regions of the silk fibre, containing a higher proportion of amino acid residues with large side chains, that mordant and dyestuff can bond. D. Kaplan, W. Wade Adams, B. Farmer and C. Viney, 'Silk: Biology, Structure, Properties and Genetics', in *Silk Polymers: Materials Science and Biotechnology*, ed. D. Kaplan, W. Wade Adams, B. Farmer and C. Viney, Washington DC 1994 (American Chemical Society Symposium Series 544), pp. 2–16; Y. Takahashi, 'Crystal Structure of Silk of *Bombyx mori*', in the same volume, pp. 168–75; H.-J. Jin and D.L. Kaplan, 'Mechanism of silk processing in insects and spiders', *Nature*, 424, 2003, pp. 1057–61. For an example of the extraction of dyestuff before redyeing the textile see Rosetti 1969 (cited in note 13), pp. 17, 107.

30 Jin and Kaplan 2003 (cited in note 29); Hofenk de Graaff (cited in note 2), pp. 286–7, 291, 335–6.

31 Recipes for alkalis are very common and are often included in pigment recipes; see, for example, G. Rosetti 1969 (cited in note 13), pp. 17, 107; Wallert 1991 (cited in note 3); *Middelnederlandse verfrecepten voor miniaturen en 'alderhande substancien'*, ed. W.L. Braekman, Scripta 18, Brussels 1986, text 1 (London, Wellcome Historical Medical Library, MS 517), no. 45: 'Om synober te maken ..', pp. 46–7.

32 EDX analysis was carried out on samples of the alkalis evaporated to dryness and on kermes and lac lakes prepared using them, from dyed wool in the first case and from sticklac in the second, by Ashok Roy. See also M. Verità, 'L'invenzione del cristallo muranese: un verifica analytica delle fonti storiche', *Revista della Stazione Sperimentale di Vetro*, 1, 1985, pp. 17–35.

33 C. Singer, *The Earliest Chemical Industry: An Essay in the Historical Relations of Economics and Technology illustrated from the Alum Trade*, London 1948; D. Cardon, *Le monde des teintures naturelles*, Paris 2003, pp. 27–38.

34 Singer 1948 (cited in note 33), pp. 70, 203-6; V. Biringuccio, [*De la pirotechnia*] *The Pirotechnia of Vannoccio Biringuccio*, tr. C.S. Smith and M.T. Gnudi, Cambridge, Mass., 1942 (1966 reprint; originally published Venice 1540), pp. 98–105.

35 Singer 1948 (cited in note 33), pp. 177–81, 193–7, 226–8; G. Agricola, *De re metallica*, tr. H.C. Hoover and L.H. Hoover, New York, 1950 (originally published Basel 1556), pp. 564–72.

36 Clarke, Fredrickx, Speleers, Vanden Berghe and Wouters, in course of publication (cited in note 3). We are grateful to Dr Mark Clarke and his colleagues for allowing us to consult the text of their article before publication.

37 N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Oxford 1984 (1990 reprint), pp. 243–95, esp. p. 253.

38 J. Williams, 'Hydrated Aluminium Oxide', *Pigment Handbook*, ed. T.C. Patton, New York 1973, Vol. 1, pp. 293–304; T. Sato, 'Precipitation of Gelatinous Aluminium Hydroxide', *Zeitschrift für anorganische und allgemeine Chemie*, 391, 1972, pp. 69–78.

39 V.C. Farmer, 'The anhydrous oxide minerals', *The Infrared Spectra of Minerals*, ed. V.C. Farmer, Mineralogical Society Monograph 4, London 1974, pp. 183–204, and Y.I. Ryskin, 'The vibrations of protons in minerals: hydroxyl, water and ammonium', in the same volume, pp. 137–81. Broad bands associated with the hydrated Al–O lattice are seen centred at *c.*950 (Al–(OH)–Al bend) and *c.*600 (Al–O lattice) cm^{-1}. No bands associated with hydroxide vibrational modes are seen (*c.* ν(OH) 3660–3000; δ(OH) 1080–950; γ(OH) 770–20 cm^{-1}).

40 T. Sato and K. Sato, 'Preparation of Gelatinous Aluminium Hydroxide from Aqueous Solutions of Aluminium Salts Containing Sulphate Group with Alkali', *Journal of the Ceramic Society of Japan, International Edition*, 104, 1996, pp. 359–63. Exact band positions depend on the precipitation pH. It should be noted that S–O infrared vibrations are more intense than equivalent Al–O modes, presumably because the S–O bond is more polar.

41 Sato and Sato 1996 (cited in note 40); N. Le Bozec, D. Persson, A. Nazarov and D. Thierry, 'Investigation of Filiform Corrosion on Coated Aluminium Alloys by FTIR Microspectroscopy and Scanning Kelvin Probe', *Journal of the Electrochemical Society*, 149, 2002, pp. B403–8. Monodentate carbonate coordination gives rise to bands at 1520, 1430, 1090 and 850 cm^{-1}. The carbonate present in the hydrated alumina substrate may also derive from reaction with atmospheric CO_2. In real samples it can be difficult to determine the nature of anions incorporated into the substrate because of the contribution of the medium and other pigments to the infrared spectrum.

42 Tingry 1830 (cited in note 21).

43 This substrate resembles the modern material used in the pigment making industry known as light alumina hydrate, approximate formula $Al_2O_3{\cdot}0.3SO_3{\cdot}3H_2O$: T.C. Patton, 'Light Alumina Hydrate and Gloss White', in *Pigment Handbook* 1973 (cited in note 38), pp. 319–21.

44 L.S. Burrell, C.T. Johnston, D. Schulze, J. Klein, J.L. White and S.L. Hem, 'Aluminium phosphate adjuvants prepared by precipitation at constant pH. Part I: composition and structure', *Vaccine*, 19, 2001, pp. 275–81.

45 Dunkerton, Penny and Spring 2002 (cited in note 3), p. 34.

46 M. Matteini, A. Moles, G. Lanterna, C. Lalli, M.R. Nepoti, M. Rizzi and I. Tosini, 'Characteristics of the materials and techniques', in *Giotto. The Crucifix in Santa Maria Novella*, ed. M. Ciatti and M. Seidel, Florence 2002 (English edition), pp. 393–4; J. Dunkerton, 'Mantegna's painting techniques' in *Mantegna and 15th Century Court Culture*, ed. F. Ames-Lewis and A. Bednarek, London 1993, pp. 26–38.

47 Certain constituents present in the dyestuffs as extracted from the scale insect and madder raw materials do not dye the textile. Their absence in an HPLC analysis of a lake pigment is therefore an indication that it was probably prepared using dyestuff extracted from textile matter.

Table 1. Examples of red lake pigments examined

Artist, painting title and date	Area sampled and results of analysis of red lake pigments
Austrian School, *The Trinity with Christ Crucified* (NG 3662), *c.*1410, oil on wood.	Red of God the Father's robe: madder (HPLC; much alizarin). S, some Al, small K, Ca, Cl (EDX). The lake particles contain protein (FTIR, ninhydrin test), and are rich in S (EDX, S peak larger than Al peak) due to extraction from wool (S not present as sulphate inside the red particles, FTIR). Calcium sulphate associated with the red lake in the matrix between large red particles (FTIR), and small amounts of silicates and calcium phosphate (EDX). A small amount of kermes lake pigment is also present (HPLC).
Domenico Beccafumi, *The Story of Papirius* (NG 1430), probably 1540–50, oil on wood.	Red glaze of dress of woman centre of group below steps: lac (HPLC; erythrolaccin detected). Al, some S, small K, Ca, Si, P (EDX).
Attributed to the workshop of Giovanni Bellini, *The Adoration of the Kings* (NG 3098), *c.*1475–80, oil on canvas.	Red of kneeling King's cloak: Old World cochineal (Polish? HPLC). Mainly Al, some S, K (K and S associated in some areas), small Si, P, Na (EDX). The EDX results suggest that there is potash alum in the red lake pigment as well as amorphous hydrated alumina.
Joachim Beuckelaer, *The Four Elements: Air* (NG 6587), 1570, oil on canvas.	1) Red sleeve of figure, right; 2) cloth below birds, centre: Mexican cochineal (HPLC; ellagic acid detected).
Francesco Bissolo, *The Virgin and Child with Saints Michael and Veronica and Two Donors* (NG 3083), probably 1500–25, oil on wood.	Red of Saint Veronica's dress: kermes (HPLC). Al, small S, K, Ca, P, Si (EDX). Within the homogeneous red glaze are small particles that contain Ca (sometimes combined with S or P), together with some silicaceous particles (EDX).
Workshop of Sandro Botticelli, *The Virgin and Child with a Pomegranate* (NG 2906), probably *c.*1480–1500, egg tempera on wood.	Red of Virgin's robe: kermes (HPLC). Al, small S, P, Si, Ca, K (EDX). Within the homogeneous red glaze are small particles that contain Ca (sometimes combined with S or P). FTIR microscopy confirms amorphous hydrated alumina and a small amount of sulphate.
Workshop of Dirk Bouts, *Christ Crowned with Thorns* (NG 712), probably *c.*1470–5, oil on wood.	Red of Christ's cloak: two layers containing red lake. Madder in lower layer (HPLC); large particles, Al and S (EDX, S peak slightly smaller than Al), protein detected in the pigment particles therefore probably extracted from wool (FTIR, ninhydrin test), and some sulphate in the matrix between the red particles. Kermes in upper layer (HPLC, ellagic acid detected); smaller particles, mostly Al, small S, Ca, K, P and Na (EDX). FTIR microscopy shows amorphous hydrated alumina, with some sulphate and possibly some phosphate.
Canaletto, *A Regatta on the Grand Canal* (NG 4454), *c.*1740, oil on canvas.	Red of textile: cochineal (HPLC; probably Mexican). Al, with small Ca, K, Si, P, and Cu (EDX). Starch particles mixed with the red lake pigment (FTIR, optical microscopy).
Annibale Carracci, *The Three Maries* (NG 2923), *c.*1604, oil on canvas.	Red of the Magdalen's robe: cochineal (HPLC; type unclear). Al, some S and small P (EDX). FTIR detected some sulphate and phosphate, as well as amorphous hydrated alumina. EDX confirmed that calcium sulphate is present in the glaze.
Bernardo Cavallino, *Christ driving the Traders from the Temple* (NG 4778), *c.*1645–50, oil on canvas.	Dark red of Christ's robe: cochineal (HPLC; probably Mexican). Appears rather faded in cross-section, although the larger particles are still red. Large Al, some S, small Si, P, K, Ca, Cl (EDX). Some regions are richer in Ca. FTIR detected some sulphate, as well as amorphous hydrated alumina.
Philippe de Champaigne, *Cardinal de Richelieu* (NG 1449), 1633–40, oil on canvas.	Shadow in a fold of the red cloak: lac (HPLC). Shellac components seen by FTIR microscopy.
Gerard David, *The Virgin and Child with Saints and Donor* (NG 1432), probably 1510, oil on wood.	Red brocade of Saint Catherine's dress: kermes and madder (HPLC). Madder lake shows orange fluorescence in ultraviolet light. Madder lake; large S, some Al, small Si, Cl, K (EDX) and protein (FTIR), so probably extracted from wool. Kermes lake; Al, small Si, P, Cl, K, Ca (EDX). A little calcium sulphate in the matrix between the red particles (FTIR).
Workshop of Albrecht Dürer, *The Virgin and Child* (NG 5592), *c.*1500–10, oil on wood.	Red of Virgin's robe: two layers, lower layer mainly madder (HPLC; rich in alizarin), upper layer mainly kermes (HPLC). Madder lake; large S, some Al, small K, Ca, Na, Si, P (EDX) together with protein (FTIR, ninhydrin test). Suggests extraction of the dyestuff from wool, as does the positive test for organic sulphur. Calcium sulphate in the matrix between particles (FTIR, EDX). Kermes lake; large Al, small Ca, K, Ca, Si, P.
Garofalo, *The Virgin and Child with Saints Dominic and Catherine of Siena* (NG 3102), probably 1500–5, oil on wood.	Red of curtain in background: madder and kermes in separate red lake pigments (HPLC). Madder lake; S, Al, K (EDX) together with protein (FTIR), suggesting that the dyestuff was extracted from wool, and that unreacted potash alum is present. Some Zn in the matrix between the large red lake particles. Kermes lake; Al, some S and small K, Ca, P, Si, Cl (EDX).
Ridolfo Ghirlandaio, *The Procession to Calvary* (NG 1143), probably *c.*1505, oil on canvas, transferred from wood.	Saint John's red robe: kermes (HPLC; possibly tannins present). Al, small S, P, Si, K, Ca, Mg (EDX). FTIR microscopy: amorphous hydrated alumina, a small amount of sulphate and phosphate.

Table 1. Examples of red lake pigments examined (continued)

Artist, painting title and date	Area sampled and results of analysis of red lake pigments
Giannicola di Paolo, *The Annunciation* (NG 1104), late 15th century, egg tempera on wood.	Red of Virgin's robe: kermes (HPLC; ellagic acid detected) and madder (HPLC; very little alizarin). Al, small, Si, P, S, Cl, K, Ca (EDX). FTIR microscopy (of the bulk sample): amorphous hydrated alumina, with possibly a small amount of phosphate and sulphate.
Eustache Le Sueur, *Alexander and his Doctor* (NG 6576), *c.*1648–9, oil on canvas.	Cloak of seated figure, left-hand side: Mexican cochineal (HPLC; ellagic acid also detected). Al, small Ca, K, S, Si, P (EDX).
Stephan Lochner, *Saints Matthew, Catherine of Alexandria and John the Evangelist* (NG 705), *c.*1450, oil on wood.	Red robe of Saint Catherine: large particles of red lake. Large S, some Al, small Ca, Cl, K, P (EDX). Red lake particles contain protein (FTIR) which, together with the high S content, suggests that the dyestuff was extracted from wool. Some calcium sulphate (FTIR, EDX), calcium carbonate, and a Zn compound in the matrix between the red lake particles (EDX).
Marinus van Reymerswaele, *Two Tax Gatherers* (NG 944), *c.*1540, oil on wood.	Red of sleeve of left figure: underpaint contains madder lake (HPLC), upper layer contains kermes lake (HPLC). Madder lake; Al, large S (slightly smaller than Al). FTIR microscopy: the red lake particles contain protein suggesting that the dyestuff has been extracted from wool. Also amorphous hydrated alumina, some calcium carbonate and calcium sulphate. Kermes lake; Al, some S, small K, Ca, P, Na, Mg (EDX).
Marco Marziale, *The Virgin and Child with Saints* (NG 804), 1507, oil on wood.	Red of Virgin's robe: kermes (HPLC; ellagic acid detected) and a little madder. Al, small S, Si, P, K, Ca (EDX). FTIR microscopy (bulk sample): amorphous hydrated alumina, and some phosphate and sulphate.
Master of Saint Giles, *The Mass of Saint Giles* (NG 4681), *c.*1500, oil on wood.	Red of cloth on altar frontal: kermes and madder (HPLC) in separate layers. Madder lake in lower layer; rich in S, with some Al, K, Ca, Si (EDX). Protein detected by FTIR which, together with the high S content, suggests that the dyestuff was extracted from wool. Kermes lake in upper layer; mainly Al, calcium sulphate in matrix (FTIR, EDX).
Master of the Story of Griselda, *The Story of Patient Griselda, Part III* (NG 914), probably *c.*1493–1500, oil and egg on wood.	1) Red glaze on Griselda's son's gold tunic; 2) Red dress of standing woman: kermes (HPLC). Al, some S, relatively large P, small K, Ca, Si, Mg (EDX). Some calcium sulphate in the matrix between the red particles (EDX, FTIR). FTIR microscopy suggests that P is in the form of phosphate (egg tempera medium masked other characteristic substrate bands).
Matteo di Giovanni, *Saint Sebastian* (NG 1461), probably 1480–95, egg tempera on wood.	Red of angel's drapery: Al, some S, relatively large P, small Ca, Si, K, Cl, Mg, Cu (EDX).
Giovanni Antonio Pellegrini, *Rebecca at the Well* (NG 6332), 1708–13, oil on canvas.	Servant's red cloak, lower left: Mexican cochineal (HPLC); Al, with small S, P, Si (EDX). Red lake mixed with starch (FTIR, optical microscopy).
Pietro da Cortona, *Saint Cecilia* (NG 5284), 1620–5, oil on canvas.	Red shadow of Saint Cecilia's dress: brazilwood and cochineal (HPLC). Al, quite large S, some K, very small P, Na, Mg (EDX). Some small potash alum particles present, sometimes within large red particles (EDX). FTIR microscopy: amorphous hydrated alumina and some sulphate.
Raphael, *The Ansidei Madonna* (NG 1171), 1505, oil on wood.	Red of Saint John the Baptist's cloak: kermes and a trace of brazilwood (HPLC). Kermes in upper layers; large Al, small S, P, K, Ca (EDX). Brazilwood is in the underpaint and has deteriorated to a yellow colour; content of particles is variable. Some contain Al, some S, small K, Ca, Na, others contain Al combined with S and Ca (EDX).
Paolo Veronese, *The Adoration of the Kings* (NG 268), 1573, oil on canvas.	Red of kneeling King's cloak: cochineal (HPLC; perhaps Polish). Uppermost layer; contains mainly Al, relatively large P, K and S, small Cl, Ca (EDX). FTIR microscopy: amorphous hydrated alumina, with some sulphate, phosphate and carbonate. Underpaint contains a different red lake pigment, rich in S, with very little Al (EDX). Protein detected by FTIR which, together with the high sulphur content, suggests that the dyestuff was extracted from wool. Some calcium sulphate in the matrix (EDX, FTIR).
Willem van der Vliet, *Portrait of Suitbertus Purmerent* (NG 1168), 1631, oil on wood.	Red of tablecloth: madder (HPLC; much alizarin). Al, medium S (half peak height of Al), small K, Ca, P (EDX). Within the red paint are small areas containing Ca, Al, S. FTIR microscopy: amorphous hydrated alumina, some calcium sulphate and carbonate.
English School, *The Westminster Retable* (Westminster Abbey), *c.*1270, oil on wood.	Red of false enamel decoration: lac (HPLC). Shellac components detected by FTIR microscopy. Al, relatively large P, S, K, Ca, small Na, Mg, Si, Cl (EDX). Small particles containing Al, S, K, probably potash alum (EDX).