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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.

Investigation of Pigment-Medium Interaction Processes in Oil Paint containing Degraded Smalt

MARIKA SPRING, CATHERINE HIGGITT AND DAVID SAUNDERS

THE BLUE PIGMENT SMALT, a cobalt-containing potash glass, was widely used in European oil paintings from the end of the fifteenth century onwards.[1] However, it is not a stable pigment and in many paintings it has deteriorated, losing its colour and causing yellowing of the oil medium so that the paint acquires a brownish-yellow or greenish-grey colour. Often, this is accompanied by other paint defects such as drying cracks and patchy blanching. The paint can appear lighter at the surface, as if the binding medium has disintegrated and is scattering light, or as if some kind of efflorescence has occurred.

Studies of historic window or vessel glass have shown that the first stage in the deterioration involves leaching of the alkali and alkaline earth components of the glass. In 1969 Joyce Plesters suggested that this process may also be occurring in smalt-containing paint, encouraged by reaction with the acidic oil binding medium.[2] Since smalt is a potash glass, the alkaline component is predominantly potassium. More recently it has been possible to prove, with elemental and molecular mapping techniques, that leaching of potassium has taken place in paint samples containing deteriorated smalt.[3] The appearance of the deteriorated paint suggests that this is accompanied by other changes affecting the binding medium. Possible processes include reaction of the potassium with carboxylic acids in the oil to form potassium soaps, or perhaps with anion sources in the environment to form species such as carbonates and sulphates. The aims of this study were to investigate not only what is happening to the pigment when it degrades, but also to examine changes in the oil binding medium. Paint samples containing degraded smalt from a number of National Gallery paintings were examined using light microscopy, energy dispersive X-ray analysis (EDX) in the scanning electron microscope (SEM), Fourier transform infrared (FTIR) microscopy and gas chromatography–mass spectrometry (GC–MS). A series of artificially aged paint samples of smalt was also analysed, to help interpret and understand the results from the paintings.

Literature on the deterioration of window and vessel glass

The literature on the deterioration of window and vessel glass is extensive. The range of deterioration products that are formed, the mechanism of deterioration, and the effect of the composition of the glass on durability have all been studied. It is worth taking this research into account when considering the deterioration of smalt pigment, since it is likely that broadly similar processes are occurring.

The deterioration of glass is a complex process because of its variable composition and the diversity of environmental conditions to which it can be exposed. The main agent in the deterioration is water, and under acidic conditions ($pH<9$) an initial stage has been identified involving diffusion of water into the glass, followed by ion exchange and migration of alkali and alkaline earth metal ions out of the glass in the form of hydroxides. At the same time, salts of these metal ions form, creating a crust on the surface of the glass. The salts formed, and the degree of deterioration, depend on the original composition of the glass and the environment in which it has been kept; carbonates, sulphates, chlorides, nitrates and oxalates predominate.[4]

In the crusts on the surface of window and vessel glass, complex as well as simple salts have been identified. For example, on the potash-lime-silica glass that has been used in most European medieval cathedrals, syngenite ($K_2SO_4{\cdot}CaSO_4{\cdot}H_2O$), arcanite ($K_2SO_4$), schoenite ($K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$), gorgeyite ($K_2SO_4{\cdot}5CaSO_4{\cdot}6H_2O$), leonite ($K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$) and polyhalite ($K_2SO_4{\cdot}2CaSO_4{\cdot}MgSO_4{\cdot}2H_2O$) have all been reported to be present as deterioration products.[5] These crusts have also been found to contain gypsum ($CaSO_4{\cdot}2H_2O$), calcite ($CaCO_3$), and calcium oxalate ($CaC_2O_4{\cdot}nH_2O$). The source of calcium in these complex crusts is not only the glass itself, but also airborne particles that are gradually deposited on the surface and become incorporated into the crust through reaction with the rather alkaline and hygroscopic salts initially formed.[6] Biodeterioration is also thought to play a role, manifested by the presence of calcium oxalate and encouraged by the high levels of K, Ca, Mg, Fe and P that are released as the glass degrades and which are essential for microbial growth.[7] Studies have shown that with time sulphates (which are the most thermodynamically stable species) predominate, and eventually gypsum becomes the major component of the crust, while black dirt particles trapped in the crust give it a grey colour.[8]

As it degrades, the surface of the glass becomes a hydrated silica gel depleted in alkali and alkaline earth metal ions. If the deterioration is extreme, any transition or heavy metal ions present can also migrate and either make their way into the crust or become redistributed in the glass. In studies where cross-sections of deteriorated glass have been analysed, metal ions such as Mn, Al, Fe, Cu, Zn, Co and Pb have been found to concentrate in the silica gel layer at the surface of the glass.[9]

The durability of glass is closely related to its composition; the nature and proportion of the alkali and alkaline earth components are particularly important. It is well known that glass rich in potassium is significantly more unstable than a sodium glass of equivalent composition.[10] Glass generally consists of a silica network in which metal oxides are incorporated that modify the properties. Sodium and potassium oxides act as fluxes, lowering the melting temperature of the glass, while calcium and magnesium oxides are described as glass stabilisers because they can reduce the sensitivity of the glass to water. Small amounts of other metal ions can have a strong effect; for example Al and Fe can act as network formers, which improve the durability. It is, however, very difficult to predict the stability of the glass from the composition alone.[11] The proportion of silica present has also been found to be significant. Glasses with more than 66 mol% SiO_2 have been found to be far less prone to deterioration than glasses with a lower silica content.[12]

It is not surprising that smalt is prone to deterioration, since it is rich in potassium; levels of around 15 wt% K_2O have been found in this study and are reported in the literature.[13] The high surface area of the crushed smalt glass and its immersion in an acidic drying oil would be expected to facilitate leaching of alkaline components, and therefore deterioration. The change in colour of smalt as it degrades is thought to be due to the change in environment of the Co^{2+} ion as the alkali is leached.[14] It has been shown that physical changes can also occur in the smalt particles, such as pitting of the surface.[15] The general glass literature reports that shrinking of glass can occur when large amounts of the alkaline components are leached.[16] Damage to the surface in the form of pitting has been ascribed to dissolution of silica in the regions where the hygroscopic salts formed by leaching are concentrated, creating an alkaline micro-environment.[17] The physical changes in the smalt glass could affect the coherence of the paint film, which is also likely to be affected by reactions involving the metal ions leached from the smalt. These could include formation of soaps with carboxylic acids in the drying oil, or of other salts such as carbonates and sulphates.[18] Mobile metal ions in the paint film which are not from the smalt glass (particularly lead) could play a part, so that complex salts are formed rather than simple potassium salts.[19] These possibilities were all borne in mind when considering the results of the analyses on test samples and on samples from paintings.

Test samples

A number of test samples of smalt in oil were painted out and artificially aged under different conditions.[20] The test samples were designed to assess the effect of various factors on the degradation, such as particle size and composition, proportion of lead white or binding medium, and the type of drying oil. The colour changes in the test samples are not dramatic; it may be that the smalt used is reasonably durable or that the samples have not been aged for a sufficiently long time.[21] However, the FTIR microscopy and EDX analysis of the artificially aged samples revealed some interesting chemical changes, and the results reported below proved useful in interpreting the results from paintings.[22]

In infrared spectra of glasses, the exact positions and intensities of the bands depend on the composition, but the strongest band, assigned to the asymmetric Si–O–Si stretching vibration, is in the region 1000–1060 cm^{-1}.[23] The symmetric Si–O–Si vibration appears at *c.*780 cm^{-1} and the O–Si–O bending mode in the region 400–500 cm^{-1}. The presence of network modifiers such as K_2O, CaO and Na_2O in the glass results in an additional band at *c.*920 cm^{-1} (Si–O–M vibration, where M is the modifier cation).[24] In smalt, the major asymmetric Si–O–Si band is usually a very broad band at

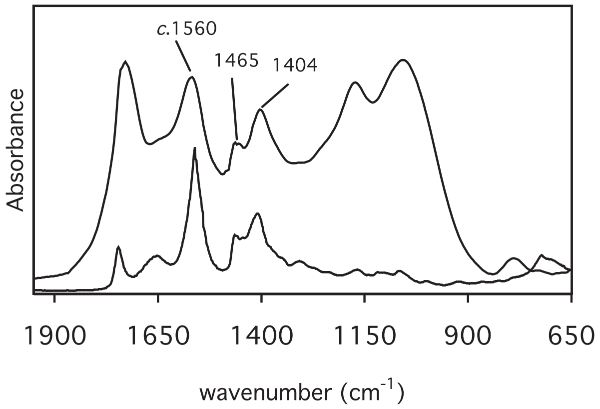


FIG. 1 Infrared spectra (1950–650 cm-1) of: (1) smalt test film exposed to heat and light (upper trace); (2) a standard sample of potassium soaps (prepared by adding KOH to fresh linseed oil, lower trace).

*c.*1040–1080 cm-1 with a shoulder to higher wavenumber (*c.*1160 cm-1). The O–Si–O bend is seen at *c.*460–470 cm-1 and the vibration associated with the symmetric Si–O–Si mode as a broad band at *c.*780–800 cm-1. The Si–O–M band is generally not resolved from the broad band at *c.*1040–1080 cm-1. When glass degrades, leaching of the network modifier cations by water causes the Si–O–M vibration to decrease in intensity and wavenumber. As water diffuses in and becomes incorporated into the structure, bands associated with Si–O–H vibrations and H_2O may develop,[25] and the spectrum begins to resemble that of a hydrated silica gel.[26] Any salts that the leached alkali has formed would also contribute to the infrared spectrum.

The infrared spectra of several of the test samples of pure smalt in oil that had been exposed to heat and light revealed the presence of bands at *c.*1560–1566 and 1404 cm-1 (with a shoulder at *c.*1465 cm-1), in addition to the bands expected for the oil medium and the pigment. These additional bands are most pronounced in the films exposed to both light and heat, but are also present in the films exposed to light at ambient temperature or to heat in the absence of light.[27] These bands match spectra obtained for potassium soap standards (FIG. 1), showing that potassium from the smalt had reacted with fatty acids in the oil. EDX analysis confirmed that potassium had migrated from the pigment into the binding medium.[28]

EDX analysis also detected cobalt in the medium between the pigment particles. It is not possible to determine by FTIR spectroscopy whether cobalt soaps have formed in addition to potassium salts as the band positions are very similar.[29] Moreover, smalt contains much less cobalt than potassium, and cobalt is less easily leached, so very little cobalt soap would be expected to be present. Studies of the formation of lead soaps in paint films, due to reaction of lead-containing pigments with the oil medium, have shown that lead carbonate is also produced, probably as a result of subsequent reaction with CO_2 that has diffused into the paint film from the air.[30] Analogous carbonate formation and other reactions with atmospheric components such as SO_2 could be occurring in smalt films, but as with the cobalt soaps, band overlap in the infrared spectra makes it very difficult to detect the salts that would be expected to form.[31]

The various potassium and cobalt species that might be present have different solubilities. Samples from the films described above that showed the greatest degree of reaction were treated with either water or methanol, with the aim of separating the components; this had the added advantage of removing the interference from the oil and pigment in the infrared spectra.[32] The methanol extract contained some lipid material, but the strongest bands in the infrared spectrum were at 1566 and 1405 cm-1, with a shoulder at 1465 cm-1. EDX analysis showed that only potassium, and no cobalt, was present in the extract, which confirms that the bands in the infrared spectrum are from potassium soaps.[33] Potassium soap bands were also seen in the water extract and again no cobalt was detected by EDX analysis. In addition, highly scattering well-formed acicular crystals containing potassium and sulphur were visible in the back-scattered image in the SEM, embedded in a matrix of potassium soaps. These crystals are probably a potassium sulphate such as arcanite (K_2SO_4), a material found on corroded glass.[34]

Several soluble cobalt and potassium salts were mixed with oil and exposed to the same ageing regime as the other test samples, with the intention of producing potassium and cobalt soaps for comparison.[35] There was no sign of either potassium or cobalt soap formation in the infrared spectra of these samples, perhaps because the environment is not sufficiently alkaline for the salts to react with the oil. When glass degrades, the metal oxides are believed to leach out as hydroxides, creating a sufficiently alkaline environment for hydrolysis of the oil medium.[36] The free carboxylic acid functional groups thus produced could then react with available metal cations and encourage further leaching of cations from the smalt.[37]

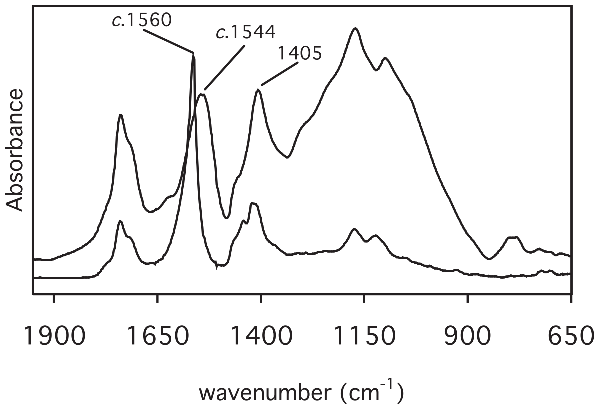


FIG. 2 Infrared spectra (1950–650 cm^{-1}) of: (1) smalt test film over lead white priming exposed to light at 90% RH (upper trace); (2) methanol extractables from the same film (lower trace).

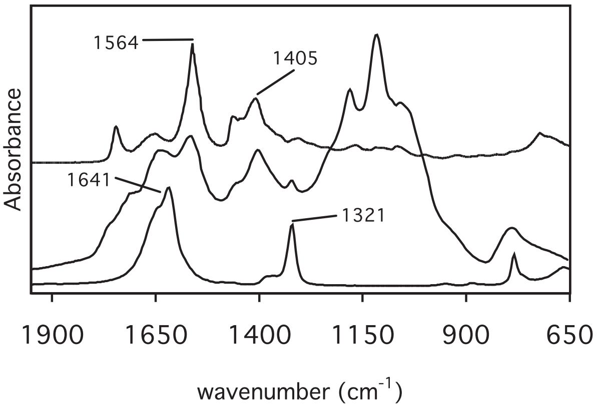


FIG. 3 Infrared spectra (1950–650 cm^{-1}) of: (1) a standard sample of potassium soaps (prepared by adding KOH to fresh linseed oil, upper trace); (2) smalt test film prepared by Plesters in 1964 and subsequently aged naturally (middle trace); (3) a standard sample of calcium oxalate prepared in the laboratory (lower trace).

In one set of test samples the smalt in oil was painted over paper primed with lead white in oil. Again, bands that can be ascribed to metal soaps were seen in the infrared spectrum, particularly in the samples exposed to higher relative humidity,[38] but the asymmetric carboxylate stretch is shifted by about 20 cm^{-1} to c.1544 cm^{-1}. In the methanolic extract from these films, the band appears at c.1560 cm^{-1}, confirming the presence of potassium soaps (FIG. 2). A possible explanation for the shift in the band is that other metal carboxylates are also present. These are likely to be lead soaps, since Pb as well as K was detected by EDX in the matrix between the pigment particles in the smalt layer.[39] This is significant because the test film did not initially contain any lead; it must instead have migrated (possibly as lead soaps) from the lead white priming.[40]

Smalt films prepared by Joyce Plesters in the 1960s which have aged naturally for the last forty years were also examined.[41] Although there is no record of their original colour, these samples are rather brown and have therefore almost certainly degraded. They have also accumulated much surface dirt, and seem to have developed a surface crust. FTIR microscopy and EDX analysis again suggested that potassium soaps had formed (1564, 1460 and 1403 cm^{-1}), but in these older samples further bands were seen that correspond to calcium oxalate (1641 and 1321 cm^{-1}), a material commonly mentioned in the context of glass corrosion and degradation of many types of works of art (FIG. 3).[42] EDX analysis also demonstrates the presence of other salts containing combinations of K and S (perhaps arcanite), or K, S and Na, or K, Na, P, Al, Si, S, and Cl. Particles of these types have been reported on naturally aged glass where, as in this sample, it is not always possible to identify the exact compounds present.[43]

The results from the test samples are reasonably consistent. They demonstrate the formation of potassium soaps by reaction of the oil binder with smalt. Other salts were also seen in some of the samples, notably what appears to be a potassium sulphate and, in the most aged samples, calcium oxalate. The combination of oxalate and potassium soaps in the same sample gives an infrared spectrum with bands at both c.1560 and c.1640 cm^{-1}. Two of the amide bands of proteins occur in the same positions, so an accurate assignment of the spectrum is crucial to avoid misidentification of the binding medium. This pattern of bands was seen in test films containing only degraded smalt and linseed oil, confirming that they can arise simply from the interaction of the smalt with the medium or the environment, and in the absence of proteinaceous components.

Analysis of degraded smalt from National Gallery paintings

In *The Conversion of the Magdalen* (NG 1241), attributed to Pedro Campaña, the cloak of the figure of Christ is painted with smalt. The pigment has lost its colour entirely, and the paint now appears yellowish brown as a result of discoloration of the binding medium (PLATE 1). In the cross-section of Christ's cloak, there is no sign of any blue

PLATE 1 Attributed to Pedro Campaña, *The Conversion of the Magdalen* (NG 1241). Detail showing the figure of Christ.

colour and it is difficult to see the smalt particles (PLATE 2). Under ultraviolet light, however, the typical jagged shape of the glass particles is visible (PLATE 3). FIGS 4a–d illustrate the back-scattered image of this cross-section in the SEM, together with maps for silicon, potassium and cobalt. The silicon map and the back-scattered image help to locate the smalt particles, which are 6–15 microns in size. In the potassium map it can be seen that only one of the smalt particles contains enough potassium to register clearly in the map, demonstrating that it has been leached from the pigment. Even in this particle the potassium is confined to the centre and is depleted in the rim. There is also potassium in the matrix between the pigment particles and a line of potassium at the surface of the paint sample, which is likely to have migrated from the smalt particles. The quantitative analysis results in Table 1 (see p. 70) illustrate the degree of depletion of potassium in the degraded particles; the centre of the well-preserved particle, which has a greyish-blue colour, contains around 14 wt% K_2O, while the deteriorated particles, which are all colourless, contain only 1–2%. There are a few cobalt-rich areas, visible in the cobalt map, in the crust on the surface of the paint, and spot spectra of these show that nickel is also present, which is a common impurity in the cobalt ore from which smalt was manufactured. The glass literature, surveyed above, states that transition metals in the glass can also be leached out when the degradation is severe, and this appears to have happened here. However, in the smalt in the other paintings in this study, only potassium had leached to any appreciable extent, and the smalt in the Campaña appears to be exceptionally deteriorated.

The grey paint of the trees in the background landscape of Gainsborough's *John Plampin* (NG 5984) consists of smalt mixed with a small amount of Naples yellow and lead white. In a cross-section of a sample from one of the trees, the smalt particles still retain some blue colour, although the hue is rather dull and greyish (PLATE 4). Here it is difficult to determine whether the smalt has deteriorated or whether it was always a dull colour. However, as in the painting by Campaña, the EDX analysis reveals that there is potassium in the matrix between the pigment particles as well as in a crust on the surface and, while some smalt particles contain 12–15 wt% K_2O, others contain only 4–7% (Table 1). Leaching

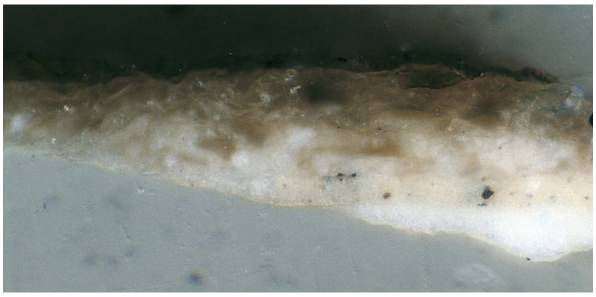


PLATE 2 Attributed to Pedro Campaña (NG 1241). Cross-section from the yellow-brown paint of Christ's cloak showing several layers containing smalt mixed with different proportions of lead white. Photographed at a magnification of 450×; actual magnification 400×.

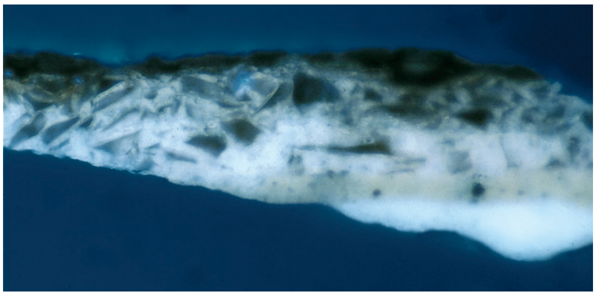
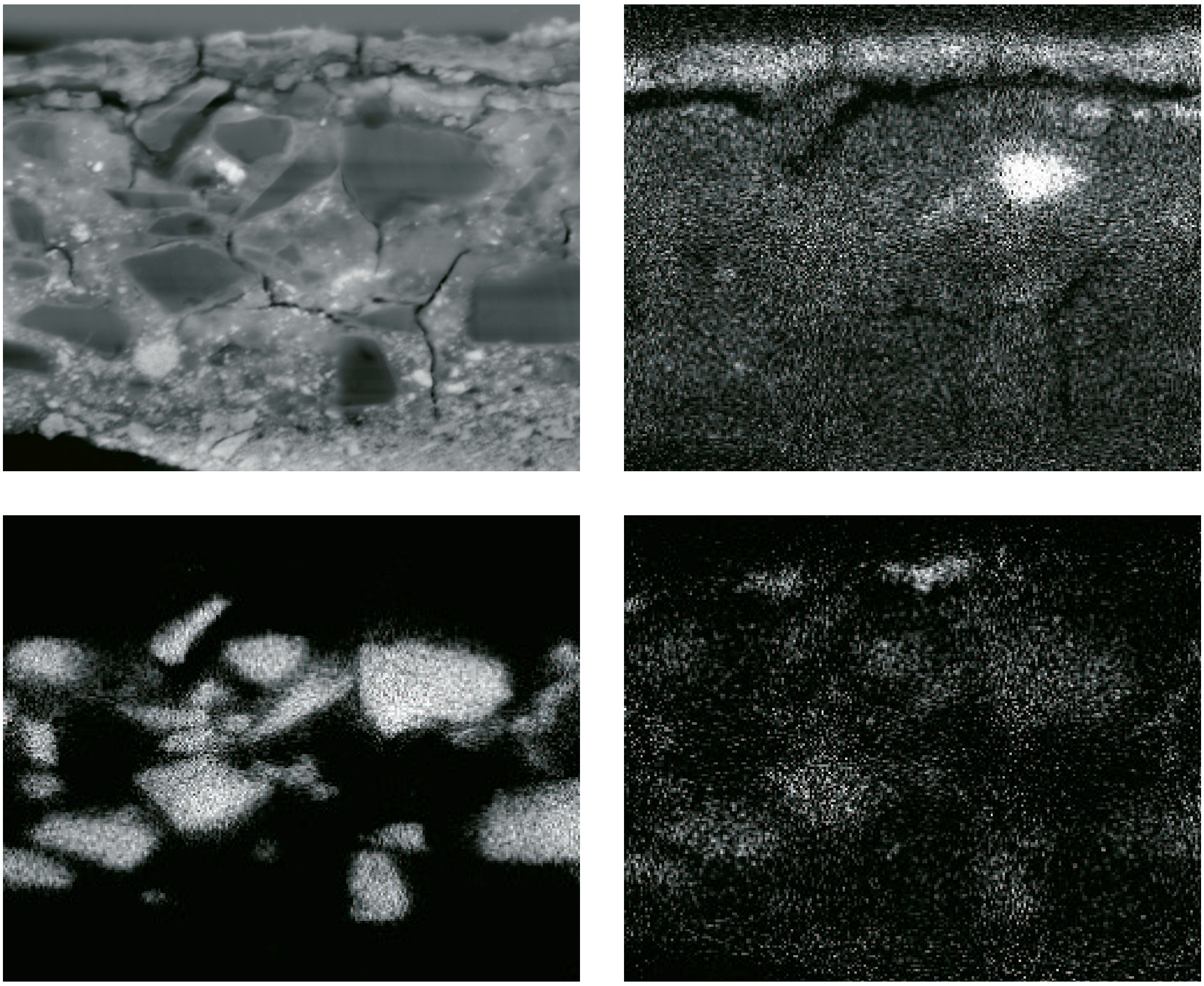


PLATE 3 Attributed to Pedro Campaña (NG 1241). Cross-section in PLATE 2 under ultraviolet light.



FIGS 4a–d Back-scattered image of part of the cross-section in PLATES 2 and 3 (*upper left*), with EDX maps for silicon (*lower left*), potassium (*upper right*) and cobalt (*lower right*).

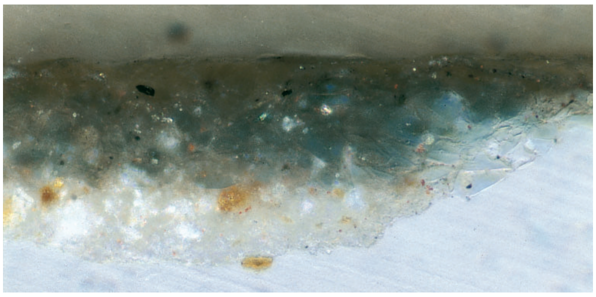


PLATE 4 Thomas Gainsborough, *John Plampin* (NG 5984). Cross-section from the dark grey trees in the distant background landscape. The uppermost paint layer consists of bluish-grey smalt mixed with a small amount of lead white, Naples yellow, vermilion and black. Photographed at a magnification of 500×; actual magnification 440×.

of potassium has occurred and the smalt is therefore degraded, although to a lesser degree than in the painting by Campaña.

The sky in Paolo Fiammingo's *The Sons of Boreas pursuing the Harpies* (NG 5467) is also painted with smalt that has degraded. The EDX maps of a cross-section from the sky (PLATE 5 and FIGS 5a–c) demonstrate clearly the relationship between the potassium content and colour. The EDX map of silicon reveals that the lower layer, which appears yellow, contains discoloured smalt. In the potassium map, only the particles which appear blue still contain potassium, and these are all in the uppermost layer where the smalt is mixed with more lead white. The lead white appears to have protected the smalt from discoloration; it may be that it inhibits the leaching by reacting with the oil itself, or it could be that the paint in the upper layer is less medium rich. Again, the quantitative results (see Table 1) show a considerable difference in the potassium levels of the particles; 13–14 wt% in the well-preserved smalt in the upper layer compared to only around 2% in the degraded particles in the lower layer. Clearly, light is not the primary factor in the degradation of smalt.

Reliable quantitative analysis of smalt pigment

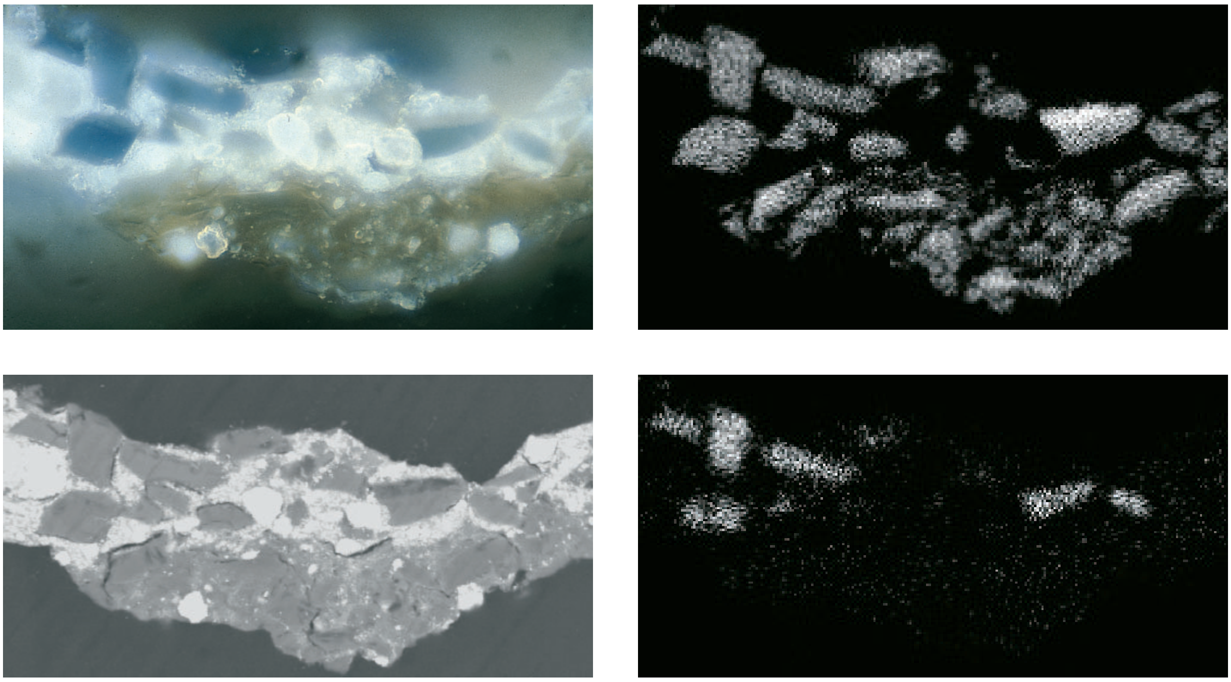


PLATE 5 Paolo Fiammingo, *The Sons of Boreas pursuing the Harpies* (NG 5467), 1592–6. Cross-section from the greenish-grey paint of the sky (*upper left*). The lowest layer in the cross-section, which appears a translucent yellow, contains smalt alone. In the upper layer smalt is mixed with lead white and retains a strong blue colour. Photographed at a magnification of 750×; actual magnification 650×. FIGS 5a–c Back-scattered image of the cross-section in PLATE 5 (*lower left*), with EDX maps for silicon (*upper right*) and potassium (*lower right*).

particles is a challenge, because of their small size and because they are usually intimately mixed with other pigments in the paint. In each cross-section, a series of particles which contained enough potassium to register in the EDX map was analysed, followed by a series in which very little potassium could be seen, to compare the composition of well-preserved and degraded smalt in the same paint. Where possible, the largest smalt particles were chosen for analysis, to minimise the contribution of other pigments in the paint. The accuracy of the analysis was assessed by comparing the results with those for a standard sample of Corning Glass D of known composition that was analysed under the same conditions.[44] A range of values is given in Table 1 because the colourless particles show different degrees of deterioration, and therefore vary in potassium content. The analysis of the well-preserved particles in each cross-section gives some idea of the original bulk composition of the smalt.[45] A range of values is also quoted for the well-preserved glass, because it is conceivable that even where the smalt is still blue some deterioration may have occurred. Generally the well-preserved smalt in the samples is rich in potassium (10–15 wt% K_2O) and contains almost no other alkali and alkaline earth ions. The cobalt levels are variable; in several samples cobalt was detected at 7–9 wt%, but lower levels of around 3% were quite common, which would produce a paler variety of smalt.[46] The arsenic, which is associated with the cobalt ore, is at notably high levels in all the samples, often equal to or greater than the cobalt levels. It is thought that the cobalt ore was roasted before use to remove the arsenic, but the high levels suggest that this was not done thoroughly, if at all.[47]

In Pieter Bruegel's *Adoration of the Kings* (NG 3556), the smalt in the Virgin's robe is remarkably well preserved, while the smalt in the sky is badly degraded and almost completely colourless. The two smalts appear to be of different composition; that in the Virgin's robe contains a relatively high proportion of calcium (3–4.5 wt%), which may explain its good state, although it also differs in that it contains less arsenic and bismuth. It is difficult, however, to predict the durability of the glass from the composition alone, and other factors, such as the proportion of lead white in the paint or particle size may be more significant.[48] Both the degraded and the well-preserved smalt in this painting were high in cobalt, at between 6 and 9 wt%. As very little cobalt is needed to give glass a blue colour, this level would give a very dark almost black colour to the bulk glass, but this intensity of colour would be necessary to give a strong blue colour when the glass is crushed to prepare the pigment.[49]

The smalt in *The Nativity* (NG 297.1) by Romanino is unusual in that it is a soda glass rather than a potash glass, containing around 11 wt% Na_2O, with low levels of potassium and calcium.[50] A few other examples of sodium-containing smalt have been published, but they seem to be rather rare.[51] Generally, soda glass is more durable, and in the cross-section from the Virgin's robe it can be seen that the smalt particles retain their colour. The paint as a whole, however, has a dark brown colour and is also severely cracked. The quantitative results (Table 1) suggest that some leaching of alkali ions (particularly sodium) has taken place, perhaps enough to cause discoloration of the oil medium, but not enough to cause a loss of colour in the smalt particles themselves.[52]

In the painting by Romanino, the smalt layer is applied over a layer of azurite, even though azurite was generally more expensive than smalt; usually a cheaper blue was used in the underpaint. The same layer structure was found in the sky paint of Parmigianino's *Portrait of a Man* (NG 6441), which is now a greyish-brown colour. The quantitative analysis for this painting in Table 1 is for degraded smalt particles only, because no well-preserved particles were seen in the cross-section that was analysed.

The elements arsenic, nickel, iron and bismuth, found in all the smalt samples, originate from the cobalt ore used to colour the glass, and reflect the geographical location of the cobalt ore deposit. Studies on blue glasses, glazes and enamels dating from the Bronze Age to the eighteenth century have identified four patterns of trace elements, which relate to particular geographical sources of the ore.[53] The paintings examined here date from the sixteenth to the eighteenth century. The studies of blue glass found that during this period only one type of ore was used, which contained Co, As, Fe, Ni and Bi. Our results from paintings also found only this pattern of cobalt ore impurities (see Table 1), in agreement with a recent study of the impurities in smalt on eleven polychrome sculptures of the same period.[54]

PLATE 6 Joachim Beuckelaer, *The Four Elements*: *Air* (NG 6587), 1570. Detail of the girl at the left of the painting.

PLATE 7 Joachim Beuckelaer, *The Four Elements*: *Air* (NG 6587). Macrophotograph of the girl's sleeve.

In Joachim Beuckelaer's series of paintings of *The Four Elements* there are many areas of severely degraded smalt, which have drastically altered the tonality of the paintings.[55] The smalt is often used in layers and mixtures with red lake, with the intention of producing a subtle range of shades of purple and blue, which have now been completely lost. For example, in the painting representing *Air* (NG 6587, PLATE 6), brushstrokes of smalt have been applied over a red layer in both the waistband and sleeves of the woman on the left. In the detail of the sleeve (PLATE 7), there are a few strokes that still retain a pale blue colour, but most of the cream-coloured strokes also contain smalt and must originally have been blue. In PLATE 8, showing a paint sample from the sleeve, the surface appears lighter and rather opaque, as if the binding medium has disintegrated, or some kind of crust has formed. In a cross-section

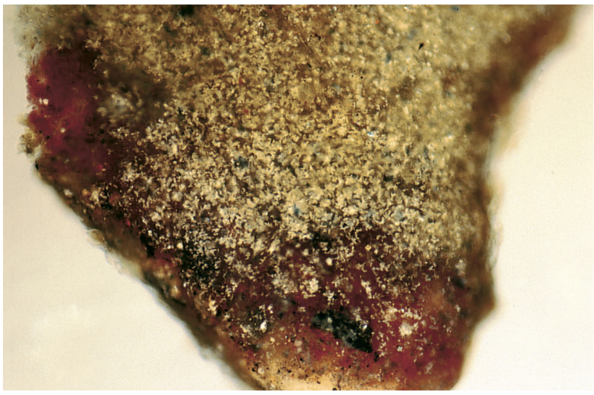


PLATE 8 Joachim Beuckelaer, *The Four Elements*: *Air* (NG 6587). Sample from the girl's sleeve, showing the deteriorated opacified surface of the paint. The uppermost layer consists of smalt, applied over a layer of red lake. Photographed at a magnification of 100×; actual magnification 90×.

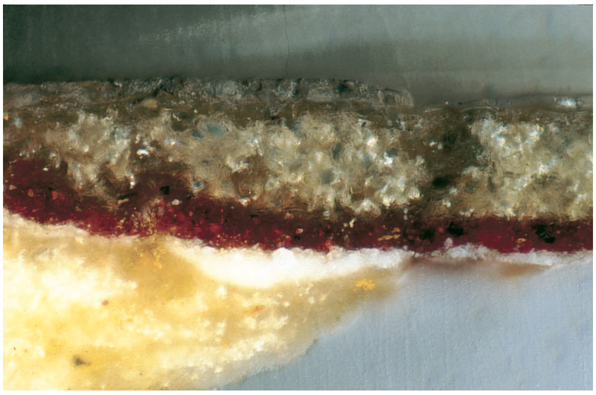


PLATE 9 Joachim Beuckelaer, *The Four Elements*: *Air* (NG 6587). Cross-section of the paint sample in PLATE 8. The uppermost layer, containing smalt, is very degraded. There are lighter patches in the layer, not because it contains lead white, but because the layer is very degraded. Photographed at a magnification of 500×; actual magnification 440×.

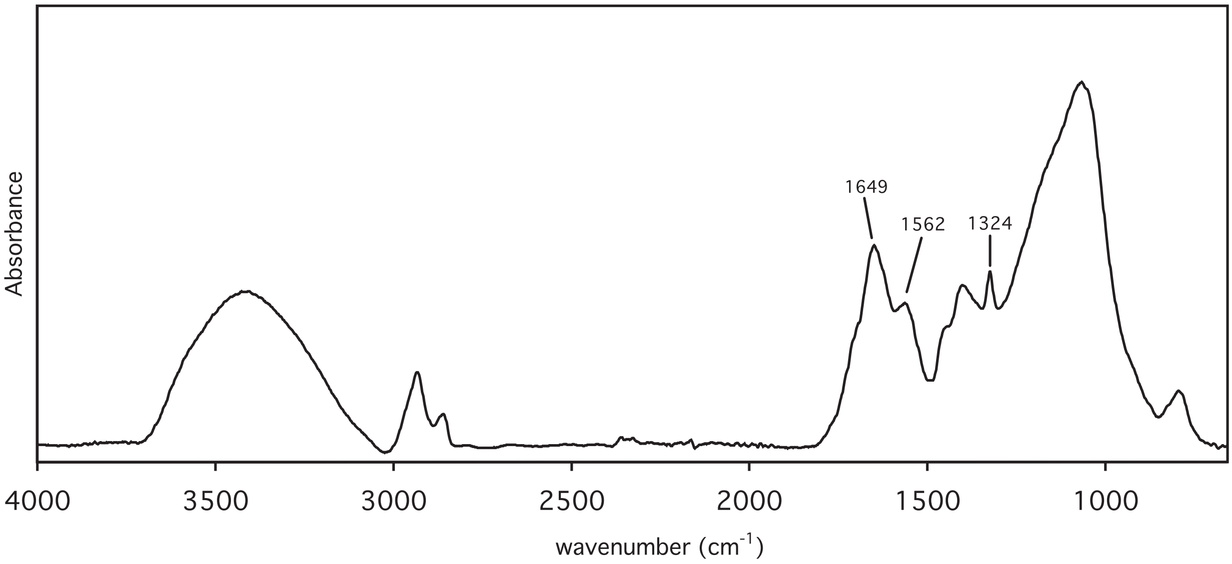


FIG. 6 Joachim Beuckelaer, *The Four Elements*: *Fire* (NG 6588). Infrared spectrum (4000–650 cm^{-1}) of the discoloured smalt layer in the beige apron of the girl.

of the sample (PLATE 9) a few particles of smalt that are still blue are visible, but again the paint layer appears very disrupted.

As in the other paintings examined, EDX analysis of a sample from the painting by Beuckelaer demonstrated that potassium has been leached from the smalt. It was also quite clear that the binding medium has altered. FTIR microscopy was carried out on a number of samples of degraded smalt from Beuckelaer's series of paintings, to investigate whether there was any evidence that potassium soaps, or other potassium salts, had formed. In several samples a band was present at 1562 cm^{-1}, which can be assigned to the asymmetric stretch of potassium soaps, demonstrating that in real paint samples, as well as in the test samples discussed earlier, leached potassium from degraded smalt reacts with carboxylic acids in the oil. The infrared spectrum illustrated in FIG. 6 is from a sample from the beige apron of the woman at the left of *Fire* (NG 6588). Here a smalt layer was painted over a layer of red lake, so that the apron was, presumably, originally a purplish-blue colour. As well as the peaks from potassium soaps, there are peaks at 1649 and 1324 cm^{-1} which can be ascribed to calcium oxalate; this was also seen (at low levels) in the oldest of the test samples and has, as mentioned above, been found in crusts on the surface of

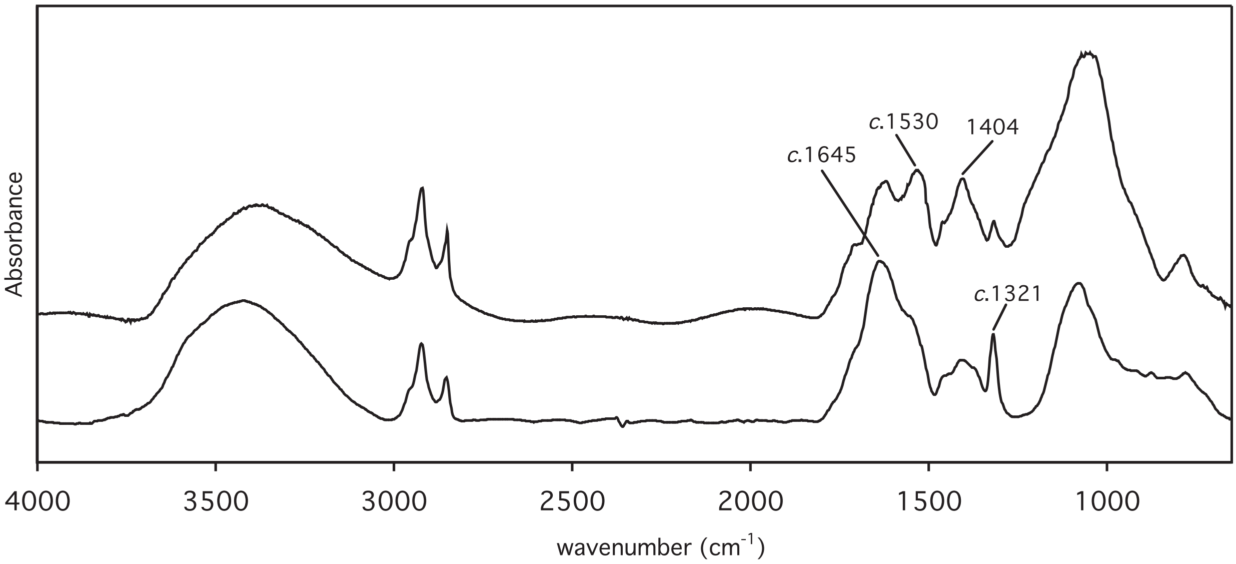


FIG. 7 Attributed to Pedro Campaña (NG 1241). Infrared spectra (4000–650 cm^{-1}) of: (1) a sample from Christ's yellow cloak (upper trace); (2) the surface layer over the cloak (lower trace), showing a strong peak for the symmetric oxalate stretch at *c.*1320 cm^{-1}.

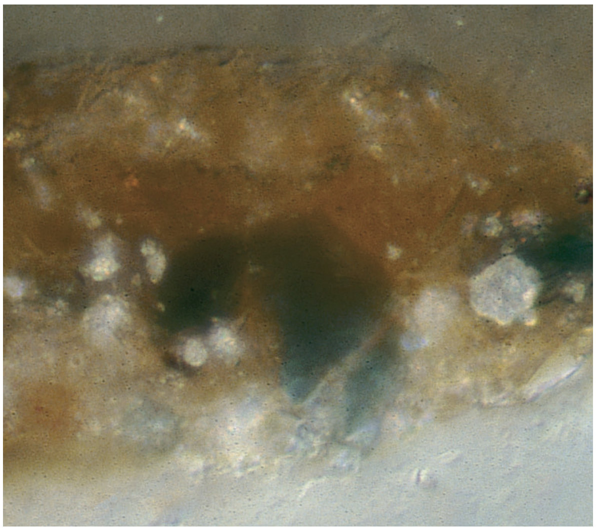


PLATE 10 Joachim Beuckelaer, *The Four Elements: Water* (NG 6586). Cross-section from the beige paint of the girl's apron. Two large smalt particles retain a blue colour, while the rest of the smalt is completely degraded. Photographed at a magnification of 500×; actual magnification 1150×.

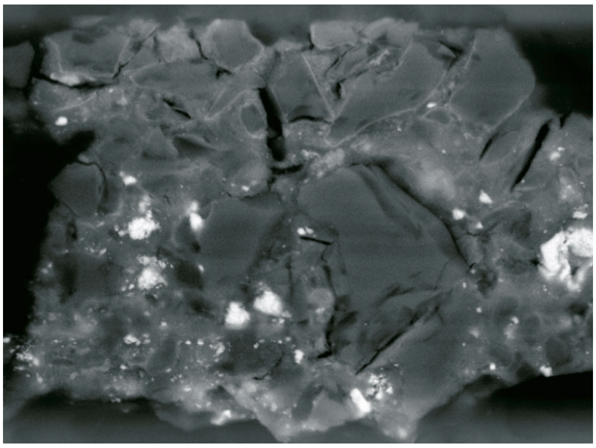


FIG. 8 Back-scattered image of the cross-section in PLATE 10. There are lighter lead-rich rims around all the smalt particles except the two large well-preserved particles which are still blue.

degraded glass. Where the crust on the surface of the paint was analysed separately from the bulk of the paint, the proportion of oxalate was generally found to be higher and associated with gypsum, and was therefore rather similar to the crusts found on the surface of glass.[56]

As in the samples from the paintings by Beuckelaer, broad bands were observed at around 1560–70 and 1410 cm^{-1} in the infrared spectra of the samples from all the other paintings examined using FTIR microscopy (Table 1). In some examples these bands are of fairly low intensity but in others the bands are quite pronounced and the shoulder at *c.*1465 cm^{-1} can be resolved. In the majority of the samples, calcium oxalate was also seen, particularly near the surface of the paint (FIG. 7, lower trace). Occasionally, calcium carbonate could be detected in the crust (FIG. 7), but generally band overlap made it impossible to determine whether other salts such as sulphates were present.

In a few cases, the asymmetric carboxylate band is shifted to *c.*1530 cm^{-1} (FIG. 7), suggesting the presence of both lead and potassium soaps, as seen in the test samples that were painted over lead white (Campaña NG 1241, Gainsborough NG 5984 and

Parmigianino NG 6441). Lead in conjunction with potassium was detected by EDX in both the bulk of the paint and the surface crust of all three of these paintings. Another phenomenon relating to the presence of lead in the smalt paint films was seen in the painting attributed to Campaña and in a sample from the beige paint of the girl's apron in Beuckelaer's *Water* (NG 6586), where the smalt particles can be seen in the back-scattered image to have lead-rich rims. In the sample from the Beuckelaer it is clear that this effect is associated with the deterioration, since it is not seen around two large well-preserved particles (PLATE 10, FIG. 8). Enrichment of the surface of a glass with lead (even when the glass did not originally contain lead) has been reported in glass buried in an environment where there was lead in the soil, perhaps a similar effect to that seen in these paint samples.[57]

Conclusion

When smalt pigment in oil degrades, potassium is leached from the glass, as observed in all the paintings in this study and shown by quantitative analysis. The potassium has not only migrated into the matrix between the pigment particles but has made its way to the paint surface. In the painting attributed to Campaña, where the smalt was particularly degraded, cobalt and nickel were also found to have leached from the glass and migrated to the surface. FTIR microscopy demonstrated that potassium soaps are present in all the samples from paintings containing degraded smalt. Some calcium oxalate was also seen in many of the samples, particularly in the crusts that had formed on the surface of the paint, which are similar in composition to crusts reported in the literature on the surface of degraded glass.

The infrared spectra of artificially aged test samples of smalt showed bands which can be ascribed to potassium soaps and, in the most aged samples, calcium oxalate at *c*.1560 and *c*.1640 cm^{-1} respectively. Analysis of the methanol and water extracts, which separated the soaps from the oxalate, confirmed the assignment of the infrared peaks. It was important to demonstrate that these bands arise from interaction of the oil with the pigment, since they are in the same region as two of the amide vibrations of proteins, and might otherwise be interpreted as an indication of the addition of a proteinaceous component such as egg or glue to the paint. This is particularly significant for blue pigments, since some historical documentary sources suggest grinding smalt or other blues in egg yolk or glue before grinding with drying oil, to improve the working properties.[60]

The smalt pigment does not simply lose its colour when it degrades, but causes chemical and physical changes in the paint film. As well as forming soaps, alkaline material from the degrading smalt can cause darkening of the oil medium, which gives certain smalt paint films their characteristic grey-brown appearance. The chemical changes that this study has revealed could account for the physical changes that occur in smalt films. The loss of a large amount of alkali and other cations alters the surface of the glass particles, changing the nature of the pigment–medium interface; soaps and salts are formed in the medium surrounding the particles, and migration of metal ions to the surface of the paint creates crusts that can be further modified by reaction with the environment. The action of solvents used in cleaning and fluctuations in the environment, particularly the relative humidity, could further alter the vulnerable and hygroscopic salts in the crust. All the changes caused by deterioration could disrupt the physical integrity of the paint film, and may begin to explain the blanched and disintegrated appearance of discoloured smalt in paintings.

Acknowledgements

In addition to our colleagues in the scientific and conservation departments, we are grateful to Joanne Russell for her help with FTIR microscopy and to Emma Richardson for preparing various cobalt, potassium and calcium salts for use as standards. We would also like to thank Ian Freestone (Cardiff University) for useful advice on the quantitative analysis of glass, and for helping us find our way through the extensive glass literature. Mikkel Scharff and Bent Eshøj at the school of conservation at the Royal Danish Academy of Fine Arts, and the Danish State Workshop for Arts and Crafts made it possible for one of the authors (DS) to use the weatherometer to age smalt samples, while on sabbatical leave.

Notes and references

1 Until recently it has been thought that smalt was introduced as a pigment in paintings around the end of the fifteenth century. Recent research has shown that it was being used much earlier, although it was most common in the sixteenth and seventeenth centuries. See H. Stege, 'Out of the Blue? Considerations of the early use of smalt as blue pigment in European easel painting', *Zeitschrift für Kunsttechnologie und Konservierung*, 18, 2004, pp. 121–42. M. Richter, 'Smalt in Polychromy and Painting of German-Speaking Countries. Study on the History, Technical Sources and Composition', *Historical Polychromy. Polychrome Sculpture in Germany and Japan*, eds M. Kühlenthal and S. Miura, Munich 2004, pp. 175–203. B. Mühlethaler and J. Thissen, 'Smalt', *Artists' Pigments. A Handbook of Their History and Characteristics*, vol. 2, ed. A. Roy, Washington 1993, pp. 113–30.

2 J. Plesters, 'A Preliminary Note on the Incidence of Discolouration of Smalt in Oil Media', *Studies in Conservation*, 14, 1969, pp. 62–74.

3 H. Paschinger and H. Richard, 'Blaupigmente der Renaissance und Barockzeit in Österreich', *Naturwissenschaften in der Kunst*, Vienna 1995, pp. 63–6. M. Spring, N. Penny, R. White and M. Wyld, 'Colour Change in *The Conversion of the Magdalen* attributed to Pedro Campaña', *National Gallery Technical Bulletin*, 22, 2001, pp. 54–63. J.J. Boon, K. Keune, J. van der Weerd, M. Geldof and J.R.J. van Asperen de Boer, 'Imaging microspectroscopic secondary ion mass spectrometric and electron microscopic studies on discoloured and partially discoloured smalt in cross-sections of 16th century paintings', *Chimia*, 55, 2001, pp. 952–60.

4 G. Woisetschläger, M. Dutz, S. Paul and M. Schreiner, 'Weathering Phenomena on Naturally Weathered Potash-Lime-Silica-Glass with Medieval Composition. Studies by Secondary Electron Microscopy and Energy Dispersive Microanalysis', *Microchimica Acta*, 135, 2000, pp. 121–30. I.C. Freestone, 'Post-depositional Changes in Archeological Ceramics and Glasses', *Handbook of Archeological Sciences*, eds D.R. Brothwell and A.M. Pollard, Chichester 2001, pp. 615–25. R. Newton, 'Deterioration of Glass', in R. Newton and S. Davison, *Conservation of Glass*, Cambridge 1989, pp. 135–64.

5 Woisetschläger et al. 2000 (cited in note 4).

6 R.A. Lefèvre, A. Chabas and I. Munier, 'Modern and Ancient Glass in the Polluted Atmosphere: What is the Prevailing Phenomenon? Leaching, Corrosion, Soiling, Encrusting…?', *Art 2002. 7th International Conference on Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, June 2002, Antwerp. Proceedings*, eds R. Van Grieken, K. Janssens, L. Van't dack and G. Meersman, Antwerp 2002, unpaginated.

7 R. Drewello and R. Weissman, 'Microbially influenced corrosion of glass', *Applied Microbiology and Biotechnology*, 47, 1997, pp. 337–46. Medieval glass is said to be particularly prone to microbial growth because of the high K and Ca content of the glass, and because the low durability means that they are readily released. The degree of microbial growth on the surface can also be increased by the presence of certain metal ions; for example more microbial growth was found on pink stained-glass windows, ascribed to the presence of manganese in the glass.

8 Lefèvre et al. 2002 (cited in note 6).

9 J. Sterpenich, 'Cristallochemie des produits d'altération des vitraux médiévaux: application au vieillissement des déchets vitrifiés', *Bulletin of Engineering, Geology and the Environment*, 61, 2002, pp. 179–93. Freestone 2000 (cited in note 4). R. Procházka, V. Goliás, I. Hlásensky, L. Strnad and J. Lněničková, 'Natural corrosion of old potash glass coloured with uranium compounds', *Ceramics – Silikáty*, 46, 2002, pp. 86–96. In this last study, the uranium in the glass, which is more firmly bound than alkali ions, was found to have been redistributed and concentrated in the corroded surface.

10 Woisetschläger et al. 2000 (cited in note 4). The instability is due to K being more easily leached from the glass than Na. See also L.L. Hench, R.G. Newton and S. Bernstein, 'Use of infrared reflection spectroscopy in analysis of durability of medieval glasses, with some comments on conservation procedures', *Glass Technology*, 20, 1979, pp. 144–8. Glass containing around 10 mol% K_2O is reported to be fairly durable, while that with 17 mol% K_2O is not.

11 Newton 1989 (cited in note 4). The relationship between composition and stability is complicated. For example, the addition of lime (CaO) increases the resistance of the glass to the action of water up to a level of 10 mol%, but above 15 mol% the stability has been found to be decreased. The effect of different transition metal ions is also very complex and difficult to predict.

12 T.M. El-Shamy, 'The chemical durability of K_2O–CaO–MgO–SiO_2 glasses', *Physics and Chemistry of Glasses*, 14, 1973, pp. 1–5. Freestone 2000 (cited in note 4). The addition of lime (CaO) to a glass made using a potassium-rich ash can make the glass less water-sensitive, as discussed earlier. In Austrian medieval glasses, however, the proportion of CaO and K_2O has been found to be so high that the SiO_2 content can be as low as 40 wt%, and the glass is highly prone to deterioration. See M. Schreiner, 'Analytical Investigations of Medieval Glass Paintings', *Recent Advances in the Conservation and Analysis of Artifacts, Jubilee Conservation Conference Papers*, compiled by J. Black, London 1987, pp. 73–80.

13 Mühlethaler and Thissen 1993 (cited in note 1). I.C. Freestone and V. Tatton-Brown, 'The Bonus Eventus Plaque: Changing Materials, Changing Perceptions', *Annales du 16e Congrès de l'Association Internationale pour l'Histoire du Verre, London 2003*, in press, to be published 2005.

14 Mühlethaler and Thissen 1993 (cited in note 1). Boon et al. 2001 (cited in note 3).

15 A.R. Burnstock, C.G. Jones and A.D. Ball, 'Morphology of the Blue Artist's Pigment Smalt using Scanning Electron Microscopy', in *Art 2002* (cited in note 6).

16 Procházka et al. 2002 (cited in note 9). Here loss of around 14 wt% K_2O has been shown to have caused contraction of the glass.

17 Freestone 2000 (cited in note 4) discusses pitting caused by salts on the surface of the glass creating an alkaline micro-environment. Burnstock et al. 2002 (cited in note 15) report scaling and surface roughness (visible in SEM images) on degraded smalt particles.

18 In paint films where lead-containing pigments have reacted with the oil binding medium to form lead soaps, lead carbonate has also been found, possibly formed by reaction with CO_2 that has diffused into the paint film. An analogous process might occur with potassium soaps. See C. Higgitt, M. Spring and D. Saunders, 'Pigment-medium Interactions in Oil Paint Films containing Red Lead or Lead-tin Yellow', *National Gallery Technical Bulletin*, 24, 2003, pp. 75–95.

19 See Procházka et al. 2002 (cited in note 9) where lead was found concentrated in the corroded layer on buried uranium glass, despite the fact that it was not one of the components of the glass itself. It was concluded that lead released from lead glass nearby in the soil had migrated and become incorporated in the crust on the uranium glass. This illustrates the complex interactions of the various metal ions present that can occur. See also Sterpenich 2002 (cited in note 9) where it is reported that small quantities of palmierite ($K_2Pb(SO_4)_2$), as well as anglesite ($PbSO_4$) and lead phosphate, are present in the crust on the surface of medieval window glass.

20 Three types of smalt were used in these experiments: smalt light and smalt dark supplied by L. Cornelissen and Son, 105 Great Russell Street, London, and Kremer Pigmente 10010 fine grade smalt, 0–80 micron diameter, supplied by A.P. Fitzpatrick, 142 Cambridge Heath Road, London. Quantitative analysis of Cornelissen smalt light gave the following results: 65 wt% SiO_2, 22 wt% K_2O, 12 wt% CoO, 0.5 wt% Al_2O_3. Kremer 10010 smalt showed 77 wt% SiO_2, 16 wt% K_2O, 6.5 wt% CoO, 0.2 wt% Al_2O_3. Although fairly high in cobalt, the Cornelissen smalts are not too dissimilar from the smalt found in paintings. The Kremer 10010 smalt is lower in cobalt, but has rather high silicon levels, which may mean that it is more durable than is typical. However, the relationship between composition and durability is complex.

21 Although several of the samples were light aged for the equivalent of around 350 years under museum lighting conditions, the heat ageing equated to only approximately twenty years at ambient temperature.

22 The results of these on-going experiments will be the subject of another paper.

23 S. Parke, 'Glasses', *The Infrared Spectra of Minerals*, *Mineralogical Society Monograph* 4, Chapter 21, pp. 483–514, ed. V.C. Farmer, London 1974, esp. pp. 486–9; Hench et al. 1979 (cited in note 10); G.I. Cooper, G.A. Cox and R.N. Perutz, 'Infra-red microspectroscopy as a complementary technique to electron-probe microanalysis for the investigation of natural corrosion on potash glass', *Journal of Microscopy*, 170, 1993, pp. 111–18. There is a shoulder at higher wavenumber (*c.*1170 cm^{-1}).

24 See Hench et al. 1979 (cited in note 10); Cooper et al. 1993 and Parke 1974 (both cited in note 23).

25 The infrared bands linked to the presence of Si–OH groups are seen at *c.*3400–3700 ν(SiO–H), *c.*1570–1630 δ(H_2O) and *c.*950 ν(Si–OH) cm^{-1}, see Cooper et al. 1993 and Parke 1974 (both cited in note 23), and H.H.W. Moenke, 'Silica, the three-dimensional silicates, borosilicates

and beryllium silicates', *The Infrared Spectra of Minerals*, *Mineralogical Society Monograph* 4, ed. V.C. Farmer, London 1974, pp. 365–82 and esp. pp. 365–70.

26 Moenke 1974 (cited in note 25) and Parke 1974 (cited in note 23).

27 Cornelissen smalt light or smalt dark was ground in cold pressed linseed oil (Kremer Pigmente) and painted onto an inert substrate. Two sets of samples were stored in the dark at 30 or 60 °C, and two further sets exposed to a light dose of 576 Mlux hours at either 30 or 60 °C in an Atlas Xenon Arc Weatherometer at the Konservatorskolen in Copenhagen; in all cases the relative humidity was maintained at 55%. The Xenon light source was filtered to provide a power spectrum equivalent to daylight through window glass.

28 The precise band positions observed for metal soaps are dependent on the nature of the carboxylate anion, the reaction conditions, reaction stoichiometry and the degree of hydration. A number of phases appear to be possible, even with simple soaps (where there is a single type of free fatty acid as the anion). In smalt-oil films, saturated or unsaturated, mono- or dicarboxylic fatty acids could react. Complex anions can be involved – from simple pairs of cross-linked free fatty acids to complex structures involving both C–C or C–O cross-linkages and potentially also glycosidic or ionic linkages (see J.J. Boon, S.L. Peulvé, O.F. van den Brink, M.C. Duurma and D. Rainford, 'Molecular aspects of mobile and stationary phases in ageing tempera and oil paint films', *Early Italian Paintings: Techniques and Analysis*, Symposium, Maastricht 1996, eds T. Bakkenist, R. Hoppenbrouwers and H. Dubois, Maastricht 1996, pp. 35–56 for discussion of ionomers). A mixture of potassium soaps is likely to be present, each with subtly different infrared absorption bands, explaining why broader bands are observed in the infrared spectra than are seen, for example, in lead soap inclusions (see Higgitt et al. 2003 (cited in note 18)). The spectrum obtained when KOH was added to linseed oil (three major broad bands at *c.*1560, 1465 and 1410 cm^{-1}) is a more appropriate comparison than spectra for individual simple soaps such as potassium palmitate. Furthermore, certain potassium soap phases are hygroscopic and can form acid soaps. M.N.G. de Mul, H.T. Davis, D.F. Evans, A.V. Bhave and J.R. Wagner, 'Solution Phase Behavior and Solid Phase Structure of Long-Chain Sodium Soap Mixtures', *Langmuir*, 16, 2000, pp. 8276–84; M.L. Lynch, F. Wireko, M. Tarek and M. Klein, 'Intermolecular Interactions and the Structure of Fatty Acid-Soap Crystals', *Journal of Physical Chemistry B*, 105, 2001, pp. 552–61; M.V. García, M.I. Redondo and J.A.R. Cheda, 'Temperature dependence of the vibrational spectra of potassium soaps: Fourier transform infrared study', *Vibrational Spectroscopy*, 6, 1994, pp. 301–8.

29 As discussed in note 28, precise band positions depend on the carboxylic acid, reaction conditions and stoichiometries involved. Cobalt soaps are expected to show infrared bands at around 1542 ν_a(COO), 1470 $\delta(CH_2)$, 1414 ν_s(COO), 723 $\rho(CH_2)$ cm^{-1}. See J.-M. Rueff, N. Masciocchi, P. Rabu, A. Sironi and A. Skoulios, 'Synthesis, Structure and Magnetism of Homologous Series of Polycrystalline Cobalt Alkane Mono- and Dicarboxylate Soaps', *Chemistry – A European Journal*, 8, 2002, pp. 1813–20, and E. Richardson, *Infrared and Raman Analysis of Metal Soap Formation Through Pigment and Binder Interactions in Oil Paintings*, MSc dissertation, Sheffield Hallam University, 2004.

30 Higgitt et al. 2003 (cited in note 18).

31 For the band positions of several salts commonly seen on degraded glass see J.T. Kloprogge, R.D. Schuiling, Z. Ding, L. Hickey, D. Wharton and R.L. Frost, 'Vibrational spectroscopic study of syngenite formed during the treatment of liquid manure with sulphuric acid', *Vibrational Spectroscopy*, 28, 2002, pp. 209–21; L. Robinet, K. Eremin, B. Cobo del Arco and L.T. Gibson, 'A Raman spectroscopic study of pollution-induced glass deterioration', *Journal of Raman Microscopy*, 35, 2004, pp. 662–70. See also Cooper et al. 1993 (cited in note 23).

32 Potassium soaps are expected to be soluble and cobalt soaps insoluble in both methanol and water. Potassium carbonates and sulphates are expected to be water soluble but methanol insoluble. See *CRC Handbook of Chemistry and Physics*, 68th edn, ed. R.C. Weast, Boca Raton 1987. The test films disintegrated completely on contact with water or methanol. The films are rather young, and probably do not reflect the properties of older films, but the observation that the potassium soaps and salts formed on degradation of smalt are rather sensitive to water may have implications for aqueous cleaning of smalt-containing passages in paintings.

33 A broad band centred around 3400 cm^{-1} is seen in both the aqueous and methanolic extracts, suggesting that the potassium soaps are hydrated, see note 28.

34 It seems likely that the process of extraction and recrystallisation from water is responsible for the crystal morphology, since crystals could not be seen on the surface of the intact sample. However, well-formed acicular particles of potassium sulphate have been found in studies of the deterioration of potash-lime-silica glass, see Woisetschläger et al. 2000 (cited in note 4). Fluctuations in humidity, and the high solubility of the potassium sulphates, could result in dissolution and recrystallisation on the glass surface, and may explain the well-formed crystals. It has been observed that glasses that have been exposed to high humidities contain mainly gypsum and very little potassium salts in the deterioration crust; it appears that the composition of the crust is not static, but alters as the salts dissolve and recrystallise in response to changes in humidity. The only possible source of sulphate in the test films is from the atmosphere.

35 KNO_3, $Co(NO_3)_2$ and K_2CO_3 were ground with cold pressed linseed oil (Kremer Pigmente).

36 When KOH is added to linseed oil the oil darkens. Potassium soaps are rapidly formed (confirmed by FTIR spectroscopy). Base-catalysed condensation reactions of ketones and aldehydes are believed to be the main cause of the darkening.

37 As discussed earlier, potassium is believed to be leached out of glass by water in the form of potassium hydroxide. The hydroxide could attack the glyceride linkages in the oil to release carboxylic acids with subsequent formation of potassium soaps, which may explain why soaps were not formed with potassium nitrate and carbonate.

38 These paint films comprise smalt (Kremer Pigmente 10010) ground in cold pressed linseed oil (Kremer Pigmente), painted over a lead white in oil ground. The samples were exposed to light at relative humidities between 10 and 90%; experimental conditions are given in D. Saunders and J. Kirby, 'The Effect of Relative Humidity on Artists' Pigments', *National Gallery Technical Bulletin*, 25, 2004, pp. 62–72. Some reaction between pigment and oil was seen in the infrared spectra of all the samples, but was greater in those exposed to light than those kept in the dark, and greatest in those exposed to higher RH (both in the light and the dark). Under most conditions, a metal-carboxylate band at *c.*1560 cm^{-1} was observed, but for the samples exposed to light at 75 and 90% RH, where reaction was greatest, the band was shifted to *c.*1544 cm^{-1}.

39 Methanolic and aqueous extracts from samples taken from the film exposed to light at 90% RH showed that potassium soaps were present (and sulphates in the water extract). The lead soaps are not seen in the extracts as they are insoluble in methanol and water. Infrared spectra for lead fatty acid soaps are given in Higgitt et al. 2003 (cited in note 18) and L. Robinet and M.-C. Corbeil, 'The Characterization of Metal Soaps', *Studies in Conservation*, 48, 2003, pp. 23–40. In films containing Cornelissen smalt light mixed with lead white and exposed to mid RH conditions (see note 27 for exposure conditions), a broad potassium soap band at *c.*1560 cm^{-1} was seen, although there was little indication of any lead soaps having formed under these conditions. In pure lead white films exposed to the same conditions, there was also little lead soap formation. The lead white-containing films did not discolour to the same extent as those containing no lead white. The samples mixed with lead white, and those painted over a lead white priming and exposed to high RH, were the only test films which were thoroughly dry. All of the samples of smalt alone in oil were touch-dry but had a soft and jelly-like consistency beneath the surface, evident when the films were sampled. Cobalt acts as a surface drier while lead acts as a 'through-drier' and accelerates drying of the film from the inside rather than from the surface. An excess of cobalt in a paint film is also known to result in soft films. See *Hess's Paint Film Defects, Their Causes and Cure*, 3rd edn, ed. H.R. Hamburg and W.M. Morgans, London 1979, pp. 5, 65 and 72.

40 The migration of lead soaps is discussed, in the context of the formation of lead soap pustules, in Higgitt et al. 2003 (cited in note 18).

41 The smalt sample for which results are reported here comprised smalt, supplied by Reckitt's Colours Ltd., painted out in Winsor and Newton linseed oil in 1962. The paint film was subsequently exposed to ultraviolet radiation, although the intensity and duration of exposure were not recorded. Subsequently the sample has been stored under low light levels in the laboratory at ambient temperature and humidity.

42 Two forms of calcium oxalate are commonly found on artworks: a monohydrate phase (whewellite, infrared: 1622, 1319 and 779 cm^{-1}) and a dihydrate (weddellite, infrared: 1643, 1330 and 783 cm^{-1}), see F. Cariati, L. Rampazzi, L. Toniolo and A. Pozzi, 'Calcium oxalate films on stone surfaces: experimental assessment of the chemical formation', *Studies in Conservation*, 45, 2000, pp. 180–8; M.J. Schmelz, T. Miyazawa, S.-I. Mizushima, T.J. Lane and J.V. Quagliano, 'Infra-red

absorption spectra of inorganic co-ordination complexes – IX Infra-red spectra of oxalate complexes', *Spectrochimica Acta*, 9, 1957, pp. 51–8. See Drewello and Weissman 1997 (cited in note 7) for calcium oxalate of biogenic origin on glass. Infrared assignments for potassium and cobalt oxalates are given in Schmelz et al., loc. cit., and H.G.M. Edwards and P.H. Hardman, 'A vibrational spectroscopic study of cobalt(II) oxalate dihydrate and the dipotassium bisoxalatocobalt(II) complex', *Journal of Molecular Structure*, 273, 1992, pp. 73–84.

43 Salts with these combinations of elements have been found, using EDX analysis, on deteriorated glass. Many of the elements probably originate from airborne particles and other atmospheric pollutants. See Woisetschläger et al. 2000 (cited in note 4).

44 Analysis was carried out using the Oxford Instruments INCA 300 EDX system on polished carbon-coated cross-sections. Spot spectra were collected at 25 kV, at around 3 kcps to ensure that the count rate was statistically sufficient, with an acquisition time of 50 s. Elements present at levels of less than 0.5% are not quoted in Table 1. The results are quoted as weight% oxide and are normalised. This should be taken into account when comparing degraded and undegraded particles; for example the Si content appears greater in the degraded particles because of the loss of the network modifying metal ions.

45 For elements present at levels greater than 1 wt% oxide, the results on the standard Corning D glass (Corning Museum of Glass) were all within 8% (relative) of the published values. See R.H. Brill, *Chemical Analyses of Early Glasses. The Corning Museum of Glass*, Vol. 2, Corning 1999, Tables of Analyses, p. 553. The results are a little less accurate than can be achieved with bulk glass, where values within 5% of the published values are expected.

46 Burnstock et al. 2002 (cited in note 15). The use of different paler grades of smalt is discussed, together with surface features of the particles seen in the SEM that distinguish a deliberately pale smalt from a degraded smalt.

47 Arsenic can act as an opacifier, which may have been regarded as a positive side effect of using unroasted ore. For a discussion of roasting of the ore see Richter 2004 (cited in note 1).

48 See Newton 1989 (cited in note 4) for a discussion of the effect of Ca on the stability of the glass. They suggest that the stabilising effect begins at levels greater than 5 wt% CaO. The effect of the lower levels of arsenic and bismuth on the stability is difficult to predict.

49 Mühlethaler and Thissen 1993 (cited in note 1), quote a range of values for the composition of smalt. They suggest that smalt can contain up to 18 wt% CoO. Freestone and Tatton-Brown (in press, cited in note 13) bring together several smalt analyses in the literature to compare with the Bonus Eventus Plaque (which is a smalt glass); these all contain lower levels of cobalt (1–3.5 wt%).

50 The true sodium level is probably a few percent higher than that reported in the table, because sodium tends to migrate under the electron beam. In the sixteenth century, soda glass was generally made with marine plant ashes. However, glasses made with ashes generally contain minor amounts of other elements that come from the plant, notably phosphorus, which is not present in the smalt in the painting by Romanino. See M. Verità, 'L'invenzione del cristallo muranese: una verifica analytica delle fonti storiche', *Rivista della Stazione Sperimentale di Vetro*, 1, 1985, pp. 17–35. It may be that a purified plant ash was used. Alternatively, Richter discusses recipes for smalt that involve adding NaCl to the glass, see Richter 2004 (cited in note 1) p. 202. Mühlethaler and Thissen 1993 (cited in note 1) mention that sodium gives the glass a more violet hue.

51 Richter 2004 (cited in note 1).

52 See note 36 for a discussion of base-catalysed condensation reactions causing yellowing of the oil.

53 B. Gratuze, I. Soulier, J-N. Barrandon and D. Foy, 'De l'origine du cobalt dans les verres', *Revue d'Archéometrie*, 16, 1992, pp. 97–108.

54 Richter 2004 (cited in note 1). Smalt samples from eleven polychrome sculptures dating from the seventeenth and eighteenth centuries were analysed by EDX.

55 L. Campbell, 'Beuckelaer's The Four Elements. Four masterpieces by a neglected genius', *Apollo*, 2002, pp. 40–6. The colour changes are discussed in this article.

56 Crusts containing calcium oxalate are not only found over smalt paint layers, but can form over the whole surface of the painting. The origin of the oxalate has been much discussed in the literature, and ascribed to biodeterioration as well as to extreme breakdown of organic surface coatings. See Cariati et al. 2000 (cited in note 42). It has also been suggested that microbial growth can be encouraged by availability of K and Ca on the surface (as could happen over degraded smalt); see Drewello and Weissman 1997 (cited in note 7).

57 Procházka et al. 2002 (cited in note 9) and the discussion in note 20.

58 Richter 2004 (cited in note 1) reviews the literature on protein components in oil paint containing blue pigments, and quotes an Italian manuscript that suggests that smalt should be ground in egg yolk and honey before use in oil, see p. 186.

Table 1: EDX analysis of smalt in cross-sections from National Gallery paintings

Painting and sample area		Na_2O	Al_2O_3	SiO_2	K_2O	CaO	FeO	CoO	NiO	As_2O_3	Bi_2O_3
Attributed to Pedro Campaña, *The Conversion of the Magdalen* (NG 1241), *c.*1562, oil on wood. Yellow of Christ's cloak (originally blue). Smalt and a little lead white.	Well preserved (bluish grey)		0.5	67	13.7–14.3		3.7–4.2	6.6–6.7	0.9	5.9–6.3	1.0–1.2
	Degraded (colourless)		0.5	68–72	0.7–2.1	0.4	5.0–5.1	7–9	1.5	7–10	1.0–1.2
Thomas Gainsborough, *John Plampin* (NG 5984), *c.*1752, oil on canvas. Dull grey of trees in the background landscape; smalt and a little Naples yellow, lead white, vermilion and black.	Well preserved (rather greyish blue)		0.9–1.0	63–66	12–15	0.9–1.3	3.7–4.3	3.5–5	0.4–1.1	8.1–11.7	0.7–0.8
	Degraded (pale greyish blue)		0.9–1.0	69.5–75.2	3.4–7.6	0.6–1.3	3.0–4.5	3.5–5	0.6–1.2	7.7–10.4	0.2–0.9
Gerolamo Romanino, *The Nativity* (NG 297.1), 1524–6, oil on wood. Dark brown shadow of the Virgin's drapery. Smalt mixed with a little lead white over an azurite layer.	Well preserved (greyish blue)	7.4–11.5	0.6–1.0	66.7–72.7	4.1–5.0	3.1–3.9	1.4–2.2	2.6–3.8	0.5–0.9	2.6–3.9	1.3–2.7
	Degraded	1.1–5.1	1.0–1.2	72.3–75.6	2.8–4.2	3.5–5.0	1.7–1.8	2.9–3.7	0.6–0.8	2.6–3.5	1.0–2.1
Parmigianino, *Portrait of a Man* (NG 6441), probably before 1524, oil on wood. Grey brown sky; smalt layer over azurite layer.	Degraded (colourless)		0.6–0.7	78–80	0.8–1.7	2.0–2.3	2.3–2.8	4.6–5.1	1.0–1.3	3.6–4.3	2.2–2.8
Pieter Bruegel the Elder, *The Adoration of the Kings* (NG 3556), 1564, oil on wood.	Blue of Virgin's robe: well-preserved smalt mixed with a little lead white.	0.3–0.5		60–65	10–16	3.2–4.5	5.2–7.5	6.4–8.3	0.6–0.7	3.2–4.4	0.5–1.1
	Blue of sky: smalt, completely colourless, and a little lead white.		0.5–0.7	72.5–76.2	0.7–0.9	0.6–1.9	5.2–5.8	7.9–9.1	0.8–1.8	4.8–6.2	0.4–1.7
Paolo Fiammingo, *The Sons of Boreas pursuing the Harpies* (NG 5467), 1592–6, oil on canvas. Greyish-blue paint of the sky.	Upper layer: well preserved smalt mixed with lead white.			62–8	13–14		3.6–5.1	6.5–7.5	0.9–1.3	5.4–8.6	1.1–1.7
	Underlayer: smalt with only a little lead white, completely colourless			76–78	1.6–2.2		5.1–5.7	4.2–5.5	0.3–0.4	8.6–9.1	0.1–0.4
Joachim Beuckelaer, *The Four Elements:Water* (NG 6586), 1569, oil on canvas. Pinkish-grey paint of the apron of the serving girl in the background.	Well preserved (greyish blue)			57–59	12.6–14.7	1.4–1.8	2.9–4.5	8.0–9.5	3.2–3.8	5.7–6.7	2.6–4.8
	Degraded (colourless)			73–77	1.1–1.7	0.3–0.4	3.6–4.8	6.8–7.8	1.1–1.2	8.2–9.6	1.5
Joachim Beuckelaer, *The Four Elements: Air* (NG 6587), 1570, oil on canvas. Pinkish-grey waistband of the woman on the left.	Well preserved (greyish blue)			62–63	14.2–14.7	0.8–1.0	3.6–4.1	6.4–7.2	1.0–1.5	8.6–9.0	1.7–1.9
	Degraded (colourless)			73–74	2.1–3.3	0.9–1.3	3.2–3.4	6.1–6.6	1.0–1.4	10.0–10.9	1.5–1.9