Imaging Microspectroscopic, Secondary Ion Mass Spectrometric and Electron Microscopic Studies on Discoloured and Partially Discoloured Smalt in Cross-sections of 16th Century Paintings

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Abstract: Paint cross-sections of five 16th century paintings with areas of discoloured smalt oil paint were investigated. Semi-quantitative SEM-EDX analysis revealed that potassium was relatively low in all discoloured smalts, while cobalt remained at an approximately steady level. Reflection light microscopy demonstrated the presence of partially discoloured small particles with a remaining blue core. Imaging SIMS demonstrated that cobalt has a uniform distribution in the glass particles. Potassium however shows relatively high levels in the oil paint matrix around the discoloured glass particles and an uneven distribution in small particles with a blue core. These blue cores always have a higher K level compared to the discoloured rim of the particle. The loss of potassium from smalt in oil paint is interpreted as a leaching process which lowers the basicity of the glass below a critical level for colour maintenance. The colour change of the smalt is thus an indicator of a change in alkalinity inside the glass. The critical level appears to be near a K:Co of about 1:1 in 16th century potash glass on the basis of semi-quantitative SEM-EDX data. The migrated K is thought to be accommodated on the many fatty acid groups of the mature oil network ionomer in the aged oil paint. Ca was observed in a number of blue remaining smalls which suggest a role in preservation of the blue glass or retardation of the leaching process. It is estimated that the colour change is an early phenomenon possibly related to the early stages of oxidation and hydrolysis of the cross-linking oil paint. The differences in potassium levels in the remaining blue part of the small particles point to variability in the quality of the base potash glass in the 16th century. Analysis of partially discoloured smalt from two panels of a triptych by Dirk Barendsz (1534–1592) demonstrated that he had access to two chemically different smalts.

Keywords: Imaging SIMS · Oil paint · Potash glass leaching · Potassium cobalt ratio · Smalt discoloration

Introduction

Traditional pigments for blue colours in paintings are azurite and ultramarine [1][2]. Smalt, a ground cobalt glass, was a cheap substitute for these expensive pigments and has been found in paintings since the middle of the 16th century. Riederer wrote a very detailed account of the history of smalt, its physical properties and behaviour in oil painting and fresco [3]. The paper on smalt from Mühlethaler and Thissen [4] was updated and appeared as a review of the occurrence and properties of smalt in Artists' Pigments volume 2 [5]. With the invention of Prussian blue early in the 18th century, the use of smalt declined, although Riederer [3] relates its decreased occurrence mainly to the decreased production of Netherlandish paintings. Smalt production [3] was still about 3400 tonnes in the middle of the 19th century, but this smalt was not used in paintings.

Oil painting with smalt was not without problems. Armenini [6] and Van Mander [7] knew about the problems of painting with smalt. De Mayerne [8] mentions the problem of the rapid surface drying of smalt paint and the need to use coarse glass to maintain the colour. Indeed, the covering ability of smalt is poor especially when low contents of cobalt are used, because the refractive index of cobalt-poor glass approaches that of linseed oil [3]. The instability of the colour of smalt in oil paintings is now a well-known problem and a major cause of the loss of blue coloured areas in paintings. Blue clothes turn into a brownish white. Blue skies become grey skies. The colour can be reconstructed in discoloured areas of the original by clever digitisation techniques applied to painting photographs, facilitated when a contemporary copy is available, in which the original colours are better preserved [9]. Discolouration of smalt-containing oil paint may already have been observed in the early 17th century, but it was considered to be a prob-
lem of the oil (see [8], p. 42) and not seen as a problem of the stability of smalt itself. De Mayerne even advises the use of walnut oil instead of more strongly yellowing linseed oil.

Several causes for the discoloration phenomenon have been suggested [5]. Northern European glass at that time was potash glass, a soft potassium-rich glass, which is prone to deterioration [10]. This deterioration could affect the coordination chemistry of cobalt in the glass matrix [11]. Other explanations are that cobalt may have simply leached out from the glass matrix or may have changed its oxidation state [5]. The quality of the cobalt oxide produced in the 16th century is poor and it is likely that many minor and trace elements were present that could affect the stability of the colour as well. In fact, the method of purification of the cobalt raw material was greatly improved in the Netherlands in the early 17th century. Riederer also points to the ratio of quartz, potash and cobalt ore in the glass as an important factor [3]. His reconstructions of smalt at the Doerner Institute produced very different working properties and colour shades dependent on this ratio. The best working properties and colour are obtained above a SiO$_2$ percentage of 30%, a percentage of K$_2$O between 5 and 40% and a cobalt content of 5-40% (as CoO). High contents of cobalt produce a stronger blue, but the resulting glass itself has poor handling properties. The relative amount of silica is a critical factor. Potash glass panes in Austrian churches made with less than 60 at% silica are much less durable [12].

No studies exist on the optical properties of cobalt in potash glass. The optical absorption of cobalt in modern soda-lime glass has been discussed by Bamford [13] and more recently by Bartecki and Burgess [14]. Cobalt in base glass occurs normally in the divalent form in four-fold coordination with the glass oxygen atoms. The replacement of sodium by potassium leads to a bluer glass due to a bathochromic shift in the light absorption of about 10 nm. The absorption spectra in soda-lime cobalt glass resemble those from reconstructed potash cobalt glass published by Riederer [3]. One reason for the blue colour is the strong light transmission in the 380-450 nm range. The absorption spectrum of cobalt-coloured glass (see [13]) shows several absorption maxima in the range 500-700 nm. In glass with cobalt oxides a pattern of bands at about 600 nm is mostly related to tetrahedral coordinated Co$^{2+}$(Co II), i.e. the chromophore CoO$_4$ [14].

Several paint cross-sections studied earlier by Van Asperen de Boer and students [15-17] provided the opportunity to study the discoloration phenomenon of smalt in more detail using modern imaging microspectroscopic and imaging secondary ion mass spectrometric techniques. A fraction of the small particles in the cross-sections of the selected paintings in this paper are only partially discoloured and present themselves as remaining cores of blue glass surrounded by a shell of greyish discoloured glass (see Fig. 1 and 2). This phenomenon is a unique opportunity to compare the spatial distribution of cobalt, silica, potassium and other elements in the glass, and in the paint matrix. The data from imaging visible microspectroscopy and imaging secondary mass spectrometry on a typical partially discoloured small particle are used to test whether cobalt is a fugitive element in the glass or whether the stability of the potash glass is related to the discoloration. Secondary electron microscopy in combination with energy dispersive X-ray analysis (SEM-EDX) was used to survey a larger set of discoloured smalt particles in cross-section.

Fig. 1. Reflection light microscopic photographs of a paint cross-section (A102/11) of the discoloured robe of Mary Magdalene in the Seven Sorrows of Mary painted c.1554 by Pieter Aertsen. The glass particles are more visible under UV-fluorescence conditions (B). The small particle (marked a) is partially discoloured showing a preserved blue core surrounded by discoloured glass (coded A102/11,1 in Fig. 3).
A103/2 from Pieter Aertsen (1509–1575), Seven Joys of Mary (dated 1554), [St. Leonardus Parish, Zoutleeuw, (B)]. Cross-sections and remaining paint samples are held by J.R.J. van Asperen de Boer. Detailed descriptions of these cross-sections have been deposited in the archive of the Netherlands Institute for Art History (RKD, Den Haag). Samples were embedded in polyester resin. After initial grinding and polishing using silicone carbide paper of increasing mesh size, the surface was dry polished using Micromesh™ cloths (final step 12 000 mesh).

Microscopy
Microscopic studies on cross-sections were performed on a Leica DMR microscope (Leica, Wetzlar, Germany). Normal light was provided by a 100 W Halogen projection lamp. An Osram HBO 50 lamp and Leica filter D (excitation 360–425 nm, emission >460 nm) were used for fluorescence microscopy.

SEM-EDX
SEM-EDX measurements were carried out on a JEOL JSM 5900 LV scanning electron microscope scanning with a 25 kV electron beam. Samples were coated with a thin carbon coating to improve the conductivity of the sample and so prevent the accumulation of charge. EDX analyses were performed at various point throughout the cross-section by measuring the emitted X-rays with a Noran Vantage EDS-system with Pioneer Norvar detector.

TOF-SIMS
Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) measurements were performed on a TRIFT II instrument of PHI Electronics Inc. (USA) [18]. The surface of the sample was scanned with a 25 keV primary ion beam from an Indium liquid metal ion gun which has an input beam diameter of about 30 nm releasing secondary ions from the sample with a exit diameter of about 100 nm. The triple ESA ion focusing system guarantees a spatial resolution of at least 1 micron at a mass resolution of about 5000. The surface of the sample was charge compensated with electrons pulsed in between the primary ion beam pulses.

Imaging Visible Light Microspectroscopy
Visible light spectroscopic imaging studies were performed on a Leica...
Results

All discoloured and partially discoloured small-containing layers in the cross-sections of the paintings selected were studied routinely by reflected visible light microscopy, reflected UV-fluorescence light microscopy and SEM-EDX (data summarised in Fig. 3). The degree of discolouration in the paintings is variable and also depends on the layer structure of the painting. The degree of colour preservation in the cross-sections was estimated by counting remaining blue particles in a unit area. Glass particles are relatively easy to recognise in SEM by their high silicon content, angular outline, and moderate secondary emission of electrons compared to the omnipresent lead white. The small particles in oil paint of the 16th century paintings studied here are poorly solved. The glass particles are recognised easily under UV-fluorescence conditions. A120/11 contains a few larger glass fragments (about 30-40 μm) in which a blue core remains (see Fig. 1A and 1B). The partially discoloured glass particle a (coded SEM-EDX A120/11,1 in Fig. 3) is our type locality on which the imaging microspectroscopy and imaging SIMS is applied and reported here. Other discoloured and blue glass particles in this layer are coded SEM-EDX A120/11,2 and SEM-EDX A120/11,4, respectively.

The small in sample A21/19 from the shadow in the blue robe of Mary is mostly discoloured (>90%), but the colour of the glass in the lower part of the small layer is better preserved (total thickness of the paint is 60 μm). Two brownish glass particles (A21/19,4 and 19,5) in the top layer and three bluish glass particles (A21/19,1; 19,2 and 19,3) in the lower layer were selected for analysis by SEM-EDX.

The small paint layer in the samples from the Dirck Barendsz painting (A233/7 and A233/11) clearly consists of two layers. The lower layer of sample A233/7 (total thickness 60 μm) from the now brownish robe of Mary in the central panel is 100% discoloured, but some larger glass fragments in the top layer show preserved cores of blue colour around a discoloured rim. One example is shown in Fig. 2A and 2B, marked as a. The core and rim of the partially discoloured glass fragment are coded A233/7,1C; A233/7,2R and 7,3R, respectively in Fig. 3. Another particle of completely discoloured glass (marked as b) selected in this cross-section is A233/7,6 and 7,7 of which the centre and outer rim were analysed. The two paint layers of cross-section A233/11 from the greyish blue sash of a standing man with stick in the interior of the right wing show the opposite situation. The top layer (thickness 50 μm) is completely discoloured while the lower layer (40 mm thick) has about 70% of the blue glass preserved. Two discoloured particles were selected: one in the top layer (A233/11,1) and one in the partially blue layer (A233/11,2). A glass particle with a
blue core and discoloured rim (A233/11,3) was selected in the lower layer. One painting with partial smalt discolouration, which is reliably dated at 1557 but painted by an unknown South Netherlandish painter (A351), shows much less discolouration. Examination of the paint cross-section of sample A351/9 from the bluish-grey robe of the man to the right of St John in the central panel shows that about 80% of the blue colour is preserved in the paint. Two blue glass samples were analysed by SEM-EDX (coded A351/9,1 and 9,2).

The SEM-EDX data in Fig. 3 were ordered as a function of increasing relative potassium content. The measurements were standardised on a 60 s acquisition time at 25 kV. All samples analysed show a high silicon content and smaller concentrations of cobalt, arsenic, iron and potassium. All blue samples have a relatively high potassium content, while discoloured cobalt glass has a low potassium concentration. The ratio of Si:K:Co derived from the peak heights of blue in A233/11,3 is 100:45:6, while the most discoloured cobalt glass has a ratio of 100:2:8 (sample A102/2,1). The transition from blue to discoloured glass in the sample series analysed is sample A102/11,4 (still blue) with a ratio of 100:13:7 while A102/11,3 (discoloured) has a Si:K:Co ratio of 100:8:8. Since both sample points are from the same paint layer, we can safely conclude that the colour threshold in 16th century smalt is near a K:Co ratio of 1:1 on the basis of SEM-EDX.

The partially discoloured glass particles, in which a core of blue glass still remains can help us in comparative studies of the material properties on the assumption that the blue core represents the composition of the original glass. Partially discoloured particles with a preserved blue colour in the centre, i.e. A102/11,1; A233/7,1, and A233/11,3 were analysed. The data in Fig. 3 are marked with R or C to indicate discoloured rim (R) or blue centre (C), respectively. The K:Co in the blue cores of the partially discoloured particles is not the same and decreases in the order of A233/11,3C; A233/7,1C; A102/11,1C. The K:Co of the discoloured rims decreases very slightly in the order of A102/11,1R, A233/7,2R and A233/7,3R, to A233/11,3R (note that A233/7,2 and A233/7,3 are spot analyses in the rim of the same particle, where A233/7,1 represents the blue centre).

These differences in composition of the blue cores can be explained as differences between batches of smalt or as an indication that potassium is also partially lost from the central parts of smalt particles. The compositional difference between the centre and rim of a completely discoloured large glass particle in A233/7,6 (coded A233/7,6 (C) and 7,7(R)) is very small suggesting that such large particles can become completely depleted in potassium. In the case of A102/11 the difference between being blue or discoloured is very small, which leaves open the possibility that potassium could have been lost from the blue core as well, but that the K:Co of the centre has not yet reached the critical level for colour loss. The difference in composition between A233/11,3C and R on the other hand is very substantial. The depletion of K is almost complete in the discoloured rim, but the blue core has a very high K content. Considering the depletion of K in the rim, it is surprising that a blue core even exists. We discovered, however, that both A233/11,3 C and R have relatively high calcium content (compare the EDX-traces in Fig. 3. Note the high Ca peak, while the K is almost gone in the leached rim). It is interesting that calcium is preserved upon discolouration in A233/11,3R while most of the K is lost. SEM-EDX studies of other blue as well as discoloured smalt particles in A233/11 also reveal some calcium. It seems that calcium might have a barrier function in ancient potash glass which changes the mechanism of potassium release.

The small in the cross-sections A233/7 and A233/11 are from the same painting and we expected approximately the same composition of the small on the assumption that Dirck Barendsz would have used the same batch of smalt while painting the blue robes on the central and right panel. However, A233/11,3C not only has a different potassium content, but also has a much higher content of Ca than A233/7,1, which implies that Barendsz must have used two different types of smalt. Was he aware of this? Perhaps he took a batch of smalt from Venice when returning from his period (1555–1562) with Titian and ran out of this supply during the completion of the triptych. Fact is that the composition of the smalts used on the same triptych differs. This observation makes it more credible that small composition may have been quite variable in the 16th century. A planned larger survey of smalts in paintings with the aim to obtain more quantitative chemical composition data from that and later periods should give valuable insights into the history of the manufacture of this pigment.

**Imaging Microspectroscopy of a Partially Discoloured Small Particle in A102/11**

Further studies were focussed on a partially discoloured particle of about 0.1 micron diameter (marked as a in Fig. 1) in the discoloured small layer of the painting the *Seven Sorrows of Mary* by Pieter Aertsen (A102/11). The discoloured outer part of the small particle follows its circumference suggesting that substances have been lost by diffusion, which resulted in the change in colour. The microspectral map of particle a at 550 nm with a spatial resolution of about 1 micron shows that there is indeed an absolute difference in colour around the central core (Fig. 4A). The spectral characteristics of the core of the particle shown in Fig. 4B resemble the visible reflection spectrum of modern smalt reference material [5]. Reflection spectral data taken of a non-discoloured small particle in a cross-section obtained from the painting the *Seven Joys of Mary* by the same painter (Fig. 4C) reassured us that modern and 16th century small do not differ much in their visible light spectra. A separate non-discoloured blue smalt particle analysed in transmission (red curve) has a stronger absorption in the 400–500 and the 700–750 nm regions compared to the reflection spectrum. The diffuse reflection spectrum of the blue core region of A102/11 in Fig 4B and the non-discoloured small particle in A103/2 shows high reflectance in the red range (above 650 nm). The most characteristic features are the two reflection maxima near 570 and 630 nm. These features are preserved in the spectra of the discoloured outer rim, which suggests that some of the postulated interactions of cobalt with the glass matrix are preserved [14]. The discoloured rim shows a lower absorption in the 450 nm region. Comparative studies demonstrate that these changes in the reflectance spectra upon discolouration are a fairly general phenomenon.

**Imaging SIMS of a Partially Discoloured Smalt Particle in A102/11**

Sample A102/11 was subjected to imaging secondary ion mass spectrometry to study the distribution of silicon, cobalt, potassium and other elements in relation to the partial discolouration of the smalt. Fig. 5 compares the visible image with the imaging SIMS elemental maps of cobalt and lead. The visible image of A102/11 is horizontally flipped compared to the microscopic picture in Fig. 1 to facilitate the comparison with the elemental...
Fig. 4. Imaging reflectance microspectroscopy of the area around particle a in the cross-section A102/11 taken from the discoloured robe of Mary Magdalene in the Seven Sorrows of Mary painted c.1554 by Pieter Aertsen (see Fig. 1). Fig. 4A represents the false colour image at 550 nm. Fig. 4B represents the visible spectra of an average of ten pixels in the central (blue) core region and the discoloured rim of particle a. Fig. 4C shows the transmission spectrum and reflectance spectrum of non-discoloured smalt in the triptych Seven Joys of Mary by the same painter (dated 1554).

Fig. 5. Imaging SIMS maps of the lead (A) and cobalt (C) distribution of smalt particle a in cross-section A102/11.

Note, for example, particle b in Fig. 1A and Fig. 5. Lead, a marker for the binding medium of the oil paint (highest concentrations are shown as white decreasing via yellow to red) shows highest concentrations between the glass particles, but some discoloured glass particles in the middle of the map show higher numbers of lead secondary ions, which suggests that lead might not be confined to the oil paint alone.

Fig. 6 presents results at higher magnification of positive ion images of the total ion current (TIC+), the elements Si, K, Ca, Co and Pb and the negative ion image of palmitic acid (m/z 255) of the partially discoloured small particle a and, its surroundings. For instrumental reasons there is a slight difference in magnification between the positive and negative image. The differences in grey tonality in the TIC+ demonstrate that there is a difference in secondary ion yield of the glass particles and the binding media matrix. The glass particles have a uniform emission. The oil paint matrix, which is more prominent on the left hand side of
the TIC+ picture shows a bright, somewhat cloudy distribution, which coincides perfectly with the distribution of the secondary ions of lead from lead white (lead hydroxycarbonate), a common constituent of oil paint. Relative yields in positive secondary ions are unknown for oil paint but have been determined for an aluminium oxide matrix and the approximate order in yields for the elements relevant here is K ~ Ca > Si ~ Co >> Pb [19]. The high emission in the region of the binding medium would thus point to relatively large concentrations of lead compared to cobalt and potassium. The distribution of the palmitic acid (m/z 255) as marker for oil paint matches the lead distribution. Cobalt has a very specific distribution, which coincides perfectly with the glass particles that are visible in the light microscopic picture (Fig. 1). The cobalt is very uniformly distributed and does not show any evidence for selective migration or leaching. Silicon, a main component of the glass, matches the cobalt distribution although the contours of silicon in the glass particles are not as sharp as those of cobalt. Note that some silicon ions may have been generated from a thin coating of silicones in or on the polyester resins. Silicones are unfortunately a common contaminant in existing cross-sections, since silicone-containing putty is used in light microscopy as a mounting medium for the polyester embedding blocks. Regrettably, it is detected in SIMS with an extremely high sensitivity.

There is a gradient of potassium in the partially discoloured particle a. The part coinciding with the preserved blue colour appears to have a higher potassium concentration (lighter grey). The distribution of K and Co was plotted along the transect outlined in Fig. 1. A different colour coding of the potassium contours in the SIMS map in Fig. 7 more clearly outlines the high abundance region in the core of the particle. A transect was drawn that sections a number of smaller smalt particles and the big particle a. The red graph in Fig. 7B represents the potassium secondary ion yields, which are highest where a glass particle is sampled. Potassium is also detected at lower levels in the oil paint medium between the glass particles, which is interpreted as a sign of migration from the glass, because potassium is not normally an oil paint component. Although there is some uncertainty in the distribution curve due to a relatively high noise-level, the core of particle a shows a higher average level compared to the sides of the particle. This higher level coincides with the blue colour in the visual image. The cobalt distribution on the other hand is zero between the particles and remarkably flat in particle a. This is proof that cobalt remains, while potassium migrates by diffusion to the binding medium around particle a and the other glass particles. It is interesting that cobalt tends to drop off near the edges of particle c, which could point to some corrosion of the glass. Although sodium is present in considerably lower concentrations, the distribution pattern of Na follows that of potassium. Calcium, usually a minor component in potash glass, mainly follows the contours of the glass particles.
Fig. 7. Line scans of cobalt and potassium along the transect displayed in the potassium imaging SIMS map of particle a in cross-section A102/11. The potassium contours ranging from high to low are colour coded from black via red to yellow. Particle c is completely discoloured. Cobalt is confined to the glass particles. The highest K levels form a 'levee' with an average intensity level of 16 in the blue coloured centre of particle a, while the 'banks' coincide with the discoloured rim at an average level of 12. The relatively small difference in K levels between core and rim suggest that the K:Co is close to a critical level.

We conclude from these image data that the cobalt is still present in the glass and has not been lost by diffusion. The preservation of cobalt and silicon was earlier indicated by the SEM-EDX spot analyses. The picture for K and Ca is different. Potassium is present in and around the glass particles. Recent studies on a mid 16th century painting by Pedro Campagna (possibly originating from Flanders) by SEM-EDX also demonstrate a drop in potassium content of the smalt and an increase around the glass particles [9]. Preliminary SIMS data on non-discoloured smalt containing oil paint in the triptych the Seven Joys of Maria by Pieter Aertsen, dated 1554 and present in the same St. Leonardus church in Zoutleeuw as the discoloured Seven Sorrows of Mary by Pieter Aertsen, demonstrate that the images of Si, K and Co match closely implying that K is hardly leached from the glass. Since this sample is rich in calcium carbonate and lead white, we presently infer that the buffering capacity of the oil paint by other pigments or fillers may be a factor of importance in this case. Further studies of smalt particles with imaging SIMS are in progress.

Discussion

The main conclusion from the imaging SIMS and microspectroscopic data on A102/11 is that cobalt is a conservative element in the glass, while potassium and perhaps some silica is leached out. The specific role of calcium in the stability of the potash glass needs further study. As confirmed by the SEM-EDX data of the samples investigated, we infer that the discolouration of smalt in the 16th century is mainly due to instability of the glass and not caused by cobalt loss from the glass. The discolouration is directly related to the loss of basicity of the glass leading to the transition of cobalt (II) from a tetrahedral to octahedral symmetry. Octahedral cobalt (II) reacts with basic glass to form tetrahedral cobalt (II), a reaction which is used to determine the acid-base chemistry of the glass [11]. On the assumption that the same physicochemical behaviour of cobalt (II) takes place in ancient potash glass, we conclude that a blue colour (tetrahedral symmetry) relates to a basic glass composition and that discolouration implies a loss of alkali below the critical value leading to cobalt (II) in primarily octahedral symmetry. Another factor of importance for the spectroscopic behaviour is the difference in extinction coefficient between acid and basic glass, which in modern cobalt (II) containing potassium borate glasses depends on the molar concentration of potassium [11]. At lower potassium concentrations the extinction coefficient is an order of magnitude lower, resulting in a much weaker blue [11].

The analysis of the preserved blue cores in the smalt particles in 16th century paintings provides a unique possibility to draw conclusions about smalt composition in the past. We now have strong indications that the quality of smalt used is variable even within a triptych by the same painter. The high potassium content of the smalt suggests that the glass was made with beech wood; a common practice in the Middle ages and later on [20]. Newton also mentions that beech wood potash may contain too much lime for a satisfactory stability and the combination of K and Ca would make the glass even more vulnerable to damp atmospheres. Recent studies of Austrian medieval window glass made with potash and lime show very severe forms of degradation due to the loss of glass network modifier ions such as potassium, sodium, calcium, magnesium, barium and lead by leaching [12]. Calcium in modern soda glass improves durability and slows down, but
does not prevent, the loss of monovalent alkali [11]. Does the presence of calcium imply that there is a boundary condition, which determines the onset and rate of potassium loss? This behaviour could explain the relatively large difference in composition between the core and the discoloured rim of the partially preserved small particle in A233/1 (A233/13C and A233/113R).

We infer that the reasons for the enhanced deterioration of small must be sought in the nature of the oil paint, the poor buffering capacity of most small oil paints and the exposure to moisture absorbed from the environment. The general mechanism for the deterioration of potash glass by moisture according to Newton and Davison [10] requires the inward diffusion by water, which reacts with the non-bridged oxygen atoms of the silica to produce hydroxyl ions that migrate out with the alkali cations. Moisture in oil paint tends to produce hydrolytic reactions that affect its stability. Van den Berg et al. [21] have shown that 25 years is sufficient for a substantial degree of hydrolysis of all ester bonds in lead white oil paint, while almost none of the glycerol ester bonds remain in oil paints after about hundred years. The cross-linked part of oil paint hydrolysates in the course of time to form a three-dimensional cross-linked structure with many exposed fatty acid groups [21–23]. Titration of the hard and brittle lead coordinative ionomeric networks in aged oil paint by moisture absorbed from the environment would result in an ion-exchanger in the paint that could easily absorb potassium diffusing away from the glass. Such a finely dispersed cation exchanger developing during ageing of the oil paint combined with high potash glass that is also finely divided, appears to be a sure recipe for glass deterioration [10].

Relatively large amounts of small organic acids that are produced in the early stages of the drying of oil paint [24] could also endanger the stability of the small, if sufficient buffering of the fresh oil paint, for example by calcium carbonate or lead white, is absent. Potassium hydroxide released from small would be readily absorbed by reaction with the cross-linking ester linked network leading to potassium fatty acid soaps and water. If the pH around the glass particles reached a value near 9.0, silica would also become soluble and migrate away from the glass. Deterioration of the silica network in the smalt particles is not so evident in the samples examined in this paper, but has been observed elsewhere [5].

The postulated drifts in pH of the oil paint, which are detrimental to the stability of blue potash glass, suggest that the onset of the discoloration process, i.e., the loss of solid phase basicity of the glass below a critical potassium level, would be a relatively rapid phenomenon, which would take 25–50 years to be noticeable by the viewer. Some evidence for problems with smalt can indeed be deduced from the late 16th and early 17th century treatises of Armenini, van Mander and De Mayeur, although they interpret the problems as related to the yellowing of the drying oil. Our interpretation is that these observers have seen the colour changes in the smalt itself when they saw paintings from the mid 16th century in the late 16th or early 17th century. On the other hand, the final stages of the process might take much longer depending on the relative humidity and chemical quality of the atmosphere since the 16th century. In any event, discolouration of smalt seems to be the rule in oil paintings and preservation of the blue colour of smalt the exception.

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