

# Investigation of the Discoloration of Smalt Pigment in Historic Paintings by Micro-X-ray Absorption Spectroscopy at the Co K-Edge

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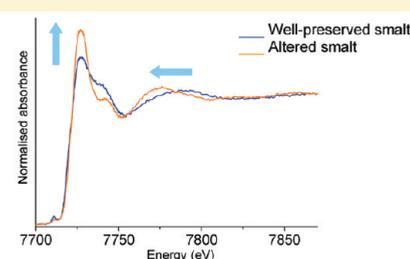
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**ABSTRACT:** Smalt was commonly used as a pigment by artists between the 16th and 18th centuries. It is a powdered blue potash glass colored by cobalt ions and often degrades causing dramatic changes in the appearance of paintings. The aim of the work presented in this paper was to investigate the changes in the structure and environment around the cobalt ion on deterioration, to further our understanding of the basis of the loss of color. Particles of well-preserved and altered smalt in microsamples from paintings in the National Gallery, London, and the Louvre, Paris, were analyzed using synchrotron micro-X-ray absorption spectroscopy at the Co K-edge. X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) measurements showed that in intense blue particles the cobalt is predominantly present as  $\text{Co}^{2+}$  in tetrahedral coordination, whereas in colorless altered smalt the  $\text{Co}^{2+}$  coordination number in the glass structure is increased and there is a shift from tetrahedral toward octahedral coordination. The extent of this shift correlates clearly with the alkali content, indicating that it is caused by leaching of potassium cations, which act as charge compensators and stabilize the tetrahedral coordination of the cobalt ions that is responsible for the blue color.



The blue pigment smalt is a potash glass with the color given by cobalt ions. It was most common as an artists' pigment between the 16th and 18th centuries and was widely used in all types of painting, including in oil, watercolor, wall paintings, and polychrome sculpture. The history, occurrences in works of art, recipes, and trade relating to smalt have been described by several authors, including Riederer,<sup>1</sup> Mühlethaler and Thissen,<sup>2</sup> Stege,<sup>3</sup> Richter,<sup>4</sup> and Delamare.<sup>5</sup> It was manufactured from cobalt ore, a source of silica such as sand or pebbles, and potash as the flux. The glass was ground, washed, and separated into grades of different particle size, with the finer smalt being less intense in color. The various grades that were sold could differ in cobalt content too, which also influenced the hue; the quantitative analyses that have been published indicate that the cobalt content is about 1–2 wt % in pale varieties such as those used for tinting paper or as a laundry blue<sup>5</sup> and can be as much as around 15 wt % in the grades used in painting, although a range of 3–7 wt % is more usual.<sup>1,2,6,7</sup>

In addition to potassium, silicon, and cobalt, historical smalt contains other elements in varying amounts, most commonly arsenic (often present at higher levels than cobalt), nickel, bismuth, iron, magnesium, and aluminum, indicative of the origin of the cobalt ore or the silica source.<sup>8</sup> The high arsenic levels can be explained by the fact that the most abundant cobalt ores were arsenides or sulphoarsenides. These would have been added in

the form of “zaffre”, which was prepared by roasting the ore, converting it to an oxide, and eliminating at least some of the arsenic, followed by mixing with varying proportions of silica depending on the grade of the product. The amount of arsenic present can be related to either the origin of the ore or the degree of roasting.<sup>5,7</sup>

Smalt is almost always a potash glass, and in fact cobalt in association with potassium gives a purer blue than with sodium.<sup>9</sup> This is reflected in some of the historical recipes where potassium-rich tartar is mentioned as an ingredient.<sup>3</sup> A few rare examples of smalt containing a significant amount of sodium in addition to potassium have been reported,<sup>4,6</sup> but soda glass containing cobalt has a slightly more purple-blue hue that is less desirable.<sup>2,10</sup>

Smalt has frequently degraded causing the paint to appear brown or gray, resulting in sometimes dramatic changes to the appearance of a painting. The smalt particles themselves become colorless or gray. In oil paintings the binding medium is also affected, especially when the smalt is not mixed with lead white; it becomes yellow-brown in color causing the overall brown

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appearance of the paint, but can also become broken up so that it scatters light and the paint appears blanched.

The discoloration of smalt-containing paint is mentioned already in 17th century treatises on painting technique, although these ascribe the change only to yellowing of the binding medium.<sup>11</sup> It was appreciated already in the 19th century that “excess alkali” in the smalt glass could affect durability and that even after immersion in water for a relatively short time the potassium was leached and the solution became alkaline.<sup>12–14</sup> More recently, scanning electron microscopy—energy-dispersive X-ray (SEM-EDX) analysis has demonstrated in samples from paintings that loss of potassium from the smalt particles is indeed associated with the deterioration.<sup>6,10,15</sup> Fourier transform infrared (FT-IR) analyses have shown that the leached potassium goes on to react with fatty acids in an oil binding medium to form soaps,<sup>6</sup> which can then migrate to the surface of the paint and undergo further reactions with environmental pollutants. As a result a crust is formed on the paint surface containing complex insoluble potassium salts very similar to that which has long been known to develop on vessel and window glass.<sup>6,16</sup>

A certain amount of knowledge therefore exists about both changes within the glass on alteration of smalt and its interaction with the surrounding binding media, particularly oil. The exact physicochemical origin of the color change, however, has not yet been fully explored. Various hypotheses have been formulated. These include leaching of the coloring cobalt cation,<sup>17,18</sup> but although this has been demonstrated to have occurred in a few extreme cases where the smalt is very degraded,<sup>6</sup> SEM-EDX analyses have shown that loss of color is often observed without significant loss of cobalt, and this cannot therefore be the primary mechanism.<sup>6,10,17</sup> It has also been proposed that the color change results from a modification of the cobalt speciation with a change in the coordination from tetrahedral to octahedral.<sup>6,10,19</sup> Boon et al. postulated that the threshold for loss of color occurs at a particular potassium/cobalt ratio, measured as a ratio of the peak height of these elements in the EDX spectrum, of 1:1.<sup>10</sup> It has also been suggested that a change in the oxidation state of the cobalt ion is involved.<sup>19</sup>

The objective of this study was to investigate further the various hypotheses that have been put forward regarding the processes responsible for the color change within the smalt glass on degradation. Microsamples from paintings in the National Gallery, London and various museums in France were selected that included both particles of smalt that were still blue and degraded particles that had lost their color so that the cobalt environments and speciation in each could be compared. The size of the samples—the paint cross sections were 300–400  $\mu\text{m}$  across and the smalt particles were 10–50  $\mu\text{m}$  in size—put certain constraints on the analytical techniques that could be used. Optical absorption spectroscopy has been applied in the past to investigate the coordination in cobalt compounds but was not suitable for these samples.

X-ray absorption spectroscopy (XAS) is particularly suitable for investigating structural information such as the oxidation state, coordination, nearest neighbors, or more generally the environment around the cobalt ion. For this reason, synchrotron micro-XAS at the Co K-edge with a beam size and flux capable of analyzing individual smalt particles was chosen to examine the changes in structure that occur on degradation and loss of color. Complementary analyses were performed using SEM-EDX, as it was important to correlate the changes in elemental composition on degradation with the XAS analyses. As these analyses were

part of a broader project aiming to gain as comprehensive an understanding of smalt deterioration as possible, the samples were also examined by synchrotron FT-IR and Raman microspectroscopy. These two techniques provided information about changes in the silicate network<sup>20</sup> which will be discussed in detail in a separate publication. This paper will concentrate on the XAS analysis—which instead probes the local environment of the cobalt in smalt—and its relationship with the elemental composition.

## MATERIALS AND METHODS

**Samples and References.** The microsamples from historic paintings were prepared as cross sections by mounting in polyester resin, followed by cutting with a diamond saw or grinding on silicon carbide (SiC) paper. Polishing was carried out with fine grades of SiC paper or Micromesh polishing cloth. Five samples from paintings dating between the 16th and 18th century that were considered to be representative were selected from the archives of the Scientific Department, National Gallery, London and the Centre de Recherche et de Restauration des Musées de France (C2RMF). Details of the paintings and the location of the sample points are as follows. François Lemoyne, *Hercule tuant Cacus*, 1718, oil on canvas, Louvre museum, Paris: the sample L4346 is from the drapery of Cacus. Paolo Veronese, *Les Dieux de l'Olympe*, 1557, fresco transferred to canvas, Louvre Museum, Paris: the location of the sample L2925 is not known. Bartolomé Esteban Murillo, *The Heavenly and Earthly Trinities* (NG 13), 1675–1682, oil on canvas, National Gallery, London: the sample NG13S8 is from the grayish-blue sky. Paolo Veronese, *The Consecration of Saint Nicholas* (NG 26), 1562, oil on canvas, National Gallery, London: the sample NG26S6 is from the brown discolored shadow of the bishop's blue drapery. Paolo Fiammingo, *Landscape with the Expulsion of the Harpies* (NG5467), around 1590, oil on canvas, National Gallery, London: the sample NG5467S1 is from a light blue area of the sky.

The references measured for comparison included a modern Kremer Pigmente smalt powder with a very simple composition (only K, Si, and Co are present) (Table 1) and silica gel colored by cobalt chloride. Silica gel was examined both in dry (blue) and hydrated (pink) forms.

**Analytical Techniques.** The paint cross sections were examined and photographed with a light microscope (Leica DM4000M) under normal and ultraviolet light (filter block A; excitation BP, 340–380 nm; emission LP, 430 nm).

The cobalt coordination of the reference compounds was examined by optical absorption spectroscopy. Spectra were collected in absorbance mode between 350 and 800 nm on a Varian Cary 4000 UV–vis spectrophotometer fitted with an integration sphere. Modern Kremer Pigmente smalt and blue dry silica gel displayed the triply split band centered at 600 nm characteristic of  $\text{Co}^{2+}$  in tetrahedral coordination, whereas the pale pink hydrated silica gel displayed the single weaker band centered at 520 nm characteristic of  $\text{Co}^{2+}$  in octahedral coordination. The results agree with published measurements on alkali silicate and borate glasses.<sup>21</sup>

Quantitative elemental analysis and elemental mapping was conducted in a Carl Zeiss EVO MA10 SEM with an Oxford Instruments INCA 350 EDX system and X-max 80 mm<sup>2</sup> EDX detector. Variable pressure conditions allowed charge compensation on the non-conducting samples, avoiding the need for carbon

**Table 1. Elemental Composition of Well-Preserved and Altered Smalt in Historic Paintings and a Smalt Reference Measured by SEM-EDX<sup>a</sup>**

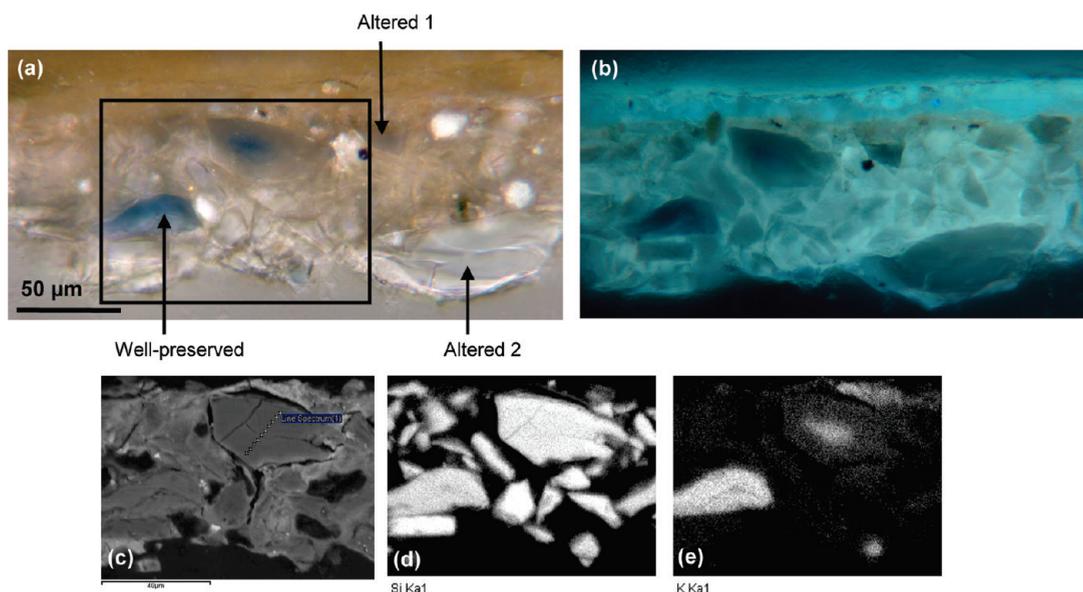
wt %	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	FeO	CoO	As <sub>2</sub> O <sub>3</sub>	NiO	PbO	Bi <sub>2</sub> O <sub>3</sub>
NG13S8—Murillo, <i>The Heavenly and Earthly Trinities</i>												
well-preserved	70.2	1.4	0.9	11.9	1.7	0.3	2.9	2.6	4.5	0.5	2.4	0.5
altered 1	77.9	1.3	0.2	3.0	1.5	0.4	3.4	3.0	4.3	0.6	3.2	0.7
altered 2	90.9	0.5	0.1	1.4	1.2	0.2	1.2	0.9	0.7	0.8	2.0	0.1
L2925—Veronese, <i>Les Dieux de l'Olympe</i>												
well-preserved	64.4	1.8	1.2	16.0	7.0	0.8	2.0	2.1	4.2	0.1	0.4	—
altered 1	77.7	1.4	0.1	0.9	7.8	0.5	2.3	2.2	6.2	0.4	0.4	—
altered 2	76.2	0.7	0.4	1.8	6.0	0.5	2.2	4.1	7.0	0.9	0.2	—
NG26S6—Veronese, <i>The Consecration of Saint Nicholas</i>												
well-preserved	60.0	0.4	0.2	13.7	0.3	—	3.1	5.9	13.8	1.1	—	1.5
altered 1	66.6	0.5	0.2	5.0	0.4	—	3.6	6.6	14.9	1.1	—	1.2
altered 2	67.4	0.5	0.1	2.7	0.3	—	3.8	6.8	14.8	1.0	1.9	1.4
NG5467—Fiammingo, <i>Landscape with the Expulsion of the Harpies</i>												
well-preserved 1	64.5	0.2	0.3	14.2	1.5	—	2.9	4.1	8.8	0.6	2.9	—
altered 1	67.3	0.2	0.1	10.9	1.6	—	3.1	4.4	8.7	0.6	3.2	—
well-preserved 2	67.2	0.0	0.3	14.1	1.3	—	2.7	4.0	8.2	0.5	1.8	—
altered 2	72.5	0.3	0.2	6.3	1.6	—	2.9	3.9	9.3	0.6	2.5	—
altered 3	77.4	1.1	0.2	2.4	0.3	—	3.4	3.0	10.1	0.1	2.2	—
L4346—Lemoyne, <i>Hercule tuant Cacus</i>												
well-preserved	64.0	0.6	0.3	14.4	0.4	—	3.5	4.2	1.1	1.9	9.7	—
altered 1	80.1	1.6	0.1	2.5	0.4	—	2.6	3.3	2.3	1.5	5.6	—
altered 2	81.9	2.1	0.2	2.4	1.0	—	2.8	1.4	2.2	0.3	5.8	—
Reference												
smalt Kremer	74.1	—	0.3	16.1	—	—	—	9.5	—	—	—	—

<sup>a</sup> —, not detected.

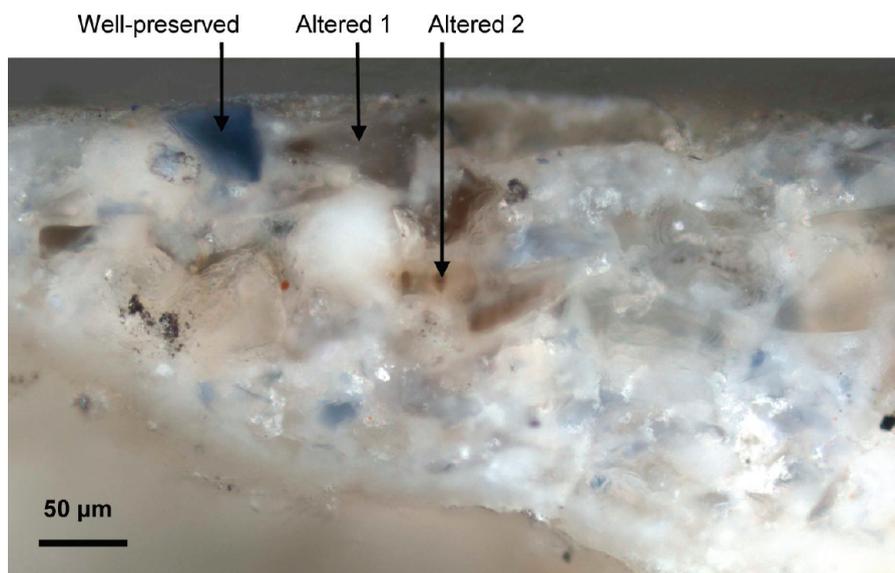
coating and allowing further analysis by other techniques. The operating parameters were 20 kV, 200 pA beam current, 30 Pa chamber pressure (the minimum necessary to limit charging), and water vapor as the chamber gas. The accuracy of the quantitative analysis was evaluated by analysis of Corning Museum of Glass reference glass D, and the measured values were found to be well within 0.2 wt % oxide of the reference values for the majority of the elements.<sup>22</sup> Quantitative EDX analysis was carried out on each particle analyzed by XAS, averaging several spectra from a single particle. Only results relating directly to smalt particles for which XAS spectra are reported are listed in Table 1, but as many particles as possible within the paint cross section were analyzed to gain a general idea of how representative these were. The glass is not perfectly homogeneous in composition, accounting for the small variations in the cobalt content within one paint sample evident in Table 1. The apparently higher concentration of cobalt in the degraded particles relative to the well-preserved is a consequence of normalizing the measurements.

X-ray absorption spectra were collected at the cobalt K-edge on the LUCIA beamline at SOLEIL synchrotron.<sup>23</sup> The beamline was equipped with a Si(111) double-crystal monochromator. The smalt particles in the cross sections were analyzed in fluorescence mode using a mono-element SDD detector with a microbeam. A spot size of  $4 \times 2 \mu\text{m}^2$  was achieved using dynamically bendable mirrors in Kirkpatrick–Baez configuration. The depth analyzed is far greater as the beam passes through the

whole particle due to the beam energy and the low cobalt concentration in smalt, leading to averaging in partially altered particles and making it difficult to obtain quantitative information from the XAS results. For this reason, only data collected from homogeneous particles will be considered in this paper. First  $\mu\text{XRF}$  mapping of the cross section was carried out over the region of interest. On the basis of the cobalt and potassium maps, between 6 and 10 locations that included well-preserved and altered smalt with different degrees of alteration were selected for the XAS measurements. The Kremer smalt reference was analyzed in transmission mode, and the silica gels were analyzed in fluorescence mode. In order to avoid structural change due to dehydration in the vacuum chamber, silica gel was sealed in X-ray transparent Kapton tape. The spectra were collected between 7670 and 8000 eV (energy limit of the beamline) with a step of 2 eV in the pre-edge region (7670–7705 eV), 0.2 eV in the X-ray absorption near-edge spectroscopy (XANES) region (7705–7755 eV), and 1 eV in the extended X-ray absorption fine structure (EXAFS) region (7756–8000 eV) and a counting time of 2 s. Two scans were collected on each point to be averaged. The data was treated using the Athena and Artemis software from Ifeffit.<sup>24</sup> Athena was used to process the spectra by normalization of the pre-edge and post-edge line and to establish linear combinations between spectra in the range of  $-20$  to  $30$  eV. The Co–O distances were obtained in Artemis by fitting the Fourier transforms of  $k^3$ -weighted EXAFS spectra checked by reference to crystalline pyroxene  $\text{CaCoSi}_2\text{O}_6$ .



**Figure 1.** Cross section from Murillo, *The Heavenly and Earthly Trinities* (NG 13S8): (a) visible light; (b) UV light; (c) backscattered image in the SEM of the area in the black box marked on the visible light image; (d) silicon EDX map of the same area; (e) potassium EDX map of the same area.



**Figure 2.** Optical microscope image of the cross section from Veronese, *Les Dieux de l'Olympe* (L2925).

## RESULTS AND DISCUSSION

**Appearance and Elemental Composition of the Smalt Samples.** Smalt particles have a distinctive blue color, as well as an angular shape characteristic of crushed glass that is easily recognizable under a microscope (Figures 1 and 2). On degradation they become pale blue-gray, or lose their color entirely, and can be invisible under normal light due to the similarity of their refractive index with that of the oil medium but are more easily seen under UV light (Figure 1). The cross sections in this study contained smalt particles showing different degrees of degradation (some blue and well-preserved, others completely altered). Some, including that in Figure 1, include

partially altered particles which have a discolored rim but retain a blue core.

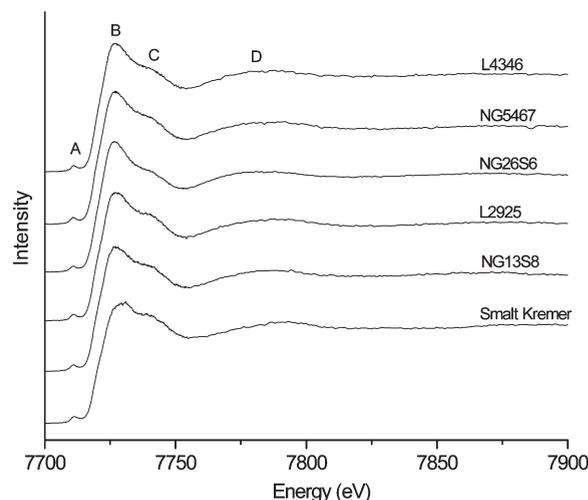
The quantitative SEM-EDX measurements from the most well-preserved particles indicate the original composition of the smalt. The measurements confirm that in every painting the smalt is a potash silicate glass colored by cobalt containing, in well-preserved particles, about 60–70 wt % silica, 12–16 wt % potassium, and 2–7 wt % cobalt (Table 1). The smalt richest in cobalt, at around 6–7 wt %, is that in Paolo Veronese's *Consecration of Saint Nicholas* (NG26). The variation in cobalt content could indicate the use of different grades of smalt, more or less intense in color, or might be due to the quality of the raw materials from which it was manufactured.<sup>5,7</sup>

Arsenic from the cobalt ore is almost always found at significant levels in smalt pigment and here varies between 1 and 15 wt % oxide. The highest level measured was in Paolo Veronese's *Consecration of Saint Nicholas* (NG26), but this reflects the correspondingly high level of cobalt. Comparison instead of the ratios of the atomic % values of cobalt to arsenic brings out variations between the paintings that could relate to the ore that was used or its preparation. In Fiammingo's *Landscape with the Expulsion of the Harpies* (NG5467) it reveals that two different smalts are present within one sample, since that in the lower layer is significantly richer in arsenic than that in the upper layer.

Calcium is present at low levels in some of the smalt particles, which could be of significance when considering degradation since it is known to have a stabilizing effect on glass. The high concentration found in the detached fresco painting by Veronese (L2925), however, is mainly from the calcium carbonate matrix around the smalt. The calcium is appearing in the EDX spectrum either because the interaction volume of the electron beam is larger than the smalt particle or because "beam-skirting" under variable pressure conditions causes scattering from elements away from the beam. Similarly, lead is present in the quantitative results because the smalt is mixed with at least some lead white in every sample; lead is not likely to be a significant component of smalt glass.

Both the composition and the chemistry of the environment surrounding the glass influence its susceptibility to alteration. In the sample from the painting by Fiammingo the smalt in the upper layer is far better preserved than that in the lower layer, almost certainly because it is mixed with lead white. This may be because a lower proportion of drying oil is needed to make a workable paint when smalt is mixed with lead white, making it less permeable to moisture and also decreasing the availability of free fatty acids for potassium soap formation. The formation of lead soap might be a competing reaction that also has an influence on the degree of degradation.<sup>6</sup> The smalt in the lower layer does also differ in composition; it contains more arsenic, as has already been mentioned above, but there are also other differences, such as a lower calcium and nickel content. It is difficult, however, to correlate differences in stability with composition in glass as complex as this.

The loss of color in smalt correlates with depletion of potassium, the concentration of which drops from 12–16 wt % in the most well-preserved particles in this study to 1–2 wt % in the most degraded (Table 1). Veronese's *Les Dieux de l'Olympe* (L2925) shows the largest difference in potassium content between particles, with one of the well-preserved particles containing 16 wt %, whereas the most leached contains only 0.9 wt %. The relationship of alkali leaching to the color loss can be most directly demonstrated by the particles where the core is still blue and the rim has lost its color, as the potassium EDX maps indicate that the rim is depleted in potassium relative to the center (Figure 1). The other cations, including cobalt, are retained in the structure. This alteration process is common for glasses since alkalis, and particularly potassium ions, are the most mobile ions in the structure and are therefore easily leached and replaced by hydrogenated species via an ion-exchange reaction.<sup>25</sup> In the case of smalt this probably involves either water resulting from the painting being subjected to conditions of high humidity at some point in its history or free fatty acids in the drying oil binding medium, or a combination.

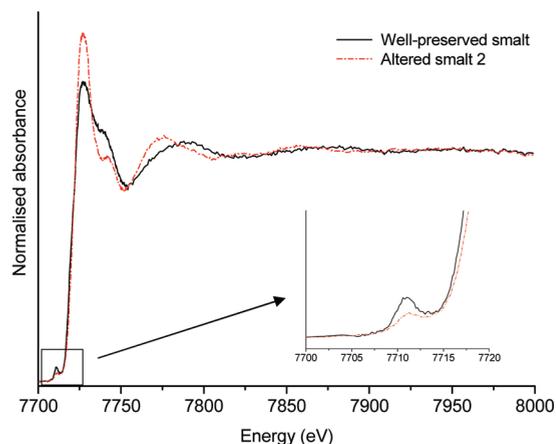


**Figure 3.** X-ray absorption spectra from the well-preserved smalt from paintings and the smalt reference listed in Table 1.

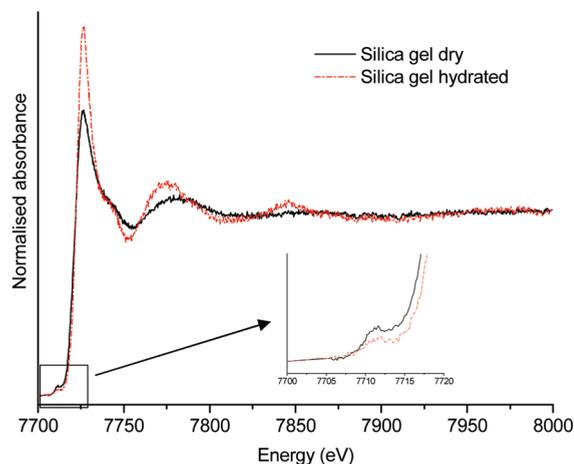
**Structure and Environment around the Cobalt Ion.** The blue color of cobalt-containing compounds is associated with tetrahedral coordination of the cobalt cation, whereas a pink color is expected when the cation is in octahedral coordination.<sup>9</sup> The crystal field transitions of cobalt d-orbitals associated with coordination of the ion and responsible for the color have been described in detail in the literature.<sup>21,26,27</sup> It is generally agreed that in silicate glasses only  $\text{Co}^{2+}$  is present, as  $\text{Co}^{3+}$  is not stable in the temperature range required for melting, unless the alkali content is higher than 40 wt %.<sup>9,21,26</sup> The coordination of cobalt in a glass may vary from tetrahedral to octahedral depending on the glass composition, creating a variety of colors. In alkali borosilicate glasses both environments can occur, with the cobalt coordination decreasing as the alkali content increases or the aluminum content decreases.<sup>27–29</sup> In alkali silicate glass, however, cobalt always gives a blue color as tetrahedral coordination is more stable than octahedral coordination, although an equilibrium does exist between the two.<sup>30</sup> In addition, Terczynska-Madej has demonstrated that potassium stabilizes tetrahedral coordination better than sodium in alkali silicate glasses, leading to a blue color of higher intensity.<sup>21</sup>

Typical X-ray absorption spectra of well-preserved smalt in the cross sections and the Kremer smalt reference are reported in Figure 3. In the XANES region, the pre-edge (A) corresponds to the  $1s \rightarrow 3d$  electronic transition, and the white line (B) is associated with the transition of the  $1s$  electron to the  $4p$  molecular orbitals.<sup>31</sup> Both features are revealing the electronic structure and coordination of the element. The shoulder (C) following the white line corresponds to multiple scattering and/or multielectronic excitations. The large oscillation (D) at the start of the EXAFS region is mostly assigned to multiple scattering of the first neighbor, in this case  $\text{Co}-\text{O}$ .<sup>31</sup> The profiles and band positions of the XANES spectra in Figure 3 are very similar, both to each other and to the Kremer smalt reference, reflecting a similar environment around the cobalt ion and, therefore, the presence of  $\text{Co}^{2+}$  in a mostly tetrahedral coordination. There are, however, small variations in the intensity of features B and C between samples due to differences in the composition of the smalt, since this region is sensitive to the other elements in the glass.

Clear differences between the XAS spectra of altered and well-preserved smalt could be seen in both the XANES and the



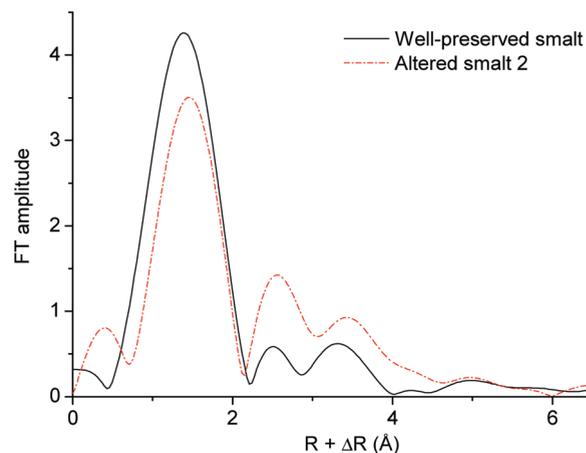
**Figure 4.** X-ray absorption spectra of well-preserved and altered smalt in the cross section from Veronese, *Les Dieux de l'Olympe* (L2925).



**Figure 5.** X-ray absorption spectra of hydrated (pink,  $\text{Co}^{2+}$  octahedral) and dry (blue,  $\text{Co}^{2+}$  tetrahedral) silica gel.

EXAFS regions. The spectral modifications were observed in all the samples to differing extents but were greatest in L2925 from one of the paintings by Veronese (Figure 4), consistent with the fact that this sample also showed the largest difference in potassium content between the two particles from which spectra were collected. However, the pre-edge centered at 7711 eV and the single white line centered at 7727 eV in the XANES region are in the same position in both the altered and well-preserved particles. The degree of oxidation is therefore not modified, and cobalt remains as  $\text{Co}^{2+}$  in the altered glass structure. There are instead changes in the profile on alteration; the pre-edge intensity decreases and the white line becomes sharper and increases in intensity, suggesting an increase in the cobalt coordination.<sup>32</sup> In silica gel, similar spectral differences were observed when going from the dry ( $\text{Co}^{2+}$  tetrahedral) to the hydrated form ( $\text{Co}^{2+}$  octahedral) (Figure 5). A study of alkali borate glasses has correlated these spectral and color changes with the  $\text{Co}^{2+}$  coordination number in the glass, which increased from 4 to 5 and then 6.<sup>28</sup> This suggests that a similar coordination increase occurs in the smalt on alteration.

In the EXAFS region of the spectra from historic smalt, there is a shift of the first oscillation toward lower energy in the altered pigment relative to the well-preserved, indicating an increase in

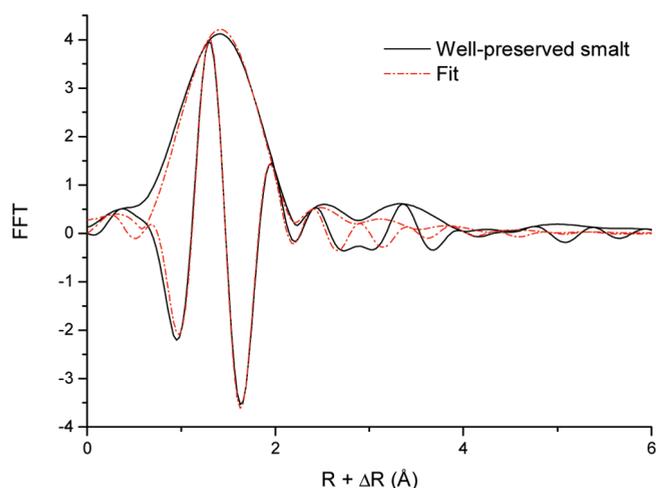


**Figure 6.** Fourier transforms of EXAFS spectra of well-preserved and altered smalt in the cross section from Veronese, *Les Dieux de l'Olympe* (L2925).

the average Co–O distance (Figure 4).<sup>29</sup> In the Fourier-transformed domain this appears as an intensity decrease and a shift of the Co–O peak toward higher values (Figure 6). Again, similar variations can be seen when comparing the spectra of the blue hydrated silica gel and the dry pink silica gel in which the coordination number is increased (Figure 5).

The fitting of the Fourier-transformed domain was carried out in two steps. In a preliminary fit, in which none of the parameters were fixed, we noted an increase in the Co–O distances and the Debye–Waller factors (disorder factor) with alteration of the smalt. To refine the fitting and allow comparison of the different glasses, the Debye–Waller factors were fixed at 0.008 Å for well-preserved smalt and 0.013 Å for altered smalt and the fitting was repeated. Good fit quality was achieved regarding both the amplitude and the imaginary part of the first coordination sphere up to 2.2 Å (Figure 7). The results of these calculations for all the paintings in the study as well as the references (Table 2) show that the Co–O distances, and also the coordination numbers, are indeed consistently greater in the smalt which has lost its color relative to that which is blue. In the Kremer smalt reference, the Co–O distance measured was 1.89 Å and the coordination number was 4.4, which is consistent with the predominantly tetrahedral coordination indicated by the optical absorption measurements. The Co–O distances are greater in the silica gel references, with 2.02 Å when  $\text{Co}^{2+}$  is tetrahedral and 2.11 Å as the coordination is increased to octahedral; this agrees with the published values for various cobalt-containing gels.<sup>33</sup> In the paint samples, the Co–O distance in the well-preserved smalt varies between 1.95 and 1.96 Å with a coordination number between 4.4 and 4.9. These values are close to those that have been obtained for alkali borosilicate glass containing tetrahedral  $\text{Co}^{2+}$  where the Co–O distance has been reported as 1.97 Å.<sup>34</sup> In the altered smalt the Co–O distance and the coordination number can be seen to have increased, reaching a Co–O distance of 2.06 Å with a coordination number of 6 in some particles. These results are consistent with the Co–O distance of 2.07 Å reported in low-alkali borosilicate glass containing mostly octahedral  $\text{Co}^{2+}$ .<sup>28</sup>

The EXAFS measurements confirmed quantitatively the conclusion drawn qualitatively from the XANES region and specified that the discoloration of smalt is associated with an increase in the



**Figure 7.** Fitting of the EXAFS Fourier transforms (amplitude and imaginary part) of well-preserved smalt in the cross section from Veronese, *Les Dieux de l'Olympe* (L2925).

**Table 2.** EXAFS Fitting Results for the References and the Well-Preserved and Altered Smalt in Historic Paintings<sup>a</sup>

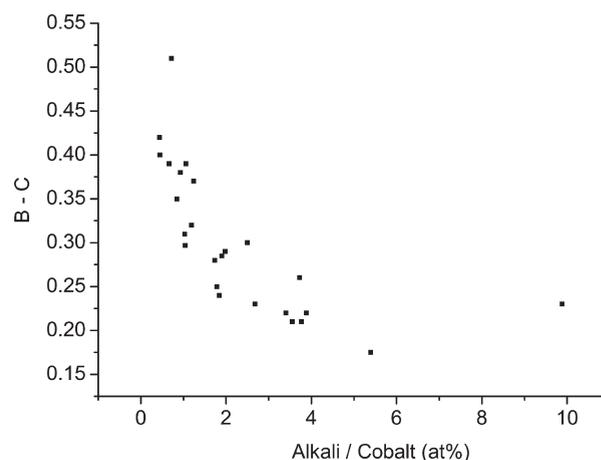
sample	state	R (Å)	N (dN)
Kremer smalt		1.89	4.4 (2)
silica gel	dry (blue)	2.02	4 (fixed)
	hydrated (pink)	2.11	6 (fixed)
L2925	well-preserved	1.95	4.4 (2)
	altered 1	2.03	5.5 (2)
	altered 2	2.06	6.0 (3)
NG13S8	well-preserved	1.95	4.7 (2)
	altered 1	1.97	5.5 (2)
NG5467	well-preserved	1.95	4.9 (1)
	altered 1	2.00	6.2 (1)
NG26S6	well-preserved	1.96	4.4 (3)
	altered 1	2.02	5.6 (1)

<sup>a</sup> R is the Co–O distance given with a minimum error of  $\pm 0.02$  Å, and N is the coordination number given with the associated error dN.

Co–O distance and an increase in the coordination of cobalt from mostly tetrahedral toward octahedral.

Further information could be gained from the concurrent examination of the elemental composition and the XANES spectra collected from the smalt particles. A correlation was established between the intensity of the XANES white line B relative to the shoulder C (B–C) and the alkali content relative to the cobalt content measured in atomic % (Figure 8). The correlation shows that the intensities in the XANES spectra, and therefore the Co–O distance and cobalt coordination, are affected by the alkali/cobalt ratio, indicating that potassium is a close neighbor of the cobalt ion in the glass structure. XANES spectra of cobalt-containing alkali borate glasses synthesized with different alkali contents showed similar changes, with the Co<sup>2+</sup> coordination increasing from 4 to 5 and then 6 together with a change in color, as the alkali content decreased.<sup>28</sup>

The direct effect of alkali on the cobalt environment may be explained by the role of the different cations in the glass structure. Cobalt, as well as the arsenic, iron, aluminum, or nickel present in



**Figure 8.** Correlation between the intensity of the XANES white line B relative to the shoulder C (B–C) and the ratio alkali/Co content in atomic %.

smalt, requires additional positive charges when in tetrahedral coordination to compensate the charge of the four surrounding oxygens. In glass this charge compensation is generally provided by alkali ions.<sup>35,36</sup> In well-preserved smalt, where Co<sup>2+</sup> ions have a tetrahedral coordination, it is potassium that plays this role. The electronegativity of the specific alkali ion that is present influences the coordination and valence around the cobalt ion (and therefore the color), because it affects the optical basicity of the glass and the polarizability of the oxygen ions. The lower electronegativity of potassium stabilizes tetrahedral coordination better than other alkali ions with higher electronegativity, giving a glass with a stronger blue color.<sup>21</sup> The leaching of the potassium ions from the glass creates a deficiency in charge-compensating cations in the structure. The hydrogenated species that replace the alkali cannot take over their role as charge compensators as they form strong covalent bonds with oxygen (modifying the polarizability of the oxygen ions), which influences the cobalt–oxygen bond valence. For this reason, the tetrahedral coordination of Co<sup>2+</sup> responsible for the blue color is not maintained and the Co–O distance together with the number of oxygen neighbors increases.

## CONCLUSION

Smalt was historically very widely used as a pigment as it was cheaper than alternatives such as azurite and ultramarine. The inherent instability of smalt means that the degradation phenomenon addressed in this paper is very common. For this reason there has been a strong interest in understanding the various processes involved. A more complete knowledge can improve our ability to interpret analytical findings, which in turn informs hypotheses as to the original appearance of a painting as well as issues relating to conservation treatment.

Although it has long been postulated that the loss of color in smalt is associated with a change in coordination of the cobalt from the tetrahedral structure that is responsible for the blue color, this was based on extrapolation from studies of cobalt compounds and bulk glass. The techniques used here have allowed investigation of the structural changes in microscopic pigment particles in samples from real paintings directly, confirming that the loss of color is due to an increase in the coordination number of Co<sup>2+</sup> from mainly tetrahedral to octahedral

and that the postulated mechanism holds true in smalt that has degraded naturally over several centuries.

The new data on the local environment of cobalt in alkali silicate glass, including the Co–O distances and the coordination number of cobalt, are also of broader interest to the scientific community, since earlier XAS studies have instead been on alkali borosilicate glass. In addition, the smalt glass investigated here is of far more complex composition. Nevertheless, the results show the same fundamental relationship between the alkali content and structure around the cobalt ion that was seen in the borosilicate glasses synthesized with different compositions, even though in smalt pigment the decrease in alkali content (in this case potassium) was caused by leaching during degradation. This loss of potassium ions results in a decrease in the number of charge-compensating ions available in the structure, which can create a charge deficiency around the cobalt. As a result, the cobalt cations cannot retain a tetrahedral coordination, and it increases toward octahedral coordination with a concurrent loss of the blue color in the smalt.

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