



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

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<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

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Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



**Experiment title:**

Looking for new insight into the fading mechanism of Prussian Blue by FF-XANES and micro-FTIR 2D mapping of Fe(III)/Fe(II) and bridging cyanide on original and model paintings

**Experiment number:**

HG-107

**Beamline:**

ID21

**Date of experiment:**

from: 05/07/2017 to: 11/07/2017

**Date of report:**

03/03/2020

**Shifts:**

18

**Local contact(s):**

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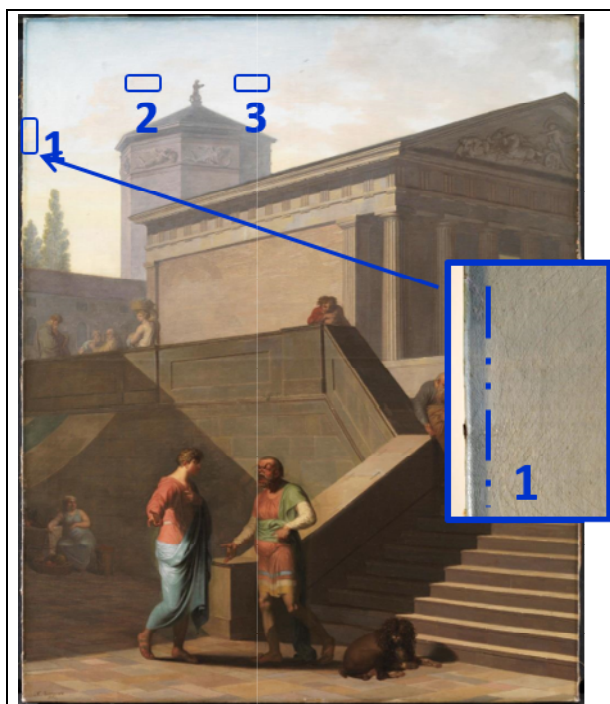
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**1. INTRODUCTION**

The fading of the mixed-valence pigment Prussian blue (hereafter referred to as PB;  $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}/\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ ) in oil paintings has been ascribed to a photo-induced reduction of  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$ . The process depends on the presence of others pigments/extenders, the environmental conditions to which PB is exposed as well as to its synthesis process [1-6].

However, an overall comprehension of the fading mechanism and its extend through the paint layer at the (sub)micrometer-scale is still lacking due to the sensitivity of the pigment towards the exposure to SR X-ray micro-probes [7,8]. In this experiment we have investigated the photo-fading process of PB at the sub-micrometer length by employing a combination of different 2D XANES-based approaches at the Fe K-edge. Measurements have been performed on photochemically aged PB oil paint models and in microsamples taken from discoloured areas of a selection of 18th C. Danish paintings of the Statens Museum for Kunst (SMK) collection (Copenhagen, DK) (Figure 1).



**Figure 1.** Photograph of one of the analyzed painting *Pamphilus and his Servant Davus* by N. Abildgaard (KMS588, 1802; Statens Museum for Kunst collection, Copenhagen, DK) with magnification of the area exposed to environmental light, that shows the dramatic fading of the blue colour

## 2. EXPERIMENTAL

The following set of samples have been investigated at ID21:

- a) photochemically aged PB-based oil model paints (ca. 10 in total) obtained by mixing either the soluble (SPB) or the insoluble Prussian blue (IPB) in different mass ratios with 2 different white pigments: lead white [LW;  $\text{PbCO}_3/\text{Pb}_3(\text{CO}_3)_2 \cdot (\text{OH})_2$ ] or zinc white (ZW;  $\text{ZnO}$ ).
- b) Original paint micro-fragments (4 in total) obtained from selected (un)discoloured regions of two 18<sup>th</sup> C paintings (SKM collection).
- c) set of Fe-reference powders (ca. 10 in total).

Model paint samples were analyzed before and after photochemical aging in the form of thin sections (2-10  $\mu\text{m}$  in thickness), while micro-samples from real paintings were investigated as resin-embedded cross-sections.

Measurements were performed at the scanning X-ray microscope (SXM) end-station of ID21 by means of a fixed exit double-crystal Si(220) monochromator.

The energy calibration was performed using an iron metallic foil and by setting the position of the peak maximum of its first order derivative spectrum at 7112 eV. The incident beam was focused by means of Kirkpatrick-Baez mirrors down to a diameter of  $0.88 \times 0.4 \mu\text{m}^2$  (h $\times$ v). Measurements in unfocused mode were performed using a beam with a diameter size between 100  $\mu\text{m}$  and 250  $\mu\text{m}$ . XRF signals were collected in the horizontal plane and at 69° with respect to the incident beam direction by means of either a single energy-dispersive silicon drift detector (Xflash 5100, Bruker) or a photodiode. Single point XANES spectra were acquired in XRF mode by scanning the primary energy across the Fe K-edge (7.100-7.297 keV; energy step: 0.5 eV; exposure time per energy step: 0.1 s).

A photon flux up to ca.  $1 \times 10^{10}$  ph/s was employed and it was varied using attenuators. Fluence values between  $6 \times 10^7$ - $6 \times 10^8$  ph/ $\mu\text{m}^2$  were estimated for the spectra recorded in unfocused mode, while fluences of  $1$ - $3 \times 10^{11}$  ph/ $\mu\text{m}^2$  were calculated for those collected by means of the focused beam.

The ATHENA software [9] was used for the normalization and the linear combination fit (LCF) of the spectra against a library of XANES spectra of Fe -reference compounds.

During the  $\mu$ -XRF mapping experiments, the fluorescence signals were produced by employing a monochromatic primary beam of fixed energy across the Fe K-edge. Maps of the same region of interest were recorded using 100 ms/pixel at three different energies: (i) 7.124 keV to favor the excitation of  $\text{Fe}^{\text{II}}$  -species and other Fe-based compounds (e.g. oxyhydroxides/oxides, oxalates and or/sulfates); (ii) 7.1304 keV and (iii) 7.3 keV to obtain the fluorescence intensity of  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ -species and all Fe-species, respectively.

The software PyMca was used to fit the fluorescence spectra and to separate the contribution of different elements.

Total fluence values between  $4 \times 10^8$  and  $2 \times 10^9$  ph/ $\mu\text{m}^2$  were employed during the  $\mu$ -XRF mapping at the three different energies.

Full spectral (FS)  $\mu$ -XANES mapping in XRF mode of regions of interest of the original paint micro-samples were performed using dwell times of 100 ms/pixel. A stack of n. 173  $\mu$ -XRF maps at energy increments around the Fe K-edge was recorded with the following step sizes: 2 eV before the pre-edge peaks and the absorption edge (7.092-7.108 keV), 0.5 eV around the pre-edge peak and the absorption edge (7.1085-7.136 keV), 1 eV just after the absorption edge (7.136-7.208 keV) and 2.5 eV in the post-edge absorption region. The deconvolution into elemental maps of the FS  $\mu$ -XRF data (XANES stack) was performed using PyMCA. The spectrocrunch library was employed to correct for the alignment of frames in the XANES stack, while TXM-Wizard [10] was used to fit the Fe K-edge XANES spectra and to produce the maps of different Fe-phases.

Total fluence values between  $2 \times 10^{10}$  and  $3 \times 10^{11}$  ph/ $\mu\text{m}^2$  were employed during the FS  $\mu$ -XANES mapping investigations.

It should be noted that full-field XANES imaging investigations have been also performed on a selection of the model paints. Nevertheless, for most of them, especially for those containing higher relative amounts of lead white and zinc white with respect to Prussian blue, the analysis did not yield reliable results.

### 3. RESULTS

#### 3.1. Assessment of Prussian blue stability under exposure to SR X-ray micro-beam

$\mu$ -XANES measurements and  $\mu$ -XRF mapping at Fe K-edge have been performed to map the distribution of different  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ -cyanide compounds within the stratigraphy of (un)faded PB painting fragments with (sub)micrometric lateral resolution. It is reported that a high-flux X-ray radiation may cause damages on Prussian blue pigments, by inducing a reduction of  $\text{Fe}^{\text{III}}$  ions [7,8]. This makes tricky any detection of changes in the  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  ratio, that results from the original aging process of the pigment.

To face this shortcoming, first of all we have performed radiation damage tests on PB paint models, with the aim to find the safest working conditions in terms of time exposure and fluence ( $\text{ph}/\mu\text{m}^2$ ).

As shown in Figure 2, the XANES spectra recorded by means of a focused beam do not show visible changes for fluence values up to of about  $2\text{-}3 \times 10^{11} \text{ ph}/\mu\text{m}^2$ ; clear variations are clearly detectable instead for fluence values  $\geq 1 \times 10^{12} \text{ ph}/\mu\text{m}^2$ . Specifically, such spectral modifications consist in a shift of the absorption edge toward lower energies accounting for the reduction of  $\text{Fe}^{\text{III}}$  into  $\text{Fe}^{\text{II}}$ . Furthermore, the intensity decrease of the white line (at ca. 7.1305 keV) and the intensity increase of the pre-edge peaks is attributable to the greater disorder and deformation of the octahedral coordination sphere of Fe-ions [2,7,11].

The variations induced by the exposure to X-ray microbeam have been also exploited for selecting the energies for performing  $\mu$ -XRF mapping at multiple energies around the Fe K-edge (see section 2 for details).

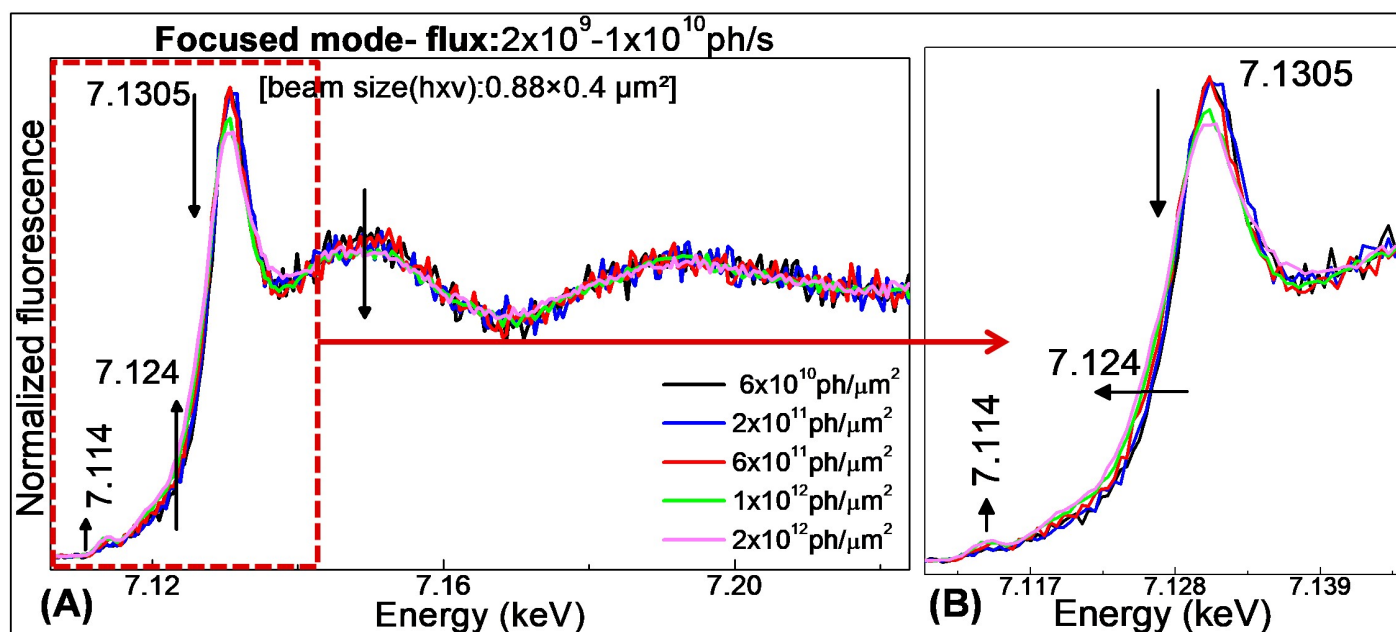


Figure 2. (A) Fe K-edge  $\mu$ -XANES spectra collected from an oil paint model composed of a mixture of Prussian blue and zinc white (in a 1:50 weight ratio) at different fluence values to test the radiation damage. (B) Enlarged visualization of the spectral range highlighted by dotted red rectangle shown in (A).

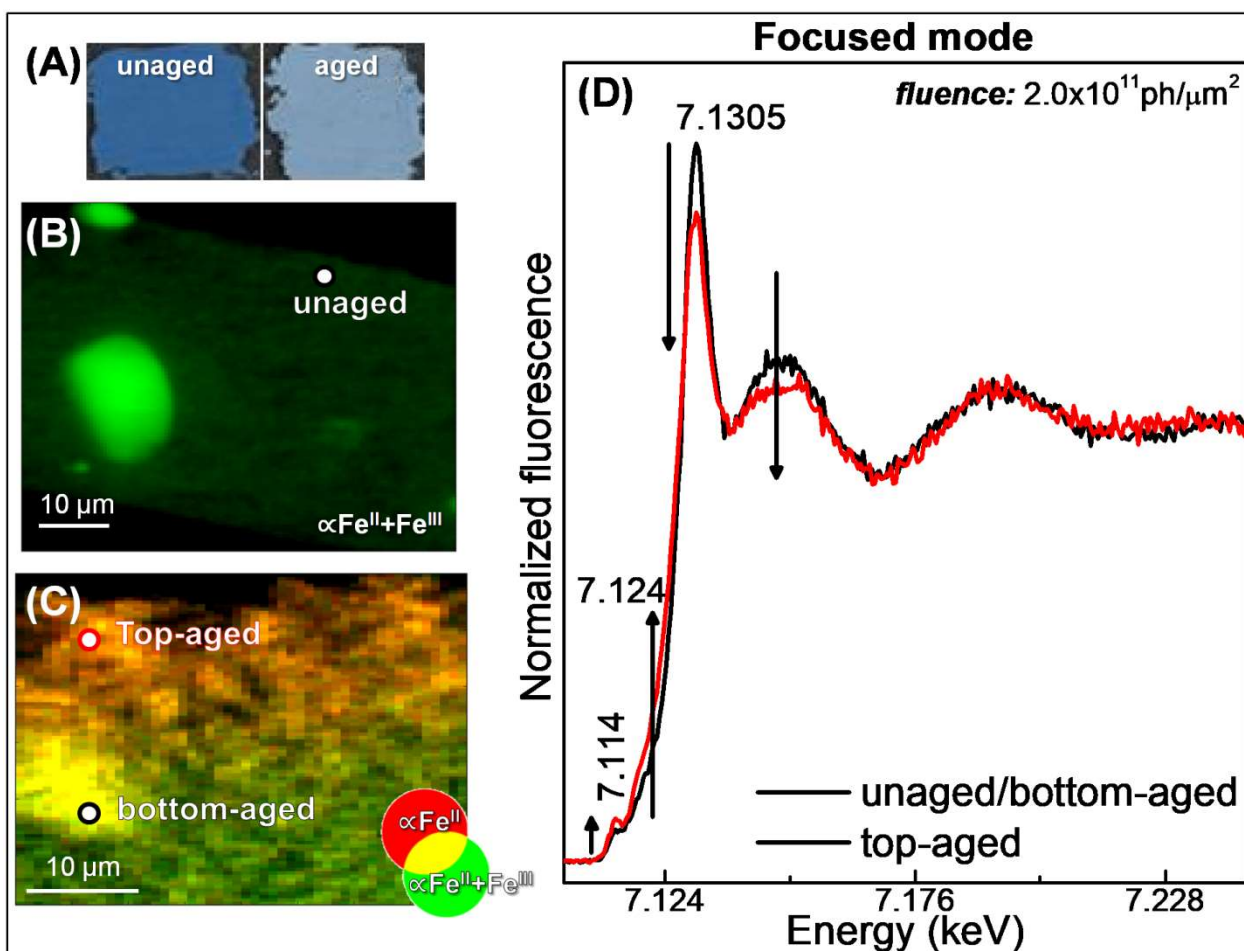
### 3.2. Photochemically aged PB-based model paints

After having found the safe working conditions of analysis and the appropriate energies to map variation of the Fe<sup>II</sup>/Fe<sup>III</sup>-cyanide distributions,  $\mu$ -XRF mapping and single point  $\mu$ -XANES analyses at Fe K-edge have been performed on the set of PB-based model paints.

As an example, the Fe-speciation results obtained from the unaged and aged mock-ups, prepared by mixing Prussian blue (soluble form) and lead white (1:50 weight ratio), are shown in Figure 3.

After light exposure, the paint surface exhibits a clear discoloration (Figure 3A).

Fe-speciation maps (Figure 3B,C), show the presence of a higher relative amount of Fe<sup>II</sup>-species only within the uppermost 3 – 10  $\mu$ m of the aged sample. This is further confirmed by  $\mu$ -XANES analysis (Figure 3D): the spectrum acquired from the superficial degradation layer (red line) appear modified if compared with the profiles collected from the bottom part of the aged sample and from the unaged one (black line). Such modifications of the XANES profile resemble the changes observed during the beam damage tests (*cf.* Figure 2) as well as those reported in the literature [2,7,8,11] and they can be assigned to the partial reduction of Fe<sup>III</sup> to Fe<sup>II</sup>.



**Figure 3.** (A) Photographs of the oil paint models composed of a mixture of Prussian blue (soluble form) and lead white (1:50 weight ratio) (left) before and (right) after UVA-Visible light exposure. (B) Composite RG Fe-speciation maps obtained from a region of interest of thin sections of the (B) unaged sample [step size:  $0.5 \times 0.5 \mu\text{m}^2$ , exp. time: 100 ms/pixel, Fluence (3 energies):  $5 \times 10^8 \text{ ph}/\mu\text{m}^2$ ] and (C) photochemically aged paint [step size:  $0.8 \times 0.3 \mu\text{m}^2$ , exp. time: 100 ms/pixel, Fluence (3 energies):  $2 \times 10^9 \text{ ph}/\mu\text{m}^2$ ]. (D) Selection of the Fe K-edge  $\mu$ -XANES spectra recorded from the spots shown in (B,C).

### 3.3 Original paint micro-samples

Figure 4 shows the full spectral (FS)  $\mu$ -XANES mapping results obtained from the analysis of a cross-section taken from the light exposed/faded blue area of the painting KMS588 (cf. Figure 1).

The Fe-speciation maps and the corresponding  $\mu$ -XANES spectra (Figure B,C) reveal that the superficial faded layer is mainly composed of  $\text{Fe}^{\text{III}}$ -oxyhydroxide along with minor abundances of  $\text{Fe}^{\text{II}}$ -compounds, including sulfates and oxalates. Prussian blue is instead the main component of the blue paint underneath.

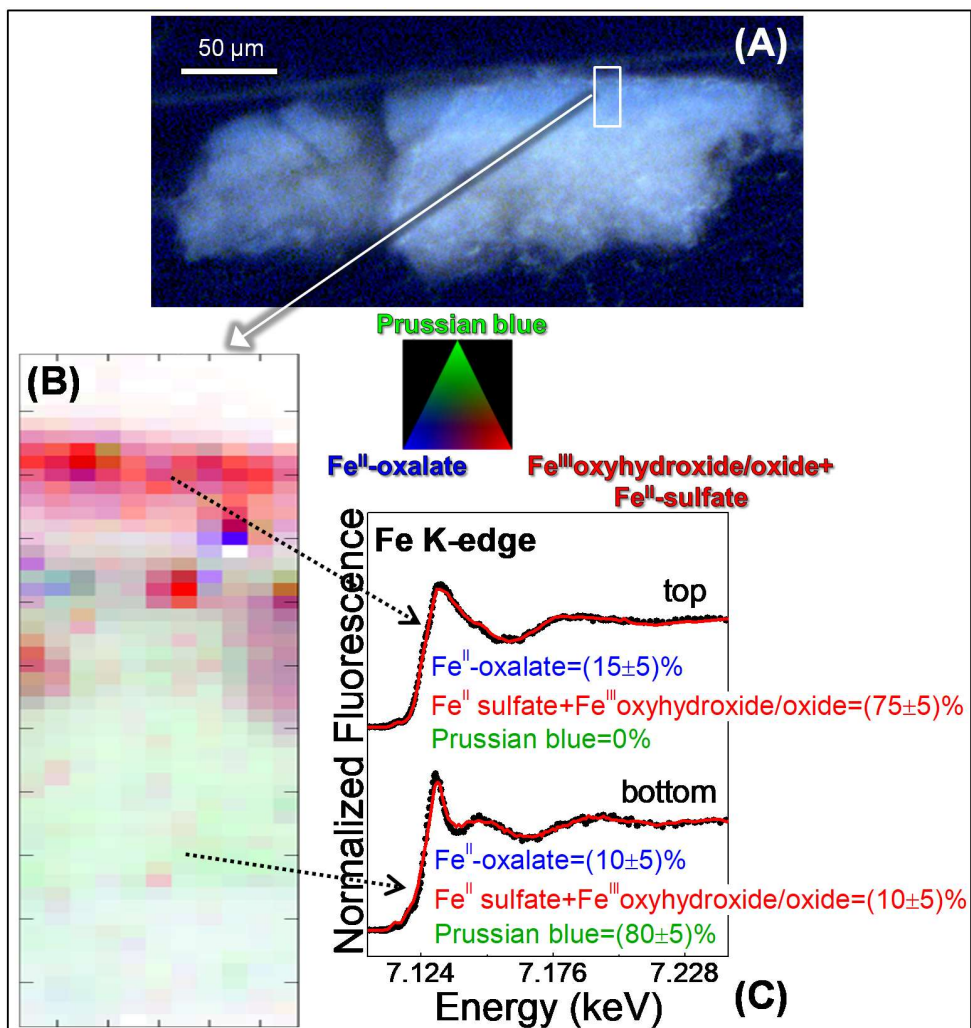
Based on earlier studies, [5,11] the presence of  $\text{Fe}^{\text{III}}$ -oxyhydroxide has been interpreted either as a final degradation product of a deep fading of the original Prussian blue or as a residue of the manufacturing process of the pigment.

Nevertheless, considering that similar analyses performed on the unexposed/not faded cross-section (results not reported) reveal that Prussian blue is the dominant component of the entire paint stratigraphy, we can reasonably assume that, in the faded cross-section,  $\text{Fe}^{\text{III}}$ -oxyhydroxide is a degradation product of the original PB pigment.

Overall the obtained results provide new significant information on the redox process involved in the photo-degradation mechanism of Prussian blue as well as on the conservative story of the analyzed paintings. In addition, the present experiment lays the foundation for the development of a safe analytical working protocol for the analyses of Prussian blue pigments by synchrotron radiation X-ray micro-beams, by avoiding any radiation damage issue.

### REFERENCES:

- [1] Kirby, J. and D. Saunders, *The National Gallery Technical Bulletin*, 2004, **25**, 73-99; [2] Samain, L., et al., *JAAS*, 2011, **26**, 930-941. [3] Samain, L., et al., *JAAS*, 2013, **28**, 524-535; [4] Samain, L., et al., *J. Synchrotron Radiat.*, 2013, **20**, 460-473; [5] Samain, L., et al., *J. Phys. Chem. C*, 2013, **117**, 9693-9712; [6] Monrad, K., et al., *Science and Art. The painted Surface*, 2014. RSC Publishing. Ch. 17, pp. 354-372. [7] Gervais, C., et al., *Appl. Phys. A*, 2013, **111**, 15-22; [8] Gervais, C., et al., *Appl. Phys. A*, 2015, **121**, 949-955; [9] B. Ravel, M. J. Newville, *Journal of Synchrotron Radiation*, 2005, **12**, 537-541. [10] Y. Liu et al., *Journal of Synchrotron Radiation* 2012, **19**, 281-287. [11] Gervais, C., et al., *Langmuir*, 2015, **31**, 8168-8175.



**Figure 4.** (A) Photomicrograph of a cross-section taken from an exposed/faded blue area of the painting KMS 588 (cf. Figure 1). (B) Full-spectral (FS)  $\mu$ -XANES composite RGB maps of  $\text{Fe}^{\text{III}}$ -oxyhydroxide+ $\text{Fe}^{\text{II}}$ -sulfate/Prussian blue/ $\text{Fe}^{\text{II}}$ -oxalate recorded from the area indicated by the white rectangle in (A) [step size (v×h):  $0.5 \times 1 \mu\text{m}^2$ , exp. time: 100 ms/pixel, Fluence (173 energies):  $\sim 2.5 \times 10^{10}$  ph/ $\mu\text{m}^2$ ]. (C) Fe K-edge  $\mu$ -XANES spectra (black) extracted from region of interests of the FS  $\mu$ -XANES stack shown by arrows in (A) [average pixel number: 3-5; pixel sizes:  $0.5 \times 1 \mu\text{m}^2$ ] and corresponding linear combination fit results of different Fe-based compounds (red).