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A multimodal study of smalt preservation and degradation on the painting "Woman doing a Libation or Artemisia" from an anonymous painter of the Fontainebleau School

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Abstract The blue pigment smalt, a synthetic potash glass tinted with cobalt, was widely used between the sixteenth and the eighteenth centuries. As part of a study on the alteration of smalt and the reconstitution of its original color, the painting: *Woman doing a Libation or Artemisia* (Fontainebleau school, 1570) was examined in which the artist used smalt as a blue pigment, which is now degraded. Noninvasive imaging was performed using macro-2D X-ray fluorescence and reflectance imaging spectroscopy to get an overview of the artist's palette and its distribution. Samples prepared as cross sections were also analyzed by scanning electron microscopy coupled with energy dispersive spectroscopy, micro-X-ray absorption near-edge structure spectroscopy and synchrotron micro-X-ray diffraction imaging to determine the preservation state of the smalt as well as structural information on other pigments adjacent to smalt grains in individual paint layers, which could play a role in the degradation process. On the one hand, the study conducted on the alteration of smalt has shown that it is very weathered and mixed with hydrocerussite, which could be a factor that would facilitate the alteration. On the other hand, these analyses have made it possible to identify and locate the pigments used, which will be the basis for the virtual reconstruction of the color of the painting.

1 Introduction

The appearance of historical paintings can change due to alteration of over time [1, 2]. Some alterations, such as the discoloration of smalt, are irreversible and cannot be restored. Smalt is a blue potash glass colored by the addition of cobalt oxides during the preparation of the glass and milled to be used as a pigment. It is commonly found between the sixteenth and the eighteenth centuries in oil paintings, murals and polychromy [3–5].

This blue pigment existed in different hues depending on the thickness of the grains and on the Co concentration which can vary between 1 and $2\%_{wt}$ of the total weight of a grain, in smalt used as brightener [3] to $15\%_{wt}$ in the ones used in painting. The most common concentrations of Co found in this pigment in paintings lie between 3 and $7\%_{wt}$ [6]. Depending on the region where smalt is manufactured, the grains of this pigment may contain several other elements. For example, smalt from the Erzgebirge mountains is known for containing arsenic (As), iron (Fe), nickel (Ni) or bismuth (Bi) in smalt grains [7].

Smalt has the tendency to degrade in oil painting from blue to a yellowish hue [8]. The alteration involves an ionic exchange between the H^+ ions from the painting medium and the K^+ ions contained in the glass grains. This leads to the leaching of K^+ ions

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Fig. 1 *Woman doing a libation or Artemisia*, anonymous, around 1550, Fontainebleau School, Louvre Museum (Inv n° : RFML.PE.2019.40.1). **a** Image before restoration, position of the samples taken from the painting are shown (cross section A, inv n° C2RMF 20070 and cross section B n° C2RMF 20071). **b** Image after restoration. ©C2RMF/Thomas Clot

with several consequences: the leached K^+ ions can react in the medium and form K soaps able to migrate at the paint surface, creating crust on the painting [6]. In the smalt grains, the leaching of the K^+ induces rearrangement of the silicate matrix and creates a charge deficit around Co^{2+} ions. This deficit forces the Co^{2+} complexes to rearrange in the glass matrix going from a tetrahedral coordination to an octahedral one, explaining the loss of color of the pigment in paintings [6, 9].

Whereas the smalt alteration mechanism has already been well studied and understood, the different factors which can play a role in the alteration process have not yet been understood.

A previous study where an overview of the alteration state of smalt in paintings from French museum collections has shown that the weathering mechanism is not a time-dependent process and that the depth of the smalt containing paint layer in stratigraphies does not seem to have a role in the weathering of the pigment either [10, 11].

Therefore, other components in the smalt containing paint layer, such as other pigments mixed with smalt or the binding medium, are potential alteration factors. In order to target those potential criteria, we studied a painting from the Louvre's collection. Visual and microscopic observations of the painting had first shown a potential presence of a particularly altered smalt in the sky and in the garment of the woman at the center. Therefore, noninvasive analyses on the painting were performed: macro-2D X-ray fluorescence (MA-XRF) and reflectance imaging spectroscopy (RIS) to confirm the presence of smalt and to characterize the composition of the artist's palette. Then, two samples were taken from the painting to perform microscale analysis. Observations under optical and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) have allowed the exact composition of the paint layers and smalt grains to be determined. Micro-X-ray absorption near edge spectroscopy at the Co K-edge (XANES) was performed to quantify the weathering state of the pigment and 2D synchrotron micro-X-ray diffraction (2D-µXRD) was used to investigate the crystalline phases of other pigments especially lead white which exist in two crystalline forms in paintings: cerussite and hydrocerussite [12].

2 Experimental section

2.1 Materials

The painting studied here is *Woman doing a Libation or Artemisia* and is painted by an anonymous artist of the School of Fontainebleau from around 1550 (Inv n°: RFML.PE.2019.40.1) (Fig. 1).

The painting could represent the scene where Artemisia drinks the mixture of bones and ashes reduced to powder of her deceased husband. A little to the right a fire seems to be burning on a table. This painting had been under restoration during several months at the C2RMF, which allowed us to perform several analyses.

2.1.1 X-ray fluorescence imaging spectroscopy (MA-XRF)

Scanning X-ray fluorescence imaging of paintings, labeled here MA-XRF, is nowadays a well-established method using synchrotron radiation and laboratory X-ray generators [13].The detailed experimental description of the instrument is reported elsewhere [14]. The head integrates a 50-kV Mo X-ray generator (ROENTEC X1 generator, RTW MCB 50-0.6, 50 kV, 0.6 mA max) with a 1 mm collimator producing a 1 mm beam spot on the painting. XRF spectra were collected using a silicon drift detector (10 mm^2 KETEK model AXAS-A) placed at 15 mm distance from the paining surface and an Amptek 8000A multichannel analyzer. In our case, the maps were acquired with a step size of 0.7 mm. Each point is acquired with a 100 ms dwell time. The data set was processed with the open-source program PyMCA [15]. Elemental maps were obtained by fitting the global spectrum of the scan and by performing a deconvolution of the spectrum in order to select the region of interest (ROI) of each element on it.

2.2 Reflectance imaging spectroscopy (RIS)

Spectral reflectance data were collected using a pushbroom visible-near-infra-red hyperspectral camera (HySpex VNIR1600 manufactured by Norsk Elektro Optikk), which acquires data with a spatial resolution of 15 pixels per mm and within the spectral range of 414 to 992 nm. The pushbroom camera acquires only a single line of data spatially and is, therefore, mounted on an automated XY translation stage in order to scan the entire surface of a painting. For this acquisition, 80 spectral bands were captured with a center wavelength spacing of 7.29 nm. The data were then calibrated radiometrically to absolute reflectance and corrected for geometric distortions to produce a final data cube using the methodology described in [16].

Spectral analysis was then carried out using the Python programming language and the Spectral Python and Numpy modules. Spectral angle mapping (SAM) classification was carried out using five end-members chosen on the painting, which were chosen according to the elemental distribution provided by MA-XRF. SAM classification then allowed visualization of the areas assigned to each end-member with each end-member labeled as the pigment they were supposed to represent.

2.3 Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX)

Two samples were taken from the painting at two different locations in the sky where smalt could be found (Fig.1: one at the left under the arc (cross section A, n° C2RMF 20070) and one at the top of the painting (cross section B, n° C2RMF 20071). Both samples were embedded in sody33 polyester resin as cross sections and were analyzed by SEM-EDX. Quantitative elemental and elemental mapping were conducted in a JEOL 7800F SEM coupled with two Bruker AXS 6|30 EDX detectors. The non-conductive samples were platinum (Pt) coated in order to avoid charge accumulation. The operating parameters were: an acceleration voltage of 15 kV, a beam current of 3.6 nA and a pressure in the chamber of less than 100 Pa.

All spectra were analyzed with the Bruker Quantax Duo 400 analytical platform (Esprit software). An internal reference provides the quantitative analysis for the determination of the elemental ratios and results were expressed in oxide percentage.

2.4 Micro-X-ray absorption near edge spectroscopy (XANES)

Micro-XANES spectra were collected at the Co K-edge on the PUMA beamline at the SOLEIL synchrotron. The beamline was equipped with a Si(111) double crystal monochromator. Smalt grains were analyzed in fluorescence mode with a micro-beam of 5 x 5 μm^2. 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. The spectra were collected between 7670 and 8000 eV with a step of 2 eV in the pre-edge region (7670 to 7705 eV), 0.2 eV in the XANES region (7705 to 7755 eV) and 1 eV in the EXAFS region (7755 to 8000 eV) and a counting time of 2s. The data were treated using PyMCA.

2.5 2D micro-X-ray diffraction (2DμXRD)

2D-μXRD maps were recorded on the ID13 beam-line [17] at ESRF synchrotron benefitting from the historical materials “Block Allocation Group” (BAG) access HG-172 [18]. The incident energy (13 keV) was selected thanks to a Si(111) crystal monochromator. The beam was focused down to 2.5 x 2.5 μm^2 using compound refractive lenses (CRL) mounted in a transfocator. XRD signals were recorded in transmission geometry using a Dectris EIGER X 4M detector (2,070 × 2,167 pixels, pixel size 75 ×75 μm^2) with an acquisition time of 25 ms/pixel. Calibration of the setup was performed using an Al_2O_3 reference sample. The recorded 2D diffraction images were azimuthally integrated using the PyFAI software package. Crystalline phases were identified using the Match! software [18]. The phase maps were obtained using PyMCA by selecting the ROIs corresponding to characteristic and unique peaks of the phases.

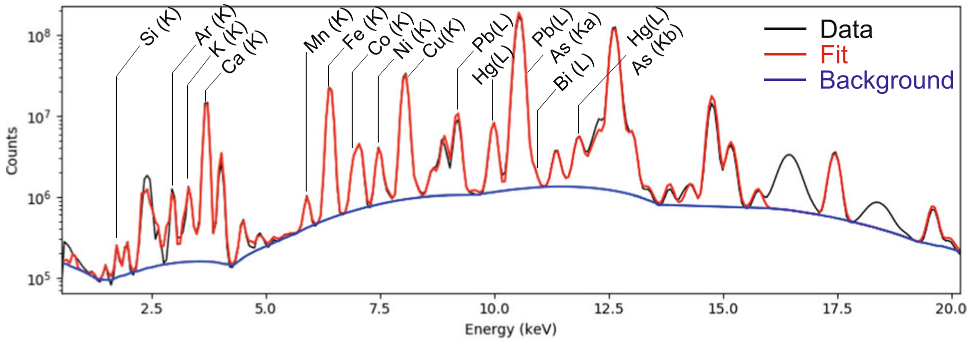

Fig. 2 Overall spectrum of the MA-XRF scanning of the painting

3 Results and discussion

3.1 Distribution of the pigments on the painting

The first goal was to characterize the artist's palette. Thus, a MA-XRF scan of the whole painting was performed and the global spectrum is shown in Fig. 2.

Elemental distribution maps were extracted and these distributions compared to extract information on the pigments used within the painting.

The elemental distributions maps indicated the presence of several pigments. The tin (Sn) distribution shares common areas with the lead (Pb) distribution which indicated the presence of lead tin yellow. The copper (Cu) distribution indicated the presence of a Cu-based pigment. The fact that Cu-rich areas appear blue suggested the presence of azurite. The mercury (Hg) distribution indicated the presence of vermilion and high concentrations of Fe in some areas of the painting suggest the use of different earth pigments or ochres. By looking at the Co, Ni, As and Bi distributions, which are elements found in the smalt composition, we observed that the distribution of these elements were correlated (Fig. 3), which indicated that smalt was present in the painting. Moreover, the brown color of the areas, where smalt is present, could indicate that the pigment is highly weathered.

Then, RIS mapping and SAM classification were carried out. The resulting spectral angle mapping and related spectra are shown in Fig. 4. The first observation was that pixels which are classified as azurite are clustered in three locations: the dress of the character at the top of the painting, the amphora and the part of the sky on the right. The comparison of these results and those obtained by the MA-XRF mapping of Cu gave very similar results. The spectrum associated with these zones are also characteristic of the reflectance spectrum of azurite, which confirmed the presence of this pigment.

Many elements of the foreground as well as some of the clothing of the figures were attributed to vermilion and lead tin yellow, which is consistent with the MA-XRF elemental distributions. However, we expected the statues on the right and left columns on the painting, to be attributed to lead tin yellow which is barely the case. For the earth pigments or ochres we expected more areas of the background to be assigned to this end-member given the Fe MA-XRF elemental map. The distribution of smalt correlated rather well with the Ni, Co and As MA-XRF maps. Also, the right part of the sky should contain smalt according to the MA-XRF maps but the SAM did not assign these area to smalt. Besides, the classification assigned areas to smalt even if they did not contain Co, Ni or As according to MA-XRF. These areas, mainly on the left and right edges of the painting, appeared yellow/brown on the reflectance image of the painting. The fact that smalt also appeared yellow/brown on this painting indicated that the pigment must have lost its original color and it confirmed the advanced state of alteration of the pigment. This could explain why the areas at the right and left ends of the painting, which were also yellow/brown were mistakenly attributed to smalt as their colors were close.

Moreover, the yellowing of the varnish, which resulted in a loss of clarity and legibility of the colors of the work, could play a role in these inconclusive results of the SAM for pigments with colors close to yellow and brown.

3.2 State of preservation of smalt

To test for the presence of some of these pigments and to get more information about the smalt used on the painting, elemental mapping was carried out on both cross sections A and B. Cross section B is represented in Fig. 5.

The cross section is composed of three layers: a ground layer and two painted layers. The ground layer is brown and mainly composed of calcite, alumino-silicates and lead white. The second layer is yellowish with some blue grains. It contains mostly smalt and lead white. The blue grains are identified as azurite. The third layer is composed of smalt and lead white and appears gray/yellow. Cross section A had a comparable stratigraphy: the same number of layers, a similar preparation and also two painted layers. The only difference between the painted layers of cross section A with respect to that of the B was that they did not contain azurite.

The composition of smalt grains was quantified in both cross sections. The results are given in Table 1 with only the main elements indicated.

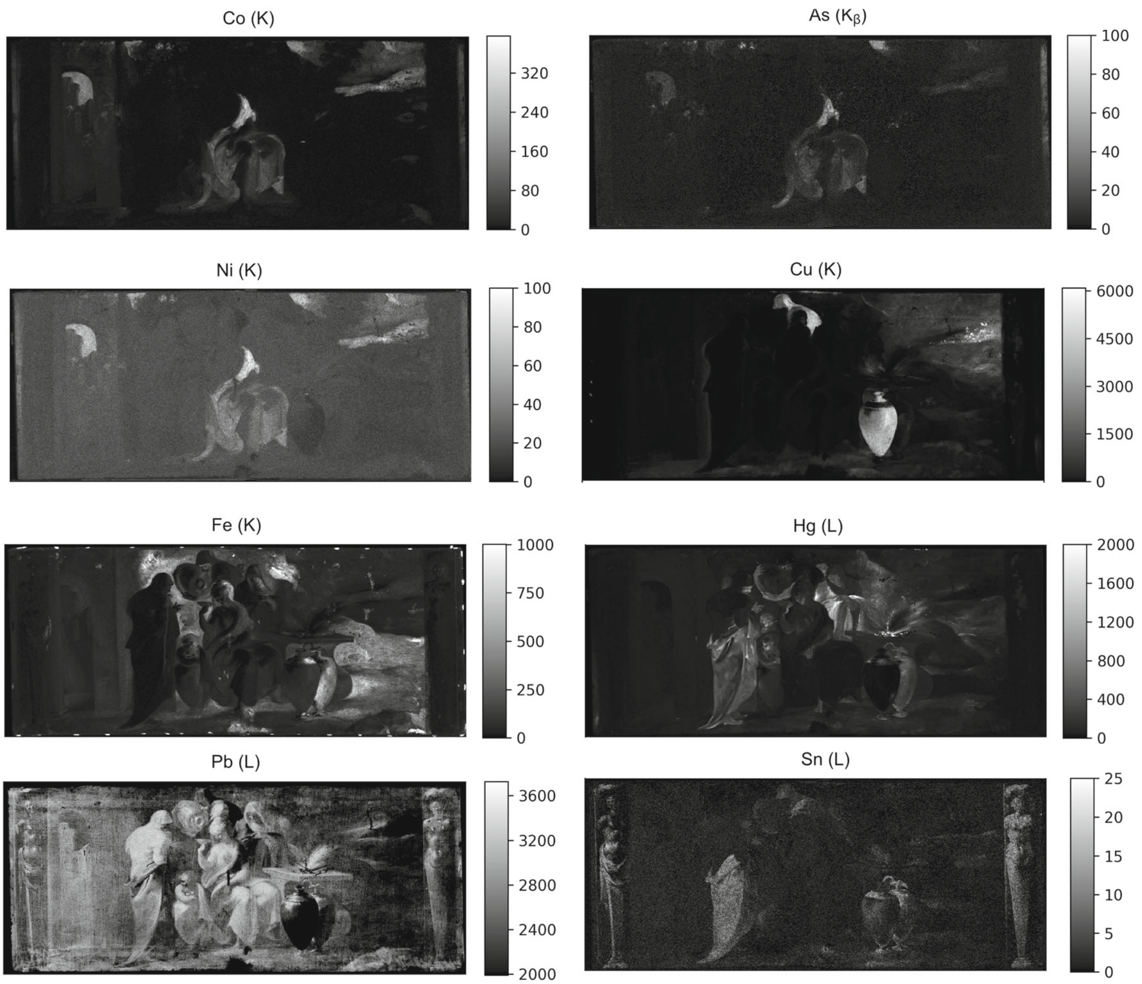

Fig. 3 Elemental distribution extracted from MA-XRF scan

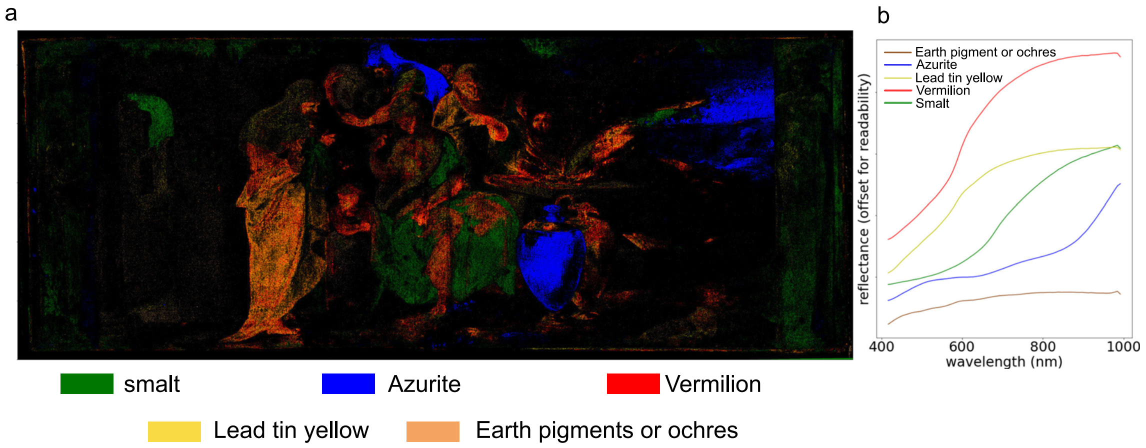

Fig. 4 Reflectance spectra and associated distribution map obtained from reflectance imaging spectroscopy (RIS). **a** SAM map corresponding to reflectance spectra shown in b. **b** Reflectance spectra of end-members labeled as : smalt (green color), vermilion (red color), azurite (blue color), lead tin yellow (yellow color), earth pigments or ochres (brown color)

Notably, the Co content of the grains is comparable to other smalts used in oil paintings [6]. As the loss of color of smalt grains is due to the modification of the Co^{2+} coordination state which is induced by the leaching of K^+ ions [19], the K concentration in smalt grains is a first indicator of the state of alteration of the pigment. Here, the content of K is low (2.13 $\%_{wt}$ on average for cross section A smalt and 1.40 $\%_{wt}$ on average in cross section B). The low K concentration is a first indicator of the state of preservation

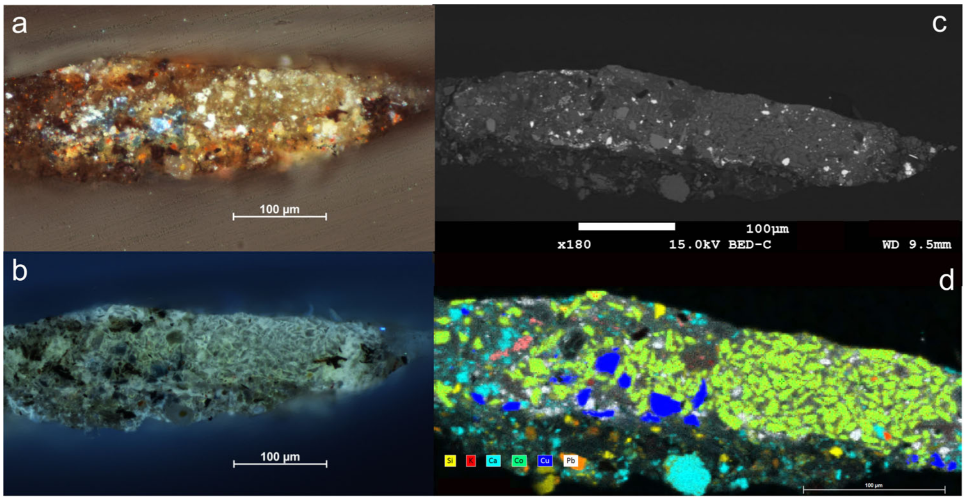

Fig. 5 **a** Image of cross section B under white light. **b** Image of cross section B under UV light. **c** back scattered electron image of cross section B. **d** elemental map of cross section B, in yellow the Si, in red the K, in cyan the Ca, in green the Co, in blue the Cu and in white the Pb

Table 1 Composition of the smalt grains, average over the grains, in the painting determined by quantitative SEM-EDX (MC for mean composition and SD for standard deviation)

		Na_2O	SiO_2	K_2O	Fe_2O_3	CoO	NiO	AS_2O_3	Bi_2O_3	K_20/CoO
A	MC (wt%)	0.25	73.73	2.13	3.54	4.62	1.24	2.35	2.61	0.46
	SD (wt%)	0.6	4.9	0.3	0.3	0.8	0.2	0.3	0.7	
B	MC (wt%)	0.05	80.97	1.40	3.86	5.38	1.38	2.5	2.67	0.26
	SD (wt%)	0.08	1.2	0.4	0.2	0.3	0.1	0.3	0.4	

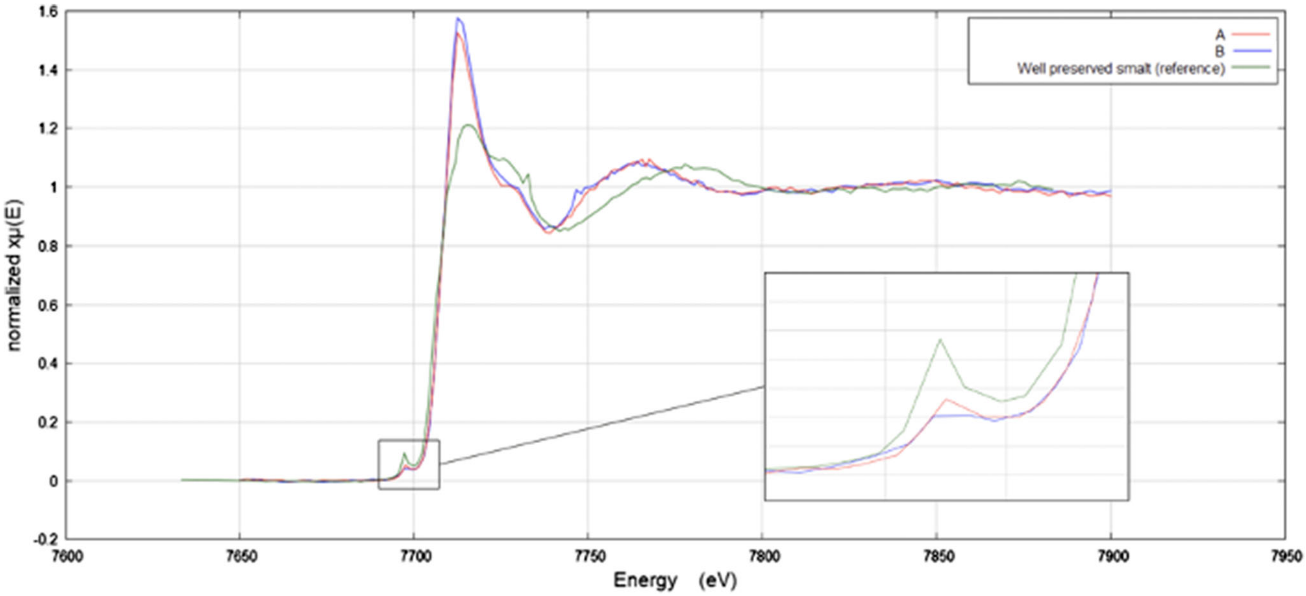

Fig. 6 XANES spectra at the Co K-edge of smalt from both cross sections A and B and from a commercial smalt (Deffner & Johann Smalte 9001050)

of smalt in the painting. Here, it is highly probable that K has leached greatly and that the smalt is very altered. Moreover, the K concentration in the smalt of cross section B is on average lower than in cross section A, which indicates that smalt is more altered in this area of the painting.

XANES at the Co-K edge was performed on both cross sections and on a well-preserved reference smalt to verify this hypothesis. During the weathering, tetrahedral Co^{2+} ions, responsible for the blue color, change their coordination to an octahedral one. This can be observed on XANES spectra by a decrease of the pre-edge intensity and the increase of the white line intensity. In Fig. 6, XANES spectra at the Co K-edge of smalt from both cross sections A and B are plotted and compared to that of a commercial, well-preserved smalt.

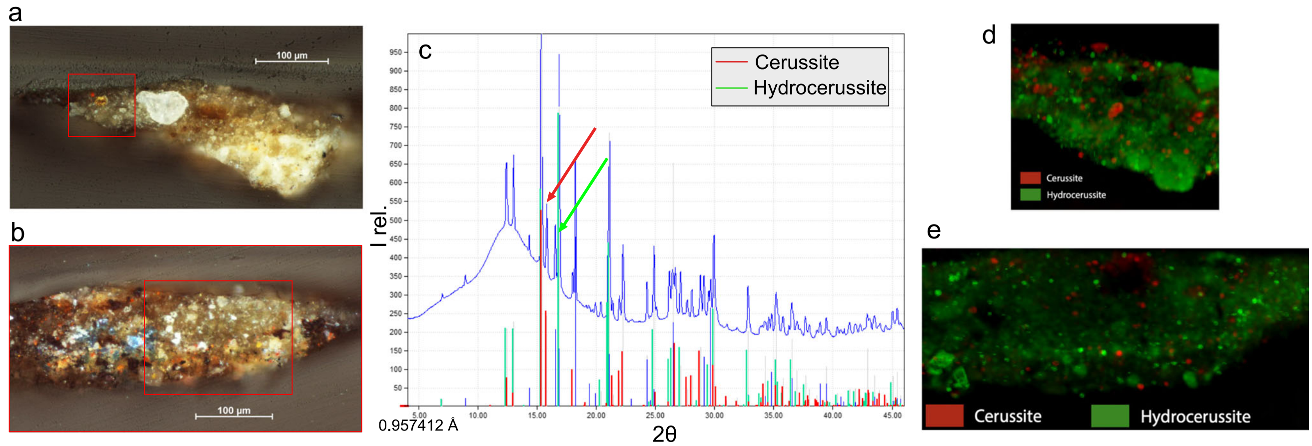

Fig. 7 **a** Optical image of cross section A where area of the 2D-μXRD mapping is indicated. **b** Optical image of cross section B where area of the XRD analysis is indicated. **c** Diffractogram of cross section A, characteristic peaks of cerussite and hydrocerussite are indicated. Arrows indicate peaks used to extract maps. **d** Superposition of cerussite and hydrocerussite maps of the studied zone of cross section A. **e** Superposition of cerussite and hydrocerussite maps of the studied zone of cross section B

Pre-edge intensities of spectra from the smalt of the painting were lower than the reference one and white lines were sharper and more intense. This suggested that Co is not in tetrahedral coordination anymore and that smalt is in an advanced alteration state. Moreover, these spectra confirmed that smalt from cross section B was more weathered than the smalt from cross section A. Its pre-edge was less intense and its white line more intense. The fact that this alteration difference was visible by XANES spectroscopy was interesting in order to characterize with precision the state of alteration of a grain. Thus, these interesting results made us wonder why smalt could be more altered in some areas of the paint than in others. This led us to study the environment near the smalt grains.

3.3 Factors influencing the alteration of smalt

In order to understand the factors playing a role in the alteration of the pigment, a first approach was to probe the environment of the smalt grains in the hypothesis that the type of lead white, commonly mixed with smalt in paint layers and existing in two different crystalline forms (cerussite and hydrocerussite) in acid-based equilibrium, could influence the alteration process.

2D-μXRD maps of both cross sections have been performed at the ID13 beamline of the ESRF synchrotron facility to determine the main crystalline phases present. In Fig. 7, the cerussite and hydrocerussite maps of both cross section are shown. In both cross sections hydrocerussite is dominant. Lead carbonates in aqueous medium can react with protons H^+ according to the following reactions [20, 21] :

$$PbCO_3 + 2H^+ \rightleftharpoons Pb^{2+} + H_2CO_3 \quad \log(K) = 3.5$$

$$Pb(CO_3)_2(OH)_2 + 6H^+ \rightleftharpoons Pb^{2+} + 2H_2CO_3 \quad \log(K) = 14$$

These equilibria depend on various parameters such as pH, temperature, carbonates and Pb concentrations and the other ions in solution [22]. When cerussite or hydrocerussite are mixed with smalt in paint layers, the ionic exchange between smalt's K^+ ions and protons from the medium could compete with the solubilization reaction of cerussite and hydrocerussite [23]. We hypothesize that when smalt is mixed with cerussite, the dominant reaction is the solubilization of the cerussite which would attenuate the alteration of the blue pigment and when it is mixed with hydrocerussite, the ionic exchange is dominant leading to the weathering of the grains. The study of smalt mock-ups mixed with pure cerussite or pure hydrocerussite is under way to validate this hypothesis.

4 Conclusion and perspectives

For the study of the degraded painting *Woman doing a Libation or Artemisia* several analytical and imaging methods resolved from the macrodown to microscale have been performed. MA-XRF and RIS have provided information on the artist's palette and the distribution of the pigments in the painting. The study of smalt at a microscopic scale thanks to SEM-EDS, XANES and 2D-µXRD analysis provided information on the smalt composition, the alteration state and the near chemical environment in the paint layer. In order to better understand the factors playing a role in the alteration process of the pigment, further studies on smalt and lead white-based model samples could provide more precise answers on its influence on the alteration mechanism. Furthermore, we aim to use these results to develop methods for virtual reconstruction of the original appearance of the painting.

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Data Availability Statement This manuscript has associated data in a data repository of the ESRF. The 2D-μXRD datasets generated during and analyzed during the current study are available in the ESRF repository: DOI 10.15151/ESRF-ES-527799901. All the other datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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