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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: Role of CdCl(OH) and other Cl-compounds in the degradation of CdS-based yellow in "The Scream" by Munch and model samples	**Experiment number**: HG-95
Beamline: ID21	**Date of experiment**: from: 23/11/2016 to: 28/12/2016	**Date of report**: 31/01/2020
Shifts: 12	**Local contact(s)**: Marine Cotte	*Received at ESRF:*

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1. INTRODUCTION

The bleaching of cadmium yellows, a class of pigments of different stoichiometry ($CdS/Cd_{1-x}Zn_xS$) and crystalline structure (hexagonal/cubic), has been reported in a number of paintings by Ensor, [1] Van Gogh, [2] and Matisse. [3-5]

Our previous SR-based X-ray and FT-IR investigations of artificially aged paint mock-ups allowed us to achieve the following results: [6]

(i) the photo-oxidation of yellow $CdS/Cd_{0.76}Zn_{0.24}S$ to white $CdSO_4/CdSO_4 \cdot nH_2O$ and their photocatalytic activity are triggered by moisture, occurring at a relative humidity (RH) ≥95% but not at environmental humidity (~45% RH).

(ii) The stability of CdS-based yellows and the chemical nature of the corresponding alteration products depends on both the Cd:Zn stoichiometry and aging conditions but not on the crystalline structure of the pigment. Notably, $Cd_{0.76}Zn_{0.24}S$ undergoes photo-oxidation more readily than CdS and it is a more efficient photocatalyst for the oil oxidation, giving rise also to the formation of Zn-oxalates.

In dark and highly moist conditions (RH≥95%), the $S^{2-} \rightarrow SO_4^{2-}$ conversion is hindered instead. However, preliminary investigations performed on a late 19th century cadmium yellow paints containing also Cd(OH)Cl (present as a residue of early manufacturing processes) and treated with moisture have revealed the formation of $CdSO_4$. [7] This finding, in line with the fact that Cl-species were identified in degraded CdS-based paints of some artworks by Matisse [3-5] and Munch, [6] leaves open the question of whether and to what extent Cl-compounds and moisture affect the decay of CdS-based paints.

To this aim, the experiment has focused on the study of a series of CdS-based oil paint mock-ups as well as historical oil paint tubes containing chlorides

Figure 1. Optical microscope pictures of two of the analyzed micro-flakes taken from the painting *The Scream (1910?)* by E. Munch (Munch Museum, Oslo, Norway).

before and after different artificial aging treatments (with light or moisture). Investigations of the oil paint mock-ups were also combined with the analysis of several micro-flakes obtained from the painting *The Scream (1910?)* by E. Munch (Figure 1).
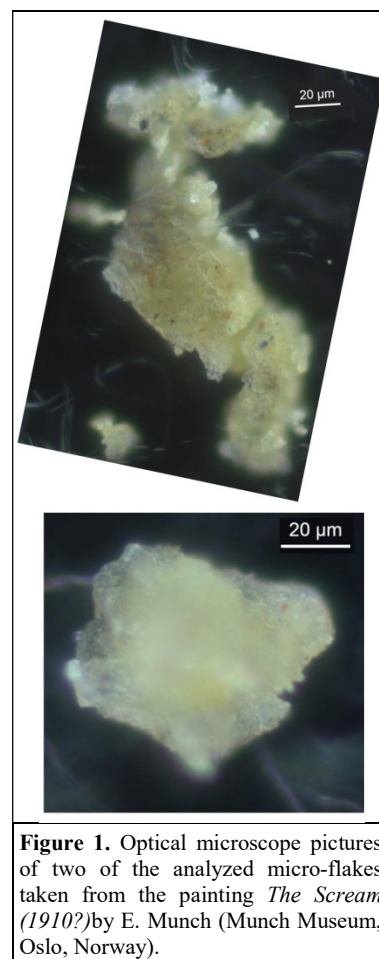
2. EXPERIMENTAL

The following materials have been analyzed at the ID21 beamline:

a) S-/Cd-/Cl-reference compounds (about 10 in total);
b) CdS-based oil paint mock-ups and late 19th century cadmium yellow paint tubes (20 in total) before and after exposure to different aging conditions (exposure to either UVA-Visible light or RH≥95%);
c) Original paint micro-flakes (6 in total) obtained from a flaked-off CdS-based yellow paint of the lake region of *The Scream (1910?)* (Munch Museum, Oslo, Norway).

By using the microtome avalialble at the ID21-beamline, all oil paints were prepared as thin sections (average thickness of 5 μm). Both thin sections and original paint micro-flakes have been fixed on sulfur-free tape and then covered with an ultralene film.

Measurements were performed at the scanning X-ray microscope (SXM) and the full field (FF)-XANES end-stations.
Investigations were carried out by means of a fixed exit double-crystal Si(111) monochromator at both the SXM and FF-XANES end-stations. The energy calibration was performed using $CaSO_4 \cdot 2H_2O$, NaCl and a Cd foil as standards and by setting the position of the peak maximum of their first order derivative spectrum at 2.4829, 2.8261 and 3.5418 keV, respectively.
At the SXM-end station, the incident beam was focused with Kirkpatrick-Baez mirrors down to a diameter of *ca.* 0.6×0.4 μm² (h×v). XRF signals were collected in the horizontal plane and at 69° with respect to the incident beam direction by means of a single energy-dispersive silicon drift detector (Xflash 5100, Bruker).
Single point μ-XANES spectra were acquired in XRF mode by scanning the primary energy at the absorption edge of the following elements: S K-edge (2.46-2.53 keV; energy step: 0.18 eV), Cl K-edge (2.79-2.89 keV; energy step: 0.25 eV), and Cd L_3-edge (3.5-3.7 keV; energy step: 0.4 eV).
μ-XRF mapping experiments were performed using a monochromatic primary beam of fixed energy around the S K- and Cd L_3-edges. Maps of the same region of interest were collected by employing either 80 or 100 ms/pixel at the three following energies: (i) 2.473 keV and 2.482 keV to favor the excitation of the S^{-II}- and S^{VI}-species, respectively and (ii) 3.7 keV to obtain the XRF intensity of all S-, Cl- and Cd-species. The software PyMCA was used to fit the XRF spectra and to separate the contribution of different elements, whilst ATHENA [9] was employed to perform the normalization of the XANES spectra.
Cd L_3-edge FF-XANES imaging of thin sections (~5 μm thickness) obtained from a selection of the artificially aged oil paints and original paint micro-flakes was carried out by an unfocused beam (size of ~1.5×1.5 mm^2). A Lu_2SiO_5:Tb scintillator (located less than 2 mm downstream the sample) was used to convert X-ray transmission images into visible images. A 10× optical objective was employed to magnify the image onto a CMOS camera (PCO edge, Germany), giving a pixel size of ~0.65×0.65 μm^2 and a spatial resolution of ~1.5 μm. The maximum field of view is around 1.5×1.5 mm^2. A stack of 214 X-ray radiographs was recorded, while tuning the X-ray energy across the Cd L_3-edge with the following variable step sizes: i) 5 eV in the 3.4880-3.5239 keV and 3.6380-3.7180 keV range, ii) 0.5 eV in the 3.2530-3.5980 keV region and iii) 1 eV in the 3.5980-3.6380 keV range. The dark and flat field correction and the images alignment were performed by employing the Spectrocrunch library. The TXM-Wizard software package [10] was used to produce the chemical state maps of different Cd-compounds.

3. RESULTS

3.1. Artificially aged CdS-based oil paints. As an example the SR μ-XRF and μ-XANES results obtained from a thermally aged oil paint mock-up prepared by mixing CdS and Cd(OH)Cl (called CdS$_{Cd(OH)Cl}$) before and after exposure to moisture (RH=95%, T=40°C, 100 days), is shown in Figure 2.
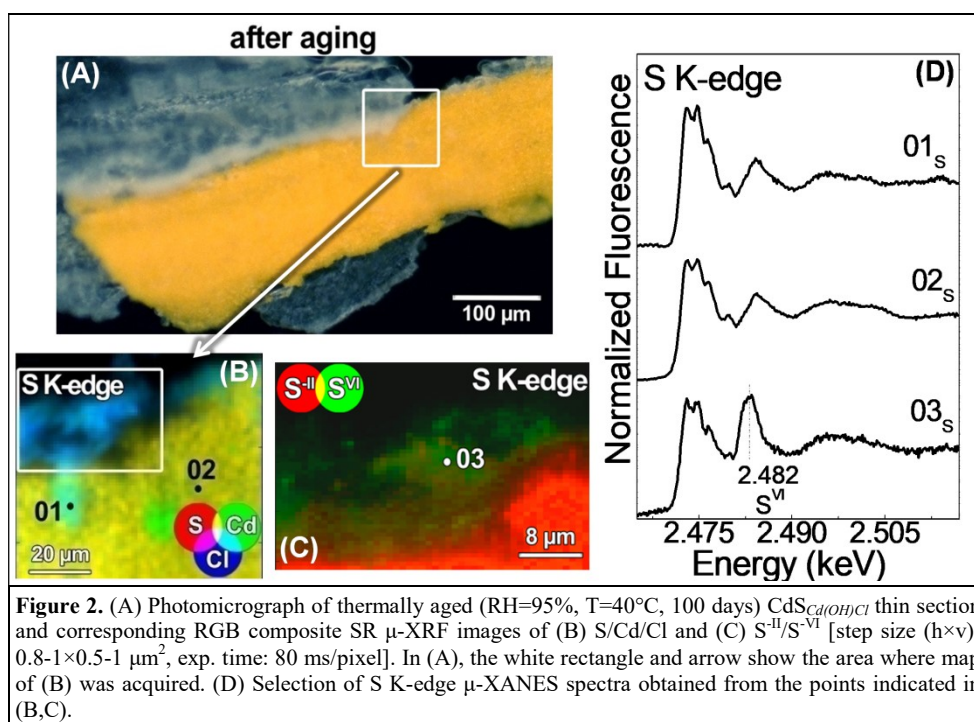
Before aging (results not reported), S- and Cl-speciation investigations reveal that Cd(OH)Cl particles/aggregates are homogenously distributed within the yellow paint, where only S^{-II}-species (CdS) were found.

As a consequence of the aging, a bleaching appears in selected areas of the paint surface (Figure 2A). SR μ-XRF maps (Figure 2B) show that these whitish regions are mainly composed of Cd and Cl with minor abundances of S. The S-speciation maps (Figure 2C) and the S K-edge μ-XANES spectra (Figure 2D: pt 03$_S$) show the formation of sulfate-based compounds in the (Cd,Cl)-rich area at the surface, whereas only CdS (pts 01$_S$, 02$_S$) is present in the Cl-free/poorest regions underneath.

Comparable results have been obtained from other CdS-based oil paint mock-ups and late 19th century cadmium yellow paint tubes containing other types of Cl-based compounds (i.e. CdCl$_2$, KCl) and aged under similar conditions. In addition, the sporadic presence of sufiltes has been also frequently observed in such samples.

Diversely, no evidence of the formation of oxidized S-species has been observed instead in the equivalent paints aged with UV-Visible light and at environment moisture conditions (RH≈45%) (results not reported).

Overall these analysis show that moisture and Cl-compounds promote the oxidation of CdS to cadmium sulfates.

Figure 2. (A) Photomicrograph of thermally aged (RH=95%, T=40°C, 100 days) CdS$_{Cd(OH)Cl}$ thin section and corresponding RGB composite SR μ-XRF images of (B) S/Cd/Cl and (C) S^{-II}/S^{-VI} [step size (h×v): 0.8-1×0.5-1 μm^2, exp. time: 80 ms/pixel]. In (A), the white rectangle and arrow show the area where map of (B) was acquired. (D) Selection of S K-edge μ-XANES spectra obtained from the points indicated in (B,C).

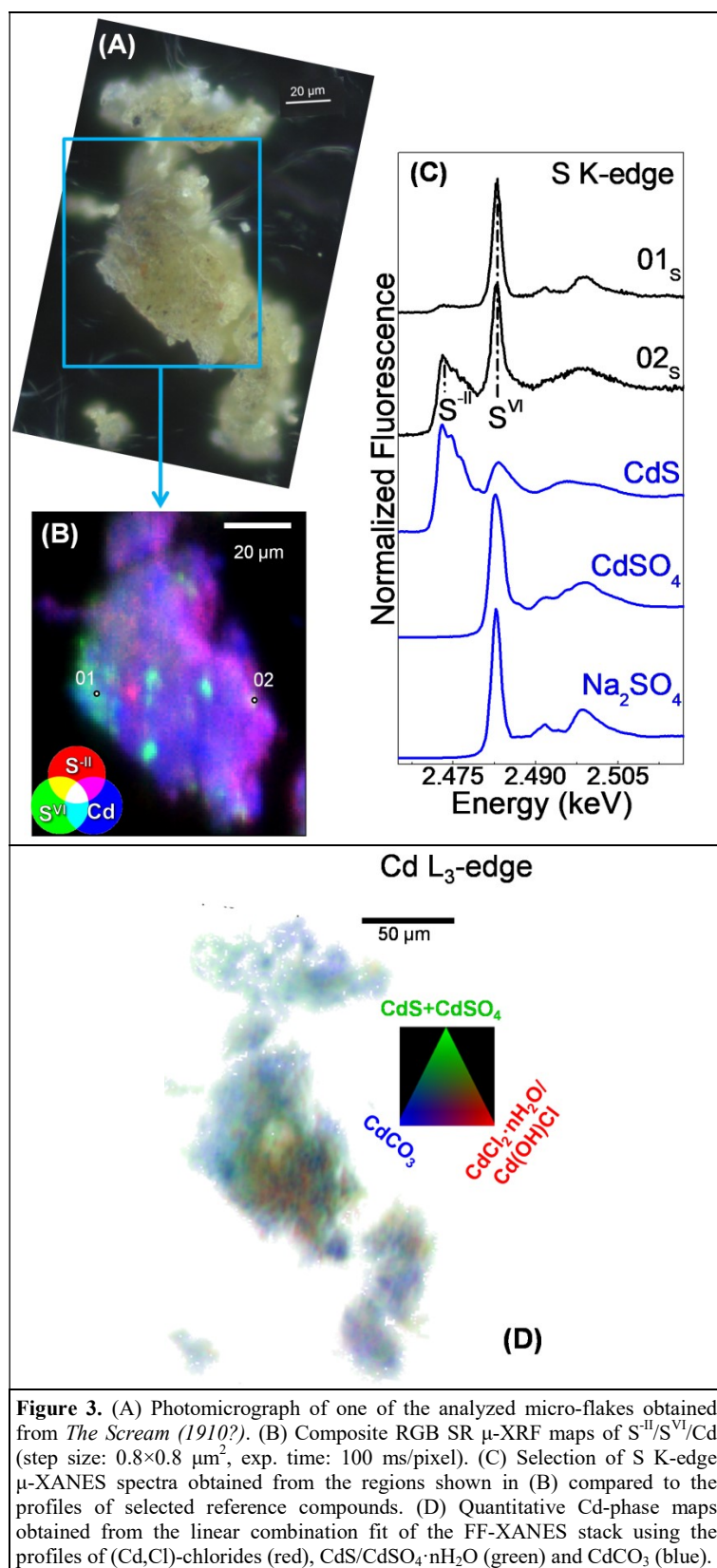## 3.2 Original paint micro-flakes from "The Scream (1910?)"

Figure 3. (A) Photomicrograph of one of the analyzed micro-flakes obtained from *The Scream (1910?)*. (B) Composite RGB SR µ-XRF maps of $S^{-II}/S^{VI}/Cd$ (step size: 0.8×0.8 µm^2, exp. time: 100 ms/pixel). (C) Selection of S K-edge µ-XANES spectra obtained from the regions shown in (B) compared to the profiles of selected reference compounds. (D) Quantitative Cd-phase maps obtained from the linear combination fit of the FF-XANES stack using the profiles of (Cd,Cl)-chlorides (red), CdS/CdSO$_4$·nH$_2$O (green) and CdCO$_3$ (blue).

SR µ-XRF and S-chemical speciation maps of original paint micro-flakes obtained from *The Scream (1910?)* (Figure 3A,B; as an example, only the results of one of them are reported) revealed that Cd and S^{-II}-species are homogenously distributed throughout the yellowish paint, while S^{VI}-compounds are localized as agglomerates. S^{-II}- and S^{VI}-species are unambiguously identified in the S K-edge µ-XANES spectra (Figure 3C) by the signals at ~2.473 and ~2.482 keV, for sulfides (S^{-II}) and sulfates (S^{VI}) respectively.

Among the S-containing phases, the comparison with the XANES spectra of selected reference compounds reveals that the paint matrix is mainly composed of CdS (spectra not shown in Figure 3C), whereas the sulfate agglomerates are made of Na$_2$SO$_4$ and/or CdSO$_4$. (Figure 3C: pts 01$_s$,02$_s$).

The original and newly formed Cd-species are better visualized in the FF-XANES Cd-phase images (Figure 3D) in which, within the CdS/CdCO$_3$–based paint matrix, CdSO$_4$ and CdCl$_2$·nH$_2$O/Cd(OH)Cl are also present.

The identification of highly water soluble materials, such as Na$_2$SO$_4$ and (Cd,Cl)-compounds opens the question whether and to what extent their solubility influences the degradation state of the cadmium yellow paint under high humidity conditions. This was further studied by analyzing before and after aging (RH≥95%, T=40°C) two additional oil paint mock-ups prepared by mixing CdS with Na$_2$SO$_4$ and CdCl$_2$. The results (not shown) clearly revealed that after exposure to moisture, soluble Na$_2$SO$_4$ and CdCl$_2$ dissolve, migrate through the paint and, upon re-crystallization, give rise to CdSO$_4$- and NaCl-based compounds. Based on these results, it follows that CdSO$_4$ may not only be present as an oxidation product of the original CdS pigment (see Figure 2) or as a leftover synthesis reagent but also as a secondary product arising from the dissolution and re-crystallization of soluble leftover reagents.

The results obtained from this experiment will be published soon.

REFERENCES: [1] G. Van der Snickt et al., *Analytical Chemistry* **81** (2009), 2600-2610; [2] G. Van der Snickt et. al.,*Analytical Chemistry* **84** (2012), 10221–10228; [3] J. Mass et al., *Applied Physics A* **111** (2013), 59-68; [4] J. Mass et al., *Analyst* **138** (2013), 6032-6043; [5] E. Pouyet et al., *Applied Physics A* **121** (2015), 967-980; [6] L. Monico et al., *Chemistry–A European Journal* **24** (2018), 11584-11593; [7] Exp. report HG-64; [8] T. Froysaker, N. Streeton, H. Kutzke, F. Hanssen-Bauer, B. Topalova-Casadiego, *Public Paintings by Edvard Munch and His Contemporaries: Change and Conservation Challenges* (Archetype Publications Ltd, London, UK, 2015; [9] B. Ravel, M. J. Newville, *Journal of Synchrotron Radiation* **12** (2005), 537–541; [10] Y. Liu et al., *Journal of Synchrotron Radiation* **19** (2012), 281-287.