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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.
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- 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:**

Study of the physico-chemical parameters influencing the chromatic alteration and destabilization of cadmium sulfide-based pigments

Experiment number:

HG-64

Beamline: ID21	Date of experiment: from: 25/11/2015 to: 01/12/2015	Date of report: 04/03/2016
Shifts: 18	Local contact(s): Marine Cotte	<i>Received at ESRF:</i>

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1. INTRODUCTION

Cadmium sulfide-based yellow-orange-red pigments is a class of compounds of different composition ($\text{CdS}/\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{CdS}_x\text{Se}_{1-x}$) and crystalline structure (hexagonal, cubic or amorphous), widely used by many painters of late 19th C-early 20th C. [1-3] The fading of CdS-based yellow paints, has been already documented for masterpieces by Ensor, [4] Van Gogh, [5] and Matisse. [6-8] In these case studies, Cd-sulfates, oxalates, carbonates, chlorides have been identified and suggested as possible degradation products, originated by a process that starts with a photo-activated step. Additives and other environmental factors have been also suggested as other possible triggering factors for the degradation of CdS-based pigments.

Nevertheless, these hypotheses have been never experimentally proved by accelerated aging tests.

With the final aim to assess the physico-chemical parameters influencing the chromatic alteration and/or destabilization of CdS-based pigments, this experiment has focused on the investigations of a series of oil paint models composed of commercial/historical CdS-based pigments of different composition (with additives and/or synthesis residues) before and after exposure to light or different relative humidity (RH) conditions.

The study of the model paints was also combined with the analysis of several micro-samples (Figure 1) obtained from the painting *Alchemy* (1947) by J. Pollock.

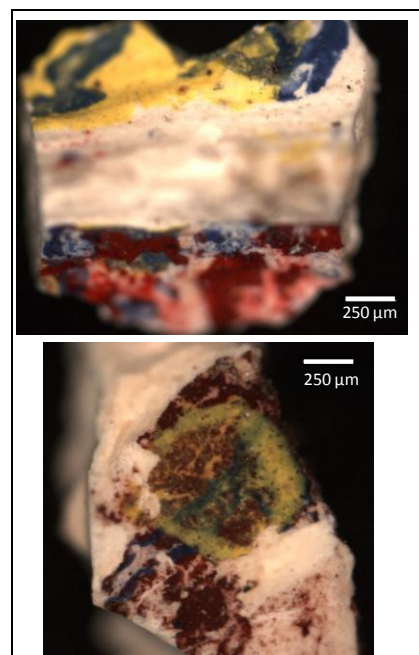


Figure 1. Optical microscope pictures of two of the paint microsamples taken from the painting *Alchemy* by J. Pollock (1947, Peggy Guggenheim collection, Venice).

2. EXPERIMENTAL

The following materials were analyzed by means of μ -XRF/ μ -XANES at the S K-, Cl K- and Cd L₃-edge:

a) *S-/Cd-/Cl-reference compounds (10-15 in total)*;

b) *CdS-based oil paint models (20 in total)* before and after exposure to different aging conditions (Table I);







c) *Original paint micro-samples (5 in total)* obtained from different CdS-paint areas of the painting *Alchemy*.

By using the microtome available at the ID21-beamline, all the paint samples were prepared and analyzed as thin sections (thickness of 5-20 μ m). A highly monochromatic primary beam (with $\Delta E/E=10^{-4}$) was produced using a Si(111) fixed-exit double-crystal monochromator. The incident beam was focused with Kirkpatrick-Baez mirrors down to a diameter of $0.6 \times 0.6 \mu\text{m}^2$ (h \times 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).

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 L₃-edge: 3.5-3.7 keV (energy step: 0.4 eV). The energy calibration was performed using CaSO₄·2H₂O, NaCl and a Cd foil as standards. The software ATHENA, [9] was used to perform the normalization of the XANES spectra.

During the μ -XRF mapping experiments, the fluorescence signals were produced by employing a monochromatic primary beam of fixed energy (around the S K- and Cd L₃-edges). Maps of the same region of interest were recorded using 100 ms/pixel at three different excitation energies: (i) at 2.473 keV and 2.482 keV to favor the excitation of the S^{-II}- and S^{-VI}-species, respectively; (ii) at 3.7 keV to obtain the fluorescence intensity of all S-, Cl- and Cd-species. The software PyMca was used to fit the fluorescence spectra and separate the contribution of different elements. [10]

Table I. List of the unaged/aged oil paint model samples analyzed by S K-, Cl K-, and Cd-L₃-edges μ -XRF/ μ -XANES spectroscopy (20 in total).

Sample	Characterization before aging ^(a)	Thermal aging ^(a)		Photochemical aging ^(a)	S K-, Cl K-, ^(b) and Cd L ₃ -edges μ -XRF/ μ -XANES results	
		95% RH, T=40°C (90 days)	50% RH, T=40°C (150 days)	UVA-Vis light, $\sim 1 \times 10^5$ lux, ~ 650 h	unaged	aged
7914* 	CdCO ₃ , CdCl(OH), hexagonal-CdS, Cd _{0.82} Zn _{0.12} S	X	X	X	CdS, CdCO ₃ Cd-chlorides. S ^{VI} -species (amount below 10%)	<i>Thermal aging.</i> Localized formation of CdSO ₄ often combined with that of CdC ₂ O ₄ and Cl-compounds. Appreciable changes in the post-edge spectral features of the Cl K-edge XANES profiles. ^(c) <i>Photochemical aging.</i> Neither significant increasing of S ^{VI} -species nor formation of new Cd-based phases were detected. Appreciable changes were observed only in the post-edge absorption region of the Cl K-edge XANES profiles collected from the upper 50 μ m of the thin section.
7913* 	hexagonal-CdS, cubic-CdS	X	X	X	CdS, K/Cl-species	<i>Thermal aging.</i> Localized formation of CdSO ₄ . ^(d) <i>Photochemical aging.</i> The formation of S ^{VI} -species and new Cd-based phases was not identified/negligible.
2791* 	Cd _{0.91} Zn _{0.09} S, BaSO ₄	X	-	X		No change after neither thermal nor photochemical aging
844* 	CdS _{0.62} Se _{0.38} , BaSO ₄ , carbonates	X	-	X		No change after neither thermal nor photochemical aging
CdS _{hexagonal} [§] 	hexagonal-CdS	X	-	X		No change after neither thermal nor photochemical aging
CdS _{cubic} [‡] 	cubic-CdS (90%), hexagonal-CdS (10%)	X	-	X		No change after neither thermal nor photochemical aging

*Historical powder (early 20th C). §Commercially available powder. ‡In-house synthesized powder.

^(a)Characterization performed using the following laboratory techniques: XRPD, macro reflection/ATR mode FTIR, UV-Vis, Raman spectroscopies (for further details, see [1,2]). ^(b)Analysis performed only on the unaged/aged samples 7914. ^(c)Additional identification of Cd-carboxylates by FTIR. ^(d)Detection of CdC₂O₄ by FTIR/XRD.

3. RESULTS

3.1. Artificially aged CdS-based paint models. An overview of the SR μ -XANES and μ -XRF results obtained from the analyzed paint models samples is summarized in Table I.

S- and Cd-speciation results obtained from samples 2791, 844, CdS_{hexagonal} and CdS_{cubic} (not shown) did not reveal significant changes after neither light exposure nor treatment with moisture. A mixture of CdS and BaSO₄ was identified in samples 2791 and 844, while only CdS was detected in CdS_{hexagonal} and CdS_{cubic}.

On the contrary, clear indications about the local S^{II} \rightarrow SO₄²⁻ conversion and the formation of new organo-Cd-compounds (*i.e.*, oxalates— result also supported by μ -FTIR and μ -XRD) were observed for the samples containing Cl-compounds (*i.e.*, 7914 and 7913) and aged with different relative humidity conditions. In both samples, chlorides are likely present as additives/residues of early synthesis procedures.[1,3]

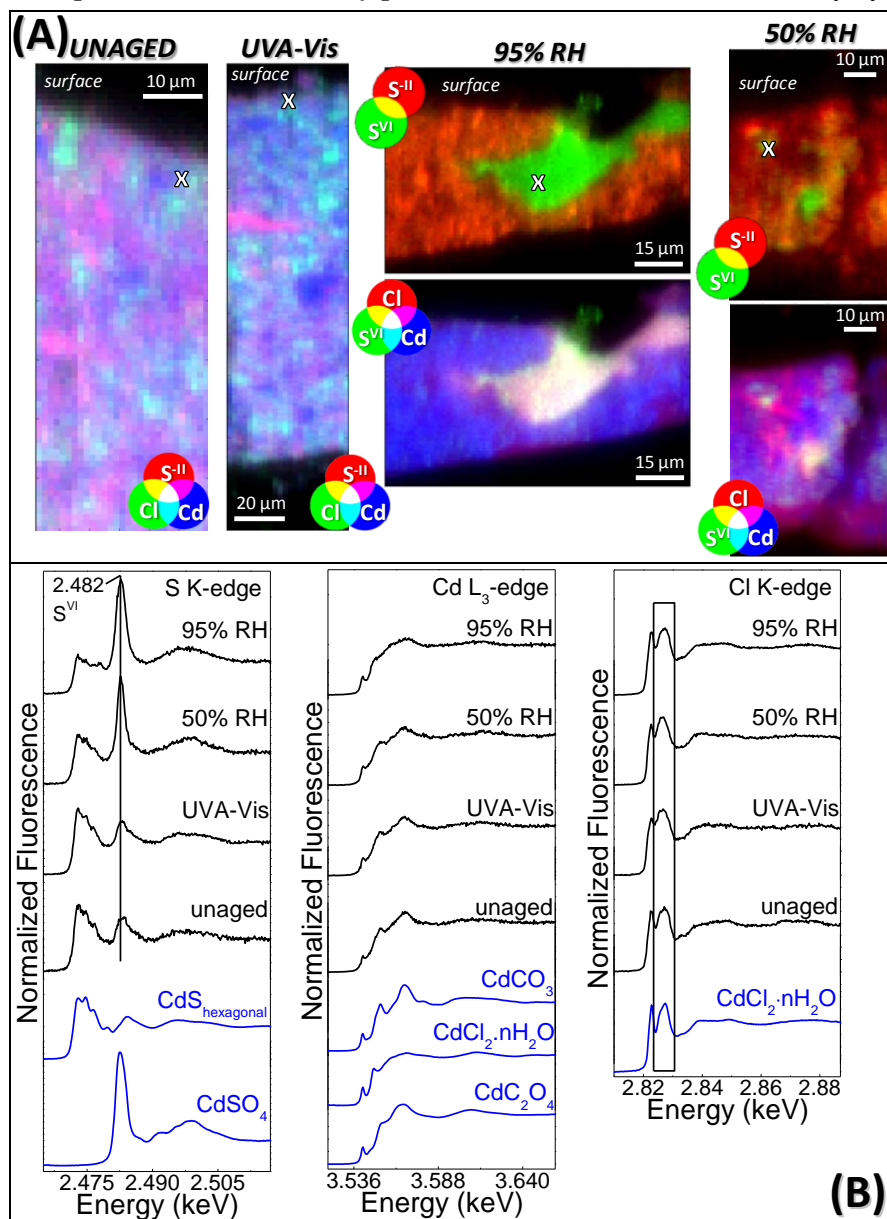


Figure 2. Paint model sample 7914. (A) RGB composite μ -XRF S^{II}/S^{VI} chemical state maps and Cl/Cd distributions acquired from 7914 (from left to right) before and after exposure to light (UVA-Vis) or different relative humidity conditions (95% RH or 50% RH) [step sizes (h \times v): 1 \times 1 μ m²; dwell time: 100 ms/pixel]. (B) Selected (from left to right) S K-, Cd L₃- and Cl K-edges μ -XANES spectra obtained from the areas indicated by the symbol “X” in (A). In blue, spectral profiles of the reference compounds.

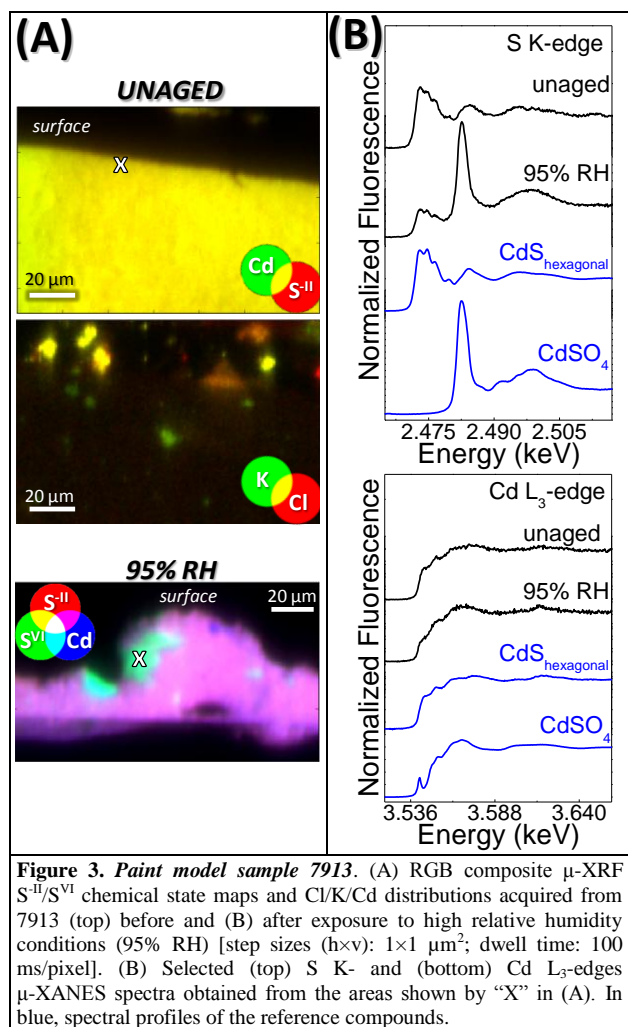
(95% RH or 50% RH) are consistent with the presence of newly formed S^{VI}-rich aggregates/spots, often co-localized with Cd and Cl-species too. The S K-edge XANES spectra recorded from these areas strongly resemble to that of the CdSO₄ reference compound, while the corresponding Cd L₃-edges profiles are more similar to those of CdCl₂ and/or CdC₂O₄. In the Cl K-edge μ -XANES spectra, changes very similar to those present in the profiles obtained from the equivalent UVA-Vis light-exposed material are observable.

Figure 2 shows the μ -XRF distribution of S^{II}, S^{VI}, Cl and Cd along with a selection of the corresponding S K-, Cl K and Cd-L₃-edges μ -XANES spectra obtained from the sample 7914 before (unaged) and after exposure either to light (UVA-Vis) or different relative humidities (95% RH/50% RH).

In the unaged sample, S^{II}, Cl and Cd, appear to be homogeneously distributed within the paint (Figure 2A). On the basis of the comparison between the μ -XANES spectra (Figure 2B) obtained from the sample (black lines) and those of the reference compounds (blue lines), these species are ascribable to CdS, CdCO₃ and Cd-chlorides [CdCl(OH)]. In the S K-edge XANES spectrum, the energy-shift and increase of the intensity of the white-line at *ca.* 2.482 keV suggest also lower amount of S^{VI}-species (*cf.* CdS reference profile).

After UVA-Vis light exposure, the elemental distribution does not reveal significant changes (Figure 2A). Neither the formation of oxidized-S species nor that of new Cd-based compounds is revealed by S K- and Cd L₃-edges μ -XANES analysis. Only in the Cl K-edge μ -XANES spectra collected from the upper 50 μ m of the thin section, the appreciable broadening of the post-edge feature at 2.824–2.83 keV is observable.

The μ -XRF/ μ -XANES results obtained from the sample 7914 aged with two different relative humidity conditions



In Figure 3, the S and Cd-speciation results obtained from the sample 7913 before (unaged) and after exposure to high relative humidity conditions (95% RH) are reported.

In the unaged sample, CdS is the main constituent of the yellow-orange paints. K and Cl-particles are also widespread within the paint (Figure 3A, top). Similarly to the sample 7914, neither the formation of oxidized-S species nor that of new Cd-based compounds was detected after UVA-Vis light exposure (results not reported), while the *in situ* formation of CdSO₄ is detectable after exposure to moisture (Figure 3A, bottom; Figure 3B).

3.2 Original paint micro-samples from “Alchemy” (results not shown). S and Cd-speciation investigations of four out five analyzed samples (Figure 1, top) revealed that CdS and BaSO₄ are the main constituents of the yellow layer. In the remaining sample (Figure 1, bottom), the yellow pigment, strongly diluted in a Cl/Pb-rich matrix, was found to be composed of CdS and CdCO₃. No evidence of other S/Cd/Cl-based compounds ascribable to the degradation of the original CdS-yellow pigments were identified.

4. SUMMARY AND CONCLUSIONS

The results obtained from this experiment (to be published soon) have revealed that: *a*) the CdS-pigments are stable under UVA-Vis light exposure; *b*) the composition and crystalline structure of the pigment itself do not influence its stability; *c*) the formation of Cd-alteration products (CdSO₄, CdC₂O₄, and Cd-carboxylates) appears to occur only for historical pigments containing Cl-compounds (residues of early synthesis procedures) and that it is favored under exposure to high relative humidity condition ($\geq 50\%$ RH). These experimental findings open up the way to additional investigations that will focus on the role of Cl-compounds in the mechanism of oxidation of Cd-yellows.

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