

The photodegradation of cadmium yellow paints in Henri Matisse's *Le Bonheur de vivre* (1905–1906)

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Abstract Evidence for the alteration of the yellow paints in Henri Matisse's *Le Bonheur de vivre* (1905–1906, The Barnes Foundation) has been observed since the 1990s. The changes in this iconic work of Matisse's Fauvist period include lightening, darkening, and flaking of the yellow paints. Handheld X-ray fluorescence (XRF) and multispectral imaging surveys reveal that the degradation is confined to cadmium yellow (CdS) paints. The discoloration of cadmium yellow paints in Impressionist, Post-Impressionist and

early modernist work from the 1880s through the 1920s has been ascribed to the photo-oxidative degradation of CdS. Preliminary investigations of the degraded yellow paints in this work involved Cd L_{III}-edge X-ray Absorption Near Edge Spectroscopy (XANES) at the Stanford Synchrotron Radiation Light Source (SSRL Menlo Park, California) and Scanning Electron Microscopy-energy dispersive X-ray analysis (SEM-EDS) at the Winterthur Museum Scientific Research and Analysis Laboratory. To determine if the visual changes in the paints did in fact indicate photo-oxidative degradation and if different chemistries could be observed for the lightened versus darkened regions, synchrotron radiation-micro Fourier Transform InfraRed (SR- μ FTIR) spectroscopy, X-ray Fluorescence (SR- μ XRF) mapping and micro X-ray Absorption Near Edge Spectroscopy (μ XANES) mapping at the Cd L_{III}-edge of the altered paint cross-sections were carried out at the European synchrotron radiation facility (ESRF, Grenoble, France) beamline ID-21. The goal is to elucidate the discoloration mechanisms observed in the paint using elemental and speciation mapping. The μ XANES mapping and SR-FTIR imaging showed a substantial enrichment of CdCO₃ in the off-white surface crust of the faded/discolored CdS paint. This suggests that the CdCO₃ is present as an insoluble photodegradation product rather than solely a paint filler or starting reagent. Additionally, oxalates and sulfates were found to be concentrated at the alteration surface.

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1 Introduction

Recent research has revealed that the synthetic inorganic pigments used in Impressionist and early modernist paintings at the turn of the twentieth century are undergoing degradation phenomena ranging from lightening and

color shifts to flaking and spalling. These phenomena have been particularly notable in the yellow pigments of this time period, with discoloration of zinc yellow ($K_2O \cdot 4ZnCrO_4 \cdot 3H_2O$), chrome yellow ($PbCrO_4$), and cadmium yellow (CdS) paints being observed in the works of Georges Seurat (zinc yellow and cadmium yellow), Vincent van Gogh (chrome yellow and cadmium yellow), and Pablo Picasso (cadmium yellow) [1–3].

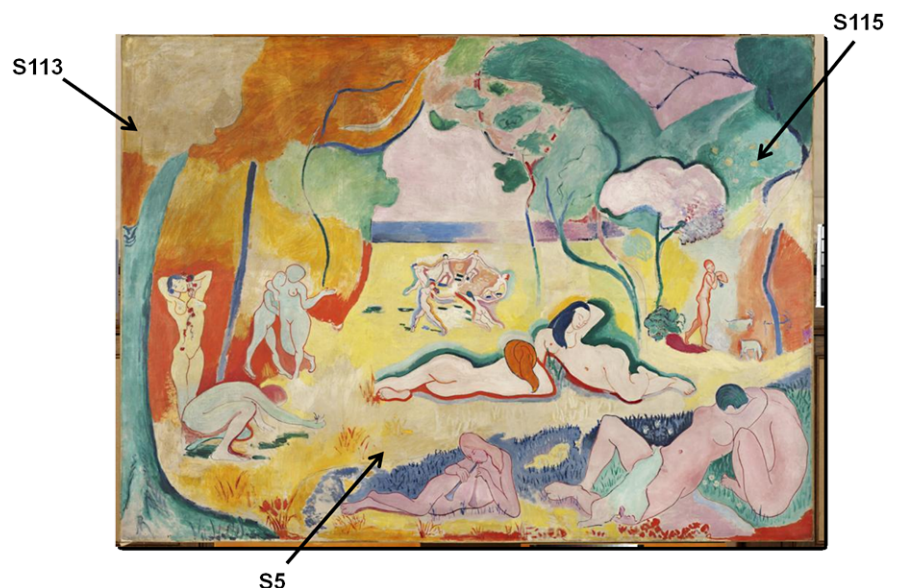
Henri Matisse's *Le Bonheur de vivre*, also called *The Joy of Life* (between October 1905 and March 1906, $69\frac{1}{2} \times 94\frac{1}{2}$ in [176.5×240.7 cm] The Barnes Foundation, BF719) is a seminal early work in the creation of his Fauvist identity. *Le Bonheur de vivre*, was highly controversial and widely criticized upon its display in the 1906 Salon des Independents in Paris, but it is now considered to be one of the icons of modern art, responsible for cementing Matisse's reputation in the art world. The painting has been on view at The Barnes Foundation since its purchase in 1923. Several regions of alteration in the yellow paints have been identified in *Le Bonheur de vivre*, most notably the yellow foliage in the upper left corner of the work (see Fig. 1) the yellow foreground beneath the central reclining figures, and the yellow fruits in the tree in the upper right quadrant (see online supplementary material for a version of this work that does not appear to have undergone alteration or color change). A 1990 conservation assessment of the work first reported that regions of the yellow paint had turned light brown, and that other areas of the yellow paint had "disintegrated into a fragile powder". The problem was most pronounced in the high impasto brushstrokes of yellow paint under the central reclining figures.

Matisse painted three other works related to this final version (*Le Bonheur de vivre*, 1905–1906, The Barnes Foundation BF719); *Sketch for Le Bonheur de vivre*, The Barnes

Foundation BF35, *Esquisse pour "Le Bonheur de vivre"*, Museum of Modern Art, San Francisco, 91.160, and *Landscape at Collioure/Study for Le Bonheur de vivre*, Statens Museum fur Kunst, Copenhagen). In a first attempt to understand the changes that the Barnes painting is undergoing, the Barnes work was compared visually to the related works prepared by Matisse, especially the oil sketch for *Le Bonheur de vivre* at the Museum of Modern Art, San Francisco (91.160). The San Francisco painting has warm yellow foliage in its upper left corner and a pure bright yellow foreground under the central reclining figures (see online supplementary material). This comparison suggests that the warm yellow foliage of the upper left corner of the Barnes painting has altered to a tan color, whereas the yellow paint beneath the central reclining figures has lightened to an ivory color. Regions of chalking, flaking, and spalling paint were also identified beneath the central reclining figures.

Since the late 19th century cadmium yellow paints (in particular the paler shades) were observed reacting to undergo disfiguring lightening and discoloration [4], and the phenomenon was noted in the art conservation literature in 1986 [5]. At the time this deterioration was attributed to adulterants or to the use of smaller particle sizes of the paler shades. In conjunction with the lightening and discoloration one often observes an irreversible degradation of the oil paint binder resulting in a chalky, crumbling, flaking, and ultimately spalling paint layer—this degradation proceeds from the exterior to the interior of the paint layer. The phenomenon has been observed in works by Piet Mondrian (1872–1944) and in the work studied here [6]. Leone et al. [3] performed the first systematic study of the alteration of cadmium yellow pigments, including the characterization of 12 works from 1887–1923, including those by Vincent van Gogh, Pablo Picasso, Georges Seurat, and Fer-

Fig. 1 Matisse's *Le Bonheur de vivre*, also called *The Joy of Life* (1905–1906), The Barnes Foundation, BF719. Note the lightening and dirty appearance of the yellow paint below the central reclining figures, the darkening of the yellow paint in the upper left corner of the work, and, less visible in this image, the simultaneous lightening and discoloration of the yellow fruit in the tree in the upper right quadrant. Cross-section sample locations are noted



nand Leger. Notably amorphous or nanocrystalline CdS was identified in seven of the twelve paintings (based upon their absence of XRD patterns). Potential CdS photodegradation products identified in the paintings included cadmium carbonate (CdCO_3), cadmium oxide hydroxide, cadmium carbonate oxide, and cadmium sulfate (CdSO_4). It is important to note that CdCO_3 and CdSO_4 are reagents for the dry and wet process syntheses of CdS, respectively, and so their identification alone does not constitute conclusive proof of photo-oxidation (CdCO_3 has also recently been noted to be used in an indirect wet process method) [5, 7]. However, the phases identified, together with their identification at the paint's surface as discolored degradation crusts, suggested a photo-oxidation mechanism. Artificial aging experiments on period cadmium yellow paints were also carried out by Leone et al. at 45 % RH and 85 % RH. The samples aged under high RH conditions were noted to have a matte or etched appearance, and TOF-SIMS analysis revealed a lower concentration of fatty acids at the degraded surface, suggesting that the paint binding medium is being attacked during the degradation process [3]. This led the researchers to propose a mechanism in which amorphous or nanocrystalline (and thus reactive) CdS pigment was photo-oxidized to produce CdO, CdSO_4 , and SO_2 gas. In the presence of high RH environments, the SO_2 is proposed to convert to H_2SO_4 , resulting in acid hydrolysis of the paint binding medium. van der Snickt et al. have observed the formation of $\text{CdSO}_4 \cdot 2\text{H}_2\text{O}$ and $[\text{NH}_4]_2\text{Cd}(\text{SO}_4)_2$ on the surface of faded cadmium yellow paints in the works of James Ensor (1860–1949) [8]. μXANES was used in the Ensor study to demonstrate that the sulfur in the CdS was oxidized to SO_4^{2-} , and it was hypothesized that the soluble cadmium sulfate was re-precipitating at the surface of the painting to form the observed white globules on the yellow paint layer. The ammonium phase was ascribed to a potential reaction with a previous cleaning treatment. The cadmium yellow pigments on Edvard Munch's painting *The Scream* (1910, the Munch Museum) are recently reported to have altered to a gray color [7] and have been studied by X-ray diffraction (XRD), SEM-EDS, and FTIR analysis. These paints were found to be mixtures of CdS and CdCO_3 . Evidence for small amounts of CdSO_4 -based phases was also found using XRD, and only a minor proportion of the pigment remained as CdS. The authors concluded that CdCO_3 was not a photo-oxidation product, but rather that its high concentration and low refractive index (1.6–1.8) suggested that it was a bulking agent. CdCO_3 , along with cadmium oxalate, were intentionally added to CdS paints as extenders during this period [5]. As mentioned above, CdCO_3 was also documented to have been used as a starting material for the dry process and indirect wet process syntheses of CdS yellow paints [5, 7].

The goal of the current research is to identify the cadmium-based compounds in the altered yellow paints

of *Le Bonheur de vivre*, and determine their positions within the paint layers so that their identities as photodegradation products, fillers, or leftover starting reagents can be determined. This will also allow us to determine the species involved in the discoloration (including potential catalysts and intermediates), and also to propose the mechanisms of degradation involved. While we have studied the alteration of the yellow paints in *Le Bonheur de vivre* comprehensively, using handheld XRF, multispectral imaging, microRaman spectroscopy, FORS (fiber-optic reflectance spectroscopy), cross-section photomicroscopy in ultraviolet and visible light, μFTIR spectroscopy, XPS (X-ray photoelectron spectroscopy), SEM-EDS, GC-MS (gas chromatography-mass spectrometry) and HPLC (high performance liquid chromatography) here we will present primarily the characterization of the intact and degraded yellow paints in *Le Bonheur de vivre* that were carried out using synchrotron-based analysis methods. These methods included Cd L_{III}-edge and S K-edge XANES and μXANES , SR- μXRF imaging, and SR-ATR (synchrotron radiation—attenuated total reflection)- μFTIR mapping.

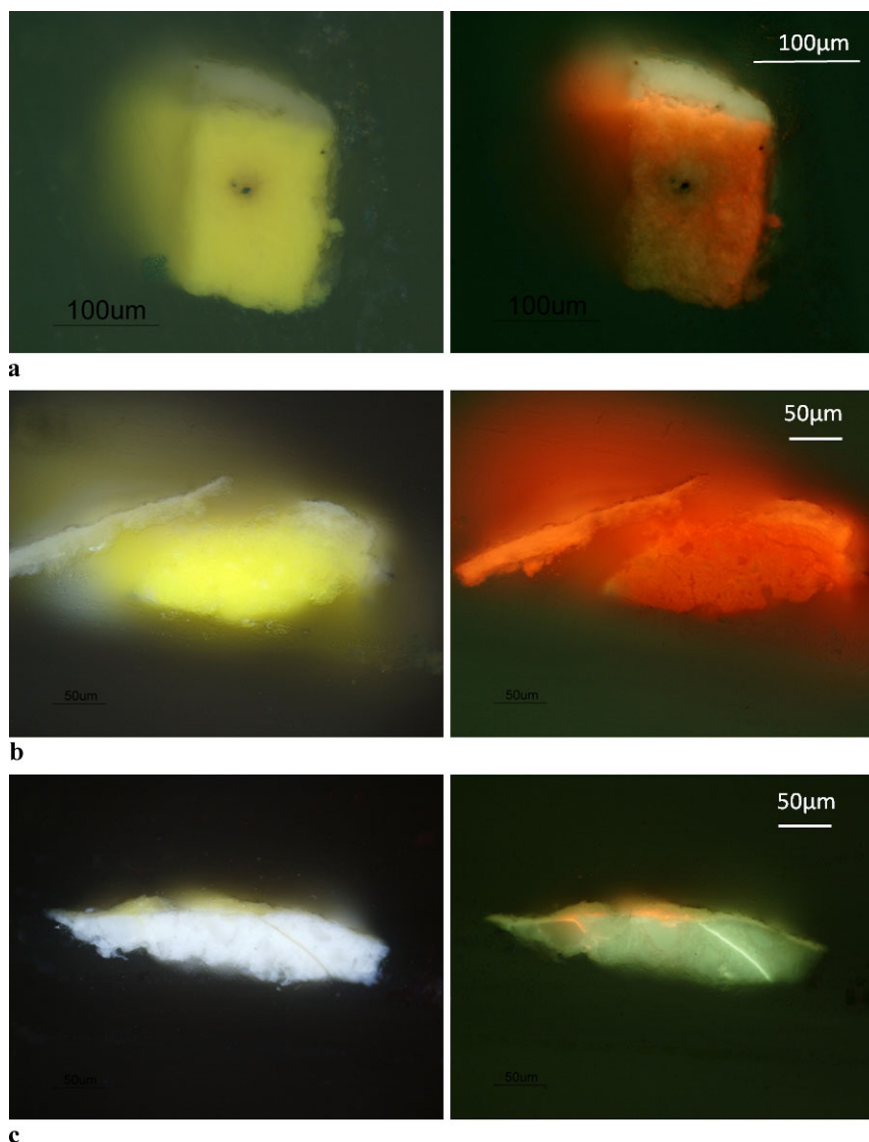
2 Experimental

2.1 Materials

As mentioned above, reference standards were chosen for XANES measurements based upon their use as cadmium-containing CdS precursors, fillers, or photodegradation products. Reference standards employed for the XANES and μXANES mapping experiments at SSRL and ESRF thus included powders of: cadmium sulfate (CdSO_4), Acros Organics; cadmium sulfide (CdS, 99.995 % metals basis), cadmium nitrate tetrahydrate [$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], cadmium iodide (CdI_2), cadmium oxide (CdO, >99.99 % pure), cadmium sulfate (CdSO_4), cadmium chloride (CdCl_2 , >99.99 % pure), cadmium carbonate (CdCO_3), and hydrated cadmium sulfate ($\text{CdSO}_4 \cdot n\text{H}_2\text{O}$), all from Sigma-Aldrich. The FTIR spectrum of cadmium oxalate (CdC_2O_4) is well-characterized, and the prominent absorbance at 1320 cm^{-1} was used to monitor the presence of this compound in the SR-ATR- μFTIR maps [9].

Samples S5, S115, and S113 were removed from the painting using a size 11 steel scalpel blade from the lightened region below the central reclining figures (S5), the lightened and discolored yellow fruit in the upper right corner tree (S115), and the darkened top left corner foliage (S113) (see Fig. 1). The samples were then mounted in 1 cm^2 cubes of Extec polyester resin (with methyl ethyl ketone peroxide catalyst, Extec Corporation®, Enfield, CT) that was allowed to cure for 24 hours under ambient light at room temperature. A cross-section of each sample was

Fig. 2 Visible (*left*) and ultraviolet (*right*) light photomicrographs of cross-section samples (a) S5 altered cadmium yellow paint cross-section from below the central reclining figures. The alteration layer ranges in thickness from 15 to 30 μm . (b) S115 altered cadmium yellow paint cross-section removed from the lightened and discolored fruit in the upper right quadrant of the painting. The alteration layer, which appears white in cross-section, ranges in thickness from 15 to 24 μm . (c) S113 darkened cadmium yellow paint cross-section removed from the upper left corner foliage



then exposed using a jeweler's saw, and the resulting sample surface dry polished using MicroMesh SiC polishing papers from 1500–12000 grit. Sample locations are shown in Fig. 1. Visible and ultraviolet light images of each sample are shown in Fig. 2. Note the white alteration layers/crusts on the surface of samples S5 and S115.

2.2 Methods

The cross-section samples were examined under reflected visible and ultraviolet light using the Nikon Eclipse 80i microscope at 200 \times magnification using the X-cite[®] 120 Fluorescence Illumination System with BV-2A cube. Images were taken with the Nikon digital camera DXM 1200F using ACT-1 software.

Handheld XRF Qualitative XRF analysis was carried out to determine appropriate sample locations using a Bruker

Tracer III–V with a rhenium tube and analysis conditions of 40 kV and 1.2 μA with a real time of 100 seconds.

Scanning Electron Microscopy X-ray microanalysis A Topcon ABT-60 SEM with a Bruker Quantax EDS detector was used to identify the elemental composition of the paint samples in cross-section. A 20 mm working distance was used, in addition to a 20 $^\circ$ stage tilt. All samples were examined at 20 kV in backscattered electron mode.

μXRF mapping, μXANES and SR- μFTIR , at ID21, ESRF The samples and reference standards were shipped to the European synchrotron radiation facility (ESRF, Grenoble, France) for cadmium and sulfur speciation and elemental distribution mapping. The X-ray microscopy beamline (ID21) at ESRF was used for both elemental imaging (μXRF mapping) and spectroscopic analysis (μXANES Cd L_{III}-

and S K-edges). This allowed the distribution and speciation of the Cd- and S-containing compounds in the paint cross-sections to be imaged at sub-micron resolution. The ID21 Scanning X-ray Microscope (SXM) operates in an energy range of 2.1–9.1 keV for μ XRF and μ XANES measurements. The microscope consists of a fixed-exit double-crystal multilayer monochromator (Si(111) used for this experiment) for selection and scanning of the X-ray beam. XRF and XANES experiments were performed in vacuum to minimize air absorption of the important low energy XRF lines such as S K, Cd L, and Pb M. The monochromatic incident beam was focused with Fresnel zone plate to a size of 0.3 (ver.) \times 0.7 (hor.) μm^2 at the Cd L_{III}-edge (3.7 keV) and 0.2 (ver.) \times 0.6 (hor.) μm^2 at the S K-edge (2.5 keV). The samples were raster scanned in the micro-beam to collect 2D images of their XRF using a Bruker SDD XFLASH 5100 detector. The incident X-ray flux at the samples was 6×10^9 photons/s/Si(111) bandwidth in the focused mode. μ XANES spectra were acquired by scanning the primary energy around the Cd L_{III}-edge (3.52–3.65 keV with a step size of 0.3 eV), and around the S K-edge (2.46–2.53 keV with a step of 0.2 eV). The PyMca software package was used to fit XRF spectra and to map the different elemental positions for μ XRF [10]. SIXPACK was used to decompose the Cd L_{III}-edge μ XANES spectra [11].

To obtain chemical maps, the energy of the incoming X-rays is set to a few particular values, where the absorption and consecutively the XRF of particular species is overexcited. As an example, at 2.4728 KeV sulfides ($\text{S}^{-\text{II}}$) are overexcited while at 2.4825 keV, sulfates ($\text{S}^{+\text{VI}}$) present a strong absorption [12].

Prior to the analysis of the paint cross-sections, powdered reference samples (described above) were prepared for XANES analysis by dusting the finely ground powder onto an adhesive tape and using a 200 mm diameter X-ray beam in transmission mode. Cross-section samples were maintained in a vertical plan, oriented at 30° with respect to the incident beam.

SR-FTIR was also carried out at ID21 using an SR-FTIR microscope [13]. The FTIR end-station is equipped with a Continuum microscope coupled to a Nexus Spectrometer (Thermo). The infrared emission of the synchrotron is collected on the edges on a bending magnet and directed to the beamline. For this experiment, the beam was focused using a Ge ATR tip, mounted on a $\times 15$ Schwarzfild objective. The beam size on the sample and the step size were set to 6 μm in both directions. Analyses were carried out on the surface of polished samples. Data analyses were performed using PyMca software.

Cd L_{III}-edge and S K-edge XANES at SSRL The powdered reference standards were mounted on adhesive films as described above for the ESRF experiments and analyzed

in XRF mode using a Lytle detector or a four element Si solid state detector (Vortex). Experiments were carried out at beamline 4-3 for S K-edge and Cd L_{III}-edge spectroscopy using a 100 μm incident beam. XANES was collected in XRF mode. BL4-3 is dedicated to X-ray absorption spectroscopy measurements with special capabilities for soft-energy (2.4–6 keV) studies. Equipment includes a Lytle detector or a four element Si solid state detector (Vortex). This station enables soft X-ray measurement from S K-edge and up. SIXPACK data decomposition software was employed for the quantitative determination of the XANES spectra.

The cadmium standards used for this study included: CdCO_3 , CdSO_4 , $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$, CdCl_2 , CdO , and $\text{Cd}(\text{OH})_2$. The sulfur standards used included H_2SO_4 on cotton, CdSO_4 , and $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ (see Materials section for suppliers). SIXPACK was used to decompose the Cd L_{III}-edge and S K-edge XANES spectra and obtain best fit local compositions by linear combination of reference spectra.

3 Results

3.1 Preliminary characterization

The three altered samples removed from *Le Bonheur de vivre*, S5, S113, and S115, (see sample locations and images above in Figs. 1 and 2) were all confirmed to be cadmium yellow paints (as opposed to chrome yellow, also used in this painting) using handheld XRF prior to sampling.

3.2 Sample S5 (from the ivory-colored altered paint below the central reclining figures)

Previous analysis by μ FTIR and μ Raman spectroscopies as well as XPS confirmed the presence of CdCO_3 as the major phase in this altered yellow paint region (data not shown). XPS also confirmed the presence of a CdSO_4 -based minor phase. CdS, the compound responsible for the yellow color of the paint, was identifiable only by XPS, suggesting that the CdS yellow pigment used by Matisse is amorphous or nanocrystalline. XANES analysis of this sample was carried out to determine the overall concentration of CdCO_3 , $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$, and CdS contained in this altered region of the painting (see Fig. 3).

The best fit local composition determined using the SIXPACK decomposition program for these data was 69 % CdCO_3 , 14 % CdS, and 17 % $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$, as shown in Fig. 3. It is important to note that while museum-based preliminary analyses only detected the major CdCO_3 phase, substantial $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ was also present. CdCO_3 and $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ are both white compounds, and so their presence explains the ivory color of this passage of the painting. That this ivory color was not Matisse's original intent for

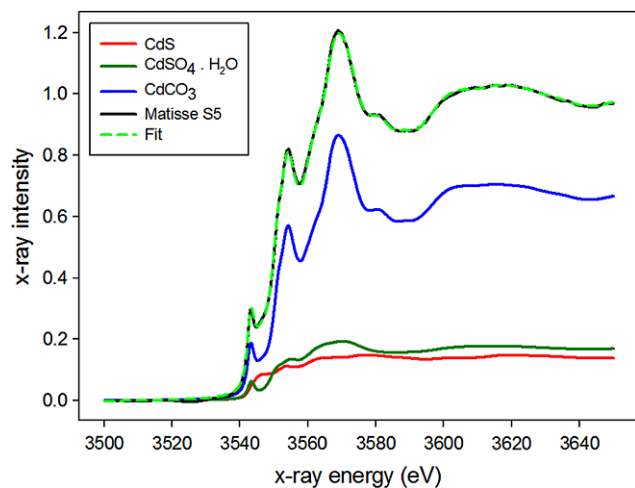


Fig. 3 Cd L_{III} XANES spectra of Cd references as well as *Le Bonheur de vivre* sample S5. Data collected at SSRL beamline 4-3 using a 100 μm spot size and XRF detection

this passage can be demonstrated by comparison with related works such as his final oil sketch at the Museum of Modern Art in San Francisco (see supplementary electronic material), and also the appearance of the original bright yellow paint color visible in this region where high impasto (thickly applied) regions of the ivory crust has fallen away. Both cadmium sulfates and cadmium carbonates have been identified previously as photo-oxidation products of cadmium yellow paints from the turn of the 20th century [3, 8]. However, cadmium carbonate was also used as a paint filler during this period to prepare pale cadmium yellow paints, and as a starting material for the dry process synthesis of CdS and an indirect wet process synthesis method [5, 7]. As a result, the identification of CdCO₃ does not provide conclusive evidence for a photo-oxidative degradation of the paint layer. High concentrations of CdCO₃ have been observed in grayish-yellow regions on Edvard Munch's *The Scream* (Munch Museum, Oslo, c. 1910), and interpreted as being from an indirect wet process starting material and/or a CdCO₃ filler rather than being conclusive evidence for photo-oxidation [7]. Similarly, CdSO₄ was also used as a wet process starting material and so its presence in a cadmium yellow paint cannot conclusively demonstrate that it is a photo-oxidation product [5]. To determine the origins and roles of CdCO₃ and CdSO₄·nH₂O in the altered *Le Bonheur de vivre* cadmium yellow paint then, μXANES, SR-μXRF mapping, and SR-μFTIR mapping were used so that the speciation of the cadmium compounds as a function of depth could be determined in sample S5 as well as S113 and S115.

Figure 4 shows the S K-edge μXANES spectra for two points, one within the yellow region of sample S5 (point 1) and one within the white alteration crust (point 2). The spectrum from point 1 shows pre-edge features for CdS at

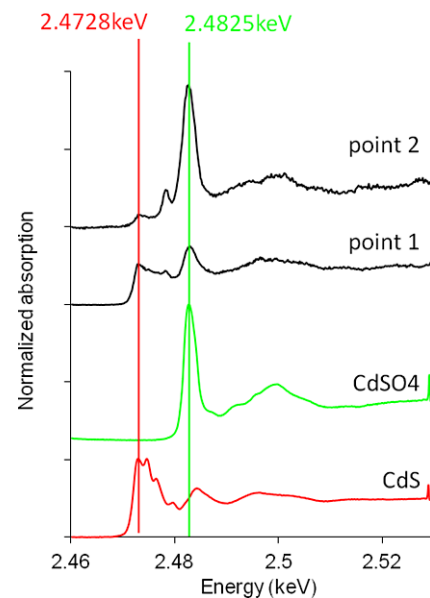


Fig. 4 μXANES spectra of the yellow interior and alteration crust of sample S5 (points 1 and 2, respectively), showing that the yellow portion of the sample (point 1) still contains CdS, while the white surface crust (point 2) is predominately composed of CdSO₄. That CdSO₄ is a photo-oxidation product is suggested by its high concentration in the white surface crust

2.4728 keV in addition to a peak at 2.4825 keV for CdSO₄, demonstrating that they are both present in the yellow portion of the paint. However, the spectrum from point 2, in the white alteration region, shows almost entirely the features of the CdSO₄ spectrum. The depletion of CdS from the alteration zone and the enrichment of CdSO₄ in this region, are suggestive of a photo-oxidation process in which the S²⁻ in CdS is oxidized to SO₄²⁻. This is consistent with previous studies of this system, including those of Leone and van der Snickt et al. [3, 8]. However, the presence of CdSO₄ in the yellow region of the sample has two possible interpretations. One is that alteration is already occurring in this region of the paint layer although it is not yet visible as a color change, and that this alteration is detectable in the form of the CdSO₄ identified there. The second interpretation is that the yellow region represents a truly unaltered region of the paint film, and that the CdSO₄ is present in this region as a leftover starting reagent. Further study of this sample, examining the distribution of carbonate phase as well, is required to help determine which of these is the case.

3.3 Sample S115 (sample from the altered yellow fruit in the painting's upper right quadrant)

Cross-section photomicrographs of the yellow fruits show that the dirty white surface color of the fruits is actually an alteration crust concealing the original bright yellow fruits (see Fig. 2b). Figure 5 shows the macroscopic appearance of this paint in visible light.

The off-white alteration crust is visible in cross-section both in visible light and in ultraviolet illumination (see Fig. 2b). The alteration layer appears pure white in cross-section, and varies in thickness between 15 and 24 μm . Figure 6a shows a backscattered SEM image of this same cross-section at 340 \times magnification, revealing the loss of structural integrity of the surface crust in the white upper right corner of this cross-section (see Fig. 2b), and the SEM-EDS map of Fig. 6b shows the sulfur depletion of this corner and the detached surface crust on the upper left when compared to the intact yellow interior of the paint layer. The loss of sulfur in the off-white surface crust is suggestive of a photo-oxidation in this region.

Cd L_{III}-edge μXANES analysis was carried out on this cross-section to determine the speciation of the cadmium in the altered and unaltered regions of this paint layer. The results are shown in Fig. 7.

Note the high concentration of CdCO_3 in the off-white altered paint surface/crust, up to 91 % whereas in the unaltered yellow portions of the paint layer CdCO_3 can be a major phase, up to 46 %, but not enriched to the levels observed in the alteration zone. $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ is more commonly ob-

served in the alteration zone, but it is also observed at locally high concentrations in the bulk yellow region of the paint layer (at 52 %). It is notable that CdS is completely absent from the alteration zone, as might be predicted by its off-white color, and that even in the bulk yellow region of the paint layer it is only present at a maximum of 37 %. Finally, it is important to note the presence and substantial concentrations of CdCl_2 in the bulk yellow region of the paint layer, up to 28 %. These high concentrations of CdCl_2 were also observed in the darkened foliage of the upper left corner of the painting—with concentrations up to 52 % (see this displayed graphically for sample S113 in Fig. 8). While small amounts CdCl_2 were observed in the faded cadmium yellow paint below the central reclining figures, it was typically less than 5 %. CdCl_2 is a starting material used in the wet process synthesis of CdS , and is likely present as a leftover synthesis reagent.

The enrichment of CdCO_3 in the off-white alteration crust of the paint layer suggests that it is a photo-oxidation product. Its high concentration in the yellow interior of the paint layer, however, is open to two interpretations. It may suggest an advanced progression of the photo-oxidation such that photodegradation products are present throughout the paint layer, although concentrated at the surface. How-



Fig. 5 Photomicrograph of cadmium yellow “fruits” from *Le Bonheur de vivre* upper right corner showing altered surface appearance

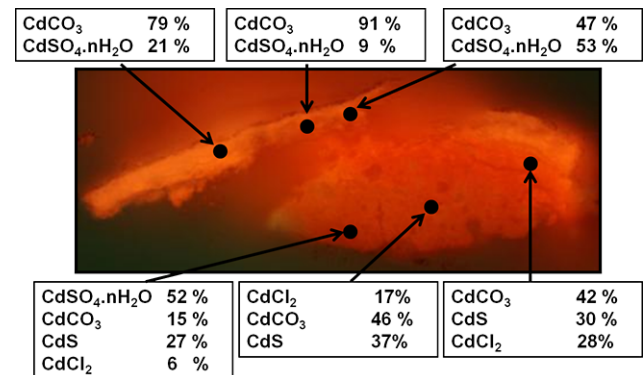
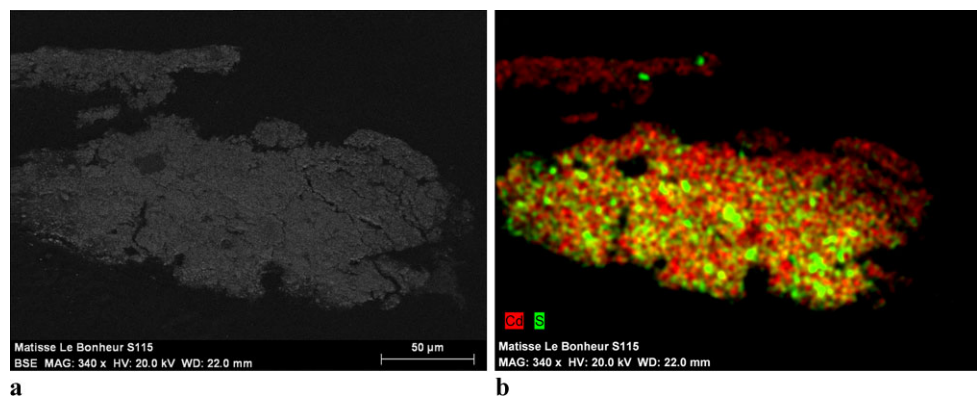


Fig. 7 Cd L_{III}-edge μXANES data from ESRF BL ID-21 collected using a $\sim 1 \mu\text{m}$ beam on *Le Bonheur de vivre* sample S115 from the altered cadmium yellow fruit shown in Fig. 5

Fig. 6 (a) Backscattered SEM image of sample S115 from the altered cadmium yellow fruit of *Le Bonheur de vivre* showing the breakdown of the paint layer in the upper right region, corresponding to the white altered surface layer visible in Fig. 2b. (b) SEM-EDS map showing the loss of sulfur in the off-white surface crust



ever, it may also demonstrate that the original cadmium yellow paint formulation contained a CdCO_3 filler [7], a known formulation during this period. In either case, the enrichment of CdCO_3 in the alteration layer suggests its presence here is at least a partially as photo-oxidation product. At ESRF ID21, the FTIR analysis of sample S115 (data not shown) also indicated the presence of carbonates (more concentrated in the alteration crust than in the bulk) as well as oxalates, which were specifically detected in the alteration layer.

The more even distribution of $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ throughout the unaltered and altered regions of the paint layer (based on point analysis data, see Fig. 7 for representative point analyses) makes its role in this particular region of the *Le Bonheur de vivre* cadmium yellow paint unclear, although its concentration at the surface of S5 suggests its role as a photo-oxidation product, and it has been identified as a direct photo-oxidation product of CdS in cadmium yellow paints previously [8]. The distribution of $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ in S115 suggests it could be present as a leftover synthesis reagent, or as a photo-oxidation product in a paint layer that has undergone an advanced degree of photo-oxidation. The high solubility of $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ could also explain its distribution throughout the paint layer (CdSO_4 is highly hygroscopic with a solubility of 76.4 g/100 mL).

3.4 Sample S113 (sample from the darkened foliage in the painting's upper left corner)

Elemental mapping using SR- μXRF for the degraded yellow paint layer and a portion of the ground layer for this sample are shown in Fig. 8.

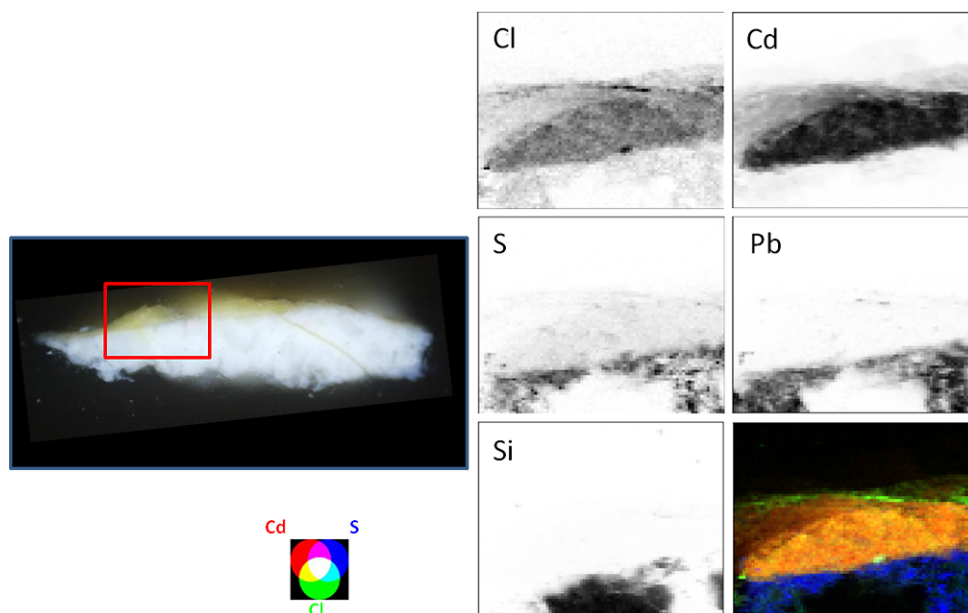
The high sulfur concentration in the lower part of the map is due to large clastic barium sulfate particles present in the

lead white ground—this was a common commercial paint ground for the turn of the 20th century. Note in this highly altered region of the painting that a high concentration of chlorine is observed in the cadmium yellow paint layer. This suggests that CdCl_2 was a starting material for the wet process synthesis of the cadmium yellow paint in this region, and that its high levels of degradation may result from chlorine's role in decreasing the band gap of CdS and thus increasing its photosensitivity [14]. μXANES data from this sample (data not shown) reveal an increased concentration of CdSO_4 at the surface of the paint layer, confirming the S5 results suggesting its role as a direct photo-oxidation product of CdS.

4 Discussion and conclusions

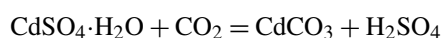
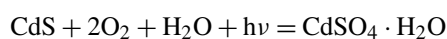
These data can be applied to a greater understanding of the regions of lightening and darkening/discoloration in the cadmium yellow paints of *Le Bonheur de vivre*. There were likely several different tubes of paint used on a work of this size, and the starting material for the synthesis of the cadmium yellow in at least one of these tubes appears to have been CdCl_2 based on this compound's presence in all of the discolored cadmium yellow regions on the painting (using, for example, the following synthesis reactions: $\text{Cd} + 2\text{HCl} \rightarrow \text{CdCl}_2 + \text{H}_2$ and $\text{CdCl}_2 + \text{H}_2\text{S} = \text{CdS} + 2\text{HCl}$). Given its high concentration and distribution throughout the paint layers, it is also likely that CdCO_3 was present initially as a paint filler/extender in these commercial paints [5, 7, 8]. As a result, the as-applied paint was already impure, likely a mixture of CdS, CdCl_2 , and CdCO_3 . The darkening/discoloration of the paint layers is worst in the re-

Fig. 8 Photomicrograph of sample S113 (removed from the darkened foliage in the upper left corner of *Le Bonheur de vivre*) under ultraviolet illumination. The region mapped is outlined in red. The map sizes are $100 \times 80 \mu\text{m}^2$ and the pixel size is $1.2 \times 1 \mu\text{m}^2$



gions where the CdCl_2 concentrations are highest (the foliage in the upper left corner and the fruits in the upper right quadrant). As mentioned above, CdS synthesized from CdCl_2 is known to have a smaller band gap than CdS synthesized from other starting materials, and so the cadmium yellow paints with the highest concentrations of CdCl_2 are expected to be the most sensitive to photodegradation [14]. Additionally, CdCl_2 is hygroscopic and so will increase the amount of water and the overall hydrophilicity of the paint film [135 g/100 mL (20 °C)]. The lightening/whitening of the surface of these regions can be explained by the high concentrations of $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ and CdCO_3 found at the surface (see Figs. 4 and 7) as these are both white compounds. It is also likely that a large fraction of the CdCO_3 found near the surface is the product of a gradual secondary reaction of CdSO_4 with atmospheric CO_2 . The pale brownish appearance of these regions of the painting cannot be ascribed to the formation of the dark brown photodegradation product CdO , as this compound was not identified by μXANES . Similarly, no evidence for the formation of the black PbS compound could be identified in these paint films [a possible secondary photodegradation product that forms when sulfur-containing pigments decompose in the presence of lead white pigment $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ observable using SEM-EDS and SR- μXRF mapping]. The surface darkening/discoloration appears rather to be organic in nature, the result of entrained surface soil in the interstices of the crumbling paint surface (see Fig. 6), a degradation pathway that may be initiated and enhanced by attack from dilute H_2SO_4 produced on the painting surface as the photo-oxidation takes place in a high RH environment [3]. The presence of dilute H_2SO_4 may also result in the formation of chromophores contributing to the darkened appearance of these surfaces as a result of the acid hydrolysis of the drying oil paint binder, and further organic analysis of the paint is needed to more fully understand the observed darkening. In the upper left corner of the painting the interpretation of the current color of the foliage is made more difficult by the presence of an overlying layer of lead white-based paint. The date of application of this overlying layer is not yet known, but it is likely a restoration layer. As a result, the current appearance of the fruit in the upper right quadrant of the painting (see Fig. 5), is the most representative of the altered cadmium yellow paint film.

The reactions that can be put forward for the visible changes in the paint film are as follows, with chloride ions, as noted above, likely acting as a catalyst for the photodegradation of the CdS by reducing its band gap and therefore increasing its photosensitivity.



Note that CdSO_4 is also hygroscopic, with solubility of 76.4 g/100 mL while CdCO_3 is highly insoluble, with a K_{sp} of 1.0×10^{-12} . As a result, CdCO_3 may represent the insoluble endproduct of a series of photodegradation reactions that include the formation of CdSO_4 . The high solubility of CdSO_4 may explain its distribution throughout the paint layer.

Cadmium oxalate was used as an inert filler/lightener for the production of pale cadmium yellow paints in the turn of the 20th century. Further research is needed to determine if its presence in the alteration crust is due to its initial presence in the paint layer, or due to a photodegradation phenomenon, as has been proposed by other researchers (see van der Snickt et al. this volume).

To conclude, the cadmium yellow paints of Matisse's *Le Bonheur de vivre* have developed a dirty off-white alteration crust on their surfaces, particularly in the regions below the central reclining figures, the foliage in the upper left corner, and the yellow fruits in the upper right quadrant. Elemental mapping and speciation mapping with SR- μXRF , μXANES and SR- μFTIR methods have revealed the presence of cadmium sulfates and cadmium carbonate in these crusts, and suggested the presence of cadmium oxalates. The spatial distribution of sulfate and carbonate phases suggests that they are photo-oxidation products rather than solely left-over starting reagents from dry or wet process syntheses or fillers. However, in the case of CdCO_3 its presence throughout a visibly unaltered portion of the paint layer suggests that it may also have been initially present as a filler or starting reagent. Leone et al. have demonstrated that high RH conditions increase the loss of the degrading cadmium yellow paint film's structural integrity, likely due to acid hydrolysis of the drying oil binder due to the formation of dilute H_2SO_4 [3]. As a result, while the observed alterations cannot at present be reversed, they can be slowed by the environmental conditions that are now in place at The Barnes Foundation.

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