ESRF	**Experiment title:** Photo-Oxidative Degradation Cadmium Sulfide Yellow Pigments in works by van Gogh, Matisse, and Their Early Modern Contemporaries	**Experiment number:** EC-880
Beamline: ID21	**Date of experiment:** from: 21 September 2011 to:27 September 2011	**Date of report:** 27 August 2012
Shifts: 18	**Local contact(s):** Dr. Marine Cotte	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Jennifer Mass – Winterthur Museum and University of Delaware Department of Art Conservation

Robert Opila*, Ismat Shah, and Jonathan Church* – University of Delaware Department of Materials Engineering

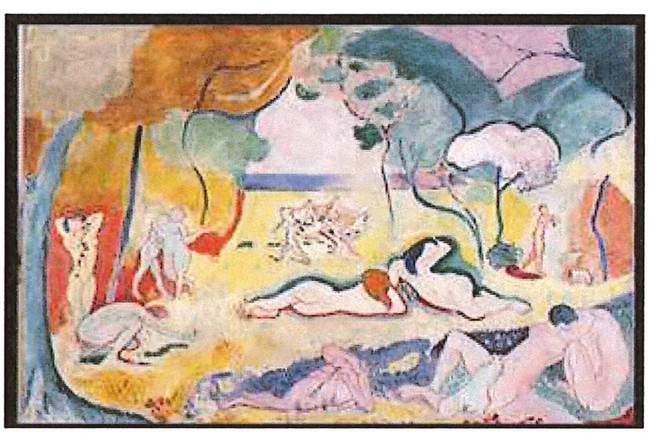
Apurva Mehta* – Stanford University Synchrotron Radiation Light Source

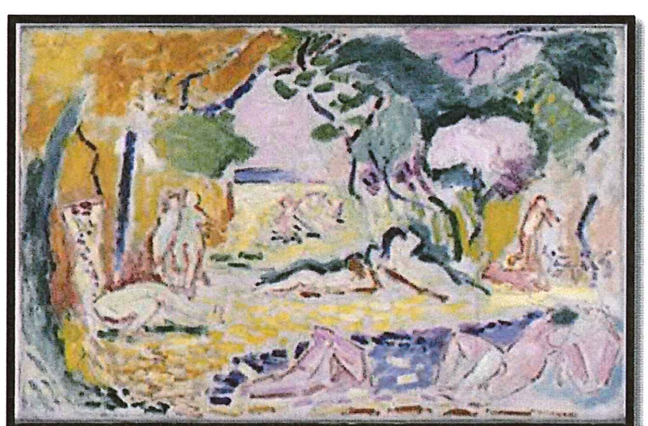
Barbara Buckley – The Barnes Foundation

Joris Dik – Technical University of Delft

Report:

The goal of the proposed research was the elucidation of the photo-oxidative degradation mechanisms of CdS (cadmium yellow) pigments in Henri Matisse's *Le Bonheur de vivre* (1905-6). The experiment focused on microsamples removed from the darkened foliage in the upper left corner of the work (shown below on the left), the lightened region below the central reclining figures, and the yellow fruits in the upper right quadrant that have a dirty white photo-oxidation crust. These regions are visible below, compared to an unaltered version of the painting from the Museum of Modern Art, San Francisco.





SR-μXRF imaging, μXANES imaging, and SR-μFTIR analysis was carried out on samples from these three regions at beamline ID21 with Dr. Marine Cotte. The positions of the Cd-containing phases identified (such as cadmium sulfate, cadmium carbonate, and cadmium chloride) were used to help discern the role of these materials as synthesis starting reagents, paint fillers, or photodegradation products.

The data collected during this experiment, described below, was presented at:

"Synchrotron Studies of Pigment Degradation" ***Synchrotron Research in Cultural Heritage Science*** (Argonne and Evanston Illinois, October 11th-12th, 2011), Jennifer L. Mass, Jonathan Church, Fang Fang, Robert Opila, Ismat Shah, Apurva Mehta, John Moulder, Marine Cotte, and Barbara Buckley. *Invited lecture*

"Imaging of CdS Degradation in Matisse's *Le Bonheur de Vivre* (1905-6): microXANES and SR-FTIR Methodologies", ***Synchrotron Radiation in Art and Archaeology*** (New York, June 5th-8th, 2012) Jennifer Mass, Jonathan Church, Robert Opila, Marine Cotte, Carol Hirschmugl, Apurva Mehta, Catherine Patterson, John Delaney, and Barbara Buckley

"Imaging the Light-Induced Degradation of Henri Matisse's *Le Bonheur de vivre*" ***Gordon Research Conference: Scientific Methods in Cultural Heritage Research – Non-Destructive Imaging and Micro-Analysis in Cultural Heritage*** (West Dover, Vermont, July 29th – August 3rd 2012) Jennifer Mass, Jonathan Church, Robert Opila, Marine Cotte, Carol Hirschmugl, Apurva Mehta, Catherine Patterson, John Delaney, and Barbara Buckley. *Invited lecture*

"Surface Analysis Meets Microscopy: Chemical Changes in Matisse Paintings", ***Microscopy and Microanalysis 2012*** (Phoenix, Arizona, July 29th - August 2nd, 2012) Robert L Opila, Jonathan Church, Fang Fang; University of Delaware; Jennifer L Mass; Winterthur Museum

A manuscript was also submitted on this work to ***Applied Physics A***, "The Photodegradation of Cadmium Yellow Paints in Henri Matisse's Le Bonheur de vivre (1905-6), Jennifer L. Mass, Robert L. Opila, Barbara Buckley, Marine Cotte, Jonathan Church, and Apurva Mehta. The abstract is reproduced below:

Evidence for the alteration of the yellow paints in Henri Matisse's *Le Bonheur de vivre* (1905-6, 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 works 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 Laboratory (SSRL Menlo Park, California) and Scanning Electron Microscopy-energy dispersive x-ray analysis (SEM-EDS) at the Winterthur Museum. 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-μFTIR) spectroscopy, X-Ray Fluorescence (SR-μXRF) mapping and micro X-ray Absorption Near Edge Spectroscopy (μXANES) 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 μXANES mapping and SR-FTIR imaging showed a substantial enrichment of $CdCO_3$ in the off-white surface crust of the faded/discolored CdS paint. This suggests that the $CdCO_3$ 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.

The ESRF experiment focused on cross-section samples S112 and S113 from the darkened cadmium yellow upper left corner of the painting, cross-section sample S115 from the lightened cadmium yellow fruit in the upper right quadrant of the painting, and samples S117 and S5 from the lightened cadmium yellow region below the central reclining figures.

Figure 1 below shows samples S5 (a) S115 (b) and S113 (c) in visible in ultraviolet light illumination. White alteration/ photodegradation crusts are clearly visible on the surfaces of both samples S5 and S115. The μXANES spectra of sample S5 in Figure 2 (both in the unaltered and altered regions, data points 1 and 2 respectively) show the enrichment of cadmium sulfate in the alteration layer. This can also be observed in the μXANES map of this sample, and demonstrates that cadmium sulfate is likely present as a photo-oxidation product in this region of the painting rather than as a synthesis starting reagent. Individual μXANES measurements revealed that cadmium carbonate was also a major phase in this sample, with measurements containing up to 70% $CdCO_3$. The presence of high concentrations of $CdCO_3$ and $CdSO_4$ explain the lightening of the cadmium yellow in this region of the painting (below the central reclining figures), as these are both white compounds.

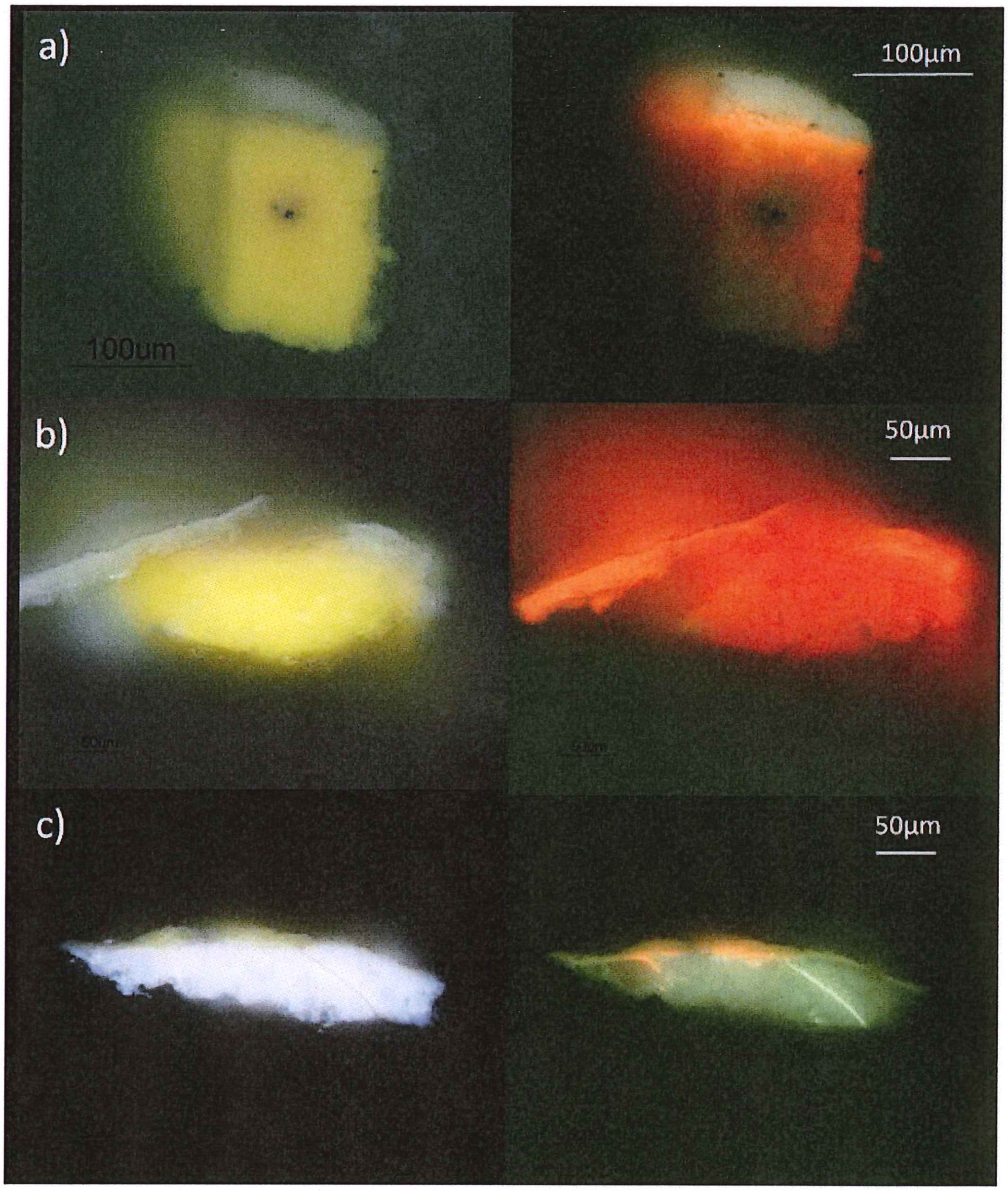
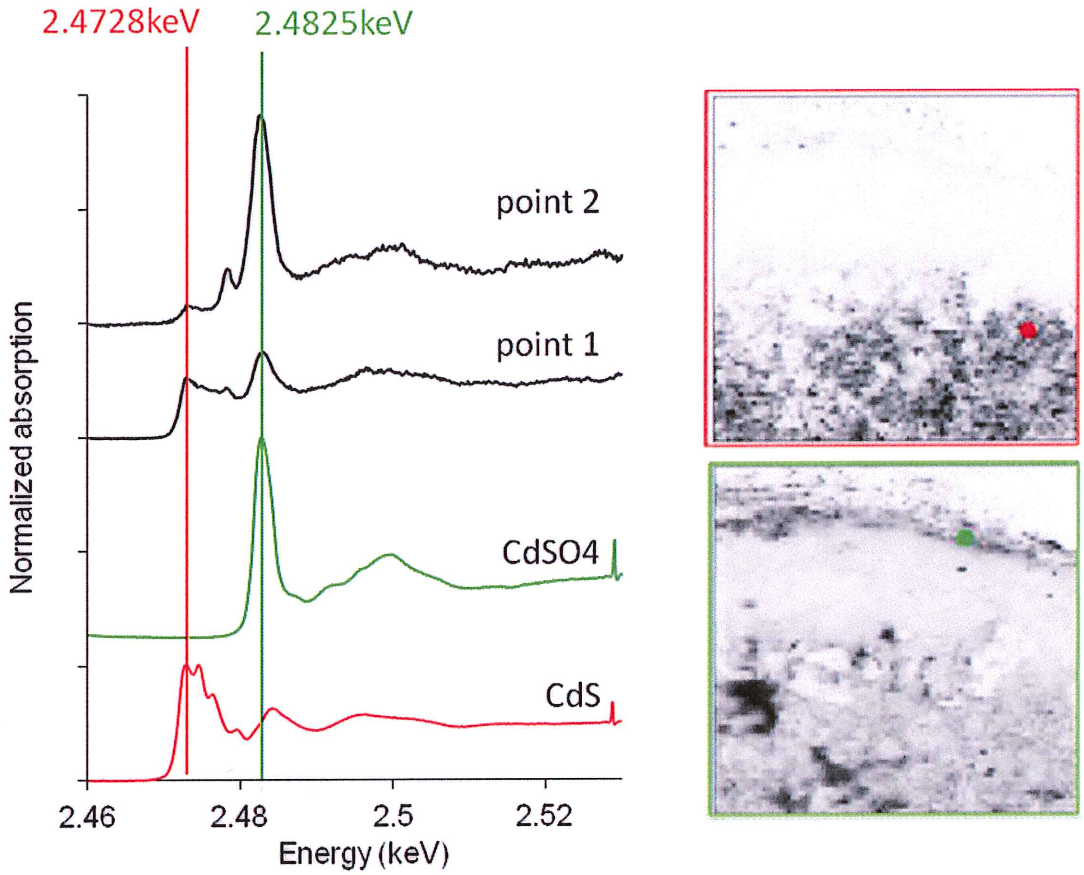


Figure 1. Photomicrographs of samples S5, S115, and S113 in visible and ultraviolet illumination.



Data point 1 (shown in red) = yellow unaltered layer
Data point 2 (shown in green) = white alteration layer

The position of the region studied on the paint cross-section is shown by the red box on the ultraviolet image below, and the sulfide and sulfate concentrations in this region are shown by the red and green data points respectively.

Figure 2. μXANES spectra and speciation map from sample S5 showing the enrichment of $CdSO_4$ on the altered surface of the CdS yellow paint layer.

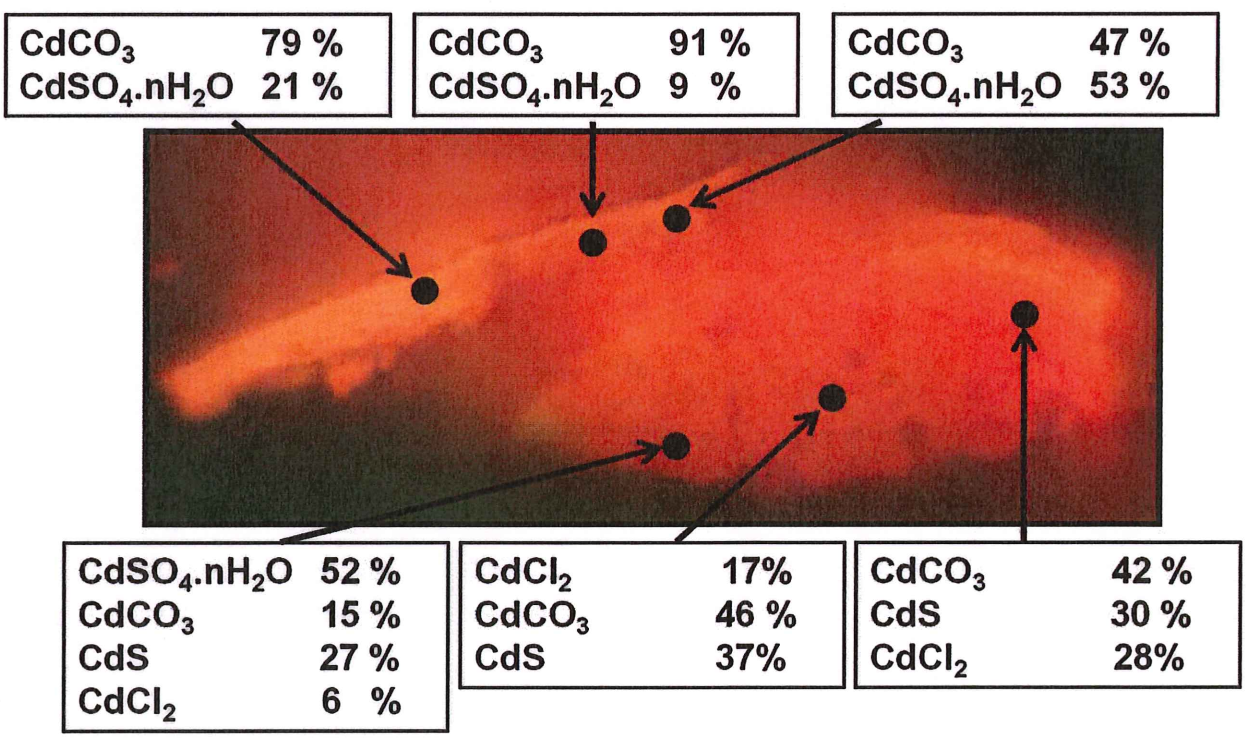


Figure 3. Quantitative μXANES data for sample S115, cross-section sample of cadmium yellow fruit from the upper right quadrant of Matisse's *Le Bonheur de vivre*.

Figure 3 shows the quantitative μXANES results for sample S115, removed from the cadmium yellow fruit in the upper right quadrant of the painting. It is clear from this data that the white alteration crust observable on this fruit is fully oxidized, with no cadmium sulfide remaining, and that the major phase is cadmium carbonate. The predominance of cadmium carbonate in the alteration crust of the paint rather than the yellow interior of the paint layer suggests that this compound is present as a photodegradation product rather than as a synthesis starting reagent or as an inert filler. FTIR imaging of this sample confirms the enrichment of carbonates in the alteration surface, and further points to the presence of oxalates, compounds that are commonly found in degraded oil paint films (see Figure 4). Further research is required to determine if these compounds are cadmium oxalates, as has been observed by other research groups (Koen Janssens et al.)

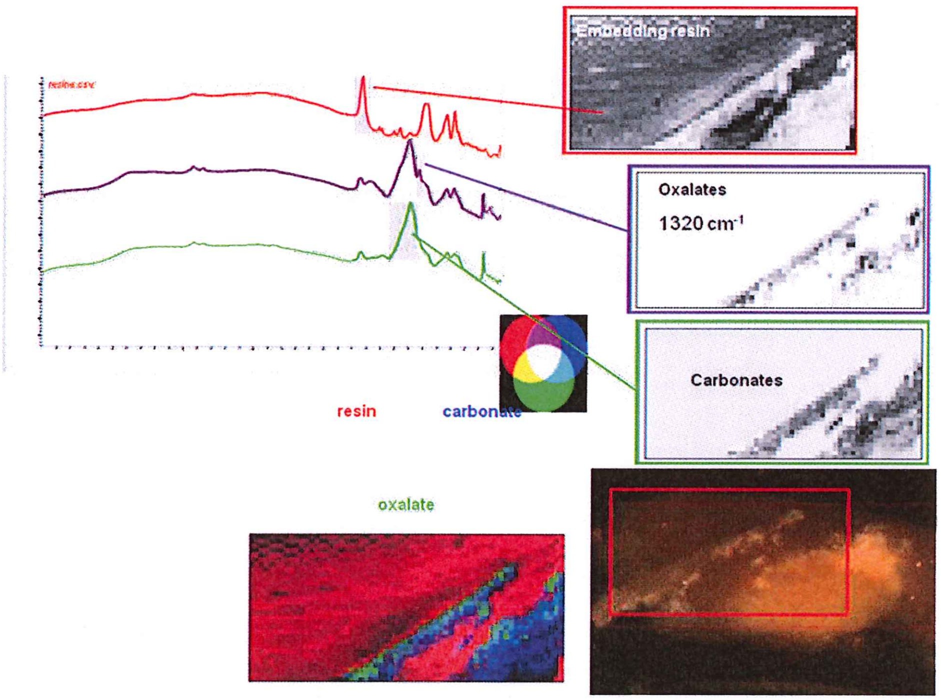


Figure 4. μFTIR imaging of sample S115 showing the enrichment of oxalates in the alteration crust as well as carbonates.

Elemental and speciation maps of sample S112 from the darkened yellow foliage in the upper left corner of the painting (see Figure 5) show a depletion of sulfur at the surface of the altered cadmium yellow paint layer, and an enrichment of sulfate at this surface. The high concentration of chloride in this paint film, also observed in sample S115 (see Figure 3), suggests that the highly altered cadmium yellow paints in both the upper left corner and the fruit was prepared from a cadmium chloride starting material.

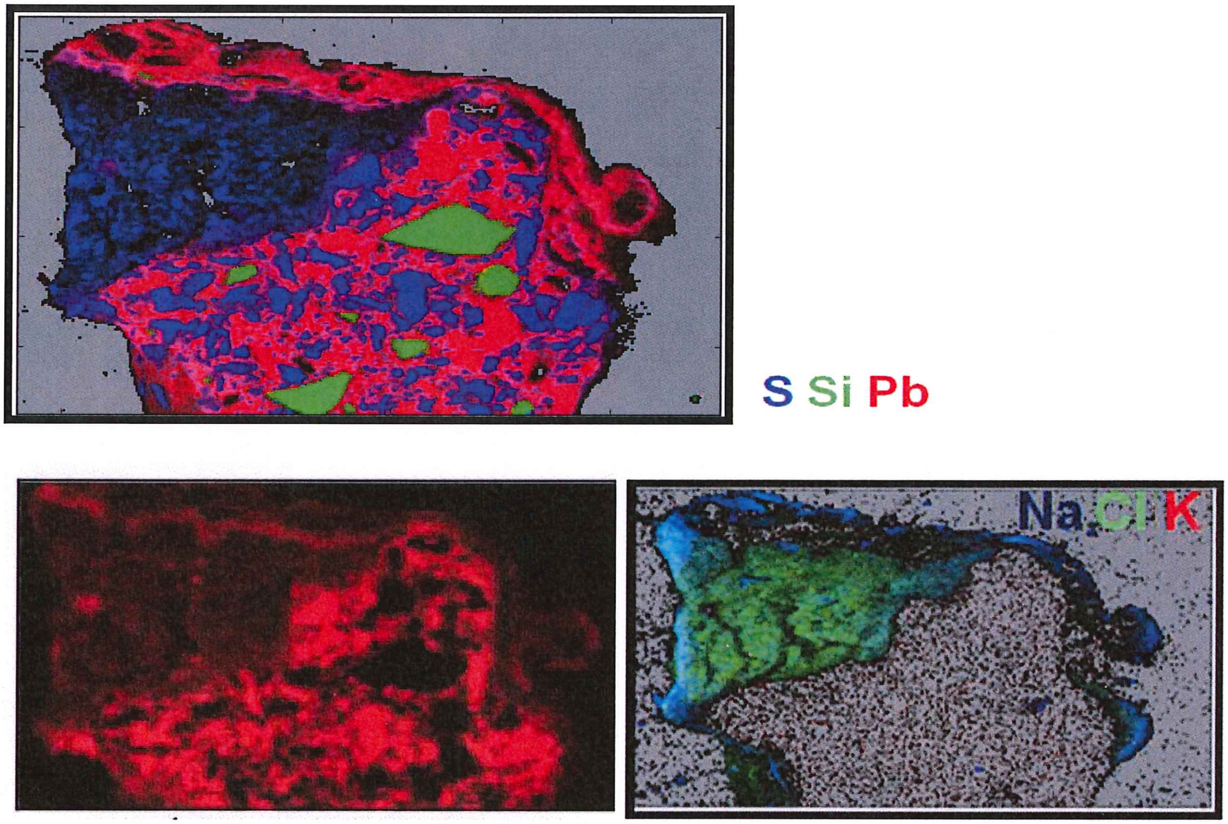


Figure 5. Elemental maps and sulfate speciation map (shown in red, lower left) for sample S112 from the darkened cadmium yellow paint in the upper left corner of Henri Matisse's *Le Bonheur de vivre*

In conclusion, the degradation mechanisms of the cadmium yellow paints in Henri Matisse's *Le Bonheur de vivre* were sought in the September 2011 run at ID21. The data collected during this experiment demonstrate:

1. The lightening of the cadmium yellow paint below the central reclining figures is due to the formation of an off-white alteration crust. The conversion of CdS to $CdSO_4$ has occured in this crust, and there is also a depletion of sulfur in this region compared to the paint layer interior. $CdCO_3$ is also present at high concentrations in the lightened yellow paint below the central reclining figures, but it remains somewhat unclear whether it is present in this region as a photo-oxidation product, a paint filler or a synthesis reagent for the paint in this region. (A slight increase in $CdCO_3$ toward the surface suggests, but does not prove, that it is at least in part a photo-oxidation product). Note that given the monumental scale of this painting (and also the different shades of cadmium yellow observed) it is likely that Matisse used several different tubes of cadmium yellow paint, and so different initial formulations and different degradation mechanisms for different regions of the canvas are to be expected.

2. The white alteration crust on the yellow fruit in the upper right quadrant of the painting is due to the photo-oxidation of cadmium sulfide to cadmium sulfate and cadmium carbonate. The high concentration of cadmium carbonate in the alteration crust suggests it is a photodegradation product rather than a paint filler or a synthesis reagent. In fact, the cadmium yellow paint in this region is rich in cadmium chloride, suggesting that cadmium chloride was the synthesis starting reagent rather than cadmium carbonate. The dirty appearance of the white alteration crust in this region is NOT due to the presence of cadmium oxide. Rather, it appears that the crumbling of the paint film as a result of photodegradation (visible by scanning electron microscopy) has caused surface soil to be entrained in the alteration film. Further data is required to confirm this hypothesis.

3. The cadmium yellow paint in the upper left corner has a lead white-based overpaint applied on top of it (see Figure 5). The extent of this overpaint is not yet known. However μXRF and sulfur speciation maps reveal a sulfur depletion at the surface of the cadmium yellow paint layer, and an enrichment of sulfate at this surface. The photodegradation revealed by these phenomena may explain the presence of overpaint in this region of the painting. The brownish appearance of the overpaint may be a result of the formation of PbS in the presence of degrading CdS. Lead XANES measurements are needed to confirm this hypothesis.

The data thus far suggest a direct photo-oxidation of cadmium sulfide to sulfate, as has been observed by other researchers, and also what appears to be a conversion of cadmium sulfate to cadmium carbonate. The formation of cadmium carbonate can also be caused by the oxidation of cadmium sulfide to cadmium oxide, followed by a reaction with atmospheric carbon dioxide. Atmospheric carbon dioxide is likely involved in the formation of any cadmium oxalates as well. Further research is needed for a full mechanistic elucidation, but the ID21 data has provided many answers to our group's initial questions concerning degradation materials and possible mechanisms.