Cadmium yellow degradation mechanisms in Henri Matisse's *Le Bonheur de vivre* (1905-6) compared to the Munch Museum's *The Scream* (1910) using chemical speciation as a function of depth

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There is a growing awarness of the alteration of cadmium sulfide pigments in the works of Edvard Munch and his contemporaries, including works by van Gogh, Picasso, Matisse, and Seurat (see, for example, U. Plahter and B. Topalova-Casadiego, *Cadmium Yellow in "The Scream" painted by Edward Munch*. in *The National Gallery Technical Bulletin 30th Anniversary Conference*. 2011. London: Archetype and J. L. Mass et al., *The Photodegradation of Cadmium Yellow Paints in Henri Matisse's Le Bonheur de vivre (1905-6)*, *Applied Physics A*, Published online 23 November 2012). 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. The photodegradation of cadmium yellow pigments can lead to a variety of photo-oxidation products, including cadmium oxides, cadmium sulphates, and cadmium carbonates. For example, the cadmium yellow pigments on Edvard Munch's iconic painting *The Scream* (1910, the Munch Museum, Woll 896) have altered to a grey colour, and are mixtures of CdS and $CdCO_3$. $CdCO_3$ is not thought to be a photo-oxidation product, but rather a bulking agent added to the paint. It is notable that $CdCO_3$ is documented to have been used both as a starting material for the wet process synthesis of CdS yellow paints, and that $CdCO_3$, along with cadmium oxalate, is thought to have been intentionally added as an extender for CdS paints during this period.

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. In contrast to *The Scream* 1910, changes in this iconic work of Matisse's Fauvist period include lightening, darkening, and flaking of the yellow paints. The data presented here focuses on microsamples removed from the darkened foliage in the upper left corner of the work (see Figure 1), 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 final oil sketch of the painting from the Museum of Modern Art, San Francisco (see Figure 2)

Figure 1. Henri Matisse's *Le Bonheur de vivre* (1905-6) (Image courtesy of The Barnes Foundation)

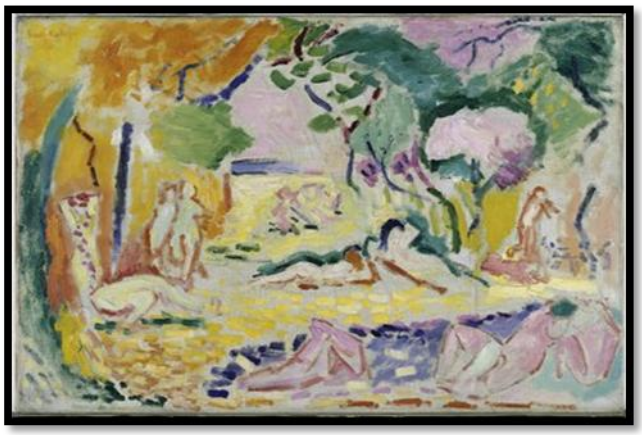

Figure 2. Final oil sketch for Henri Matisse's *Le Bonheur de vivre* (1905-6) (Image courtesy of the Museum of Modern Art, San Francisco)

Handheld X-Ray Fluorescence (XRF) and Multispectral Imaging surveys reveal that the alteration is confined to cadmium yellow (CdS) paints. Preliminary investigations of the degraded yellow paints in this work involved Cd L_{III}-edge X-Ray Absorption Near Edge Spectroscopy (XANES) and Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDS), Fourier Transform Infrared (FTIR), and Raman Microscopy. 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. These experiments were done to elucidate the discoloration mechanisms observed in the paint using elemental and speciation mapping. The positions of the Cd-containing phases identified (such as cadmium sulphate, 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 μXANES mapping and SR-FTIR imaging showed 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 in this painting rather than as a paint filler or starting reagent. Additionally, oxalates and sulphates were found to be concentrated at the alteration surface. Cadmium chloride, however, was found throughout the paint layers and interpreted as a synthesis starting reagent, unfortunately one that contributes to the photosensitivity of the cadmium sulphide pigment.