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Understanding and Predicting Cadmium Yellow Pigment Failure Mechanisms in the Works of the Early Modernists Using STEM Methodologies

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The new painting materials used by the early modernists were a critical part of their break with traditional modes of representation. These artists explored the synthetic organic and inorganic pigments that were newly available due to the chemical revolutions of the 19th century. However, the bright and novel hues that made their way onto these artists' palettes and in many cases defined their signature styles were not always synthesized properly. As a result, a number of their most commonly used pigments could be prone to rapid degradation and discoloration.

Many artists working in this period of the 1880s to the 1920s were aware of the limitations of the materials that were available to them, and they attempted to make choices based upon the most stable options at hand. Likewise, paint manufacturers were aware that not all of their offerings were equally stable, and would note the stability of the various hues of a pigment offered for sale. Given this context, however, we still have a number of important works from this period that have been substantially altered due to their pigment choices. Two examples of these works will be discussed: Edvard Munch's c. 1910 version of *The Scream* (Munchmuseet) and Henri Matisse's *Flower Piece* (1906-1907, The Barnes Foundation). The cadmium yellow paints in *The Scream* have faded to an ivory white in the neck of the central figure and in one prominent brushstroke in the sky. Flaking is observed in cadmium yellow brushstrokes in the water. Cadmium yellow paint in *Flower Piece* has developed an ivory crust in one region (the center of a daisy), and darkened in a second (to the right of the pitcher).

The cadmium-containing regions of *The Scream* were identified using x-ray fluorescence, ultraviolet-induced visible fluorescence, and ultraviolet-induced infrared fluorescence. Samples removed from the yellow brushstrokes in the water in the 1970s were studied using scanning electron microscopy and energy dispersive x-ray microanalysis. The growth of crystalline degradation products was visible as rod-shaped particles exuded from the surface of the samples (Figure 1). EDS data suggested that these are crystals of cadmium chloride. FIB lift-out of a sample for TEM revealed a highly heterogenous particle size distribution for the paint. Cadmium carbonates and sulfates were identified, as well as cadmium chlorides, hydroxychlorides, and cadmium oxide. Direct confirmation of the cadmium carbonate phase was provided by electron energy loss spectroscopy (EELS). Cadmium sulfide was a minor phase of the sample, explaining the color change observed in the painting. Electron diffraction data, high angle annular dark field (HAADF) images, and energy filtered transmission electron microscopy (EFTEM) images revealed that the particles of cadmium sulfide are polycrystalline, and that the cadmium sulfide particle size is on the order of 7 nm. The high surface area caused by this, in

addition to the presence of what appears to be chloride doping in the CdS lattice, help to explain the reactivity of the cadmium yellow in *The Scream*. Similar findings were observed for Henri Matisse's *Flower Piece*. The rotational average of the Fourier transform of the lattice images revealed that the CdS particles were polytype phases, containing stacking faults that prevent the formation of fully cubic or hexagonal phases. The absence of any large CdS grains (compared to the cadmium carbonate grain size) is consistent with an indirect wet process precipitation synthesis for the pigment. A combination of large and small cadmium carbonate grain sizes suggest that this phase is present both as a residual starting reagent and as an alteration product.

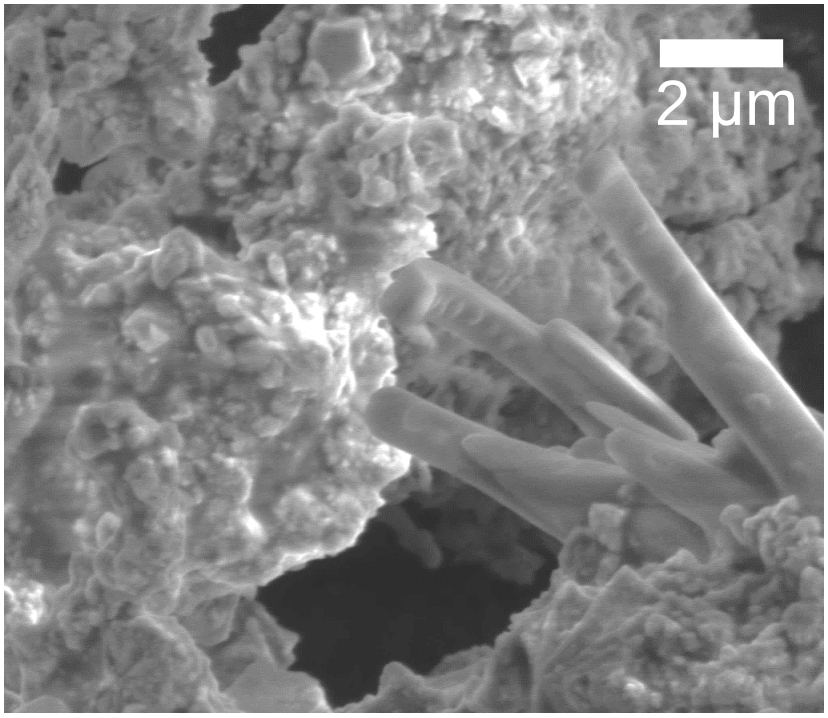

Figure 1. Rod-shaped crystals of cadmium chloride growing from *The Scream* (c. 1910) sample 1.

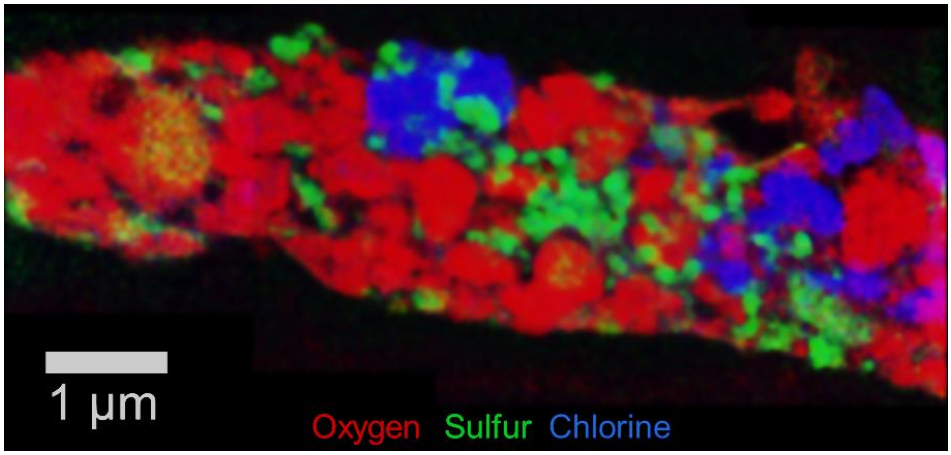

Figure 2. X-ray map of Sample 1 from *The Scream* (c. 1910) showing the small amount of sulfide remaining.