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Reverse Engineering Cadmium Yellow Paint from Munch's "The Scream" with Correlative 3-D Spectroscopic and 4-D Crystallographic STEM.

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Cadmium sulphide (CdS) based yellow paint in art masterpieces from the late 19th and early 20th centuries by artists such as Picasso, Matisse, van Gogh, and Munch are undergoing fading, flaking, and discoloration as they age. Characterization of the CdS and cadmium carbonate ($CdCO_3$) distribution within these yellow paints, are crucial for understanding degradation of the CdS pigment, and the role of $CdCO_3$ in paint synthesis and aging [1]. Here, we present a multidimensional and correlative scanning transmission electron microscopy (STEM) analysis of a focused ion beam milled section of cadmium yellow paint from the 1910 version of Edvard Munch's "The Scream". The painting has regions of cadmium yellow paint that have altered, resulting in the paint either flaking or fading. The sample selected for analysis is from a region of flaking yellow paint in the water adjacent to the two background figures on the bridge (Figure 1a).

Spectroscopic mapping of the paint sample by x-ray energy dispersive spectroscopy (XEDS) reveals the paint to be primarily composed of ~ 1 µm sized $CdCO_3$ and cadmium chloride particles, intermixed with smaller CdS, $CdCO_3$, and chloride particles (Figure 1b & 1c). The presence of carbon in carbonate particles is confirmed by EELS (Figure 1d). The observation of large $CdCO_3$ particles is consistent with the theory that in the Scream, $CdCO_3$ is present in yellow paint as a residual starting reagent from CdS synthesis [1]. The role and origin of the chloride is not yet fully understood, but its presence can result in increased reactivity/photosensitivity of the CdS pigment, so its presence is significant.

A 4-dimensional crystallographic dataset, consisting of a CBED pattern recorded in under 1 ms at each pixel of a series of 256x256 pixel scans of the sample, was acquired using a new high-speed pixel array detector with single electron sensitivity, and a dynamic range of 1 to 10^6 electrons. [2]. Mapping variations in the center of mass of the CBED patterns allowed us to to display the crystal orientation of the particles in the sample, revealing that many of the paint particles are polycrystalline, with ~ 10s – 100s nm grain size (Figure 2). Further analysis promises new insights into the relationship between pigment aging and synthesis, and crystal grain size and structure. [3]

References:

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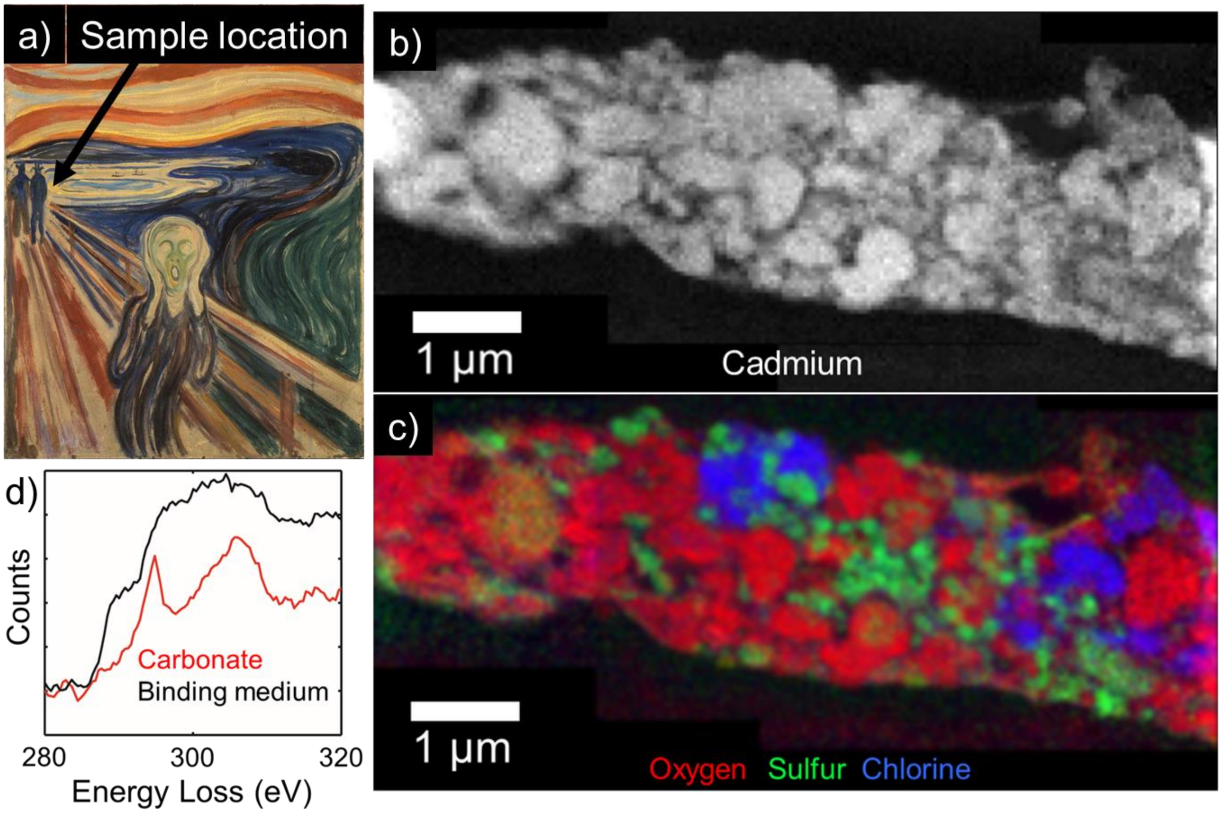

Figure 1. a) Approximate paint sampling location on "The Scream" indicated by arrow (Photo © Munch Museum). XEDS maps of FIBed section of paint showing b**)** Cadmium present throughout paint layer, and **c)** oxygen, sulfur and chlorine signals, which correspond to $CdCO_3$, CdS, and $CdCl_2$ respectively. **d)** Carbonate identity confirmed by EELS, also mapped.

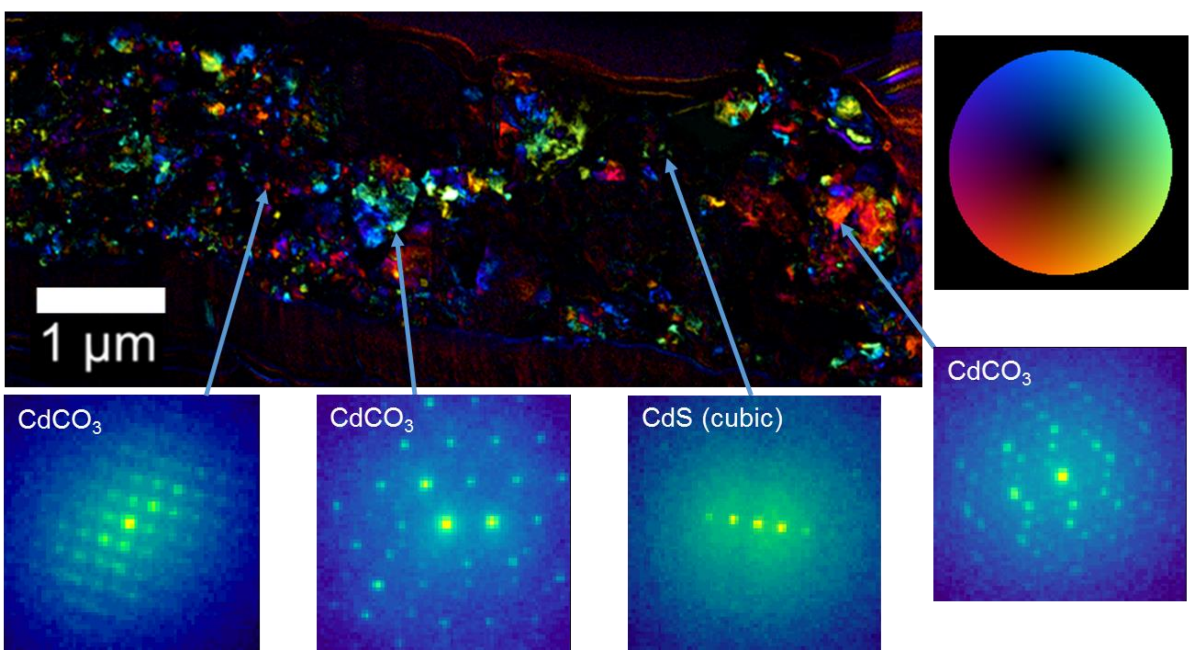

Figure 2. Center of mass map of the same region of paint sample. Colorwheel brightness indicates amplitude, and hue indicates angle of deflection of center of mass of CBED pattern from the origin. Comparison with XEDS maps (Figure 1) shows many paint particles are polycrystalline with 10s – 100s nm grain size. Selected diffraction patterns from dataset are shown with their location indicated on the map by arrows. Cubic CdS identified from diffraction spots matching (200) d-spacing (~2.9 Å).

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