White Paper

Fast Structural and Compositional Analysis of Cross-section Samples from an 18th Century Oil Painting with "Shuttle & Find"

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Fast Structural and Compositional Analysis of Cross-section Samples from an 18th Century Oil Painting with "Shuttle & Find"

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Date: June 2011

Introduction

Cross-section sample analysis is essential for obtaining layered structural and compositional information on many kinds of artworks, especially paintings. While non-invasive analytical techniques such as infrared microspectroscopy, Raman microspectroscopy, fiber optic reflectance spectroscopy, and X-ray fluorescence spectroscopy are effective in characterizing artists' materials, they usually provide either only surface information or mixed atomic information of all layers. Collecting micro-samples and preparing cross-sections is the most convenient and easiest way to identify and characterize the layered structure of a painting.

Here we present the cross-section sample analysis of an oil painting on canvas. The painting, *The Madonna Appearing to St. Philip Neri*, was created by Italian artist Sabastiano Conca (1680-1764) in 1740 (Fig. 1). It has been previously heavily restored, and numerous losses and fills can be seen clearly as featureless white patches in the X-radiograph (Fig. 1). The radiograph also shows that a thick impenetrable white fill material, probably lead white pigment ($2PbCO_3.Pb(OH)_2$), was applied over the entire lower area of the painting during a previous restoration, probably to cover losses and damages.

Correlative Light and Electron Microscopy (CLEM) is convenient for analyzing cross-section samples since it combines the optical properties of light micros-copy (LM) with the detailed structural and chemical analysis of the scanning electron microscope (SEM) with energy dispersive X-ray spectrometer (EDS). LM shows the optical appearance of layered structures in the samples, while SEM-EDS provides information on pigment particle morphology and composition at high spatial resolution within different layers.

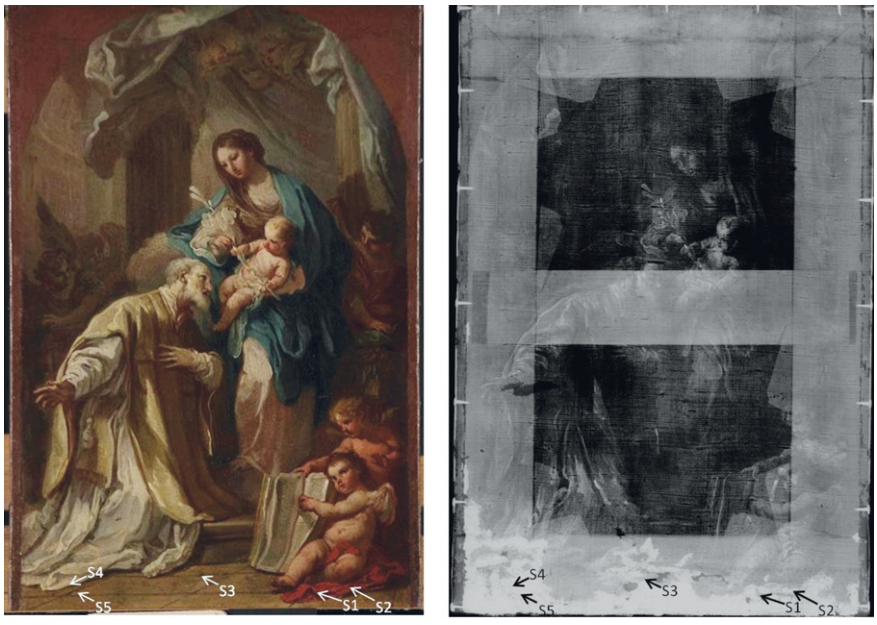

Figure 1
Left: The Madonna Appearing to St. Philip Neri, 1740, Sabastiano Conca, oil on canvas. The Indianapolis Museum of Art, James E. Roberts Fund gift (71.6), © The Indianapolis Museum of Art. Right: Corresponding X-radiograph. Arrows indicate the sampling locations.

The conservator charged with preparing the painting for an upcoming exhibition had two questions for which cross-sectioning was warranted: are there any original paint layers under the lead white fill, and if so, does the original layer show the same image as the current restored layer?
To answer these questions, five microsamples were removed from the lower area of the Conca painting and prepared as epoxy mounted cross-section samples.

Sample Preparation and Imaging

Five samples (~100 to 200 µm) were removed from the lower area of the painting at sites of existing losses or cracks (indicated by arrows in Fig. 1). All samples were mounted and embedded in epoxy resin, after which the mounted sample was hand polished on Micro-Mesh™ cloths to a grit fineness of 12,000. The cross-section samples were mounted in a sample holder especially designed for CLEM by Carl Zeiss. This holder can be used to transfer samples between the LM and SEM swiftly. The holder has three L-shaped registration markers defining a coordinate system that can be quickly located and calibrated semi-automatically in the "Shuttle & Find" software module.

LM imaging of the samples was performed on an Axio Imager.M2m motorized reflected light microscope using a 20 x darkfield objective. The microscope was equipped with an AxioCam MRc5 digital camera for image capture. Darkfield images of the regions of interests (ROIs) were collected in the reflected light mode. Auto-fluorescence ($\lambda > 488$ nm) images of the ROIs were also obtained by UV excitation from an X-Cite series 120 Q halogen lamp.

The sample holder assembly with mounted cross-section samples was then transferred to an EVO® MA15 variable pressure SEM. No sample coating is necessary for the embedded samples when using variable pressure mode (70 Pa air or water vapor). The SEM is coupled with detectors for secondary electron (SE), back-scattered electron (BSE), variable pressure secondary electron (VPSE), and EDS (Bruker). After calibration of the sample holder in the SEM, the ROIs in the LM images were relocated within a few seconds by clicking on stored points in the imported LM images. Corresponding SEM images were taken at an acceleration voltage of 15 kV using the BSE detector. A full spectrum EDS mapping of the same area was also performed to provide elemental characterization of the ROIs.

Results

Similar layered structures were found for all the cross-section samples under the light microscope. Figure 2 shows a schematic drawing of the general structure. From bottom to top, there exists the original red ground or preparatory layer, the original paint layer(s), a thick restoration lead white fill layer, and a restoration paint layer. Importantly, the restoration paint layer was shown via optical microscopy to be the same color as the corresponding paint layer(s) in all samples, thus confirming that the restorer carefully imitated the original painting's coloration in these areas.

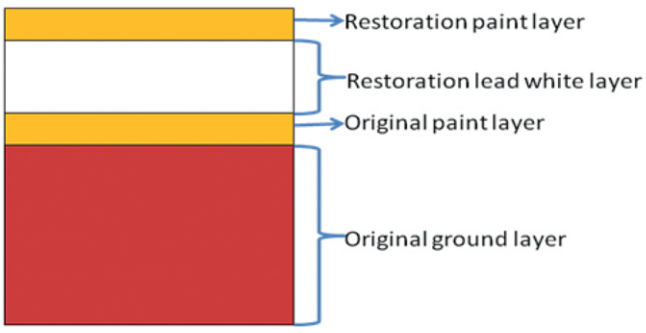

Figure 2
Schematic structures of the cross-section samples.

A darkfield image and an auto-fluorescence ($\lambda > 488$ nm) image of the cross-section sample S5 are shown in Figure 3. The aforementioned layered structures can be seen in both images. In this particular area, two layers of original paint are present, which is seen most clearly in the auto-fluorescence image due to their differing luminescence.

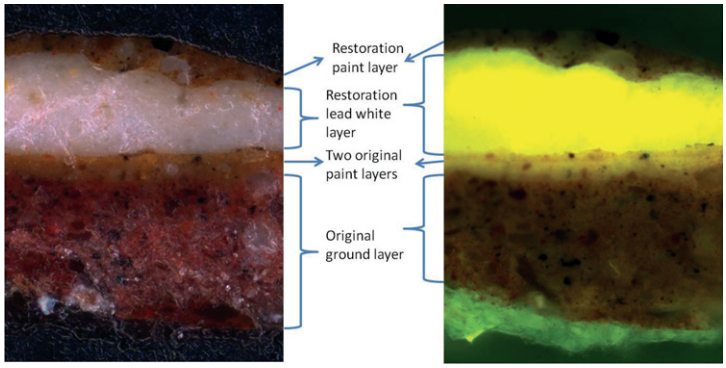

Figure 3
Darkfield (left) and auto-fluorescence ($\lambda > 488$ nm) (right) images of the cross-section sample S5.

Figure 4 shows the BSE image and element specific maps from EDS on sample S5. The bright areas in the BSE image (Fig. 4a) match with the lead map (Fig. 4b), showing that lead white is not only present in the thick lead white fill layer, but also was mixed to different degrees in all other layers. Iron is concentrated in both the restoration and original paint layers as well as in the original ground layer (Fig. 4c). Given the different colors, yellow ochre (primarily goethite, FeO(OH)) was probably used in the restored and original paint layers, while red ochre (primarily hematite, Fe_2O_3) is responsible for the red color of the ground layer. EDS mapping (Fig. 4d) also shows Ca, Si, Al, K, Na, and Mg in the ground layer, indicating the usual clay and silicate mixture of red ochre as well as chalk and/or gypsum typical of painting ground layers.

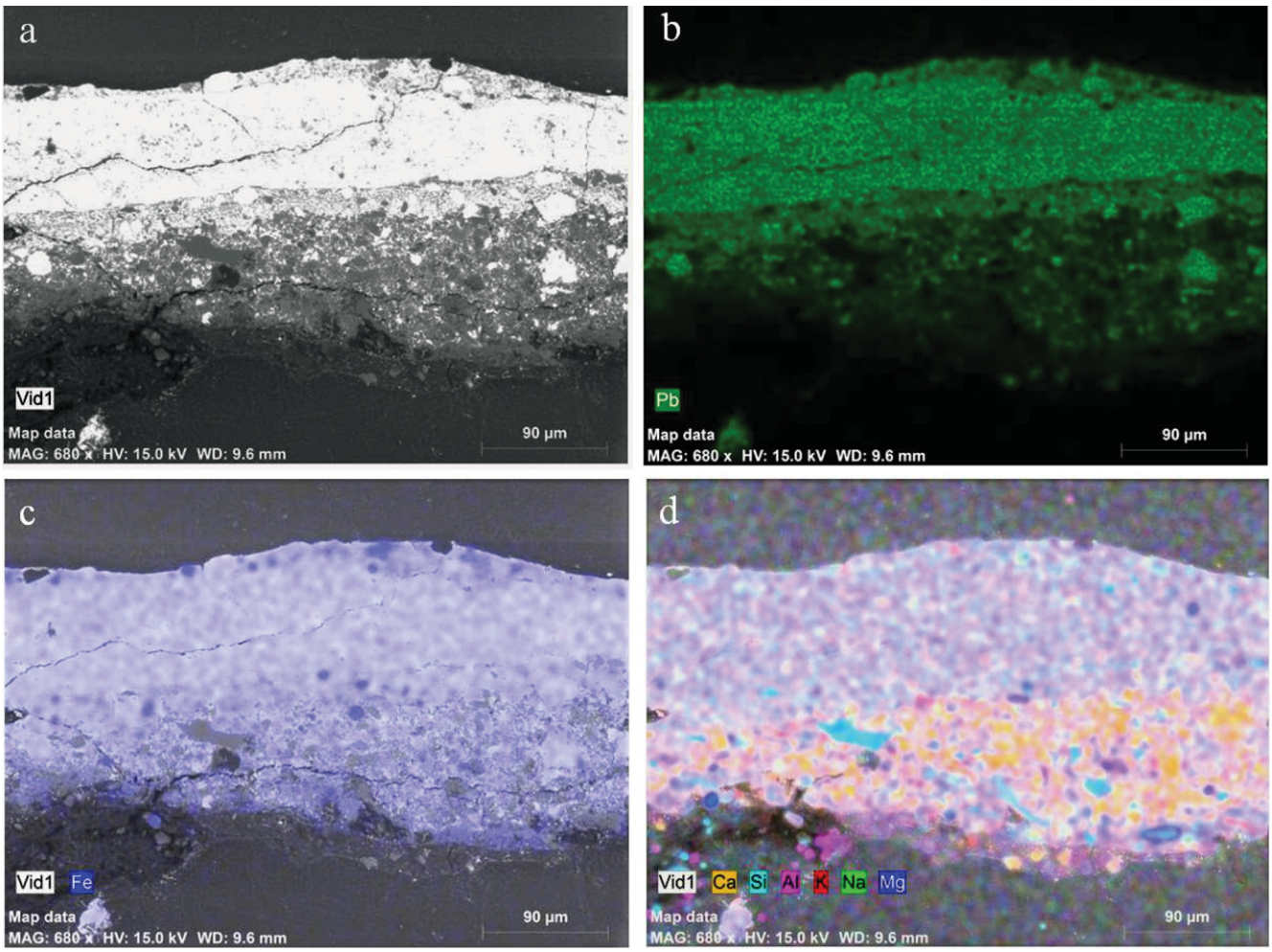

Figure 4
SEM images from cross-section sample S5. a) BSE image, EDS mapping of b) lead, c) iron, and d) elements typical of chalk or gypsum and clays (Ca, Al, Si, K, Na, Mg).

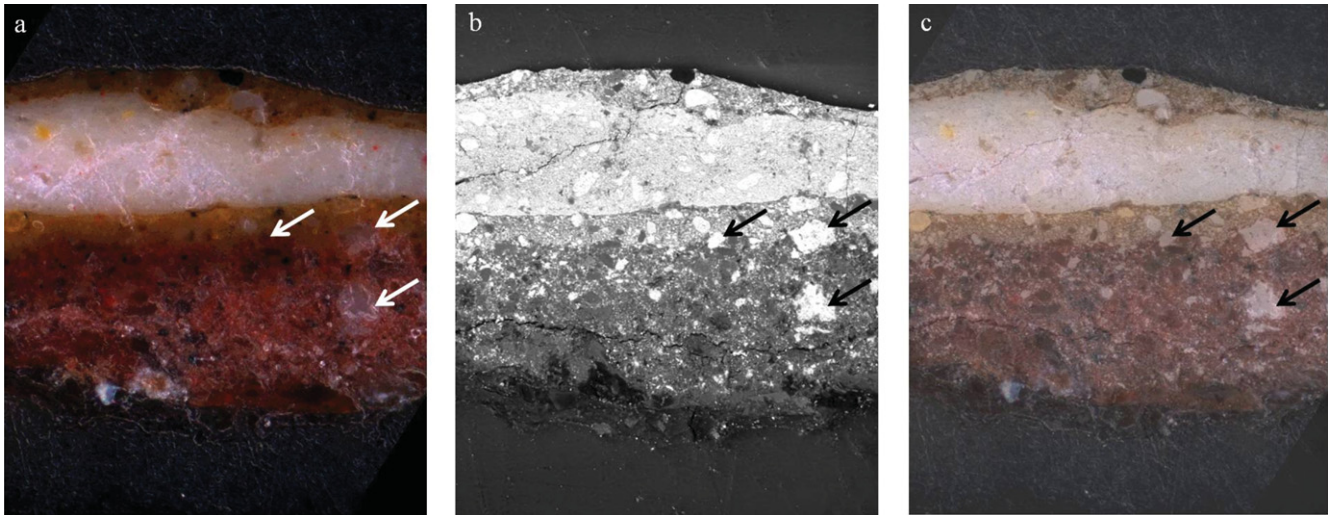

Figure 5

CLEM comparison of exact location on the cross-section sample S5 with (a) darkfield, (b) BSE, and a (c) 50:50 mixture of darkfield and BSE images. Arrows indicate translucent particles (darkfield) containing lead (BSE).

"Shuttle & Find" enables precise relocation of ROIs between the light microscope and the scanning electron microscope for fast, convenient correlative microscopy. Figure 5 shows the side-by-side comparison of the darkfield image and BSE signal of the exact same ROI on the cross-section sample S5. AxioVision software allows additive blending of the two into a single image for effortless comparison as well as movies showing the gradual overlapped transition from an SEM image to an optical image.

Careful comparison of the two images reveals that some bright spots from the BSE image appear translucent in the darkfield image (marked by arrows in Fig. 5). EDS mapping shows the major component of the bright spots to be lead. All the information combined suggests the translucent particles could be a result of incipient lead soap formation in the original paint layers. Saponification reactions in paintings can lead to stability issues, and knowing this in advance could affect the treatment and handling of the painting in the future.

Conclusion

The "Shuttle & Find" interface for correlative microscopy makes analysis of cross-section samples fast, reliable, and precise. LM images of the cross-section samples from the Conca painting suggest the existence of original paint layers covered by a previously heavy-handed restoration and that the original painting probably resembles the restored image. Conservation efforts are underway to uncover intact areas of the original painting. The precise overlay of the LM and SEM images of the ROIs possibly reveals the early stages of lead soap formation, which could be a potential conservation issue for this painting.

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