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When New and Improved Becomes Outdated and Degraded: The Technical Study and Treatment of a 1964 Pop Art Painted Collage

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ABSTRACT

A painted collage by New York Pop artist Marion Greenstone, entitled *Spoonk* (1964), was recently given to the Zimmerli Art Museum at Rutgers University, New Jersey. This gift was accepted on the condition that the damaged collage would be treated by a graduate student in the Winterthur/University of Delaware Program in Art Conservation. Before treatment began, technical analysis methods including visual examination, polarized light microscopy, x-ray fluorescence, cross-sectional microscopy, scanning electron microscopy-energy dispersive spectroscopy, Raman spectroscopy, Fourier-transform infrared spectroscopy, and gas chromatography/mass spectrometry were conducted in order to better understand the condition of the various components of the artwork. Many colorants, binders, and fillers in the paints and paper elements were identified. Some compounds which are likely products of degradation were also identified. The information gained from the analysis aided in the development of a treatment plan for this painting, which was completed successfully, and it is believed that the results of this study will also be a useful addition to currently available information on Greenstone's materials and working methods as well as those of her contemporaries.

Fig. 1. *Spoonk* (1964) by Marion Greenstone

I. INTRODUCTION

A. Background Information

Historical Context of the Artist and Artwork

Marion Greenstone (1925-2005) was born in New York City. After discovering her artistic talent through an evening art class, Marion trained as an artist at the Art Students League and at Cooper Union from 1951 to 1954 (Archives of American Art 2008). After a two-year Fulbright in Italy, Greenstone began exhibiting as an abstract expressionist painter showing in various galleries and museums including the Whitney Museum and the Brooklyn Museum of Art, both in 1953. However, by 1963 her art began to reflect the new colors and images of the young artists associated with the rising Pop Art movement (Kriff 2008). *Spoonk,* painted in 1964, is an example of the pop art collages Greenstone was then creating (fig. 1).

The phrase “Pop Art” (short for popular art) was first coined by British art critic Lawrence Alloway to characterize the new movement of art that was emerging in the late 1950s (Madoff 1997). The esoteric and introspective paintings of the abstract expressionists were being pushed aside by a younger generation who embraced the new technologies and commercialism that quickly invaded America after the war. In the words of Andy Warhol, Pop Art encompassed “all the great modern things that the Abstract Expressionists tried so hard not to notice at all” (Eccher 2005, 158). Along with Warhol, the American Pop artists included Lichtenstein, Wesselmann, and Rosenquist, who created montage images from advertisements, television, magazines, packaging, and comics on a larger-than-life scale. These vibrant artworks were immediately recognized by the public as celebratory of commercialism and the rise of America’s power and economy after World War II, while simultaneously criticizing America’s over consumption and waste, a seemingly inevitable consequence of newly-won prosperity.

Between 1957 and 1961, Greenstone lived in Ontario, Canada and became active in the Toronto art community, gaining recognition and momentum in her career as an abstract expressionist. Upon moving back to New York City in 1961, Greenstone continued to show regularly in Canadian exhibitions. But by 1963, Greenstone’s style had changed dramatically. On November 24, 1964 Greenstone wrote a letter to the International Gallery Limited in Toronto inquiring whether her new works would be accepted in the local art community. Gallery employee Jerrold Morris’s reply, dated December 3 of that year stated:

> Dear Marion… Emilio and I both feel that Toronto will not be receptive to the change in your work (at the same time we understand the motives behind it). (Archives of American Art 2008)

Despite the reluctance that some Toronto galleries seemed to have in embracing Greenstone's new Pop style, she continued to show at the Albert White Gallery between 1964 and 1966, including at least one exhibit of her new Pop Art collages. A tag adhered to the back of *Spoonk* as well as written gallery records leave little doubt that this painting was shown at the Albert White Gallery during these years.

Greenstone's painting, *Spoonk,* is constructed of six mixed-media images on canvas. Each was stretched over a separate wooden support and then attached to one another to create a unified work. The composition consists of bright, matte paints on canvas and adhered paper collage elements from advertisement images including food, cars, and sports. The bright, flat colors and mass-media images relate to works made by other Pop artists in New York City at that time, especially James Rosenquist and Tom Wesselmann. While Greenstone was not a prominent New York Pop artist, her work reflected the same energized palette and sensational images used by the leaders of the movement. In fact, the same cake batter advertisement image inspired both Greenstone, as seen in *Spoonk*, and Rosenquist in his later painting, *Highway Trust* (1977) (figs. 2, 3).

Fig. 2. *Spoonk;* batter detail 90° CCW

Fig. 3. *Highway Trust* (1977) by Rosenquist

Condition of the Artwork

During the initial examination, the auxiliary supports (including the wood stretcher bars and plywood backing boards) were found to be stable but dusty. The screws and staples on the back proper left of the artwork had rusted but were still firmly attached. This suggested that the painting had been exposed to moisture, sufficient to cause metal corrosion but not enough to cause deformation or warping of the wood supports. The entire surface of the artwork was covered with dirt and fingerprints, and areas of orange paint exhibited mold growth. There were also a few areas of abrasion, and there was noticeable fading and discoloring of some paper elements. The discolored and splotchy green paint on the right side of the art work and tacking edges was actively flaking. There were many losses in the green paint exposing the ground and causing the lifting of the paper lips element, which was originally adhered directly to the paint. Corner draws were visible in the diagonal corners on these canvases. While external circumstances are often the cause of damage to artworks, damage can also be caused by inherent properties of the artwork materials themselves. This has become increasingly more apparent in artworks containing modern paints and materials that artists began to embrace beginning in the early twentieth century.

B. Statement of the Problem

Spoonk was recently given to the Zimmerli Art Museum at Rutgers University in New Jersey. The purchase of this painting was agreed upon on the condition that it would be treated by a graduate student in the Winterthur/University of Delaware Program in Art Conservation. The painting arrived at the Winterthur Museum on November 11, 2007, and the artwork was examined by the author. During the condition documentation of this painting, several questions arose:

1. What are the media, pigments, and fillers in the ground layer(s)?
2. What are the media, pigments, and fillers in the paints?
3. What are the components in the printed paper images?
4. Are the identified media, pigments, and other components consistent with the proposed date and movement for the artwork?
5. What is the composition of the dirt and grime collected from the paint surface, and what does this suggest about the environment and damage the artwork has experienced?

These questions were addressed using various analytical techniques as discussed in Experimental Procedures. The analytical results from this experiment aided the author in formulating and completing an appropriate plan for treatment and preventive care for the artwork. The information gained from this analysis has not only been of benefit to this painting, but will also be useful in comparison with the present information on the materials and working methods for Greenstone's other works as well as for works by her contemporaries. There is still relatively little known about the deterioration of many modern and contemporary materials, and it is crucial in preserving and caring for these artworks that the chemical composition and reactivity of these materials are better understood.

C. Review of Literature

In the search for technical literature relating to the artwork presented for analysis, no publications or records on the technical analysis of artworks by Marion Greenstone were found. Therefore, preparatory literature research focused on the techniques reportedly most used to successfully identify reference standards of modern synthetic organic media and colorants and technical analysis done using pigment and binder samples from actual modern paintings.

Reference Standards for Modern Materials

Many of the traditional paint media and pigments on works dating from antiquity up to the late nineteenth century have been successfully analyzed and identified using various techniques including FTIR, GC/MS, and Raman. Modern synthetic polymer resins and the various additives often differ significantly in molecular structure and handling properties from traditional media, but FTIR spectroscopy and pyrolysis-gas chromatography with mass spectrometry (Py-GC/MS) are also often successful in identifying these new twentieth-century media.

The differences between analyzing traditional pigments and the synthetic organic pigments developed in the last 150 years are much more significant than the differences between analyzing traditional and modern paint media. Pigments used before the mid-nineteenth centuryare primarily inorganic with the exception of a few organic pigments, red lakes being the most prominent. Because of the inorganic and crystalline nature of most traditional pigments and their long, established histories of use, techniques including PLM, ultraviolet/visible spectroscopy, SEM-EDS**,** and x-ray diffraction have been used successfully in their identification and cataloguing. Synthetic organic pigments have proven to be much more difficult to detect and identify using these techniques due to the inability of these techniques to identify complex organic molecules, the lack of established reference libraries for these relatively new compounds, and the small amounts of these colorants typically found in samples (Lomax and Learner 2006). Like modern synthetic organic media, synthetic organic pigments have been more successfully identified using FTIR, Py-GC/MS, and Raman analytical techniques.

Fourier-Transform Infrared Spectroscopy:

Numerous authors have reported on the usefulness of FTIR spectroscopy in the identification of modern paint media and colorants, especially with the use of a diamond cell (Lake et al. 2004; Lomax and Learner 2006) which is not only less expensive than other FTIR preparations, but also requires less time and a smaller sample size than microtomed samples (Learner 1996). Although Learner (2004, 81) stated that “the only modification needed to make FTIR a more suitable technique for modern paint analysis is the collection of a range of new standard spectra from all the synthetic binders and modern pigments and extenders,” he did not discuss the compound concentration requirements for detection using this method. Because of their color strength, many synthetic organic colorants are not present in paints in high enough concentrations to be detected using FTIR spectroscopy.

Pyrolysis-Gas Chromatography and Mass Spectrometry:

One technique that has been discussed repeatedly in literature on the analysis of modern materials is pyrolysis-gas chromatography/mass spectrometry, which uses heat in the absence of oxygen to degrade the sample before analysis with GC/MS. Learner (2004) discussed the pros and cons of Py-GC/MS which can produce very distinct spectra for most azo pigments (the main class of synthetic organic pigments), but is not able to volatilize the large phthalocyanine and quinacridone pigments sufficiently enough to run through the GC column. Although this technique has been able to identify both pigments and media from a single sample (Boon et al. 2004), the fragments of some pigment molecules identified using Py-GC/MS may not be enough to identify a specific structure. Learner (2004) has used this technique to successfully break apart the polymers found in synthetic organic resins (including acrylics, PVACs, and alkyds) which GC alone is generally unable to do. Lomax and Learner (2006) have found that direct temperature resolved mass spectrometry (DTMS), which uses a higher temperature than Py-GC/MS and operates with the sample in a vacuum to volatilize the sample compound, is able to detect many of these larger pigment structures.

Raman:

Peter Vandenabeele has authored many articles on the use of Raman spectroscopy to analyze modern synthetic organic paint resins and pigments. In one of the most relevant papers regarding the analysis of organic paint media using Raman, Vandenabeele and B. Welhing et al. (2000) described the use of micro-Raman-spectroscopy (MRS) using a laser with a wavelength in the near IR to minimize fluorescence. Other articles suggested that FT-Raman often has better results than dispersive Raman when identifying organic samples because it operates using a laser wavelength in the near IR, out of the range of fluorescent transmissions. However, Vandenabeele et al. (2006) observed that highly-colored samples like organic pigments and dyes give a much stronger signal when using a laser with a wavelength similar to that reflected by the pigment. While Vandenabeele has reported on various successes with this technique relating to synthetic organic media and colorants, he also discussed the limitations of this technique on organic samples due to the lack of substantial reference databases and fluorescence interference (Vandenabeele and L. Moens et al. 2000). However, the small sample size required (smaller than a cross section), the non-destructive nature of this technique (referring to the ability to reuse samples), and the potential for highly-specific compound identification make Raman analysis worth pursuing and developing further.

Analysis of Modern Paintings

Only one technical report on an artwork by one of Greenstone's fellow New York Pop artists was found (Tsang et al. 2008). This study, currently unpublished, was instigated by condition and treatment investigations by the author, Grow (2008) regarding Tom Wesselmann's 1962 assemblage, *Still Life #12*, currently owned by the Smithsonian American Art Museum. FTIR-ATR analysis confirmed the presence of an acrylic ground and two layers of oil-based paint. SEM-EDS analysis detected Ti and Ca in the paint layers, suggesting the use of titanium white and calcium carbonate. In addition, the absence of heavy elements in the top red paint layer as observed using SEM-EDS suggested that a red organic pigment is present in the top paint layer, but this was not investigated further.

Although there seems to be a lack of published analytical studies on materials identified in works by artists closely related to Greenstone, a few papers discussing artworks by other prominent artists working between the late 1950s and early 1970s were found. Learner's (1996) investigation of a 1970/1 Hockney painting and a 1962 Stella painting using FTIR confirmed Hockney's use of an acrylic emulsion binder with a chalk extender, barium sulfate, and a cadmium yellow pigment which was confirmed using SEM-EDS. Stella was found to have used an alkyd resin house paint with large amounts of a chalk extender and a Prussian blue pigment. Burnstock (1999) used FTIR with similar success on an Ellsworth Kelly painting from 1970 and a Mark Rothko painting from 1958, and she was even able to identify Rothko's mixed-media binder which included oil, egg proteins, and possibly beeswax. Several white inorganic pigments were easily identified. However, the specific identification of an organic red pigment was not successful using FTIR.

Crook and Learner's (2000) research on ten artists working in the 1950s and 1960s discussed their use of synthetic media as discovered through artist interviews, FTIR, and Py-GC/MS analysis. While the specific data and the successes and failures of these analyses were not discussed, the media used by specific artists - when and why they were used, and how they were applied – were discussed in detail.

Few technical papers were found to discuss the technical analysis and identification of synthetic organic pigments in samples taken from actual artworks (Ropret et al. 2008 is one of the few). Most of the synthetic organic pigments discussed were analyzed from dry pigment samples collected by the authors from artist suppliers and not from artworks. This seems to suggest that, while databases for the technical identification of these pigments are growing, the practical use of these databases and successful compound identification is still limited.

II. EXPERIMENTAL PROCEDURES

A: Experimental Design

A wide range of analytical techniques was used to answer the previously-stated questions for this study. In order to accomplish the proposed analysis with the least amount of sampling, a specific order was proposed for the analytical techniques to be used. Visual examination (using normal light, UV light, and infrared reflectography) and X-ray fluorescence were conducted first as these techniques did not require sampling of the artwork. Cross-sectional microscopy followed, and these cross-sectioned samples were also used for electron microscopy and Raman spectroscopy respectively. Un-mounted samples were taken for Fourier-transform infrared spectroscopy. These samples were then used for gas chromatography-mass spectrometry. Results from polarized light microscopy and cross-sectional microscopy done by the author in the spring of 2008 are also included in this study (see appendix for sample location diagrams).

B. Instrumentation, Materials, and Preparations

Visual Examination

The painting was first examined under visible reflected light, UV (long wave) light, and under low magnification (up to 60x) using a Wild Heerbrugg Stereomicroscope with an Intralux 6000 light source to closely examine the surface characteristics of the visible paint layers, collage elements, and damaged areas on the painting. This method of examination also aided in locating optimal sites for sampling. Infrared reflectography was done using a re-calibrated Nikon D-70 camera which had the IR filter removed and an IR pass filter inserted.

Polarized Light Microscopy

A Nikon Labophot2-Pol polarized light microscope was used to examine six pigment and canvas fiber samples using transmitted visible light and cross-polarized light at magnifications between 40x and

400x. Samples were removed from the artwork by scraping the surface using a #15 scalpel blade. Samples were mounted on glass slides using Cargille mounting medium (refractive index 1.66).

X-Ray Fluorescence

X-ray fluorescence did not require sampling and provided elemental information, which directed further analysis. XRF was used to identify the elements in certain pigments, fillers, and surface dirt.

The ArtTAX µXRF spectrometer that was used can provide qualitative and quantitative information on elements of equal to or higher atomic mass than potassium (Z = 19). The ArtTAX µXRF is equipped with a metal/ceramic molybdenum tube x-ray source, a microcapillary focusing optic (diameter 70-75µm), and an energy dispersive silicon detector. An ArtTAX voltage tube (accelerating voltage 50 kV) was used with a current of 600 µA. Data was collected for approximately 100 seconds with no filter in non-vacuum (air) conditions. Resulting data was analyzed using ArtTAX Ctrl Software by Röntec GmbH Berlin.

Cross-Sectional Examination

Sixteen samples were taken from the painting for cross-sectional examination, five of which were taken and prepared in the spring of 2008. The layer structure and color of each sample were noted as well as the results from fluorescent dye staining for carbohydrates, proteins, and lipids.

A #15 scalpel was used to take the cross section samples. Extec Polyester Clear Resin (polyester methacrylate resin and methyl ethyl ketone peroxide catalyst) was used to cast the samples which were then placed under a tungsten halogen bulb for approximately one hour and let to sit 10-12 hours to finish curing. An electrical grinder was first used to grind down the polyester resin sample cubes. Final polishing was done using a gradation of micro mesh cloths (1,500 to 12,000 grit) beginning with the roughest and ending with the finest mesh, working the sample in a figure-eight motion.

The embedded cross section samples were wetted with an aliphatic hydrocarbon solvent and then covered with a glass cover slip in preparation to be viewed under the Nikon Eclipse 80i binocular microscope (4x, 10x, and 20x objectives X 10x ocular) equipped with a Nikon Excite 120 Mercury Lamp. Samples were viewed using reflected visible light, ultraviolet light, and several filter cubes. Fluorescent staining was performed on the sample cross sections using the Nikion Eclipse 80i

Binocular Microscope and several fluorescent stains (see appendix for details on the filter cubes and fluorescent stains used).

Digital images were viewed using the DXM 1200F Nikon Digital Camera, and Nikon ACT-1 (Automatic Camera Tamer) control software for PC systems captured digital images of the cross sections viewed with the Nikon Eclipse 80i microscope.

Fourier Transform Infrared Spectroscopy

Ten un-mounted samples of paints, ground, and adhesives from the artwork were analyzed using FTIR in order to identify binding media, pigments, and fillers.

A Nicolet 6700 FTIR Spectrometer (Thermo Fischer Scientific) supporting a Nicolet Continuum FTIR Microscope (Thermo Fischer Scientific) was used in transmission mode. Samples were prepared by flattening on a diamond cell with a stainless steel roller and a #11 scalpel under a Nikon SM2800 Microscope. For each spectrum, 128 scans were taken over a range of 4000-650 cm^{-1} (with a spectral resolution of 4 cm^{-1}) using OMNIC ESP 8 Software which includes background subtraction and baseline correction. Data analysis was done within the OMNIC program using IRUG and commercial reference spectral libraries.

Gas Chromatography-Mass Spectrometry

The un-mounted paint samples used for FTIR spectroscopy were also used for GC/MS in order to identify synthetic organic pigments and binding media. Four surface dirt samples were also tested, collected on cotton swabs using water and mineral spirit solvents.

Methanol was used as the rinse solvent in the syringe preparation. Samples were placed in a tightly-capped, heavy-walled vial (100-300µL) and approximately 100µL (or less for smaller samples) of 1:2 MethPrep II reagent (Alltech) in benzene was added. The vials were warmed at 60°C for one hour in the heating block, removed from heat, and allowed to stand to cool.

Samples were analyzed using the Hewlett-Packard 6890 gas chromatograph equipped with 5973 mass selective detector (MSD) and 7683 automatic liquid injector. The Winterthur RTLMPREP method was used with conditions as follows: inlet temperature was 300°C and transfer line temperature to the MSD (SCAN mode) was 300°C. A sample volume (splitless) of 1µL was injected onto a

30m×250µm×0.25µm film thickness HP-5MS column (5% phenyl methyl siloxane at a flow rate of 2.3mL/minute). The oven temperature was held at 55°C for two minutes, then programmed to increase at 10°C/minute to 325°C where it was held for 10.5 minutes for a total run time of 40 minutes. Analysis was done using Hewlett-Packard software with chromatogram and mass spectra libraries.

Scanning Electron Microscopy –Energy Dispersive X-ray Spectroscopy

The prepared paint sample cross sections were also analyzed using SEM-EDS in order to more specifically locate elements within paint layers to aid in the determination of pigments and fillers within the paints. The cross section samples were mounted on carbon stubs and the area around the embedded samples was coated with a carbon suspension in isopropanol. Two un-mounted samples were taken of a paper collage element and of the mold on the orange paint surface. These samples were mounted on carbon stubs, coated with vaporized carbon, and were then observed using SEM in secondary electron detection mode in order to observed the surface structure of the samples.

Samples were examined using a Topcon ABT-60 scanning electron microscope with a high voltage of 20 kV, working distances of 26.5mm, 27mm, 31mm, and 57mm, and a sample tilt of 20°. Samples viewed using SEM in secondary electron detection mode were run using a high voltage of 11 kV. The Silicon Drift Detector used was able to detect elements down to boron ($Z = 5$). The EDS data was analyzed with the Bruker X-flash detector and microanalysis Quantax model 200 with Esprit 1.8 software.

Raman Spectroscopy

The paint cross sections were also analyzed using Raman spectroscopy in order to identify pigments and fillers. Raman Spectroscopy was performed using a Renishaw inVia Raman Microscope and microscope enclosure with a diode laser at 785nm and an argon laser at 514nm. The spectral resolution of the system is approximately 3cm^{-1}, and the diffraction grating has 1200 lines/mm. Cross-sectioned samples were placed in the microscope enclosure and analyzed using a 50x objective (X 10x ocular). Scans were 10 seconds, 20 seconds, or one minute in length, having a spectral range between 3200-100cm^{-1}. The data was collected using Wire 2.0 Software and analyzed using the Winterthur SRAL database and the University College of London online Raman spectroscopic library.

III. RESULTS

A. Ground

Comparative cross sectional analysis of the ground layers in samples from five of the six image panels consistently showed two distinct layers on the canvas substrate (table 2 in appendix). The top layer was white and the bottom layer was transparent and slightly darker (fig. 4). Under UV light, the bottom layer fluoresced a slightly brighter blue-white than the top ground layer (fig. 5). Fluorescent staining suggested the presence of oil and carbohydrate components in the top ground layer, and possibly a protein binder in the bottom ground layer. Analysis of SEM-EDS elemental mapping identified the presence of elements relating to titanium white, calcium sulfate, and alumino silicates (table 3 in appendix). The FTIR spectrum of the ground had stretches relating to the presence of gypsum and calcite, and the sharp upward slope of the base line between 850 and 700 cm^{-1} suggested the presence of titanium dioxide (figs. 6, 7).


Fig. 4. Cross section of the ground under normal light

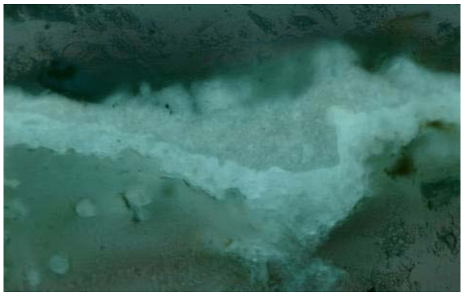
Fig. 5. Cross section of the ground under ultraviolet light

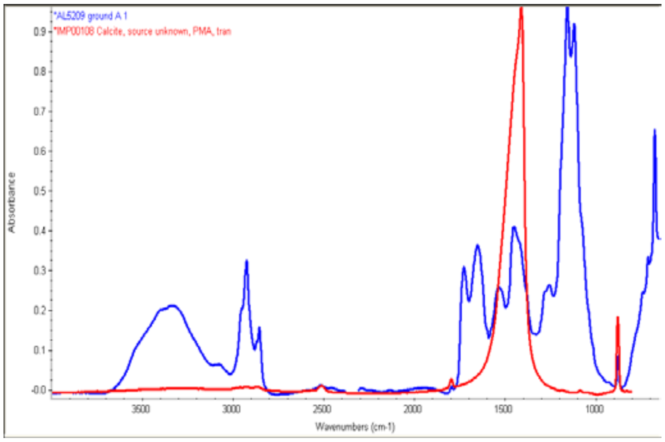

Fig. 6. FTIR spectrum of the ground with calcite spectrum overlay

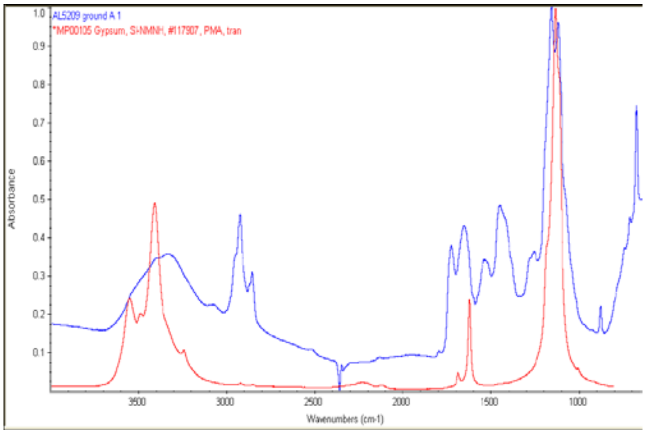

Fig. 7. FTIR spectrum of the ground with gypsum spectrum overlay

Raman analysis of the ground layers produced a spectrum with numerous sharp peaks, which was characteristic of a synthetic organic dye. However, Raman analysis did not produce peaks relating to titanium dioxide (perhaps the small sample area analyzed did not contain TiO_2 pigments). The two strongest peaks in the Raman spectrum occurred at 1290cm^{-1} and 1205cm^{-1} but this did not match any of the spectra in the available reference libraries at Winterthur or in online databases and article searches. The ground Raman spectrum was also compared to Raman spectra for Rhodamine B (used as a fluorescent stain in cross sectional analysis) and the polyester resin used to mount the cross section, as possible sources of sample contamination. Neither spectrum correlated with that of the ground sample. The Raman spectra for two of the most common optical brighteners, stilbene and coumarin were also compared to the ground Raman spectra, but neither matched the spectrum of the ground sample.

B. Paints

Deteriorated Green

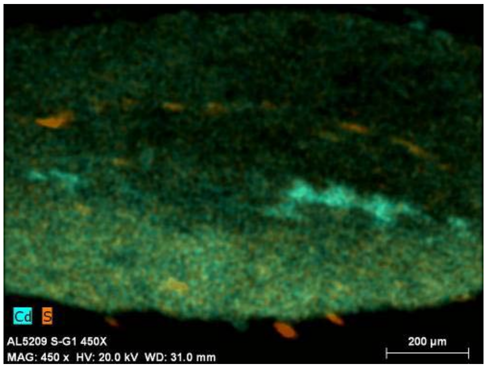

Fig. 8. SEM-EDS elemental mapping of Cd and S in deteriorated green paint

Fig. 9. Corresponding cross section of deteriorated green paint (normal light)

XRF and SEM-EDS elemental mapping of the deteriorated green paint suggested the presence of elements including O, S, Cu, Zn, As, and Cd (tables 1, 3 in appendix). These elements indicated the likely presence of emerald green, cadmium yellow, and zinc white pigments. PLM analysis of the deteriorated green paint also suggested the presence of emerald green pigments. Cross-sectional microscopy defined at least two layers of green paint over the ground; one or two layers of light green paint could be seen over a dark green paint. None of the paint layers in the cross section fluoresced under UV light. SEM-EDS elemental mapping detected a higher concentration of cadmium and sulfur (presumed to be cadmium yellow pigment) in the bottom dark green paint layer (figs. 8, 9). The Raman spectrum collected from analysis of the deteriorated green paint showed a peak at 475 cm^{-1}, which was consistent with several copper sulfide spectra including covellite-CuS, villamaninite-CuS_2, and anilite-Cu_7S_4 which also had strong peaks near 470 cm^{-1} (fig. 10). Neither Raman nor FTIR spectra collected from the green paint corresponded with known spectra for emerald green.

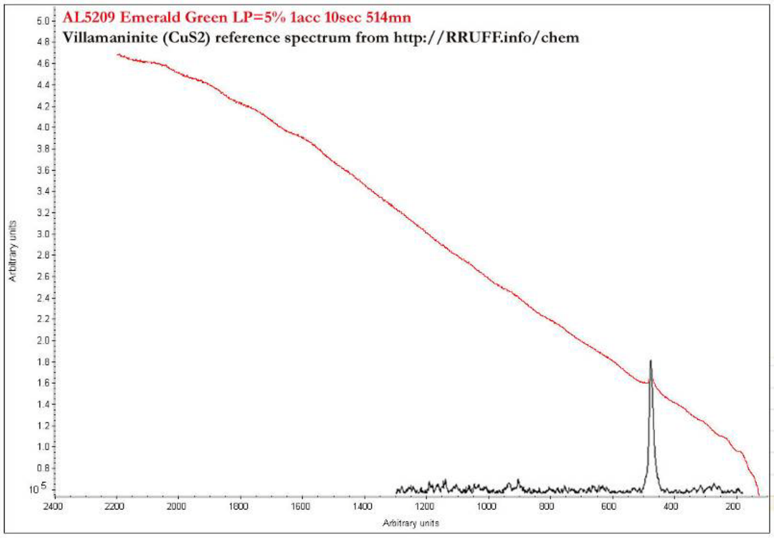

Fig. 10. Deteriorated green paint and villamaninite Raman spectra overlay

Results from fluorescent staining of the cross section suggested lipids present in the top lighter green paint layers. GC/MS analysis detected the prominent presence of palmitic, stearic, and azelaic fatty acids peaks, characteristic of a drying oil.

Orange

Three paint layers were distinguished in cross-sectional analysis of the orange paint; there was a single orange layer over the two ground layers. Under UV light, the orange paint layer did not fluoresce, and results from fluorescent staining were inconclusive. XRF and SEM-EDS elemental mapping detected the presence of elements including C, O, Mg, S, Zn, Se, Cd, and Ba, suggesting the possible presence of cadmium orange and/or a cadmium lithopone, barium sulfate, and zinc white in the orange paint layer. FTIR analysis of the orange paint layer produced a spectrum which closely matched reference spectra for magnesium carbonate and barium sulfate (fig. 11). Two C-H stretches at 2926 cm^{-1} and 2854 cm^{-1} and the carbonyl stretch at 1741 cm^{-1} were also observed in the FTIR spectrum of the orange paint. The gas chromatogram for the orange paint contained strong peaks for palmitic acid, stearic acid, azelaic acid, and a weak peak for oleic acid. Solvent tests indicated that the orange paint is sensitive to water and polar solvents.

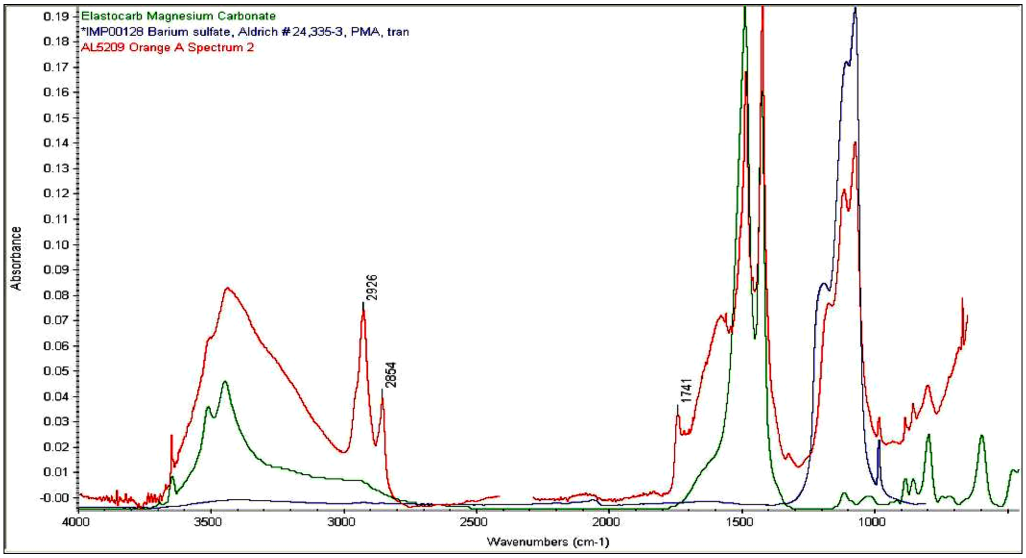

Fig. 11. FTIR spectrum of orange paint with magnesium carbonate and barium sulfate spectra

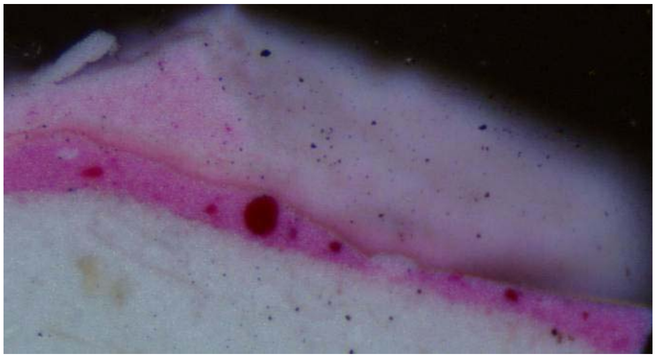

Fig. 12. Cross section of pink paint under normal light

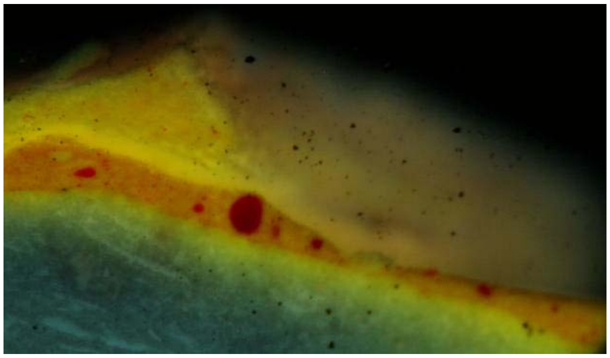

Fig. 13. Cross section of pink paint under UV light

Pink

Microscopic surface examination and cross-sectional micrographs of the pink paint indicated two pink paint layers over the ground layers; there is a lighter pink paint layer over a darker pink paint layer (figs. 12, 13). Under UV light both pink layers fluoresce bright orange. Fluorescent staining of the cross section suggested that there are no carbohydrates or proteins in the pink paint layers, and fluorescent staining for lipids was not possible due to the already-fluorescent nature of the pink paints when using the G-1B filter. XRF analysis in an area of pink paint detected the elements Ti and Zn, suggesting the possible presence of titanium white and zinc white in the pink paints. PLM observations characterized white pigment particles in the pink paint sample as having a cloudy birefringence under cross-polar transmitted light, which is characteristic of zinc white. The bright, transparent color and isotropic nature of the pink pigment particles when viewed using PLM are traits often observed in modern red organic pigments. The gas chromatogram of the pink paint had a strong peak at just over thirty minutes which was not present in any of the other paint sample chromatograms (fig. 14). The mass spectrum for this peak indicated the presence of Rhodamine 6G in the paint sample. The gas chromatogram of the pink paint contained peaks for palmitic acid, stearic acid, azelaic acid, and a more intense peak for oleic acid than in any of the other paint sample chromatograms. FTIR analysis of the pink paint produced a spectrum which closely matched a reference spectrum of linseed oil.

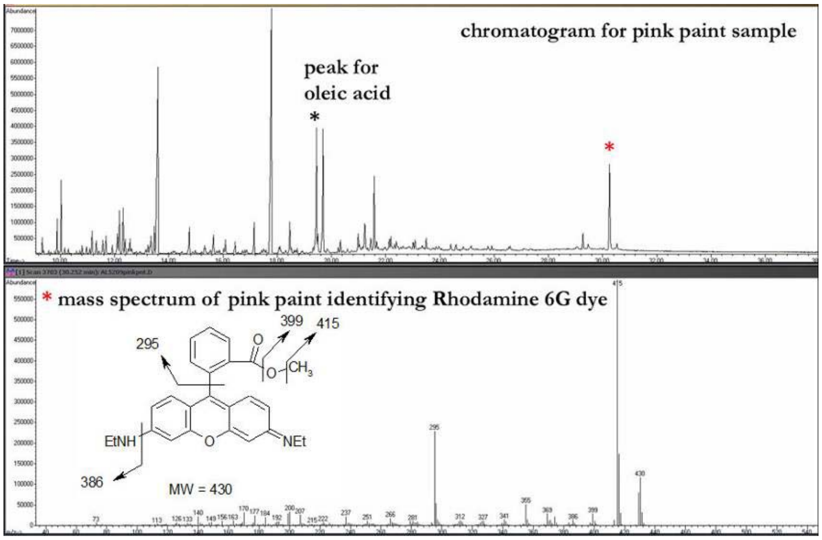

Fig. 14. Gas chromatogram and mass spectrum for pink paint sample

Black

Analysis was conducted on samples of black paint from four separate areas of black paint on the artwork (tables 1-3 in appendix). Cross section analysis of black paint samples from two areas of the artwork exhibited different stratigraphy. The black paint sample S-B1 consisted of a single black paint layer over layers of the deteriorating green paint. Sample S-B2 was found to contain a single black paint layer over layers of metallic paint and a pigmented white layer. SEM-EDS elemental mapping detected the presence of elements including C, O, Si, P, S, and Ca suggesting the presence of a carbon-based black pigment, possibly calcium phosphate. XRF analysis of an area of black paint detected elements including P, Ca, Cu, Zn, As, and Ba, which suggested pigments such as calcium phosphate, emerald green, and zinc white. Raman analysis yielded a spectrum containing two broad peaks at 1203 cm^{-1} and 1288 cm^{-1}, which suggested the presence of a carbon- based pigment, but the spectrum did not contain a peak at 961cm^{-1} which would have been characteristic of calcium phosophate. FTIR analysis, however, did produce a spectrum which is a close match for reference spectra of calcium phosphate and linseed oil as well (fig. 15).

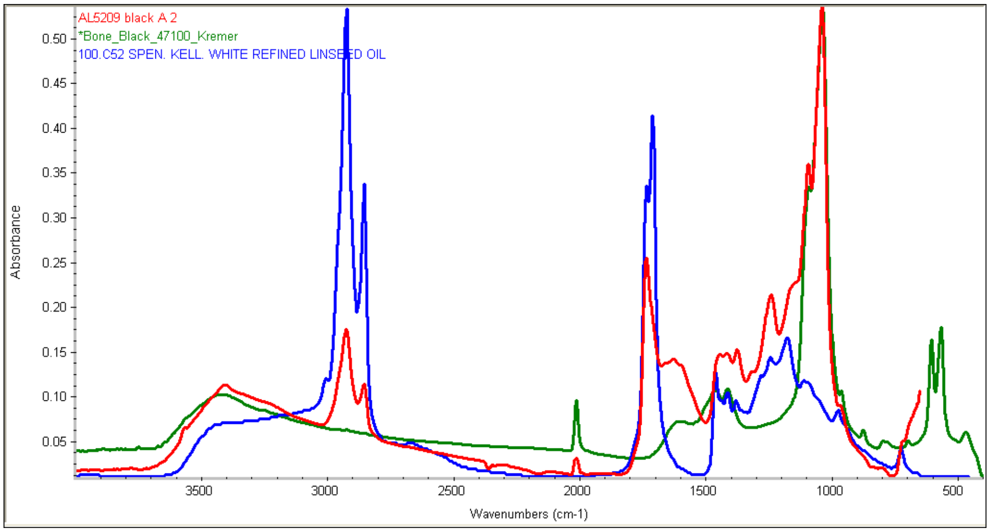

Fig. 15. Overlay of black paint sample, bone black reference, and linseed oil reference FTIR spectra

Silver

Using cross-sectional microscopy the metallic paint layer in samples S-Sl, S-B2, and S-DG1 under normal light appeared to be a transparent medium with flecks of a highly-reflective metal imbedded in it. Under UV light the medium fluoresced a faint blue and the metallic flecks appeared black. Fluorescent staining of the metallic paint layer appeared to have a positive result for the presence of lipids. SEM-EDS elemental mapping of cross sections containing the metallic layer identified the metallic flecks as aluminum.

Dark Green

The dark green paint was first analyzed using XRF spectroscopy, which detected elements including Zn, Ba, and possibly Ti and Cd. SEM-EDS elemental mapping detected S, Ti, Cr, Fe, Zn, and Cd, suggesting the possible presence of a chromium oxide green, cadmium orange, titanium white, and zinc white pigments. Cross section images of the dark green paint layer showed a green paint matrix containing orange-red pigments. The Raman spectrum for the dark green paint contained several sharp peaks (fig. 16). This is characteristic of many synthetic organic dyes. The strongest peaks in the spectrum were at 1541 cm^{-1}, 687 cm^{-1}, and other prominent peaks included 1288 cm^{-1}, 1216 cm^{-1}, and 742 cm^{-1}.

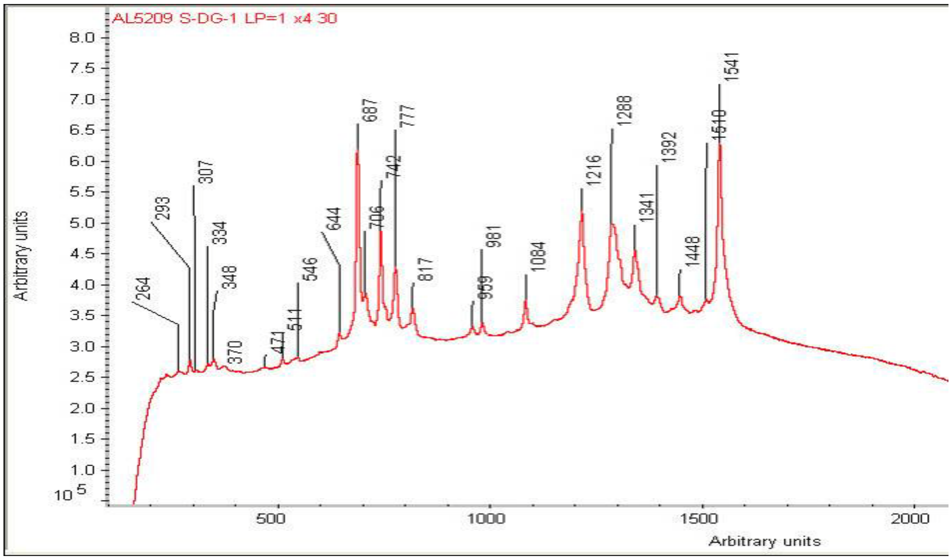

Fig. 16. Raman spectrum for dark green paint

Yellow

XRF analysis detected elements including Zn and Cd in the yellow paint suggesting the presence of zinc white and cadmium yellow.

C. Paper Elements

XRF analysis was conducted on three different paper collage elements from *Spoonk*. Intense peaks for Ti were observed in all three sample spectra (fig. 17). SEM-EDS results of analysis on a brown paper

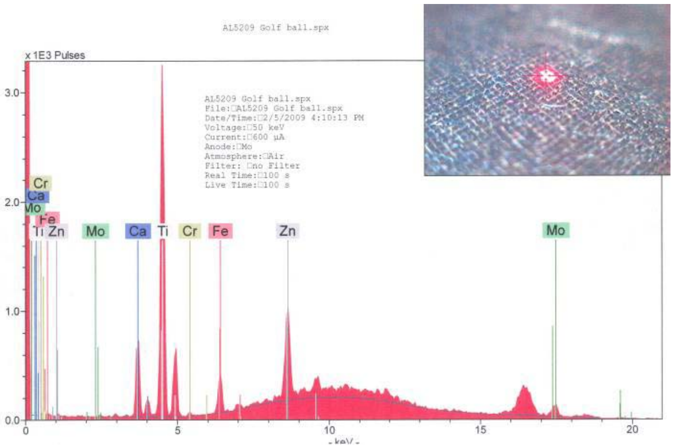

Fig. 17. XRF spectrum of golf ball paper element

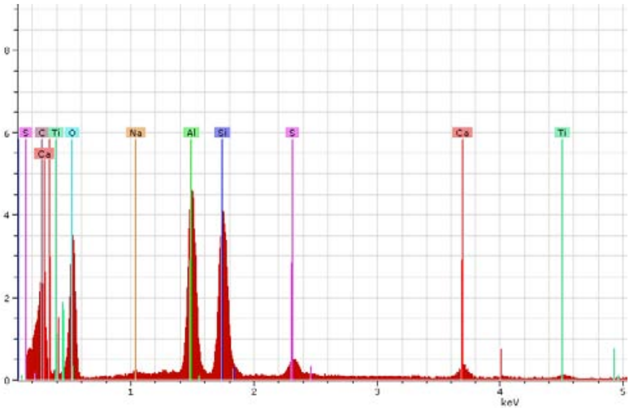

Fig. 18. SEM-EDS spectrum of brown paper element

sample from *Spoonk* was conducted and compared with the spectra of known paper samples from a glossy magazine paper and from a matte paper. Strong peaks for O, Al, Si, and weak peaks for Ca and Ti were noted in the spectrum for the brown paper sample (fig. 18). The spectrum of the known glossy magazine paper also had strong peaks for Al, Si, and Ca. The spectrum for the known matte paper had strong peaks for O and Ca, but very weak peaks for Al and Si. A sample of an adhesive used to attach the paper elements to the artwork was analyzed using FTIR, and the resulting spectrum closely matched a reference spectrum for polyvinyl acetate resin. Microscopic examination of the paper surfaces showed the individual printing dots of the separate ink colors. While most of the colored dots still appeared to be saturated, some colors, namely the reds, appeared comparatively lighter in certain areas.

D. Dust and Mold

Samples of dirt from the paint surfaces were analyzed using GC/MS. The sample taken with mineral spirits on a cotton swab produced a chromatogram with peaks indicating the presence of squalene and palmitoleic acid, and selected ion (71) monitoring of this chromatogram showed the presence of petroleum wax. A mineral spirit extraction of a wooden swab stick was also analyzed using GC/MS for comparison with the mineral spirit-extracted surface dirt sample to investigate the swab stick as a possible source of the petroleum wax and therefore of sample contamination. A peak relating to petroleum wax was observed in the chromatogram of the wooden swab stick sample.

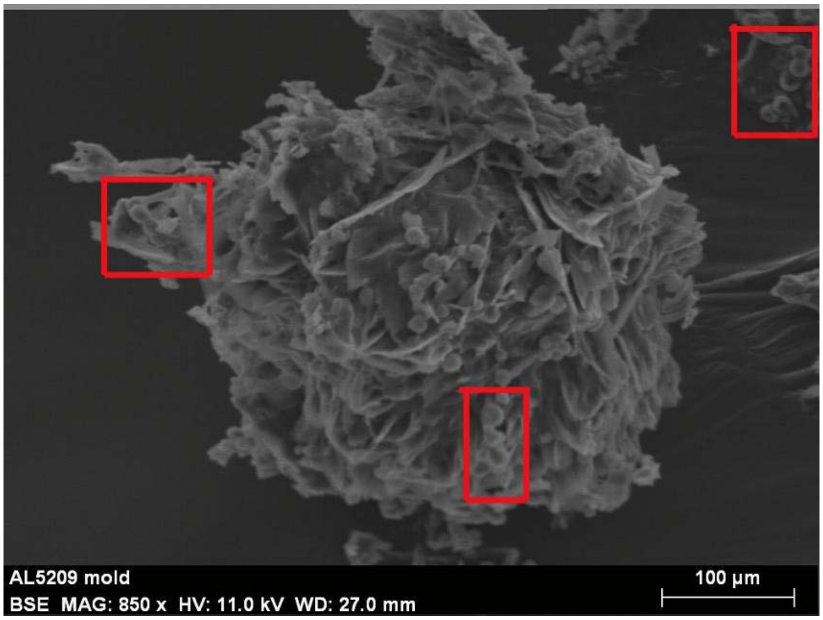

Fig. 19. SEM-SE image of mold spores taken from orange paint surface

Visual examination of the orange paint surface suggested the presence of mold hyphae. Fluorescent staining of a surface dirt sample from the orange paint resulted in a positive reaction for mold hyphae, which fluoresced bright green after staining with lyophilized FITC (see table 4 in appendix for stain information). A sample of the mold was examined using SEM secondary electron imaging, and mold spores and hyphae were identified (fig. 19).

IV. DISCUSSION

A. Ground

The similarities between the ground layers found in cross section samples from five of the six prepared canvases suggested that the same prepared canvas was used for all of the separate image panels. The presence of protein in the bottom layer and its observed transparence in normal light and blue fluorescence in UV light may suggest that the bottom ground layer is actually a canvas size layer which did not fully penetrate into the substrate fibers. The inorganic compounds identified were available as pigments and fillers for paints and grounds at the time the painting was made.

After confirming that the ground Raman spectrum did not match those of possible contaminants such as Rhodamine B and polyester resin, it was suggested that the spectrum and the fluorescence of the ground in UV light might be characteristic of a synthetic organic optical brightener used to brighten the white ground. Chemical compounds classified as fluorescent whitening agents were discovered at the beginning of the twentieth century (Mustalish 2000). These compounds absorb light waves in the near UV range and then emit light waves in the visible violet/blue spectral range. The addition of these compounds to paper and textiles was found to negate the yellowing of these materials as well as give them the appearance of being whiter than white. In the 1960s there were over 250 optical brighteners in use, organized into approximately 10 classes of compounds (SDC and AATCC 1971). Today the compound class stilbene (discovered in 1933) accounts for more than 80% of optical brighteners in use (Mustalish 2000).

Though neither of the optical brightener standards tested was found to be a successful match for the ground spectrum, there are still hundreds of other optical brightener compounds that would need to be further investigated before the presence of an optical brightener could be confirmed or denied. As suggested by the literature and these experimental results, Raman spectroscopy still has limited reference standards, and the use of Py-GC/MS or DTMS, as suggested in the literature review, may yield more specific information leading to compound or class identification.

B. Paints

Deteriorated Green

Emerald green is a copper aceto-arsenite $Cu(C_2H_3O_2)_2{\cdot}3Cu(AsO_2)_2$ (Gettens and Stout 1966) which was first produced around 1814 as a replacement for the less-stable Scheele's green, and by 1822 emerald green had become widely used as a pigment in artists' paints. But by 1960 emerald green was no longer manufactured as a pigment in paints because of its toxicity (Fiedler and Bayard 1997). This suggests that Greenstone may have used emerald green paint that had been purchased several years prior to the creation of *Spoonk.*

Copper-based greens are known to darken in the presence of sulfur-containing compounds due to the formation of black copper sulfides (White 2006). There are records of several artists noting this darkening when combining paints containing cadmium sulfide pigments with emerald green (Fiedler and Bayard 1997). In a study on the reaction between the copper-containing malachite pigment and cadmium yellow in the presence of water, White et al. (2006) identified the copper sulfide compound covellite (CuS) as the degradation product. The sample Raman spectrum, in comparison with several copper sulfide Raman standards, suggested that the deterioration seen in the emerald green paint on *Spoonk* was caused by the formation of black copper sulfides, likely formed from copper in the emerald green pigment and sulfur in the cadmium sulfide pigment. This would explain the greater darkening of the lower green layer, which had a higher concentration of sulfur, allowing for more copper sulfide formation than in the top green paint layer. This likely deterioration of the emerald green could also explain the lack of Raman peaks and FTIR stretches in the collected sample spectra that correlate with known standard spectra for emerald green.

Although the paint contained an oil binder which would normally inhibit this interaction, the leanly-bound nature of the paint and the past moisture damage likely exacerbated this deterioration mechanism. This reaction will probably continue throughout the life of the artwork, though at a significantly slower rate if the work is protected from humid conditions in a stable environment. In order to stabilize the flaking paint, and in an effort to mitigate future deterioration, the green paint was consolidated using a combination of 95% methyl cellulose and 5% Aquazol 500 in a 50:50 water:isopropanol solvent solution. This consolidant was found to be strong at a low concentration, could penetrate through the paint layers for good adhesion, and did not change the color or gloss of the paint after drying. Because of the fragile nature of the paint, several types of consolidant application methods were considered including an ultrasonic mist consolidation system. After testing, it was decided that using a small brush to drip the consolidant on the damaged paint and allow it to penetrate into the paint layers, was the most effective method, and the least complicated. The flaking green paint received three applications of the consolidant.

After consolidation, the losses in the deteriorated green paint were filled and textured using Modostuc, a water-soluble fill material consisting of polyvinyl acetate and calcium carbonate, which can be removed without dissolving the original paint. The fills were then inpainted and discolorations toned using Golden Mineral Spirit Acrylic colors, which are soluble in a solution of approximately 80% mineral spirits and 20% xylene, and can therefore be applied and removed without reactivating or weakening the methyl cellulose consolidant and paint.

Orange

Cadmium sulfides are generally characterized as yellow pigments and cadmium sulfo-selenides are characterized as red pigments; the range from yellow to red, including cadmium oranges depends on the ratio of cadmium to sulfur, and additionally for the reds, the sulfur to selenium ratio (Fiedler 1986). Cadmium sulfides were discovered by Stromeyer in 1818 but were not actually used as pigments until the 1840s (Fiedler 1986). The cadmium lithopone pigments, which are a co-precipitate with the cadmium pigments and barium sulfate, were available beginning in the late 1920s (Gettens and Stout 1966). Cadmium sulfide- and sulfo-selenide-based pigments became quite popular as artist's pigments by the 1920s due to improved manufacturing procedures and subsequently cheaper costs. The continued popularity of these pigments today, along with the analytical data in this study, point to their probable presence in the orange paint. Barium sulfate and magnesium carbonate are likely present as fillers in the paint (Gettens and Stout 1966). Both the carbonyl stretch in the FTIR spectrum and the fatty acid peaks present in the chromatogram were likely due to the presence of a drying oil in the paint binding medium, which at first seemed incongruous with the observed water-sensitivity of the paint film. However, the water sensitivity of a modern oil paint could be due to the presence of stearates, originally added as dispersion agents, which can form water-soluble soaps over time (Burnstock 2007). Further analysis using FTIR and GC/MS could be done to detect the possible presence of stearates in the paint.

Pink

Rhodamine 6G is the fluorescent ethyl ester of diethyldiamino-*o*-carboxyl-phenyl-xanthenyl chloride, categorizes as a cyanine-type chromogen dye (Streitel 1995). It is one of the more stable synthetic organic dyes and is used in the form of a red lake pigment in paints (Gettens and Stout 1966). It was discovered by Bernethsen in 1892. Because of their bright fluorescence, many fluorescent colorants were used on aircraft trafficking signals during World War II, and by the 1950s Rhodamine pinks and other fluorescent colorants had become popular as interior and artists paints (Tsang 2004). The

Rhodamine B dye is even used in conservation today as a fluorescent tag for lipids during cross sectional analysis. Coincidentally, the presence of the Rhodamine 6G dye as a colorant within the pink paint cross section made the application of the Rhodamine B stain for analysis ineffective.

The fatty acids detected in the pink paint sample as shown in the above chromatogram (fig. 9) suggested the presence of an oil component in the binding medium. The relatively high amount of oleic acid present (especially in comparison to the chromatograms of the other paint samples analyzed using GC/MS) suggested a non-drying or slow-drying oil. It is possible that the Rhodamine dye interacted with the binder in a way that inhibited the oxidation process that allows drying oils to form a solid film. The presence of the light pink paint layer over the darker pink paint layer suggested that the artist changed her mind about her color choice during the painting of *Spoonk* and painted over the darker pink areas with the lighter pink.

Black

The results from SEM-EDS elemental mapping, FTIR, and Raman analysis of areas of black paint pointed to the use of carbon-based black pigments, likely including calcium phosphate pigments such as bone or ivory black. The absence of the phosphate peak in the Raman spectrum could be due to the absence of a phosphate-based pigment in the small area analyzed by the instrument laser. FTIR results also suggested the presence of an oil-based binder in the black paint. Although it is possible that the same paint was used for all the black areas on the artwork, the paint stratigraphy below these areas differed greatly as observed in results from cross-sectional analysis and XRF analysis. This may suggest that the artist made her final decisions of where to apply the black paint within the composition during its creation, after several other color layers had been applied.

Silver

The presence of metallic aluminum as the colorant in the metallic paint layers accounted for the inability of the FTIR spectrometer and Raman spectrometer to identify any components in the metallic paint; the reflective nature of the metallic aluminum prevented the absorbance of the FTIR and Raman radiation.

Dark Green

Analysis of the dark green paint using FTIR spectroscopy was hindered by the presence of the aluminum paint layer which proved inseparable from the dark green paint sample. The presence of inorganic pigments such as chromium oxide green, which has been available as a pigment since the nineteenth century, (Gettens and Stout 1966) and cadmium orange (possibly in the orange-red pigments dispersed within the green paint matrix) could not be confirmed or denied using Raman spectroscopy because of the strong signal of another component within the paint. This component produced a spectrum including several sharp peaks, which was similar to many synthetic organic dyes. However, this spectrum has not yet been identified; the peaks do not specifically correlate with any spectra in the available spectral reference databases. The inclusion of synthetic organic dyes with inorganic pigments in paints and inks was already occurring at the beginning of the twentieth century in order to boost the color intensity (Centeno 2006), and it is not unlikely that this is also the case for some paints from the mid-twentieth century, such as the dark green paint used by Greenstone. Further investigation into the identity of the compound(s) in the dark green paint should include Py-GC/MS and DTMS, which -as suggested in the literature review- are more successful techniques in identifying large synthetic organic compounds in mixtures.

Due to the insolubility of these paints in water (with the exception of the water-sensitive orange paint and the fragile deteriorated green paint), they were surface cleaned using a 0.5% citrate solution, pH 6 and rinsed with deionized water applied using moistened cotton swabs, removing the layer of dirt and grime that dulled the visual effect of the colors.

C. Paper Elements

The presence of Ti in all the paper element samples analyzed suggested the presence of titanium dioxide in the paper, likely present as a whitening agent (Beazley 1991). The Ca detected in the brown paper sample was likely from calcium carbonate, which has been used as a filler and coating for papers in the United States since the 1920s (Beazley 1991). Al and Si are often present in magazine papers in the form of kaolinite, which acts as a filler and can impart a high gloss to a paper surface (Beazley 1991). The strong peaks for Al and Si in the known glossy magazine paper and the weak peaks for Al and Si in the known matte paper further suggested that the Al and Si are present as clay. The strong peaks for Al and Si in the brown paper sample were likely due to the presence of clay and suggest that the image may have come from a glossy page in a magazine rather than a matte paper like newsprint. The absence of other elements that would suggest inorganic pigments makes the use of synthetic organic colorants in the printing inks most likely. Many synthetic organic dyes are fugitive and may fade or discolor with light exposure. The minimal fading of the inks observed on the paper elements suggested that the artwork had largely been kept in dark storage. Because these inks are likely to fade and discolor further, it was recommended that the artwork be exhibited using low light levels appropriate for paper objects rather than the relatively high light levels used to exhibit paintings. In order to further investigate the dyes used in the paper printing inks Raman, Py-GC/MS, and DTMS could be used to analyze the available brown paper sample. The identity of these dyes would allow for greater knowledge of colorant stability and their potential for future fading.

The brilliance of the colors still intact on much of the paper surface was dulled by a layer of dirt which was removed during treatment using non-latex cosmetic sponges and the kneaded Design 1224 eraser, avoiding the introduction of moisture to the paper. In small areas of paper loss and abrasion, a barrier layer of methyl cellulose was applied and then toned using water colors.

D. Dust and Mold

Comparison of the chromatograms for the mineral spirit-extracted surface dirt sample and the mineral spirit-extracted wooden swab stick sample suggested that the petroleum wax found in the surface dirt chromatogram was actually from the wooden swab stick and not from the artwork. Squalene and palmitoleic acid are secreted from human skin tissue (Nikkari 1974; Kotani 2002). The presence of these compounds in the surface dirt chromatogram was likely due to the touching and handling of the artwork.

The presence of mold on the orange paint further supported the theory that the painting had encountered extended exposure to moisture, and the low relative humidity storage conditions recommended to mitigate the deterioration of the emerald green paint would also help prevent a recurrence of mold growth on the orange paint. Once the presence of mold was confirmed, the dark mold stains in the orange paint were reduced using a solution of 0.5% citrate, pH 6 with 1% (w/w) lysing enzymes dissolved into the solution. The enzymes break up the cell walls of the mold making it possible to remove the mold remnants with a damp swab. Because of the sensitivity of the orange paint, an application of cylcomethacone (a slow evaporating non-polar solvent) was first applied to an area of orange paint, and then the aqueous enzyme solution was applied in areas of mold using tiny cotton swabs. The cyclomethacone acted as a protective layer on the paint, repelling the water, but still allowing the enzyme to break up the mold.

The selective growth of the mold, only on the orange paint, was not fully explained by the results of this study. However, mold growth on the deteriorating emerald green paint was likely prevented due to the arsenic in emerald green, which is a natural fungicide, and the hydrophobic nature of Rhodamine dyes likely made the pink paint and unattractive site for mold growth. Further chromatographic analysis of the orange paint could yield more information about other components that may have contributed to the selective mold growth, especially considering the possible presence of water-sensitive stearate soaps.

V. CONCLUSIONS

Before treatment of artist Marion Greenstone's *Spoonk* (1964), a Pop Art painted collage now owned by the Zimmerli Museum, technical analysis was conducted in order to better understand the condition of the various artwork components. Many colorants, binders, and fillers in the paints and paper elements were identified and found to be consistent with the date of creation. Most notable of the technical results was the probable presence of emerald green and cadmium yellow in the deteriorated green paint. These two pigments likely reacted to form black copper sulfides, causing the discoloration and flaking of these paint layers. Unfortunately, this deterioration process is likely to continue. The presence of mold on the artwork and the corrosion of metal attachments suggested that the artwork has suffered from exposure to moisture. The likely presence of synthetic organic dyes printed on the paper collage elements suggested that some of these colorants are probably prone to fading and discoloring upon light exposure. However, the minimal fading of the colorants that has been observed on the paper collage elements suggests that the artwork has thus far been protected from excessive light exposure. This information aided in the treatment of *Spoonk* and in the formulation of storage and exhibition guidelines for the artwork. This research will also contribute to the present information on Greenstone's materials and working methods as well as that of her contemporaries.

VI. ACKNOWLEDGEMENTS

I would like to thank the Scientific Research and Analysis Laboratory at the Winterthur Museum including my project supervisor Dr. Joseph Weber, Dr. Jennifer Mass, Dr. Chris Petersen, Catherine Matsen, Melanie Gifford, and Chris Cole for all their assistance and advice with technical analysis and the interpretation of results. I would also like to thank Dr. Joyce Hill Stoner, Richard Wolbers, Mary McGinn, and Joan Irving for their guidance in treatment decisions and implementation, and thanks to the Zimmerli Art Museum Registrars Leslie Kriff and Margaret Molnar and Curator Jeff Wechsler for allowing me to conduct this study on an artwork from the Zimmerli collection. Others who encouraged and aided me along the way include Brian Baade, Jim Schneck, Debbie Hess Norris, Jae Gutierrez, Bruno Pouliot, and my classmates of WUDPAC 2010.

VII. REFERENCES

Archives of American Art. 2008. Marion Greenstone. Unpublished personal archives of Marion Greenstone. Smithsonian Archives of American Art, Washington D.C.

Beazley, K. 1991. Mineral fillers in paper. *The paper conservator: journal of the Instittue of Paper Conservation* (15): 17-27.

Boon, J.J., N. Wyplosz, F. Hoogland, M. Duursma, K. Keune, and T. Learner. 2004. Molecular Characterization and Mapping of Twentieth-Century Synthetic Organic Pigments and Additives in Paints. Proceedings of the IIC Biennial Congress Modern Art, New Museums. Bilbao, Spain. The International Institute for Conservation. 219.

Burnstock, A. et al. 2007. An Investigation of Water-Sensitive Oil Paints in Twentieth-Century Paintings. *Modern Paints Uncovered.* eds. Learner, T. et al. Los Angeles: Getty Conservation Institute. 177-188.

Burnstock, A. and A. Langley. 1999. The analysis of layered paint samples from modern paintings using FTIR microscopy. *ICOM-CC Committee for Conservation 12th triennial meeting.* Lyon, France. London: James & James. 234-241.

Centeno, S.A. et al. 2006. Raman study of synthetic organic pigments and dyes in early lithographic inks (1890-1920). *Journal of Raman Spectroscopy* 37: 1111-1118.

Crook, J. and T. Learner. 2000. *The Impact of Modern Paints.* London: Tate Gallery Publishing Ltd.

Eccher, D. 1005. *Tom Wesselmann*. Rome: Museo D'Arte Contemporania.

Fiedler, I. and M. Bayard. 1986. Cadmium yellows, oranges and reds. In *Artists' pigments: a handbook of their history and characteristics*, ed. R.L. Feller. London: National Gallery of Art. 65-108.

Fiedler, I. and M. Bayard. 1997. Emerald green and Scheele's green. In *Artists' pigments: a handbook of their history and characteristics.* ed. E.W. FitzHugh. London: National Gallery of Art. 219-271.

Gettens, R.J. and G.L. Stout. 1966. *Painting Materials: A short encylcopaedia.* New York City: Dover Publications, Inc.

Grow, S. 2008. Condition Report and Treatment Proposal for Still Life #12 by Tom Wesselmann. Unpublished typescript in the Lunder Conservation Center conservation files. Smithsonian American Art Museum, Washington D.C.

Kotani, A. and F. Kusu. 2002. HPLC with electrochemical detection for determining the distribution of free fatty acids in skin surface lipids from the human face and scalp. *Archives of Dermatological Research* 294: 172-177.

Kriff, L. 2008. Personal communication. E-mail message to author.

Lake, S., E. Ordonez and M. Schilling. 2004. A technical investigation of paints used by Jackson Pollock in his drip or poured paintings. In *Modern Art, New Museums: Contributions to the Bilbao*

Congress, 13-17 September 2004. Roy, A. and P. Smith, eds. 137-141. London: International Institute for Conservation of Historic and Artistic Works.

Learner, T., 2004. *Analysis of Modern Paints*. Los Angeles, California: The Getty Conservation Institute.

Learner, T. 1996. The use of FTIR in the conservation of twentieth century paintings. *Spectroscopy Europe* 8(4): 14-19.

Lomax, S., and T. Learner. 2006. A review of the classes, structures, and methods of analysis of synthetic organic pigments. *Journal of the American Institute for Conservation* 45(2): 107-25.

Madoff, S.H., ed. 1997. *Pop Art: A Critical History*. Berkeley, California: University of California Press.

Mustalish, R.A. 2000. Iptical brighteners: history and technology. In *Tradition and innovation: advances in conservation: contributions to the Melbourne Congress, 10-14 October 2000*. ed. A. Roy and P. Smith, Editors. International Institute for Conservation of Historic and Artistic Works. 133-136.
Nikkari, T., P.H. (1974) Schreibman, and E.H. Ahrens, Jr. In vivo studies of sterol and squalene secretion by human skin. *Journal of Lipid Research* (15) 563-573.

Ropret, P., S.A. Centeno, and P. Bukovec. 2008. Raman identification of yellow synthetic organic pigments in modern and contemporary paintings: Reference spectra and case studies. *Spectrochimica Acta Part A* (69): 486-497.

SDC and AATCC. 1971. *Colour Index Third Edition Volume 2*. London: The Society of Dyers and Colourists and American Association of Textile Chemists and Colorists.

Streitel, S. 1995 Fluorescent pigments (daylight). *Encyclopedia of Chemical Technology* 15: 585-607.

Tsang, J.S. 2008. Technical Report MCI 6213 Still Life #12 by Tom Wesselmann Smithsonian American Art Museum. Unpublished typescript. Smithsonian Museum Conservation Institute.

Tsang, J.S., S. E. Pinchin, K. Almond, and C.S. Tumosa. 2004. Conservation of Murals in the Alameda Theatre: Reviving Former Cutting-Edge Fluorescent Paint and Black-Light Technology. In *Proceedings of the IIC Biennial Congress Modern Art, New Museums*. Bilbao, Spain: The International Institute for Conservation. 185-188.

Vandenabeele. P., L. Moens, H.G.M. Edwards, and R. Dams. 2000. Raman spectroscopic database of azo pigments and application to modern art studies. *Journal of Raman Spectroscopy* (31): 509-517.

Vandenabeele, P., B. Welhing, L. Moens, H. Edwards, M. De Reu, and G. Van Hooydonk. 2000. Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art. *Analytica Chimica Acta* (407): 261-574.

Vandenabeele, P., H.G.M. Edwards, and L. Moens. 2006. A Decade of Raman Spectroscopy in Art and Archaeology. *Chemical Reviews* (107) 3: 675-686.

White, R. M.R. Phillips, R. Thomas, and R. Wuhrer. 2006. In-Situ Investigation of Discolouration Processes Between Historic Oil Paint Pigments. *Microchimica Acta* (155): 319-322.

VIII. APPENDIX

Table 1. X-Ray Fluorescence Spectroscopy Results

Sample	**Description**	**Results *** (relevant elements in **bold**)	**Colorants Inferred**
Orange 1	orange paint	**Zn,** Sr, **Se, Cd, Ba**	cadmium orange or cadmium red lithopone, barium sulfate, zinc white
Orange 2	orange paint	Fe**, Zn,** Sr**, Se, Cd**, **Ba,**	cadmium orange or cadmium red lithopone, barium sulfate, zinc white
Green 1	degraded green paint	Fe, **Cu, Zn, As, Cd,**	emerald green, cadmium yellow, zinc white
Green 2	degraded green paint	Ca? Fe, **Cu, Zn, As, Cd,**	emerald green, cadmium yellow, zinc white
Black 1	black paint	Ca. Mn, **Fe**, **Cu, Zn, As,** Sr, **Ba**	barium sulfate, emerald green, zinc white
Black 2	black paint	Ca, **Ti,** Mn, Fe, Zn	titanium white
Light Pink	light pink paint	Ca, **Ti,** Fe, **Zn**	titanium white, zinc white,
Dark Pink	dark pink paint	Ca, **Ti,** Fe, **Zn**	titanium white, zinc white
Lips 1	yellow print on paper over paint	Ca**, Ti,** Fe**, Cu, Zn, As**, **Cd**	titanium white, emerald green, cadmium yellow
Tail Lights 1	orange print on paper over paint	Ca, **Ti,** Cr? Fe, **Zn**, Br, Pb	titanium white, zinc white
Silver 1	metallic paint	K, Ca, **Ti,** Cr, Fe, **Zn**	zinc white, titanium white
Yellow 1	yellow paint	Fe, Cu, **Zn, Cd**	zinc white, cadmium yellow
Golf ball 1	black print on paper over ground	Ca, Fe, **Ti,** Cr, **Zn**	titanium white, zinc white
Dark Green 1	dark green paint	Ca, Ti? Fe, Cu, **Zn,** Cd?, **Ba**	barium sulfate, zinc white

*Molybdenum from the x-ray tube was found in all XRF spectra

Table 2. Cross-sectional Analysis Results

Sample	**Layers**	**Description**		**Fluorescent Staining Results**		
		Visible light	Ultraviolet light	Carbohydrates	Proteins	Lipids
S-O2	1. orange	orange	brown	?	negative	?
	2. ground	white	bright white/blue	positive	negative	positive
	3. canvas	grey	bright	negative	positive	negative

	fibers		white/blue			
S-G1	1. lt. green	lt. green	blue	?	?	?
	2. dk. Green	dk. green	blue/grey	?	?	?
C5-green	1. lt. green	lt. green	blue	?	negative	positive
	2. dk. Green	dk. green	blue/grey	?	negative	?
C2-pink	1. lt. pink	lt. pink	bright orange	negative	negative	?
	2. dk. Pink	dk. pink	bright orange	negative	negative	?
	3. ground	white	grey	?	negative	positive
	4. ground	transparent	white/blue	negative	negative	negative
C1-ground	1. ground	white	grey	positive	negative	positive
	2. ground	transparent	white/blue	negative	?	negative
S-GR1	1. ground	white (pink contaminant on top left)	light grey (yellow at top left)	positive	negative	positive
	2. ground	transparent, brown	white/blue	negative	positive	negative
	3. canvas fibers	transparent, brown	white/blue	?	negative	negative
S-GR2	1. ground	white	light grey	positive	negative	positive
	2. ground	grey, transparent	blue-white	negative	positive	negative
S-S1	1. metallic paint	shiny, warm hue	black flecks in blue medium	negative	negative	positive
	2. resin?	transparent brown	white/blue	negative	negative	negative
	3. lt. green	lt. green	dk. green	?	negative	negative
	4. d. green	dk. green	black	?	negative	negative
S-B1	1. black	black	black	?	negative	negative
	2. lt. green	Lt. green	light blue	negative	negative	negative
	3. dk. Green	dk. green	grey/blue	?	negative	negative
S-B2	1. black	black	black	negative	negative	?
	2. metallic paint	shiny, warm hue	black flecks in blue medium	negative	negative	positive
	3. ground	white	grey	positive	negative	positive
	4. ground	transparent	white	negative	?	negative
S-DG1	1. dk. green	dk. green with red	black	negative	negative	negative

	pigments				
2. metallic paint	shiny, warm hue	black flecks in blue medium (possible layer separation?)	?	?	positive
3. white	white with colored pigments	blue with dark pigments	positive	?	positive

Table 3. Scanning Electron Microscopy-Energy Dispersive Spectroscopy/Back Scattered Electron Imaging Results

Sample	**Description** (cross section unless otherwise noted)	**Results** (relevant elements in **bold**)	**Colorants Inferred**
S-G1	degraded green paint	C, **O,** Al, **S, Cu, Zn, As, Cd**	emerald green, cadmium yellow, zinc white
	orange paint layer	C, **O,** Mg, Al, Si, **S, Se, Cd, Ba**	cadmium orange or cadmium red lithopone, barium sulfate
S-O1	white paint layer	**C, O,** Na, Mg, **Al, Si, S,** Cl, **Ca, Ti**	titanium white, calcium carbonate and/or calcium sulfate, alumino-silicate
	silver paint layer	**Al**	metallic aluminum
S-S1	degraded green paint layer	C, **O,** Al, **S,** Cl, **Cu, Zn, As, Cd**	emerald green, cadmium yellow, zinc white
C1-ground	white ground layers	**O,** Na, Mg, **Al, Si, S,** Cl, K, **Ca, Ti,** Fe	titanium white, calcium sulfate, alumino silicates (possibly a clay extender)
	dark green paint layer	Mg, Si, **S,** K, Ca, **Ti, Cr, Fe,** Zn, **Cd**	chromium oxide green, cadmium orange, titanium white
	silver paint layer	**Al**	metallic aluminum
S-DG1	white paint layer	Mg, **Al,** Si, **S,** Cl, K, Ca, Ti, Fe, **Cu, Ba**	barium sulfate, alumino-silicate
	black paint layer	**O,** Na, Mg, **Si, P, S,** Cl, K, Ca, **Fe**	possibly bone black
	silver paint layer	**Al**	metallic aluminum
S-B4	white paint layer	**C, O, Ti,** Na, Mg, **Si, S,** Cl, **Ca,** Fe,	titanium white (possibly calcium sulfate, anhydrite)
Paper	brown paper sample, un-mounted	**C, O,** Na, **Al, Si,** S, **Ca, Ti**	alumino-silicates (clay), calcium carbonate, titanium white

Table 4. Information on filter cubes and fluorescent stains used during cross-sectional analysis

Microscope filter cubes used on the sample cross sections:

Blue Excitation: Nikon B-2A (ex. 450-490 nm, ba 520 nm)
Green Excitation: Nikon G-1B (ex. 546/10 nm, ba 590 nm)
Violet Excitation: Nikon BV-2A (ex 400-440 nm, ba 470nm)

Fluorescent stains used on the sample cross sections:

TTC (Triphenyl Tetrazolium chloride) with a concentration of 4.0% in anhydrous methanol (0.2g/5ml). Stains for Carbohydrates, reducing sugars, reducing compounds. Positive reading is red/brown using the UV-2A filter cube.

488 (Alexa Fluor 488) with a concentration of 0.02% in water (pH 9), 0.05%M borate and 5% DMF solution. Stains for proteins. Positive reading is yellow/yellow-green using the B-2A filter cube.

FITC (Fluorescein isothiocyanate) with a concentration of 0.2% in anhydrous acetone (0.01g/5ml). Stains for free amino containing groups (proteins). Positive reading is yellow/green using the B-2A filter cube.

FITC conjugated lyophilized powder with a concentration of 1% in water (pH 9), 0.05%M borate. Stains for chitin (mold). Positive reading is yellow/green using the B-2A filter cube.

DCF (2,7, Dichlorofluorescein) with a concentration of 0.02% in ethanol. Stains for saturated and unsaturated lipids (oils). Positive reading is pink for saturated lipids and yellow for unsaturated lipids using the B-2A filter cube.

RHOB (Rhodamine B) with a concentration of 0.06% in ethanol or 1:1 ethanol:xylene (0.003g/5ml). Stains for lipids (oils). Positive reading is red/orange using the G-1B filter cube.

XRF Sample Locations

SEM and Cross Section Sample Locations

GC/MS and FTIR Sample Locations