**INVITED PAPER** 

# Applied Physics A Materials Science & Processing



# Prior states: evolution of composition and color in two Barnett Newman paintings

Bradford A. Epley<sup>1</sup> · Corina E. Rogge<sup>2</sup>

Received: 1 March 2015/Accepted: 14 July 2015/Published online: 21 July 2015 © Springer-Verlag Berlin Heidelberg 2015

Abstract The color field paintings of Barnett Newman, one of the great American abstract expressionist painters, are seminal works of the modern era. They feature large flat fields of vibrant colors intended to allow the viewer to connect with the paintings in immediate, visceral ways. Despite the apparent simplicity of his compositions, Newman considered himself an intuitive painter and allowed his compositions to evolve during the painting process. Two paintings in the Menil Collection, Untitled 2 (1950) and Unfinished Painting [Blue and Brown 1970-#2] (1970) display visual evidence of former states, but attempts to elucidate earlier compositions by X-radiography were inconclusive due to the lack of contrast in paint densities. We applied limited sampling and used a handheld X-ray fluorescence spectrometer in a 'scanning' manner to determine the color and composition of the previous states of these paintings to help us better understand their evolution. Newman altered his initial cadmium red and alizarin composition in Untitled 2 (1950) by overpainting the alizarin region with a wider band of Mars black paint. He then modulated the surface of the black by partially covering it with a carbonaceous black with a different gloss. For Unfinished Painting [Blue and Brown 1970-#21 (1970), Newman not only changed the cadmium red to an umber but simplified the composition, removing multiple zips and refining it to its current monumental state. This evidence of Newman's decisionmaking processes permits a tantalizing glimpse of the artist consistently looking both ahead and backward, experimenting and revisiting.

# **1** Introduction

The creation of a painting involves a dialogue between the artist and the materials. Although often beginning with an idea in mind, and perhaps a preliminary sketch, the artist may revise the original concept and alter the composition of the work during painting. These changes, known by the Italian word pentimenti ('repentances'), provide an insight into the creative process and help technical art historians better understand the evolution of an artist's work. In what may be termed 'traditional' oil paintings, pentimenti are often relatively easy to find and document because of common artistic practices. Preliminary sketches made on the support with carbonaceous pigments can be detected by infrared reflectography, allowing the sketches to be compared with the surface paint. Pigments that are extremely dense and absorb X-rays well, such as lead white, can be easily detected in X-radiographs even if they have been overpainted. Unfortunately, pentimenti are often harder to find and document in modern works as most common paints are relatively X-ray transparent and artists often forgo preliminary sketches. A case in point is the work by the American Abstract Expressionist painter Barnett Newman.

Beginning with the watershed creation of *Onement I* (1948), Newman's works featured planes of color divided by vertical or horizontal lines or 'zips' of a different, often contrasting color. Despite the apparent simplicity of the finished works, Newman worked slowly, often taking years

Corina E. Rogge crogge@mfah.org

<sup>&</sup>lt;sup>1</sup> Chief Conservator at the Menil Collection, The Menil Collection, 1500 Branard St., Houston, TX 77006, USA

<sup>&</sup>lt;sup>2</sup> Andrew W. Mellon Research Scientist at the Museum of Fine Arts Houston and the Menil Collection, Museum of Fine Arts, Houston, P.O. Box 6826, Houston, TX 77265, USA

to complete pieces [1, 2]. In his provocative approach to painting he sought to eliminate the influence of others or himself: "The fact is, I am an intuitive painter, a direct painter. I have never worked from sketches, never planned a painting, never 'thought out' a painting. I start each painting as if I had never painted before." [3]. Such an approach would leave no physical record of the 'original concept' of a work, but the vagaries of the creative process might still be detectable as revisions or alterations. Importantly, Newman believed that the act of painting engendered his work, saying "The content has to be determined at the very moment it's being made" [4], and he acknowledged that he responded to the emerging painting: "It is as I work that the work itself begins to have an effect on me. Just as I affect the canvas, so does the canvas affect me" [5]. Evidence of revisions or alterations in his works might therefore be indications of how a given piece evolved during its creation.

Several previously detected alterations have confirmed that Newman made changes, reworking a painting until he was satisfied. Visual examination of Galaxy (1949) reveals that the zips were originally wider and darker than their final form [6]. Newman strengthened the cream colored zip in Vir Heroicus Sublimis (1950-1951) [7, 8], added an additional zip to Adam (1951-1952) [9], and reworked Be II (1961, 1964) [8]. These changes, although important, are mostly rather slight, and it would be reasonable to suspect that larger, more comprehensive alterations may have passed unrecognized due to limitations of standard examination techniques. An exhibition at the Menil Collection, Barnett Newman: The Late Work, March 27-August 2, 2015, presented an opportunity to revisit and reanalyze the works in the collection. During this process, it became apparent that two paintings, Untitled 2 (1950) (Fig. 1) and Unfinished Painting [Blue and Brown 1970—#2] (1970) (Fig. 2) displayed density variations in their X-radiographs suggestive of changes to composition. However, the paints used by Newman were not variable enough in density to draw firm conclusions.

To further investigate, a combination of techniques was used to analyze the media, the pigments, and the location of different paints on the canvas. A handheld X-ray fluorescence spectrometer was used to create a series of line scans on the recto, and when accessible the verso, of the canvases to document the location of specific paints. These findings were used to inform location of microsamples taken for cross-sectional visualization and pigment and media identification. The embedded and polished cross sections confirmed the stratigraphy suggested by XRF. The same samples were then analyzed by Raman and FTIR spectroscopy to identify pigments and media, and those findings were correlated with samples of historic Bocour Aqua-tec acrylic and Bellini oil paints, which Newman was **Fig. 1** Barnett Newman, Untitled 2 (1950) ( $48 \times 5 1/8''$ ), The Menil Collection, Houston). The wider zip on the proper right is red, and the smaller one on the proper left is black with a modulated gloss



Fig. 2 Barnett Newman, Unfinished Painting [Blue and Brown 1970—#2]) ( $84 \times 76''$ ), The Menil Collection, Houston). The proper left side of the canvas is a reddish-brown color, while the larger plane of color on the proper right is bright blue

known to favor [10]. As expected from its early date, Untitled 2 (1950) was painted using drying oils, but the paints present do not appear to be standard Bellini oils. The media of Unfinished Painting [Blue and Brown 1970—#2] (1970) was found to be poly(ethyl acrylate/methyl methacrylate), a copolymer consistent with early acrylic emulsion paints, but the pigments do not correspond to commercially available Bocour Aqua-tec paints represented in the historic collection. The combination of all analyses also revealed that both paintings were initially quite different in appearance: Newman reworked the compositions and dramatically altered the colors.

### 2 Experimental

#### 2.1 X-radiography

For both paintings, a ScanRay AC-120 X-ray control box and tube head (type DOB 120) were utilized in conjunction with Agfa Structurix D4DW film. For each exposure of *Untitled 2* (1950), the tube was set at 50 kVp and 3 mA for 420 s. For each exposure of *Unfinished Painting [Blue and Brown 1970—#2]* (1970), the tube was set at 75 kVp and 3 mA for 45 s.

#### 2.2 Microscopy

Samples were embedded in Bio-Plastic embedding resin (Ward's Scientific), coarse ground using Micro Mesh MX sheets (120 and 150 grit) (Scientific Instrument Services) and fine polished using Micro Mesh sheets (1500-12,000 grit) (Scientific Instrument Services). Images of the stratigraphy were obtained using a Zeiss Axio-Cam MRc5 camera controlled by Zeiss Axiovision AC software Release 4.5 and mounted onto a Nikon Labophot-Pol optical microscope equipped with  $4\times$ ,  $10\times$ ,  $20\times$ , and 40× objectives. Scale bars were created in Adobe Photoshop using images of a micrometer scale taken using the different objectives.

#### 2.3 X-ray fluorescence spectroscopy

X-ray fluorescence spectra were collected using a Bruker Tracer III-SD handheld energy-dispersive X-ray spectrometer equipped with a Peltier cooled XFlash silicon drift detector (SDD) with a resolution of 145 eV. The excitation source was a Rhodium (Rh) target X-ray tube, operated at 40 kV and 10  $\mu$ A current, 15 kV and 10  $\mu$ A current with the vacuum pump attachment, or 40 kV and 10  $\mu$ A current with an Al/Ti filter. Spectra were collected over either 120 or 180 s (live time). Spectral interpretation and peak integration were performed using the Bruker Artax Spectra 7.4.0.0 Software.

Line scans across the paintings were performed by aligning the aperture of the instrument with a soft fabric ruler stretched across the surface of the painting, obtaining a measurement, and then moving the instrument to the next desired point. For Untitled 2 (1950) a single line scan was done; for Unfinished Painting [Blue and Brown 1970-#2] (1970) three line scans were performed and the peak areas for each point were averaged and the standard deviations calculated. This averaging permits variations in the relative orientation of the instrument to painting and distance from instrument to the painting to be factored in as part of the standard deviation of each measurement. Normalization of the data to the Rh L or K lines caused by Rayleigh scattering of the primary X-rays was not performed due to the large differences in average atomic numbers in different areas of the paintings; differences which cause variations in the amount of scattering and would introduce additional error into the measurements.

#### 2.4 Transmission FTIR microscopy

Infrared spectra were collected using a Thermo Continuum microscope coupled to a Nicolet Nexus 670 FTIR spectrometer (Thermo Scientific). Samples were prepared by flattening them in a diamond compression cell, removing the top diamond window, and analyzing the thin film in transmission mode on the bottom diamond window  $(2 \text{ mm} \times 2 \text{ mm} \text{ surface})$ area). An approximately  $100 \ \mu m \times 100 \ \mu m$  square microscope aperture was used to isolate the sample area for analysis. The spectra are the average of 64 scans at  $4 \text{ cm}^{-1}$  spectral resolution. Sample identification was aided by searching a spectral library of common conservation and artists' materials (Infrared and Raman Users Group, http://www.irug.org) using Omnic software (Thermo Scientific) and through comparison with authentic Bocour paints.

#### 2.5 Attenuated total reflection FTIR microscopy

ATR spectra were collected using a Lumos FTIR microscope equipped with a motorized germanium ATR crystal with a 100  $\mu$ m tip (Bruker). Samples were placed upon glass slides and analyzed using the built-in 8x objective and a medium ATR crystal pressure. An approximately 150  $\mu$ m × 150  $\mu$ m square microscope aperture was used to isolate the sample area for analysis. The spectra are an average of 128 scans at 4 cm<sup>-1</sup> spectral resolution. An ATR correction was automatically applied by the Opus 7.0 instrument control and data collection software.

#### 2.6 Dispersive Raman microspectroscopy

Dispersive Raman spectra were collected on an InVia Raman microscope (Renishaw) using a 785 nm excitation laser operating at a power of 3.7, 7.4 or 37.5 mW at the

sample as measured using a PM100D laser power meter (Thorlabs) equipped with a S120C photodiode power sensor. A 50× objective was used to focus the excitation beam to an analysis spot of approximately 1  $\mu$ m directly on the sample supported on a glass microscope slide. The resulting Raman spectra are the average of 1–7 scans of 10 s duration. Spectral resolution was 3–5 cm<sup>-1</sup> across the spectral range analyzed. Sample identification was achieved by comparison of the unknown spectrum to spectra of reference materials and to those published in the literature.

## **3** Results and discussion

#### 3.1 Untitled 2 (1950)

Visual inspection of the painting, particularly in areas of abrasion and loss, suggests the presence of an overall white ground layer. The red paint appears to be applied directly on this ground, while the black paint, particularly on the proper left edge of the canvas, appears to overlie a deep red paint that is now revealed only in losses. The black zip also displays areas of differential gloss suggesting the presence of at least two black paints: A glossy black paint underlies a more matte surface paint; the latter does not completely cover the former and appears to be brushed on. Microsamples of each type of paint were analyzed by FTIR and Raman spectroscopy. The media of all samples appeared to be a drying oil, based upon the location of the CH<sub>2</sub> and CH<sub>3</sub> stretches and the breadth of the carbonyl peak indicative of both carboxylic acids and esters typical of partially hydrolyzed oils [11]. The FTIR spectrum of the white ground layer also displays peaks indicative of the presence of lead white (all characteristic FTIR and Raman peaks for materials identified are given in Table 1), which was confirmed by the presence of the  $v_1$  peak in the Raman spectrum. The FTIR spectrum of the red paint contained peaks attributable to barium sulfate but no absorbances related to pigments. However, XRF detected the presence of cadmium, sulfur and selenium, suggesting a cadmium sulfoselenide pigment. The pigments present in the lower, glossy black paint are FTIR and Raman silent, but XRF detected high levels of iron suggesting that the primary colorant was magnetite or Mars black. The FTIR spectrum of the upper, matte black displayed peaks indicative of calcium sulfate dihydrate and a phyllosilicate species such as talc. Raman spectroscopy suggested that the colorant was a carbonaceous black. The FTIR and Raman spectra of the bright red paint underlying the black paint suggested the presence of an alizarin lake (PR83).

Although this work is from an early stage in his career, Newman had already established a trust in the quality of Bocour paints, and so may have utilized Bellini oils on Untitled 2 (1950). To investigate this issue the collection of Bellini oils present in the Art Materials Research and Study Center at the National Gallery in Washington D.C., which included Flake White, Alizarin Crimson, Ivory Black, Mars Black and Cadmium Red Light paints, was analyzed. The Flake White paint, which had a NY 19 postal code indicating pre-1963 manufacturing date, was found to contain a mixture of lead white, zinc white and barium sulfate and therefore does not correspond to the lead white paint present on the painting. The Alizarin Crimson Bellini paint, which was simply listed as being manufactured in New York and thus provides little dating information, did contain a crimson lake, but the peak in the FTIR spectrum assigned to the inorganic component, which was described as an aluminum hydrate on the tube, was shifted almost  $100 \text{ cm}^{-1}$  from that in the sample from the painting (972 and 1087  $\text{cm}^{-1}$ , respectively) suggesting the use of different inorganic substrates. The Mars Black Bellini paint, with a Garnerville, NY address and likely dating from the late 1970s, did display high iron levels by XRF, but the FTIR spectrum indicated that silicate species were present and these were not detected in the FTIR spectrum of the iron-based black in the painting. None of the Bellini black paints contained talc or gypsum as the carbon-based black in the painting did. The Cadmium Red Light Bellini paint, again with a New York label, did contain barium sulfate, as did the red paint present on Untitled 2 (1950), but the Bellini paint also appeared to contain a naphthol-based dye, likely added as a color enhancer. No organic dyes were detected in the cadmium sulfoselenide paint present on the painting. These findings suggest Newman did not use Bellini oils on Untitled 2 (1950), although the possibility that changes in paint formulations occurred over time exist and as single representatives of authentic Bocour Bellini paints were analyzed, further Bellini paints would need to be analyzed to confirm this hypothesis.

The presence of the alizarin-based color under the black zip suggested the possibility of previous states of the painting. To investigate this, a series of scans were taken in a horizontal line stretching from the red area across the black area to the proper left edge of the canvas. Unfortunately, the verso of the canvas was inaccessible without unframing the painting from its original lathe frame and unstretching it, which was considered too great an intervention for the current study. Figure 3 shows the cadmium, iron, and lead peak areas as a function of distance from the proper left edge. Variations in the atomic signals correlate with one another and with the edges of the zip (the red/ black interface) and the upper, carbonaceous black layer. The cadmium signal is intense in the red region and falls upon crossing into the black zip, but does not plateau until

Table 1 Ch	naracteristic FTIR	and Ramar	peaks used	to identify	pigment	materials	present
------------	--------------------	-----------	------------	-------------	---------	-----------	---------

Pigment	Peak assignment	Absorption wavenumber (cm <sup>-1</sup> )	Spectroscopic mode	References
Lead white	<i>v</i> <sub>3</sub>	1419	FTIR	[12]
	$v_1$	1047	FTIR and Raman	[12]
	$v_4$	683	FTIR	[12]
Barium sulfate	<i>v</i> <sub>3</sub>	1186, 1113 and 1072	FTIR	
	<i>v</i> <sub>1</sub>	983	FTIR	[13]
Calcium sulfate dihydrate	O-H stretch	3546 and 3408	FTIR	
	O-H bending	1622	FTIR	[13]
	<i>v</i> <sub>3</sub>	1135	FTIR	[13]
	$v_4$	671	FTIR	[13]
Phyllosilicate (talc?)	O-H stretch	3676		[14]
	$e_1^1$	1019	FTIR	[14]
	$a_1^2$	671	FTIR	[14]
Carbon black	G peak	1594	Raman	[15]
	D peak	1303	Raman	[15]
Alizarin lake (PR83)	Various	1636, 1591, 1528, 1466, 1361, 1266, 840, and 722	FTIR	[16]
	Various	1479, 1327, 1290, and 488	Raman	[17]
Kaolinite	O-H stretch	3697, 3652 and 3620	FTIR	[14]
	Si-O stretch	1119, 1032, 1012 and 915	FTIR	[14]
Calcium carbonate	$v_3^u$	1447	FTIR	[12]
	<i>v</i> <sub>2</sub>	877	FTIR	[12]
	$v_4^u$	712	FTIR	[12]
Phthalocyanine blue	Various	1530, 1452, 1343, 1306, 1143, 1108, 954, 779, 748, 682, 593, 484, 286, 256, and 234	Raman	[18]
Rutile	$E_g$	452	Raman	[19]
	A <sub>1g</sub>	614	Raman	[19]

farther into the black approximately 0.75 in from the proper left side, suggesting that the black may partially cover the cadmium red paint (note that the signal does not go to zero due to overlap with other signals). This hypothesis was confirmed by a cross-sectional sample taken from the bottom edge of the painting in the black area (Fig. 4), which clearly shows the Mars black paint overlying the cadmium sulfoselenide paint. The iron signal, indicative of the Mars black paint, increases abruptly at the zip, but then decreases in the center of the zip before increasing again at the edge of the canvas. The lead signal appears to come from both the ground layer and from the carbonaceous black, where it is likely present as a drier. The lead signal is high in the cadmium red region (where only a single paint layer is present to mask the ground), low at the black zip (where both the cadmium red and Mars black paints are masking the ground), and then high in the same region that the iron signal decreases (0.875-0.25 in from the proper left edge, where the carbonaceous black has been brushed on); the lead present in the carbonaceous black may be responsible for the attenuation of the iron signal, but the presence of a thinner Mars black layer in that region cannot be excluded. Unfortunately, the light atomic weight elements present in the alizarin-based paint were obscured by the overlapping paint layers and the presence of this paint could not be mapped by XRF. However, a cross-sectional sample taken at the bottom edge approximately 0.4 in. in from the proper left edge clearly shows the ground, alizarin-based paint, Mars black paint and surface carbonaceous black paint (Fig. 5) confirming the layer structure suggested by visual examination and XRF analysis.

From these findings, we infer a possible explanation for the observed density differences apparent in the X-radiograph (Fig. 6). The apparent stripe of higher density present from 1 to 1.5 in. from the proper left side of the canvas is likely the region where the Mars black paint now partially covers the cadmium red layer. The decrease in density at 1 in. is likely where the original cadmium sulfoselenide layer stopped and the alizarin crimson zip began in a previous state. This suggests that the original state of the canvas had a vertical stripe of alizarin crimson that was 1 in. wide and a wider stripe of cadmium red that was 4.5 in. wide (Fig. 7). This would have resulted in a



**Fig. 3** Areas of the Fe  $K_{\alpha}$  (*white circle*), Cd  $L_{\alpha}$  (*white square*), and Pb  $L_{\alpha 1}$  (*white triangle*) peaks as a function of distance from the proper *left edge* of *Untitled 2* (1950). The graph is shown overlaid on the portion of the painting analyzed at a 1:1 scale. To facilitate comparison the Fe points are plotted on the primary axis at the *right* and the Pb and Cd points are plotted using the *left* secondary *vertical axis*. The cadmium signals do not end at the beginning of the *black zip*, when the iron signal from the Mars *black paint* increases, suggesting the cadmium *red zip* was once wider and is now partially covered by the *black paint*. The presence of the carbonaceous *black paint* can be detected by a decrease in iron concomitant with the increase in lead



Fig. 4 Cross-sectional sample from *Untitled 2* (1950). This sample was taken from the *black* region of the painting near the *red/black zip* and shows a *white* ground layer, followed by a cadmium *red paint*, which *underlies* the Mars *black surface paint* 

canvas with a tonality similar to *Adam* (1951–1952), *Eve* (1950), *Onement I* (1948), *Onement II* (1948), and *Untitled* 4 (1950). At some point, Newman made the decision to



Fig. 5 Cross-sectional sample from *Untitled 2* (1950). This sample was taken from the *center* of the *black zip* and reveals that the alizarin *red paint*, which is no longer visible on the surface, underlies the Mars *black paint* and carbon *black paints* 



**Fig. 6** Partial X-radiograph of *Untitled 2* (1950) showing the *bottom* portion of the canvas. Distances of observed *density lines* are indicated. The *white areas* at the edge of the canvas are due to the *stretcher bars* and lathe frame. There is a 0.5 in wide band of higher density 1 in from the proper *left* side of the canvas. This is likely due to overlap of the Mars *black paint* with the cadmium *red paint* 

alter the composition and painted over the alizarin and a portion of the cadmium paint with a 1.5 in. strip of Mars black, resulting in the second state of the canvas. The third and final state was then created when Newman brush applied the carbonaceous black paint (shown in gray in state 3 for visibility) over a portion of the Mars black zip, perhaps to create a more painterly and modulated appearance. Unfortunately, Newman never spoke about his decision to revise the composition of this work, but a series of paintings from the same time period or slightly later feature a red and black composition [*Joshua* (1950), *Untitled 5* (1950), *The Wild* (1950), and *The Way I* (1951)], so



Fig. 7 Proposed states of *Untitled 2* (1950). State 1 has a narrow alizarin crimson zip on the proper *left* of the canvas and a wide cadmium *red strip*. In state 2 the alizarin zip and a portion of the cadmium *red strip* have been covered with the Mars *black paint*. In state 3 a carbonaceous *black* (shown in *gray* for illustrative purposes) has been applied to modulate the gloss of the Mars *black* 

this piece may represent the transitional period where Newman began exploring a new color combination.

# 3.2 Unfinished painting [Blue and Brown 1970—#2] (1970)

Visual inspection of the surface and tacking margins of Unfinished Painting [Blue and Brown 1970—#2] (1970) suggested the presence a single blue paint and of at least two distinct red paints: The brownish surface paint and a bright red paint now covered over except on the tacking margins. Certain areas of the bright red paint appeared glossier than others, which could indicate that there was differential absorbance of media by the canvas in certain areas, or that Newman modulated the paint through addition of gloss or matting medium, or that two distinct types of red paint are present. No ground layer appeared to be present. Microsamples of each paint, including both matte and glossy bright red paints, and the canvas fibers were taken from the tacking margins and analyzed by FTIR and Raman spectroscopy. The FTIR analysis of the canvas fibers showed no evidence for the presence of proteinaceous or poly(vinyl acetate) sizing, the two materials most common in Newman's oeuvre [10], and the absence of protein was confirmed by a negative Biuret test result [20]. The FTIR spectra suggested that the all paints were acrylic emulsions utilizing а poly(ethyl acrylate/methyl methacrylate) copolymer (p(EA:MMA)), a binding material in common use from the 1950s until the late 1980s [21]. The spectrum of the glossy red paint did display a more prominent peak at  $1113 \text{ cm}^{-1}$ , suggestive of the presence of poly(ethylene glycol), but confirmation of different media formulations would require mass spectroscopic analysis. The FTIR spectrum of the blue paint displayed peaks suggestive of kaolinite and calcium carbonate, while the Raman spectrum indicated the presence of phthalocyanine blue and also displayed weak peaks suggestive of the rutile form of titanium dioxide. The presence of titanium was confirmed by XRF, which also detected elements likely related to the fillers/extenders (S, K, Al, Ca, Si) and bromine, which is perhaps indicative of biocides, flame retardants or other additives. Neither the bright red nor the reddish-brown paints contained IR or Raman active pigments, but the XRF spectra suggested that the bright red paint contained a cadmium sulfoselenide pigment as Cd, S and Se were detected; of note was the apparent absence of barium sulfate, a filler/extender commonly added to cadmium paints. The glossy and matte red paints did display subtle differences in XRF spectra, with the glossy paint having a higher Se/Cd ratio as estimated by peak areas and a higher Se Kalpha/Kbeta ratio suggesting less attenuation. This could indicate a slightly different paint formulation, but the origins of the observed differences are unclear. The reddish-brown paint contained significant levels of iron and manganese suggesting the use of an umber.

Unlabeled samples of acrylic paints found in Newman's studio at the time of his death and now held by the Strauss Center for Conservation and Technical Studies at Harvard University, as well as samples of Bocour Aqua-tec paints in the Art Materials Research and Study Center at the National Gallery in Washington D.C. were analyzed in order to determine whether any corresponded to materials on *Unfinished Painting [Blue and Brown 1970—#2]* (1970). Three blue paints were present in the studio materials, none of which contained phthalocyanine blue as the colorant. The Bocour Blue Aqua-tec paint, from Garnerville, NY and likely dating from the late 1970s, does contain phthalocyanine blue as a pigment, but no kaolin, calcium carbonate, or titanium-based pigments were detected by FTIR or

XRF. We infer that Newman was not using a standard commercially available material from Bocour (unless the formulation of Bocour Blue paint changed over time), but was either mixing his own paint, using a custom formulation from Bocour as has been documented [10] or using a paint from a different vendor such as Liquitex, another brand favored by Newman. Four containers of red paint were represented among the Newman studio materials, all of which utilized cadmium sulfoselenide in a p(EA:MMA) binder, one of which also contained barium sulfate. The three samples without barium sulfate were indistinguishable by FTIR and XRF and may be analogous to the bright red paint(s) found on the painting. Cadmium Red Light, Cadmium Red Medium and Cadmium Red Deep Aqua-tec paints from the NGA collection, which were likely manufactured from pre-1963 to the late 1970s given the NY 19 postal code and Garnerville, NY addresses, all contained barium sulfate as a filler, suggesting that the cadmium red paint present on Unfinished Painting [Blue and Brown 1970—#21 (1970) is not a commercially available Aqua-tec paint. No brown paints were present in the Newman studio materials, and while the NGA collection contained both Raw and Burnt Umber Aqua-tec paints, both of which contained iron and manganese, the colors of these paints do not appear to correspond to the reddish-brown paint present on the painting. These finding strongly suggest that the mythos of Newman using only commercially available paints is incorrect and that his color choices were not dependent simply upon what was available from his favored manufacturer(s).

In addition to analysis of pigments and media, the issue of stratigraphy and possible changes in composition was addressed. Visibly different areas of gloss were noted in the reddish-brown portion of the painting that appeared to follow vertical stripes (Fig. 8). The X-radiograph of this region showed vertical stripes with slightly higher densities at 0-8, 11-15 and 19-21 in. from the proper left of the canvas (Fig. 9). Traces of the phthalocyanine blue paint were found on the proper left side tacking margin, suggesting that the blue may extend under the reddish-brown area. A cross-sectional sample taken from the bottom tacking margin in the brown area confirmed this, as it contains a three layer structure with the phthalocyanine blue paint on the bottom, followed by the bright red cadmium sulfoselenide paint and then the surface reddishbrown umber paint (Fig. 10). However, this sample showed the stratigraphy in only a single location and left unresolved the issues of whether the blue paint fully extended across the canvas serving as a ground layer and whether the bright red paint formed a continuous layer underneath the surface reddish-brown paint. Discontinuities in either of these layers in the form of vertical stripes could cause the suggestive density differences seen in the X-radiograph.



Fig. 8 Visible light image of a portion of Unfinished Painting [Blue and Brown 1970—#2] showing vertical stripes of different glossiness



**Fig. 9** X-radiograph of a portion of Unfinished Painting [Blue and Brown 1970—#2]. Panel A shows the entire brown portion of the painting. The white box deliminates the area enlarged in Panel B. There are three stripes of higher density in the reddish-brown region that extend the total vertical length of the canvas, the first extends 8 in. from the proper left side of the canvas. The second is 4 in. wide and begins 11 in. from the proper left edge of the canvas. The third is 2 in. wide and begins approximately 19 in. from the edge of the canvas. The broad white line on the proper left is the wooden stretcher bar



**Fig. 10** Cross-sectional sample from *Unfinished Painting [Blue and Brown 1970—#2]*. This sample, taken from the tacking margin of the *brown zip*, shows the currently visible burnt umber layer covers the initial cadmium *red layer* that in turn overlies the phthalocyanine *blue* containing layer that covers the canvas

To address this issue non-destructively, a series of XRF spectra were taken in a horizontal line from the blue region, across the reddish-brown area on both the recto and as much of the verso as was unobscured by the proper left vertical stretcher bar. Measurements were taken from the recto (Fig. 11) shown that the copper and titanium signals are higher in the blue areas, and although they decrease in the reddish-brown region, they do not disappear, suggesting that the blue paint underlies the entirety of the reddish-brown area. This is confirmed by measurements taken from

the verso of the canvas, which shows that the Cu peak areas show no change across the entire area measured (Fig. 12). Furthermore, the Cu and Ti Kalpha/Kbeta ratios as measured from the verso also exhibit no change, which suggests that the phthalocyanine blue paint is always the lowest paint layer, closest to the canvas support. We conclude that the phthalocyanine blue paint is present as a single continuous layer and is therefore not responsible for the observed surface appearance.

Scans taken from the verso and recto of the canvas show that at the edge of the blue and reddish-brown interface the peaks areas of iron, cadmium and selenium abruptly increase (Figs. 11, 12). Although the iron peak areas are roughly constant over the reddish-brown areas, particularly as measured from the verso, the cadmium and selenium peak areas display increases in intensity at three locations: at approximately 0-8.5 in., 10.5-15 in. and 16-21 in. as measured from the proper left edge of the canvas. This suggests that while the umber paint is roughly constant across the red-brown area, the cadmium sulfoselenide paint may be thicker in areas of higher peak areas or that a paint containing more pigment is present in those areas. Because the phthalocyanine blue paint underlies the entire reddishbrown area, the Cu and Ti Kalpha/Kbeta peak ratios can serve as probes of overlying paint as thicker or more dense areas of paint should cause greater attenuation of the lower energy  $K_{\alpha}$  signal thereby decreasing the ratios. Comparison of the Cu and Ti Kalpha/Kbeta peak ratios with the cadmium and selenium intensities shows that there is an inverse correlation: Regions with high Cd and Se signals



**Fig. 11** Areas of the Fe  $K_{\alpha}$  (*white circle*), Cd  $L_{\alpha}$  (*white square*), Se  $K_{\alpha}$  (*white triangle*), Cu  $K_{\alpha}$  (*white diamond*), and Ti  $K_{\alpha}$  (*white plus*) peaks measured from the recto of the painting as a function of distance from the proper *left* edge of *Unfinished Painting [Blue and Brown 1970—#2]*. The graph is shown overlaid on the portion of the painting analyzed at a 1:1 scale. To facilitate comparison the Ti, Fe,

and Se values are plotted on the primary axis on the *right*, and the Cu and Cd values are plotted on the secondary axis on the *left*. The Cu and Ti signals diminish but do not disappear in the *reddish-brown* portion signifying that the phthalocyanine *blue paint* underlies the *reddish-brown* paint



**Fig. 12** Areas of the Fe  $K_{\alpha}$  (white circle), Cd  $L_{\alpha}$  (white square), Se  $K_{\alpha}$  (white triangle), Cu  $K_{\alpha}$  (white diamond), and Ti  $K_{\alpha}$  (white plus) peaks measured from the verso of the painting as a function of distance from the proper left edge of Unfinished Painting [Blue and Brown 1970—#2]. Note that even though the points were measured on the back of the painting, the graph is shown overlapped onto the front of the painting at a 1:1 scale in order to show the correlation

between the numbers and paint fields. To facilitate comparison the Ti and Se values are plotted on the primary axis on the *right*, and the Fe, Cu and Cd values are plotted on the secondary axis on the *left*. The Cu and Ti signals are constant across the field of measurement. The Fe signal is noisy due to the small peak areas, but largely constant across the *reddish-brown* field. The Cd and Se signals display three areas of higher intensity in the *reddish-brown* field



**Fig. 13** Area of the Cd  $L_{\alpha}$  (*white square*) measured from the recto of the painting and the Cu  $K_{\alpha}/K_{\beta}$  ratio (*white diamond*), and Ti  $K_{\alpha}/K_{\beta}$  ratio (*white plus*) measured from the recto of the painting as a function of distance from the proper *left edge* of *Unfinished Painting* [*Blue and Brown 1970—#2*]. The graph is shown overlaid on the

portion of the radiograph of the painting analyzed at a 1:1 scale. The  $K_{\alpha}/K_{\beta}$  ratios are plotted using the *left vertical axis* and the Cd  $L_{\alpha}$  areas on the *right hand axis*. The *stripes* of higher density on the X-radiograph correspond to decreases in the Cu and Ti  $K_{\alpha}/K_{\beta}$  ratios and increases in the Cd  $L_{\alpha}$  peak area

display more attenuated Cu and Ti signals. Furthermore, these cadmium sulfoselenide-rich areas correspond to areas of higher density in the X-radiograph (Fig. 13). From this body of evidence, we hypothesize that the painting has existed in at least three prior states (Fig. 14). Newman initially painted the entire canvas with the phthalocyanine blue paint, applied a cadmium sulfoselenide paint in three vertical zips (in some order), resulting in state 2, and then created state 3 by overpainting the zips as a single red field with a cadmium sulfoselenide paint. Newman then appears



Fig. 14 Proposed states of Unfinished Painting [Blue and Brown 1970—#2]. In state 1 the entire canvas was painted with the phthalocyanine blue paint. In state 2 three cadmium red zips of 2, 4, and 8 in. width were applied. In state 3 the zips were painted over with a cadmium red paint; we cannot exclude the possibility that either states 2 or 3 were completed in stages. In state 4 the cadmium red was overpainted with an umber

to have been unsatisfied with the color combination and chose to overpaint the bright red cadmium sulfoselenide paint with the umber paint, resulting in the current state. States 2 and 3 were created by applying cadmium sulfoselenide paints, and while Newman may have used the exact same paint, it is also possible that two slightly different paints were used; perhaps the matte and glossy bright red paints seen on the tacking margins. Our data cannot distinguish the sequence in which the zips were laid down, nor can they exclude the possibility that two zips may have been consolidated by overpainting prior to a third being laid down. Attempts to confirm the presence of the zips through cross-sectional analysis have been thwarted by the impeccable state of the painting, which prevents sampling directly from the surface. Samples taken from the turnover edges in regions of the putative zips show the same stratigraphy as samples taken from non-zip regions, from bottom to top: phthalocyanine blue, cadmium red and umber. Under the illumination conditions available, there is no clear evidence for the presence of multiple cadmium red layers. This could be due to the turnover edges having incomplete stratigraphy; Newman was generally careful to maintain clean edges on paintings in order to isolate the surface of the canvas from the edges and supporting walls. The lack of multiple layers could also indicate that the proposed states were very transient and that the layers of cadmium red were applied close enough in time that they cannot be visually distinguished. Given that the stripes of different gloss and higher X-ray density extend evenly across the entire vertical length of the canvas and the large size of the canvas (84" in height) it seems unlikely that these areas of density were created adventitiously through roller application.

Comparison of the hypothetical state 2 with its relatively evenly spaced zips of increasing size with the rest of Newman's oeuvre shows that it is unique in composition and relatively unusual in color choice. The closest compositional analogue is Shimmer Bright (1968), which utilized two zips of blue on a white field. However, the zips are approximately the same size unlike in state 2. Newman created only two blue and red compositions, L'Errance (1953) and Voice of Fire (1967), and the blue in those works was a truer, less lightened blue. A larger series did utilize red, blue and yellow (Who's Afraid of Red, Yellow and Blue I (1966), Who's Afraid of Red, Yellow and Blue II (1967), Who's Afraid of Red, Yellow and Blue III (1968), Chartres (1969), but again the blue in these is distinctly different in color from the phthalocyanine blue in Unfinished Painting [Blue and Brown 1970-#2] (1970). Thus, this early state appears to have been experimental both in composition and in color choices. The composition was evidently the first aspect addressed by overpainting the three zips into a solid block of color, and then the color was modulated by overpainting the cadmium red paint with an umber. This color composition is still unique, and we cannot know if Newman's untimely death prevented further alterations or if this is a state that satisfied his vision.

## 4 Conclusions

The success of this multi-analytical micro-destructive approach in revealing prior states of two Newman paintings provides an unprecedented look into the artist's working technique. The identification of major alterations in two paintings that bracket his most productive years confirms that throughout his career, the act of painting was an active process and that he approached the canvas ready to alter any composition he might have had in mind initially. We hope that the findings of this study and the relative simplicity of approach will encourage institutions to look more closely at Newman paintings within their collections and that more 'lost' compositions can be recovered, thereby increasing the appreciation of this seminal modern artist.

Acknowledgments The authors thank: Dr. Barbara Berrie and Michael Skalka of the National Gallery of Art (Washington D.C.) for

providing access to Bocour Bellini and Aqua-tec paints held in the Art Materials Research and Study Center; Drs. Tom Tague and Cruz Hinojos and Bruker Corporation for the generous loan of a Lumos FTIR instrument; Rice University Shared Equipment Authority for providing access to the Thermo FTIR and Renishaw Raman spectrophotometers; Drs. Doug Natelson and Pavlo Zolotavin of Rice University for the use of the laser power meter, and the Andrew W. Mellon Foundation for supporting conservation science at the Menil Collection.

#### References

- B. Newman in Barnett Newman: Selected Writings and Interviews, ed. by J.P. O'Neill (University of California Press, Berkeley, 1992), p. 190
- R. Schiff in *Barnett Newman: a Catalogue Raisonné*, ed. by R. Schiff, C. Mancusi-Ungaro, H. Colsman-Freyberger (Barnett Newman Foundation, New York and Yale University Press, New Haven 2004)
- B. Newman in *Barnett Newman: Selected Writings and Inter*views, ed. by J.P. O'Neill (University of California Press, Berkeley, 1992), p. 248
- 4. B. Newman, *Lecture at Hunter College*, (Audio tape, Barnett Newman Foundation Archives, New York City, 1962)
- B. Newman in *Barnett Newman: Selected Writings and Inter*views, ed. by J.P. O'Neill (University of California Press, Berkeley, 1992), p. 189
- 6. Y.-A. Bois in *Reconsidering Barnett Newman: A Symposium at the Philadelphia Museum of Art*, ed. by M. Ho (Philadelphia Museum of Art, Philadelphia, 2005)
- 7. B. Newman, *interview by Karlis Osis*, (Transcript, Barnett Newman Foundation Archives, 1962 or 1963)

- S. Penn in *Reconsidering Barnett Newman: A Symposium at the Philadelphia Museum of Art*, ed. by M. Ho (Philadelphia Museum of Art, Philadelphia, 2005)
- 9. R. Alley, Catalogue of the Tate Gallery's Collection of Modern Art Other Than Works by British Artists (Tate Gallery and Sotheby Parke-Bernet, London, 1981), p. 556
- C. Mancusi-Ungaro in *Barnett Newman: a Catalogue Raisonné*, ed. by R. Schiff, C. Mancusi-Ungaro and H. Colsman-Freyberger (Barnett Newman Foundation, New York and Yale University Press, New Haven, 2004)
- R.J. Meilunas, J.G. Bentsen, A. Steinberg, Stud. Conserv. 35, 33 (1990)
- 12. W.B. White *in Infrared Spectra of Minerals*, ed. by V.C. Farmer (Mineralogical Society, London, 1974), p. 227
- S.D. Ross in *Infrared Spectra of Minerals*, ed. by V.C. Farmer (Mineralogical Society, London, 1974), p. 423
- V.C. Farmer in *Infrared Spectra of Minerals*, ed. by V.C. Farmer (Mineralogical Society, London, 1974), p. 331
- 15. A.C. Ferrari, J. Roberston, Phys. Rev. B 64, 075414 (2001)
- J. Russell, A Study of the Materials and Techniques of Francis Bacon (1909–1992) (Northumbria University, Newcastle, 2010), p. 74
- 17. L. Burgio, R.J.H. Clark, Spectrochim. Acta A 57, 1491 (2001)
- K. Castro, M. Pérez-Alonso, M.D. Rodríguez-Laso, L.A. Fernández, J.M. Madariaga, Anal. Bioanal. Chem. 382, 248 (2005)
- T. Mazza, E. Barborini, P. Piseri, P. Milani, D. Cattaneo, A. Li Bassi, C.E. Bottani, C. Ducati, Phys. Rev. B 75, 045416 (2007)
- N. Odegaard, S. Carroll, W.S. Zimmt, *Material Characterization* Tests for Objects of Art, 2nd edn. (Archetype Books, London, 2007)
- 21. T. Learner, Conservator 24, 96 (2000)