2002.23

J. Paul Getty Museum

Leaf from a Gospel Book or New Testament

Unknown

1325-1345

tempera colors and gold leaf on parchment

Getty Conservation Institute

Scientific Report

GCI Scientist(s):
C. Patterson

JPGM Conservator:
N. Turner

JPGM Curator:

29 June 2020

The Getty Conservation Institute

Summary:

In this analysis, the pigments in *Leaf from a Gospel Book or New Testament* were studied using x-ray fluorescence spectroscopy and Raman spectroscopy. The analysis indicates the use of pigments consistent with the date of the manuscript, including lead white, vermilion, ultramarine, and one or more iron earth pigments. Small amounts of carbon, and chalk were also identified. Unidentified pigments/materials that may also be present include one or more organic colorants (likely red), and possibly a copper-containing pigment.

Introduction

This leaf was examined as part of a larger study examining the materiality of Byzantine manuscripts. The major aims of the project are to both better understand these objects (primarily from the J. Paul Getty Museum collection), and to look for changes in pigment use or painting techniques between the center of the Byzantine Empire (i.e. Constantinople) and areas farther removed from Constantinople. In this context, this leaf was considered a "center" object.

Experimental

X-Ray Fluorescence Spectroscopy

XRF spectroscopy is a non-destructive technique which can detect the majority of elements commonly found in mineral-based pigments in discrete areas of the work. The presence, or absence, of particular elements provides an indication of the pigments that are present in the examined area(s). Importantly, however, air-path XRF instruments such as those used in this analysis are generally incapable of detecting the low energy x-rays emitted by elements with atomic number less than ~20, so elements such as carbon, nitrogen, oxygen, sodium, aluminum, silicon, and sulfur cannot be detected. The technique relies on the use of x-rays, which are sufficiently energetic to excite fluorescence from materials in both the uppermost pigmented layers and, in some cases, in buried layers of the object. Elements detected, therefore, may be from a ground layer or pigments from underlying paint layers, as well as from the painted surface. Determination of the specific stratigraphy of the various paint layers would require the removal of a sample for cross-sectional analysis, which was not done as part of this study. It should be noted that XRF provides an *elemental* rather than *molecular* analysis and therefore cannot conclusively identify the presence of particular pigments. Conclusive pigment identification requires complementary analysis via a molecularly specific technique such as x-ray diffraction (XRD) or Raman spectroscopy.

In this work, the elemental composition of the major color regions were studied using a Bruker Artax x-ray fluorescence spectrometer (non-filtered W-tube, 50 kV, 600 μA, 60 second accumulations, in air) in a non-contact configuration. The spot size of incident x-rays is approximately 0.65 mm in diameter. For areas examined that are near this size, elements in a neighboring color field may contribute to the final observed spectrum.

Raman spectroscopy

To complement the elemental analysis, Raman micro-spectroscopy was used to confirm the presence of pigments and identify molecular species. The coupling of the Raman spectrometer to a microscope assembly allows spectral acquisition from individual pigment particles. The vibrational signatures apparent in the resulting spectra allow identification of pigments through comparison to known or reported spectra.[1-6] Where possible, Raman spectra were collected from the same areas of the manuscript where XRF data were collected. Raman

spectra were collected using a Renishaw inVia Raman microscope using a 785 nm laser excitation source calibrated using the 520.5 cm^{-1} silicon Raman band. The leaf was analyzed by placing it directly on the microscope stage and collecting spectra through a L50X microscope objective (N.A. 0.50, working distance ~8 mm). Laser power and collection times were varied for each area examined to optimize the signal while avoiding sample degradation.

Fiber Optic Reflectance Spectroscopy (FORS)

Fiber optic reflectance spectroscopy (FORS) measures the relative absorbance/reflectance of various wavelengths of light by a material. Taken alone, these measurements may not be sufficient to conclusively identify pigments, but can provide supporting information which, in conjunction with other analyses, may clarify the materials present.

Select areas on this folio were examined using an ASD FieldSpec4 instrument, which provides data from 350-2500 nm at 1 nm intervals. The examined area was illuminated with white light (held at ~45°) and data collected using a fiber optic probe hand-held 5-10 mm from, and perpendicular to, the surface of the object, in a non-contact configuration. The spot size of the fiber optic probe is on the order of several millimeters in diameter. At least two spectra were taken in each area, which were averaged together for analysis. Spectral matching against GCI reference libraries was done using the OPUS software suite.[1]

Results

Areas analyzed in this study are indicated in Figure 1, and results are summarized in Table 1. These results should not be interpreted as an exhaustive list of all materials present in the manuscript. Rather, these are the materials that could be identified and/or inferred in the areas examined, and by the two techniques utilized. Other pigments may be present that were not identified in this study (including areas marked in Figure 1/described in Table 1).

[1] Unless otherwise noted, libraries used were: *FORS_Catherine_Feb24* (spectra from pigment/colorant paintouts on paper), *FORS_M.Aceto* (Italian FORS data provided to M. Ganio), *CRL_MOCKMANUS* (organic colorants on modern parchment), and *GCI_FORS_COLORANTS* (organic colorants on paper provided by N. Turner), as they existed in August 2016. Search parameters used were: Spectrum search, spectrum correlation, vector normaliazation and first derivative matching, with a minimum hit quality of 100.

Figure 1: Spots analyzed on *Leaf from a Gospel Book or New Testament*. Yellow squares indicate locations of analysis point measurements.

Table 1: Analysis of areas marked on Figure 1 (*Leaf from a Gospel Book or New Testament*).

Area	Description/Color	XRF analysis[a]	Raman analysis	FORS analysis	Confirmed materials	Possible or inferred materials
1	white of bible	✓	✓		lead white, ultramarine, carbon	
2	red edge of bible	✓				lead white, vermilion, iron earth
3	red robe	✓		✓		lead white, vermilion, possible insect-based organic red, iron earth
4	red text in background	✓				vermilion, iron earth, gold (from gold leaf background)
5	red-orange exposed bole	✓	✓		lead white	iron earth, gold (from gold leaf background)
6	gold leaf background	✓				gold leaf, iron earth bole
6b	gold leaf background	✓				lead white, gold leaf, iron earth bole, silver leaf?
7	green-blue border of pedestal	✓	✓		ultramarine, carbon, calcite, lead white	iron earth (including possible hematite), lead white, gold leaf (underneath?)
8	brown footstool	✓				iron earth, lead white
9	light blue inner edge of border	✓				lead white, ultramarine; gold leaf/iron earth from underneath?
10	dark blue outer edge of border	✓				ultramarine, iron earth
11	blue robe at knee	✓	✓		ultramarine, lead white	iron earth
12	flesh tone in Saint's face	✓	✓		vermilion, carbon, lead white	iron earth, possible ultramarine
13	purple design of pedestal step	✓	✓	✓	ultramarine, lead white, vermilion, chalk	iron earth, organic colorant (possibly an insect-based red dye)[b]
14	black in design of pedestal step	✓	✓	✓	vermilion, ultramarine, lead white	iron earth, azurite or copper green, possible organic red (possibly an insect-based red dye)?
15	bare parchment	✓	✓	✓	lead white, carbon, hematite	chalk
16	red text in background		✓		vermilion	

17	blue border		✓		ultramarine, lead white	possible hematite (iron earth)

a. All XRF-based identifications (except those in area 15) were based on spectra with parchment background subtracted, so small amounts of lead, iron, or calcium actually present in some spots may not have been indicated in the analysis.

b. Organic colorants are suggested by lack of evidence for inorganic pigments consistent with overall color of the area analyzed. In some cases FORS analysis allows more specificity.

Discussion

Taken together, the XRF, Raman, and FORS analyses suggest the overall color palette summarized in Table 2.

Table 2: Palette suggested by analysis of *Leaf from a Gospel Book or New Testament*.

General color area	Pigment(s) suggested
red	vermilion (with varying amounts of lead white and iron earth), insect-based organic red
pink	--
yellow	--
green	(blue toned) ultramarine and iron earth (with carbon, chalk and lead white)
blue	ultramarine (with lead white, and sometimes iron earth)
purple	vermilion and organic colorant (insect-based) mixed with ultramarine (with lead white, iron earth)
white	lead white (with ultramarine, carbon)
brown	iron earth with lead white
black	mix of vermilion, lead white, ultramarine, iron earth, copper-containing pigment, and possible organic red colorant
flesh tone	lead white, vermilion, and carbon (with or on iron earth)
metal	gold leaf (possible zwisch gold in one area)
bole	red-orange, contains iron earth and lead white
parchment	lead white, chalk, iron earth, carbon

In general, the pigments listed in Table 2 are typical, and consistent with the date of the manuscript. Unresolved are the identities of a copper-containing pigment and whether or not any organic colorants were used in the making of this leaf.

Area 14 – the dark edging of the purple-toned pedestal – appears to contain a complex mixture of pigments. The XRF analysis of this area, a very trace amount of copper may be present; this would typically be associated with e.g. the blue copper-containing pigment azurite, the green mineral pigment malachite, or another green copper-containing pigment. However, no evidence for a copper-containing pigment was found during Raman analysis. Additional examination, including by close visual observation, may clarify whether or not a blue or green pigment was used in this area.

Organic red colorants may be present in both areas 14 and area 13. Area 13 is purple in color, yet the only materials suggested by the XRF analysis are iron earth pigment(s) and lead white. While purple-tinted iron earth pigments exist, they are not common. Thus, it may be that this area contains additional materials not identifiable by XRF. Raman spectroscopy identifies a small amount of vermilion. Additionally, fiber optic reflectance spectroscopy performed in each of these areas is suggestive of an organic red or purple dye, likely insect based. Of these, the red dyes (cochineal, kermes, lac) are more common, and may be used in both of these purple areas. Raman spectroscopy identifies ultramarine in both areas. Overall, then, the purple areas appear to be a mixture of red and blue particles: ultramarine, vermilion, and an insect-based red dye.

An interesting feature of this manuscript is the presence of both lead and chalk (calcite) in the area of 'bare' parchment examined. Chalk is often found on medieval parchment, and may have been used as a pounce (material rubbed into the surface of the parchment as part of the preparation to write)[7], or to whiten the parchment surface. In this case, lead white was also used, likely as a whitener.

Notes of interest to examine further:

- One of the gold areas (6b) shows silver, the other doesn't, and the one that shows silver also has quite a bit of lead. What's going on here? Images of the two areas?

References:

(1) Burgio, L.; Clark, R. J. H. *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **2001**, *57*, 1491-1521.
(2) Bell, I. M.; Clark, R. J. H.; Gibbs, P. J. *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **1997**, *53*, 2159-2179.
(3) de Faria, D. L. A.; Silva, S. V.; de Oliveira, M. T. *J. Raman Spectrosc.* **1997**, *28*, 873-878.
(4) Clark, R. J. H.; Cridland, L.; Kariuki, B. M.; Harris, K. D. M.; Withnall, R. *J. Chem. Soc.-Dalton Trans.* **1995**, 2577-2582.
(5) Edwards, H. G. M.; Wolstenholme, R.; Wilkinson, D. S.; Brooke, C.; Pepper, M. *Anal. Bioanal. Chem.* **2007**, *387*, 2255-2262.
(6) Castro, K.; Perez-Alonso, M.; Rodriguez-Laso, M. D.; Fernandez, L. A.; Madariaga, J. M., e-VIBRATIONAL SPECTROSCOPIC DATABASES In *Anal. Bioanal. Chem.*, 2005; Vol. 382, pp 248-258.
(7) Brown, M. P. *Understanding Illuminated Manuscripts: A Guide to Technical Terms*; The J. Paul Getty Museum and the British Library, 1994.