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Case study

An integrated approach to the study of a reworked painting "*Madonna with child*" attributed to Pietro Lorenzetti

Andrea Atrei [a], Francesca Benetti [a], Susanna Bracci [b], Donata Magrini [b], Nadia Marchettini [a,*]

[a] *Dipartimento di Chimica Università di Siena, Via Aldo Moro 2, 53100 Siena, Italy*
[b] *Istituto per la Conservazione e Valorizzazione dei Beni Culturali-Consiglio Nazionale delle Ricerche (ICVBC-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy*

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ABSTRACT

The painting "*Madonna with Child*", attributed to Pietro Lorenzetti (14th century) and reworked around the middle of the 16th century, was studied by several techniques in order to characterize the materials used in the original and in the repainted areas. FORS, light microscopy, ESEM-EDX, ToF-SIMS and GC-MS were used. Red ochre and raw sienna earth were identified by FORS in the original parts of the painting. On the repainted parts of the panel, cinnabar, ultramarine blue and lead white were found. By means of GC-MS and ToF-SIMS measurements it was possible to identify the organic binding media used in the preparatory and painted layers.

1. Introduction

The painting "*Madonna with Child*" (Fig. 1), attributed to Pietro Lorenzetti [1], now in the *Pinacoteca Nazionale* of Siena (Italy), represents the Virgin Mary and Child. In the 16th century the painting underwent restoration, which completely changed the original style of Lorenzetti, and two lateral panels were added. Different pictorial styles are clearly discernible. The flesh tones of the two figures are all that remains of Lorenzetti's style. The other areas of the panting have been completely covered by an artist of the Siena School, known as *Maestro delle Monache di Santa Marta* [2].

2. Research Aims

The painting was subject to a diagnostic campaign during restoration, aimed at characterizing the pigments, binding media and painting techniques used by Lorenzetti and *Maestro delle Monache di Santa Marta*. To identify the pigments, a preliminary investigation of various areas of the painting was carried out by fibre optics reflectance spectroscopy (FORS) [3,4]. Light microscopy (LM) and environmental scanning electron microscopy (ESEM) with energy dispersive X-ray (EDX) spectroscopy were used to determine the sequence of layers and their chemical composition, on cross-sections of samples taken from significant areas of the painting. The organic binding media were characterized by chromatography coupled with mass spectrometry (GC-MS). Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to characterize the inorganic and organic components, as well as their spatial distribution in the cross-sections. ToF-SIMS, a relatively new analytical method in the field of cultural heritage studies, makes it possible to simultaneously determine the nature and spatial distribution of organic and inorganic components in a single measurement run [5–7]. However, surface contamination and sample preparation may affect surface composition results because ToF-SIMS is very surface-sensitive. To clarify this point, ToF-SIMS results were compared with those obtained by well-established techniques, such as SEM-EDX and GC-MS.

3. Experimental

3.1. Sampling

Before restoration, six samples were taken from the edges of existing lacunae in the painting in close collaboration with the restorers. The sampling areas are shown in Fig. 1. Cross-sections were prepared embedding the fragments in epoxy resin (*Epofix resin*, Struers). After curing, they were polished using silicon carbide paper with different grit sizes (P200, P400, P800, P1200).

* Corresponding author.
E-mail address: nadia.marchettini@unisi.it (N. Marchettini).

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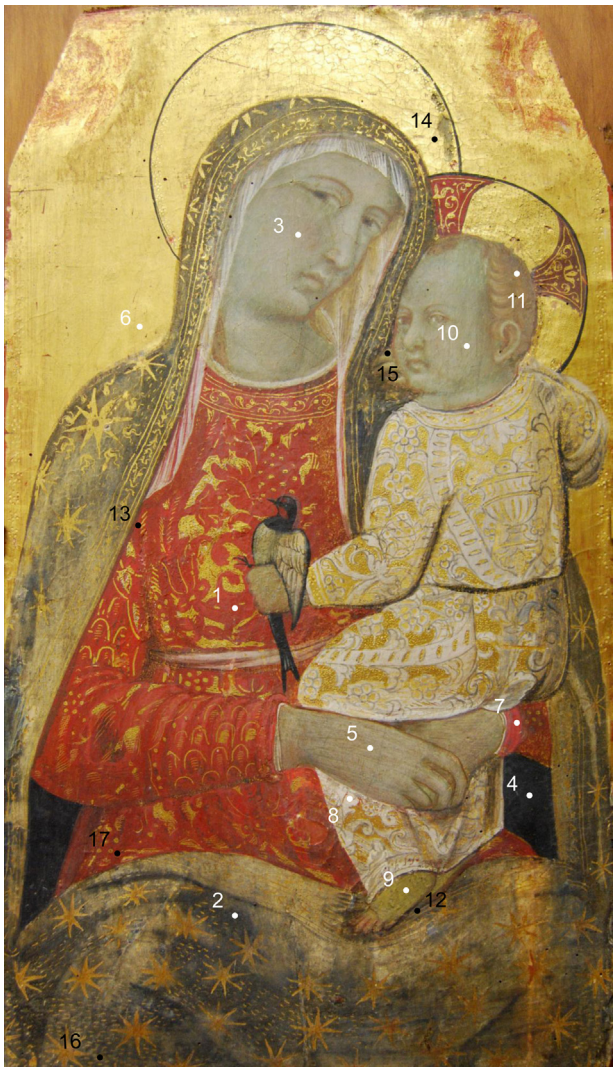

Fig. 1. The painting "*Madonna col Bambino*" by Pietro Lorenzetti and *Maestro delle Monache di Santa Marta*, Pinacoteca Nazionale di Siena (Italy), inventory no. 161, showing the analysis spots (**1–11** in white) and sampling areas (**12–17** in black).

3.2. Fibre optics reflectance spectroscopy (FORS)

The FORS measurements were performed with an Ocean Optic (*mod. HR2000*) spectrophotometer equipped with optical fibres and a tungsten lamp as light source. A measurement head with illumination at 0° and signal collection at 45° allowed acquisition of reflectance spectra from an area of approximately 2 mm^2. The map of FORS measuring points is reported in Fig. 1.

3.3. Light microscopy

The cross-sections were observed and photographed with a Nikon Eclipse 600 light microscope, equipped with an UVa source (λ_{exc} 330-380 nm), to characterize their morphology, identify the stratigraphic sequence and check for materials fluorescent to UV light.

3.4. Environmental scanning electron microscopy with energy dispersive probe

A Quanta200 FEI/Philips Electron Optic microscope equipped with an EDX microanalysis system was used for ESEM measurements. Operating in "low vacuum" mode, it was possible to perform SEM measurements without metallization of samples. Images were constructed from backscattered electrons. The energy of the primary electron beam was 25 keV.

Table 1
Summary of analysis spots (1–8, marked in white in Fig. 1) and sampling points (12–17, marked in black in Fig. 1) with short description, measurement techniques and FORS results. The FORS spectra were interpreted by the comparison with those of reference pigments.

Analysis spots/sampling points	Description	Technique	Results
1	Red robe of Virgin	FORS	Cinnabar
2	Blue drapery of Virgin	FORS	Ultramarine blue
3	Flesh tones of Virgin	FORS	Raw sienna earth and red ochre
4	Black reverse of drapery	FORS	Non identified
5	Hand of Virgin	FORS	Raw sienna earth
6	Gold background	FORS	Gold
7	Sleeve cuff of red robe	FORS	Cinnabar
8	White decoration of Child's robe	FORS	Non identified
9	Foot of Child	FORS	Raw sienna earth and red ochre
10	Flesh tones of Child	FORS	Raw sienna earth and red ochre
11	Child's hair	FORS	Raw sienna earth
12	Blue drapery of Virgin	LM, SEM-EDS, ToF-SIMS	See text
13	Red robe of Virgin	LM, SEM-EDS, ToF-SIMS	See text
14	Gold halo of Virgin	LM, SEM-EDS	See text
15	Hand of Child	GC-MS	See text
16	Blue drapery of Virgin	GC-MS	See text
17	Red robe of Virgin	GC-MS	See text

3.5. Gas chromatography coupled with mass spectrometry

A Focus gas chromatographer coupled to a DSQ II with single quadrupole mass spectrometer (Thermo Scientific) and split-splitless injector was used for GC-MS analysis. The preparation method was a combined procedure for the determination of drying oils and proteinaceous materials on the same sample, as described elsewhere [8–10].

3.6. Time-of-flight secondary ion mass spectrometry

ToF-SIMS measurements were performed with a TRIFT III instrument (Physical Electronics, Chanhassen, MN, USA) equipped with a liquid metal gold primary ion source. Au^+ ion beam energy was 22 keV and beam current 600 pA. Positive and negative spectra were acquired in high mass resolution mode. The typical mass resolution, $m/\Delta m$, in the range of interest was around 2000. Ion images were acquired with a primary ion dose density of 10^{11} ions/cm^2, i.e. below the static SIMS mode [11], and a lateral resolution of about 2 μm.

4. Results and discussion

The FORS results are summarized in Table 1. In the original areas of the painting, FORS revealed red ochre and raw sienna earth, whereas cinnabar, raw sienna earth and ultramarine blue were detected in the repainted areas.

The LM images of the cross section from the Virgin's golden halo (sample 14, Table 1) showed three layers: a white ground layer (a), an intermediate orange preparatory layer (b) and a thin metallic surface layer (c) (Fig. 2, top left). The ground layer showed strong UV fluorescence. SEM-EDX analysis showed two regions with different textures in the ground layer (fine and coarse grained) but