Beyond the youth smile: Investigating techniques and materials in Caroto's paintings by analytical single-point analyses and IR reflectography in full-field

(Original research)

Beyond the youth smile: investigating techniques and materials in Caroto's paintings by analytical single-point analyses and IR reflectography in full-field

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Highlights

- Giovan Francesco Caroto, an Italian late-Renaissance painter not deeply studied yet
- Twenty representative paintings analysed by XRF, FORS and IR reflectography
- A reliable *in-situ* non-invasive protocol based on joined spectroscopy and imaging
- Painting described at the multidisciplinary level from underdrawing to the palette
- Confirm historical sources about the painter thanks to pigments characterisation

Abstract

Giovan Francesco Caroto was a famous Renaissance who played a fundamental role in Venetian painting at the turn of the 15th and 16th centuries. Despite this, just a few of his works have been studied in depth with a multidisciplinary approach between art history and scientific diagnostics. In this study, twenty paintings spanning almost forty years of his entire production in different areas of Northern Italy were analysed. The occasion for this study was the monographic exhibition dedicated to Caroto in Verona, in the halls of the Palazzo della Gran Guardia, in 2022. The research project focused on the application of non-invasive and *in-situ* techniques on a large number of paintings, following a consolidated protocol from imaging to spectroscopic analyses. The goal was to transition the local determination into a whole pattern analysis through a chemometric statistical evaluation. Indeed, it was possible to gain an overview of the material dimension of the artist by correlating chemical data with the year and place of production. This was achieved by overlapping Vis-IR imaging data with a high number of surface analyses (UV-Vis-NIR fibre optics reflectance spectroscopy -FORS-), and stratigraphic elemental analyses (XRF spectrometry). A multi-layer reading of the analysed works was proposed from the preparatory layer to the glaze and surface finish. Full-field IR reflectography allowed the *corpus* analysed to be considered in its entirety, discriminating original materials and retouchings, for the identification of the areas most representative for chemical analyses. The application of this protocol, along with the cross-discussion of the data acquired, and the comparison with historical sources enabled the identification of the artist's palette and its evolution over time. Moreover, the determination of minerals and minor elements in pigments traced Caroto's movements between Verona and Casale Monferrato, also providing information on material supply habits.

Keywords

Non-invasive protocol, XRF, FORS, IR reflectography, Renaissance pigments, ochre pigments

1. Introduction

Giovan Francesco Caroto was an Italian artist (ca 1480-1555) who embodied the spirit of the Italian Renaissance with his curiosity. He drove the first manner to the late results among Verona, Milan, Mantua, and the Monferrato region, and was renowned for his innovative approach. As the owner of an apothecary workshop, he hung out with humanists, naturalists, and scientists and was himself open to new frontiers and experimentation. Scholar of Andrea Mantegna, and influenced by masters such as Leonardo da Vinci, Michelangelo Buonarroti and Raffaello Sanzio, Caroto refined his style over time, previously more classical and severe. His late production bore the imprint of Giulio Romano who he met between Mantua and Verona [1]. Altogether, these events make Caroto a famous artist in the Verona region, being today one of his artworks, 'A child with a drawing', one of the symbols of Verona civic heritage. Interestingly, this masterpiece inspired the description of a medical rare condition known as Angelman syndrome [2].

Despite Caroto's significance in the Italian artistic landscape, his body of work remains relatively unexplored in terms of materials characterisation and painting technique. In the international literature, there is only an in-depth analysis of one of the artworks owned by the Louvre Museum [3], with a particular focus on the blue washes, whose pigments and stratigraphy were studied. Unfortunately, investigations carried out during conservation events on other Caroto's paintings are limited. Condition reports or pieces of thesis may mention actions taken [4], but analytical data have not been exhaustively discussed.

Nowadays, it is a validated practice among museums, art collectors, and scholars to approach paintings through a non-invasive analytical protocol [5,6], possibly with a multidisciplinary panel to better understand artists' production in terms of material and art concept. Indeed, the scientific method offers valuable tools for understanding the creative process of the artist thanks to techniques such as infrared imaging to uncover underdrawings and *pentimenti* and joined single-point spectroscopies to determine the chemical composition of the palette [7,8]. This analytical protocol may also shed light on past conservation treatments not always properly recorded, or changes that occurred to the drawing due to damages or variations of taste over the centuries [9].

Research aim

The exhibition "Caroto e le arti tra Mantegna e Veronese"[1] showcased a great number of artworks from public and private collections attributed to or signed by Caroto. Such a relevant monographic exhibition presented the opportunity to characterise Caroto's palette, preparation techniques and underdrawing methods, which have not yet been systematically explored. Twenty paintings spanning nearly his entire career were selected as representative of the artist's materials and technique, ranging from 1501 ('Madonna cucitrice' the earliest painting confidently attributed) to the 1540s. However, being a challenge, the context of the analytical campaign was defined by the exhibition environment: halls dedicated to a temporary exhibition with no possibility to avoid daily light, open to the public, lack of sampling authorisation, and no possibility to remove cases when present or relocate paintings. Despite these constraints, a massive multispectral imaging campaign was possible. The focus was on optimizing a diagnostic protocol based on in-depth elaboration of single-point spectroscopic data guided by full-field IR imaging. This approach aimed at extracting information comparable to that obtained through invasive -and destructive- microscopical imaging and cross-section analyses.

[1] "Caroto and the arts, from Mantegna to Veronese", held at Palazzo della Gran Guardia, Verona (Italy), May 13, 2022 – Oct 2, 2022 [1]

2. Materials and methods

Analytical protocol

The *in-situ* diagnostic workflow included full-field imaging in the visible and infrared (Vis-IR) range and single-point spectroscopy in representative regions.

High-resolution images in the Vis and NIR band were captured using a modified full spectrum CMOS camera (32 MP Nikon D800 supplied by CHSOS) equipped with filters (bandpass Vis 400-700 nm, long pass IR> 900 nm). Infrared reflectography (IRR) was conducted in the 900-1700 nm range using InGaAs cameras by Opus Instruments (Osiris model –8-bit, 16MP and Apollo model –16-bit, 26MP). Paintings were lit up with two halogen lamps positioned one meter away at a 45° angle on both sides of the artwork. Standard image calibration was performed using a colour checker and the reflectance-certified standard Labsphere®, both placed within the scene.

Based on the imaging data, regions that seemed homogeneous were selected and further examined through single-point analyses to define the palette of each painting, thereby creating a representative pool of points covering all colour hues. The paintings under study, along with the selected points for chemical characterisation, are reported as Supplementary Materials (Figs. S1-20).

Fibre optic reflectance spectroscopy (FORS) was performed using the Ocean Optics HR2000 spectrometer (Dunedin, Florida) with a spectral range of 200-1100 nm and a spectral resolution of 0.5 nm. A double deuterium-halogen source DH-2000-BAL was directed onto the sampling area (1 mm diameter) via a fibre optic connected to a DINOLITE (Almere - The Netherlands) digital microscope equipped with a camera (resolution of 5.0 MP and magnification from 400x to 470x) useful to verify the degree of homogeneity of the colour field or the presence of pigments mixture. Acquisition integration time was set at 40 ns, except for darker areas where it was increased to 700 ns. The resulting spectra represent the average of 100 curves. Calibration was performed with the Labsphere® standard. Data processing (normalisation and spectral smoothing) was carried out with Origin®(OriginLab), with the first derivative or the relative absorbance (log 1/R) of the curve calculated when necessary. The former operation allowed to highlight inflection points characteristic of yellow, red, and brown pigments spectra, whereas the latter was calculated for green and blue pigments, to evaluate the position of maximum relative absorption. The obtained values were compared with the literature [10-12].

XRF (X-Ray Fluorescence) analyses were conducted using a portable instrument (East Greenbush, NY, USA) model XL3T GOLDD, equipped with a silver (Ag) target with a maximum current of 100 µA and voltages ranging between 8 and 50 kV. The detector was a Large Drift Detector (LDD) with a surface area of 25 mm^2 and an energy resolution of 135 eV @Mn Kα. A 30°/30° geometry with a working distance of 2 mm was employed. Each analysis consisted of four sequential measurements using four voltages and three different filters to enhance material response across the spectrum energy range. The specified conditions were as follows: main Al/Fe (40 kV); low Cu, 20 kV; high Mo (50 kV); light no filter (8 kV). The analysis was carried out on an ellipsoidal area with a maximum diameter of 3 or 8 mm, displayed using a CCD camera. The obtained data were compared with background acquisitions at the same live time and with certified reference materials (NIST, SGT, CORNING, MBH).
All measurements were conducted three times and averaged over the final value. The acquired spectra were processed with the commercial software Baxil (Brightspec NV/SA, Belgium), derived from the academic software QXAS (IAEA). A mixed analysis algorithm was applied involving the treatment of the matrix through a fundamental parameter approach (FP) scaled on comparison with a series of standards that allows to take into account the peculiarities of portable instrumentation. Matrix interactions, as well as the effects of secondary fluorescence and self-absorption, were considered through the use of a system of nonlinear

equations and relative minimization of their correlation coefficients formulated by De Jong [13]. Consequently, data are considered quantitative, although attention must be paid to their representativeness due to the unpredictable thicknesses of layers and potential influences from the support. The results are expressed as absolute percentage weight on the analyzed volume.

All results were subjected to a threshold of 0.01%, considered as the detection limit (LLD) for all elements (except aluminium, for which 0.5% was applied) [14]. This is a prudential limit, given that the instrumental sensitivity stands at tens of parts per million (ppm) [15]. In some cases, such as the simultaneous presence of sulphur and lead, the interference is too important, rendering quantification impossible.

Once elaborated, data from single-point analyses were treated through statistical methods for reducing the space of variables, capable of allowing the definition of classes useful to evaluate the presence of glazes, pigment mixtures, preparation layers and provenience. K-means clustering method was used to define groups characterized by different amounts of lead and tin based on the Euclidean distances of their centroids. The number of clusters was determined using a segmentation method (Elbow method).

Studied paintings

Twenty representative paintings on canvas and panels were analysed (Tab. 1). The selection spanned over the whole artist's production represented within the exhibition (1501-ca1540). Towards the end of his life (the last fifteen years), Caroto's production decreased, while his younger scholars, such as Paolo Veronese, were acquiring fame. The final artworks were created for the decoration of altars, often large in size and not easily accessible [1]. Additionally, the decision of the curators was not to request the relocation of artworks for the exhibition (those not frescoes) to encourage visitors to explore the original locations in Verona. The project prioritized paintings with comparable subjects and iconography to establish a cohesive narrative of Caroto's drawing and technique. It is worth remembering that FORS and XRF analyses were subjected to the permissions granted by the owners of the artworks since require intimate contact with the surface.

Table 1: Caroto's paintings analysed and analyses carried out [1], images are reported in Supplementary Materials;

Title	Year	Ownership	Support	Analyses
Madonna con il Bambino e san Giovannino (Madonna cucitrice), Madonna with Child and St. John (Stitcher Madonna) (Fig.S1)	1501	Modena, Galleria Estense, IT	Wooden panel	Vis, IRR, FORS, XRF
Adorazione del Bambino, Adoration of the Child (Fig.S2)	1500/10	Verona, Museo degli affreschi G.B. Cavalcaselle, IT	Canvas	Vis, IRR
Tre arcangeli, Three archangels (Fig.S3)	1512/13	Verona, Museo degli affreschi G.B. Cavalcaselle, IT	Wooden panel	Vis, IRR, FORS, XRF
Madonna della farfalla, Madonna of the Butterfly (Fig.S4)	1510/15	Verona, Museo di Castelvecchio, IT	Wooden panel	Vis, IRR, FORS, XRF
Madonna della farfalla, Madonna of the Butterfly (Fig.S5)	1510/15	Private collection	Wooden panel	Vis, IRR, FORS, XRF
Compianto sul Cristo morto, Lamentation over the Dead Christ (Fig.S6)	1515	Private collection	Wooden panel	Vis, IRR, FORS, XRF
San Sebastiano, Saint Sebastian (Fig.S7)	1515/18	Casale Monferrato, Santo Stefano church, IT	Canvas	Vis, IRR, FORS
Deposizione (Cristo deposto), Deposition (Christ Deposed) (Fig.S8)	1515/25	Milano, Castello Sforzesco, IT	Canvas	Vis, IRR, FORS, XRF

Pietà della lacrima, Pity of the tear (Fig.S9)	1520/24	Verona, Museo di Castelvecchio, IT	Canvas	Vis, IRR, FORS, XRF
Sofonisba, Sophonisba (Fig.S10)	1520/25	Verona, Museo di Castelvecchio, IT	Canvas	Vis, IRR
Madonna cucitrice, Stitcher Madonna (Fig.S11)	1520/25	Venezia, Gallerie dell'Accademia, IT	Canvas	Vis, IRR, FORS
Ritratto di giovane monaco benedettino, Portrait of a young Benedictine monk (Fig.S12)	1520/25	Verona, Museo di Castelvecchio, IT	Canvas	Vis, IRR
Ritratto di fanciullo con disegno, A child with a drawing (Fig.S13)	1523	Verona, Museo di Castelvecchio, IT	Wooden panel	Vis, IRR
Santa Caterina d'Alessandria, St Catherine of Alexandria (Fig.S14)	1525	Verona, Museo degli affreschi G.B. Cavalcaselle, IT	Canvas	Vis, IRR
Natività di Maria, Nativity of Mary (Fig.S15)	1527	Bergamo, Accademia Carrara, IT	Wooden panel	Vis, IRR, FORS, XRF
L'arcangelo Michele caccia Lucifero, Archangel Michael drives out Lucifer (Fig.S16)	1531/34	Verona, Museo degli affreschi G.B. Cavalcaselle, IT	Canvas	Vis, IRR, FORS, XRF
Tentazione di Cristo, Temptation of Christ (Fig.S17)	1531/34	Verona, Museo degli affreschi G.B. Cavalcaselle, IT	Canvas	Vis, IRR, FORS, XRF
Sacra Famiglia con santa Elisabetta e san Giovannino, Holy Family with St. Elizabeth and St. John child (Fig.S18)	1531	Verona, Museo degli affreschi G.B. Cavalcaselle, IT	Canvas	Vis, IRR, FORS, XRF
Madonna con il Bambino e san Giovannino, Madonna and Child with St John child (Fig.S19)	1530/40	Verona, Museo degli affreschi G.B. Cavalcaselle, IT	Canvas	Vis, IRR
Madonna con il Bambino con i santi Giovanni Battista e Cristoforo, Madonna and Child with Saints John the Baptist and Christopher (Fig.S20)	1530/40	Pavia, Pinacoteca Malaspina, IT	Canvas	Vis, IRR, FORS, XRF

3. Results and discussion

The preparation layer and the imprimitura

In Renaissance painting, it was common practice to apply a preparation of gypsum and glue in one or more layers on the paint supports, which could be covered with an additional white lead (*biacca,* $[(PbCO_3)_2{\cdot}Pb(OH)_2]$) in oil layer (*imprimitura*), sometimes supplemented with other pigments to prepare coloured bases [16]. Thanks to XRF analysis, these preparation layers were detectable and described (Tab. 2).

Painting		**Support**	**Preparation layer**	***Imprimitura***		
Title	*Year*		*Thickness*	*Pb %*	*Sn %*	*Sn/Pb*100*
Madonna with Child and St. John (Stitcher Madonna)	1501	WP	thin	0.4	-	-
Three archangels	1512/13	WP	middle	4.0	0.07	1.8
Madonna of the Butterfly, civic collection)	1510/15	WP	thin	4.7	0.11	2.5
Madonna of the Butterfly,	1510/15	WP	thin	3.5	0.11	3.1

(private collection)						
Lamentation over the Dead Christ	1515	WP	middle	1.9	0.03	1.7
Deposition (Christ Deposed)	1515/25	C	middle	15.8	0.72	4.6
Pity of the tear	1520/24	C	thick	1.0	-	-
Nativity of Mary	1527	WP	thin	24.9	0.34	1.3
Temptation of Christ	1531/34	C	middle	4.2	-	-
Archangel Michael hunts Lucifer	1531/34	C	thick	4.3	-	-
Holy Family with St. Elizabeth and St. John child	1531	C	middle	0.9	-	-
Madonna and Child with St John child	1530/40	C	middle	0.6	-	-

Table 2: composition of preparation layers in the analysed paintings based on XRF analyses, showing the percentage data of lead (Pb) and tin (Sn); legend for the support material: WP wooden panel, C canvas

The stratigraphic analysis, conducted through a machine learning approach of the XRF data, revealed systematic trends in the content of calcium (Ca) and lead (Pb) elements, corresponding respectively to a plaster/glue preparation and the *imprimitura*. Specifically, the determination of the presence or absence of gypsum [$CaSO_4 \cdot 2H_2O$], along with the establishment of the percentage threshold values for lead relative to the *imprimitura* layer (either related to its thickness and/or density), enabled correlations between different paintings to the point that they can be identified on the base of the period or place of construction.
Through an unsupervised machine learning algorithm used for clustering the quantitative values of the elements, several groups differentiated by the variables Pb and Sn were identified in areas where lead was not associated with the paint layer as a white or yellow pigment (§*The palette*, follows). Exclusion of these pigments at the surface level by comparison with digital microscopy and FORS spectroscopy data provided insight into the possible distribution of lead in the depth profile.
Average percentage values of lead associated with the practice of *imprimitura* were calculated and correlated with the amount of lead in the *biacca* layer (thickness, density), considering all errors related to absorption and secondary fluorescence phenomena generated by all the layers above.
Thus, having established that the emission of X-rays attributable to the L lines of lead comes from all possible layers above the support, and having determined the concentration values by weight for the entire analysis volume, the subsequent machine learning analysis proceeded. Through the definition of the number of clusters using the elbow method, it was possible to identify a series of groups based on the lead concentration, correlated to different chromatic areas for each painting. The chromatic difference for the larger areas was achieved using multispectral imaging and microscopic observations.
The best representation of the data was achieved through a histogram that defined the average lead concentration for each area in each painting (as reported in Figure 1**Errore. L'origine riferimento non è stata trovata.***Figure 2*), followed by a summary graph that considered only the variation in lead relative to the lowest average lead values found in each painting. The same procedure was applied to the tin concentrations by weight, allowing the evaluation of a possible correlation between the minimum average lead value and the minimum average tin value for each painting (Table 2).

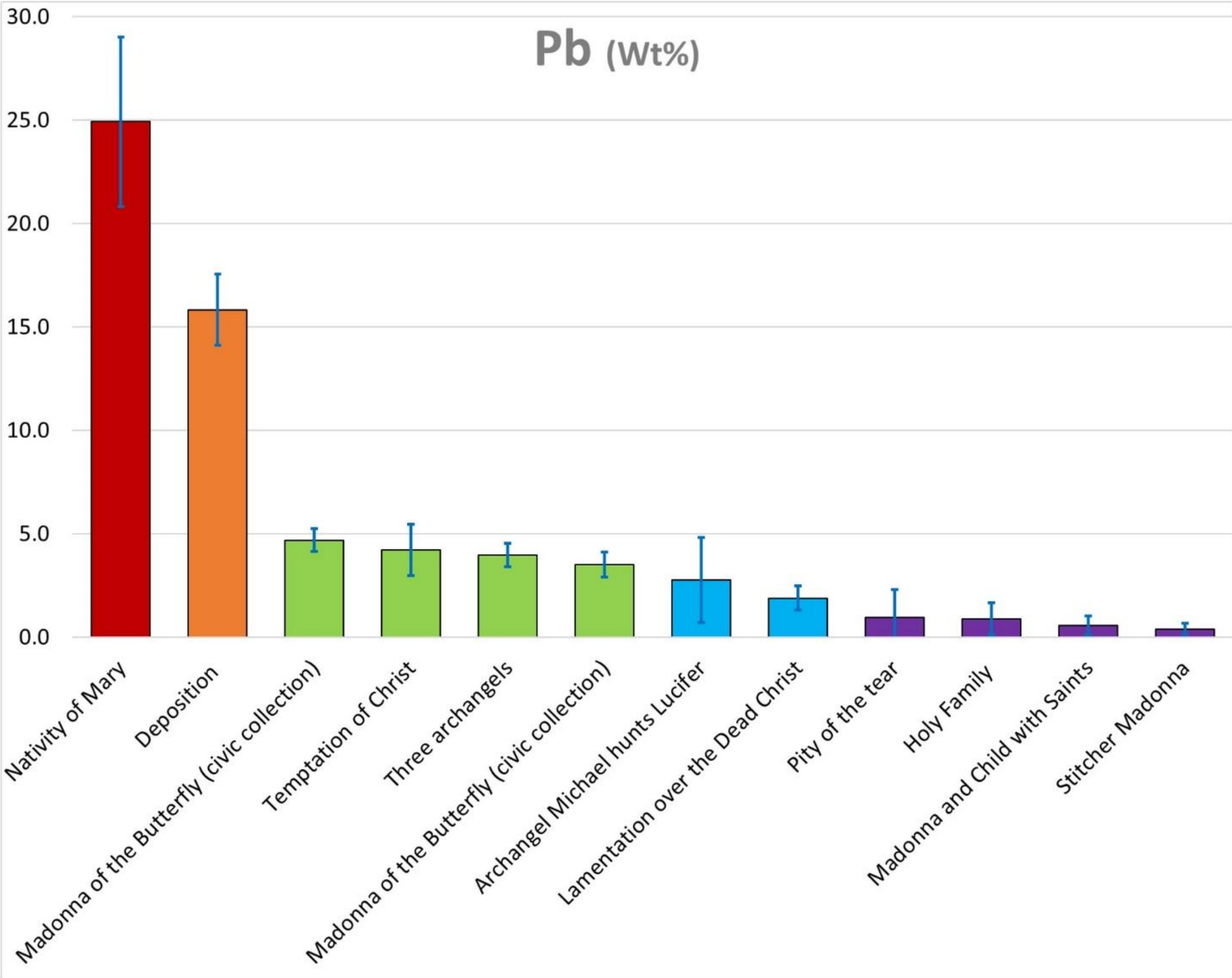


Figure 1: averaged percentage of Lead concentration due to the imprimitura layers

Giving an example, in the painting 'Three Archangels' a graph of this type (Figure 2) was obtained, where typical concentration values are visually identified, indicating a background (especially where the areas are dark or black), an intermediate value derived from areas affected by mixing with lead white to lighten the hue, and a third higher value referable to white areas.

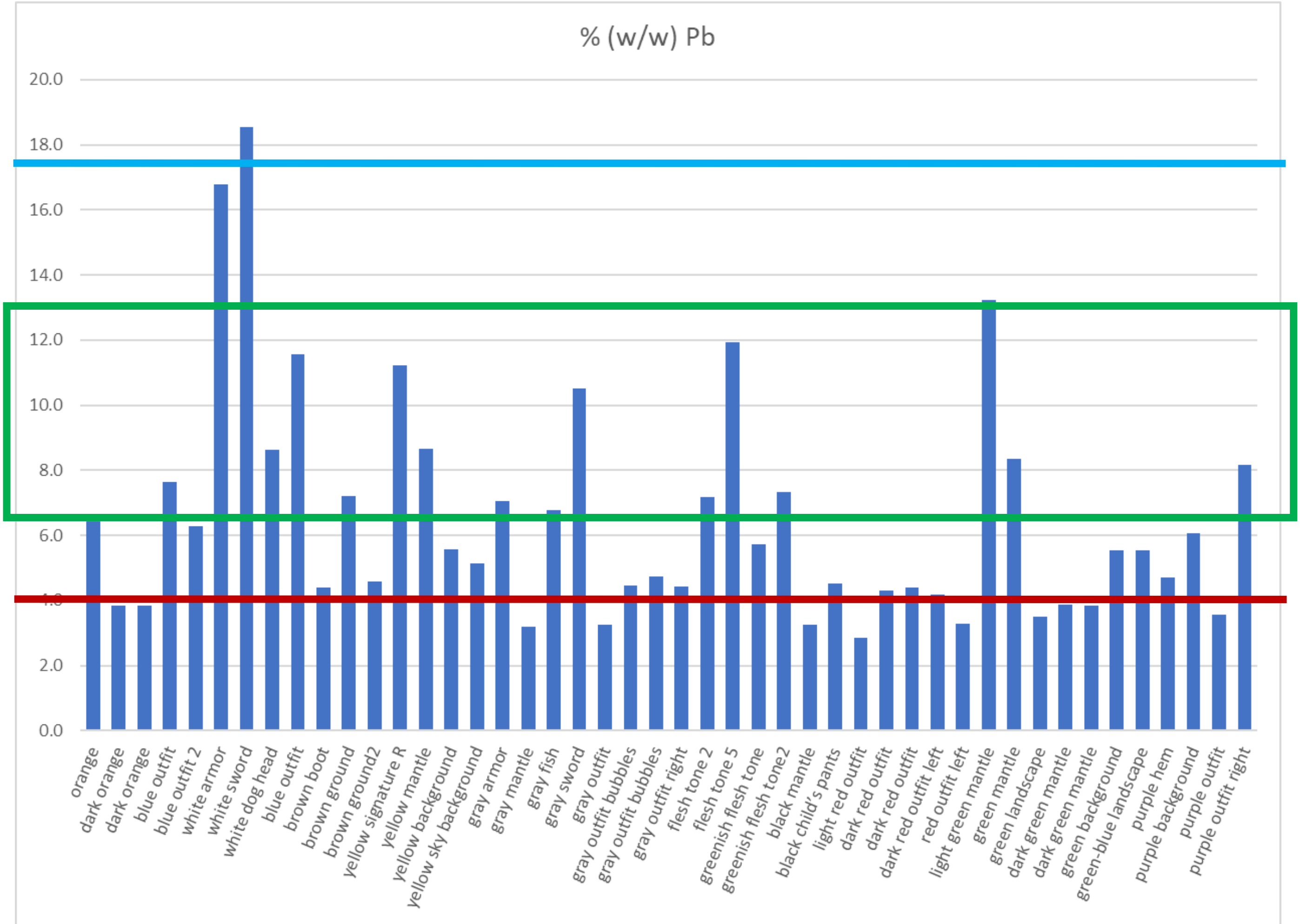


Figure 2: percentage concentration values of Pb in the different chromatic areas of the painting 'Three Archangels'; three XRF measurements were collected for each represented area.

It was not intended to define lead concentrations in what are probably pigments mixtures, where the concentration may still vary, but rather to determine a threshold of minimum values (clearly visible in the black or dark areas) that can be attributed to a preparatory layer underlying the pictorial one. The variation of these values according to the absorption of the overlying-coloured layers confirms that it is a ground layer. In this case, the minimum average lead value is around 4.0% (wt/wt).

Errore. L'origine riferimento non è stata trovata. displays the average Pb values correlated to the different paintings. Considering the most common measured value (4.1%) as an internal reference, it can be observed (Tab.2) that there are at least five distinct groups, one with nearly negligible lead values (0.7%), and others ranging between 15% and 25%.

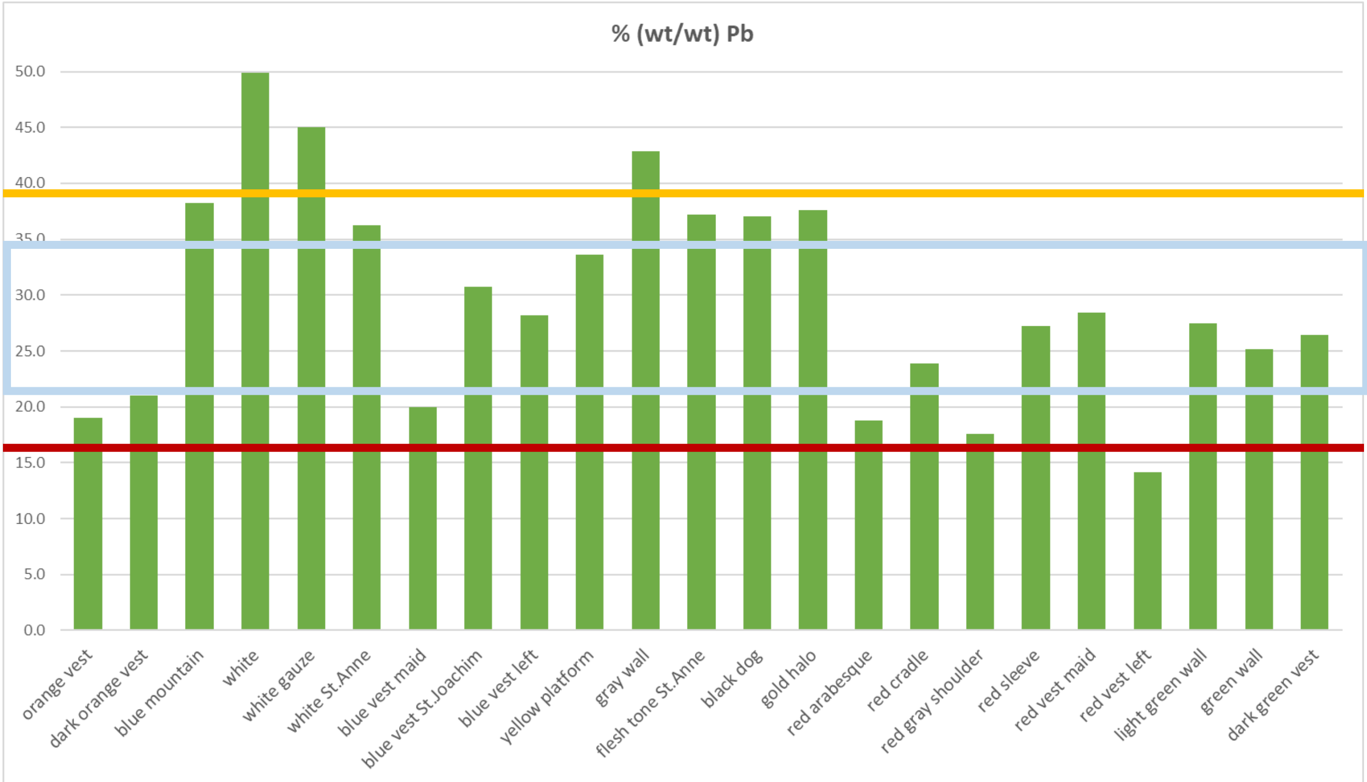
This datum provides insight into how the paintings were prepared by the painter or his workshop. In some cases, the high quantity of white lead, differing from the average values used in Caroto's works, may suggest the common practice of reusing supports with a second *imprimitura* process.

The same elaboration method was applied for the determination of tin (Sn) contents in the *imprimitura* layer, with the results (also shown in Table 2 as the percentage by weight) indicating different support preparation methods. This could be attributed to a change in the artist's technique or, more likely, changes over time in the preparation process of the support before it came to the artist.

The systematic correlation between Sn and Pb in the preparation led to two different hypotheses, one purely mineralogical and the other artistic. In the first case, it could be assumed that the lead ore used for the *imprimitura* contains a certain associated percentage of tin, suggesting a common source and/or supply market for the material used in the process of *imprimitura*.

On the other hand, the artistic technique involving the addition of *giallorino* (tin-lead yellow, [Pb_2SnO_4]) to the *biacca* for the *imprimitura* links all artworks directly to the artist based on the preparation of the supports. This consideration extends to artworks where the tin content is not evaluable, assuming its concentration is below the XRF detection limit due to the low lead values. By discussing the lead and tin data in relation to different paintings, it became apparent that for two works from the same period, 'Archangel Michael drives out Lucifer' and 'The temptation of Christ', the *imprimitura* layer thickness appears similar to those typically realised by the artist but did not present any tin contamination.
Another example might be the painting ‘Nativity of Mary’, where the same procedures guided to completely different values. As shown in Figure 3, the percentage concentration values of lead are higher than those determined in the previous case.
Although it is still possible to define clusters attributable to the pictorial layers and the preparation layer, the latter shows a rather high average value, which stands at 24.9% (wt/wt). One possible explanation is the artist’s reuse of the wooden panel, resulting in a more complex stratigraphy with a lower previous layer made of *biacca* without Sn, overlaid by a second layer (in this case with detected Sn content).

Figure 3: percentage concentration values of Pb in the different chromatic areas of the painting ‘Nativity of Mary’; three XRF measurements were collected for each represented area.



The underdrawing

The underdrawing primarily resulted from the transfer of the drawing from a primary cartoon. Caroto typically employed the *ricalco* technique to transfer the drawing onto the *imprimitura* (i.e., reporting the main lines of the drawing onto a transparent sheet later coated with carbon powder, which was then placed on the *imprimitura* and the lines traced again) (Figs.4,5). Only once the *spolvero* method was observed (Fig. 4d), with slight shifts noted during this process. The popularity of certain subjects and iconographies is evidenced not only by the use of primary cartoons but also by the existence of paintings with similar scene compositions, such as the ‘Madonna of the Butterfly’, as previously introduced, and the so-called ‘Stitcher Madonna’, with its first version dated to 1501 and the second to 1520/25. A few *pentimenti* were discovered, indicating changes in the silhouettes previously transferred by *ricalco*; examples are shown in Figures 4c, 5c and 5e.

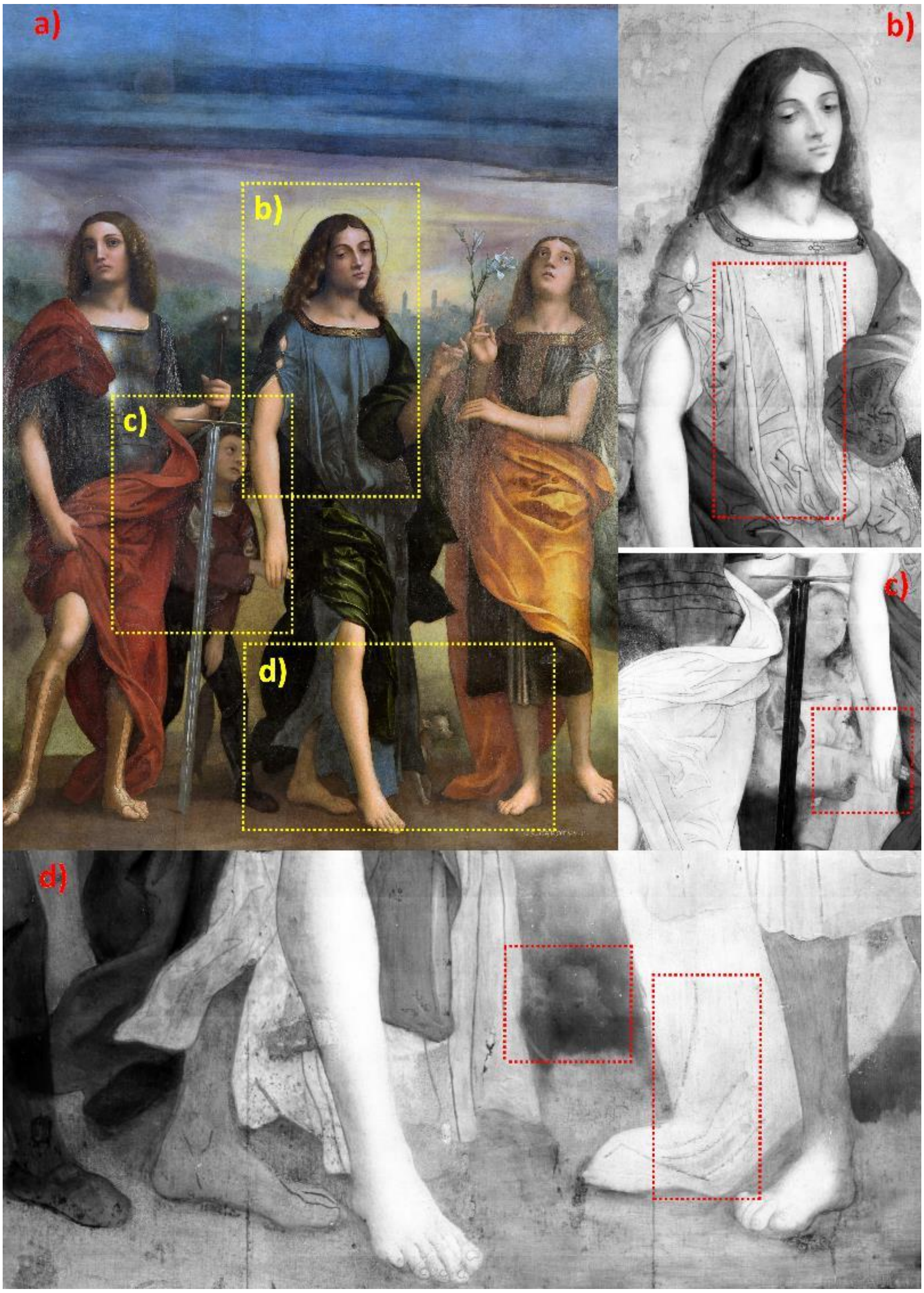


Figure 4: 'Three archangels' a) Vis image, alongside IRR image details) b) ricalco technique used for tracing the vests and lines taken up with a fine brushstroke particularly noticeable in the archangel Raphael's vestment as darker and softer lines; c) a pentimento in the handshake; d) characteristic dots of the spolvero transfer method in the drape of the cloak, whereas the dog appeared as directly painted in the executive phase

Figure 5: 'Nativity of Mary'. a) Vis image; b) IRR image c) pentimento of the on the handkerchief held by the handmaiden and in its shadow; d) construction of the handmaiden's face besides the ricalco transfer technique; e) pentimento in the figure of St. Joachim

Only in one instance, the ‘Deposition (Christ Deposed)’, a small painting resembling a study for a larger painting, revealed Caroto’s refined hand-drawing skills (Fig.6).

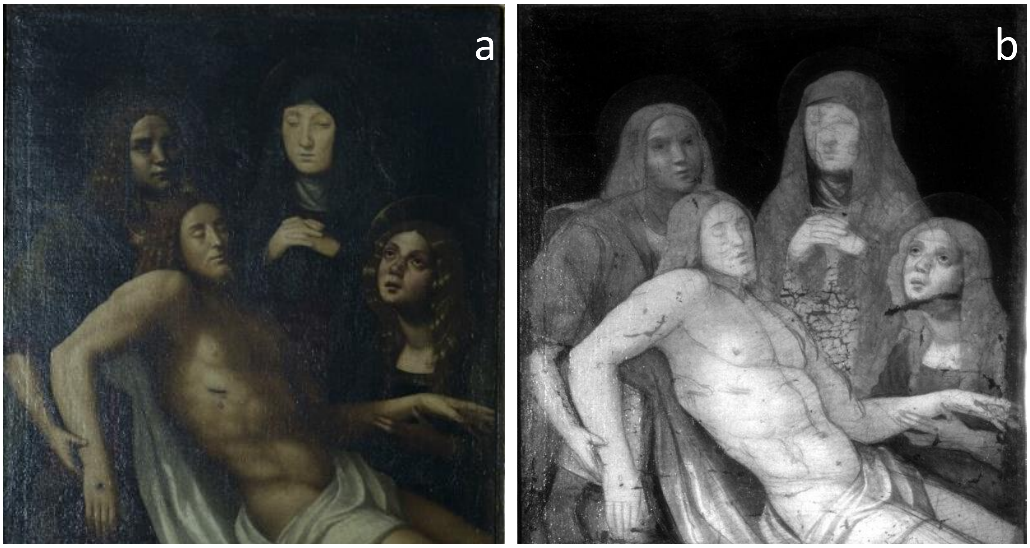


Figure 6: ' Deposition (Christ Deposed)'. a) Vis image; b) IRR image with the freehand underdrawing, clearly modify during the drawing phase in some details such as the face of Christ

The palette

Single-point analyses revealed a precise palette characteristic of the late Renaissance, which evolved in composition over the decades. Caroto began his career with a defined set of pigments, mixing them to

achieve a wider range of shades and colours. Ochres, earth pigments, smalt, azurite, cinnabar (or vermillion if synthetic, but with the employed techniques it is not possible to establish the origin of the pigment), red lake (most likely cochineal), and lead white were consistently used throughout his production. Lapislazuli-derived ultramarine blue, realgar, orpiment, and mineral black were lately introduced.
The presence of carbonates associated with ferrous compounds (e.g., iron oxides, hydroxides), typical of ochres and earth pigments, was observed in nearly all paintings, indicating the use of pigments indigenous of the Verona region [17]. Additionally, yellow areas painted with yellow in the 'Nativity of Mary' exhibited a characteristic derivative relative maximum at 435 nm in their FORS spectra, possibly indicating the presence of natrojarosite [$NaFe_3(SO_4)_2(OH)_6$] as a minor phase [18].
Significant amounts of barium were detected in azurite in four paintings, three of which were executed between 1501 and 1515, suggesting a correlation with the year of execution and possibly a common provenience of the mineral. Similar findings were observed for smalt. In this case, in addition to cobalt (Co) which is the distinctive element of this synthetic blue pigment, characteristic elements such as bismuth (Bi), arsenic (As) and nickel (Ni) were detected, indicating both the origin of the minerals and their purification process. From 1520 production sites of cobalt changed and, in addition to direct mining from ores such as 'cobaltum' also used to obtain As, cobalt was extracted by reworking bismuth slag [19].
In some paintings there are details that can refer to metals (e.g. embroidery made by golden threads, halos -Fig.7a-), whose analyses referred most of the times to lead-tin yellow. However, evidence of metal powders was found in the 'Nativity of Mary', where gold was found in the halo of St. Joachim (Fig.5). In 'Lamentation over the Dead Christ', FORS and XRF spectra led to the hypothesis that the adornment of the brocade of the vest of the figure on the left was realised with bronze powder.

Table 3 summarises pigments identified in the artworks, with the corresponding chemical formula.

Table 3: Caroto's palette according to single-point analytical data; legend: colours W-white, R-red, OR-orange, Y-yellow, O-ochre, BR-brown, B-blue, G-green, BL-black; (#) presence of barium in azurite, (*) presence of bismuth, arsenic and nickel in smalt, underlined the introduction in the palette of a new pigment

Title	Year	Supposed place of painting realisation	Palette [pigment formula]
Madonna with Child and St. John (Stitcher Madonna)	1501	*Verona, IT*	W: Lead white (*biacca*) [$(PbCO_3)_2{\cdot}Pb(OH)_2$] R: Cinnabar [HgS], red lake Y: Lead-tin yellow type I (*giallorino*) [Pb_2SnO_4] O: 'Verona' ochres (light brown, red) [mostly iron oxides and hydroxides] B: Smalt [mostly SiO_2, K_2O, Al_2O_3, and CoO], azurite(#) [$Cu_3(CO_3)_2(OH)_2$] G: Copper resinate [$Cu(CH_3CO)_2 \cdot 2Cu(OH)_2 \cdot nH_2O$ and $Cr_2O_7 . nH_2O$]
Three archangels	1512/13	*Verona, IT*	W: Lead white R: Cinnabar, red lake Y: Lead-tin yellow type II [$PbSnO_3$] O: 'Verona' ochre (light brown, red) B. Smalt, azurite G: Copper resinate, <u>verdigris</u> [$Cu(CH_3COO)_2{\cdot}H_2O$] BL: <u>Bone black</u> [C and $Ca_3(PO_4)$]
Madonna of the Butterfly (civic collection)	1510/15	*Verona, IT*	W: Lead white R: Cinnabar, red lake Y: Lead-tin yellow type II O: 'Verona' ochre (light brown) B: Smalt, azurite(#)

Madonna of the Butterfly (private collection)	1510/15	*Verona, IT*	W: Lead white R: Cinnabar, red lake Y: Lead-tin yellow type II O: ‘Verona’ ochre (light brown) B: Smalt, azurite(#)
Lamentation over the Dead Christ (private collection)–	1515	*Casale Monferrato (Turin), IT*	W: Lead white R: Cinnabar, red lake Y: Lead-tin yellow II BR: Burnt earth (burnt sienna) [$Fe_2O_3 \cdot nH_2O + Al_2O_3$] B: Smalt, azurite (#) G: Verdigris
Saint Sebastian	1515/18	*Casale Monferrato (Turin), IT*	R: Red ochre [iron oxides, mostly hematite FeO] O: Light brown ochre BR: Brown earth G: Verdigris
Deposition (Christ Deposed)	1515/25	*Casale Monferrato (Turin), IT*	W: Lead white R: Cinnabar, red lake, red ochre O: Light brown earth (Sienna) BR: Burnt earth (burnt Sienna) B: Azurite G: Verdigris
Pity of the tear	1520/24	*Verona*	W: Lead white R: Cinnabar, red lake, red ochre Y: Lead-tin yellow type I O: ‘Verona’ ochre (light brown, black) B: Smalt (*), azurite, indigo [$C_{16}H_{10}N_2O_2$] G: Verdigris BL: Bone black
Stitcher Madonna	1520/25	*Verona*	W: Lead white R: Cinnabar, red lake, red ochre OR: Realgar? [As_4S_4] O: ‘Verona’ ochre (light brown) B: Azurite
Nativity of Mary	1527	*Verona*	W: Lead white R: Cinnabar, red lake OR: Realgar Y: Lead-tin yellow II O: ‘Verona’ ochre (light brown, yellow, red) BR: Burnt earth (burnt Sienna) B: Smalt, azurite, ultramarine blue [$2Na_2Al_2Si_2O_6 + NaS_2$] G: Verdigris Gold [Au]
Temptation of Christ	1531/34	*Verona*	W: Lead white R: Cinnabar, red lake O: ‘Verona’ ochre (light brown, red) BR: Raw umber earth B: Smalt (*), azurite BL: Bone black
Archangel Michael drives out Lucifer	1531/34	*Verona*	W: Lead white R: Cinnabar BR: Burnt earth (burnt Sienna) O: ‘Verona’ ochre (light brown, red) B: Smalt (*), azurite

Holy Family with St. Elizabeth and St. John child	1531	*Verona*	W: Lead white, calcium carbonate (‘bianco di San Giovanni’) R: Cinnabar Y: Orpiment [As_2S_3] O: ‘Verona’ ochre (brown, light brown, red) B: Smalt (*), azurite, lapislazuli BL: Mineral black [$Fe^{2+}Al_2O_4$]
Madonna and Child with Saints John the Baptist and Christopher	1530/40	*Verona*	W: Lead white R: Cinnabar OR: Realgar O: ‘Verona’ ochre (brown, light brown, red) B: Smalt (*), azurite (#) BL: Bone black

The case of the two versions of the ‘Madonna of the Butterfly’, painted between 1510 and 1515, is particularly significant as a case of overpainting (Figure 7). The unveiling of the preparatory drawing showed that the works were initially very similar, likely transferred onto the support from the same cartoon, with the throne occupying a significant portion of the foreground. However, the version belonging to the collection of Castelvecchio Museum (Verona) underwent structural modification of the composition later on: the Virgin’s robe, becoming wider, covered the left knob of the throne. XRF data indicate that this complement may have been initially painted, as revealed by a change in the ratio of mercury (Hg, related to cinnabar) and manganese (Mn, related to light brown ochre) in two proximal areas.

The overlay of fluorescence spectra for the two aforementioned areas is shown in Figure 7d. Statistical processing of the quantitative values determined for each analyzed three-dimensional point enabled the creation of homogeneous clusters that define average values for each element across the different areas.

In this particular instance, variations in Mn and Hg concentrations were observed at different points within the red area corresponding to the Virgin's robe in the painting ‘Madonna of the Butterfly’ (civic collection). The results indicated that manganese levels (likely originating from yellow ‘Verona’ ochre) increase only within the boundaries of the preparatory drawing, visible in the IR image, that outlines the throne knob (blue spectrum and purple arrows).

Conversely, outside the boundaries of the preparatory drawing (seen through the IR image) that outlines the throne knob, an increase in mercury concentration was observed, attributable to a greater thickness of the cinnabar layer (red spectrum and green arrows).

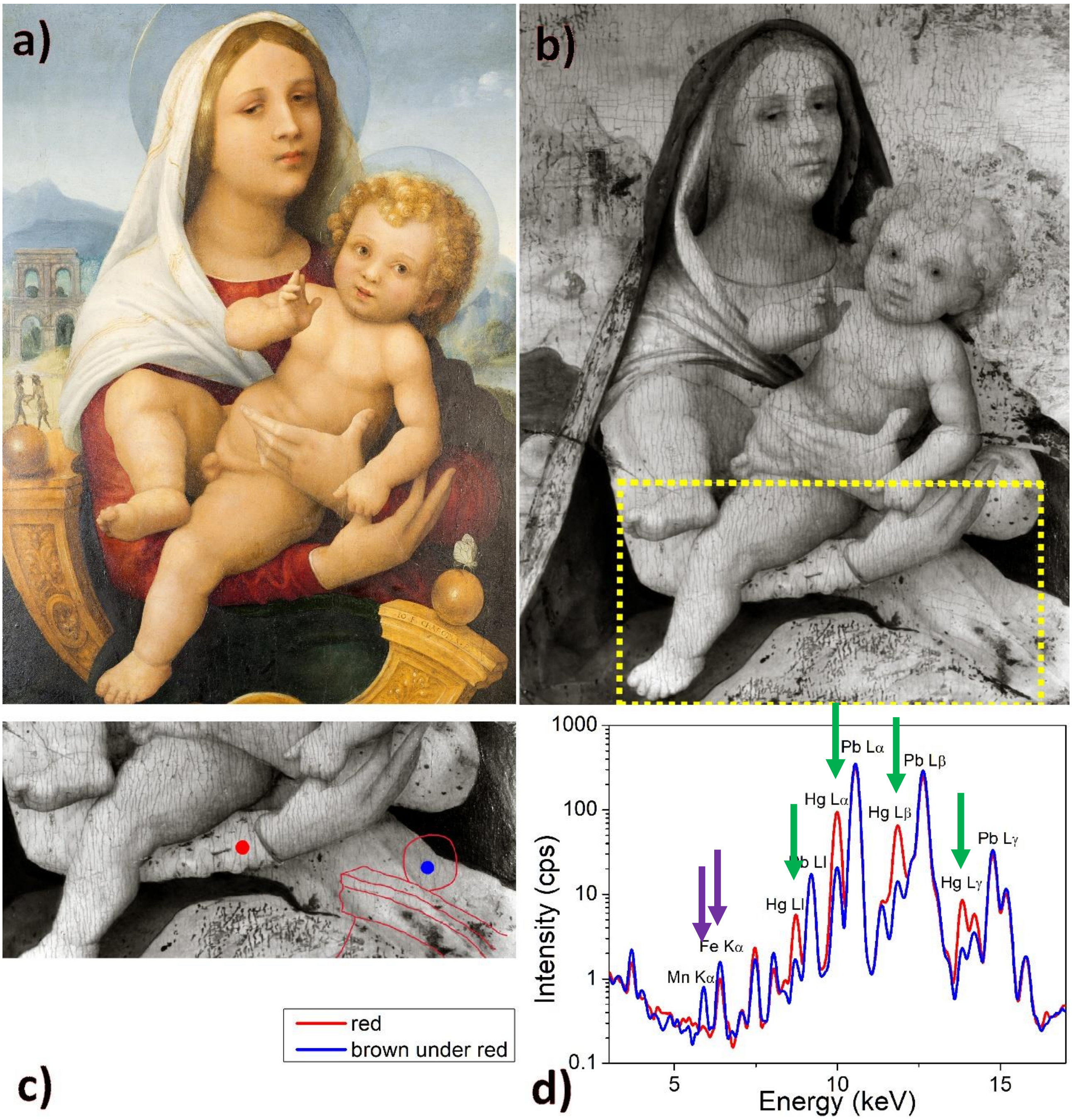


Figure 7: a) 'Madonna of the Butterfly', private collection, Vis image; b) 'Madonna of the Butterfly', collection of Castelvecchio, Verona – IR image (for Vis image see Fig.S4); c) detail of b, knob in the underdrawing, with highlighted points of XRF analysis; d) XRF spectra showing the presence of Hg, Fe, and Mn

Discussion

Aligned with the contemporary practice, for the majority of his early production, Giovan Francesco Caroto worked on wooden support prepared with the glue/gypsum layer, followed by a lead white layer, varying in thickness, possibly coloured yellow by the addition of *giallorino* (lead-tin yellow). When detected, the presence of tin is homogeneous throughout the entire painting, as suggested by a consistent Pb/Sn ratio in all XRF spectra collected on the same artwork. Conversely, the preparation seems lighter in the late works (1530/40), mostly canvas paintings: the low values detected by XRF analysis might indicate the presence of

very thin preparation layers rather than the application of lead white without tin for the *imprimitura*. This characteristic was quite common in the first half of the 16th century among painters of Northern Italy [20]. As previously noted, the presence of tin might not only be linked to the use of the yellow pigment but could also indicate the use of *biacca* containing tin for particular mining extraction.
It is unrealistic to think about the existence of a workshop owned by the artist, given the itinerant nature of his production. Nevertheless, the existence of cartoons allowed the creation of multiple copies of the same subject, identifying a certain artistic fortune among patrons for certain subjects. The succession of support preparation practices throughout the entire artistic production does not align with Caroto's movements between Verona and the Monferrato area. This might be the clue that the preparation may have been the responsibility of someone other than the artist. Caroto, originally from Verona, spent part of his career in Piedmont. This aspect in the artworks analysed results in a different palette, characterised by 'Verona' ochres and earth pigments, which were not used in the artworks: 'Saint Sebastian', still located in the church of Santo Stefano in Casale Monferrato, 'Deposition (Christ Deposed)', both documented as realised in Monferrato [21] and 'Lamentation over the Dead Christ'. Separate from this discussion on ochres is the 'Nativity of Mary', in which yellow ochre was assumed to contain natrojarosite (or another minor mineral phase) unique to this painting. This artwork also presented other singularities: the use of gold (shell gold) and of tin-yellow type II not in areas of this colour (realised by yellow ochre instead), but to lighten and brighten the verdigris used to depict the wall of the room, emphasizing the opulence of brocade and velvet. Moreover, the Pb content of the inner layers of the painting stratigraphy was particularly high, leading to the hypothesis of a reused wooden panel.

What has been documented for ferrous pigments is not as well documented for other pigments. One example is azurite, which showed traces of Ba, indicative of its mineral ore [22], in artworks painted in Verona and Monferrato. These data suggest that the artist initially brought the most precious pigments used in his Verona activity during his travels, and subsequently found suppliers locally. Monferrato was a land he frequented often since 1515 and even after the death of his patron (Marquis Guglielmo) thanks to a land bequest [23], and which was imagined to be a place for purchasing materials for his palette.

The painting phase involved the use of pure pigments to impart colour, with the addition of white or black to define highlights and shadows. Blue pigments in the landscape were usually smalt for the mountains and azurite for the sky, with red ochre used to depict sunlight at the horizon. For the ruddiness, either cinnabar (or vermillion) or red ochre was mixed with lead white, depending on the character depicted. Robes instead were often realised using glazes. This was particularly evident for blue and red vests: a thin layer of smalt was often applied over azurite (e.g., 'Nativity of Mary', 'Lamentation over the dead Christ', 'Pity of the tear') and indigo ('Pity of the tear'). Glazes were also pinpointed on 'Flight into Egypt' owned by the Louvre Museum: the Virgin's robe was painted with azurite (pure or mixed with lead white) with a glaze of lapislazuli [3]. Nevertheless, studies on paintings of the same period and in the Veneto, region attested the progressive substitution of ultramarine blue with azurite and smalt, especially from the second decade of the 16th century [24,25]. For the red robes, initially, the sequence was a base made with cinnabar (or vermillion) followed by the application of a red lake (most likely cochineal), as seen in 'Temptation of Christ'. However, late production saw the use of the cinnabar (or vermillion) for the glaze over a red ochre layer, as in 'Three archangels' and in 'Nativity of Mary' (here for the brocade).

4. Conclusion

This work underscores the significant opportunity that a monographic exhibition offers to characterise substantial artworks by the same artist using consistent techniques, instruments and operators, thus allowing a comprehensive description of the artist's entire production in terms of style and materials. Artworks undergoing exhibition are typically in good conservation state, either already on display like most of the paintings examined or undergoing conservation treatment just before the exhibition opens.

An analytical diagnostic protocol based on full-field Vis-IR imaging and single-point spectroscopy was adopted to systematically investigate the artistic production of Giovan Francesco Caroto. Imaging was used to identify representative regions for FORS and XRF analyses, enabling a deeper exploration of the palette and the executive technique, reaching a chemometric statistical level.
Imaging results highlighted conservation treatments performed over the decades, although documented in only a few cases. Integrations were discernible in IR reflectance, even in homogeneous areas under visible light. FORS spectra identified in some cases the nature of the synthetic protective varnish. Among the canvases studied, two belonged to the decorative cycle for Giulio Della Torre's *studiolo*: 'San Michele Arcangelo scaccia Lucifero' ('Saint Michael the Archangel drives out Lucifer') and 'Temptation of Christ'. For the first painting, visual observation identified a different conservation aspect: the left side was characterised by a diffuse yellow hue, while the right side appeared lighter, with a thinner paint film, especially on the suit of St. Michael (Fig.8). Despite this, the comparison of single-point data collected from the two halves did not allow to identify clear differences, requiring further investigation. In general, the identification of materials added by conservation treatments is beyond the scope of this study.

Figure 8: a) 'San Michele Arcangelo caccia Lucifero', Vis image; it is possible to notice the homogeneous yellow aspect of the left side and the thinning of the paint film (especially for St. Michael'vests) on the right side; b) IRR

Moreover, the employed protocol showed its effectiveness in confirming how Caroto is positioned not only stylistically but also technically in a specific moment of the general evolutionary framework between the 15th and 16th centuries. Peculiarities such as minor mineral phases or trace elements identified in some pigments gave support to the historical sources of the painter, being coherent with the century and the place of production of the paintings.
Furthermore, the data obtained with a non-invasive protocol applied *in-situ*, even during site opening time, underscored the potential of complementary techniques in reconstructing the stratigraphy of the paintings, from varnishes and glazes to preparatory layers, with a good degree of accuracy.

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