



ORIGINAL ARTICLE OPEN ACCESS

Nineteenth-Century Watercolour Reproductions of Old Masters in the Ruskin Teaching Collection, Ashmolean Museum, Oxford: Materials and Techniques of 'Heaven-Borne' Copyist Charles Fairfax Murray

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Keywords: 19th century | elemental analysis | FORS | multispectral imaging | pigment | Renaissance | watercolour | X-ray diffraction | X-ray fluorescence

ABSTRACT

This study presents the first comprehensive analysis of the pigments and techniques used by Charles Fairfax Murray (1849–1919), a leading expert in Italian Renaissance attribution, influential art collector and primary copyist for John Ruskin. Using a multi-disciplinary approach combining MA-XRF, single-point XRF and XRD, FORS and advanced imaging techniques, this research identifies the materials Murray employed while replicating works by Italian Old Masters, including Tintoretto and Botticelli, during the Italian Renaissance revival of the 19th century. This study examines eight artworks from the Ruskin Teaching Collection at the Ashmolean Museum, identifying the use of both traditional pigments, such as vermilion and red, yellow and brown ochres, and newer, industrially produced pigments including cobalt blue and Prussian blue-based greens. XRF mapping reveals localized use of chrome, zinc and cadmium-based pigments, suggesting later modifications. Created between circa 1870–1881, these works demonstrate Murray's application of traditional artistic teachings and colour theory used during the Renaissance in the scope of pigment innovations during the Industrial Revolution. Multispectral imaging and infrared reflectography reveal the preparatory underdrawings made of each work, including the use of the grid technique to ensure accuracy and proportion. This research underscores the importance of interdisciplinary scientific analysis in exploring the Victorian-era art of replication, a practice that elevated copying to a celebrated artistic pursuit. It reveals the profound influence of John Ruskin's teachings and Pre-Raphaelite ideals on Charles Fairfax Murray's material choices and artistic approach, particularly his emphasis on authenticity, fidelity to historical methods and the use of lightfast, durable materials. Furthermore, it highlights the pivotal role of the Ruskin Teaching Collection in art education and demonstrates how industrial advancements in pigment technology not only enhanced artistic production and longevity but also broadened public access to the visual language of the Italian Renaissance.

1 | Introduction

During the 19th century, Victorian Britain (1837–1901) experienced a significant revival of interest in Renaissance art.

One of the key figures in promoting Renaissance art during the 19th century was polymath, art critic and Slade Professor of Art at Oxford University, John Ruskin. His writings such as *The Stones of Venice* (1851–53) and *Modern Painters*

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(1843–60) emphasised the moral and aesthetic superiority of early Renaissance artists, which, in turn, inspired collectors, artists and institutions to re-evaluate the importance of this period. The revival had a profound impact on Victorian collecting practices and inspired wealthy patrons, including industrialists and aristocrats, to acquire Renaissance paintings, sculptures and decorative objects. This demand fuelled the market for both authentic masterpieces and high-quality copies. Ruskin hired the talented copyist, Charles Fairfax Murray, to reproduce the works of Italian Old Masters for his altruistic projects including the Guild of St. George, the teaching collection at Oxford and for his personal collection. Murray's copies therefore played a crucial role in bringing the Italian Renaissance to Britain, providing accessibility to a broader audience.

Murray had trained under Edward Byrne-Jones between 1866 and 1867 and received substantial academic instruction on the Renaissance masters. In addition to creating copies, Murray became deeply committed to the methodical study of attribution of Italian works, a practice that he had begun to develop during his time in the workshops of the pre-Raphaelites (Elliott 2000a, 31; Elliott 2000b, 37; Hilton 2002, 555). Murray was termed a 'heaven borne copyist' (Elliott 2000a, 43), with the Masters Report to the Guild of St. George in 1884 stating 'the most skilful of the artists thus employed was, beyond comparison, Mr Charles Fairfax Murray, and the sketches that we possess by his hand are among the principle treasures that we can boast at Oxford' (Guild of St. George 1884). Between 1873 and 1883, Charles Fairfax Murray created approximately 60 copies of early Renaissance works for John Ruskin. Of these, around 40 were intended for the Guild of St. George, while the rest, mostly lost, were intended for the Arundel Society and Ruskin's Oxford lectures (Elliott 2000b). Murray's artistic skill, his Pre-Raphaelite training, passion for attribution and his role under Ruskin uniquely positioned him to create reproductions of the highest quality and accuracy.

The reproductions of Renaissance works, which include Botticelli and Tintoretto, were undertaken during a transformative period in art technology, characterised by ground-breaking innovations. New, vibrant shades of watercolours and paints were released onto the artists market, with colour choices nearly doubling from the 1840s to the 1880s. The advancements in 'moist watercolour technology' marked an unprecedented leap for artists, providing unmatched convenience and portability (Mills and Nichols 2023). Newly released paint tubes also enabled artists to create stronger washes, distribute larger quantities of paint and work more freely and rapidly, achieving deep, vibrant hues with greater ease than traditional pans allowed. In addition, watercolours were quick to dry, allowing artists to create several works in a single session to be immediately transported. However, many watercolour paints lacked stability and standardisation due to inconsistent manufacturing and variable pigment quality, leading to inconsistencies in colour, transparency and permanence. The introduction of mass produced and synthetic pigments expanded the Victorian palette but were often chemically unstable, with some, like early aniline dyes, fading rapidly (Hagan et al. 2022).

Therefore, the collection serves as a bridge between historical painting traditions and industrial advancements, offering

valuable insights into 19th-century artistic practices, Ruskin's influence on material choices, and the evolving understanding of colour permanence in the wake of rapid technological change. Containing over 900 drawings and watercolours, many pieces in the Teaching Collection were created by Ruskin himself or commissioned from his contemporaries and followers, including Edward Burne-Jones (1833–1898), the renowned Pre-Raphaelite painter; William Henry Hunt (1790–1864), whom Ruskin hailed as the finest living still-life artist; and J.M.W. Turner (1775–1851), the eminent landscape artist whom Ruskin held in the highest esteem. John Ruskin emphasised the importance of studying historical techniques, and his collection provided artists and students with high-quality copies of Old Masters, particularly from the Italian Renaissance. The pigments and materials used in by Renaissance artists were well understood during the revival period. Notably, Cennino Cennini's (c. 1370–1440) seminal work, 'Il Libro dell'Arte', which detailed the materials required for tempera and fresco painting, was rediscovered and printed in 1821, with the first English translations published in 1844 (Cennini 1440). Concurrently during this period, research was conducted by the artists Maria Callcott and Charles Lock Eastlake, who each produced writings exploring the materials used by artists in the past (Callcott 1836; Eastlake 1847). More recently, the scientific study of Renaissance paintings has produced a vast body of published research, with non-destructive analytical techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF) and infrared reflectography (IRR) identifying key pigments used by Italian Old Masters. These include lead-tin yellow, vermilion, ultramarine and verdigris and contain materials used for fresco, gesso and oil painting. Overall, such investigations offer valuable insights into historical painting methods, artists' material choices and strategies for the long-term preservation of these masterpieces.

Utilising a multidisciplinary non-destructive analytical approach, this study aims to produce a chemical characterisation survey of the pigments and materials used by Charles Fairfax Murray in his reproductions of Italian Old Masters for John Ruskin's Teaching Collection. It further aims to assess the impact of industrially produced synthetic pigments on the Murray's material choices, Ruskin's teachings on authenticity in replicating Renaissance artists' materials as well as style and form and the importance of choosing lightfast materials for longevity.

2 | Works Analysed in This Study

The Ruskin Teaching Collection includes 10 works by Murray, eight of which were selected for analysis in this study. Of the works, seven are copies of Italian artists, with only one work, *Fragments of a Mosaic Pavement in the Sistine Chapel*, being an observational work of an architectural feature. All were created between approximately 1870 and 1883, with those from 1871 to 1883 likely painted in situ, Italy (Table 1).

3 | Methods

Multispectral images were recorded by a digital camera (Canon-EOS-90D) with both the IR and Bayer filters removed (by MaxMax Llc) through an apochromatic lens (Jenaoptik

TABLE 1 | Collection of works by Charles Fairfax Murray in the Ruskin Teaching Collection.

Accession number	Dimensions	Title	Original artist	Date created	Original work creation date	Material and technique
 WA.RS.WAL.13.a	252 × 160 mm	Drawing of 'Saint Peter enthroned and Saints'	Jacopo Palma il Vecchio	Pre-1870	c. 1520	Watercolour over graphite on wove paper
 WA.RS.STD.049bis	308 × 254 mm	Drawing of Tintoretto's 'Saint Louis, Saint George and the Princess'	Jacopo Robusti (Tintoretto)	1870	c. 1553	Watercolour over graphite on wove paper
 WA.RS.LC.01	193 × 253 mm	Drawing of 'Saint Mark Enthroned with Saints Andrew and Francis'	Andrea Busati di Stefano	1871–1883	c. 1510	Watercolour over graphite on wove paper
 WA.RS.LC.04	245 × 212 mm	Drawing of Portrait of a Man, called 'Francesco Querini'	Jacopo Palma il Vecchio	1871–1883	c. 1527–1528	Watercolour over graphite on wove paper
 WA.RS.LC.06	224 × 209 mm	Drawing of Portrait of a Woman, called 'Paola Priuli'	Jacopo Palma il Vecchio	1871–1883	c. 1527–1528	Watercolour over graphite on wove paper

(Continues)

TABLE 1 | (Continued)

Accession number	Dimensions	Title	Original artist	Date created	Original work creation date	Material and technique
 WA.RS.LC.08	207 × 203 mm	Copy of a painting of the Virgin and Child with Saint Jerome, Saint Roch and two Others	Attributed to Francesco Morone	1871–1883	Artist c. 1471–1529	Watercolour over graphite on wove paper
 WA.RS.REF.094	521 × 356 mm	Fragments of a Mosaic Pavement in the Sistine Chapel	Charles Fairfax Murray	1874	1874	Watercolour and bodycolour over graphite on wove paper
 WA.RS.WAL.02	815 × 560 mm	Drawing of Botticelli's fresco of 'Lorenzo Tornabuoni presented to the Liberal Arts'	Sandro Botticelli	1881–1882	c. 1483–1486	Watercolour and bodycolour over graphite on paper

60 mm) and a custom-made, computer-controlled 16-position filter wheel equipped with 15 bandpass filters, with centre wavelengths (and bandwidths) at 365(25), 400(25), 450(25), 475(25), 500(25), 525(25), 550(25), 575(25), 600(25), 625(25), 650(25), 700(25), 750(25), 825(50) and 925(50) nm (Edmund Optics Ltd). An additional position has a 400-nm long-pass filter that allows direct imaging of the sample and was the filter used for 1050-nm imaging reported herein. The works were illuminated by a bank of LEDs, which allow selective illumination whilst minimising the exposure to light. For a typical exposure, the light level at the page is $< 1 \text{ mW cm}^{-2}$. The system allows the recording of both reflectance images and UV or visible light induced fluorescence images using any combination of the excitation LEDs and/or emission filters. Additional IRR was performed using an Opus Instruments Apollo camera to determine underdrawing materials and technique. The camera is fitted with a $128 \times 128 \text{ px}$ InGaAs area sensor with an operational wavelength of $0.9\text{--}1.7 \mu\text{m}$. Lens specification: 6-element 150-mm focal length F/8–11. Works were illuminated using an ELIO Halogen lamp (240 V) (VIS to IRR range) from chsource.org.

A Bruker CRONO Macro-X-ray Fluorescence (MA-XRF) spectrometer was used to characterise pigments in each painting by mapping elemental distributions and classifying elements specific to individual colours. The CRONO system features a rhodium target X-ray tube and a 50-mm^2 SDD detector, delivering $< 140\text{-eV}$ energy resolution for Mn $K\alpha$ with an input count rate of up to 500,000 cps. Elemental maps were acquired in ‘automatic acquisition’ mode (speed: 13.89 mm/s , spectra time: 30 ms) with an analysis range from Mg ($Z=12$) to U ($Z=92$) using a 1-mm collimator for WA.RS.WAL.02 and a 0.5-mm collimator for the remaining works. A full map of each object guided the single-point analysis strategy, performed with a 0.5-mm collimator at 50 kV, $200 \mu\text{A}$ and 100 s per analysis. All single point

analyses were performed in triplicate for each colour area and compared with readings taken from unpainted areas of the original paper, or the mountboard support where unpainted paper was not present in the original work. Data were processed using Bruker ESPRIT Reveal software.

X-ray diffraction (XRD) analysis, conducted with a Bruker HYDRA system, identified chemical compounds in each pigment colour. The system includes a 30-W micro-focus X-ray generator with a Cu anode, parallelising poly-optics, and a 50-mm^2 SDD detector. A photon-counting 2D detector performed XRD measurements at $20^\circ\text{--}40^\circ$ 2-theta in the first run and $40^\circ\text{--}60^\circ$ in the second. Measurements used a $500\text{-}\mu\text{m}$ collimator with 300-s acquisition time per run, totalling 10 min per analysis. Diffraction patterns were processed using Panalytical HighScore Plus software and compared to the International Centre for Diffraction Data (ICDD) database (<https://www.icdd.com/>) for phase identification.

4 | Results

4.1 | Multispectral Imaging and Infrared Reflectography

All of the works show preparatory underdrawings with varying levels of detail mapping the composition before pigment application (Figure 1). *Lorenzo Tornabuoni Presented to the Liberal Arts* shows the standard practice of using grid lines to accurately map compositional elements and maintain proportion.

4.2 | MA-XRF, XRD and FORS

The pigment identification summary can be viewed in Table 2.



FIGURE 1 | (Left) IRR image of *Lorenzo Tornabuoni Presented to the Liberal Arts* reveals the artistic technique of using grid lines for the fresco copying process. (Right) Multispectral image (825 nm) showing the detailed underdrawing of *Saint Louis, Saint George and the Princess* by Charles Fairfax Murray.

TABLE 2 | Pigments identified in the examined works by artist Charles Fairfax Murray.

Work	Drawing of Tintoretto's 'Saint Louis, Saint George and the Princess'	Drawing of 'Saint Mark Enthroned with Saints Andrew and Francis'	Drawing of Portrait of a Man, called 'Francesco Querini'	Drawing of Portrait of a Woman, called 'Paola Priuli'	Copy of a painting of the Virgin and Child with Saint Jerome, Saint Roch and two Others	Drawing of Botticelli's fresco of 'Lorenzo Tornabuoni presented to the Liberal Arts'
Original artist	Drawing of 'Saint Peter enthroned and Saints'	Jacopo Palma il Vecchio	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Jacopo Palma il Vecchio	Charles Fairfax Murray
Material and technique	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on paper
Accession number	WA. RS.WAL.13.a	WA. RS.STD.049bis	WA. RS.LC.01	WA.RS.LC.04	WA.RS.LC.06	WA. RS.REF.094
Proposed date	Pre 1870	1870	1871-1883	1871-883	1871-1883	1881
Dimensions	252 × 160 mm	308 × 254 mm	193 x 253 mm	245 × 212 mm	224 × 209 mm	521 × 356 mm
Group	Pigment	Elements	Chemical formula			
Blue	Cobalt blue	Co, Al	CoAl ₂ O ₄	1, 3	1, 2, 3	1, 2, 3
	Prussian blue	Fe, K	KFe[Fe (CN) ₆]. xH ₂ O	3	3	3
	Indigo		C ₁₆ H ₁₀ N ₂ O ₂	3	3	3

(Continues)

TABLE 2 | (Continued)

Work	Drawing of 'Saint Peter enthroned and Saints'	Drawing of 'Saint Louis, Saint George and the Princess'	Drawing of 'Saint Mark Enthroned with Saints Andrew and Francis'	Drawing of 'Portrait of a Man, called 'Francesco Querini'	Drawing of 'Portrait of a Woman, called 'Paola Priuli'	Copy of a painting of the Virgin and Child with Saint Jerome, Saint Roch and two Others	Drawing of Botticelli's fresco of 'Lorenzo Tornabuoni presented to the Liberal Arts'
Original artist	Jacopo Palma il Vecchio	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Francesco Morone (attributed)	Charles Fairfax Murray
Material and technique	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on paper
Accession number	WA. RS.WAL.13.a	WA. RS.STD.049bis	WA. RS.LC.01	WA. RS.LC.04	WA.RS.LC.06	WA.RS.LC.08	WA. RS.WAL.02
Proposed date	Pre 1870	1870	1871–1883	1871–883	1871–1883	1871–1883	1881
Dimensions	252 × 160 mm	308 × 254 mm	193 × 253 mm	245 × 212 mm	224 × 209 mm	207 × 203 mm	815 × 560 mm
Group	Pigment	Elements	Chemical formula				
Green	Chrome green	Cr	Cr ₂ O ₃	1	1, 2	1	1
	Copper arsenate based green	Cu, As	Cu + As compounds	1	1, 2	1, 2	1
	Mixed green			3	1 (indicated), 3	2 (indicated)	

(Continues)

TABLE 2 | (Continued)

Work	Drawing of 'Saint Peter enthroned and Saints'	Jacopo Palma il Vecchio	Drawing of 'Saint Louis, Saint George and the Princess'	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Drawing of 'Saint Mark Enthroned with Saints Andrew and Francis'	Jacopo Palma il Vecchio	Drawing of 'Portrait of a Man, called 'Francesco Querini'	Drawing of 'Portrait of a Woman, called 'Paola Priuli'	Drawing of 'Portrait of Saint Jerome, Saint Roch and two Others'	Copy of a painting of the Virgin and Child with Saint Jerome, Saint Roch and two Others'	Drawing of Botticelli's fresco of 'Lorenzo Tornabuoni presented to the Liberal Arts'
Original artist	Jacopo Palma il Vecchio	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Jacopo Robusti (Tintoretto)	Jacopo Robusti (Tintoretto)	Jacopo Robusti (Tintoretto)	Jacopo Robusti (Tintoretto)	Jacopo Robusti (Tintoretto)	Jacopo Robusti (Tintoretto)	Jacopo Robusti (Tintoretto)
Material and technique	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper
Accession number	WA. RS.WAL.13.a	WA. RS.STD.049bis	WA. RS.LC.01	WA. RS.LC.04	WA. RS.LC.06	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.WAL.02
Proposed date	Pre 1870	1870	1871-1883	1871-1883	1871-1883	1871-1883	1871-1883	1871-1883	1871-1883	1871-1883	1871-1883	1881
Dimensions	252 × 160 mm	308 × 254 mm	193 × 253 mm	245 × 212 mm	224 × 209 mm	207 × 203 mm	521 × 356 mm	815 × 560 mm	815 × 560 mm	815 × 560 mm	815 × 560 mm	815 × 560 mm
Group	Red	Vermillion	Hg, S	HgS	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
Pigment	Red madder	Red madder	Red madder	Red madder	Red madder	Red madder	Red madder	Red madder	Red madder	Red madder	Red madder	Red madder
Elements	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti	Fe, Si, Ti
Chemical formula	Fe ₂ O ₃	—	—	—	—	—	—	—	—	—	—	—
Continues	(Continues)	(Continues)	(Continues)	(Continues)	(Continues)	(Continues)	(Continues)	(Continues)	(Continues)	(Continues)	(Continues)	(Continues)

TABLE 2 | (Continued)

Work	Drawing of 'Saint Peter enthroned and Saints'	Jacopo Palma il Vecchio	Drawing of 'Saint Mark Enthroned with Saints Andrew and Francis'	Andrea Busati di Stefano	Jacopo Palma il Vecchio	Drawing of 'Portrait of a Man, called 'Francesco Querini'	Drawing of 'Portrait of a Woman, called 'Paola Priuli'	Drawing of 'Portrait of Saint Jerome, Saint Roch and two Others'	Copy of a painting of the Virgin and Child with Saint Jerome, Saint Roch and two Others'	Fragments of a Mosaic Pavement in the Sistine Chapel	Drawing of Botticelli's fresco of 'Lorenzo Tornabuoni presented to the Liberal Arts'
Original artist	Jacopo Palma il Vecchio	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Francesco Morone (attributed)	Charles Fairfax Murray	Charles Fairfax Murray	Sandro Botticelli
Material and technique	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on paper
Accession number	WA. RS.WAL.13.a	WA. RS.STD.049bis	WA. RS.LC.01	WA. RS.LC.04	WA. RS.LC.06	WA. RS.LC.08	WA. RS.LC.094	WA. RS.LC.08	WA. RS.REF.094	WA. RS.WAL.02	WA. RS.WAL.02
Proposed date	Pre 1870	1870	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1874	1881	1881
Dimensions	252 × 160 mm	308 × 254 mm	193 × 253 mm	245 × 212 mm	224 × 209 mm	207 × 203 mm	521 × 356 mm	815 × 560 mm			
Group	Yellow ochre	Organic yellow	Lemon yellow	Cadmium yellow/orange							
Pigment	Fe	Fe ₂ O ₃	—	Ba, Cr	Cd, S						
Elements											
Chemical formula											
Yellow	Yellow ochre	Organic yellow	Lemon yellow	Cadmium yellow/orange							
	1, 3	1, 3	3	3	3	3	3	3	3	3	3
	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)
	1, 2	1, 2	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3
	1, 2	1, 2	1, 2	1, 2	1, 2	1, 2	1, 2	1, 2	1, 2	1, 2	1, 2

(Continues)

TABLE 2 | (Continued)

Work	Drawing of 'Saint Peter enthroned and Saints'	Jacopo Palma il Vecchio	Drawing of 'Saint Mark Enthroned with Saints Andrew and Francis'	Andrea Busati di Stefano	Jacopo Palma il Vecchio	Drawing of 'Francesco Querini'	Portrait of a Man, called 'Paola Priuli'	Drawing of a Woman, called 'Paola Priuli'	Copy of a painting of the Virgin and Child with Saint Jerome, Saint Roch and two Others	Fragments of a Mosaic Pavement in the Sistine Chapel	Drawing of Botticelli's fresco of 'Lorenzo Tornabuoni presented to the Liberal Arts'
Original artist	Jacopo Palma il Vecchio	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Francesco Morone (attributed)	Charles Fairfax Murray	Sandro Botticelli
Material and technique	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on paper
Accession number	WA. RS.WAL.13.a	WA. RS.STD.049bis	WA. RS.LC.01	WA. RS.LC.04	WA. RS.LC.06	WA. RS.LC.08	WA. RS.LC.094	WA. RS.LC.08	WA. RS.LC.08	WA. RS.REF.094	WA. RS.WAL.02
Proposed date	Pre 1870	1870	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1874	1881
Dimensions	252 × 160 mm	308 × 254 mm	193 × 253 mm	245 × 212 mm	224 × 209 mm	207 × 203 mm	521 × 356 mm	815 × 560 mm			
Group	Pigment	Elements	Chemical formula								
Purple	Organic purple			3	3	3					
Black	Bone/ivory black	Ca, P	Ca ₃ (OH)(PO ₄) ₃ with CaSO ₄	1	1 (indicated), 3						

(Continues)

TABLE 2 | (Continued)

Work	Drawing of 'Saint Peter enthroned and Saints'	Jacopo Palma il Vecchio	Drawing of Tintoretto's 'Saint Louis, Saint George and the Princess'	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Drawing of 'Saint Mark Enthroned with Saints Andrew and Francis'	Jacopo Palma il Vecchio	Drawing of Portrait of a Man, called 'Francesco Querini'	Jacopo Palma il Vecchio	Drawing of Portrait of a Woman, called 'Paola Priuli'	Copy of a painting of the Virgin and Child with Saint Jerome, Saint Roch and two Others	Fragments of a Mosaic Pavement in the Sistine Chapel	Drawing of Botticelli's fresco of 'Lorenzo Tornabuoni presented to the Liberal Arts'
Original artist	Jacopo Palma il Vecchio	Jacopo Robusti (Tintoretto)	Jacopo Robusti (Tintoretto)	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Andrea Busati di Stefano	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Francesco Morone (attributed)	Charles Fairfax Murray	Sandro Botticelli
Material and technique	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on paper
Accession number	WA. RS.WAL.13.a	WA. RS.STD.049bis	WA. RS.LC.01	WA. RS.LC.04	WA. RS.LC.06	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.LC.08	WA. RS.WAL.02
Proposed date	Pre 1870	1870	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1871–1883	1874	1881	
Dimensions	252 × 160 mm	308 × 254 mm	193 × 253 mm	245 × 212 mm	224 × 209 mm	207 × 203 mm	521 × 356 mm	815 × 560 mm					
Group	Pigment	Elements	Chemical formula										
Brown	Ochre	Fe	Fe ₂ O ₃	1	1, 2, 3	1, 2	1, 2	1, 2	1, 2	1, 2	1, 2, 3		
	Mixture		—			3	3	3	3	3	3		
	Umber	Fe, Mn	Fe ₂ O ₃	1, 2									
	Raw sienna	Fe, As	Fe ₂ O ₃		1	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1 (indicated)	1, 2		1, 2
	Brown madder	Cu (substrate)	C ₁₄ H ₈ O ₄ , C ₁₄ H ₈ O ₅	1 (Cu-substrate)		1	1	1	1	1			
	Iron-based brown	Fe	Fe—			1, 2, 3	1	1	1	1			

(Continues)

TABLE 2 | (Continued)

Work	Drawing of 'Saint Peter enthroned and Saints'	Drawing of 'Saint Louis, Saint George and the Princess'	Drawing of 'Saint Mark Enthroned with Saints Andrew and Francis'	Drawing of 'Portrait of a Man, called 'Francesco Querini'	Drawing of 'Portrait of a Woman, called 'Paola Priuli'	Copy of a painting of the Virgin and Child with Saint Jerome, Saint Roch and two Others	Drawing of Botticelli's fresco of 'Lorenzo Tornabuoni presented to the Liberal Arts'
Original artist	Jacopo Palma il Vecchio	Jacopo Robusti (Tintoretto)	Andrea Busati di Stefano	Jacopo Palma il Vecchio	Jacopo Palma il Vecchio	Francesco Morone (attributed)	Charles Fairfax Murray
Material and technique	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on wove paper	Watercolour and bodycolour over graphite on paper
Accession number	WA. RS.WAL.13.a	WA. RS.STD.049bis	WA. RS.LC.01	WA. RS.LC.04	WA.RS.LC.06	WA.RS.LC.08	WA. RS.WAL.02
Proposed date	Pre 1870	1870	1871–1883	1871–883	1871–1883	1871–1883	1881
Dimensions	252 × 160 mm	308 × 254 mm	193 × 253 mm	245 × 212 mm	224 × 209 mm	207 × 203 mm	815 × 560 mm
Group	Pigment	Elements	Chemical formula				
White	Zinc white	Zn	ZnO	1	1	1, 2	1, 2
	Barium sulphate	Ba, S	BaSO ₄	1 (indicated)	1, 2	1, 2 (indicated)	1, 2

Note: 1=XRF, 2=XRD, 3= FORS.

4.2.1 | Blues

MA-XRF elemental maps detected cobalt in blues on all eight works examined, primarily in areas of bright mid-blue, such as skies and robes, but also in more subtle blue tones, including the armour of *St. George in Saint Louis*, *Saint George and the Princess* (Figure 2).

Cobalt was also detected in blue-green hues, such as the robes in *Lorenzo Tornabuoni Presented to the Liberal Arts* and the landscape elements in *Saint Mark Enthroned with Saints Andrew and Francis*. XRF point analysis on areas of high elemental intensity indicated by MA-XRF consistently revealed high concentrations of cobalt with corresponding elevated aluminium. The resulting diffractograms matched the pattern for cobalt aluminium oxide (CoAl_2O_4), confirming the presence of cobalt blue. Additional FORS analysis on this area also showed the characteristic spectra of cobalt blue, specifically an absorption band at 500–675 nm showing some fine structures and a broad absorption in the 1150- to 1600-nm region (and with reference to samples of cobalt blue from Windsor and Newton 'Modern Water Colours Twenty third Thousand'; Taylor 1887).

Cobalt blue, a cobalt aluminate pigment, became available in England from approximately 1815 (Harley 2001, 54) and was widely embraced by artists for its attractive deep blue hue, excellent lightfastness, stability and versatility in blending with other pigments (Field 1841, 204; Harley 2001, 54). Cobalt blue was sold under several names, including Thenard's Blue (a cobalt phosphate with alumina) and Leithner's Blue (cobalt arsenate) (Church 1901, 210–211), with these names distinguishing variations in composition and purity (Field 1841, 204). XRF analysis on areas containing cobalt in Murray's works confirmed no

associated or correlating arsenic, thereby indicating that Murray only used cobalt aluminate pigments (Roy 2007, 152).

MA-XRF applied to darker blue shadows in the robes in *Saint Peter enthroned and Saints* and St. Louis' robe in *Saint Louis*, *Saint George and the Princess*, revealed high iron content correlating with potassium, sulphur and aluminium and the absence of significant copper and cobalt (Figure 2). Further FORS analysis in these regions showed a strong absorption band extending from the red into the near infra-red, which is characteristic for Prussian blue (by comparison to reference samples and The Windsor and Newton 'Modern Water Colours Twenty Third Thousand' catalogue). We note that this extended NIR absorption spectrum probably contributes to the dark shading seen in the NIR multispectral image of *St Peter Enthroned and Saints*, thereby confirming the use of this pigment in three of Murray's early works in the collection, specifically for the bright blue upper sky and robes of the figures in *Saint Peter Enthroned and Saints*. Prussian blue was also identified by FORS in the green hued robes in *Saint Louis*, *Saint George and the Princess* and *Saint Mark Enthroned with Saints Andrew and Francis*. However, XRF data do not show the same higher concentrations of sulphur/potassium/aluminium elemental correlation, suggesting a different formulation of Prussian blue used to create a mixed green, which is discussed further in the green pigment section. Described as the first of the modern pigments, Prussian blue was serendipitously discovered in Berlin between 1704 and 1710 (Berrie 1997, 191), but its manufacturing process remained a trade secret until 1724 when it was determined that sulphate of iron, treated with nitric and sulphuric acid, created persulphate of iron (Kirby 1993). Ferrocyanide of potassium (yellow prussiate of potash) was added to create a precipitate which was then washed and thoroughly dried providing the chemical formula

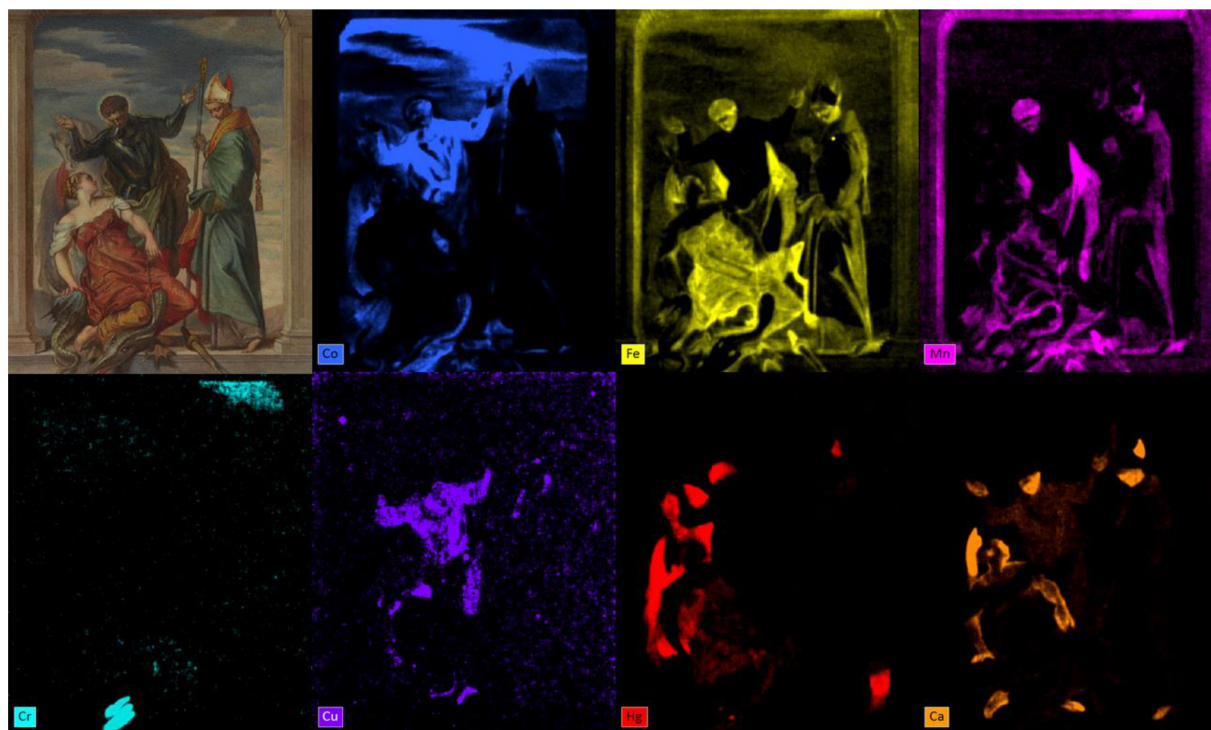


FIGURE 2 | XRF maps of *Saint Louis*, *Saint George and the Princess* showing (top left to right) cobalt (Co), iron (Fe) and manganese (Mn) and (bottom left to right) chromium (Cr), copper (Cu), mercury (Hg) and calcium (Ca).

$\text{KFe}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ or $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$. Furthermore, aluminium was introduced through alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), which was used to modify the pigment's handling properties or as an extender. Rapidly gaining popularity in the 1700s, Prussian blue filled the need for a stable, affordable blue pigment (Berrie 1997, 193). However, pure Prussian blue appears almost black in colour and therefore was frequently adulterated in the manufacturing process with additives such as starch, chalk, iron oxide, alumina, magnesia and zinc oxide (Riffault des Hêtres et al. 1874, 239–243; Salter 1869, 203), which continued into the later 1800s thereby potentially accounting for the observed variations in composition during the time Murray was actively painting. Prussian blue was also sold in different formats and guises, specifically Antwerp blue, which Salter describes as a lighter, brighter Prussian blue (Salter 1869, 208).

Dark blue areas on five of the eight works created between 1871 and 1883, the MA-XRF maps showed the notable absence of elements commonly associated with blue pigments including cobalt, copper or iron. These areas included the dark blue robe of the central figure in *Virgin and Child with Saint Jerome, Saint Roch*, the small dark decorative elements on the throne in *Saint Mark Enthroned with Saints Andrew and Francis* and the extensive blue-black background in *Lorenzo Tornabuoni Presented to the Liberal Arts*. FORS analysis on these areas confirmed the use of indigo, an organic blue pigment ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$), which was used as an artist's pigment in the 15th-century oil painting and was widely used as a watercolour in the 18th and 19th century (Dunkerton et al. 1987; Harley 2001, 64). FORS also identified indigo in the marriage portraits of *Francesco Querini* and *Paola Priuli*, with XRF and XRD analysis indicating that Murray combined indigo and iron-based browns to achieve muted or darker blue and green tones to create shadows and depth to these works (Gameson et al. 2023).

4.2.2 | Reds

MA-XRF maps of all eight works by Murray showed a strong correlation of mercury with sulphur detected in areas of red, ranging from light or subtle red hues to deeper tones of red. This was confirmed by single point XRF analysis, which confirmed the high corresponding concentrations of mercury and sulphur, with XRD analysis returning diffraction patterns matching the standard diffraction patterns for mercuric sulphide. FORS analysis also confirmed the reflectance spectrum for vermilion, characterised by a sharp increase in reflectance at 600 nm. These results therefore confirm the use of a vermilion (HgS), a vibrant red mercuric sulphide pigment that has been widely used since antiquity (Eastaugh 2008, 392; Gettens et al. 1993, 160). Murray employed vermilion extensively for clothing, decorative elements and flesh tones, often blending it with browns to achieve a red-brown hue. In *Fragments of a Mosaic Pavement in the Sistine Chapel*, he combined vermilion with red ochre, characterised by XRF, XRD and FORS, to capture subtle tonal variations. In *Virgin and Child*, the high correlation of mercury and barium shown by MA-XRF corresponds with areas of vibrant red, seen in *Virgin and Child* where vermilion is used for bright red-orange decorative border elements, clothing and the subtler flesh tones. XRD analysis on these areas also returned a strong match for barium sulphate (BaSO_4) (Figure 3) indicating the use of a barium sulphate pigment or extender (Feller 1986, 49). Barium white pigments are discussed further in the later section.

MA-XRF identified areas of high iron in notably red hues in four of the eight works. The high iron content was confirmed using single point XRF, with XRD analysis returning diffraction patterns matching iron oxide (Fe_2O_3). Correlating areas of high calcium corresponding with red areas were also

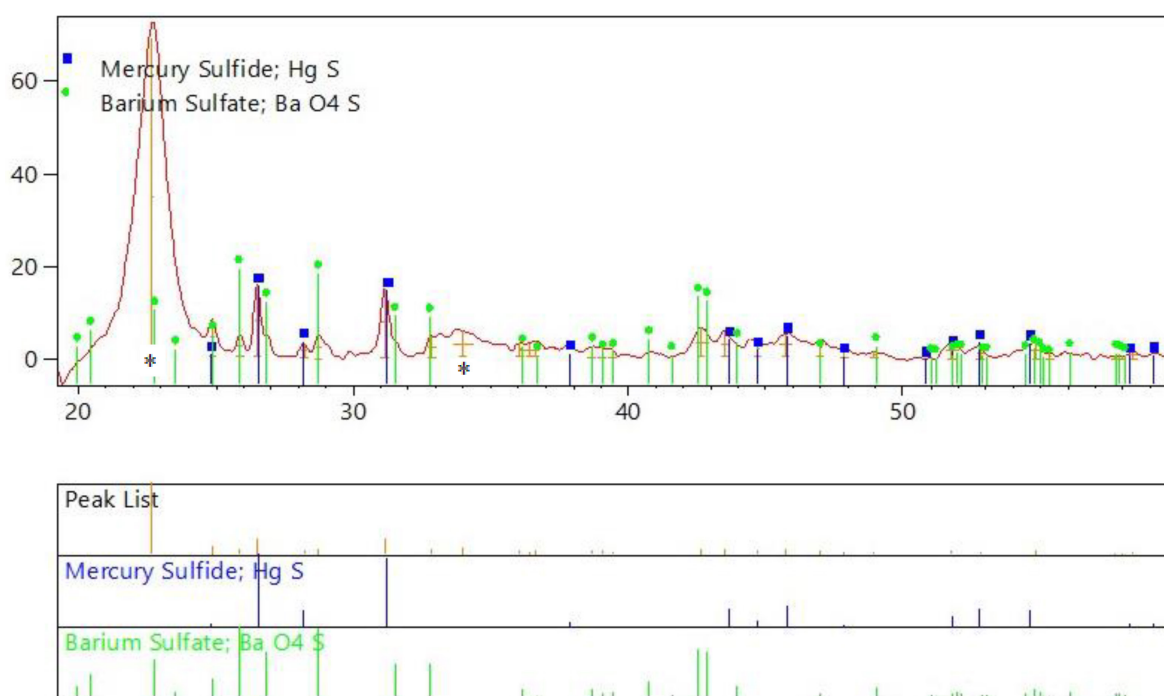


FIGURE 3 | XRD diffractogram of the red scroll detail in *Virgin and Child with Saint Jerome, Saint Roch and two Others* (WA.RS.LC.08) confirming the presence of vermilion (HgS) and a barium sulphate component. Support peaks are labelled with *.

seen in the MA-XRF maps of *St Mark* and *Virgin and Child*, with XRD analysis indicating the presence of the mineral calcium sulphate hydrate ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), or gypsum, which is frequently present in Venetian red, providing a brighter hue (Uebele 1913). FORS analysis further validated the use of red ochre in these works. Red ochre (Fe_2O_3) is a naturally occurring, permanent iron-based pigment used since antiquity (Helwig 2007). MA-XRF revealed high copper concentrations in three of Murray's works, each displaying a distinctly red or brown hue. Notably, no corresponding elements such as mercury, iron or lead, which are typically associated with red pigments, were detected, suggesting the use of a madder pigment prepared with a copper substrate (Kirby et al. 2007). This can be seen in the MA-XRF maps of *Virgin and Child*, where a high concentration of correlating copper is detected, corresponding with the middle left figure painted in a deep red. Derived from *Rubia tinctorum*, madder has been used as a pigment since antiquity. In the 19th century, it was manufactured by precipitating the raw material with barium sulphate, alum, and potassium carbonate onto a tin- or copper-based substrate (Field 1804; Kirby et al. 2007; Schweppe and Winter 1997). Madder is also used to define deep orange tones of the dress in *Paola Priuli*. However, the discrete areas of copper and mercury, shown by MA-XRF, show that these pigments were applied separately, rather than mixed together.

4.2.3 | Yellows

XRF analysis shows elevated levels of iron in areas where yellow pigment has been applied in six of Murray's works, with XRD confirming diffraction patterns of Fe_2O_3 indicating yellow ochre. Used since antiquity, yellow ochre was a staple of artists from pre-history (Helwig 2007, 40–41). The use of an organic yellow was also detected by FORS in four works. Two distinct areas in the copy of Tintoretto's *Saint Louis*, *Saint George* and the *Princess*, the dragon's head and the yellow-white cloud in the top right, show concentrations of chromium and barium, indicating the use of lemon yellow (BaCrO_4), confirmed by MA-XRF (Figure 2) and single-point XRF analysis. Other yellow hues in Murray's works were identified as ochre or organic yellow, suggesting that the presence of lemon yellow and cadmium yellow/orange suggests augmentation or modification. Discrete areas of cadmium were detected in *Saint Louis*, *Saint George* and the *Princess*, specifically the yellow-orange cloth draped over the princess's leg, her red robe and a small section of the lance at *St. Louis's* feet. The orange-yellow mantle of *St. Louis* shares tonal similarities with the princess's leg covering; however, XRF and FORS indicate that the mantle was rendered with iron-based pigments, likely ochre and an organic yellow, with no evidence of cadmium pigments elsewhere in the orange/yellow hues. Cadmium yellow (CdS) was not widely commercialized until the mid-1840s due to the scarcity of raw materials with the pigment varying from pale yellow to deep orange, depending on particle size and crystallinity (Fiedler and Bayard 1986, 65). Given that cadmium red was not available until 1910, the pigment in this work is likely yellow-orange (Eastaugh 2008, 76). Notably, cadmium yellow was often adulterated with orpiment, chromate and lead (Salter 1869, 88; Townsend et al. 1995), which was not detected in XRF analysis, indicating that the cadmium pigment used by Murray was relatively pure.

4.2.4 | Greens

XRF mapping revealed a strong correlation between copper and arsenic in greens in four artworks, a finding confirmed by XRF point analysis. XRD analysis of these points identified diffraction pattern matches for copper arsenate compounds, specifically copper arsenate ($\text{Cu}_3(\text{AsO}_4)_2$) and copper acetate arsenate ($\text{C}_4\text{H}_6\text{As}_6\text{Cu}_4\text{O}_{16}$). The latter corresponds to the proposed molecular formula for the pigment Paris Green (also known as Emerald Green), which has the composition copper acetoarsenite ($3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{COO})_2$) (Fiedler and Bayard 1997, 219). Paris Green was considered an improved version of Scheele's Green, a copper arsenite; however, it has been suggested that the manufacturing process of Emerald Green inadvertently led to small amounts of Scheele's Green. In addition, Scheele's Green has been assigned multiple molecular formulas, including CuHAsO_3 , $2\text{CuHAsO}_3 \cdot \text{H}_2\text{O}$, $2\text{CuHAsO}_3 \cdot \text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{AsO}_2)_2$, without a universally agreed-upon structure, highlighting the complexity of these pigments. This structural ambiguity complicates the distinction between Paris Green and Scheele's Green (Pantoja Munoz 2024), in addition to the confusing 19th-century practice of marketing different compositions of pigments under the same or the same composition under different names (Eastaugh 2008, 394). Given the challenges in distinguishing these pigments, historical manufacturers' records can provide valuable insights. Winsor & Newton catalogues from circa 1848 list Emerald Green and French Green (a less common name for Emerald Green; Eastaugh 2008, 167) but do not mention Scheele's Green or its more common alternative names (Eastaugh 2008, 341). Most importantly, contemporary references condone the use of Scheele's Green as an artist's material, drawing attention to its 'rankly poisonous' nature (Church 1901; Harley 2001, 76; Salter 1869). Therefore, it seems more likely that Murray as a professional artist working in the later part of the 19th century selected Emerald Green for his works.

MA-XRF showed high concentrations of chromium in other green areas, with XRD returning a strong diffraction pattern match for chromium oxide (Cr_2O_3) in five of the works, thereby confirming the use of chrome green, or the hydrated form known as viridian ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). MA-XRF showed the presence of cobalt and chromium in the same areas but with no relative ratio between the two elements, suggesting that while cobalt blue was applied in conjunction with chrome green, they were likely not pre-mixed on the palette or a commercialised pigment.

A distinctive olive-green hue was used extensively in the work *Saint Mark Enthroned with Saints Andrew and Francis* and the foliage forming the border in *Virgin and Child with Saint Jerome*, *Saint Roch*. Macro-XRF and single-point XRD analysis revealed that this pigment contained high levels of iron with corresponding elevated concentrations of silicon and arsenic, but no significant traces of copper, chromium or cobalt typically observed in green pigments. FORS analysis on the robe of *St. Francis* and the green ground confirmed that the pigment included an indigo/Prussian blue component and an organic pigment. Therefore, it is likely that the olive-green colour was created by mixing indigo or Prussian blue with an organic yellow, and toned with a brown pigment such as ochre or sienna. It should be noted that pre-prepared olive-green watercolour pigments were available from 1835 containing a combination

of blue, yellow and brown pigments including Prussian blue, indigo, quercitron lake, Indian yellow, umber and bone brown (Field 1835, 152–153). FORS analysis on the light and dark green areas of St. Louis's robe in *Saint Louis*, *Saint George*, and *the Princess* showed the characteristic spectra of Prussian blue combined with an organic pigment. This denotes the use of manufactured mixed green such as Prussian green or Hookers Green, or implies that Murray combined the available pigments in his collection. Contemporary sources, such as Field (1841, 238), describe several formulations of Prussian green, including the addition of cobalt nitrate or a mix of Prussian blue and gamboge, or yellow ochre (Eastaugh 2008, 316; Salter 1869, 281–282), but it was generally described as an inferior, therefore rarely used colour (Harley 2001, 81). The formulation for Hooker's Green is more conclusive, produced using only using Prussian blue (or its paler variant, Antwerp blue) combined with gamboge (Eastaugh 2008, 26, 192). Two shades were available; No. 1 was 'light grass green' whereas No. 2 was 'dark, powerful green' and is described as stable and durable by Salter (1869, 281). Therefore, such reported compositional similarities pose interpretational challenges when trying to identify a specific pigment. Comparisons between the darker and lighter green areas of the robe showed significantly higher concentrations of iron, manganese and cobalt in the darker green denoting the folds of the robe, indicating that cobalt and umber were used to create these shadowed areas.

4.2.5 | Browns

Traditional iron-based brown pigments such as umber, sienna and ochre had been used since antiquity and remained widely favoured by Victorian artists for their proven permanence, stability and versatility. The combined MA-XRF and XRD and FORS analysis demonstrate that Murray used ochres, umbers and sienna in his works; strong correlations between Fe and Mn establish the extensive use of umber throughout *Saint Louis*, *Saint George and the Princess* and the portrait of *Francesco Querini* as observed in the MA-XRF maps and confirmed with single point analysis. In four works, relatively high concentrations of arsenic were detected in the XRF point analysis and confirmed visually correlating only with iron in the MA-XRF maps. This potentially signifies the use of Italian-based ochres or sienna pigments, specifically raw sienna, which is typically high in arsenic (Manasse and Mellini 2006), therefore indicating that Murray used locally sourced pigments from both Italy and England. In *St Mark*, indigo and ochre are used for the brown-black trunks of trees, and vermilion is used in conjunction with an ochre for the cross carried by St. Andrew. Brown madder was likely used in *Francesco Querini* and *Paola Priuli*—this is represented in areas with high copper content but without associated pigment-relevant elements. It also appears to have been used extensively in *Saint Louis*, *Saint George and the Princess* to tone areas of the cobalt blue armour worn by St. George. Analysis on Murray's browns shows the most variation from the use of the traditional ochre, umber and sienna with brown madder with a copper substrate and possibly iron-based mixed browns and multiple mixed pigments to create brown. The challenges to identify specific brown pigments in the 19th century are an acknowledged one; the industrial revolution brought numerous new synthetic

brown pigments onto the artists market that were inexpensive to produce and often subject to substitution and adulteration. Compounding the issue, inconsistent nomenclature led to confusion, as different manufacturers released pigments of varying compositions under multiple names, and the longstanding artistic tradition of mixing residual pigments or deliberately blending colours to create brown further complicates the identification of specific brown pigments in Murray's works.

4.2.6 | Blacks

XRF analysis on the visually black robe of *Francesco Querini*, shows the entire robe to be high in calcium with elevated phosphorus. Analysis with FORS confirmed the use of a carbon-based black, most likely bone black (a mixture of calcium phosphate, calcium carbonate and carbon). The combined analysis across the eight works show that Murray rarely used pure black pigments, preferring indigo and mixtures of blues and browns to render dark, or visually 'black' appearing objects.

4.2.7 | Whites

MA-XRF maps reveal a strong correlation between barium and sulphur in areas of white in seven of the eight works examined. XRD analysis consistently produced diffraction patterns for barium sulphate (BaSO_4) in areas with high barium intensity on the elemental maps, a finding further confirmed by single-point XRF analysis. These results confirm that Murray used barium sulphate white, a widely employed white pigment in the 19th century, valued for its chemical stability, opacity and permanence (Eastaugh 2008, 44–45). Unlike toxic lead-based whites, barium pigments offered a safer alternative and were marketed as 'permanent white' or 'blanc fixe' (Harley 2001, 164). Additionally, the analysis detected barium in close correlation with mercury in areas of skin tone and decorative details, suggesting that barium sulphate was used to add opacity to the paint, create pinks or softer, brighter reds. Barium sulphate pigments were also commonly used to 'extend' costly colours, serving as an inert additive that enhanced paint durability, therefore its presence in Murray's works is consistent with artists practices of the time. MA-XRF reveals high concentrations of zinc in five of the eight works examined, with XRD analysis confirming the presence of zinc oxide (ZnO) in these areas. Zinc oxide is the principal component of zinc white pigments, which were also sold under the name 'Chinese white' from 1834 (Eastaugh 2008, 412; Harley 2001, 167). MA-XRF shows that zinc white was prominently used in *Saint Louis* and *Saint George and the Princess*, where it enhances the luminescence of St. George's halo, as well as in *Mosaic Pavement in the Sistine Chapel*, where it represents the mortar. Beyond these applications, zinc appears in discrete areas in three other works and then seemingly overpainted, suggesting that zinc white was used to conceal the original paint layer over which later modifications were made. This is exhibited in *St. Peter Enthroned with Saints* and *Francesco Querini*, where zinc is present in areas which appear visibly dark brown or black. In *Virgin and Child*, a high concentration of zinc is detected in three small, distinct areas: two on the brown 'trunk' at the Virgin's feet and one on the leg of the figure in red hose; none of which appear white or pale.

5 | Discussion

The analysis reveals that Charles Fairfax Murray employed a carefully curated watercolour palette to replicate works of the Italian Old Masters and architectural details. His selection included cobalt blue, Prussian blue, and indigo. While both cobalt and Prussian blue are deep blues, Prussian blue is darker with a green undertone, whereas cobalt is lighter and more vibrant, each serving a distinct role in the palette. Indigo may have been a contentious choice as his employer reportedly found it 'ugly' (Ruskin 1908, 142), but it was known to handle better than Prussian blue (Harley 2001, 64). Murray used a range of reds, including vermilion, red madder on copper substrate, red ochre and organic reds. In *Saint Louis*, *Saint George*, and *the Princess*, vermilion, red ochre and madder appear in both St. Louis's mitre and the princess's dress. FORS also identified an organic purple in St. Louis's lower robe. A similar red mixture in Virgin and Child highlights Murray's commitment to Old Master-style multi-tonal reds. He selected modern greens

like chrome green and a copper arsenate (likely emerald green), combining these with cobalt blue for turquoise hues. Murray also used Prussian blue-based 'mixed greens', possibly Hooker's or olive green, common in artist boxes, though given his primary pigment collection, he may have mixed these hues himself. MA-XRF of Paola Priuli shows localised chromium in the brown pattern of the dress (Figure 4); no correlation was found with lead, zinc, or barium, elements typically linked to yellow or orange pigments, suggesting chrome green was applied later to revise the work. IRR imaging reveals discrepancies between pigment placement and the original underdrawing, also pointing to later modification.

The pigment analysis compared with analysis from the works of the Old masters reveals both commonalities and distinctions in the palettes of Charles Fairfax Murray, Tintoretto, Vecchio and Botticelli, reflecting each artist's era, material choices and techniques. Tintoretto and Vecchio used the costly pigments ultramarine, indigo and smalt (Plesters 1984), while analysis

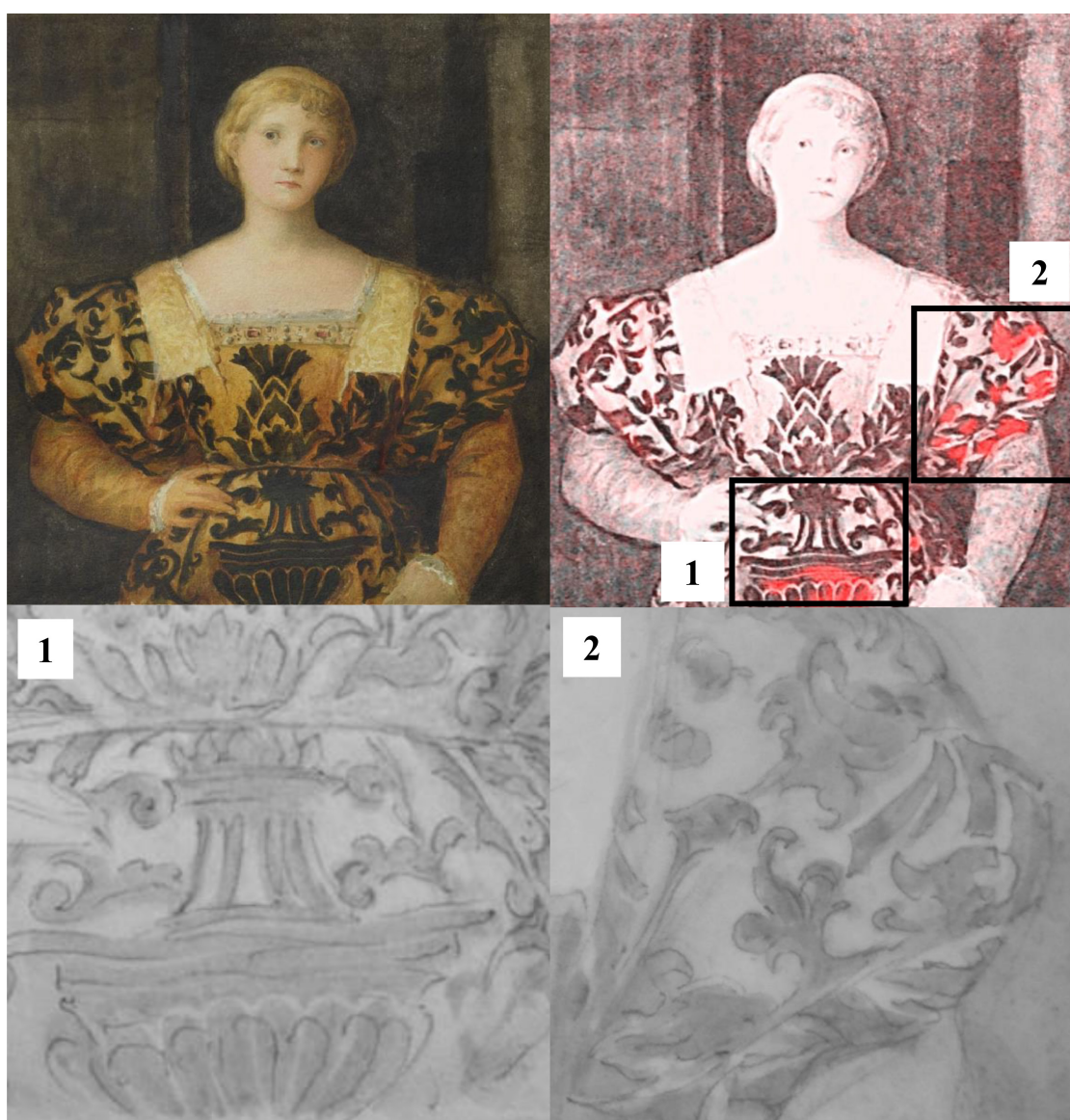


FIGURE 4 | (Top left) Charles Fairfax Murray's copy of *Portrait of a Woman, called Paola Priuli* by Vecchio, (Top right) MA-XRF map of chromium highlights discrete application areas in red. (Bottom left) IRR image reveals dress details and pigment application differences from the initial underdrawing. (Bottom right) Multispectral image shows sleeve details and pigment application variations

of *Three Graces Presenting Gifts to a Young Woman* confirms Botticelli's use of azurite (Delbourgo 1972), a blue basic copper carbonate ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$; Eastaugh 2008, 39). Ultramarine has long been a revered blue, but its prohibitive cost inspired 18th- and 19th-century colourmen to develop a synthetic, affordable equivalent, known as 'French Ultramarine' or 'New Blue' (Eastaugh 2008, 381). However, Murray selected cobalt blue, which may reflect Ruskin's influence who, despite acknowledging ultramarine's beauty, commended cobalt blue as a sufficient alternative (Ruskin 1908, 426). Financial concerns may have also played a role as from 1871, Ruskin lamented expenses related to the Guild of St. George, despite inheriting a substantial sum from his father (Hilton 2002, 348). Azurite, one of the most important blue pigments in European painting during the Middle Ages and Renaissance, was a more affordable alternative to ultramarine, reflecting Renaissance painters' ongoing pursuit of cost-effective blues (Eastaugh 2008, 39). A synthetic version, blue verditer, emerged in the 17th century before being largely replaced by Prussian blue (Gettens and West Fitzhugh 1993a, 25), which Murray employed to replicate Renaissance works. This continuity in blue pigments reflects a direct lineage, as older pigments were supplanted by modern alternatives. Markedly, Murray still used indigo, a traditional Renaissance pigment, despite the availability of more stable substitutes.

Vermilion, or cinnabar, in addition to the traditional ochres were used by both Murray and his renaissance originators to render red hues. Organic pigments were also used by both eras: Red lake was identified in works by Tintoretto, and the analysis in this study indicates that Murray used red and/or brown madder. The comparison of the yellow pigments across the two periods revealed a clear commonality. Previous analytical studies show that Tintoretto specifically used several yellows in his works, including lead tin yellow (a lemon yellow hue) (Kühn 1968), orpiment (a deep orange yellow arsenic trisulphide, As_2S_3) and realgar (an orange-red arsenic disulphide, AsS or As_4S_4), closely related to orpiment (West Fitzhugh 1997, 47). Murray used multiple yellow pigments: ochre, lemon yellow, cadmium yellow-orange and an organic yellow to replicate Tintoretto's *St. George*, effectively emulating the Renaissance method; rather than relying on a single version of a colour, artists of the period carefully tempered pigments to enhance contrast and depth. This technique is extensively described in Cennino Cennini's seminal work, *Il Libro dell'Arte*, which details how multiple tones should be applied to model form and create a sense of volume (Cennini 1440).

The greens used by Murray and his Renaissance counterparts appear to diverge the most, thereby reflecting the materials of their respective times; Renaissance painters relied on various copper-based greens, including verdigris (a vivid blue-green) (Kühn 1993, 142–145) and malachite (bright green) (Gettens and West Fitzhugh 1993b, 196–198), with terre verte providing an earthy, olive-green tone. Botticelli, in *Three Graces Presenting Gifts to a Young Woman*, layered azurite over St. Jean white, mixed with yellow ochre and green earth. In contrast, Murray used emerald green (a deep green copper arsenate), chrome green (blue-green) and Prussian blue-based greens, which ranged in hue, including olive green. As discussed, Murray largely omitted black pigments in these works, favouring dark

indigo and browns with only one instance of bone/ivory black. In comparison, the Old Masters used largely charcoal black; specifically, Tintoretto used charcoal black for grounds and shading, and Botticelli, who often mixed carbon black with red ochre and St. Jean white to create dark tones (Delbourgo 1972). The whites used by Murray and his Renaissance counterparts reflect the materials of their time. Lead white, commonly used by Tintoretto, and calcium sulphate ground were prevalent (Plesters 1984). Botticelli employed St. Jean white as a base layer in *Three Graces Presenting Gifts to a Young Woman*, notably beneath azurite and terre verte, therefore illustrating the comparative ease in which contemporary watercolours could be employed to replicate these works.

6 | Conclusion

The scientific examination of Charles Fairfax Murray's works reveals a deliberate and meticulous approach to replicating the techniques of the Italian Old Masters. Analysis of the underdrawings in the eight works studied demonstrates a consistent use of detailed preliminary drawings before the application of watercolour, highlighting Murray's methodical working process. His material selection integrates both traditional pigments such as ochres and vermilion commonly used by Renaissance painters, alongside newer, more vibrant pigments, including Prussian blue, cobalt blue, chrome green and emerald green. Murray's preference for stable and lightfast pigments suggests a commitment to producing faithful and enduring copies and his adherence to John Ruskin's teachings is evident, particularly in his use of a controlled yet versatile palette, as advocated in *The Elements of Drawing*. Murray's approach in employing multiple hues of the same colour aligns with the Renaissance tradition of utilizing warm, cool, and neutral hues of primary and secondary colours to achieve depth and tonal variation in addition to mastering the mixing of hues from the available materials. Additionally, advanced imaging and the use of MA-XRF of Murray's works reveal modifications on these works, evident in the use of zinc white under overpainted areas and the singular use of pigments, which do not appear in the remaining work.

While advanced analysis techniques provide a solid methodology for pigment identification, distinguishing between pigments such as copper arsenate-based greens and the unstandardised nomenclature of pre-manufactured pigments, which often contained popular hues like Prussian blue, reveals the challenges of interpreting materials from this period. The difficulty in identifying specific brown hues is compounded by Murray's technique of mixing pigments such as cobalt blue and chrome green, to create rich, dark tones and browns. This analysis not only deepens our understanding of Murray's technical prowess but also underscores his role in the 19th-century revival of Renaissance art and the cultural shift towards appreciating the mastery of past artists in the context of the Industrial Revolution.

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The Ruskin Teaching Collection can be viewed online at <https://ruskin.ashmolean.org/welcome>.

Data Availability Statement

Data are available on request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.