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Exploring the private universe of Henri Matisse in *The Red Studio*

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Abstract

The exhibition *Matisse: The Red Studio* allowed for an in-depth study of *The Red Studio* (1911) and six of the works featured in the painting by Henri Matisse (1869–1954) of his studio in Issy-les-Moulineaux near Paris. The grouping includes three paintings from the collection of the Statens Museum for Kunst (*Le Luxe II*, 1907, *Nude with White Scarf*, c. 1909, and *Bathers*, c. 1909), one painting from the collection of The Metropolitan Museum of Art (*Young Sailor II*, 1906), a painting from a private collection (*Cyclamen*, c. 1911), and a glazed and hand-painted earthenware plate from the collection of the Museum of Modern Art (*Untitled (Female Nude)*, 1907). The six paintings were investigated using technical (X-radiography, ultraviolet-induced fluorescence, infrared reflectography) and chemical imaging (MA-XRF) and, in some cases, spectroscopic techniques (FORS, SEM–EDS, Raman, SERS, and μ -FTIR), to better elucidate Matisse's materials and working techniques for this selection of paintings; the plate was also analyzed using MA-XRF. New findings revealed the full extent to which Matisse had completed *The Red Studio* before applying its hallmark color, referred to as Venetian red in his correspondence, over the original palette of blue, pink, and ochre that dominated the composition. Particular attention was given to identifying the wide range of pigment choices made by Matisse in the execution of the works from 1906 and 1911 that are depicted in *The Red Studio*. These pigments include lead white, zinc white, bone black, earth reds, madder lake, carmine lake, vermilion, cadmium yellow, yellow ochre, aureolin (cobalt) yellow, orpiment, viridian green, chromium-oxide green, cobalt blue, ultramarine blue, Prussian blue, cobalt violet (deep and light), and other cobalt violets, as well as possibly manganese violet and eosin red lake. The results of these analyses allowed for a direct comparison between the original works and their depictions and revealed that Matisse, unsurprisingly given his strong association with color, often translated the pigment choices faithfully between the actual works and their depictions in *The Red Studio*.

Introduction

Upon the occasion of the exhibition *Matisse: The Red Studio* [1], co-organized by The Museum of Modern Art (MoMA) and the Statens Museum for Kunst in Copenhagen (SMK), came the opportunity for an in-depth scientific study of *The Red Studio* (Fig. 1), one of four large interior scenes Matisse painted in 1911. *The Red Studio*, together with *The Artist's Studio (The Pink Studio)* (1911,

The Pushkin State Museum of Fine Arts, Moscow), illustrates a panoramic view of the interior of Matisse's *atelier* in Issy-les-Moulineaux near Paris. *The Red Studio* includes depictions of seven paintings, four sculptures, furniture, and a textile together with artist's materials and other objects that were in Matisse's studio at the time.

While *The Red Studio* is now recognized as a defining work of the early 20th century, it was not always regarded as such, nor was its significance recognized by audiences or critics. The painting was not sold immediately and later changed hands several times. After the painting was initially rejected by Matisse's patron Sergei Shchukin (Russian, 1854–1936), it appeared in London

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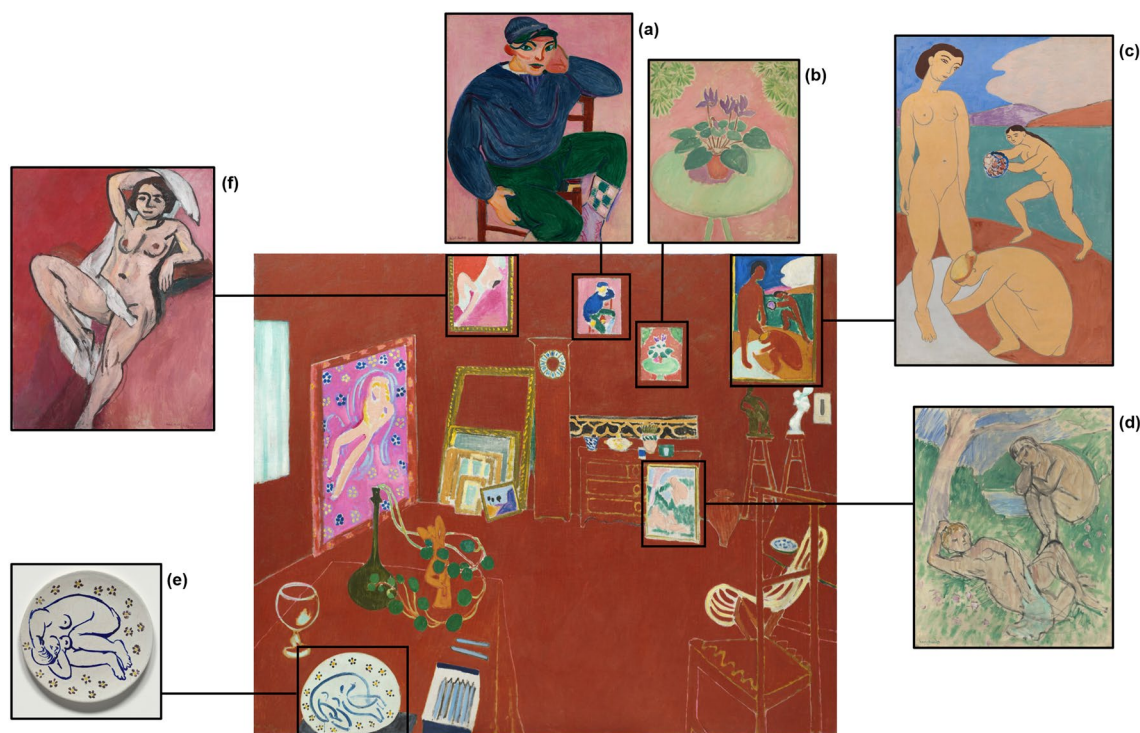


Fig. 1 Henri Matisse, *The Red Studio*. 1911. Oil on canvas (181 × 219.1 cm). The Museum of Modern Art, New York. Mrs. Simon Guggenheim Fund. The contents of *The Red Studio* analyzed in this study include: **a** *Young Sailor II*, 1906. Oil on canvas (101.3 × 82.9 cm). The Metropolitan Museum of Art, New York. Jacques and Natasha Gelman Collection, 1998; **b** *Cyclamen*, 1911. Oil on canvas (72.5 × 59 cm). Private collection, courtesy of Andrew Strauss Fine Art, Paris; **c** *Le Luxe II*, 1907–08. Distemper on canvas (209.5 × 139 cm). SMK—National Gallery of Denmark. Johannes Rump Collection, 1928; **d** *Bathers*, 1907. Oil on canvas (73 × 59 cm). SMK—National Gallery of Denmark. Gift of the Augustinus Foundation and the New Carlsberg Foundation, 2018; **e** *Untitled (Female Nude)*, 1907. Tin-glazed earthenware (Diam. 24.8 cm). The Museum of Modern Art, New York; and **f** *Nude with White Scarf*, 1909. Oil on canvas (116.5 × 89 cm). SMK—Statens Museum for Kunst. Johannes Rump Collection, 1928
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at the Grafton Galleries during the 1912 Second Post-Impressionist Exhibition and in New York at the 1913 edition of the Armory show, which traveled to Chicago and Boston. *The Red Studio* was then acquired by British aristocrat David Pax Tennant (1902–1968) in 1927, sixteen years after its creation, and the work was installed in the mirrored ballroom of his storied Gargoyle club for thirteen or so years, before moving to the Redfern Gallery in 1941, which showed contemporary British art. The painting was then sold c. 1945 to Georges Frédéric Keller (1899–1981), a Swiss-born art dealer who lived and worked in New York and was then director of the Big-nou gallery, which lent *The Red Studio* to a 1948 Matisse retrospective at the Philadelphia Museum of Art. During this time, the painting was recognized by Alfred H. Barr Jr (1902–1981), then director of MoMA, as a stroke of genius in Matisse's oeuvre, calling it “one of Matisse's most daring and original inventions” [2]. This led to the swift acquisition of *The Red Studio* by MoMA in 1948,

where it eventually came to be the renowned painting it is today [1].

In addition to a technical examination of *The Red Studio*, this exhibition also proved to be a unique opportunity for collaboration and a comparative study of some of the sculptures and paintings in *The Red Studio*, since all but one of the works originally portrayed in this setting were brought together for this show. The only painting not included in the exhibition was *Large Nude* from 1911, which Matisse considered unfinished and following his instructions was destroyed after his death. While objects depicted in *The Red Studio* other than paintings were included in the exhibition, the results presented in this study are primarily focused on the paintings. The works studied here (Fig. 1), in addition to *The Red Studio*, include three paintings in the collection of the SMK, *Le Luxe II*, 1907, *Nude with White Scarf*, c. 1909, and *Bathers*, c. 1909; one painting from the collection of The Metropolitan Museum of Art (MMA), *Young Sailor II*, 1906; and another, *Cyclamen*, c. 1911,

from a private collection. A glazed earthenware plate in MoMA's collection, *Untitled (Female Nude)* (1907), was also investigated, and this analysis presents the first scientific study of a ceramic decorated by Matisse.

This study considerably augments what is known about Matisse's palette. Previous publications have examined his use of cadmium yellow paints and their discoloration, as exemplified by *The Joy of Life* (1905–06; The Barnes Foundation, Philadelphia) [3–5], but did not publish an analysis of other pigments in the painting. Pozzi et al. [6] elucidated the nature of the natural pink lake used in *Young Sailor II* (1906; The Metropolitan Museum of Art, New York), a painting that was included in this study to investigate the other pigments used to create this work. An essay in *Becoming Matisse: The Greatest Gift of the Masters: 1890–1911* published by the Centre de Recherche et de Restauration des Musées de France (C2RMF) summarized the number of pigments used by Matisse in an early work, *La Pourvoyeuse d'après Chardin* (1893, Musée Départemental Matisse, Le Cateau-Cambrésis), where researchers identified lead white, earth pigments, cobalt blue, chromium-based pigments, Prussian blue, lithopone, calcium carbonate, and possibly orpiment. An entry in *Techniques of the World's Greatest Painters* listed some pigments used by Matisse for executing *André Derain* (1905, Tate Modern, London), including cobalt blue, cobalt violet, cadmium orange, chrome yellow, viridian, and vermilion; however, it is unclear whether scientific methods were used in their identification [7]. Other research on the color choices made by Matisse concentrated on his later oeuvre, in particular the “cut-outs,” [8] where the analysis identified the pigments found in a series of gouache-based paints, including his *Jazz* series [9], a maquette for a set of red and yellow liturgical vestments [10], and studio reference samples [8, 11]. Technical research was published in the catalog accompanying the exhibition *Matisse: Radical Invention, 1913–1917* (MoMA and The Art Institute of Chicago, 2010) covering some aspects of Matisse's working methods in painting and bronze, however, no pigment identification was included [12].

All works were studied using large area X-Ray fluorescence mapping (MA-XRF). Microscopic samples were taken from *The Red Studio* for Raman and surface-enhanced Raman (SERS) as well as micro-Fourier transform infrared (μ -FTIR) spectroscopies, and cross sections were prepared for analysis using optical microscopy (OM) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS). Technical imaging of *The Red Studio* was undertaken using X-radiography (XRR), infrared reflectography (IRR), and ultraviolet-induced fluorescence (UVF). The works at the SMK were analyzed by fiber optic reflectance

spectroscopy (FORS), in addition to analysis of cross sections and samples using Raman spectroscopy and SEM–EDS. Some works from the SMK were imaged using IRR and UVF. The MMA examined *Young Sailor II* using IRR, XRR, and UVF, in addition to Raman spectroscopy on two samples.

The Red Studio, together with the group of works analyzed here, represents a period of Matisse's experimentation with color, anatomical form, technique, and decorative motifs. This investigation resulted in a comprehensive interpretation of the materials and techniques Matisse used for all the works in this study spanning the years 1906–1911. This paper constitutes a major contribution to the technical literature on Matisse, especially his pigment choices for an artist highly preoccupied with color [1]. The results and discussion in this paper are divided into two main sections. The first section presents technical imaging and analysis of *The Red Studio*, revealing the materials and techniques Matisse used to create this unique painting. The second section presents technical imaging and analysis of five paintings and one ceramic plate portrayed in *The Red Studio*, and at the end of each object entry in this section, a comparison between the original works and their depictions is undertaken, with a particular focus on the pigments identified non-invasively using p- and MA-XRF in *The Red Studio*. The methods and materials used in this study are summarized following the conclusion.

Results and discussion

The Red Studio

Beneath the Red

After unframing *The Red Studio* at The David Booth Conservation Center, an initial examination of the tacking edges revealed the presence of pink, blue, and ochre paint peeking out from under the overall red paint (Fig. 2). A closer inspection of the surface of the painting confirmed the full extent of the blue, pink, and ochre hues observed on the tacking edges. These underlying colors appeared beneath the entire final red painting, as part of the initial stages of the work, and subsequently influenced the appearance of the overall red color, lending dimension and nuance to the composition. Matisse's ultimate addition of red paint to the walls, floor, a frame, some furnishings, and figures considerably flattened and abstracted the overall composition. Three cross sections, taken from the left tacking edge of the painting, were imaged using OM under visible light and ultraviolet (UV) radiation which showed the paint layer structure most clearly (Fig. 3). These underlying colors appeared as thin discrete layers which do not intermix with the topcoat of red, indicating they had fully dried before Matisse painted them over.

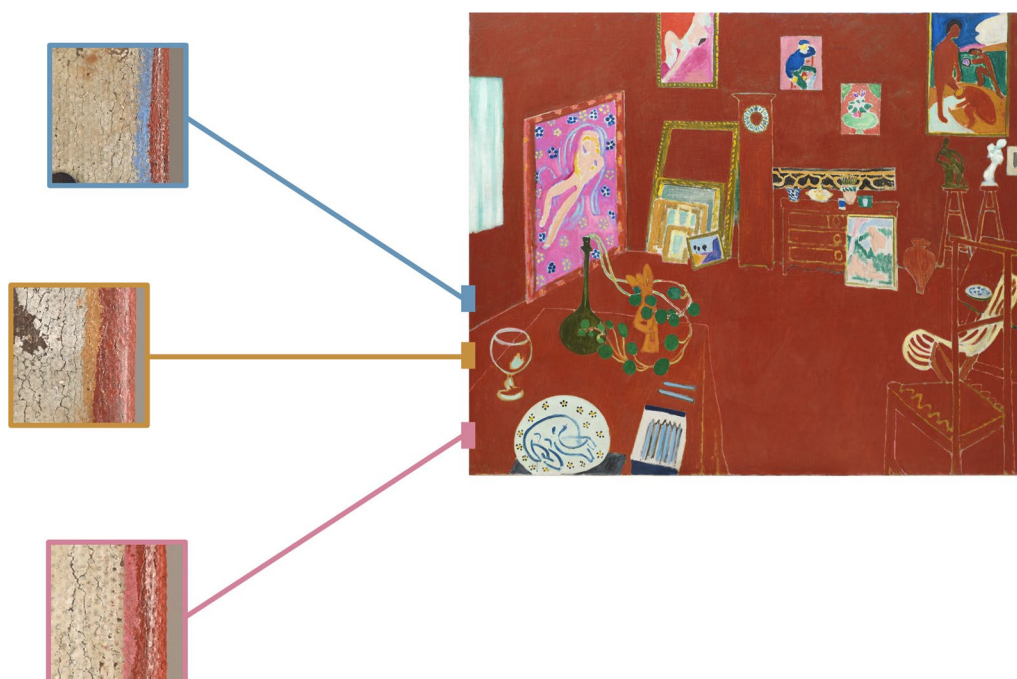


Fig. 2 Once *The Red Studio* was unframed and the edges became visible, slivers of blue, ochre, and pink, were revealed beneath the red paint. Details from the lower left edge of the painting are illustrated above

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Preparing the canvas The green fluorescence observed under UV radiation in the lowermost layers of all three cross sections indicated a zinc white preparation (Fig. 3), which was confirmed using SEM–EDS (not illustrated). Elemental mapping indicated that the ground layer contains zinc white (ZnO), some lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), and a calcium-based filler, identified as calcium carbonate (CaCO_3) by Raman spectroscopy ($\text{ca. } 1094 \text{ cm}^{-1}$) [13]. The fine distribution of particles throughout the ground layer, seen under magnification, suggested the priming was commercially prepared. The unpainted, white ground was left visible in some areas, most prominently in the foreground box of drawing implements at the lower left and in the background of the *Bathers* depiction. XRR further confirmed that *The Red Studio* was mapped out carefully at the earliest stages (Fig. 4b). No significant painted adjustments were found in the X-radiograph, which revealed only one minor change: in the window of the door at the left edge. Here, Matisse initially painted a small horizontal bar near the bottom that was subsequently painted over.

Evidence of carbon-based underdrawing (Fig. 4c) on the ground preparation was seen around the perimeter of some forms throughout *The Red Studio* in the infrared reflectogram, suggesting that Matisse partly outlined the composition during this initial stage. IRR did not reveal

any major deviations between the underdrawing and the final painting, other than a more elaborate scrolling pattern that was initially present on the chest of drawers; Matisse ultimately painted over this detail with red. In addition to the underdrawing, Matisse inscribed forms on top of the paint in pencil, as seen defining the figures in the depiction of *Bathers*.

Notably, microscopic examination of the cross section taken from the area of the studio wall (Fig. 3a, b) revealed the presence of another light gray paint layer on top of the commercial priming, but only in the background, i.e., the area depicting the studio walls. This layer did not fluoresce green under UV, indicating that it is composed of lead white, which was confirmed by SEM–EDS analysis. Raman analysis of this layer further confirmed the presence of lead white ($\text{ca. } 117, 422, \text{ and } 1058 \text{ cm}^{-1}$) [14], together with calcium sulfate ($\text{ca. } 1010 \text{ cm}^{-1}$) and a carbon-based black identified through the signature D and G bands ($\text{ca. } 1355 \text{ and } 1603 \text{ cm}^{-1}$, respectively), characteristic of carbonaceous materials [15]. This black pigment appeared as discrete particles in the cross section (Fig. 3a). The reason for this additional layer remains unknown at this time; however, it is possible that Matisse used gray paint to block in the positions of the objects on the wall (Additional file 1: Fig. S1a). In this hypothesis, Matisse would have first left areas of white ground

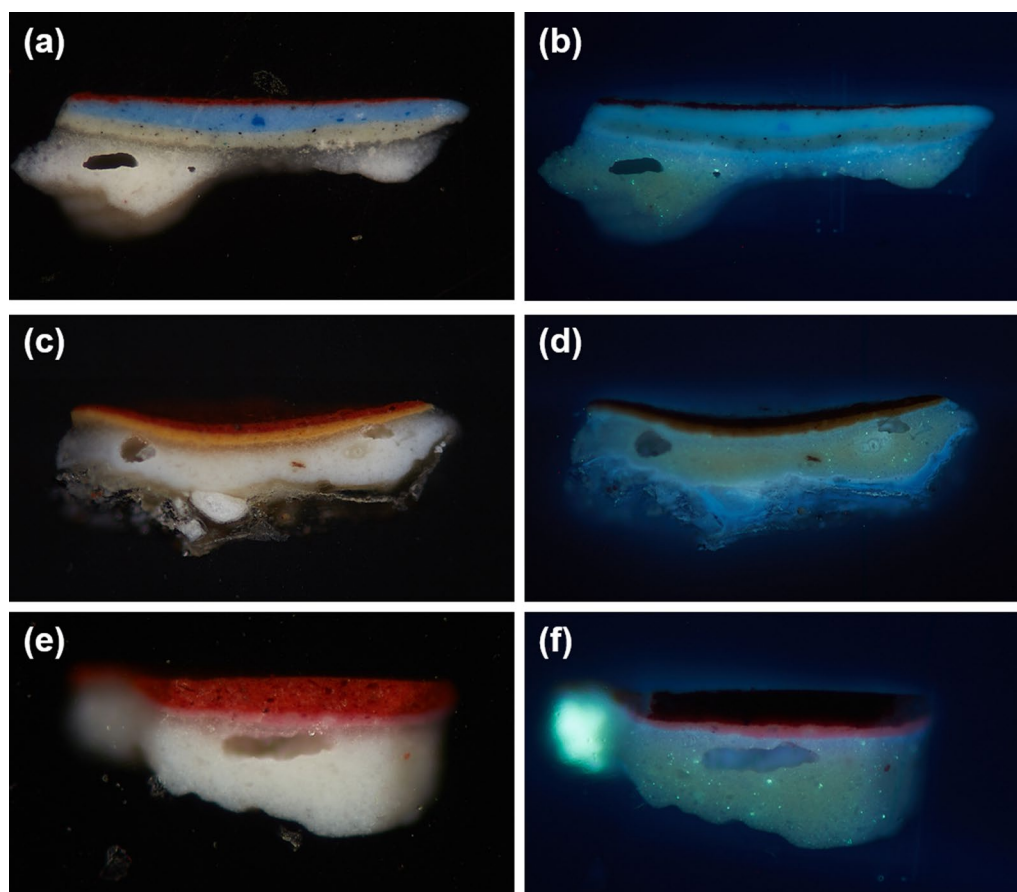


Fig. 3 Cross sections were taken from *The Red Studio* tacking edges and examined under visible (left) and ultraviolet (right) illumination. **a** and **b** show the blue, **c**, **d** show the ochre, and **e**, **f** show the pink underlayers covered by the final Venetian red paint layer, visible in all three cross sections. The reasons for the prominent lacunae in the ground preparation are unknown at this time

in reserve for the objects, as seen by the exposed ground visible in the background of *Bathers*, for example. He then would have filled the remaining space around these objects with gray paint throughout the background walls. Curiously, the presence of drips of blue and pink paint, but none of the gray, can be found on top of the depicted objects and furniture throughout *The Red Studio* (Additional file 1: Fig. S1b, c). Therefore, it follows that Matisse painted at least some of the objects on the white ground reserve, in addition to other objects in the foreground, after which he applied dilute blue and pink paint to fill in the wall and floor, respectively.

Intermediate colors and first stage Examination of the cross sections conclusively indicated the presence of an intermediate layer in *The Red Studio* made up of either blue, ochre, or pink. Visual examination of the painting indicated that blue was used in the wall area, ochre to color most of the wooden furniture, such as the table, chair, dresser, and grandfather clock, and pink was used

in the foreground to color the floor. Some of these colors remain visible as outlines, where Matisse exploited them to delineate forms throughout the monochrome red expanse, like around the table or chair.

To further characterize the pigments Matisse employed, additional microsamples were taken from the left tacking edge and used to confirm or complement the p- and mapping XRF analysis with spectroscopic techniques. The blue was identified as a mixture of cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$), based on SEM-EDS results, and lead white, which was identified by Raman spectroscopy through a characteristic $\nu_1(\text{CO}_3^{2-})$ symmetric stretch at *ca.* 1051 cm^{-1} (Fig. 5a) [14].

The yellow pigment was identified as a natural ochre based upon the detection of high levels of iron accompanied by weaker signals for aluminum, silicon, potassium, and titanium by p-XRF [16]. Analysis of this ochre with μ -FTIR confirmed the presence of silicates, including kaolin minerals (*ca.* $3696, 3669, 3654, 3619, 1165, 1115, 1081, 1011, 935, 914, \text{ and } 880 \text{ cm}^{-1}$) [17, 18] and quartz

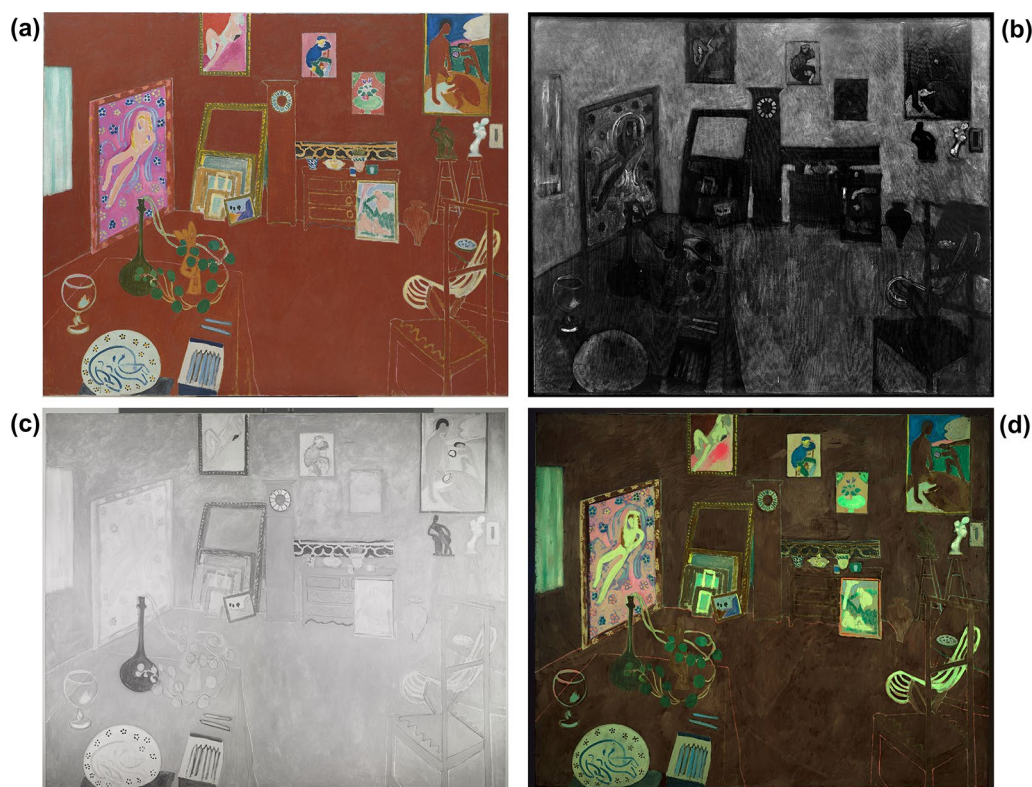


Fig. 4 *The Red Studio* was imaged using four different techniques: **a** normal light, **b** XRR, **c** IRR, and **d** UVF

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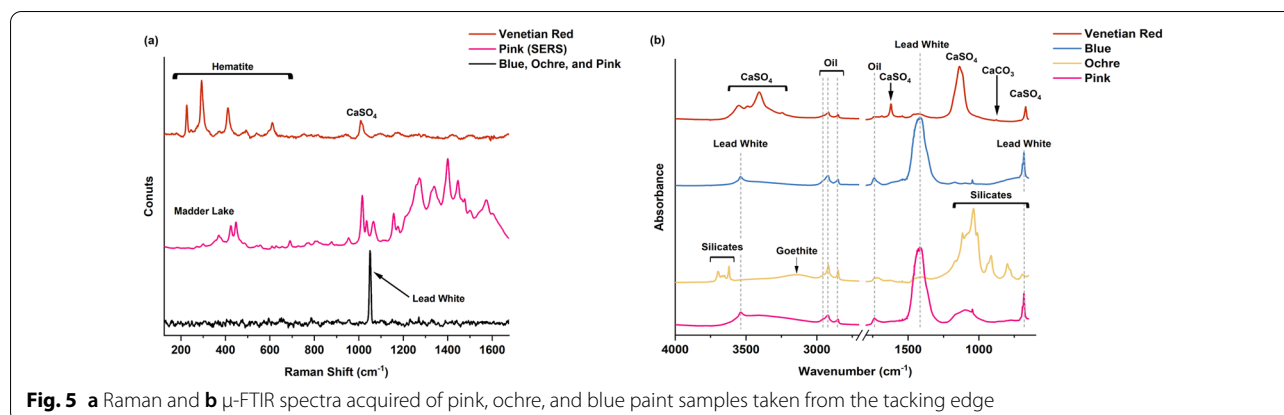
(*ca.* 799, 778, and 693 cm^{-1}) [18], in addition to lead white, identified by its asymmetric $\nu_3(\text{CO}_3^{2-})$ stretch at *ca.* 1412 cm^{-1} [19] (Fig. 5b). Bands due to these components masked the characteristic hydroxyl bending modes for goethite, the α -polymorph of iron(III) oxide-hydroxide, *ca.* 892 and 795 cm^{-1} , but there remained an observable goethite hydroxyl stretch at 3145 cm^{-1} that further confirmed the natural source of the iron-based pigment (Fig. 5b) [16].

The pink is a mixture of lead white, as identified by Raman (*ca.* 1051 cm^{-1}) [20] (Fig. 5a) and μ -FTIR (*ca.* 3537, 1412, 1046, 691 and 681 cm^{-1}) [19] (Fig. 5b) and an organic pigment, which could not be successfully identified with XRF. While normal Raman analysis was equally unsuccessful due to overwhelming fluorescence [21], SERS clearly identified the presence of natural madder lake, with lines for both alizarin (*ca.* 1602, 1573, 1476, 1464, 1400, 1357, 1360, 1340, 1272, 1176, 1167, 1035, 1015, 954, 877, 803, 776, 628, and 485 cm^{-1}) and purpurin (*ca.* 1649, 1432, 1258, 1210, 1110, 1065, 832, 813, 726, 690, 657, 609, 447, 424, 381, 370, and 300 cm^{-1}) [22] (Fig. 5a). Examination of the painting using UVF strongly suggested this lake is made from naturally-derived raw materials, as the pink seen as outlines around the

furniture fluoresces a characteristic bright orange color (Fig. 4d) [23].

While Matisse did not include any interior or architectural details in the final stage of *The Red Studio*, MA-XRF surprisingly revealed a series of chromium-rich vertical brushstrokes beneath the red (Fig. 6), in the wall area, that indicated a similar paneled wall design to the one seen in *The Artist's Studio (The Pink Studio)*. This, in combination with some observed green-colored vestiges of the intermediate layer seen along the edges of the depiction of *Young Sailor II* and beneath the stool on the right side of the picture (Fig. 7), indicated that the paneled design was executed in viridian. The original appearance of the studio walls would have resembled the vertical paneling in *Still Life with Geranium* (1901; Pinakothek der Moderne), which features a blue wall with green lines. MA-XRF also revealed that viridian appears beneath the red under the head of the clock, along with the baseboard between the blue wall and pink floor, and was used for shadows beneath the clock and to the left of the dresser.

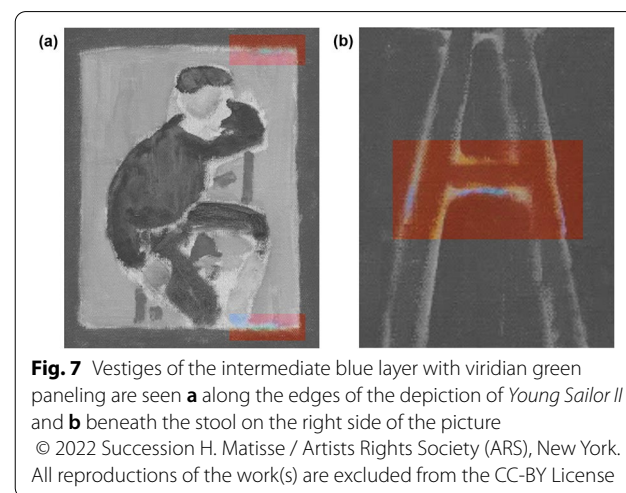
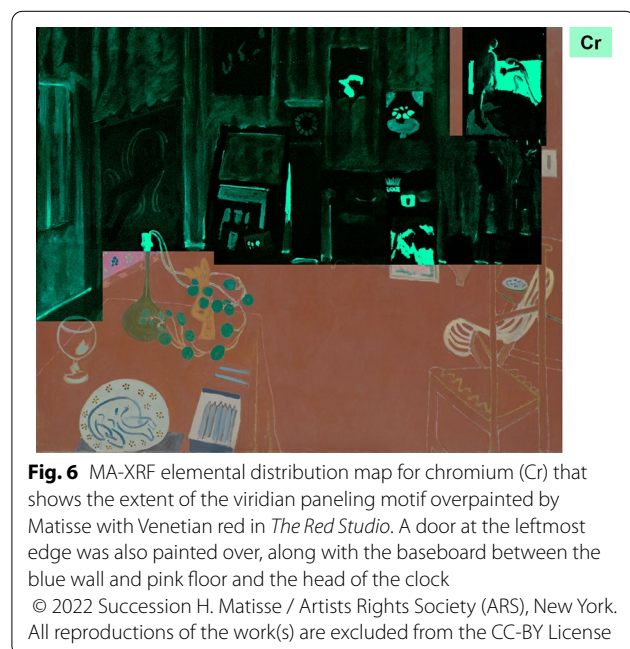
The chromium distribution map also revealed that the window, at the left of the composition, was originally conceived as one of the double doors with windows that



led into Matisse's studio. The bottom half of the door was eventually painted over with red, leaving only the window in place. Matisse also applied a vertical pencil line on top of the red paint, extending from the bottom right corner of the window curtain to the floor, indicating the outline of the lower half of one of the studio's exterior doors. The curtain of the window is characterized by long parallel strokes of the brush; incidentally, these lines appeared to be a continuation of two viridian lines from the original green paneling of the wall (Fig. 6).

Venetian red In a letter to Sergei Shchukin, the artist described *The Red Studio*, writing "[the] whole is Venetian red. This red, which is a little warmer than red ochre, is a precise color of the palette." [1] Matisse selectively covered the intermediate colors of the composition with

a red earth pigment, which sometimes was marketed as Venetian red by color merchants; overall, Matisse covered two-thirds of the original composition with this hue. While the name Venetian red has alluded to different shades and preparation methods [24], a red earth pigment was decisively identified due to the presence of hematite as observed by Raman spectroscopy (*ca.* 226, 292, 411, 492, and 610 cm^{-1}) [25] (Fig. 5a), and this paint was also found to contain calcium sulfate in the form of gypsum, as identified by Raman (*ca.* 1009 cm^{-1}) [26] and μ -FTIR (*ca.* 3548, 3490, 3405, 3244, 1684, 1621, 1139 and 669 cm^{-1}) [27] (Fig. 5b). A weak peak at *ca.* 875 cm^{-1} could indicate the presence of CaCO_3 , although all other diagnostic peaks are masked by other components. The $\nu_3(\text{CO}_3^{2-})$ stretch at *ca.* 1412 cm^{-1} in the μ -FTIR spectrum further confirmed the use of lead white with the red paint [19], which was also observed by XRF and SEM-EDS. Since Matisse referred to this shade as "Venetian red" in his correspondence, this term will be used throughout to differentiate this shade of red from other reds.



Furthermore, UVF imaging of *The Red Studio* showed intense green fluorescence only in the red passages which suggested that Matisse selectively added natural resin to the red paint [23] to enhance the gloss of the dominating red passages while leaving other areas matte (Fig. 4d). Viewing the painting under UV also revealed Matisse's vigorous brushwork in applying the red. Analysis of the red paint using μ -FTIR confirmed the presence of a natural resin (ca. 3438, 3224, 2957, 2932, 2873, 1712, 1645, 1463, 1412, 1247, 1182, and 1099 cm^{-1}) (Additional file 1: Fig. S2) [17]. In other areas, however, Matisse appeared to have instead opted for a natural resin varnish that he applied selectively over certain details. This is particularly evident in a partially varnished petal-shaped yellow highlight on the frame of *Large Nude*, where the varnish had the benefit of preserving the saturation and chroma of the cadmium yellow and zinc white paint of the highlights while the unvarnished parts have darkened.

The Red Studio color palette

The pigments in Matisse's palette for *The Red Studio* included the following: lead white, zinc white, bone black [identified through hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3]$ [28], vermilion (HgS), a red ochre, madder lake (alizarin and purpurin), a yellow ochre (Fe, Al, Si, K, Ti), cadmium yellow (CdS), chromium (III) oxide green (Cr_2O_3), viridian green ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$), ultramarine blue ($\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$), Prussian blue ($\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^{3-}$), and cobalt violet light $[\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$. The use of certain pigments to depict the remaining objects not further analyzed for this study, including the two paintings *Large Nude* and *Corsica, the Old Mill* (1898, Wallraf-Richartz-Museum and Fondation Corboud), will be discussed in this section.

Matisse used lead and zinc white in *The Red Studio*, and their distribution was mapped using MA-XRF. Matisse used lead white mainly where the paint is thickly applied as accents alone or in mixtures. In other cases, he used zinc white mixed with other colors, for example, Matisse mixed ochre and zinc white to produce lighter skin tones.

A dilute, ink-like bone black, which contains hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3]$ [28], was identified by the presence of calcium and phosphorus in the p-XRF spectra. This paint was used in the horizontal Persian textile pinned on the wall above the dresser and in the outlines of the blue drawing implements. Cadmium yellow was also mixed with a carbon-based black to create darker, bronze hues, as seen in the frame of *Nude with White Scarf* or *Decorative Figure*. (1908, Art Gallery of Ontario); this carbon-based black did not contain the calcium or phosphorus associated with hydroxyapatite from animal sources and could be plant-derived instead.

Matisse employed Venetian red not only as a final layer but also in a dilute wash of paint depicting an urn, which left the ground application and canvas texture readily visible. Yellow ochre is the only other earth pigment identified in the painting. Vermilion red was identified by the elemental maps for mercury. Passages of vermilion appear orange in the tendrils of the nasturtium and beneath the ochre of *Upright Nude with Arched Back* (Winter 1906–1907, private collection), where bright patches of orange can be glimpsed around its edges. An underlying layer of vermilion was further revealed by MA-XRF, where mercury was observed (Additional file 1: Fig. S3).

A chromium-based green, most likely hydrated viridian based on tone, predominates in the nasturtium leaves and the vase, but it is also found in a sliver of the shadow between the clock and the leaning frames in the center of the painting. In many areas, Matisse applied flat swaths of color on the canvas; however, there is some limited wet-into-wet blending, as seen in the mixing of lead white with what is likely viridian in the modeled depiction of the plaster bust, *Jeanette IV*. At the center right edge, a diagonal stroke of pure green accentuates the straight edge of the table and the curved side of a dish. A darker, more olive-toned green used in depicting the horizontal shadow of the leaning frames and the vase of the nasturtiums also appeared rich in chromium and could be evidence of Matisse's probable use of anhydrate chromium (III) oxide. It was not possible to differentiate between the two varieties due to the limited paint samples taken only from the tacking edges.

A bright cadmium yellow features predominantly in the painting. It is used in the gilded frames and in the petals of the flowers in the background of *Large Nude* and its ornate frame. Matisse also mixed cadmium yellow with chromium (III) oxide green variety to create the deep green of the vase with the nasturtium vine, and with lead white to create shades of mint green seen in the clock face and the window curtain. Cadmium yellow has a characteristic deep red–orange fluorescence when used without mixing [23], seen in the flowers of the *Female Nude*, or bright orange when mixed with zinc white, which itself fluoresces a greenish hue [23], as seen in some of the gilded frames and the flower motifs in the *Large Nude*.

In addition to the blue under paint Matisse used for the wall, a nickel-rich cobalt blue was identified in the box of light-blue drawing implements on the table. Nickel is regularly identified in the naturally sourced ores from which cobalt is extracted for pigment use [29]. As for other blues, ultramarine blue accents are found throughout, including the petals in the background of *Large Nude* and the objects on top of the bureau; this was derived from observing aluminum, silicon, and potassium in those

regions by spot p-XRF analysis. Matisse limited his use of Prussian blue to the dark rectangle beneath the *Female Nude* plate, which was identified through the presence of iron with p-XRF in that passage.

Early cobalt violets were made of toxic cobalt arsenate [24], and in this instance, cobalt violet light was identified by the presence of arsenic in mauve-hued passages, such as the background of *Large Nude* and foreground of *Corsica, the Old Mill*. Matisse perhaps used this color sparingly because it was expensive and hard to obtain at the time.

The private universe of *The Red Studio*

Young Sailor II (MMA)

Young Sailor II is the second version of a portrait Matisse painted of a young local man living in the fishing village of Collioure, in southern France. Made in the summer of 1906, it is the earliest painting included in this study. Matisse completed two versions of *Young Sailor*. While both portraits were painted within weeks, the second version is stylistically distinct from *Young Sailor I* (Collection of Sheldon H. Solow, New York), which is sketchy but comparatively naturalistic, even with its striking Fauve palette. Matisse exaggerated the sitter's features in *Young Sailor II*, which prompted a genuine misunderstanding from both fellow painters and collectors alike [30].

Visual and microscopic examination, imaging, and chemical analysis of *Young Sailor II* revealed that Matisse directly sketched his composition in pencil on a canvas prepared with a white ground mostly composed of lead

white (Fig. 8a). The uneven opacity of the ground layer across the canvas, along with diagonal striations visible in the lead distribution map (Fig. 8a) and the X-radiograph (Additional file 1: Fig. S4a) suggested that the artist probably primed the canvas. The ease with which Matisse drew the figure in pencil is clearly visible through the thin oil paint and in the infrared reflectogram (Additional file 1: Fig. S4b). Matisse made no changes or revisions in drafting the figure, using fine repetitive lines to block out the composition. This style of rendering is indicative of Matisse's deliberate approach to the second version of this portrait.

The oil paint was fluidly and thinly applied, and the bristle brush strokes allow the white ground to show through prominently, which further articulates the forms and defines the volume of the figure. Matisse painted the composition with a palette of blue, green, purple, and pink, and used contrasting strokes of brown, yellow, and red paint in the chair. Apart from the flesh tones, colors appear to be used directly from the tube. For the sweater, and most likely the cap, Matisse used ultramarine blue. This pigment was identified by Raman spectroscopy of a microscopic sample taken from the sweater (Additional file 1: Fig. S5). The dark blue shading on the proper right side of the cap contains cobalt blue. In the sitter's trousers, facial features, and cap visor, chromium was identified with MA-XRF, which most likely indicates the presence of viridian green based on hue (Fig. 8a). MA-XRF also revealed the presence of manganese, phosphorous, and cobalt in the thick purple outlines of the figure's sweater (Additional file 1: Fig. S6a–c), which suggests a

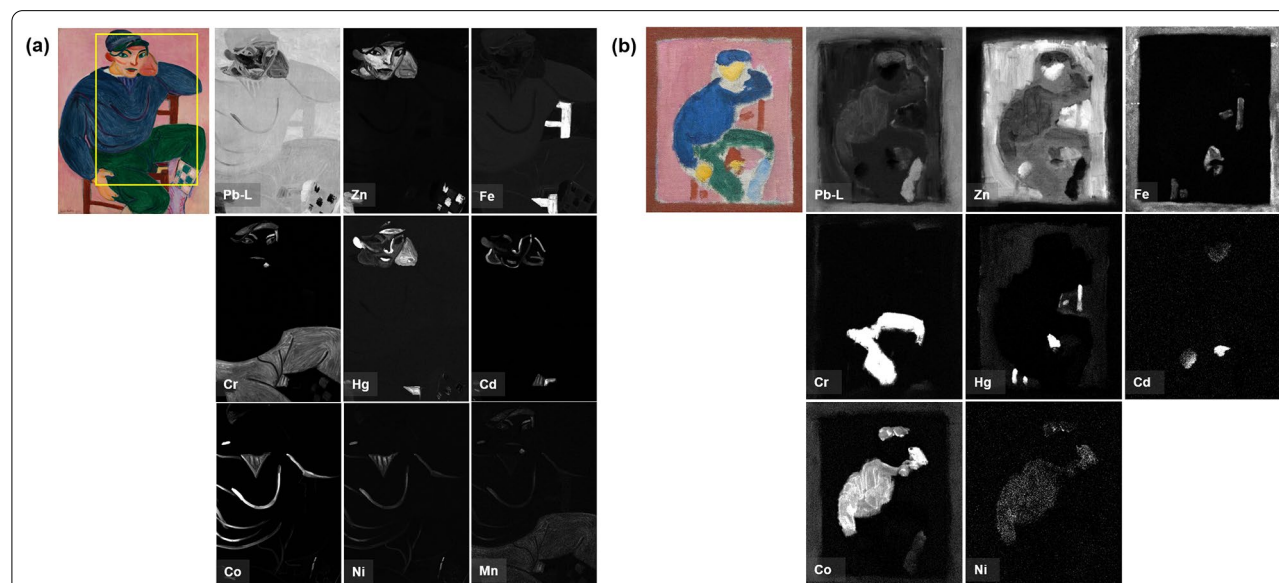


Fig. 8 Elemental distribution maps of **a** *Young Sailor II* versus **b** its depiction in *The Red Studio*

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mixture of a violet manganese phosphate [24] and cobalt blue was used. This analysis does not eliminate the possible additional presence of a cobalt (II) phosphate violet pigment [31], which would have been available to Matisse as well. Other outlines, such as those in the trousers, appear to contain only cobalt blue (Fig. 8a and Additional file 1: Fig. S6b). Matisse painted the solid pink background with a mixture of lead white and a lake pigment previously identified by SERS as a carminic acid-based lake [6].

The figure's face and hands are distinctly abstracted, as Matisse painted these features using outlines of single brushstrokes of yellow, green, and red, along with some blue outlining the sitter's right hand. Matisse juxtaposed these colors, working wet in wet without blending them. MA-XRF showed that the face contours were painted with thick strokes of cadmium yellow. The orange-hued outlines defining the nose, ear, forehead shadow, and the proper left hand, are all mercury-rich, which indicated the use of vermilion (Fig. 8a). This paint appears to have been applied directly under or on top of some of the yellow strokes to modulate their tint. The skin tones are composed of zinc white mixed with varying lesser amounts of red and pink paint. Visual examination of the face suggested that Matisse may have used an organic lake pigment in the pink paint while mercury was observed by MA-XRF, indicating the presence of vermilion in the darker red areas. MA-XRF analysis suggested that bromine, indicative of eosin lake, may be present in the pink paint (Additional file 1: Fig. S7); however, the overlap of the mercury $L\beta$ (11.869 keV) and bromine $K\alpha$ (11.902 keV) lines prevented its identification using MA-XRF alone. The bromine $K\beta$ line was not strong enough in the spectra acquired in these areas to calculate a reliable elemental distribution map, and the pristine condition of the painting prevented the sampling of the pink areas.

Matisse painted the sitter's lips in two broad strokes of a chromium-containing green and vermilion, with a hint of a warmer red applied on top of the lower lip's proper right half. The sailor's exaggerated almond-shape eyes were partially outlined and filled in with a chromium-based green and zinc white, with a dash of blue, possibly ultramarine, to define the pupils (Fig. 8a).

Matisse painted the brown wooden chair with an ochre composed mainly of iron and relatively smaller amounts of manganese, possibly an umber, and with cobalt blue outlines (Fig. 8a). Notably, Matisse may have initially used vermilion paint in the chair, as mercury was identified in the chair's front cross-rung seat rail located directly under the figure's proper right thigh. For the few strokes of the chair's seat, Matisse used pure bright colors: cadmium yellow, a chromium-based green, likely viridian, a red pigment, possibly a lake, cobalt blue, and another

blue pigment, perhaps ultramarine. Matisse finally articulated the small space between the young sailor's proper left calf and the chair with casual strokes of cobalt blue mixed with pink, possibly a mixture of zinc white and a red lake.

The representation of *Young Sailor II* in *The Red Studio* is faithful to the original, except that the figure lacks facial features and there is no pattern on his woolen sock (Fig. 8b). Both sailors' sweaters are painted blue. The sweater in *Young Sailor II* is rendered in ultramarine with cobalt blue or a mixture of cobalt blue and violet pigment outlines. In the depiction, Matisse reversed the colors by using cobalt blue with ultramarine outlines. Matisse used a similar color scheme with ultramarine in the sailor's cap of *Young Sailor II*, while in the depiction, the cap is rendered with cobalt blue. Both sailors' trousers are painted with a chromium-based green, likely viridian. The traditional Basque woolen sock in *Young Sailor II* features a checkerboard design of chromium-based green and pink (mainly a mixture of zinc white and vermilion), while the shoe is mostly painted purple with vermilion criss cross laces. However, in *The Red Studio*, both the sailor's sock and shoe are depicted as a solid block of cobalt blue mixed with relatively copious amounts of lead white.

As discussed above, the chair in *Young Sailor II* is primarily painted with an iron-based earth pigment while the seat is comprised of a multicolor pattern including some cadmium yellow, which is more loosely represented in *The Red Studio* where only an iron-based pigment and cadmium yellow were found. It is interesting to note that the front seat rail of *Young Sailor II*'s chair contains some vermilion as in the chair depicted in *The Red Studio*, however, vermilion can also be found mixed in with the iron-based earth pigment throughout the chair of the depiction. In *Young Sailor II*, Matisse painted the chair primarily with earth pigments. The skin tones in *Young Sailor II* and the depiction appear visually as different colors since the flesh tones in *Young Sailor II* are composed of zinc, vermilion, and possibly an organic lake pigment with cadmium yellow outlines, resulting in a pinkish tone, while the skin tones in the depiction in *The Red Studio* are composed of cadmium yellow mixed with a significant amount of zinc white. The background of both the painting and the depiction is a similar pink color, however, in *Young Sailor II* this pink is a mixture of a carmine lake pigment and lead white, whereas in the depiction the pink is vermilion mixed with zinc white.

Bathers (SMK)

For *Bathers*, Matisse used a plain-weave canvas primed with a white ground. The ground remains visible throughout the painting due to Matisse's sketch-like technique. XRR (Additional file 1: Fig. S8) revealed that

Matisse applied the ground using a palette knife after he stretched the canvas. Drips around the edges suggest that the ground was diluted before application. The contours of the figures are loosely painted in oil, with numerous visible changes. While it appears that the composition was executed swiftly, two types of the painted outline are observed: a more delicate rendering with numerous changes, followed by a bolder contour painted with a thicker brush that defines the figures' position. Dark contour lines were painted with bone black as observed in the maps for calcium and phosphorus associated with hydroxyapatite (Fig. 9a). Matisse used several techniques to fill his outlines with color. In some passages, he used dilute oil paints, resulting in visible drips on the surface. In other areas, the paint was applied in thicker layers using zigzag brushstrokes.

The *Bathers* color scheme incorporates shades of green, blue, brown, purple, and pink. The distribution of lead seen by MA-XRF (Fig. 9a) suggested a lead-based ground, likely composed of lead white mixed with barium and zinc; the three elements are observed throughout the composition in MA-XRF (Fig. 9a). The striated appearance of the lead-based ground in the MA-XRF elemental distribution map for lead was similar to that seen in the X-radiograph, indicating application by a palette knife.

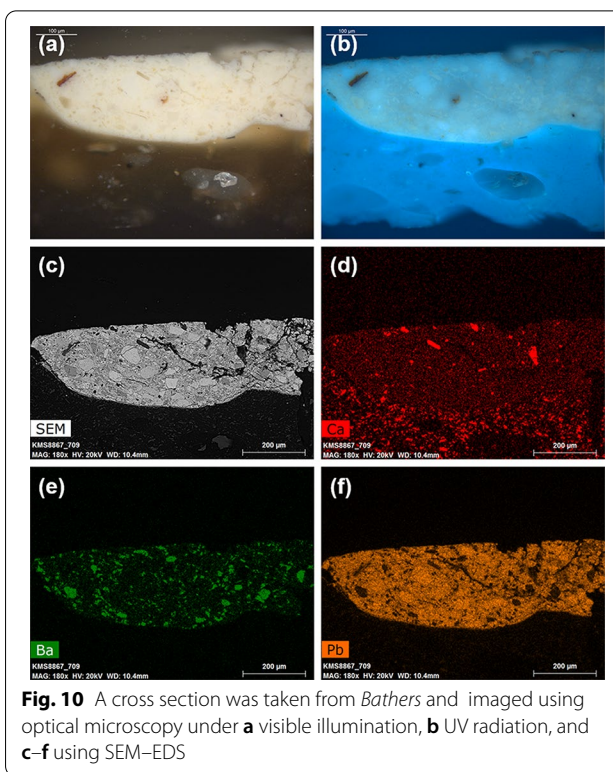


Fig. 10 A cross section was taken from *Bathers* and imaged using optical microscopy under **a** visible illumination, **b** UV radiation, and **c-f** using SEM-EDS

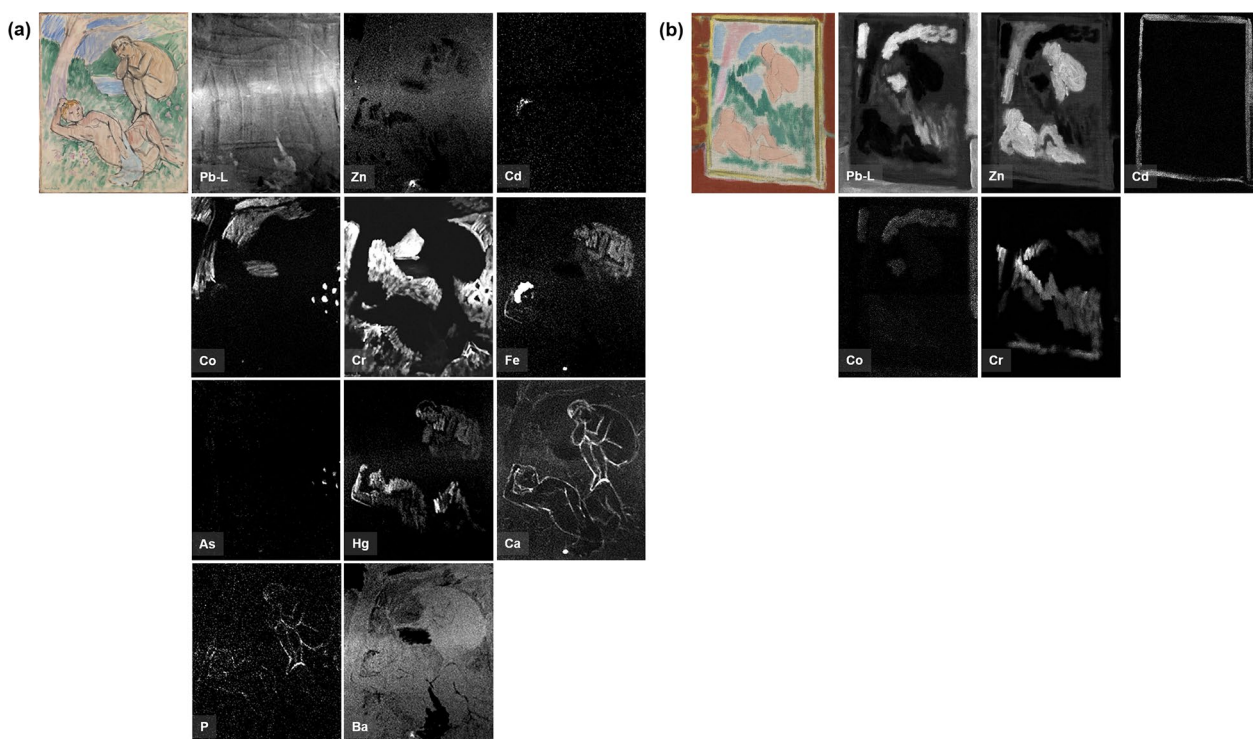


Fig. 9 Elemental distribution maps of **a** *Bathers* versus **b** its depiction in *The Red Studio*

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The use of lead white and a barium-based pigment (likely barium sulfate, BaSO_4) used in the preparation layer of *Bathers* was confirmed by SEM–EDS analysis of a cross section taken from the upper right edge (Fig. 10). Little zinc was detected in the cross section and the net intensity of barium was ten times higher than that of zinc, which safely excluded the presence of lithopone; standard lithopone is, by weight, 70–72% BaSO_4 and 28–30% zinc sulfide (ZnS) [32]. The presence of lead seen in the M-lines MA-XRF elemental distribution map (not illustrated) also indicated the use of lead white in areas of the composition such as the scarf, the left corner of the sky, and mixed with cobalt blue in the water.

MA-XRF elemental distribution maps also suggested the presence of a chromium-based green, evident in the foliage of the background. The presence of chromium (III) oxide green in the foliage was confirmed by FORS spectra that exhibited transitions to high and low reflectance at *ca.* 510 nm and 630 nm, respectively (Additional file 1: Fig. S9) [33]. The same pigment was also identified in the draped bluish-green cloth covering the reclining figure by FORS and MA-XRF.

Cobalt blue was identified in all the blue-colored areas as seen in the cobalt distribution by MA-XRF, except for the light bluish-green draped cloth. Additional analysis of the sky and water passages using FORS revealed spectra with features attributed to cobalt blue, identified by a strong absorbance at *ca.* 590 nm (Additional file 1: Fig. S9) [34]. Additionally, the co-localization of cobalt and arsenic in MA-XRF elemental distribution maps for the faint purple of the flowers on the right edge suggested that Matisse used cobalt violet (light) (Fig. 9a).

The presence of vermilion was inferred from MA-XRF elemental distribution maps for mercury (Fig. 9a), which Matisse used to depict the reddish-brown skin tones of the two figures. Vermilion also appeared to be mixed with earth browns to depict the crouching nude, as suggested by the correlation between the iron and mercury MA-XRF elemental distribution maps. Reflectance spectra from the red area in the thigh of the reclining figure exhibited spectral signatures that corresponded to vermilion mixed with a yellow ochre. Earth pigments were also observed elsewhere in the composition, such as the yellowish-brown hair that could be attributed to a naturally-occurring yellow earth pigment. FORS, as a technique, can separate between vermilion and earth pigments; yellow–brown earth pigments show transitions to high reflectance at *ca.* 450, 600, and 770 nm [35], whereas the sharp absorption transition edge at *ca.* 600 nm is characteristic of vermilion (Additional file 1: Fig. S9) [35]. In addition, MA-XRF revealed the presence of cadmium yellow mixed

with natural yellow earth in the hair of the reclining figure (Fig. 9a).

UVF imaging showed an intense pink fluorescence in the flowers at the bottom left, the top part of the tree, and some details in the lower, purple-colored trunk (Additional file 1: Fig. S10); this was attributed to the presence of a naturally-derived, organic lake pigment. FORS spectra acquired from the pink areas of the landscape showed spectral features at *ca.* 485, 515, and 550 nm that are characteristic of tin-treated cochineal lake (or tin carmine) [36], an insect-derived anthraquinone dye precipitated on a tin (IV) chloride substrate (Additional file 1: Fig. S9) [24]. In some cases, to obtain a deeper shade of pink, found in the tree and the flowers on the right, cochineal lake was mixed with cobalt blue and violet as indicated by the MA-XRF elemental maps for cobalt and arsenic, respectively (Fig. 9a). Cochineal lake mixed with cobalt blue in the bottom part of the trunk was further confirmed by UVF imaging.

The depiction of *Bathers* in *The Red Studio* captures the composition of the original painting it represents but without many of the details (Fig. 9b). This representation includes a simplified rendering of the sky, water, tree, and foliage of the background as well as the figures; however, Matisse eliminated the flowers of the background and any details in the figures. A comparison of the MA-XRF results shows that the water in both the depiction and the original painting is composed of a mixture of cobalt blue and lead white, similar to the sky of the depiction in *The Red Studio*. The sky of *Bathers*, however, is composed of cobalt blue and zinc, not lead, white. The paint of the tree in *Bathers* is blended in a gradient from purple at the bottom of the trunk, composed of cobalt blue and cochineal lake, to a cochineal lake pink near the top. Matisse repeated this technique in the depiction in *The Red Studio* by layering cobalt blue beneath a mixture of madder lake and zinc white at the bottom of the trunk, gradually transitioning to vermilion and zinc white at the top; vermilion was deduced through spot p-XRF analysis. The foliage of *Bathers* are painted in a mixture of chromium-based green and zinc white while the foliage of the depiction in *The Red Studio* is made of a chromium-based green mixed with lead white. The figures in the depiction of *Bathers* in *The Red Studio* appear much lighter, painted with a mixture of zinc white and an earth pigment (the latter was observed clearly by p-XRF) while the figures in *Bathers* are painted with vermilion or vermilion and earth red.

Nude with White Scarf (SMK)

This composition of a reclining female figure draped in a white scarf is heavily modeled with thick paint layers covering the entire surface. The thickness of the paint

layers is due to the considerable reworking of the composition by Matisse. IRR revealed numerous changes that allude to at least two other stages before Matisse arrived at the final composition; all depict variations on the same pose, outlined in black paint (Fig. 11). Nevertheless, the interpretation of these stages is complicated. Matisse often finished his figures by accentuating the contours with black paint, likely the same black paint he used for the earlier iterations. In both campaigns, the figure's proper left leg extends to the bottom right corner with the proper right leg raised and the foot placed adjacent to or under the left thigh. The scarf flows from the top of the figure's head and terminates at her proper left calf. However, in the first stage (Fig. 11a), the figure's head was likely tilted further back, and the scarf had a squared-off end by her head. Additionally, her right hand was raised, as in the final composition, but was slightly slimmer and lowered. Overall, her left side was shifted to the edge of the canvas and lowered. This first stage is most evident in the X-radiograph (Fig. 11a). The second stage of the motif seen by IRR (Fig. 11b) resembles an earlier painting from 1909, *Seated Nude* (The Pierre and Tana Matisse Foundation, New York). In the second stage, the proper left leg is lowered towards the final position. The proper right leg is raised upwards and the heel rests on an undefined object. The head is tilted slightly towards the final placement (Fig. 11c).

The MA-XRF elemental distribution map associated with lead indicated a lead white ground was present (Fig. 12a). The maps for lead and zinc also indicated the use of two different white pigments throughout the painting, lead white and zinc white. While lead white was used in the scarf and the background, zinc white was used in the skin tones and some background highlights.

Vermilion was mainly found in the background and some areas of the figure as observed in the MA-XRF elemental distribution map for mercury. The use of vermillion in the deep red passage in the top-left quadrant was confirmed by FORS with an inflection point at *ca.* 600 nm (Additional file 1: Fig. S11) [35]. The mercury map also shows that vermillion was painted under the final position of the figure's proper right leg and in a small area above her head, which is now covered by her arm and the white scarf. The MA-XRF elemental distribution map for mercury, along with visual examination, suggested that a part of the red background was added between the second and final stages. The MA-XRF elemental distribution maps for calcium, phosphorus, iron, cobalt, and chromium (Fig. 12a) showed the use of bone black, earth pigments, cobalt blue, and a chromium-based pigment, respectively. Bone black was used for outlining the figure, but also in mixtures, most notably with iron-based pigments present in the hair along with

a chromium-based green. The maps showed how Matisse mixed paints, wet-into-wet, to model three-dimensional effects; this was best seen in the zinc and lead maps (Fig. 12a). A carnation pink hue was achieved by mixing zinc white and iron-based earth pigments, and this is observed most extensively in the final position of the proper left leg. Cobalt blue was primarily used to render shadows and imbue coolness to select colors, such as the red in the lower of the painting. Finally, mixtures with chromium-based greens were observed in the maps, used mainly to add dimension to the space in the area around the proper left side of the figure's hips and arms.

A cross section taken from the bottom left corner, where a significant change in the composition was observed, contained at least six layers, including several tones of red as well as blue, black, and ground layers (Fig. 13a). The presence of several layers containing red indicated that Matisse always intended for the background in *Nude with a White Scarf* to be red. SEM-EDS analyses showed the presence of lead white and, to a lesser extent, calcium carbonate in all the layers of the cross section, but most predominantly in the ground. The lower red layers contained cobalt violet (deep) particles, a cobalt phosphate pigment [31], due to the co-localization of cobalt and phosphorus, which could indicate the presence of underlying violet tonalities now masked by the upper layers (Fig. 13 d, f). The presence of cobalt, calcium, and phosphorus throughout the SEM-EDS maps possibly indicated the presence of a cobalt violet (cobalt and phosphorus), a bone black (calcium and phosphorus), or a mix of both; however, that remains unclear at this time. UVF imaging (Additional file 1: Fig. S12) indicates the presence of an organic lake pigment in the top-right quadrant of the picture due to pink fluorescence; lead white was also identified by MA-XRF in this passage. FORS confirmed the presence of a madder lake by a characteristic absorption feature at *ca.* 510 nm (Additional file 1: Fig. S11) [36]. A superficial layer containing a madder lake was also seen in the cross section (Fig. 13a). The intensity of the aluminum signal in the upper red layers suggested that the natural madder dye was precipitated on a hydrated alumina substrate. The presence of madder lake was confirmed by Raman analysis of the cross section due to spectral bands at *ca.* 250, 476, 1321, and 1479 cm^{-1} (Additional file 1: Fig. S13) [22].

Pentimenti associated with the object under the figure's arm and legs can also be observed in the MA-XRF iron elemental distribution map (Fig. 12a). Based on the iron and cobalt elemental distribution maps it can be deduced that the figure was resting on a wedge-shaped pillow. The cobalt map also indicates that cobalt blue was used by Matisse to cover areas and make significant modifications, as is clearly visible in the lower part of the white

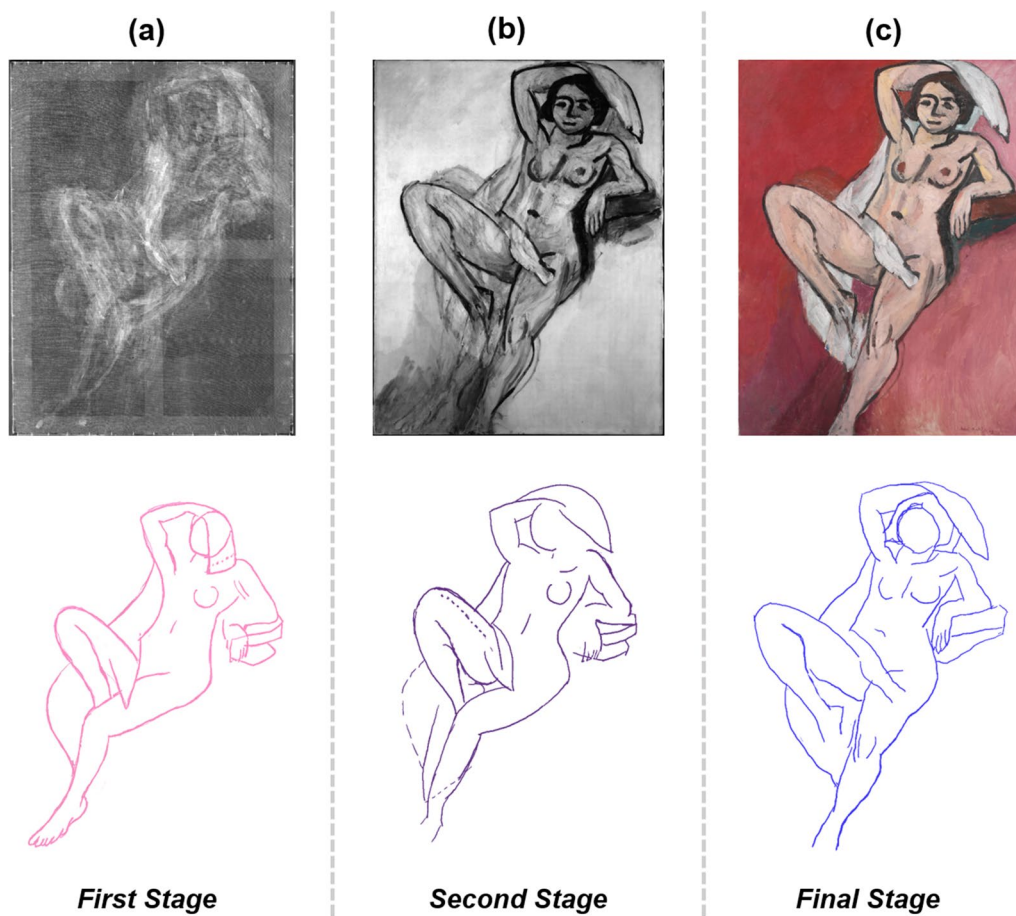


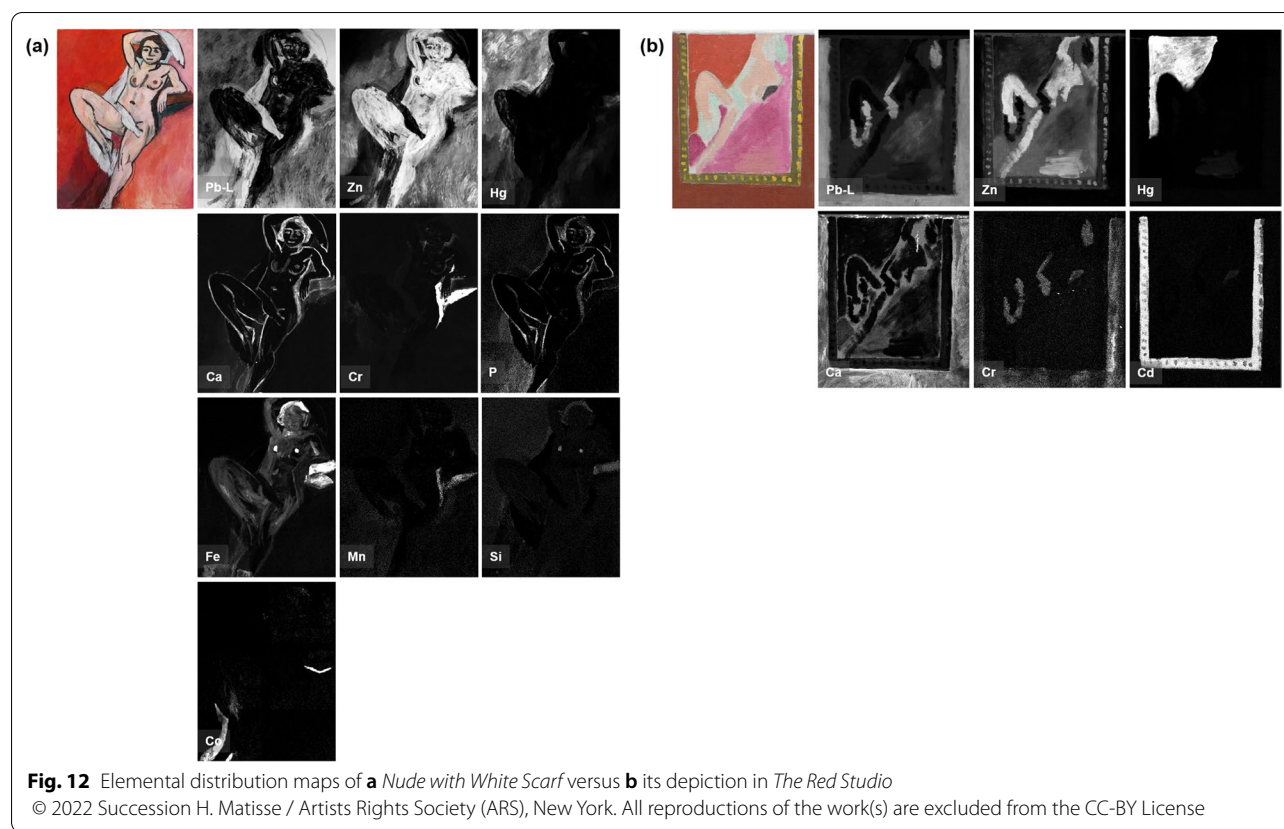
Fig. 11 Technical imaging of *Nude with White Scarf* shows the three distinct stages of the composition as developed by Matisse, where the first stage is most visible by **a** XRR and **b** the second by IRR. The final pose is also illustrated in **c**. Colored outlines of the first, second, and third stages assist in visualizing changes in the figure's poses

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scarf. Equally interesting are the maps for lead and zinc, which together showed changes in the position of the left leg. Along with the X-radiograph, it can be inferred that the right leg was slightly bent when Matisse first painted the figure, similar to *Seated Nude* (1909), as previously suggested.

The depiction of *Nude with White Scarf* in *The Red Studio* represents the original painting without many of the details, including the figure's head, hair, nipples, and shadow details (Fig. 12b). It is notable that Matisse either translated the different positions of the figure's legs from the original painting or continued to work out the positions in the depiction of *Nude with White Scarf* in *The Red Studio*, which can be seen clearly in the IRR image (Fig. 2b). If Matisse was replicating the process of painting *Nude with White Scarf* or further reworking the original composition remains unknown. The upper left portion of the background in the painting and the

depiction are both executed in a mixture of vermilion and zinc white. The lower right portion of the background in the depiction in *The Red Studio* is covered with a mixture of zinc white and madder lake, however, the lower right portion of the original painting is more complicated, composed of two different pink mixtures: lead white and madder lake as well as zinc white and vermilion. Both figures are painted with an earth pigment and zinc white. The representation of the object on which the figure rests in the depiction in *The Red Studio* is composed of bone black and chromium-based green, whereas in *Nude with White Scarf*, the shape is composed of only bone black. It is interesting to note that the scarf painted with pure lead white in the original painting is rendered with a mixture of lead white and a chromium-based green in *The Red Studio*, giving it a mint green color.



Le Luxe II (SMK)

This is the largest of all the extant paintings included in the composition of *The Red Studio* and is the second painted version of this motif to be depicted by Matisse. Unlike the oil paint he most extensively used, this version is painted in glue distemper, a material that Matisse used only rarely [37]. Matisse used a grid to transfer the motif freehand, presumably from the gridded pencil preparatory drawing (1907, Center Pompidou, Musée National d'Art Moderne, Paris) which also contains an identical red chalk grid [38]. Matisse was known to use red chalk for his preparatory drawing grids [37]. Infrared imaging along the edges showed pencil marks along all sides with an approximate distance of 20 cm. The pencil marks correspond with the red chalk traces visible in the painting. For the most part, the grid was obliterated with the application of the paint layers. Considering that glue distemper dries far more quickly than oil, this technique left Matisse little time for reworking and modeling. The paint layers were applied in large opaque color planes, creating a visual impression of contrasting matte and opaque fields of color with a two-dimensional, flat appearance. Contour lines were painted in gray rather than black, and a close examination of the figure with the bouquet and the red mountain behind her shows that the gray lines

cover darker, preliminary outlines painted in a reddish-brown tone.

While Matisse used distemper instead of oil to execute *Le Luxe II*, the analysis revealed a palette similar to the other paintings included in this study. Based on MA-XRF and FORS, chromium (III) oxide green was most likely used alone in the landscape area (Fig. 14a). Raman analysis of a layer in a paint cross section from the green landscape showed a band at $ca. 485\text{ cm}^{-1}$ that can be assigned to chromium (III) oxide in its hydrated form, known as viridian (Additional file 1: Fig. S14) [20]. Viridian was also found underneath the pink cloud in the sky and the white cloth as indicated by the chromium elemental distribution map. MA-XRF elemental distribution maps for cobalt and arsenic revealed the use of cobalt violet (light) in the purple-colored mountain (Fig. 14a), which was confirmed by reflectance minima occurring at $ca. 550, 575, \text{ and } 590\text{ nm}$, characteristic of the pigment (Additional file 1: Fig. S15) [39].

The MA-XRF elemental distribution map for iron suggested the use of a yellow ochre in the skin tones of the main figures. Additionally, the presence of cadmium and mercury together in areas such as the hair of the seated woman and the flowers in the bouquet was associated with the use of cadmium yellow and vermillion,

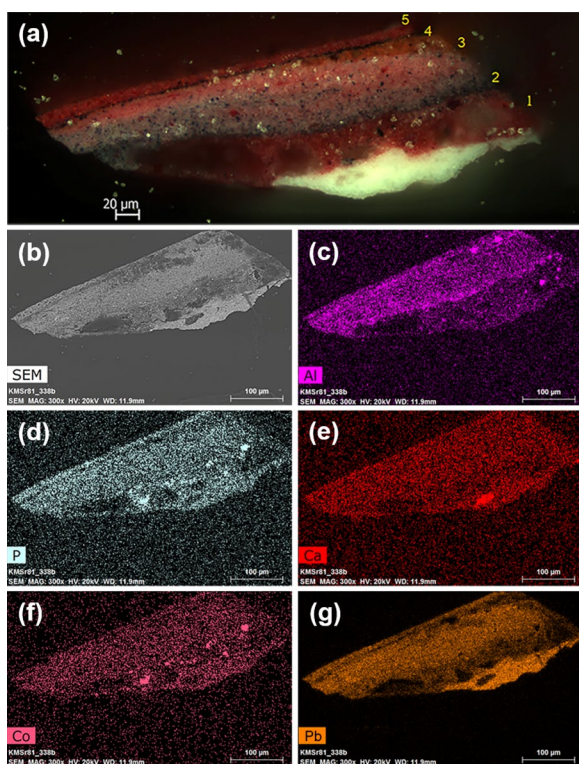


Fig. 13 A cross section taken from *Nude with White Scarf* shows the ground preparation and subsequent layers. The cross section was imaged using optical microscopy under **a** visible illumination and **b–g** using SEM–EDS

respectively. MA-XRF elemental distribution maps of calcium and zinc may suggest the use of two different white pigments: calcium carbonate and zinc white. However, calcium was found in higher concentrations throughout the composition and suggested the presence of a calcium-rich ground. Cross section analysis with SEM–EDS confirmed the use of a calcium carbonate ground with some aluminosilicate particles (Fig. 15). Moreover, the white in the cloth is composed of calcium carbonate. Zinc appeared to be associated with specific areas of the composition, such as the cloud, or it appears mixed with cobalt violet in one of the mountains of the landscape and with an iron-based pigment in the other.

MA-XRF distribution maps for calcium and phosphorus in the darker areas of the composition, including the gray contours, corresponded to bone black. SEM–EDS analysis of a cross section taken from the right edge where the green foreground meets the brown mountain (Fig. 15) revealed the use of an iron-rich earth pigment containing aluminosilicates mixed with calcium carbonate in the brown paint layers. Black particles in the top brown layer were found to be rich in calcium and phosphorus, confirming the presence of bone black.

Ultramarine blue was identified non-invasively with FORS in the blue sky and the blue of the bouquet. The FORS spectra showed a strong absorbance at *ca.* 600 nm followed by a steep rise towards lower frequencies

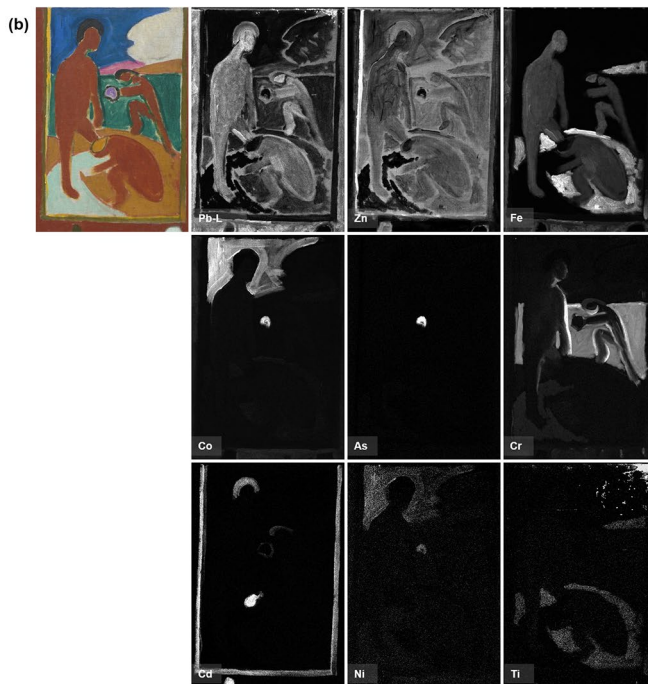
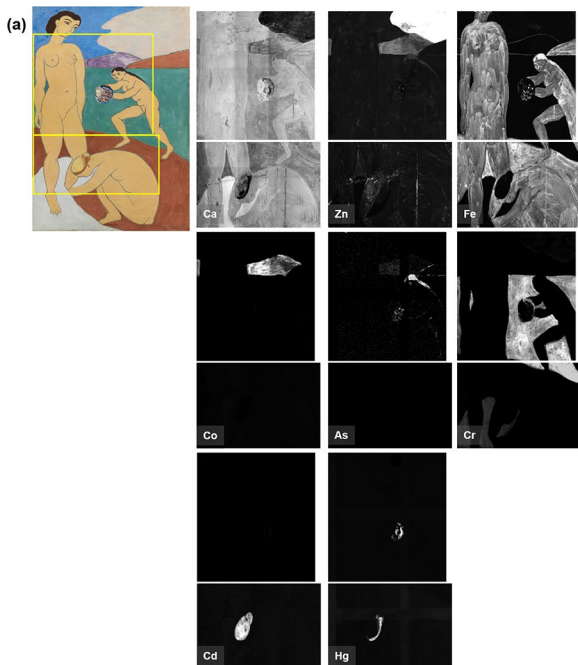


Fig. 14 Elemental distribution maps of **a** *Le Luxe II* versus **b** its depiction in *The Red Studio*

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characteristic of ultramarine blue (Additional file 1: Fig. S15) [40]. Raman analysis on a cross section sampled from the sky confirmed the presence of ultramarine blue due to an intense band at $ca. 544\text{ cm}^{-1}$ (Additional file 1: Fig. S14) [41].

MA-XRF examination of the dark reddish-brown hair of the two standing figures showed the presence of iron, zinc, and arsenic. The strong signal obtained for arsenic did not correspond to the presence of an arsenic-based pigment such as cobalt violet or emerald green. Due to the unexpected amount of arsenic found, a sample was taken from an area near the edge for further analysis. Raman analysis of orange-brown particles contained in the sample showed bands at 154, 181, 222, 231, 294, 312, and 378 cm^{-1} (Additional file 1: Fig. S14), which are attributed to orpiment [20]. Arsenic-containing yellow pigments were commercially available as artist's materials by the early 20th century, and they also occurred in wall-paper decorations [42, 43]. An area examined next to a yellow brushstroke in the bouquet exhibited fluorescence under UV radiation, which could indicate the use of a yellow colorant that has now faded.

The portrayal of *Le Luxe II* in *The Red Studio*, unlike representations of other works, is strikingly different, with figures painted in the same Venetian red as the background (Fig. 14b). Originally, Matisse appears to have faithfully represented the painting in *The Red Studio*, using ochre for the figures and an earth red color for the foreground. Ultimately, Matisse reversed the color scheme, overpainting the figures with an earth red and the foreground with an ochre yellow; remnants of the initial colors can be seen under the final colors. The figures in both the original painting and the depiction are painted with a mixture of an earth pigment and white paint, but the mixture in *Le Luxe II* contains zinc white while the mixture in the depiction contains lead white.

In the background, the orange color of the mountain and field in *Le Luxe II* and the yellow over red mountain and field in the depiction contain iron. In the original painting, yellow ochre is mixed with zinc white, while in the depiction, the ochre layer is mixed with zinc white and the lower layer is an earth pigment mixed with lead white (inferred from the lead M-line maps, not illustrated).

The hair of the seated figure is composed of cadmium yellow, yellow ochre, and vermilion in both the depiction and the painting. The hair of the main figure and the background figure both contain an iron-based pigment and an arsenic-containing pigment in the original work. For the hair of the main figure, Matisse layered bone black over cadmium yellow, while the hair of the

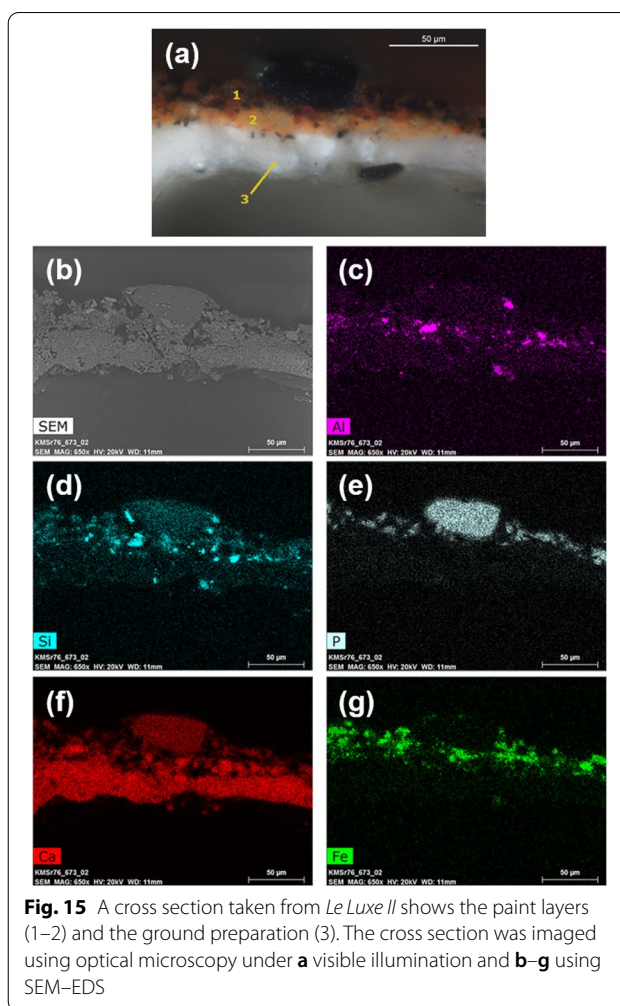


Fig. 15 A cross section taken from *Le Luxe II* shows the paint layers (1–2) and the ground preparation (3). The cross section was imaged using optical microscopy under **a** visible illumination and **b–g** using SEM-EDS

background figure is comprised of a cadmium yellow layer first, followed by bone black in *The Red Studio*.

The green field of *Le Luxe II* contains a chromium-based pigment as does the depiction, but in the representation, green was also mixed with lead white. The sky and the bouquet of flowers in the original work were both painted with ultramarine blue. The blue sky was painted with cobalt blue and lead white, while in the depiction in *The Red Studio*, the bouquet is purple and is composed of cobalt violet light. Cobalt violet was found in the landscape of *Le Luxe II*, but this area in the depiction was painted with a madder lake. The white cloth in the lower left corner of the original painting contains calcium carbonate, in contrast to the cloth in the depiction which has a pale mint-green hue made from a chromium-based green mixed with lead white. The cloud in the top right corner of *Le Luxe II* also appears white but is made of zinc white mixed with an organic pink pigment with a chromium-based green pigment underneath. The cloud

in the depiction of *Le Luxe II* is white and composed of lead white and calcium carbonate.

Cyclamen (private collection)

Matisse painted *Cyclamen* using oil paints on canvas in 1911, the same year he painted *The Red Studio*. The painting depicts a violet-colored cyclamen plant in a bright orange pot sitting on a mint green table with stylized leaves featured in the upper left and right corners of the pink background. As part of *Matisse: The Red Studio*, the painting was analyzed noninvasively in the Conservation Center at MoMA.

Similar to the underdrawing visible in *The Red Studio*, a pencil underdrawing is also visible throughout the thinly painted composition of *Cyclamen*. IRR confirmed that there is an underdrawing outlining the entire composition, including delineations of the starburst-shaped leaves in the upper right and left corners (Additional file 1: Fig. S16a). In some areas, particularly the edge of the table and the bottom right leaf, multiple drawn lines are evident along the edges of some shapes, in contrast to the fewer, more decisive lines present in other parts of the painting. These multiple lines defining some shapes are visible evidence of Matisse's process of adjusting the exact shape and location of some objects in the composition. Pencil lines are also found on top of the paint in the starburst-shaped leaves at the top corners. Matisse also used a pencil to outline the figures on top of the paint in the depiction of *Bathers* in *The Red Studio*.

In the UVF image (Additional file 1: Fig. S16b), areas of bright green fluorescence characteristic of zinc white were seen in the top center, right and left center, as well as the lower right quadrant. The use of zinc white was confirmed with MA-XRF (Fig. 16a), which showed the extent to which Matisse used this pigment for lightening the pink background, green table, terracotta pot, and starburst-shaped leaves. In contrast, lead white was used to lighten the leaves and the petals of the cyclamen and the fuchsia shadow. The presence of lead white in the ground was confirmed by MA-XRF (Fig. 16a) and can be readily seen in the exposed ground of the still life. In UVF the flowerpot's shadow fluoresces a bright pink, suggesting an organic lake pigment, much like the depiction of *Cyclamen* in *The Red Studio* [23]. Further analysis to confirm the precise composition of the lake pigment was not possible for *Cyclamen*.

In *The Red Studio*, the depiction of *Cyclamen* is one of the most faithful, if simplistic, representations of the original paintings (Fig. 16b). A comparison of MA-XRF results indicated that in both renderings, the background was executed with zinc white and vermilion, the leaves with a chromium-based green, and the terracotta

pot with vermilion. The stems of the nasturtium, not depicted in *The Red Studio*, were described with long, continuous brushstrokes of a red ochre pigment also used for Matisse's signature in *Cyclamen*. Red ochre was also used in dilute washes under vermilion in some passages of the background. The petals of the cyclamen flowers were painted with more attention. In *The Red Studio*, the petals are described with daubs of cobalt violet (light) mixed with nickel-rich cobalt blue, while in *Cyclamen* the petals were laid in with thinned cobalt violet paint and further articulated with a nickel-rich cobalt blue applied *alla prima*. The starburst-shaped leaves that decorate the upper corners of *Cyclamen*, were painted with a mixture of a chromium-based green pigment with touches of cobalt yellow ($K_3[Co(NO_2)_6]$, or aureolin, indicated by the co-localization of cobalt and potassium signals in MA-XRF elemental distribution maps associated with yellow passages. Cobalt yellow was a relatively expensive pigment with a low refractive index more commonly in use for watercolors than oils, however, it was supplied by color merchants in oil tubes [24]. In *The Red Studio* depiction, the starburst-shaped leaves were simply rendered with a solid block of color composed of cadmium yellow, a chromium-based green, and lead white. This color scheme is also used to depict the table in *Cyclamen* which has cobalt yellow and a chromium-based green mixed with zinc white, while in *The Red Studio*, Matisse used a mixture of cadmium yellow, chromium-based green, and lead white.

Untitled (female nude) (MoMA)

Untitled (Female Nude), depicts a female figure in blue outlines encircled by flowers with purple petals and yellow centers painted onto a white circular glazed ceramic plate. Matisse sourced the earthenware plate from André Metthys (French, 1871–1920) who had a studio in Asnières, near Paris. Metthys crafted his clay from local sources, such as green earth from Fresnes, marl (sedimentary rock made of clay and lime) from Meudon, and sand from Fontenay-aux-Roses, resulting in a pinkish-buff bisque [44]. The firing occurred in a kiln of Metthys' construction. After firing the ceramics, Metthys typically applied an opaque glaze and provided brilliant blue, yellow, purple, and green colors for painted decoration. This type of ceramic style, known as faïence, harkens back to the ceramic ware popular in France during the seventeenth and early eighteenth centuries that eventually fell out of favor as soft paste porcelain gained in production [45]. Metthys guided Matisse, along with other artists, including André Derain, Georges Rouault, Pierre Bonnard, Jean Puy, and Maurice de Vlaminck in their experiments with the

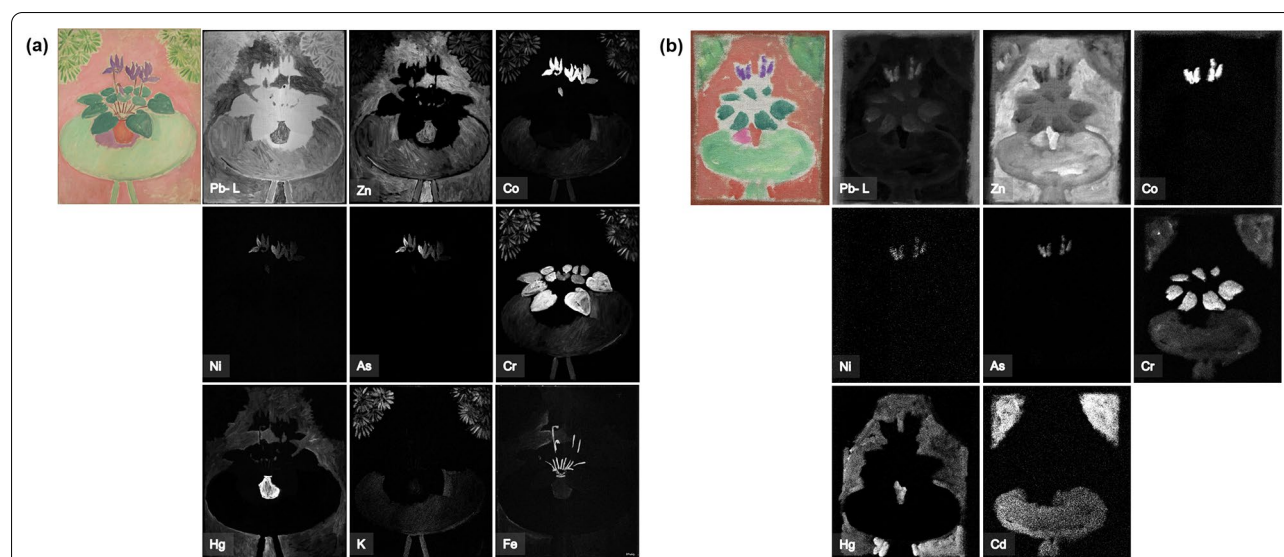


Fig. 16 Elemental distribution maps of **a** *Cyclamen* versus **b** its depiction in *The Red Studio*

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technique. Over one hundred pieces of faience, including *Untitled (Female Nude)*, were exhibited in a cabinet dedicated to the Metthys studio at the Salon d'Automne in 1907 [46].

The actual plate was cast in a mold. The first firing is assumed to be greenware, a shaped but not yet fired clay, to bisque, or a fired and unglazed ceramic. The hanging holes were made during the greenware stage before firing. The second firing was done bottom-up, as evidenced by the almost fully glazed bottom foot and glaze in the hanging holes. Each firing was done at a progressively lower temperature so as not to disturb previous applications of decorative glazing. The clear glaze on the back of the plate appears light pink in tone. A third firing for the opaque white glaze occurred with the plate face up. The plate was fired for a fourth and final time after Matisse painted on his design using a brush and a slurry of pigments in water. The front of the plate is opaque white with prominent craquelure in the glaze, which is the result of a difference between the expansion coefficients of the ceramic body and the glaze [47]. On the plate verso, only the opaque white glaze exhibits craquelure while the adjacent glaze does not.

Untitled (Female Nude) was analyzed with p- and MA-XRF (Fig. 17) to better understand the composition of the colorants and glazes used. The earthenware appears to have been coated with a lead–tin glaze, which was applied thinly in the first firing and thickly only on the recto in the second [48]. The glaze on the back appears pink in part due to a large amount of iron found in the

clay itself, which was also rich in oxides of silicon, potassium, calcium, and titanium [18].

On the face, the blue outlines of the nude figure are rich in cobalt, likely a cobalt aluminate spinel pigment; aluminum was observed in p-XRF spectra. Nickel and iron, which are used to darken and enhance the blue color, as well as potassium, which is used to eliminate green undertones, were also observed in the spectra [49]. MA-XRF shows that the flower petals were rich in manganese, possibly a manganese oxide (MnO), which turns a dark purple upon firing [49]. The pigment also contained calcium and tin, perhaps as oxides to increase the opacity of the purple pigment [48]. Lead and antimony are observed in the yellow centers of the flowers and indicated a Naples yellow pigment ($\text{Pb}_2\text{Sb}_2\text{O}_7$), which is commonly found in decorative ceramics of this period [49].

In *The Red Studio*, the ceramic plate occupies a prominent and outsize position in the bottom-left corner of the picture, with the nude curled downward as if viewed from the vantage point of Matisse himself. The background color of the plate was painted thinly, directly on the white ground, using the mint-green combination of cobalt blue, cadmium yellow, viridian, and zinc white seen elsewhere in the composition. In this way, the canvas texture appears to mimic the heavy craquelure found on the recto of the plate. The outline of the female nude was painted in cobalt blue using similar brushwork to that observed in the ceramic. While cobalt pigments were the most common and easily obtained blues for fired ceramics at that time, the use of cobalt blue in *The Red Studio* may have been a deliberate choice by Matisse.

The purple petals were instead rendered in black on the painting, done in daubs of bone black. The yellow flower centers were done in cadmium yellow, which faithfully replicated the colored glaze since it is far deeper in tone than the straw-hued Naples yellow used in oil paints.

Conclusion

The findings of this in-depth investigation substantiate *The Red Studio* as an unprecedented and bold exploration of color in Matisse's oeuvre. It has long been surmised that *The Red Studio* had a different appearance before Matisse covered the majority of its surface with a final layer of Venetian red paint. As a result of the advanced technical imaging and scientific analyses undertaken for this study, it was possible to reveal the painting's original components and successive stages, offering a broadened understanding of the painting. Specifically, previously unknown features of the painting have been revealed, including the green lines of the paneling and molding that factually represented the studio walls and a large door depicting the entrance into the artist's studio.

The occasion of the exhibition *Matisse: The Red Studio* further expanded the breadth of this study to include an investigation into Matisse's techniques and color choices through scientific analysis and in-depth examination of six depicted works in *The Red Studio* (Table 1). These works represent an experimental, post-Fauve moment

for Matisse, executed during a time of critical backlash to his style and output. In comparing the original works with their depictions, it becomes evident that certain features of Matisse's technique and his use of color were paramount to his style, as they are faithfully reproduced in the miniature versions of his works in *The Red Studio*. While not depicted to scale, the color choices and the figure positions were all translated by Matisse to the smaller and simplified, though remarkably accurate, depictions of these 1906–1911 works. For example, the purple to pink gradation of the tree in *Bathers*, the two-tone pink and red background of *Nude with White Scarf*, and the outlines of *Bathers*, executed in pencil in *The Red Studio*, stand out as examples of specific details Matisse chose to transfer from the original paintings to their depictions. Interestingly, the latest included work, *Cyclamen*, done in the same year as *The Red Studio*, is the most faithfully represented work in color and composition. The studio painting even serves as a testament to Matisse's frame choices, where many of the works are rendered in their gilded frames, and a stack of frames leaning against the wall behind *Corsica, the Old Mill* also features yellow and gold details.

In conducting this study, some patterns emerged within Matisse's approach to color, which is arguably central to his oeuvre. In this selection of works, Matisse seems to favor a chromium (III) oxide, most likely viridian, as his

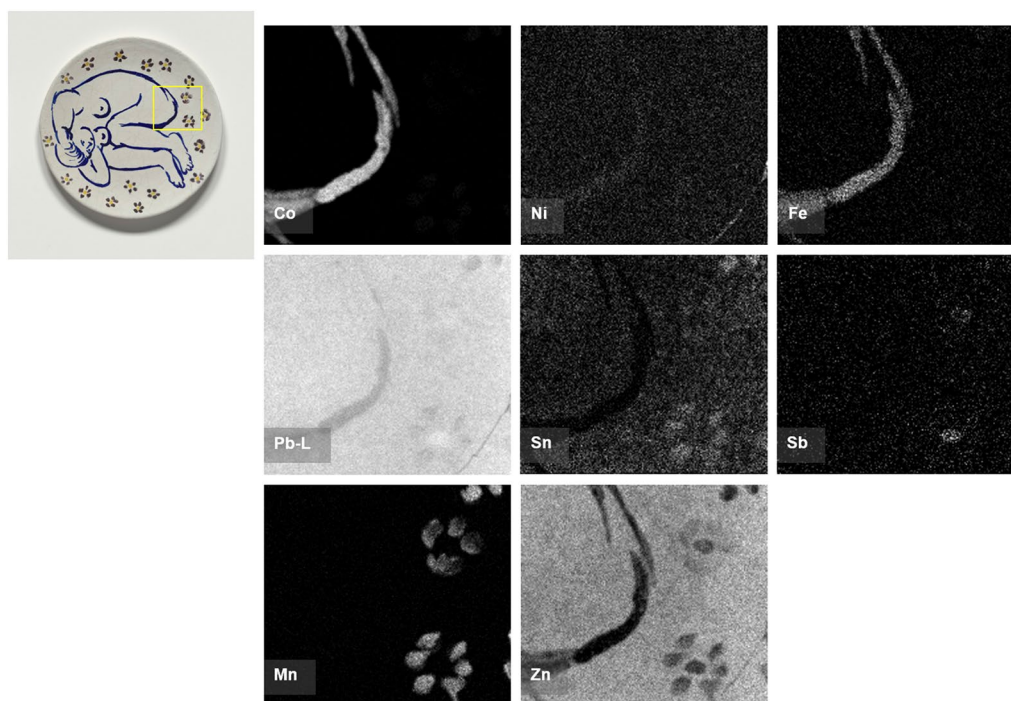


Fig. 17 Elemental distribution maps of a section from *Untitled (Female Nude)*

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principal green. Matisse uses viridian for foliage throughout these works and their depictions in *The Red Studio*, such as the leaves of *Cyclamen* and the nasturtium in *The Red Studio*, and natural scenes in *Bathers* and *Le Luxe II*. Elsewhere, the pigment is also used as his green of choice, as seen in the trousers depicted in *Young Sailor II* and the many green features in *The Red Studio*—including those overpainted architectural details uncovered by MA-XRF. Matisse also appears to favor pink backgrounds for works that are not set within a landscape. Those pinks are comprised of naturally derived lake pigments and unify a number of the works included in *The Red Studio*, such as *Cyclamen*, *Nude with White Scarf*, and *Young Sailor II*. *The Large Nude*, unable to be studied since it no longer exists, also features a pink background. Similarly, Matisse shows an apparent fondness for cobalt violet, using the pigment to depict many of the flowers in these scenes, like the petals in *Cyclamen*, the bouquet in *Le Luxe II*, and the flowers that dot the foreground in *Bathers*.

Like Matisse's use of color, his technique presents many unifying features among these works. The modeling of his figures, though done in different media, is often defined by the dark outlines that give form to the nudes

in *Bathers*, *Nude with White Scarf*, and *Le Luxe II*. While *Young Sailor II* features outlines of a darker purple color, they offer the figure's clothing form like the outlines of the nudes. The nudes are also sketched similarly in these works, with long arms and legs, rounded bosoms, and cinched waists. Furthermore, in the works that include figures, there seems to be some consistent choices of body positioning, either crouching, as seen in *Le Luxe II*, *Bathers*, and *Untitled (Female Nude)*, or reclining with a hand behind the figures' heads, as seen in *Bathers*, *Nude with White Scarf*, and the now destroyed *Large Nude*. The depiction of *Upright Nude with Arched Back* also features the figure's arms behind her head. Interestingly, the positioning of the sitter in *Young Sailor II* combines both poses, where the sitter is crouched with his hand behind his head. Curiously, Matisse eliminated all facial features from the depiction of the figures in *The Red Studio*, simply opting to depict faces only as areas of color.

Why Matisse chose to alter the painting with Venetian red, and eliminate the more varied palette, clearly influenced the final color scheme of the work, altering how the red pigment is perceived when laid over another color. The fact that Matisse did not choose to scrape away

Table 1 Listing of pigments identified in Henri Matisse paintings analyzed in this study

		<i>Young Sailor II</i> (MMA)	<i>Bathers</i> (SMK)	<i>Le Luxe II</i> (SMK)	<i>Nude with White Scarf</i> (SMK)	<i>Cyclamen</i> (private collection)	<i>The Red Studio</i> (MoMA)
Date		1906	1907	1907–08	1909	1911	1911
Pigment	Elements identified by XRF						
Zinc white	Zn	X	X	X	X	X	X
Lead white	Pb	X	X		X	X	S
Bone or ivory black	Ca, P		X	X	X		X
Red or brown ochre	Fe (Al, Si, K, Ti)	X	F	X	X	X	S
Vermilion	Hg	X	F	F	F	X	X
Madder lake	n/a				F	X	S
Cochineal Lake	n/a	S	F				
Eosin lake	Br	?					
Yellow ochre	Fe (Al, Si, K, Ti)		F	X	X		S
Cadmium yellow	Cd	X	X	X			X
Aureolin (Cobalt) yellow	Co, K					X	
Orpiment	As, S			X			
Chromium-based greens	Cr	X	F	F	X	X	X
Prussian blue	Fe, K						X
Cobalt blue	Co, Ni	X	F		X	X	X
Ultramarine blue	Al, Si, K	S		F			X
Cobalt violet (light)	Co, As		X	F		X	X
Cobalt violet (deep)	Co, P	?			X		
Manganese violet	Co, Mn, P	?					

(X) indicates pigments identified by XRF or SEM-EDS, (S) indicates pigments confirmed by Raman and/or μ -FTIR spectroscopy, and (F) indicates pigments confirmed with FORS. (?) indicates pigments tentatively identified

or overpaint this intermediate stage of blue, pink, ochre, and viridian further speaks to his daring and deliberate act of transformation. Responding to *The Red Studio* in its final state, Matisse admits to a Hungarian writer in late 1911 or early 1912, “it has not turned out the way I originally imagined. I like it but I don’t quite understand it; I don’t know why I painted it precisely the way I did” [1]. Even though Matisse did not comprehend this radical painting, through this study, it becomes apparent that there are coalescing stylistic techniques, color choices, and compositional elements among the works studied here. So much so that *The Red Studio* itself could be imagined as a snapshot that displays the evolution of Matisse’s experimentation during this post-Fauve era. Taken as a whole, the painting acts as a preview of the shift in Matisse’s work during this decade towards more abstract compositions with large areas of color and simplified forms, a theme he returns to later in his career, culminating in his signature cutouts.

Methods and materials

Analysis at MoMA

X-ray radiography (XRR) was performed with a 200 kV Portable Industrial NDT X-Ray Imaging System (35 kV, 4.5 mA, 2.54 m distance, and 480 s exposure). The radiographic image was recorded with a CareStream INDUSTREX Flex HR Digital Imaging Plate (36×43 cm), which was scanned with a CareStream HPX⁻¹ Computerized Radiography (CR) System. Forty images were visualized and processed using the Carestream Industrex Digital Viewing Software and PhotoShop.

UV-induced visible fluorescence photography (UVF) was taken using two Spectra Series CYC 100 LED Blacklights, 100–240 V (Altman Lighting, Yonkers NY) as an excitation source. Capture was made with an unmodified Hasselblad H6D-400MS in pixel-shift mode to create a 230ppi image at original scale (approximately a 325 Megapixel image). A 2E filter was used to supplement the camera sensor’s built-in filtration to minimize reflected UV and IR. Six exposures at 25 s each were required.

Infrared reflectography (IRR) was done using a modified Canon 5Ds CMOS sensor camera with a Peca 910 filter (#87C Wratten filter) to remove wavelengths shorter than 830–850 nm. To increase the resolution, three vertical images were captured of the left, center, and right of the canvas, and those images were then stitched and aligned to the visible and UVF images.

Cross sections were embedded in BioPlastic[®], [Aldon Corp., Avon, NY, USA] a blend of polyester and methacrylate monomers in a styrene solvent and dry polished with Micro-Mesh[®] [Micro-surface Finishing Products, Wilton, IA, USA] silicon carbide or aluminum oxide abrasives.

Portable, handheld X-ray fluorescence (p-XRF) was carried out using a Bruker Tracer 5i with a Rh target and silicon drift detector (SDD) operated at 40 kV and 4.5 μ A; spectra were acquired using the Bruker Artax 8.0 software for 120 s at a spot size of 8 mm without He purge. Several spots of similar colors were acquired for better comparison of the spectral data across each picture. A total of 215 spectra were acquired and further examined with the Bruker Artax 8.0 software.

Large area X-Ray fluorescence mapping (MA-XRF) was carried out using Bruker M6 JetStream with a Rh target and SSD at 50 kV and 600 μ A, with a 550 μ m spot size 550 μ m pixel size and dwell time of 10 ms/pixel under ambient conditions. The spectra were processed by employing a combination of PyMca and Datamuncher software as described in [50] and by using the Bruker M6 Jetstream software.

μ -FTIR spectroscopy was carried out in transmission mode using a Nicolet iS50- μ -FTIR coupled with a Thermo Nicolet Continuum infrared microscope equipped with an MCT detector. Spectra were collected in the 4000–600 cm^{-1} range with a 4 cm^{-1} resolution and 128 scans using the Thermo Scientific OMNIC 9.0 software package. Spectra were examined using the Spectral Search and Multicomponent Search tools available in the Thermo Scientific OMNIC Spectra 2.0 software.

SEM-EDS was carried out under low vacuum and using a Hitachi TM3000 microscope (Tokyo, Japan) fitted with a Bruker Xflash MIN SVE and Quantax 70 software. Images were acquired using analysis mode at 15 kV and a four-segment backscatter electron (BSE) detector. The cross sections were not coated as imaging was carried out under low vacuum; the remaining gas molecules in the chamber ionize the negative buildup up on the surface of uncoated, organic samples.

Raman spectroscopy was carried out using a Renishaw In-via Raman system equipped with a 785 nm diode laser operated between 0.3 and 3 mW, a 1200 lines/mm grating, and a Leica confocal microscope with a $50 \times$ LWD or $100 \times$ objective. Final spectra represent an average of five acquisitions of 10 s. Spectra were examined using the Spectral Search and Multicomponent Search tools available in the Thermo Scientific OMNIC Spectra 2.0 software.

Silver nanoparticles (AgNPs) for surface enhanced Raman spectroscopy (SERS) were prepared according to a method developed by Lux et al. A solution of 12.5 mL of 0.5 mM silver sulfate (Ag_2SO_4) ($\geq 99.99\%$), 0.5 mL of 1% sodium citrate dihydrate ($\text{C}_6\text{H}_9\text{Na}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$) ($\geq 99\%$), and 1 mL of 1% D-glucose ($\geq 99.5\%$) are mixed in a Hydrothermal Synthesis Autoclave Reactor PTFE Tank (Baoshishan, China) previously cleaned with nitric acid at 30%. Once closed, the vessel was positioned in the center of a Panasonic model NN-SD372S inverter

microwave and heated at 810 W for 2 min. 1.5 mL aliquots of this stock solution of citrate-capped AgNPs were centrifuged at 12,000 rpm for 15 min. The supernatant containing the citrate solution in excess was removed and replaced by distilled water to avoid sodium citrate interference in the SERS spectra. The sample was pretreated with HNO_3 to hydrolyze any lakes present into the colloidal solutions by breaking the bonds with the base onto which the dye was precipitated. All chemicals were purchased from Millipore-Sigma, USA.

SERS was carried out using the same Renishaw In-via Raman system, employing here a 532 nm diode laser operated at 0.25 mW with an 1800 lines/mm grating. Spectra were evaluated using Spectral Search and Multicomponent Search tools available in the Thermo Scientific OMNIC Spectra 2.0 software.

Analysis at the SMK

XRR was obtained with a YXLON SMART EVO 160D directional X-ray system with 1.0 mm focal spot, 20–160 kV, 0.5–7.0 mA tube range, with an additional 3 mm Al Mg_3 filter, and a Dürr HD-CR 35NDT CR scanner digital, using 30 × 40 cm HD Image plates from Dürr NDT. The distance between the tube and paintings was 110 cm.

IRR was carried out using an Apollo camera (Opus Instruments) with a bandwidth region of 1100–700 nm and fitted with an 1250–1510 nm bandpass filter. The illumination sources were two Hedler halogen spots placed at an angle of 25° to the paintings.

For *Nude with white scarf*, IRR was carried out using a modified Canon EOS 5D Mark III (22.3 MP CMOS-sensor) camera with a spectral response of 365–1100 nm and fitted with a Canon 50 mm Macro lens. To increase the resolution, two vertical images were captured of the top and bottom and digitally stitched. The illumination sources were Dedo LED lights for visual light and UV light, and Dedo halogen lights for infrared imaging and Dedo LED UV lamp for UV imaging. Different modes were achieved by placing a filter in front of the camera lens: for UVF, a Baader UV/IR Cut L filter; for visible light, a Schott BG39 filter; and for IRR, Heliopan RG830 2 mm filter.

For *Bathers*, the Phase One Rainbow system was used. The software is produced by Phase One following Charisma standards. The camera is a Phase One iXG 100MP Wide Spectrum with a CMOS-sensor (resolution of 11608 × 8708) and outfitted with Schneider Kreuznach RS 72 mm lens. Filters are placed in front of the camera in a filter wheel. The attached lighting system is a set of LED light, produced by Dedo: UV Dedolights and a Baader UV/IR Cut L filter or UG11 filters (365 nm); for visible light, a SchottBG39 filter; and for IR, a Heliopan

830 nm filter). The system was operated using Phase One Rainbow MSI software.

A Bruker CRONO Bruker MA-XRF scanner developed by XGLab S.R.L. was used for characterizing inorganic pigments. The instrument consists of a measuring head with an Rh-target microfocus X-ray tube (30 W, maximum voltage 50 kV, maximum current 0.6 mA), and a 30 mm² Xflash SDD with beryllium window (energy resolution < 145 eV at Mn-K α). The measuring spot can be varied by changing the distance between the paint surface and the measuring head. The instrument was operated at 50 kV, and 60 μA . The elemental 2D mapping of all paintings' surfaces was achieved through an automatic XY-motorized stage with a 30 ms/pixel acquisition time and a 2 mm step size. The elemental maps were produced using open-source PyMCA software. In the case when several maps were required to scan a surface larger than the instrumental limits, various maps were stitched together using registration and stitching plugins available in the open-source image processing Fiji suite.

FORS measurements were performed with a Field-Spec 4 fiber optic spectroradiometer (PANalytical-ASD Inc., CO). Spectra were collected over the range of 350–2500 nm (UV–vis–NIR), with a spectral sampling of 1.4 nm to 2 nm. The spectral resolution was 3 nm at 700 nm, and 10 nm at 1400 nm and 2100 nm. Measurements were carried out using a bifurcated fiber optic probe; each of the bifurcated ends is composed of 78 fibers and all the 156 fibers (core 2000 μm in diameter) are well mixed in the common end. The sampling spot was 4 mm in diameter and 64 spectra were averaged for each sample. The instrument was calibrated using a white reference panel from ASD, which is made of a totally reflective material.

Raman analyses on cross sections were carried out using a Bruker Senterra dispersive Raman spectrometer coupled with an Olympus microscope and equipped with a thermoelectrically cooled charge-coupled device (CCD) detector. Raman spectra were recorded by focusing a 785 nm or 532 nm laser beam through a 100 × objective; gratings with either 400 lines/mm or 1200 lines/mm were used. The power of the laser beam incident on the surface of the painting or sample was kept between 1 and 25 mW, with an acquisition time between 1 and 100 s and 1 to 3 accumulations for each measurement.

Elemental analyses on cross sections were carried out at the scientific laboratory of the Royal Danish Academy using a Hitachi S-3400 N scanning electron microscope equipped with a Bruker Quantax 200 energy dispersive X-ray spectroscopy (SEM–EDS) detection system with two Peltier-cooled XFlash SDDs, which have an active area of 20 mm² each. Measurements were performed in variable pressure mode (30 Pa) on non-coated polished

cross sections using an accelerating voltage of 20 kV, a probe current of 50 μ A, and a working distance of 10 mm. The acquisition times (live time) for analyzing each selected area and for producing the elemental maps were 60 s and 600 s, respectively.

Analysis at the MMA

IRR was undertaken using an Indigo Systems Merlin near-infrared camera (InGaAs sensor range: 900–1700 nm) with a StingRay Optics macro lens optimized for this range, in conjunction with a National Instruments IMAQ PCI-1422 frame grabber card and IRvista 2.51 software.

XRR was performed using an X-ray source and controller, a TFI “Hotshot” portable industrial X-ray unit, consisting of 603 head and 805D Control. The system has a 0.5 mm focal spot and 96.5 cm radiation beam. Exposure: 30 kV–5 mA–30 s. Images were recorded onto Industrex Flex XL Blue 5537 plates and digitized with a Carestream HPX-1 scanner.

UVF was conducted using a Canon 5DS camera with Kodak 2E and Kodak CC40R filters. Illumination was provided by two 4-foot 40 W GE F40BLB lamps (UV-A glass mercury vapor lights with a peak at 365 nm).

MA-XRF analysis of an area of the painting including part of the sitter and of the background was performed with a Bruker M6 Jetstream system equipped with a Rh source operating at 50 kV and 600 μ A. The focal spot size was 580 microns, the step size was 700 microns, and the dwell time 80 ms/pixel. The spatial distributions of the elements of interest were obtained using the Bruker software and open-source PyMCA tools.

Raman spectroscopy measurements were done on sample scrapings using a Renishaw System 1000 coupled to a Leica DM LM microscope. All the spectra were acquired using a 785 nm laser excitation focused on the samples using a 50 $\times$ objective lens, with integration times between 10 and 120 s. A 1200 lines/mm grating and a thermoelectrically cooled CCD detector were used. Powers at the sample were set between 0.5 and 5 mW using neutral density filters.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-022-00797-0>.

Additional file 1: Fig. S1. A detail (a) from *The Red Studio* shows the presence of a gray-colored layer beneath the blue wall; drips from (b) pink and (c) blue paint over some objects in the composition indicate that this gray layer was laid in first. **Fig. S2.** A μ -FTIR spectrum that shows the presence of a natural resin varnish in a sample taken from *The Red Studio*. **Fig. S3.** A detail (a) from *The Red Studio* that shows the depiction of *Upright Nude with Arched Back* and elemental distribution maps (b) for vermilion (Hg), iron-based earth pigments (Fe), and viridian (Cr) that show Matisse overpainting the originally orange-hued sculpture with a yellow ochre

paint. **Fig. S4.** (a) X-radiograph and (b) infrared reflectogram acquired of *Young Sailor II*. **Fig. S5.** A Raman spectrum that shows the presence of ultramarine in a blue sample taken from *Young Sailor II*. **Fig. S6.** Elemental distribution maps from a section of *Young Sailor II*: (a) combined chrome (Cr, yellow), manganese (Mn, violet), and iron (Fe, orange); (b) cobalt (Co, blue); and (c) phosphorus (P, yellow); the green ellipse indicates the location of an artifact in the calculated map. The presence of manganese, phosphorous, and cobalt in the sweater's stripes strongly suggests that a mixture of manganese violet (manganese phosphate) and cobalt blue was used by Matisse, however, this does not preclude the additional presence of a cobalt (II) phosphate violet pigment. **Fig. S7.** Detail of the sitter's face in (a) *Young Sailor II* and (b) combined mercury (Hg_L; 9.980 KeV, green) and bromine (Br_K; 11.902 KeV, pink) distribution maps for the same area. **Fig. S8.** An X-radiograph of *Bathers*. The curved striations in the ground preparation show that the painting was not commercially primed, but rather primed with a palette knife. **Fig. S9.** FORS spectra acquired from *Bathers* that show the range of pigments identified by the technique. **Fig. S10.** A UVF image of *Bathers* that shows the occurrence of tin-treated cochineal lake marked by intense pink fluorescence. **Fig. S11.** FORS spectra acquired from *Nude with White Scarf* that show some pigments identified by the technique. **Fig. S12.** UVF imaging indicated the presence of an organic lake pigment in the top-right quadrant of the picture due to pink fluorescence. **Fig. S13.** A Raman spectrum that confirms the presence of a madder lake pigment in a red sample taken from *Nude with White Scarf*. **Fig. S14.** Raman spectra that show the presence viridian, ultramarine, and orpiment in *Le Luxe II*. **Fig. S15.** FORS spectra acquired from *Le Luxe II* that show some pigments identified by the technique. **Fig. S16.** (a) Infrared reflectogram and (b) UVF image acquired of *Cyclamen*.

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Author contributions

MoMA: AH carried out p-XRF, MA-XRF, SEM-EDS, μ -FTIR, Raman, and SERS data acquisition and interpretation. CH, MD, and AA carried out XRR and assisted with UVF and IRR technical imaging. M.D. took samples and prepared cross sections. LZ carried out a detailed examination of *Untitled (Female Nude)*. **SMK:** ASOM and GP carried out MA-XRF, SEM-EDS, FORS, and Raman data acquisition and interpretation. L.L. carried out XRR, IRR, and multi-band technical imaging. **MMA:** SAC carried out MA-XRF and Raman data acquisition and interpretation. ID carried out UVF and IRR technical imaging. SAC and ID contextualized the results. All authors wrote and revised the main text and contributed to the study conceptualization. All authors have read and agreed to the published version of the manuscript. All authors read and approved the final manuscript.

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Declarations

Competing interests

The authors declare that they have no competing interests.

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