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"*Foundations of a great metaphysical style*": unraveling Giorgio de Chirico's early palette

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Abstract

Properly situating Giorgio de Chirico's metaphysical works within his lifetime is complicated due to incomplete provenances, his practice of deliberately falsifying dates, and the known existence of forgeries. De Chirico's palette may have altered over time, due to shifts in his personal taste, changes in availability of materials, and innovations in paints; elucidating his palette and variations thereof during his metaphysical period (1911–1919) offers analytical insights that complement traditional connoisseurship when attempting to correctly position a given work within his lifetime. To this end, eleven paintings from his metaphysical period, and two in his metaphysical style but painted in the 1940s and backdated to the 1910s, were analyzed by non-destructive portable X-ray fluorescence spectroscopy. Analysis of some works was further complemented with micro-destructive analysis by scanning electron microscopy coupled with energy dispersive x-ray spectrometry, as well as Raman and Fourier transform infrared spectroscopy. While the grounds of his paintings are variable, his metaphysical palette is consistent and includes: lead white, zinc white, ochres and umbers, magnetite, bone or ivory black, vermilion, chrome yellow, Naples yellow, copper acetoarsenite, chromium oxide green, and Prussian blue. Less commonly used pigments include cerulean blue and cadmium yellow, and the backdated paintings lack lead white and vermilion.

Keywords: Giorgio de Chirico, Metaphysical period, Pigment analysis, XRF, SEM–EDS, μ-FTIR, Raman

Introduction

Art historical context

Giorgio de Chirico (1888–1978) is one of the most enigmatic figures of the twentieth century. His metaphysical paintings preceded and inspired the dream-like scenes of the Surrealists painters of the 1920s. His output between the years of 1909 and 1919 is considered by many critics to be the apex of his career. Works from this time display his distinctive visual vocabulary of empty piazzas, colonnaded buildings, mannequins, and strangely juxtaposed everyday objects through which he tried to convey "The inexplicable that lies within the existence of phenomenal reality; the image as defined in the domain of the manifest spirit" [1]. The metaphysical style was a successful one for de Chirico; works from this period were championed by Guillaume Apollinaire, sold by Paul Guillaume, and exhibited at prestigious shows such as the Salon des Indépendents and the Salon d'Automne [2].

At the beginning of the 1920s, de Chirico abandoned his metaphysical style for a more classical one, paying special attention to techniques championed by the Old Masters such as Albrecht Dürer and Lorenzo Lotto [2]. Those works proved difficult to exhibit and sell, and with the newfound popularity of surrealism as promoted by the likes of Andre Bréton and Paul Éluard [3], de Chirico's metaphysical works far surpassed those in his new style in popularity. As collectors' desires outpaced availability, copies or forgeries of de Chirico's metaphysical works, some of which were executed by surrealist admirers of the artist like Óscar Domínguez, Max Ernst, and perhaps Remedios Varo, began to appear on the art market [1]. Further confusion was created by de Chirico himself; in the 1920s, while continuing to develop his neo-Baroque

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style, he began to revisit his metaphysical motifs. The practice started as a way to satisfy the demands of his inner circle of friends, such as Éluard, who wanted copies of metaphysical works previously sold to others and who knowingly purchased said works as copies [1]. However, by 1937 de Chirico began creating metaphysical paintings and deliberately backdating them to the 1910s to increase their market value; these are known as verifalsi, from the Italian *veri* and *falso*, meaning true/authentic and fake, respectively. This practice of self-forgery was exposed publicly in 1940 by the Ghiringhelli brothers who dealt in early works by de Chirico [4].

Detangling authentic metaphysical works by de Chirico from forgeries and verifalsi is a complex problem that scientific analysis can help address. While some pigments have been in use since antiquity, many pigments, fillers, and extenders used in twentieth century paints have 'born on dates' when they were patented or manufactured. Recently two works by de Chirico in the Menil Collection dated to the 1910s were confirmed as verifalsi due to the detection of an organic yellow pigment that was not produced until the late 1920s [5]. Unfortunately, very few technical studies have been published on de Chirico's work from any period. A red pigment in one metaphysical picture, *La Mort d'un Esprit* of 1916, was identified by Vandenabeele et al. as vermilion using Raman spectroscopy [6]. Vermilion was also detected in *The Mysterious Departure* (1930–33) along with zinc white, bone or ivory black, yellow ochre, chrome yellow, Prussian blue; the ground being zinc white, perhaps with some lead white admixed [7]. In a study of fifteen works from de Chirico's later period (1960–1970), Cesareo et al. found vermilion, lead white and zinc white [8]. Over 40 paintings of certified origin, and ten still to be attributed, have been analyzed by Ridolfi for Fondazione Giorgio e Isa de Chirico using non-invasive and invasive techniques, including X-ray fluorescence (XRF) and Raman spectroscopies, but only limited findings have been published [9].

De Chirico in his own words

In the absence of identifiably anachronistic materials, insight into the authenticity of works could be garnered by comparing analytical results to de Chirico's published accounts of his materials and process, if the methods and materials described can be substantiated by analysis. These published lists of pigments serve as a point of comparison for the findings presented in this paper (Table 1). However, care in interpretation must be taken as some of these terms are ambiguous at best and might not correspond to contemporaneous or modern-day nomenclature, especially when comparing pigment names in different languages and across borders.

De Chirico first described his painting techniques at length in his 1928 *Piccolo trattato di tecnica pittorica* (*Petit traité de technique de peinture*, hereafter *Petit Traité*) [10]. Written in several sections, he focused on all aspects of tempera and oil painting, including media, pigments, varnishes, grounds, and brushes. In the section on ground preparation, he emphasized the value of tinting zinc white grounds and gesso preparations with vine black, ochre, and burnt umber. In the section on pigments for oil, most relevant here as his metaphysical works are painted in that medium, he provided the following list: zinc white, lead white, Naples yellow, chrome yellow, "mineral yellow," yellow lakes, Veronese green, Cassel earth, bitumen, and crushed charcoal for black.

In 1940, de Chirico was one of several artists who provided a list of their preferred pigments for the publication *Arte Italiana Contemporanea,* edited by Vittoro Barbaroux and Gianpiero Giani [11]. In it, de Chirico describes his palette as consisting of lead white, bone black, vine black, burnt Sienna, burnt umber, van Dyck brown, Morellone red, red earth, vermilion, carmine lake, yellow

Table 1 A summary of the pigments listed by Giorgio de Chirico in his writings on painting and studio practice

Title	Year Published	List of pigments
Piccolo trattato di tecnica pittorica (*Petit traité de technique de peinture)*	1928	Zinc white, lead white, Naples yellow, chrome yellow, "mineral yellow," yellow lakes, Veronese green, Cassel earth, bitumen, and crushed charcoal for black
Arte Italiana Contemporanea	1940	Lead white, bone black, vine black, burnt Sienna, burnt umber, van Dyck brown, Morellone red, red earth, vermilion, carmine lake, yellow ochre, Naples yellow, chrome yellow (lemon and orange), "brilliant yellow," emerald green, Veronese green, green earth, "mineral blue," Prussian blue, cerulean blue, and cobalt violet
"The Technique of Painting" in *The Memoirs of Giorgio de Chirico*	1962	*For ground preparation*: Spanish white, lead white, zinc white, silver white, powdered black, red clay, yellow clay, and lead oxide
Undated technical note	After 1940?	Cassel brown, vermilion, emerald green, Naples yellow, green earth, dark chrome yellow, Prussian blue, burnt Sienna, yellow ochre, raw umber, zinc yellow, "straw yellow," "red brown," "black," "raw Italian earth," "dark white," "yellow and red lacquer," "white," "light chrome," "cadmium" and "cobalt"

ochre, Naples yellow, chrome yellow (lemon and orange), "brilliant yellow," emerald green, Veronese green, green earth, "mineral blue," Prussian blue, cerulean blue, and cobalt violet.

In in an essay entitled "The Technique of Painting" in the 1962 edition of his memoirs [2], he provides recipes for preparing both commercial and bare canvases for tempera and oil painting, mentioning gesso, Spanish white, lead white, zinc white, silver white [12], powdered black, red clay, yellow clay, and lead oxide in the process.

Finally, in an undated technical note found in his studio at Piazza di Spagna in Rome, which he acquired in 1948, de Chirico gives pigment combinations for specific elements of a composition, such as shadows, mountains, and flesh [13]. He lists Cassel brown, vermilion, emerald green, Naples yellow, green earth, dark chrome yellow, Prussian blue, burnt Sienna, yellow ochre, raw umber, and zinc yellow. In addition, he includes more general references to "straw yellow," "red brown," "black," "raw Italian earth," "dark white," "yellow and red lacquer," "white," "light chrome," "cadmium" and "cobalt," giving no indication of color for the latter two species. "Cadmium" could be cadmium red or yellow and "cobalt" could mean cobalt blue, violet or yellow. The inclusion of additional pigments in this note suggests that it may have been written after the 1940 *Arte Italiana Contemporanea*.

Overall, these writings record what de Chirico recommended and perhaps himself used. However, the dated documents were also published well after de Chirico's initial metaphysical period, and his practices may have evolved over his lifetime. While these texts are not contemporaneous accounts, they proffer the best insight into de Chirico's favored palette and describe what he might have considered to be best painting practices.

Scientific analysis

To better understand de Chirico's metaphysical palette, seven metaphysical paintings from the collections of The Museum of Modern Art (MoMA) and four paintings from The Menil Collection were analyzed by non-destructive portable x-ray fluorescence spectroscopy (p-XRF) (some works are illustrated in Fig. 1). For ease of reading, some of the names of the paintings will be abbreviated after this point. The metaphysical works analyzed are: *The Enigma of a Day* (early 1914, MoMA; referred to as *Enigma*), *The Song of Love* (June-July 1914, MoMA), *Metaphysical Composition with Toys* (1914, Menil; referred to as *Toys*), *The Duo* (winter 1914–15, MoMA), *The Evil Genius of a King* (1914–15, MoMA; referred to as *Evil Genius*), *The Amusements of a Young Girl* (late 1915, MoMA; referred to as *Amusements*), *The Friend's Unrest or The Astronomer* (1915, Menil; referred to as *The Astronomer*), *Metaphysical Interior with Biscuits* (1916, Menil; referred to as *Biscuits*), *Metaphysical Composition [Symbols of War]* (c. 1916, Menil; referred to as *Symbols of War*), *The Faithful Servitor* (1916 or 1917, MoMA) and *Great Metaphysical Interior* (1917, MoMA). Two verifalsi from The Menil Collection, *Melancholia* (dated 1916, painted c. 1944–45) and *Hector and Andromache* (dated 1918, painted ca. 1944-1945), were also analyzed as a point of comparison between metaphysical and back-dated works. At The Menil Collection, the p-XRF results were complemented by limited sampling from the four metaphysical works and two verifalsi for analysis by Fourier transform infrared spectroscopy (μ-FTIR), Raman spectroscopy, and scanning electron microscopy coupled with energy dispersive x-ray spectrometry (SEM–EDX).

Materials and methods

Analysis at MoMA

Portable X-Ray fluorescence spectroscopy (p-XRF)

p-XRF analysis on the seven MoMA paintings was performed with a Bruker Tracer III-SD handheld energy-dispersive x-ray spectrometer a rhodium (Rh) excitation source and silicon drift detector (SDD) with a resolution of 145 eV and a 5 mm diameter approximate spot size. The excitation source was operated at 40 kV and 3 μA, and spectra were acquired for 120 s (live time) under He purge. The spectra were acquired using the Bruker S1pXRF 3.8.30 software. Due to malfunction, a Bruker Tracer 5i replaced the Tracer III-SD midway through the analysis campaign, and was operated at 40 kV and 4.5 μA; 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.

Photography

Ultraviolet Fluorescence (UVF) Photography was carried out with a Canon EOS 5D Mark II (Zeiss Mak-ro-Planar T* 2/50 ZE lens). The standard infrared filter was replaced by 2E and Peca #918 UV blocking filters. UV illumination was provided by two Altman Spectra Cyc UV lamps, a 100 Watt cyclorama/wall wash luminaires with high output 365 nm UV LED emitters. The camera was calibrated with an X-rite ColorChecker Passport and a UV Innovation Target-UV™.

Analysis at the Menil collection

Portable X-Ray fluorescence spectroscopy (p-XRF)

p-XRF spectra were collected using a Bruker Tracer III-SD handheld energy-dispersive x-ray spectrometer equipped with a Peltier-cooled XFlash silicon drift

Fig. 1 Giorgio de Chirico. **A** *The Enigma of a Day*, Paris, early 1914 (185.5 × 139.7 cm; MoMA); **B** *The Song of Love*, Paris, June-July 1914 (73 × 59.1 cm; MoMA); **C** *Metaphysical Composition with Toys*, 1914 (55.4 × 46.3 cm; The Menil); **D** *The Duo*, Paris, winter 1914-15 (81.9 × 59 cm; MoMA); **E** *The Evil Genius of a King*, 1914-15 (61 × 50.2 cm; MoMA); **F** *The Amusements of a Young Girl*, late 1915 (47.5 × 40.3 cm; MoMA); **G** *The Friend's Unrest or The Astronomer*, 1915 (40 × 32.1 cm; The Menil); **H** *Metaphysical Interior with Biscuits*, 1916 (81.3 × 65.1 cm; The Menil); **I** *Metaphysical Composition* [*Symbols of War*]c. 1916 (33.7 × 26.7 cm; The Menil); **J** *The Faithful Servitor*, 1916 or 1917 (38.2 × 34.5 cm; MoMA); **K** *Great Metaphysical Interior*, 1917 (95.9 × 70.5 cm; MoMA); **L** *Melancholia*, dated 1916, painted ca. 1944-1945 (50.8 × 67.3 cm; The Menil); and **M** *Hector and Andromache*, dated 1918, painted mid 1940s (99.7 × 69.9 cm; The Menil). All works are oil on canvas. © Artists Rights Society (ARS), New York / SIAE, Rome; all reproductions of this work are excluded from the CC: BY License

detector (SDD) with a resolution of 145 eV and a 5 mm diameter approximate spot size. The excitation source was a Rh target x-ray tube, operated at 40 kV and 10 μA current and spectra were collected over 180 s (live time). Spectra were obtained with Bruker S1pXRF software version 3.8.30 and spectral interpretation was performed using the Bruker Artax Spectra 7.4.0.0 software.

Cross section preparation

Cross section samples (taken from all six works analyzed) were embedded in Bio-Plastic resin (Ward's Science, Rochester, NY), coarse ground using Micro Mesh MX sheets (120 and 150 grit) and fine polished using Micro Mesh sheets (1500–12,000 grit) (Scientific Instrument Services).

Optical microscopy

Images of cross section samples under both normal oblique and UV illumination using B-2A or V-2B filter cubes were obtained using a Zeiss AxioCam MRc5 camera controlled by Zeiss Axiovision AC software release 4.5 and mounted onto a Nikon Labophot-Pol optical microscope equipped with 10×, 20×, and 40× objectives. Scale bars were created in Adobe Photoshop using images of a micrometer scale taken using the same objective.

Dispersive Raman microspectroscopy

Dispersive Raman spectra were collected on a Renishaw InVia Raman microscope running WiRE software version 5.5 using a 785 nm excitation laser operating at a power of 114 µW, 635 µW, 1.27 mW, 5.43 mW or 9.71 mW at the sample as measured using a PM100D laser power meter (Thorlabs) equipped with a S120C photodiode power sensor. A 5 × objective was used to focus the excitation beam on the sample supported on a glass microscope slide. The resulting Raman spectra are the average of 1 to 15 scans of 10 s duration. Spectral resolution was 3–5 cm^{-1} across the spectral range analyzed. Sample identification was achieved by comparison of the unknown spectrum to spectra of reference materials, the KIK/IRPA Raman reference library [14] and to those published in the literature.

Micro-fourier transform infrared (µ-FTIR) spectroscopy

µ-FTIR spectra were collected in transmission mode using a Bruker Lumos µ-FTIR microscope running Opus software version 8.2. Samples were prepared by flattening them in a diamond compression cell (S.T. Japan), removing the top diamond window, and analyzing the thin film in transmission mode on the bottom diamond window. The spectra are the average of 64 or 128 scans at 4 cm^{-1} spectral resolution.

Attenuated total reflectance (ATR) µ-FTIR spectroscopy

ATR-µ-FTIR spectra from embedded cross sections were collected using a Bruker Lumos µ-FTIR microscope equipped with a motorized germanium ATR crystal with a 100 µm tip. The spectra are an average of 64 scans at 4 cm^{-1} spectral resolution and an ATR correction was automatically applied by the Opus 8.2 instrument control and data collection software. Sample identification was aided by searching the Infrared and Raman Users Group Spectral Database, a spectral library of common conservation and artists' materials [15] using Omnic software version 9.11.706 (Thermo Scientific).

Scanning electron microscopy and energy dispersive X-Ray (SEM–EDX) spectrometry

Backscatter electron images of the uncoated cross section samples were taken with a JEOL JSM-IT100 SEM with 20 kV voltage, running under low vacuum mode with a pressure of 50–55 Pa and a probe current of 40–50 (unitless). EDX analysis using the integrated detector was performed under the same voltage and pressure conditions, but with higher probe currents (65–75) to increase the counts.

Results and discussion

XRF spectral interpretation

Analysis was undertaken non-invasively for all the paintings using p-XRF. The results are summarized in Table 2. Spectra were examined globally and individually in the context of each painting. The pigments and fillers that were inferred from the elemental analysis are supported by the spectra in combination with the color of the location from which they were acquired. Interpretation can sometimes be ambiguous due to the sensitivity of the technique to the underlayers of paint, ground layer and support. Moreover, certain elements can be indicative of the presence of more than one pigment. Strontium, for example, might be present as either a pigment, strontium yellow ($SrCrO_4$), or as an impurity in calcium and barium sulfate, both common fillers found in paints. Another ambiguous element is zinc, which might be present as both zinc white (ZnO), zinc yellow ($K_2O{\cdot}4ZnCrO_4{\cdot}3H_2O$) or lithopone (mixture of barium sulfate, ($BaSO_4$) and zinc sulfide (ZnS)).

The following is a summation of the pigments identified across all the paintings (Fig. 2): lead white ($2PbCO_3{\cdot}Pb(OH)_2$), zinc white (ZnO), bone/ivory black (which contains charred bones and hydroxyapatite ($Ca_5(PO_4)_3$)), magnetite (Fe_3O_4), red, yellow and brown ochres (Fe, Al, Si, K, Ti), umber (Fe, Mn, Al, Si, K), vermilion (HgS), cadmium yellow (CdS), Prussian blue ($Fe^{III}[Fe^{II}(CN)_6]_3^-$), the cobalt stannate cerulean blue ($CoO\text{-}nSnO_2$), copper acetoarsenite (($(Cu(C_2H_3O_2)_2{\cdot}3Cu(AsO_2)_2$) or copper arsenite ($AsCuHO_3$), chromium-based pigments, including lead chromate yellow ($PbCrO_4$) and viridian ($Cr_2O_3{\cdot}H_2O$) or chromium oxide green (Cr_2O_3), and Naples yellow ($Pb_2Sb_2O_7$). The presence of barium sulfate ($BaSO_4$) and/or lithopone ($BaSO_4$/ZnS), calcium (Ca), and clay-based fillers (Al, Si) was also inferred. This list is largely consistent with the pigments listed by de Chirico in his writings in *Arte Italiana Contemporanea* and *Petit Traité* [10, 11].

Using p-XRF, manganese was detected in all spectra and not only in brown areas that may contain umber, which suggests the use of a manganese based drier added to speed up the painting process [16]. In *Petit Traité* de Chirico discusses the use of a *Siccatif de Courtrai*, which often contained manganese salts [17], claiming it to be an ideal drier when used in moderation as an additive to paints used on non-absorbent grounds [10]. Chlorine was also detected in all locations analyzed on *The Duo* and *Evil Genius* and could indicate the presence of a chlorine-bleached shellac varnish. Such shellacs are treated with chlorine gas or sodium hypochlorite to decolorize them, and result in the incorporation of small

Table 2 List of Pigments identified in Giorgio de Chirico's paintings in this study

		The Enigma of a Day	The Song of Love	Metaphysical Composition with Toys	The Duo	The Evil Genius of a King	The Amusements of a Young Girl	The Friend's Unrest or The Astronomer	Metaphysical Interior with Biscuits	Metaphysical Composition [Symbols of War]	The Faithful Servitor	Great Metaphysical Interior	Melancholia	Hector and Andromache
Accession Number		1211.1979	950.1079	V 9038	1213.1979	112.1936	1215.1979	V 104	CA 64,078	1985–020 DJ	1216.1979	1078.1969	T 704	CA 4603
place and date of execution		Paris early 1914	Paris June-July 1914	1914	Paris winter 1914–15	Paris 1914–15	Paris late 1915	1915	1916	ca. 1916	Ferrara 1916 or 1917	Ferrara April-August 1917	dated 1916, painted ca. 1944–45	dated 1918, painted ca. 1944–45
Pigment	Elements Identified by p-XRF	(X) indicates a material identified by XRF or SEM–EDX and (S) indicates materials confirmed by Raman and/or μ-FTIR spectroscopy. For the grounds, (AA) indicates artist applied, (CA) commercially applied, and (I) inconclusive.												
Ground layer				(AA) Lead white (S) $CaCO_3$(S)				(CA) Lead white (S), $CaCO_3$(S)	(AA) Lead white (S)	(I) Lead white (S) Lithopone (S, X)			(AA) Zinc white (X), lead white (S), $CaCO_3$ (S) $BaSO_4$ (X)	(AA) Lithopone (S,X), $CaCO_3$(S), silicates (X)
Zinc white	Zn	X	X	X	X		X		X		X	X	X	X
Lead white	Pb	X	X	X	X	X	X	X	X	X	X	X		
Titanium white	Ti													X
Bone or ivory black	Ca, P	X	X	X	X	X	X	X		X	X	X		
Magnetite	Fe							?	X				X	
Red /brown ochre	Fe (Al, Si, K, Ti)	X	X	X	X	X		X	X	X	X	X	X	
Yellow ochre	Fe (Al, Si, K, Ti)	X	X		X	X		X	X		X	X	X	X
Umber	Fe, Mn (Al, Si, K, Ti)		X				X	X	X		X			
Vermilion	Hg	X	X	S	X	X	X	X	X	X	X	X		
Chrome yellow	Pb, Cr	X	X	X	X	X	X	X	X		X	X	X	X
Naples yellow	Sb, Pb				X		X							
Cadmium yellow	Cd								X				X	X
PY4	n/a												S	S
Copper acetoarsenite	Cu, As	X	X	S		X	X		X		X	X		X
Chromium oxide green	Cr	X			X					?	X	X		
Prussian blue	Fe, K	X	X	S	X	X		S	S	S	X	X	S	S
Cerulean blue	Co, Sn		?						X					

Paintings in bold columns correspond to paintings in the MoMA collection, those in italics are in the Menil Collection

Fig. 2 Details from paintings showing the palette as detected across the 11 metaphysical works analyzed in this study

Fig. 3 Two paintings, **A** *The Duo* and **B** *The Evil Genius of a King*, when examined using UVF photography, show the presence of a natural resin varnish, possibly identified as bleached shellac. © 2021 MoMA, N.Y

amounts of chlorine into the resin [18, 19]. In addition to reducing the visible coloration, chlorine bleaching also eliminates the characteristic UV induced orange fluorescence of shellac. Chlorine bleached shellac varnishes exhibit greenish-yellow fluorescence [19], similar to what was observed on the surface of both *The Duo* and *Evil Genius* when examined with ultraviolet photography (UVF) (Fig. 3). UVF revealed that the fluorescent varnish was unevenly brush-applied over the surface of the works, and the chlorine signal positively correlated to areas exhibiting greater fluorescence.

De Chirico's palette

Grounds

In *The Technique of Painting* de Chirico describes how to prepare and apply a ground layer for oil painting. He specifically mentions the use of zinc white but indicates that lead white can also be used, noting that it is advisable to add small amounts of black or red pigments to tone the ground "because it is not easy to paint on an absolutely white surface" [2]. If using a pre-primed canvas, he recommends the application of a second silver white [lead white] ground on top of the commercial one followed by an isolating layer of dammar varnish. XRF suggested that the ground of *Mysterious Departure* (1930–33) [7] and fifteen other unspecified works from the 1960-70s contain zinc white and lead white [8].

Cross section samples from the six Menil paintings revealed a diversity of ground materials (Fig. 4) that do not clearly correspond to de Chirico's recommendation to use only lead white or zinc white grounds. Furthermore, none of the Menil works show pigmented ground layers or multiple grounds, and examination of the cross section samples under UV illumination gives no evidence for the presence of a varnish layer between the ground and surface paint. The general lack of correspondence between what was found and what de Chirico recommends suggests that he may have changed his working practice, as much as his style, over time; his memoirs containing the essay on painting techniques were first published in 1962, many decades after the creation of these works.

The ground of *Biscuits* only contains lead white as identified by μ-FTIR and Raman spectroscopy, and it is the only work analyzed at the Menil Collection with a ground composition that corresponds to de Chirico's recommendations; the other works contain more complex mixtures of materials. Cross sections showed that *Toys* and *The Astronomer* have very similar grounds containing lead white and calcium carbonate. μ-FTIR spectra of the grounds showed characteristic peaks for hydrocerussite ($2PbCO_3 \cdot Pb(OH)_2$) at 3535, 1400, 1045 and 683 cm^{-1} [20] and calcium carbonate ($CaCO_3$) at 1787, 1407, 872, and 712 cm^{-1} [21]. Raman spectroscopy confirmed the presence of lead white (1049 cm^{-1}) and calcium carbonate (1087 cm^{-1}) [22].

Both *Symbols of War* and the verifalso *Hector and Andromache* contain lithopone, a pigment de Chirico does not mention; the former also contains lead white while the latter also contains calcium carbonate in addition to silicates. The simultaneous presence of Ba, S, and Zn can indicate the presence of barium sulfate and zinc white and/or lithopone. While it is difficult to distinguish between lithopone and a mixture of barium sulfate and zinc white by XRF, SEM–EDX can differentiate between them based upon co-localization and elemental ratios of Zn and Ba. In lithopone, Zn and Ba co-occur in individual pigment particles, and the pigment is 70–72% barium sulfate and 28–30% zinc sulfide by weight [23], with a Zn:Ba atomic ratio of approximately 1. The grounds of *Symbols of War* and the verifalso *Hector and Andromache* likely contain lithopone, as the zinc and barium co-occur in very small particles with a 1:1 atomic ratio (Fig. 5). In contrast, the ground of the verifalso *Melancholia* is primarily zinc white with calcium carbonate and only scattered particles of barium sulfate; the Zn:Ba atomic ratio is 6.87:0.08.

Due to sampling limitations, the paintings in MoMA's collection were only analyzed non-invasively by p-XRF. In the absence of accessible tacking edges, inferring a ground preparation often relies on the ubiquitous presence of elements and the attenuation of characteristic peaks by the surface paint layers, such as the attenuation of Pb Lα with respect to Lβ in the case of lead white [24]. In the case of thinly painted works, such as those from de Chirico's metaphysical period, this attenuation can be minimal, especially in white colored areas, where he applied very thin layers of either zinc or lead white that barely cover the ground. Moreover, attenuation of the Pb Lα is difficult to confirm in the presence of As due to the overlapping As Kα line. Lead and zinc appear ubiquitously in all the paintings, but it is impossible to distinguish between the potential contribution from the ground and contribution from paints containing these same elements. Analysis of tacking edges, currently inaccessible, would be necessary to characterize the ground layers of these works by acquiring cross sections for SEM–EDS.

Whites

In *Petit Traité*, de Chirico describes lead white as the most perfect of all whites, but says that zinc white is his preferred pigment, as it "does not alter the colors with which it is mixed" [10]. Despite this statement, de Chirico appears to have used zinc white exclusively in only two of the paintings analyzed, the verifalsi *Hector and Andromache* and *Melancholia*, and there are three where he exclusively used lead white, *The Astronomer*, *Symbols of War*, and *Evil Genius.* The verifalso *Hector and Andromache* is unique in containing titanium, present either as titanium white or titanated lithopone. The high levels of barium and zinc present in the ground layer of this work preclude precise identification by XRF alone. In the rest of the works, de Chirico used both zinc and lead white paints. The use of only zinc white in the verifalsi may suggest that he may have ceased using lead white for his surface paints sometime between his early metaphysical period and when he wrote the *Petit Traité* in 1928, well before the execution of the verifalsi. Cesareo et al. reported both lead and zinc whites in de Chirico works dating from the 1960s and 1970s, but it is unclear if they attempted to distinguish between surface paints and grounds [8].

De Chirico appears to have been judicious in his choice of whites, and patterns emerge when comparing the localization of lead and zinc white across all 11 metaphysical works: architectural or sculptural forms and motifs are usually painted with lead white, either thickly like in *The Astronomer* or in thin washes that barely cover the ground like in *The Duo*, whereas non-architectural forms, such as the cloud in *The Song of Love*, the thread in *Amusements*, and mannequin heads, are painted with zinc white. Moreover, zinc white was mixed with other paints to lighten them, as described by de Chirico above. For instance, in *Biscuits,* de Chirico used zinc white to adjust the blue of the beams of the ceiling, the brown of the floorboards, and the ochre of the depicted painting's frame and foreground, and in *The Duo*, the planked yellow ochre floor and the coral hued castle are brightened using zinc white. There are exceptions to de Chirico's incorporation of zinc white into mixtures, however, as the green of the sky, and the orange of the mannequin limbs in *The Duo* contain lead white. Ultimately, additional analysis of other metaphysical works is necessary to better refine these observations.

Black

De Chirico listed ivory black, along with vine black, among his preferred pigments in *Arte Italiana Contemporanea*; in his *Petit Traité,* de Chirico also suggested the use of crushed charcoal. In the works analyzed, he appears to have used at least two different black pigments: bone or ivory black, which contain hydroxyapatite ($Ca_5(PO_4)_3$), and magnetite or Mars black (Fe_3O_4). It is important to note that the use of plant based carbonaceous blacks is impossible to establish by p-XRF and these species are often inferred when black regions exhibit no detectable phosphorus and low levels of iron.

Bone or ivory black appears to have been de Chirico's preferred pigment, used in most of the metaphysical works studied here. Magnetite appears to be present in two paintings: *Biscuits* and *Melancholia*, and may also be present, although less securely identified, in *The Astronomer.* The black ribbon in *Biscuits* and black train in *Melancholia* have higher iron levels than the underlying blue and yellow paints and no detectable phosphorus (Fig. 6), suggesting the use of magnetite. In *The Astronomer*, de Chirico used bone or ivory black for the black shoulder of the astronomer, but the black of the chart has elevated iron levels and could contain magnetite; however this

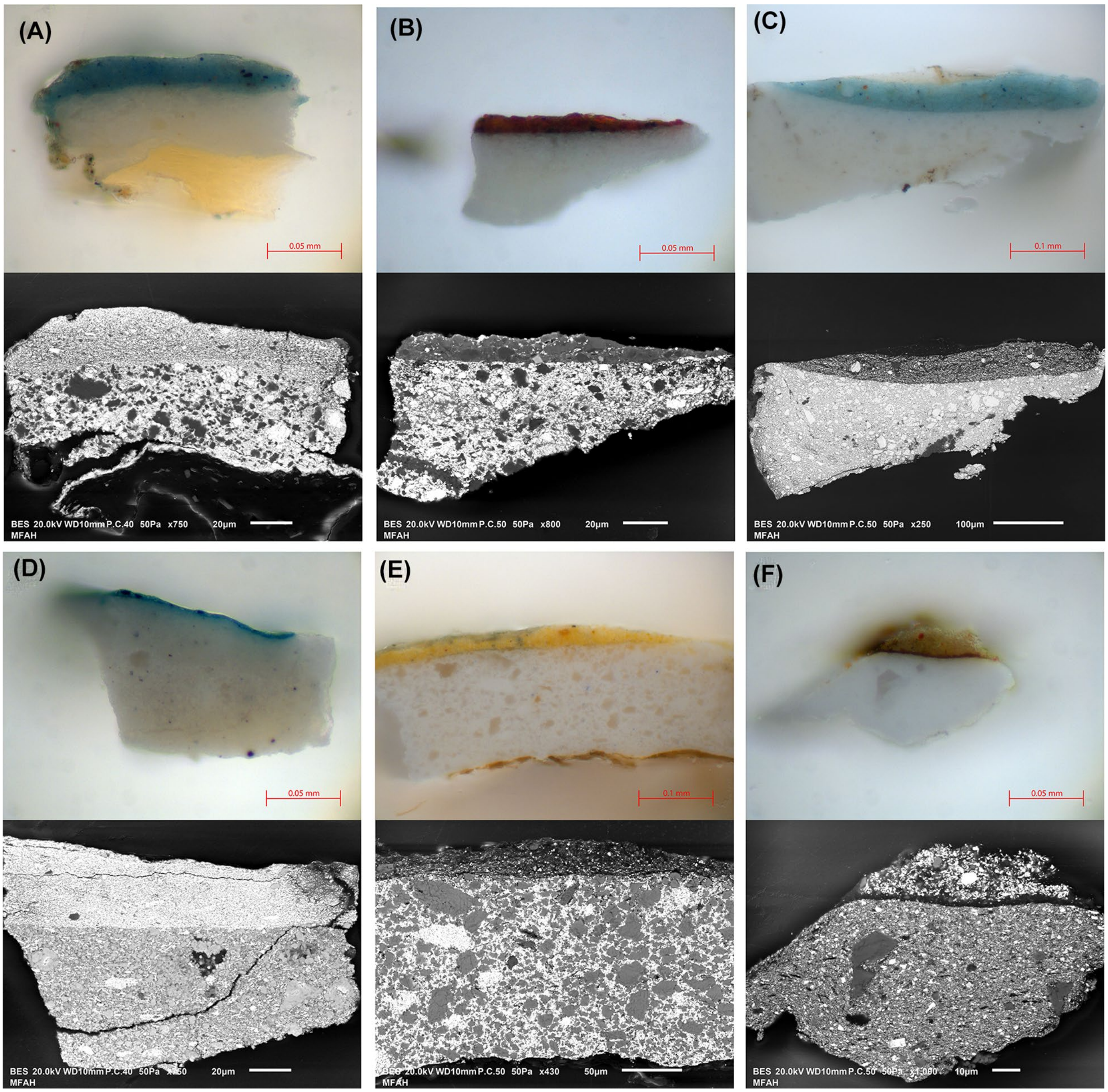

Fig. 4 Visible light and SEM electron backscatter images of cross section samples taken from de Chirico paintings. **A** *Metaphysical Composition with Toys* (1914); **B** *The Friend's Unrest or The Astronomer* (1915); **C** *Metaphysical Interior with Biscuits* (1916); **D** *Metaphysical Composition [Symbols of War]* (c. 1916); **E** *Hector and Andromache* (dated 1918, painted ca. 1944–45); **F** *Melancholia* (dated 1916, painted c. 1944–45)

region also contains manganese so the color could derive from an umber [25] mixed with a carbonaceous black.

Browns

De Chirico listed a variety of natural brown pigments, including burnt Sienna, burnt and raw umber, and van Dyck brown / Cassel earth [10, 11, 13]. Brown pigments are most often iron oxides species of varying compositions, which range in tonality depending upon calcination [25], but van Dyck brown and Cassel earth are humic earths rich in organic materials, which also contain iron [26]. Although their iron content is generally lower than mineral earth pigments, in practice, the humic earth pigments can be difficult to differentiate from Siennas and umbers using XRF alone. The calcined varieties of

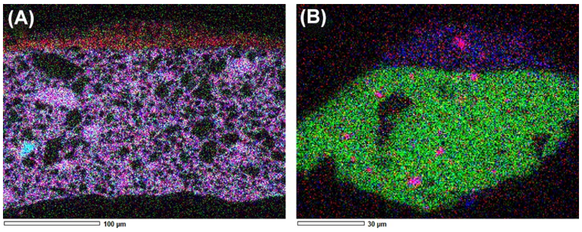

Fig. 5 SEM–EDX map showing barium (red), zinc (green) and sulfur (blue) of cross section samples of **A** *Hector and Andromache* (dated 1918, painted mid 1940s) and **B** *Melancholia* (dated 1916, painted c. 1944–45). The ground of *Hector and Andromache* likely contains lithopone, a mixture of $BaSO_4$ and ZnS; the Zn/Ba atomic ratio is 1:1. The ground of *Melancholia* is mostly zinc white, with only scattered particles of barium sulfate; the Zn/Ba atomic ratio is 6.87/0.08

umbers and Siennas are also difficult to distinguish from the raw ones by non-invasive analysis and requires the use of other invasive spectroscopic techniques [27, 28].

Nevertheless, some elemental markers, in combination with the color of the paint applied, can help suggest the type of brown used. Iron based browns are all characterized by high levels of iron, with natural earth pigments having trace amounts of elements such as Al, Si, K, and Ti. Umber is unique in that it contains 5–20% manganese oxides and hydroxides and brown regions with elevated levels of both Mn and Fe can be hypothesized to contain an umber [25]. The high manganese levels in the brown baluster form in *Biscuits* and the gray-brown walls and head of the figure in *The Astronomer* suggest umber is present (Fig. 7). Unfortunately, in many paintings de Chirico appears to have used a manganese containing siccative [10] that precludes clear identification of umber; in the MoMA works, no definitive correlation was found between the p-XRF signals of Fe and Mn in some dark passages. Aside from umber, de Chirico likely employed other brown pigments in the works analyzed here. For example, the brown in *Symbols of War* contains elevated levels of iron but very low levels of manganese, and may contain a different brown iron oxide such as a Sienna or brown ochre.

Red

De Chirico listed four red pigments—Morellone red, red earth, vermilion, and carmine lake—as his preferred ones in *Arte Italiana Contemporanea*; Morellone earth being a type of red ochre. Of these, de Chirico appears to have utilized vermilion (HgS) and red ochre (Fe_2O_3) in this selection of works, albeit Morellone red and red earth cannot be distinguished by XRF analysis alone. It is worth noting that de Chirico's use of both vermilion and red ochres was not mutually exclusive, as the two were detected in mixtures, especially in some architectural forms, like the castle in *Amusements* and chimneys in *Enigma*.

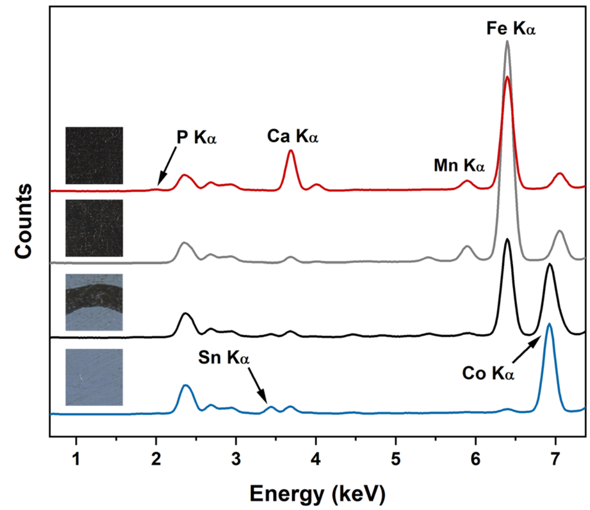

Fig. 6 XRF spectra and images of measurement area for the cerulean blue in *Metaphysical Interior with Biscuits* (blue); the black ribbon in *Metaphysical Interior with Biscuits* that may contain magnetite (black); the potential magnetite black in *The Friend's Unrest or The Astronomer* (gray) and the bone or ivory black in *The Friend's Unrest or The Astronomer* (red)

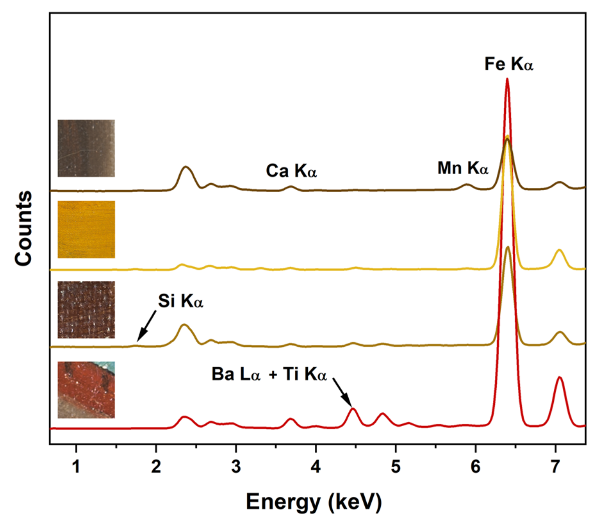

Fig. 7 XRF spectra and image of measurement area for the red rooftop of *The Friend's Unrest or The Astronomer* (red), the brown ochre in *Metaphysical Composition [Symbols of War]* (brown), the yellow ochre (yellow) in *The Duo*, and umber (dark brown) in *Metaphysical Interior with Biscuits*

XRF identification of vermilion is relatively unambiguous, and the pigment has a strong scattering cross section and was readily detected by Raman spectroscopy (256, 283, and 345 cm^{-1}) [22]. Vermilion was detected by XRF in all the metaphysical period paintings, but not in the two verifalsi; examples include the orange in the famous glove in *The Song of Love* and the castle in *The Duo*, in addition to the myriad of red and orange objects across all works analyzed. Considering that Cesareo et al. identified vermilion in de Chirico paintings dating from the 1960s and 1970s, the lack of vermilion in the verifalsi could be the result of de Chirico's specific color choices or indicate that access to this pigment was limited as a result of wartime impacts on metals trade in the mid-1940s when these works were likely painted [29]. XRF identification of red ochre is less straightforward and is based upon the detection of high levels of Fe, often accompanied by weaker signals for Al, Si, K, and Ti in red areas. Spectra of the rooftops of *The Astronomer* display these elements suggesting the presence of a red ochre.

Yellow

p-XRF suggests the presence of three yellows in de Chirico's metaphysical paintings: yellow ochre (FeOOH), Naples yellow ($Pb_2Sb_2O_7$), and chrome yellow ($PbCrO_4$), all of which are listed in *Petit Traité.* The co-occurrence of lead and chromium signals can indicate the use of chrome yellow, but chromium is also found in chromium oxide green (Cr_2O_3) and viridian ($Cr_2O_3 \cdot 2H_2O$) and the ubiquitous use of lead white in these works makes identification of chrome yellow tenuous in regions that are not visibly yellow.

The identification of yellow ochre is based upon the detection of high levels of Fe accompanied by weaker signals for trace amounts of Al, Si, K, and Ti in yellow areas. Yellow ochre is a common pigment in the de Chirico works analyzed here: it was universally used to depict all the planked and solid yellow foregrounds, like in *The Duo* and *Enigma*, and was mixed with other colors—notably earth pigments—to tone grays and shadows such as the ones created by arches.

Naples yellow was unambiguously identified by XRF as antimony occurs in no other common pigments [30]. Naples yellow was only detected in two paintings both dated 1915. Interestingly, these works were created in different locations; *The Duo* was painted in Paris but *Amusements* was made in Ferrara after de Chirico returned to Italy to serve in World War I[31]. In *The Duo*, Naples yellow provides the pale yellow of the horizon and is mixed with chromium oxide green in the sky, while in *Amusements*, it was used more liberally in red and brown mixtures across the composition.

Chrome yellow was used nearly pure in all the yellow toys and tchotchkes across the thirteen works, such as *Evil Genius* and *Toys*. De Chirico also accentuated other paints with chrome yellow quite liberally: with iron oxide pigments for deeper brown tones or shadows, to create details on the chocolates in *The Faithful Servitor*, and touches of chrome yellow were used to highlight the green balls in *Evil Genius* and *The Song of Love* and to tone the deep sky in *Amusements*.

As previously reported, two verifalsi paintings, *Hector and Andromache* and *Melancholia*, contain two additional yellow pigments, cadmium yellow and Pigment Yellow 4 (PY4, Arylide Yellow 13G) [5]. Cadmium yellow was clearly detected by p-XRF but sampling and analysis by μ-FTIR was necessary to detect PY4 (characteristic absorbances at 1666, 1597, 1557, 1518, 1489, 1446, 1399, 1305, 1287, 1261, 1244, 1209, 1182, 1165, 1110, 952, 913, 862, 845, and 749 cm^{-1}) [15], which may have been added by the manufacturer as a toner to extend the more expensive cadmium pigment. De Chirico mixed these yellows with Prussian blue to create the greens of the verifalsi skies to produce a similar tonality to those works discussed above. Of the works analyzed from de Chirico's metaphysical period, only *Biscuits* contains cadmium yellow but PY4, the anachronistic pigment found in the verifalsi, was not detected in samples taken and analyzed by μ-FTIR. The use of cadmium yellow is also very different in this work; in addition to the green tone of the sky, it is used for the yellow sponge, and in mixed greens and browns.

Green

De Chirico lists three green pigments in his treatise: emerald green, Veronese green and green earth. Care in interpretation needs to be taken here as Veronese green and emerald green are somewhat confusing terms; copper acetoarsenite ($Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$) was marketed in England under the name emerald green, but in France that name was already in use to describe viridian (hydrated chromium oxide ($Cr_2O_3 \cdot 2H_2O$)) so copper acetoarsenite was sold as Veronese green instead. It is most likely de Chirico was using the French terminology in his writing, which "translates" to a palette of viridian (hydrated chromium oxide, $Cr_2O_3 \cdot 2H_2O$), Veronese green (copper acetoarsenite ($Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$)), and green earth.

In the paintings analyzed here, only a chromium-based green and copper acetoarsenite were identified. Cu and As lines in the p-XRF spectra indicate the presence of a copper arsenic pigment, either the yellowish-green Scheele's green ($AsCuHO_3$) or the brighter, truer green copper acetoarsenite. XRF alone cannot distinguish between these two species, but they have distinct μ-FTIR and Raman spectra, and a sample taken from the blue-green sky of *Toys* was found to contain copper acetoarsenite by μ-FTIR (1557, 1454, 820, and 728 cm^{-1}) [32]. The similarity of color tone suggests that this is the species used in the other works as well. The copper acetoarsenite green was used regularly in the modeling of forms, such as balls, toys, and volumetric shapes, and de Chirico mixed it with other pigments, like iron oxides, to create gray and brown tones. Copper acetoarsenite was also used in depicting all the skies in the MoMA works, aside from *The Duo*, and in *Toys* and *The Astronomer*.

The detection of Cr in green areas suggests the use of chromium oxide, (Cr_2O_3) or hydrated chromium oxide ($Cr_2O_3 \cdot 2H_2O$), known as viridian. The former is duller in tone and was less commonly used, but secure identification of the type of chromium pigment present would require additional forms of analyses [33]. A chromium-based green was used selectively to create the dark greens of the foliage in *Great Metaphysical Interior* and darken the foreground and pedestal in *Enigma*, where it appears in very thinly painted green over yellow ochre. Chromium-containing greens were the sole green pigment de Chirico appears to have used in *The Duo*, where it is notably mixed with Naples yellow to create the pale horizon of sky, unlike the remainder of the pictures analyzed, where copper acetoarsenite was used. Interestingly, the green shrub in *The Duo* appears to contain chromium, iron, and lead and possibly indicates a combination of chrome yellow and Prussian blue, which can be commercially obtained as chrome green.

Blue

In his writing, de Chirico lists a few blues, some are clearly identifiable such as Prussian blue, others are less so such as "mineral blue" or cerulean blue, the latter of which can denote cobalt stannate or other mixtures that produce a cerulean hue. Other terms like cobalt are similarly unclear. Here, the predominant blue used by de Chirico across all time periods studied is Prussian blue, an iron-based anionic organometallic ($[Fe^{II}(CN)_6]_3^-$) pigment that is charge balanced using NH_4^+, K^+, or additional iron during synthesis [34]. The high tinting strength and ubiquity of iron makes identification by XRF more challenging. Iron is the origin of color in other pigments (such as ochres, umbers, Mars black, etc.…), a common trace element in materials, and a component in dirt and grime layers. In the works analyzed only by XRF, the presence of Prussian blue was posited based upon the detection of elevated iron levels in regions that have blue or green tonality. In those works sampled, it was identified by both μ-FTIR (2083 cm^{-1}) [35] and Raman spectroscopy (2155, 2090, 537 cm^{-1}) [36]. The identification of Prussian blue in those pictures investigated non-invasively does not exclude the presence of other pigments, such as indigo and ultramarine. Indigo is an organic blue colorant that cannot be detected by XRF, and ultramarine ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$) contains only light elements with higher XRF detection limits, so it is often difficult to identify. The transparency of regions thought to contain Prussian blue in the infrared reflectograms (not illustrated) of *Toys* and *Biscuits* confirmed the use and localization of this pigment. [37]

Based upon p-XRF, Prussian blue was mixed with copper acetoarsenite to render the skies in *Enigma*, *Evil Genius*, *The Song of Love*, *Astronomer*, and *Toys*, and possibly *The Duo*. In *Symbols of War*, Prussian blue was the sole blue in the sky, whereas in *Biscuits*, it is likely mixed with cadmium yellow. And while the blue box in *The Faithful Servitor* contains only Prussian blue, *Biscuits* contains Prussian blue and cobalt stannate cerulean blue, based upon co-detection of cobalt and tin. The cerulean blue appears to have been used for the framed blue rectangle upon which the biscuits sit and in mixed gray and brown tones. Cerulean blue was amongst the pigments de Chirico gave *Arte Italiana Contemporanea*, but it is unclear if he meant the cobalt stannate or cobalt chromate variety [38] or both.

Conclusions

In his writings, de Chirico showed a masterful knowledge of pigments, describing their qualities in different media, their properties when mixed with other pigments, and their longevity. However, as with many artists, there is sometimes a dichotomy between his writings and the materials he chose to use. The grounds of his metaphysical paintings vary widely, perhaps because he was working in both France and Italy, and they do not correspond to the recommendations made in his writings in *Petit Traité* in 1928 or in his memoirs in 1962. In general, the pigments used on the surface correlate well with his 1940 list in *Arte Italiana Contemporanea*. However, his use of cerulean blue is rare and the cadmium yellow found in *Metaphysical Interior with Biscuits* is not included in that list. Other pigments listed, like "mineral blue," cobalt violet, and carmine, the latter of which is undetectable by p-XRF, were not found in the paintings examined here, but that does not preclude their use in other works from this period. The two verifalsi analyzed are important points of comparison, in them he used exclusively zinc white, and added greens made from mixtures of cadmium yellow, PY4 and Prussian blue to his palette; he also forwent the use of vermilion, a ubiquitous pigment in his metaphysical works. This suggests the ability of material analysis to potentially help differentiate between works made during different phases of de Chirico's career.

Overall, this study sheds new light on the pigments used by de Chirico during his metaphysical period, an approach that complements art historical connoisseurship. It can also serve as a reference point for other works of uncertain origin, considering that de Chirico's oeuvre contains many works of incomplete provenance and unknown dates, whose existence are further complicated by forgeries, self-replication, and self-forgery.

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Author contributions

AH and AM carried out p-XRF data acquisition and interpretation and UVF imaging at MoMA; CER carried out SEM–EDX, Raman µ-FTIR and p-XRF data acquisition and interpretation at the Menil and drafting this manuscript. A.H CER and DD prepared figures. All authors wrote and revised the main text and contributed to study conceptualization. All authors have read and agreed to the published version of the manuscript.

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Availability of data and materials

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Declarations

Competing interests

The authors declare no competing interests.

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