

APPLIED SCIENCES AND ENGINEERING

Luminescence of coprecipitated titanium white pigments: Implications for dating modern art

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Material analysis of cultural artifacts can uncover aspects of the creative process and help determine the origin and authenticity of works of art. Technical studies on abstract expressionist paintings revealed a luminescence signature from titanium white paints whose pigments were manufactured by coprecipitation with calcium or barium sulfate. We propose that trace neodymium present in some ilmenite (FeTiO₃) ores can be trapped in the alkaline earth sulfate during coprecipitation, generating a luminescent marker characteristic of the ore and process. We show that the luminescence is linked to a specific ilmenite source used in historic TITANOX pigments, is not present in pigments produced by more advanced chemistries, and provides dating information. Facile Raman-based detection of this luminescence, along with characteristic peaks of rutile, anatase, calcium sulfate, or barium sulfate, can identify the type of titanium white pigment and narrow its manufacture date range.

INTRODUCTION

Titanium white (TiO₂) was introduced as a pigment in the early 20th century and by mid-century was as popular as lead or zinc whites. Although titanium dioxide does occur in mineral form and therefore has been found in archaeological and historic contexts (1–5), the detection of titanium white is most often a telltale sign of modern overpainting (or outright forgery) of older artworks. Because production methods for titanium dioxide have changed over the past century, pigment composition and structures can help date 20th century artworks (table S1): Some dating information can be gained by identifying the titanium dioxide polymorph (anatase versus rutile) (6, 7), and this can be refined by determining whether it is a “coprecipitated” pigment (prepared by TiO₂ coprecipitation with BaSO₄ or CaSO₄) or “pure” TiO₂ prepared without coprecipitation. Raman spectroscopy can distinguish between titanium dioxide polymorphs and identify the presence of barium or calcium sulfates from data acquired in situ or on microscopic samples, allowing non- or minimally destructive technical analysis of precious artworks. Unfortunately, co-detection of titanium dioxide and calcium/barium sulfate does not positively indicate a coprecipitated pigment, since sulfates are often included in paints as fillers that can be mechanically mixed with titanium dioxide of any origin (8, 9), and so the dating information that might be inferred by distinguishing coprecipitated and pure pigments is difficult to obtain. No proven reliable methods of identification exist, although by using large samples (2 to 30 g) inappropriate for analysis of works of art, Bancelin and Crimail (10) were able to differentiate coprecipitated pigments from pure pigments using levigation and dyeing. Transmission electron microscopy has the capability to distinguish mechanically mixed and coprecipitated pigments (11) but has not been applied to works of art. Here, we show that a set of previously unidentified luminescence peaks that appear in Raman spectra of some TiO₂ paints are a marker for coprecipitated pigments that inform on the source of the titanium used to make the pigment and provide a simple means to narrow the manufacture date of a work of art.

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RESULTS

Our technical investigations of abstract expressionist paintings revealed strong, distinctive sets of peaks in Raman spectra of certain titanium white paints (Fig. 1) that were not ascribable to known pigments or fillers and did not match spectra in common Raman databases including the Infrared and Raman Users Group (IRUG) database, RRUFF, e-vibrational spectroscopic databases of artists' materials database (e-VISART), University College London Raman Spectroscopic Library of Natural and Synthetic Pigments, Dipartimento di Fisica E Scienze della Terra, and the Romanian Database of Raman Spectroscopy. These peaks were also detected in historic samples of coprecipitated titanium white pigments manufactured by the TITANOX Pigment Corporation, and similar peaks had been reported for coprecipitated titanium white pigments from the Fogg Art Museum collection (12). The peaks occur at different Raman shifts (fig. S1) but the same absolute energies (table S2) when using 785-, 633-, or 532-nm lasers and are not observed when using a 1064-nm laser (12), indicating that they arise from luminescence (photons emitted by excited electronic states returning to the ground state) rather than the inelastic scattering that gives rise to Raman Stokes lines.

Pigment luminescence peaks match those of neodymium-doped calcium sulfate

The multiple, narrow peaks of Fig. 1 are not due to inherent photoluminescence of anatase or rutile (13–15) but are qualitatively similar to luminescence displayed by rare earth elements (REEs), which can have complex luminescence spectra that are sometimes mistaken for true Raman scattering (16). Trace elements can strongly affect the color and luminescence of inorganic solids by substituting for ions of similar size and electronic structure (17), and Goldschmidt's rules of ionic substitution indicate that REEs would be more likely to replace Ca²⁺ or Ba²⁺ in the alkaline earth sulfate than Ti⁴⁺ in titanium dioxide (18). The similarity of the luminescence spectra for the two types of coprecipitated pigment (Fig. 1) despite the relatively distinct Ti⁴⁺ environments of anatase and rutile (19) also indicates that REEs are likely substituting into the orthorhombic alkaline earth sulfates.

We used inductively coupled plasma mass spectrometry (ICP-MS) to determine whether REEs are present in luminescent titanium white paints. Calcium sulfate–coprecipitated titanium white paints from four paintings dating from 1950 to 1963 contain much higher

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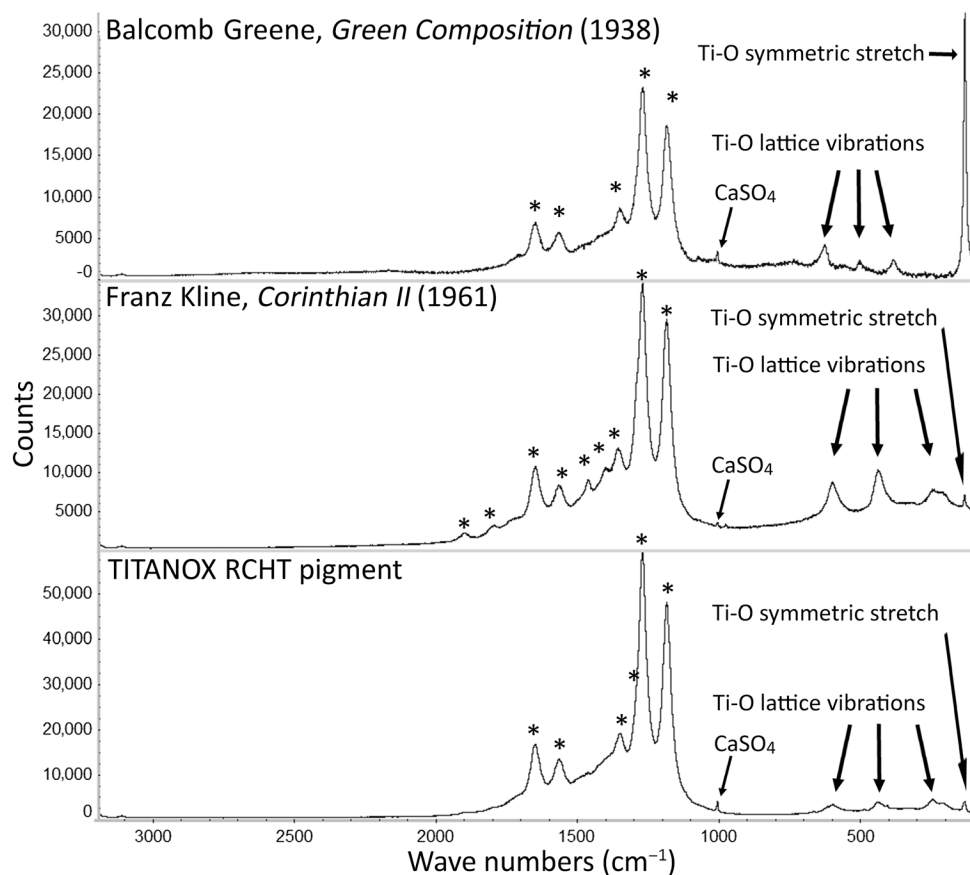


Fig. 1. Artworks and historic paints exhibit strong luminescence bands in Raman spectra. Raman spectra of titanium white paint and pigment samples taken with a 785-nm laser display peaks due to CaSO_4 , anatase (sample from *Green Composition*), or rutile (*Corinthian II* and the TITANOX RCHT pigment) and the luminescence peaks, which are marked with “*.” The manufacturer’s information indicates that the TITANOX RCHT pigment is 30% rutile coprecipitated with CaSO_4 (27).

levels of REEs than Grumbacher Titanium White paint made from non-coprecipitated anatase (Fig. 2). La, Ce, and Nd are especially abundant in the coprecipitated pigments (from 3 to 6 $\mu\text{g/g}$), whereas in non-coprecipitated anatase, Ce is present at less than 1 $\mu\text{g/g}$ and La or Nd are present at less than 0.01 $\mu\text{g/g}$. Of the three abundant REEs, only Nd could plausibly give rise to the observed luminescence. Lanthanum in its stable 3+ oxidation state has no f electrons and so will not show typical REE luminescence. Cerium luminesces primarily at 350 to 390 nm (17), much higher energy than observed here, but the Nd $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transition occurs at ~ 875 nm (16, 20, 21), in agreement with the energy of our observed luminescence. Nd^{3+} -doped anhydrite (CaSO_4) emits at 868, 874, and 879 nm (20), which correspond closely to the first three peaks of the coprecipitated pigments at 869, 875, and 882 nm. We conclude that the titanium white pigment luminescence arises from neodymium incorporated into the calcium sulfate structure.

Titanium ore REEs are found in coprecipitated pigments

Because natural anhydrite rarely exhibits this luminescence (21–26), the alkaline earth used to make the titanium pigment is unlikely to be the Nd source. We reasoned that the Nd might derive instead from ilmenite (FeTiO_3), the primary titanium source for 20th century pigment manufacture, and become incorporated into the sulfate structure during the coprecipitation process. If so, the luminescence would be indicative not only of coprecipitated pigment but also of

the composition and source of the ilmenite. To test for REE variations across ilmenite sources, we analyzed samples of ore from the McIntyre mine (Tahawus, Essex Co. NY, USA), the Faraday mine (Hastings Co. ON, Canada), Egersund (Norway), and the Middle Atlas Mountains (Morocco) by ICP-MS. The McIntyre mine was the primary source of titanium for Titanium Pigments Co., the manufacturer of the TITANOX pigments (27). The Egersund province in Norway has one of the most important deposits of titanium in Europe, and Titan Company A/S, maker of Kronos Titanvitt pigments (including coprecipitated pigments), used this source of ilmenite (11). Samples from Canada and Morocco were chosen to provide comparisons for different geologic deposits. Analysis of the ore samples (Fig. 3) reveals that the McIntyre mine in New York and the Faraday mine in Canada have high levels of La, Ce, and Nd, with significantly higher amounts of Nd in the McIntyre mine.

The high Nd levels in the McIntyre ilmenite suggest that the observed luminescence may be linked to coprecipitated pigments manufactured from this ore. To test this hypothesis, we analyzed a collection of eight historic samples of different TITANOX pigments (table S3): four coprecipitated pigments and four pure or non-coprecipitated (27). The coprecipitated pigments display the luminescence peaks, whereas the pure pigments do not. The ICP-MS analysis of samples of two coprecipitated pigments (TITANOX RCHT and TITANOX RC) and one pure pigment (TITANOX RA) shows that the coprecipitated pigments contain much higher levels of REE (Fig. 4).

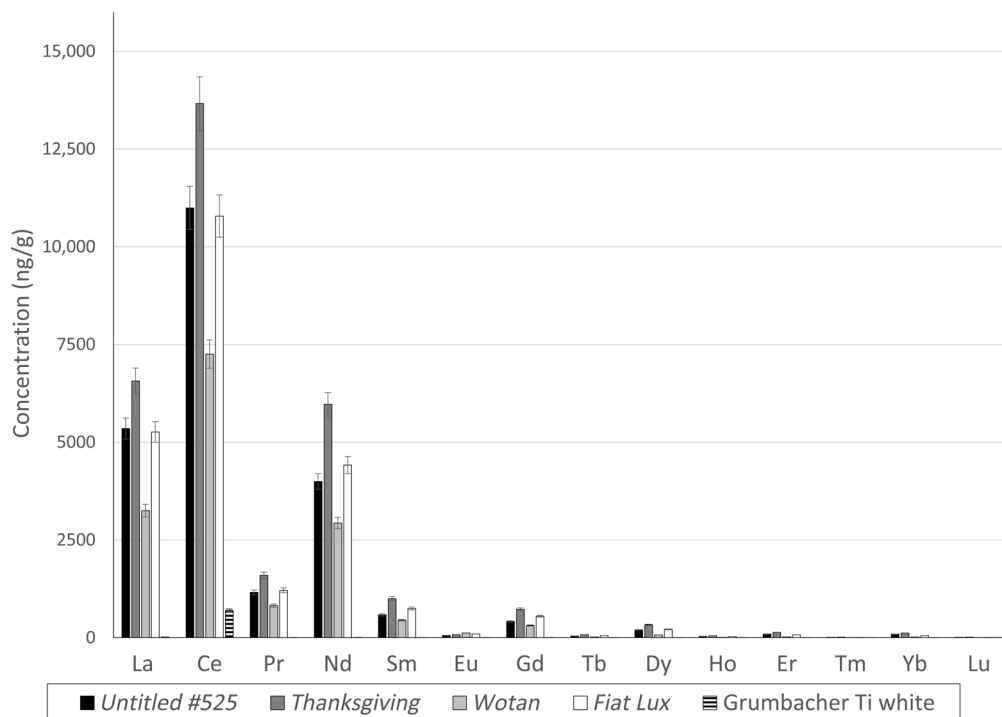


Fig. 2. Luminescent titanium white paint samples from four works of art contain similar levels of certain REEs. ICP-MS was used to determine REE concentrations in samples of coprecipitated titanium white paints from *Untitled #525* (1961) and *Thanksgiving* (1960) by Ray Parker, *Wotan* (1950–1951) by Franz Kline, and *Fiat Lux* (1963) by Hans Hofmann and in a sample of Grumbacher Titanium White paint. All samples contain the rutile form of TiO_2 , except for that from *Wotan*, which contains both rutile and anatase phases.

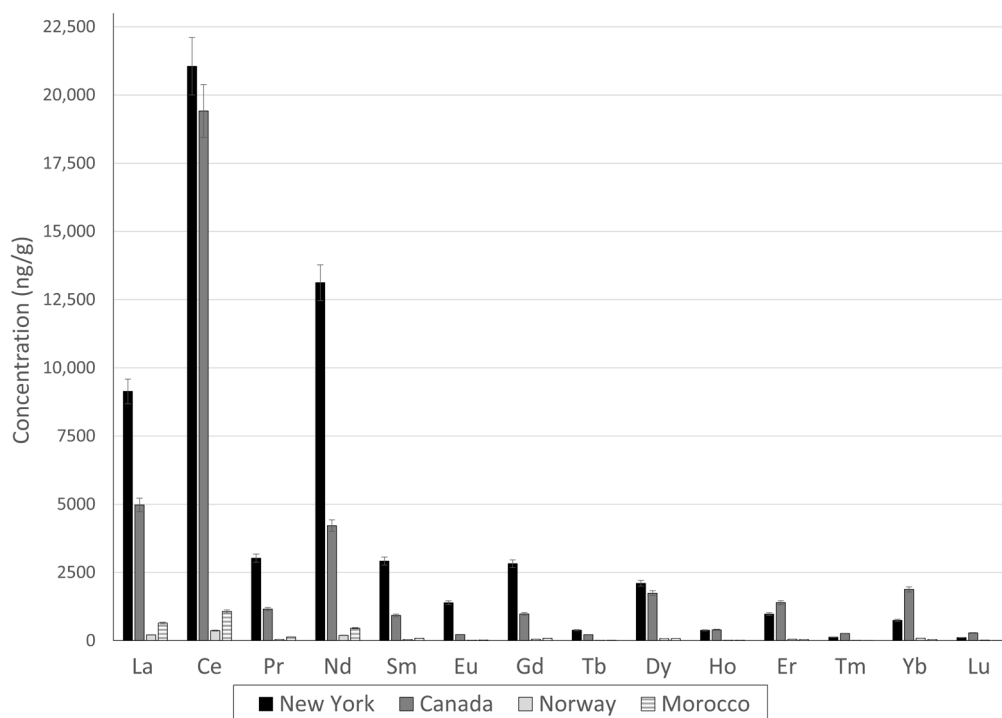


Fig. 3. REE levels vary widely in ilmenite ores. ICP-MS was used to determine concentrations of REEs in ilmenite ore samples from the McIntyre mine (New York), the Faraday mine (Canada), Egersund (Norway), and the Middle Atlas Mountains (Morocco). Error bars indicate SEM ($n = 3$).

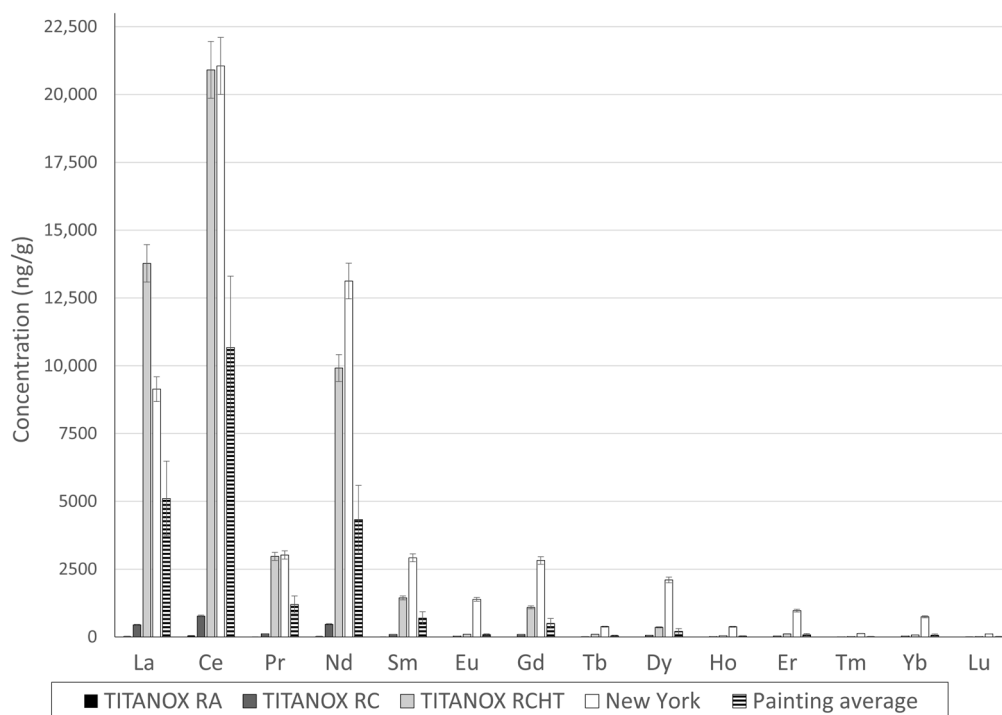


Fig. 4. REE levels are similar in an ore, a coprecipitated pigment, and paints from works of art. Concentrations of REE in different samples of TITANOX pigments compared to those of the ilmenite from the McIntyre mine (New York) and average concentrations of the four paintings analyzed in Fig. 2. Error bars on the TITANOX and ilmenite samples indicate a 5% instrumental error, while those on the painting average indicate SD of the four different paint samples. REE levels in the pure pigment TITANOX RA are within the detection limits of ICP-MS but comparatively low (for Nd, 25 ng/g), so bars are nearly invisible on this scale. The same data are presented on a log scale in fig. S3.

TITANOX RC contains 18 times as much Nd as TITANOX RA, and TITANOX RCHT contains almost 400 times as much, indicating that the different methods of pigment preparation differentially affect trace levels of REE. McIntyre ilmenite has Nd levels comparable to those found in the sample of TITANOX RCHT and the luminescent samples taken from paintings. We conclude that the luminescence detected here by Raman spectroscopy is a marker characteristic of coprecipitated pigments made from an ilmenite ore with high levels of Nd, such as are found in the McIntyre mine deposit.

Detection of luminescence refines dating information inferred from the TiO₂ polymorph

To determine whether the luminescence marker for coprecipitated pigments could be used to infer creation dates of works of art, we performed a survey of 109 oil paintings of known provenance created between 1926 and 1986 by artists working in the United States, which should contain paints dating from the period in which luminescent titanium white pigments were manufactured. Figure S2 displays the occurrence of pigments through time, and table S4 provides a summary of the works that display luminescence peaks indicative of the coprecipitated pigments. The anatase/calcium coprecipitate (as detected by the luminescence) is first found in a work dating from 1938, well after the pigment's initial manufacture date of 1925; of the 18 other paintings analyzed from 1938 or before, 5 use lead white, 6 use zinc white, and 10 use anatase titanium white that shows no luminescence. The anatase/calcium sulfate coprecipitate is last detected in 1967, much later than the reported cessation of production in the 1940s. The rutile/calcium sulfate coprecipitate is first detected in 1945, 4 years after its introduction, and is found as late as 1977. Paintings

containing the non-coprecipitated anatase form of titanium dioxide date from 1932 to 1983, and those containing the non-coprecipitated rutile form date from 1946 to 1983. The 1946 date is earlier than the date of widespread production of high-quality rutile and so could indicate that the sample came from an area of overpaint, but during World War II, the National Lead Company produced a rutile pigment, TITANOX A-NC, for military use (27), so the rutile could derive from an industrial paint. No examples of barium sulfate-coprecipitated pigments were found on the paintings, but both anatase and rutile/barium sulfate coprecipitates may be present on an Edward Kienholz sculpture, *John Doe* (1959). Occurrences of the coprecipitated and non-coprecipitated forms correspond well with generally accepted manufacturing dates of the different pigment types, suggesting that identification of the form of titanium white can provide valuable dating information.

Detection of the luminescence is a strong indicator that a coprecipitated pigment is present, although a lack of luminescence does not rule out a coprecipitated pigment. Even when the luminescence is observed, interpretation and dating can involve some caveats. If barium and calcium sulfate co-occur in a luminescent sample, then either alkaline earth sulfate could have been mechanically mixed in after coprecipitation; this ambiguity means some dating information is lost. Raman scattering intensity is laser wavelength dependent; longer wavelength lasers result in smaller Raman cross sections (28), as can be seen in fig. S1 where rutile gives much stronger signals with the 532-nm laser than the 785-nm laser. Using a 785-nm laser, which is common in cultural heritage studies because it minimizes fluorescence of paint binding media, can result in cases such as that of *Grave I* (table S4), where the coprecipitate luminescence is detected

while the Raman peaks for titanium dioxide and alkaline earth sulfates are below the detection limit. Analyzing this class of samples with a 532- or 633-nm laser can help resolve this ambiguity.

An estimate of the luminescence detection limit may be useful for those seeking to apply this tool. As can be seen in Fig. 1 and fig. S1, the strongest luminescence peaks of TITANOX RCHT are of similar intensity as the Raman peaks for rutile when using a 532- or 633-nm laser. TITANOX RCHT contains 30% rutile in CaSO_4 (27) and 10 $\mu\text{g/g}$ of Nd (Fig. 4), or 0.001% Nd; the similar signal intensities indicate approximately 3×10^5 higher sensitivity for Nd luminescence compared to rutile Raman peaks. The Raman detection limits for anatase and rutile in clay minerals are approximately 0.03 and 0.09 weight %, respectively (29); a 333-fold dilution of TITANOX RCHT would put the Nd at 30 ng/g and the rutile at its detection limit. We readily detect luminescence from TITANOX RC, a coprecipitated pigment with Nd (467 ng/g), suggesting that the effective detection limit may be well below the estimate (30 ng/g), especially with a 785-nm laser. Our inability to detect the luminescence in any of 46 titanium white oil artists' paints from the Art Materials Research and Study Center of the National Gallery of Art (NGA-MSRC) (table S5) despite the high sensitivity of the method indicates that none of these paints contains coprecipitated pigments with neodymium incorporated in the alkaline earth sulfate. Seventeen of the paints did display the characteristic Raman peaks of barium sulfate; this may have been mechanically mixed with pure titanium dioxide, but the lack of luminescence does not rule out the possible presence of coprecipitated pigments from titanium sources with low neodymium levels. Luminescence is also prone to quenching (30, 31); there may be instances where, although coprecipitates that include Nd are present, Nd^{3+} luminescence cannot be detected.

DISCUSSION

Our findings demonstrate that a luminescence signature readily detected in the course of standard Raman spectroscopic analysis of microscopic paint samples is indicative of a coprecipitated TiO_2 pigment derived from an ilmenite source with trace contaminants of neodymium. Although not every coprecipitated pigment will exhibit luminescence (since not all titanium ores are enriched in neodymium), this straightforward interpretation of data accessible by a minimally destructive method allows one to narrow the date range available from Raman-based identification of the titanium polymorph and alkaline earth sulfate.

Another possible use of the luminescence signature is to distinguish artists' paints from industrial paints. The less expensive, more poorly tinting coprecipitated pigments (27) may be a hallmark of industrial paints, which are not held to the high standards of artists' materials; the industrial literature recommends the use of coprecipitated pigments in both interior and exterior finishes (27, 32), and coprecipitated pigments were reported in a sample of a historic house paint (12). The lack of luminescence from any of 46 titanium white oil artists' paints from NGA-MSRC (table S5) analyzed by Raman spectroscopy, including at least 18 made in the United States that would be likely to use ilmenite having high-trace neodymium, suggests that manufacturers of these paints incorporated the better tinting pure TiO_2 polymorphs as they became available. We hypothesize that coprecipitated pigments are uncommon in artists' paints and that detection of coprecipitated pigments may be an indication of commercial paints. However, paint formulations often change

through time, so the absence of coprecipitated pigments in these particular samples of artists' paints does not preclude their having been used in previous formulations.

The hypothesis that coprecipitated pigments may be a marker for industrial paints is supported by the cluster of occurrences from the 1950s to 1960s in our survey. Contemporary records indicate and subsequent research has confirmed the presence of industrial paints in works by Franz Kline, Hans Hofmann, and Jackson Pollock (33–38), who created at least seven paintings that display the luminescence signature (table S4). The signature is found in paintings by other abstract expressionists, many of whom also rejected traditional artists' materials and adopted less costly industrial paints that were free from association with traditional representational art. The coprecipitated pigment luminescence signature is present in *Summer Party* (1959) by Anna Mary Robertson (Grandma) Moses, a self-taught "primitive" artist who used house paints (39). Thus, the artists in whose work the coprecipitated pigments are present support the association of these pigments with nontraditional materials.

The coprecipitated pigment luminescence has been detected only in the raw TITANOX pigments or on works of art, in oil or alkyd paints likely to be from U.S. manufacturers: It has not been found in acrylics (40) or in the hundreds of European or Latin-American paintings examined by the authors to date. European pigment manufacturers such as the Titan Company A/S in Norway made coprecipitated pigments (11) but apparently not from neodymium-rich ilmenite ores (Fig. 3). To our knowledge, the luminescence method described here represents the first positive identification of coprecipitated titanium pigments in works of art; the dependence on the composition of the ilmenite source can help determine the pigment origin but prevents the method from being completely general.

The current art market is fraught; the recent Knoedler Gallery scandal in which forged abstract expressionist paintings were sold for tens of millions of dollars has led to increased leering among collectors and museums. Distinguishing an authentic painting from a forgery depends on a combination of stylistic connoisseurship, provenance, and material analysis; for modern paintings, the minimalist compositions and brief history make material analysis an especially critical component of the authentication process. The luminescence reported here is a previously unidentified and valuable tool that allows scientists and technical art historians to easily identify coprecipitated pigments in a minimally destructive manner, providing important diagnostic information as to the age and origin of an artwork.

MATERIALS AND METHODS

Samples of ilmenite ore from the McIntyre mine (Tahawus, Essex Co. NY, USA), the Faraday mine (Hastings Co., Ontario, Canada), Egersund (Norway), and the Middle Atlas Mountains (Morocco) were purchased from online vendors. The TITANOX pigments are from the collection of P. Whitmore (Yale University), and titanium white artists' paints analyzed are from NGA-MSRC, Washington DC (www.nga.gov/content/ngaweb/conservation/materials-study-center.html).

Dispersive Raman spectra were acquired with two different systems at the Museum of Fine Arts, Houston (MFAH) and the Metropolitan Museum of Art (MMA). Most of the MFAH spectra were collected on an inVia Raman microscope (Renishaw) with 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 with a

PM100D laser power meter (Thorlabs) equipped with an S120C photodiode power sensor. To determine the laser dependence of the apparent Raman shift of the luminescence shown in fig. S1, 532- and 633-nm excitation lasers operating at 0.5 and 5% intensity, respectively, were used (the laser powers at sample were not measured for these lasers). A 50× 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 one to four scans of 10 s in duration. Spectral resolution was 3 to 5 cm^{-1} across the spectral range analyzed. Analysis at the MMA was conducted with a Bruker SENTERRA Raman spectrometer equipped with Olympus 50× and 100× long working distance microscope objectives and a charge-coupled device detector. A continuous wave diode laser, emitting light at 785 nm, was used as the excitation source, and two holographic gratings (1800 and 1200 rulings/mm) provided a spectral resolution of 3 to 5 cm^{-1} . The output laser power (10 or 25 mW), number of scans, and integration time were adjusted according to the Raman response of the different samples. Spectra were interpreted by comparison with library databases (MMA and IRUG) and published literature.

For the ICP-MS analysis, precisely weighed samples of approximately 50 mg of powdered paints, pigments, and ilmenite ores were placed into acid-cleaned 20-ml perfluoroalkoxy alkane (PFA) beakers to which 4 ml of HF and 0.5 ml of concentrated HNO_3 were added [all acids used in digestion were double-distilled and diluted with Milli-Q water (Millipore, 18.2 megohm-cm at 25°C)]. The solutions were allowed to digest overnight at 120°C, dried down, redissolved in a mixture containing 2 ml of HF and 2 ml of aqua regia, and transferred into the precleaned 15-ml Teflon digestion tubes for digestion with a Milestone UltraWAVE microwave single reaction digestion system. The total digestion time (including cooling) was approximately 90 min. After cooling, the solutions were transferred into 20 ml PFA beakers, and the digestion tubes were rinsed two to three times with 2% HNO_3 to ensure maximum sample recovery. The solutions were concentrated at 110°C to approximately 60 μl (one drop). The samples were diluted with concentrated HNO_3 and HCl until the solution clarified and then were diluted to a final dilution factor of 1:1000 with 2% HNO_3 . Solutions were then analyzed with the University of Houston ICP Analytical Laboratory & Agilent Facility Center instrument, an Agilent 8800 QQQ ICP-MS. The analytical precisions were generally better than 5% monitored by the repeated analysis of multi-element solution standard during the run. All ICP-MS data are provided in data file S1.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/5/5/eaav0679/DC1>

Fig. S1. Luminescence bands shift and change intensity with laser energy.

Fig. S2. Timeline for occurrences of six white pigments in American works of art.

Fig. S3. REE levels in an ilmenite ore are similar to those in coprecipitated titanium white pigments and paints from works of art.

Table S1. Timeline of titanium oxide pigment manufacture in the United States.

Table S2. Raman shifts and luminescence wavelengths generated by different lasers.

Table S3. TITANOX titanium dioxide pigment compositions and species detected by Raman spectroscopy.

Table S4. Works of art displaying luminescence peaks indicative of coprecipitated pigments.

Table S5. Analysis of titanium white oil paints from NGA-MSRC.

Data file S1. Rare earth concentrations in samples of ilmenite ores, TITANOX pigments, and samples of paint as determined by ICP-MS.

Reference (41)

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Acknowledgments: We thank B. Berrie and M. Skalka for allowing access to the paints held in NGA-MRSC; P. Whitmore for sharing samples of the TITANOX pigments; A. Bezur and E. Coquillette for facilitating the process; the Shared Equipment Authority at Rice University for access to the inVia Raman spectrometer; D. Natelson and P. Zolotavin of Rice University for the use of the laser power meter; Y. Gao of the University of Houston ICP Analytical Laboratory and Agilent Facility Center for performing ICP-MS analyses; S. Grow for sharing the Raman spectrum of *Spoonk*; A. de Lima Greene and K. Weber of the MFAH and B. Epley of the Menil Collection for permitting the sampling necessary for the survey; K. R. MacKenzie for critical reading and editing of the manuscript; and the Andrew W. Mellon Foundation for supporting conservation science at the MFAH and the Menil Collection. **Funding:** Funding for this project was provided by the Museum of Fine Arts Houston, the Metropolitan Museum of Art, and the Andrew W. Mellon Foundation. **Author contributions:** Both authors contributed equally to this work. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 10 August 2018

Accepted 2 April 2019

Published 17 May 2019

10.1126/sciadv.aav0679

Citation: C. E. Rogge, J. Arslanoglu, Luminescence of coprecipitated titanium white pigments: Implications for dating modern art. *Sci. Adv.* **5**, eaav0679 (2019).

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Sci Adv 5 (5), eaav0679.

DOI: 10.1126/sciadv.aav0679

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