

Supplementary Materials for

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

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Other Supplementary Material for this manuscript includes the following:

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

Supplementary Materials

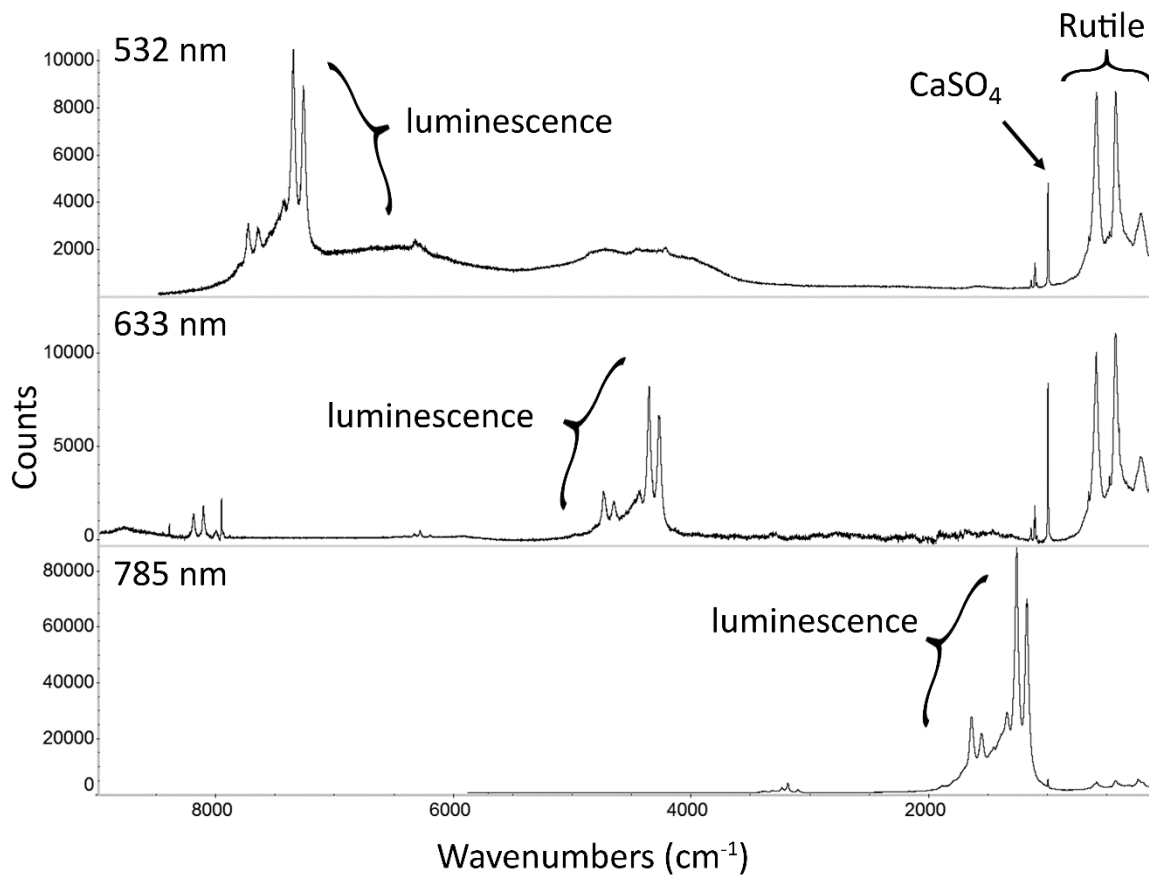


Fig. S1. Luminescence bands shift and change intensity with laser energy.

Raman spectra of TITANOX RCHT pigment, a co-precipitated species containing 30% rutile and 70% calcium sulfate, acquired using 785, 633 and 532 nm lasers. While the rutile Raman peaks at 610, 445 and 144 cm^{-1} and anhydrite peaks at 1160, 1129 and 1017 cm^{-1} occur at the same frequencies in all spectra, the apparent Raman shifts of the luminescence peaks are laser dependent (see Table S2).

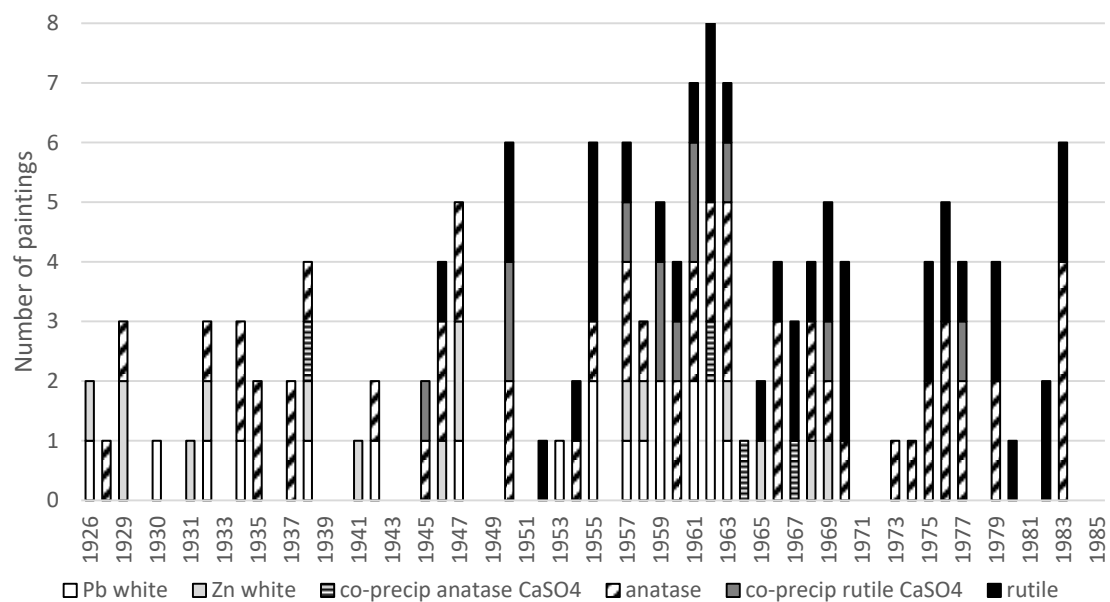


Fig. S2. Timeline for occurrences of six white pigments in American works of art.

White pigments in paintings created in the USA between 1926 and 1983 were identified using the methods described in the text and each occurrence of a given pigment type is ordered by creation date.

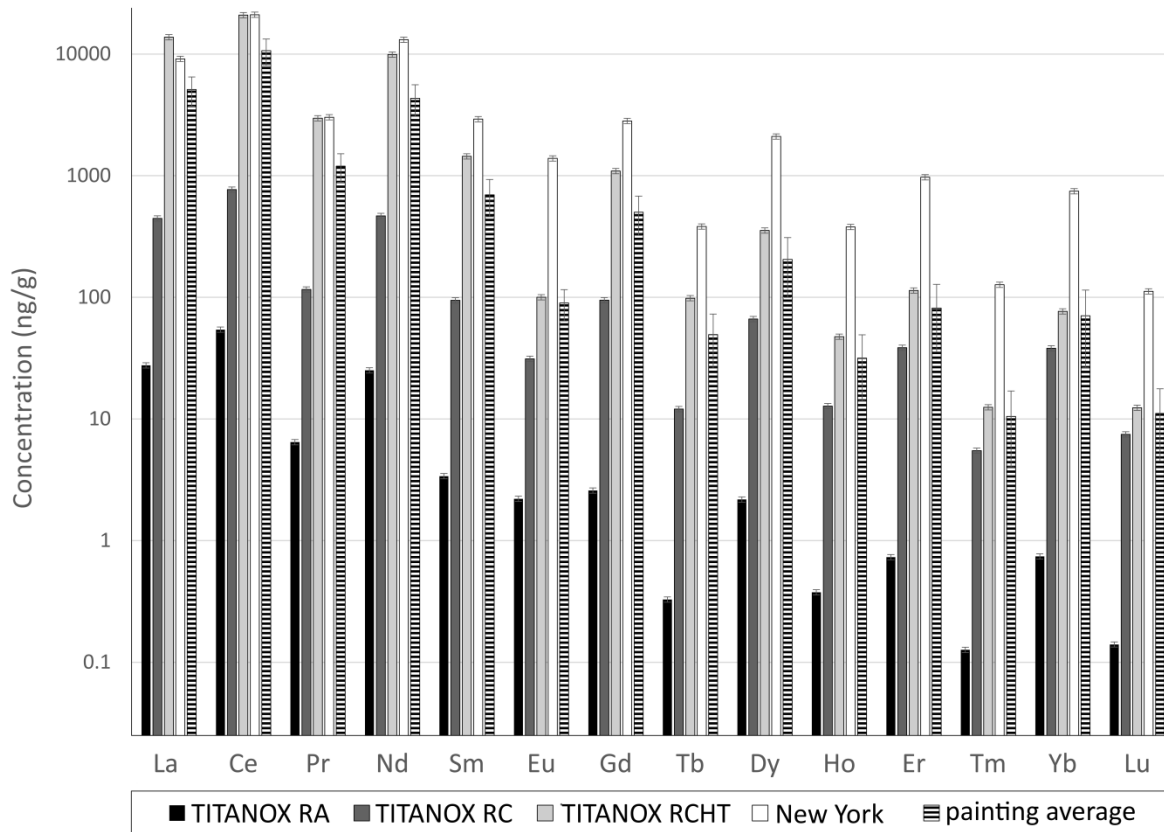


Fig. S3. REE levels in an ilmenite ore are similar to those in coprecipitated titanium white pigments and paints from works of art. Data from Fig. 4 are presented on a log scale. Concentrations of REE in different samples of TITANOX pigments compared to those of the ilmenite from the McIntyre mine (New 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 standard deviation of the four different paint samples.

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

Year		References
1916	Anatase co-precipitated with BaSO ₄	27, 11
1925	Anatase co-precipitated with CaSO ₄	6, 11
1926-7	Non-co-precipitated anatase available	6, 11
1941	Rutile co-precipitated with BaSO ₄ or CaSO ₄ patented	6, 41
1944	TITANOX Pigment corporation ceases production of anatase CaSO ₄ co-precipitated pigment	11
Late 1940s	TITANOX Pigment corporation ceases production of anatase BaSO ₄ co-precipitated pigment	27
1957	Non-co-precipitated rutile widely available	6
Late 1970s	Rutile BaSO ₄ co-precipitated pigment phased out	6

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

785 nm laser		633 nm laser		532 nm laser	
Experimental Raman shift (cm ⁻¹)	Calculated wavelength (nm)	Experimental Raman shift (cm ⁻¹)	Calculated wavelength (nm)	Experimental Raman shift (cm ⁻¹)	Calculated wavelength (nm)
1196	866	4289	869	7280	868
1281	873	4372	875	7366	875
1362	879	4450	881	7446	881
1576	896	4669	899	7663	898
1661	903	4754	905	7745	905

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

Name	Materials (27)	Materials identified by Raman	Luminescence signature ^a
TITANOX A 168 LO	97% anatase, treated with hydrated alumina	anatase	No
TITANOX A MO	98% anatase	anatase	No
TITANOX C 50 A	50% TiO ₂ co-precipitated on CaSO ₄	rutile, CaSO ₄	Yes
TITANOX RA	97% rutile	rutile	No
TITANOX RC A	30% TiO ₂ co-precipitated on CaSO ₄	rutile, CaSO ₄	Yes
TITANOX RA NC	93% rutile	rutile	No
TITANOX RCHT	30% TiO ₂ co-precipitated on CaSO ₄	rutile, CaSO ₄	Yes
TITANOX RCHT X	30% TiO ₂ co-precipitated on CaSO ₄	rutile, CaSO ₄	Yes

^a Using a 785 nm laser

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

Title	Artist	Year	Pigments identified by Raman ^a	Institution
Green Composition	Balcombe Green	1938	anatase, CaSO ₄	MFAH
Moon Vessel	Jackson Pollock	c. 1945	rutile, CaSO ₄	MFAH
Untitled (Study for Wotan)	Franz Kline	1950	rutile, CaSO ₄	MFAH
Wotan	Franz Kline	1950	rutile, anatase, BaSO ₄ , CaSO ₄	MFAH
Crucifixion and Reflection	Robert Rauschenberg	1950	rutile, CaSO ₄	Menil
Primordial Light	Barnett Newman	1954	anatase, CaSO ₄ , BaSO ₄	Menil
Sparks	Hans Hofmann	1957	rutile, CaSO ₄	MFAH
Untitled	Walter Egel Kuhlman	1958	rutile, CaSO ₄ , BaSO ₄	Menil
Summer Party	Grandma Moses	1959	rutile, CaSO ₄	MFAH
Circle and Parts	David Smith	1959	rutile, CaSO ₄	MFAH
John Doe	Edward Kienholz	1959	rutile, anatase, BaSO ₄	Menil
Thanksgiving	Ray Parker	1960	rutile, CaSO ₄	MFAH
Icebox	Andy Warhol	1961	rutile, CaSO ₄	Menil
Untitled #525	Ray Parker	1961	rutile, CaSO ₄	MFAH
Untitled	Franz Kline	1961	rutile, anatase (trace), CaSO ₄ , BaSO ₄	MMA
Corinthian II	Franz Kline	1961	rutile, BaSO ₄ , CaSO ₄	MFAH
Glider	Robert Rauschenberg	1962	rutile	MFAH
Very Low Sun-High Snow	Theodoros Stamos	1962	anatase, CaSO ₄	MFAH
Grave I	William Christenberry	1963	luminescence only	Menil
Fiat Lux	Hans Hofmann	1963	rutile, CaSO ₄	MFAH
Untitled	Knox Martin	1964	anatase, CaSO ₄	MFAH
Spoonk	Marion Greenstone	1964	anatase, CaSO ₄ ^b	
White and Hot	Barnett Newman	1967	anatase, CaSO ₄	St. Louis Art Museum
Haiti	Dorothy Hood	1969	rutile, CaSO ₄	MFAH
Evolutionary Balance	James Rosenquist	1977	rutile, CaSO ₄	MFAH

^a Using a 785 nm laser^b Personal e-mail communication from Sharra Grow, March 20, 2014.

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

Brand	Address (if given)	Name	Species detected by Raman	
			TiO ₂ polymorph	other
Alexander Oil Color	Salem, OR	Titanium White	rutile	
Archival Oils	Sydney, Australia	Formula Titanium White	rutile	
Beckers Normalfärg	Stockholm, Sweden	Titanium White	rutile	BaSO ₄
Bellini Artists' Oil Colors	New York	Titanium-Zinc White	rutile	BaSO ₄
Bellini Artists' Oil Colors	NY 19	Titanium White	rutile	BaSO ₄
Bellini Artists' Oil Colors	Garnerville, NY	Titanium White	rutile	BaSO ₄
da Vinci Paint	Irvine, CA	Titanium White	rutile	
da Vinci Paint	Irvine, CA	Non-yellowing Titanium White	rutile	BaSO ₄
Fidelis	Statesville, NC	Titanium White	rutile	
Flying Eagle	China	Titanium White	rutile	
Fragonard	France	Titanium White	anatase, rutile	
Gamblin	Portland, OR	Titanium White	rutile	BaSO ₄ , CaCO ₃
Grumbacher	NY 10001	Superba White	anatase	
Grumbacher		Titanium White Academy	anatase	
Grumbacher	NY	MG Underpainting White	anatase	BaSO ₄
Grumbacher	Bloomsbury, NJ	MG Underpainting White	anatase	BaSO ₄
Grumbacher	NY	Pre-tested Permanent Titanium White	anatase	
Holbein	Japan	Quick Drying White	rutile	CaCO ₃
Holbein l'huile ecole		Titanium White	rutile	BaSO ₄ , CaCO ₃
Hunstman Co. Speedball	Statesville, NC	Titanium White	rutile	
Lefranc & Bourgeois		Titanium Zinc White	anatase	BaSO ₄
Lefranc & Bourgeois		Titanium White	rutile	
Lumen		Titanium White	rutile	
Maimeri Brera	Italy	Titanium White	anatase	BaSO ₄
Matisson	Japan	Titanium white	rutile	BaSO ₄
Mir	Barcelona	Titanium White	rutile	
Old Holland		Titanium White	rutile	
Pebeo Fragonard		Zinc and Titanium White	rutile	
Permanent Pigments		Titanium Everwhite	rutile	BaSO ₄
Rembrandt	Apeldoorn, Holland	Titanium White	anatase	
Rowney Georgian	Bracknell, England	Titanium White	rutile	
Royal Talens van Gogh		Titanium White	rutile	CaCO ₃

Sax Colors	Urdorf	Titanium White	rutile	
Sennelier	Paris	Titanium White	anatase, rutile	
Shiva Signature	Torrance, CA	Titanium White	anatase	CaCO ₃
Shiva Victor	Torrance, CA	Titanium White	rutile	
Stevenson	Toronto, Canada	Titanium White	rutile	
Talens	Apeldoorn, Holland	Titanium White	anatase	
Talens		Underpainting White	rutile	
The Art Store by Pictor Oil Color	Torrance, CA	Titanium White	anatase	BaSO ₄
Utrecht		Unbleached Titanium White	rutile	
Weber	Philadelphia, PA	Permalba White Oil Color	anatase	
Weber	Philadelphia, PA	Titanium White	anatase	BaSO ₄
Winsor & Newton		Winsor White	rutile	BaSO ₄
Winsor & Newton		Titanium White	rutile	BaSO ₄
Yarka	St. Petersburg, Russia	Titanium White	rutile	

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