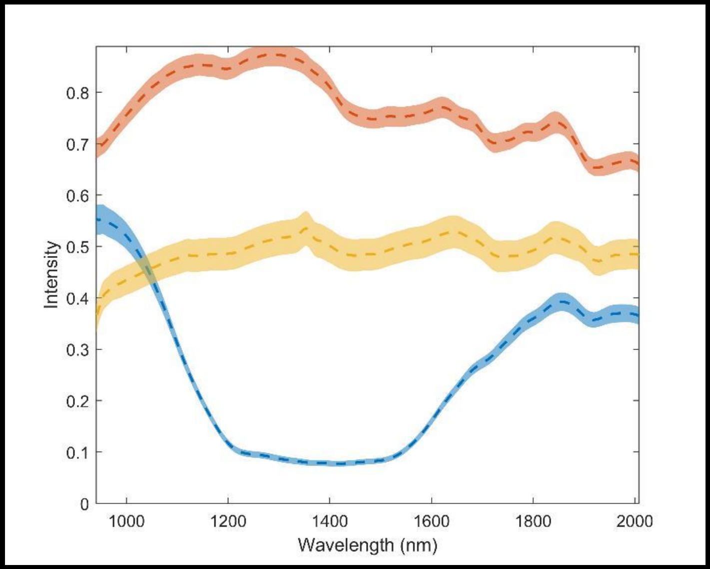
Science in art conservation and education: the role of analysis in understanding and treating paintings

Conservation aims to stabilise a painting in its present condition
If we conserve anything and it is unstable then we need to understand its present condition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0.1
0.2
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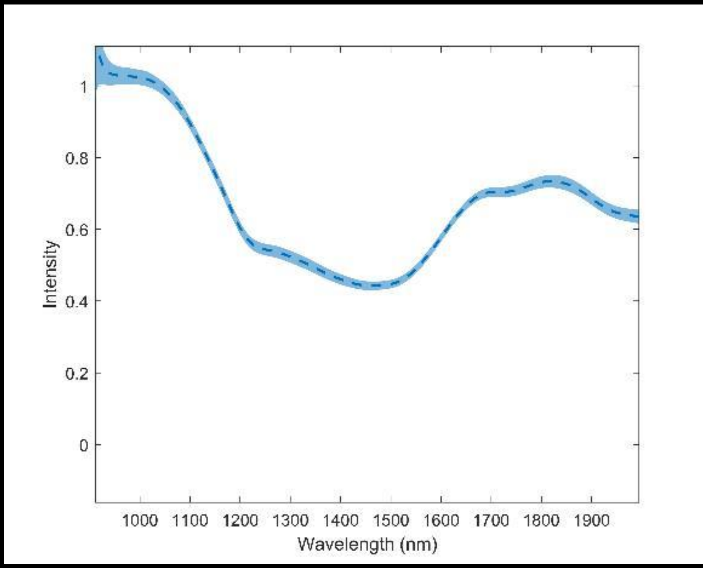
Wavelength (nm)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1300
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1700
1800
1900
Wavelength (nm)


The Courtauld

The Courtauld

The Courtauld

Science in art conservation and education: the role of analysis in understanding and treating paintings

Tel Kabri

Context

Paintings

Binding media

Significance

Middle Bronze Age (ca. 1850–1650 B.C.E.)

* Canaanite Kingdom

2000 painted Aegean style plaster paint fragments from our different schemes

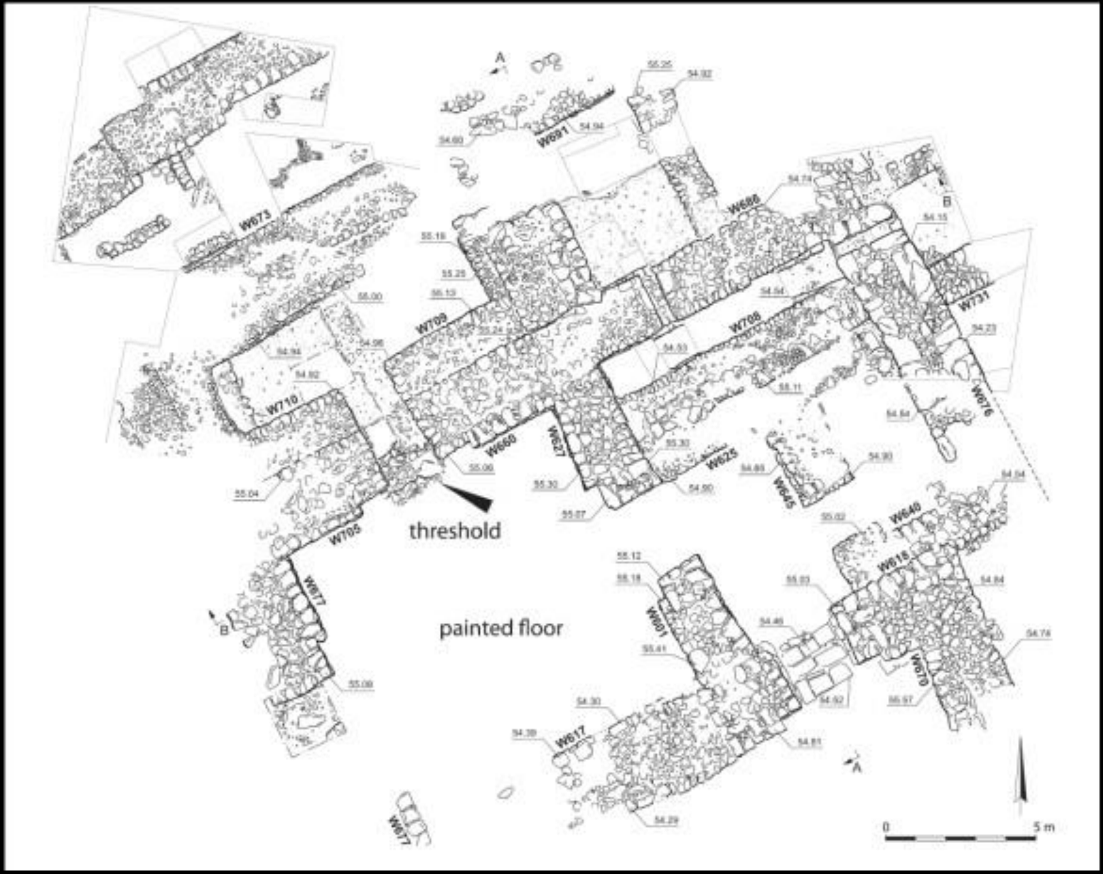
Kabri paintings can be compared to other sites: Tell el-Daba, Qatna & Alalakh

Phase **DW IV** is dated to the 18th century B.C.E

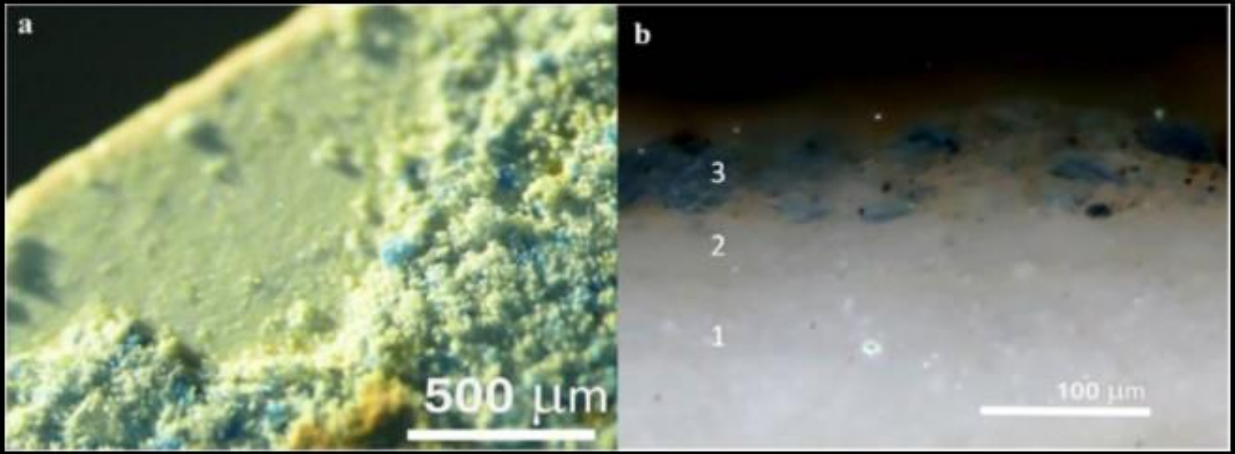
A. Yasur-Landau, E. H. Cline, A. J. Koh, D. Ben-Shlomo, N. Marom, A. Ratzlaff,

Recent excavations by Cline, Landau and Goshen

Painted plaster fragments were discovered face down on the floor, in reuse patterns similar to those reported in areas on of the wine magazine, Palace of Pylos



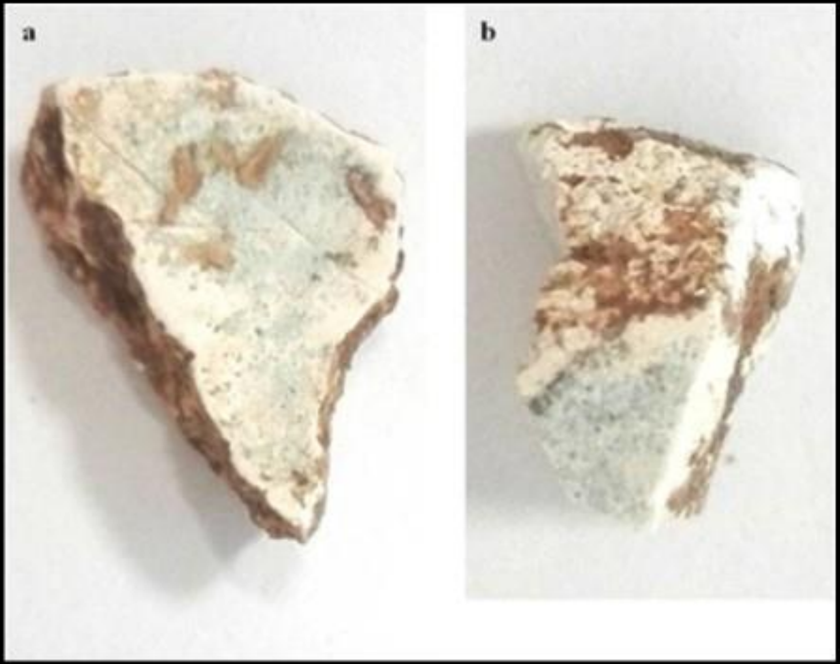
Wall painting scheme



Multiple plaster layers, with the thin topmost layer painted, like other Aegean paintings

Binding media analysis

What we know



Proteins

Mass-Spectrometry

Proteiomics

Mycenaean paintings

Egg based binding media have been identified in paintings from the "Palace of Nestor" in Pylos (Western Messenia, Greece) dated from the Late Bronze Age (ca. 1200 B.C.E.)

Journal of Archaeological Science

Characterization of organic media in the wall-paintings of the "Palace of Nestor" at Pylos, Greece: evidence for a secco painting techniques in the Bronze Age

Proteins & Amino Acids

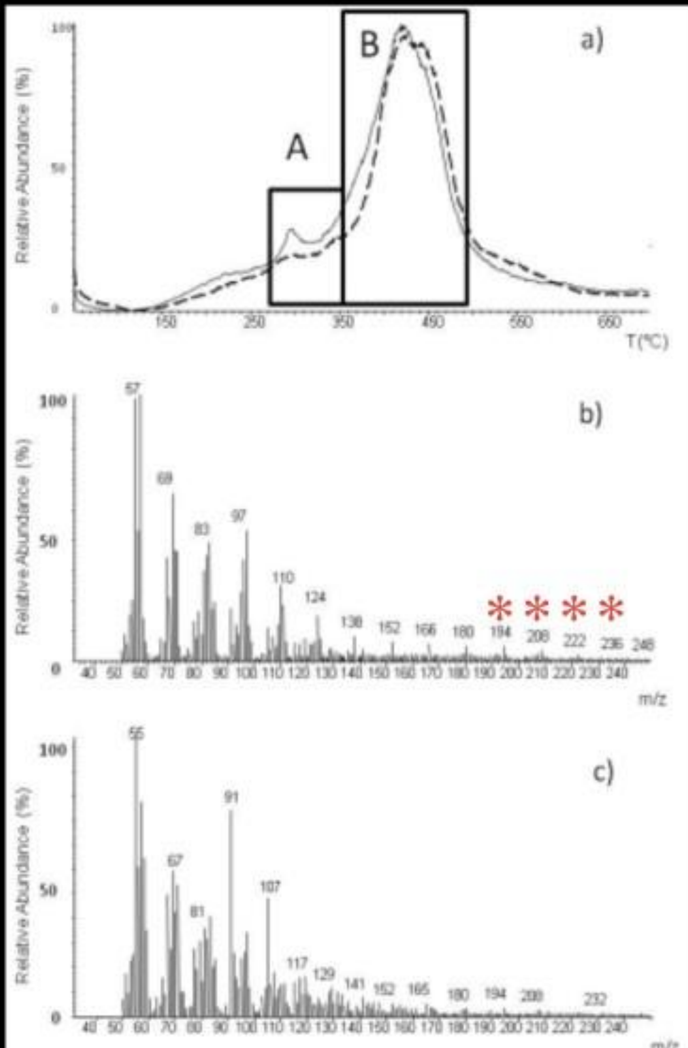
Challenges:

- Small fragments with little material for sampling
- Ancient media are degraded and poorly suited to standard methods of extraction and analysis
- Require sensitive methods to identify specific binders

Table 2

Percentage contents of amino acids and absolute amounts of protein. Al = alanine, gly = glycine, val = valine, leu = leucine, ile = isoleucine, ser = serine, pro = proline, phe = phenylalanine, asp = aspartic acid, glu = glutamnic acid, hyp = hydroxyproline.

Sample	ala	gly	val	leu	ile	ser	pro	phe	asp	glu	hyp
P1.01	10.4	13.6	8.1	9.0	6.4	8.4	2.5	4.3	17.6	19.9	0.0
004.05.01	10.7	9.2	13.6	18.7	11.9	2.1	10.3	10.3	7.0	6.0	0.0
006.02.01	9.6	10.8	13.3	14.9	8.3	2.6	9.9	5.8	16.0	8.8	0
006.04.01 *pf*	12.0	12.8	10.0	10.8	6.8	5.6	14.7	4.6	16.0	6.8	0
Dr.17.03/04	19.7	38.6	4.0	4.0	2.2	3.3	13.5	1.9	5.0	2.0	5.8
P18.06	13.8	26.0	13.1	16.6	10.8	8.8	0.3	6.4	1.9	2.4	0.0
P20.06	10.5	13.6	8.3	9.2	6.8	8.1	2.4	4.6	17.0	19.5	0.0
P23.06	11.9	18.2	8.6	9.1	5.7	6.1	2.4	4.5	17.1	16.4	0.0
P103.06	11.4	18.4	9.5	12.7	7.0	8.6	9.3	4.6	11.1	3.9	3.5
P106.06	14.8	16.0	11.3	15.4	8.2	3.5	3.7	5.7	8.9	12.5	0
P15.17	10.6	17.4	9.2	8.7	6.5	5.4	2.8	5.5	17.9	16.0	0
075.105.27/31	13.7	27.8	11.6	14.1	8.7	5.0	10.2	2.6	2.1	4.2	0.0
069.56.31	14.4	14.3	10.5	14.3	8.1	11.0	16.5	1.9	4.1	4.8	0.0
063.70.27/32	8.2	18.2	6.2	10.8	4.9	15.8	5.2	4.2	13.6	12.4	0.5
063.73.27/32	12.4	22.9	11.9	16.4	9.6	4.9	8.7	3.1	5.1	4.7	0.3
105.66.46	11.1	11.0	6.4	14.8	7.5	8.1	4	6.9	9.2	21.0	0.0
P7.64	15.7	22.4	14.9	16.2	11.0	5.8	0.5	7.3	4.1	2.4	0.0
P11.64	18.9	18.4	16.6	18.9	14.4	1.7	0.3	8.7	0.4	1.9	0.0
135.43.64	13.7	16.0	7.6	10.2	5.8	9.9	5.9	6.4	12.4	10.0	1.9
P63	10.9	11.4	6.0	7.3	4.3	7.3	3.8	4.1	15.1	29.9	0.0



Evolved Gas - Mass Spectrometry

- *No sample preparation*

The average mass spectrum reveals fragmented ions ascribable to hexadecanenitrile and octadecanonitrile (m/z 194, 208, 222, 236). Hexadecanonitrile and octadecanonitrile are known markers of egg yolk are pyrolitic profiles of degraded samples

Journal Submission

Rejection

"Given the comments made by the referees it is clear that although your findings are interesting they do not represent a sufficient basis for publication in *Angewandte Chemie* at the present time and that further experimental work and clarifications are required. "

Proteiomics Analysis

K20

CELAAAMKR + Oxidation (M)
HGLDNYR (31)
HGLDNYRGYSLGNWVCAAKFESNFNTQATNR
HGLDNYRGYSLGNWVCAAKFESNFNTQATNR + Deamidated (N)
HGLDNYRGYSLGNWVCAAKFESNFNTQATNR + 2 Deamidated (NQ) (55)
GYSLGNWVCAAKFESNFNTQATNR (51)
GYSLGNWVCAAKFESNFNTQATNR + Deamidated (N)
FESNFNTQATNR (90)
FESNFNTQATNRNTDGSTDYGILQINSR
FESNFNTQATNRNTDGSTDYGILQINSR + Deamidated (N) (51)
NTDGSTDYGILQINSR (58)
KIVSDGNGMNAWVAWR (33)
IVSDGNGMNAWVAWR (82)
IVSDGNGMNAWVAWR + Deamidated (N)
IVSDGNGMNAWVAWR.N + Oxidation (M)
CKGTDVQAWIR (72)
GTDVQAWIR (61)

Gallus gallus for both samples @ 56% coverage

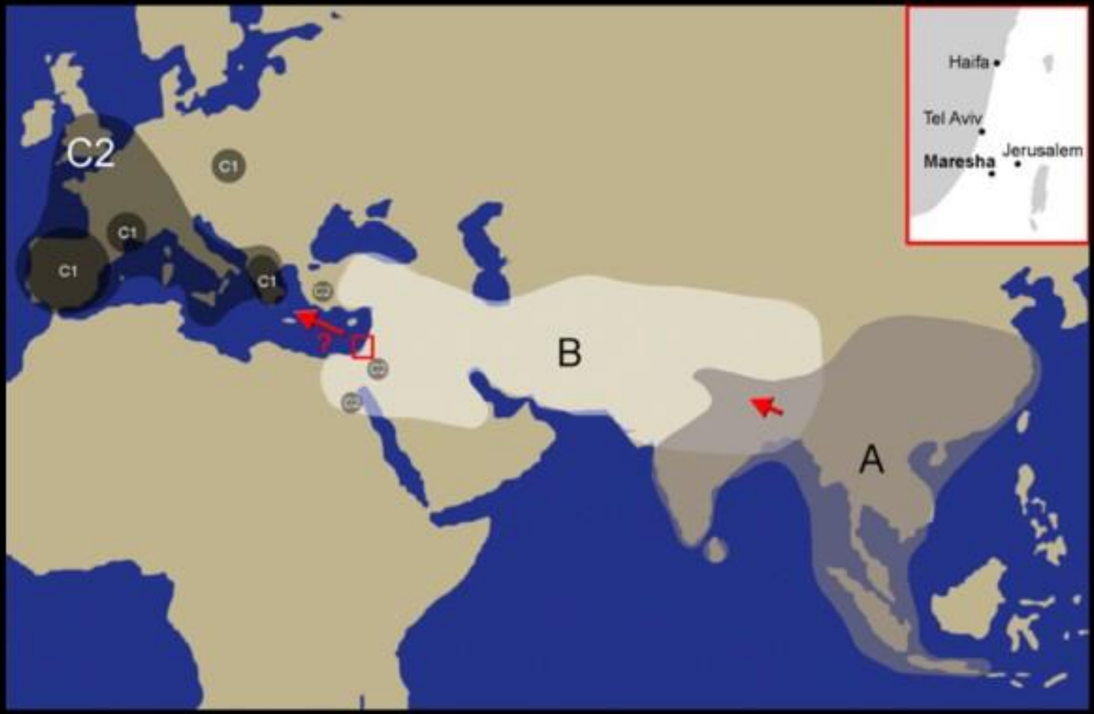
Publication in *Angew Chem Int Ed Engl.* 2018 Oct 1; 57(40):13257-13260.
doi: 10.1002/anie.201806520.

Significance:
Proteins so what?

Extend the use of an organic binder in Aegean style wall paintings back an additional 500 years and to a wider geographical area including the Eastern Mediterranean.

This is the *second oldest* identification of an organic material used as binder in wall paintings. The earliest use of egg as binder is from the Domus de Janas chamber tombs, Sardinia (3400–2700 B.C.E.)

Broader Significance :
Spread of domestic chickens?



A: 6th millennium B.C.E.
B: 2-3 millennia B.C.E
C: 8th C. B.C.E.

www.pnas.org/cgi/doi/10.1073/pnas.1504236112

Science in art conservation and education: the role of analysis in understanding and treating paintings

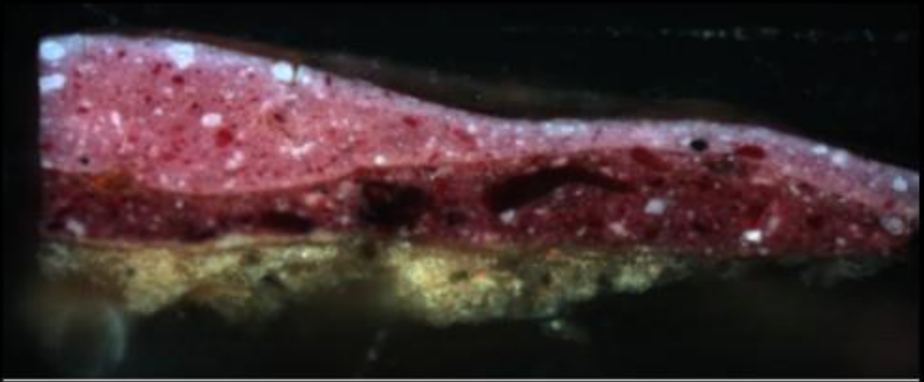
Light, & fading reds

Light-induced Colour Changes in Red and Yellow Lake Pigments

DAVID SAUNDERS AND JO KIRBY

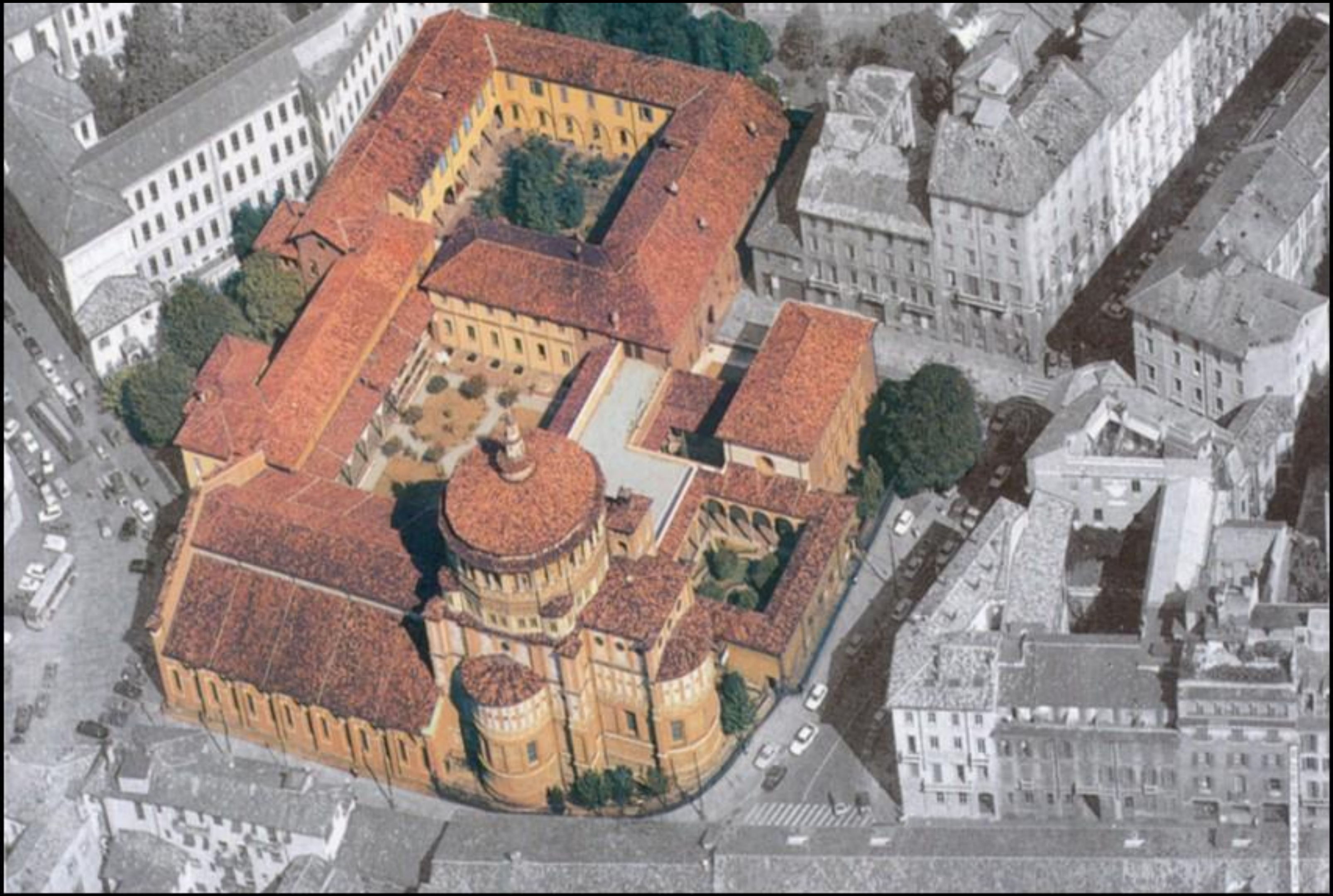
A cursory glance around the walls of any collection of western European paintings, dating from any time between the fourteenth and nineteenth centuries, will reveal numerous examples of the use of red and yellow lake pigments – translucent pigments prepared by the precipitation or adsorption of an organic dyestuff onto an insoluble substrate. Lake pigments, notably the reds, gave depth and transparency to the richly glazed shadows of draperies; red lakes were mixed with, or glazed over, white and blue to give delicate pinks and mauves; combined with yellows, browns or blues, yellow lakes gave subtle yellows and greens. Lake pigments were an essential constituent of the artist's palette.

The most casual visitor to the National Gallery could not fail to notice the striking portrait of *Anne, Countess of Albemarle* (NG 1259), painted by Sir Joshua Reynolds around 1760 (Plate 1 and Fig. 1).[1] The Countess is seated in front of a deep purplish-red curtain. Her level gaze is indicative of a formidable personality; the deep pallor of her face, enlivened only by two spots of pink on her cheeks, does not,

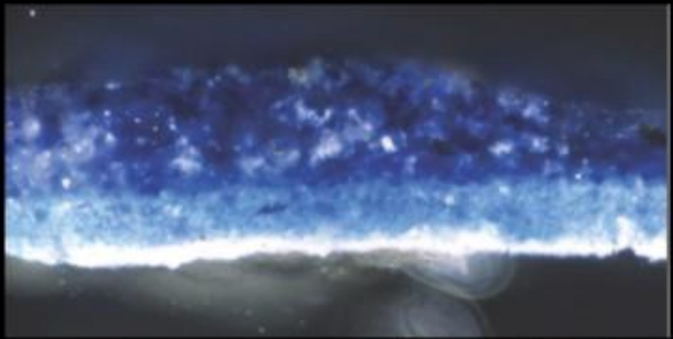


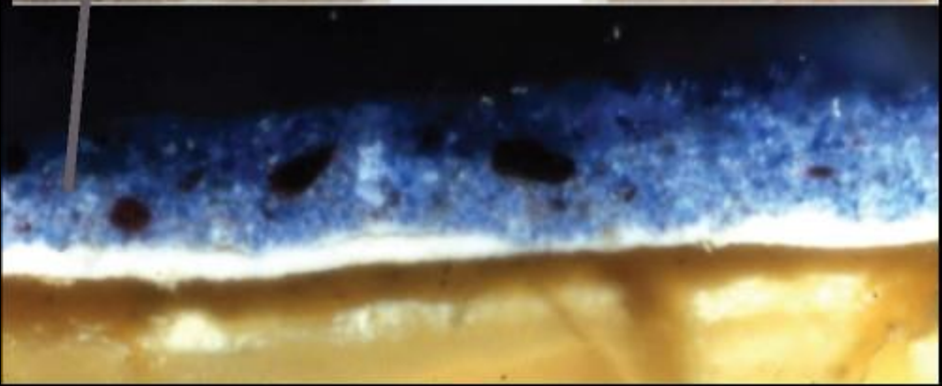
Oxidation recognized as common in paintings by Veronese @ National Gallery London

Cleaning and soluble reds



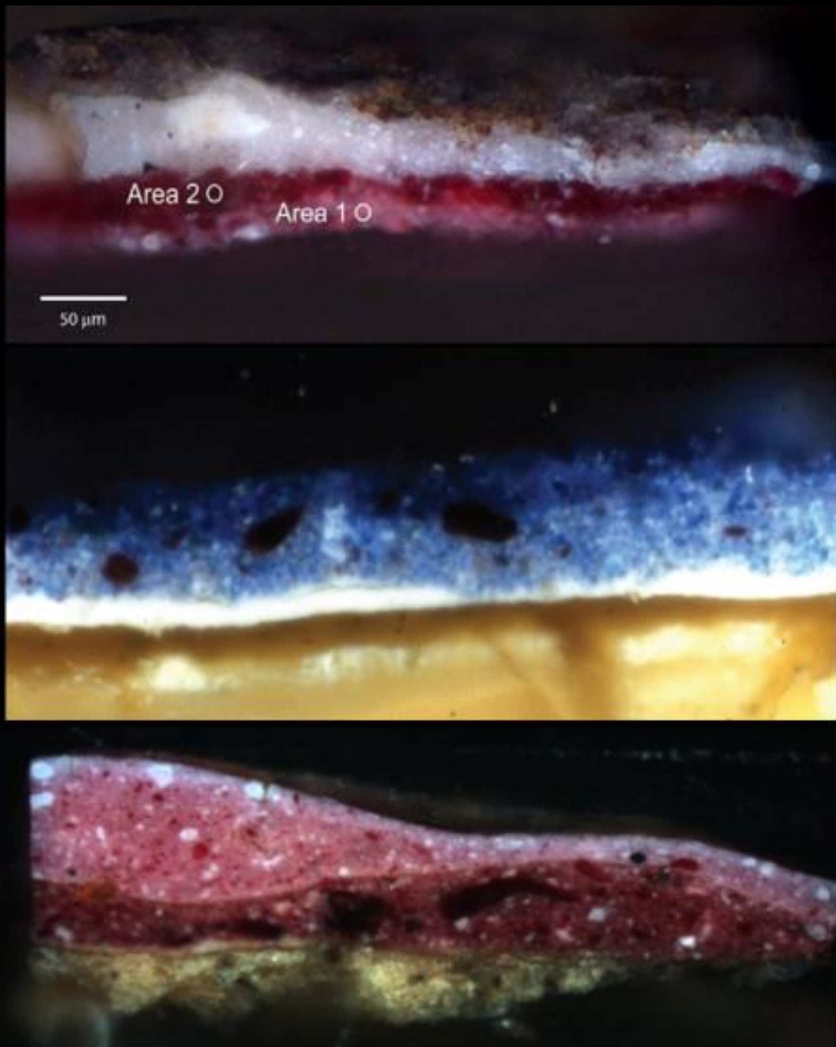
San Bartolomeo





E nota, che se la detta prìa lapis lazzari non fusse così perfetta, o che avessi triata la detta prìa che l'azzurro non rispondesse violante, t'insegno a dargli un poco di colore. Togli una poca di grana pesta, e un poco di verzino; cuocili insieme; ma fa' che il verzino o tu 'l grattugia, o tu il radi con vetro; e poi insieme li cuoci con lisciva, e un poco d'allume di rôcca; e quando bogliono, che vedi è perfetto color vermiglio

Cennino Cennini LXII.



Analysis:What reds are these?

Unique Samples

Raman Spectroscopy:
Laser excitation: 514.5 (Ar+) and 785 (Diode) nm
Objective magnification: 50X (5 µm2)
Spectral resolution: 4-6 cm-1

To overcome Fluorescence
Mathematical methods:
Subtracted Shift Raman Spectroscopy (SSRS)

Comparison of spectra with new DFT calculations *published April 2018*

RESEARCH ARTICLE

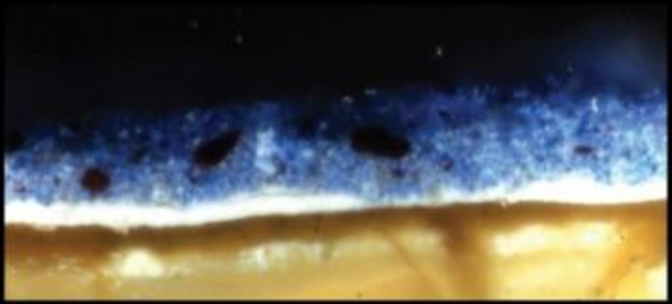
WILEY RAMAN SPECTROSCOPY

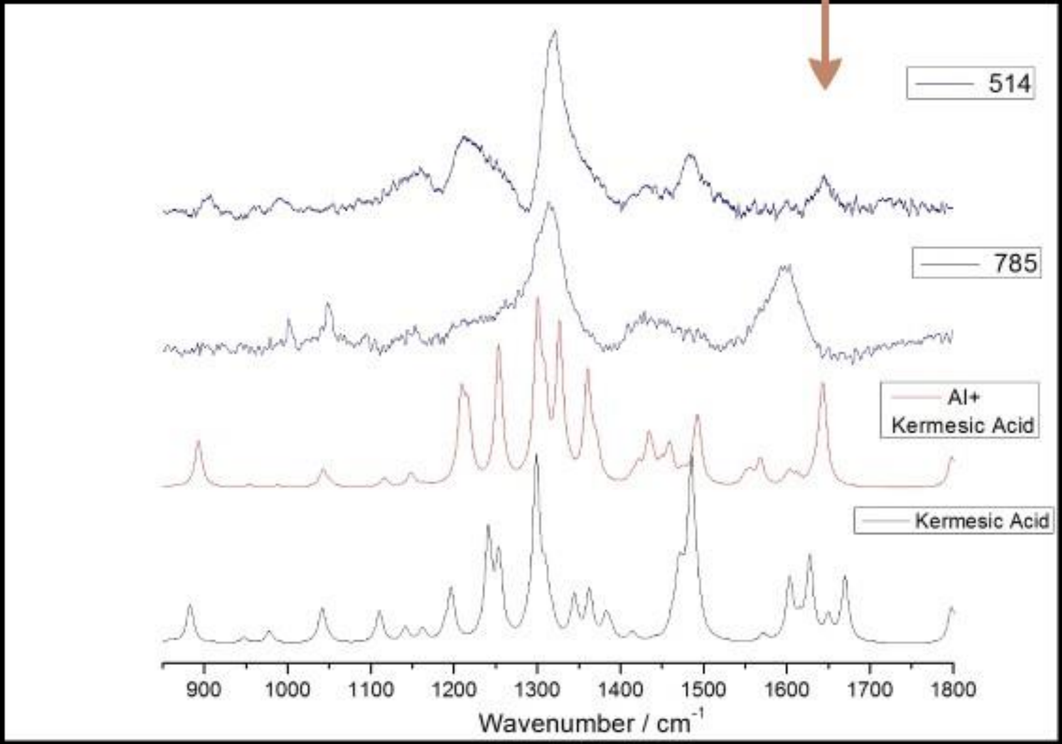
DFT calculations of the IR and Raman spectra of anthraquinone dyes and lakes

Marco Pagliai[1] | Iacopo Osticioli[2] | Austin Nevin[3] | Salvatore Siano[2] | Gianni Cardini[1] | Vincenzo Schettino[2]

Leonardo

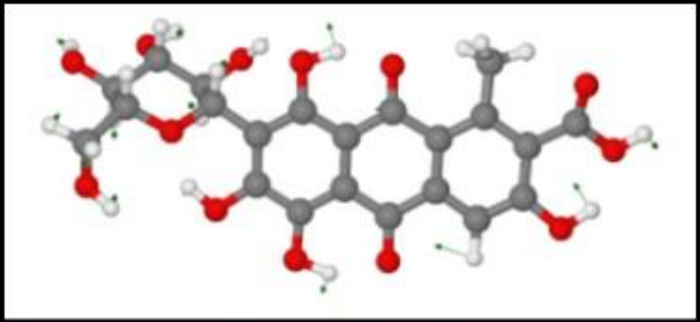
Kermes + Kermesic Acid

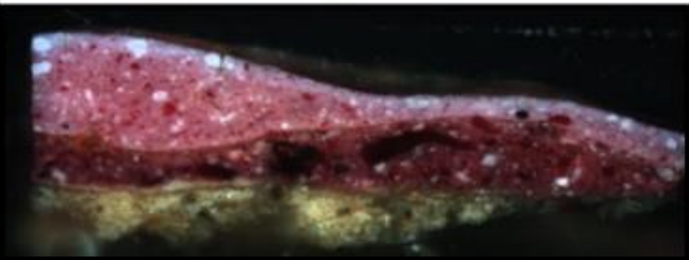


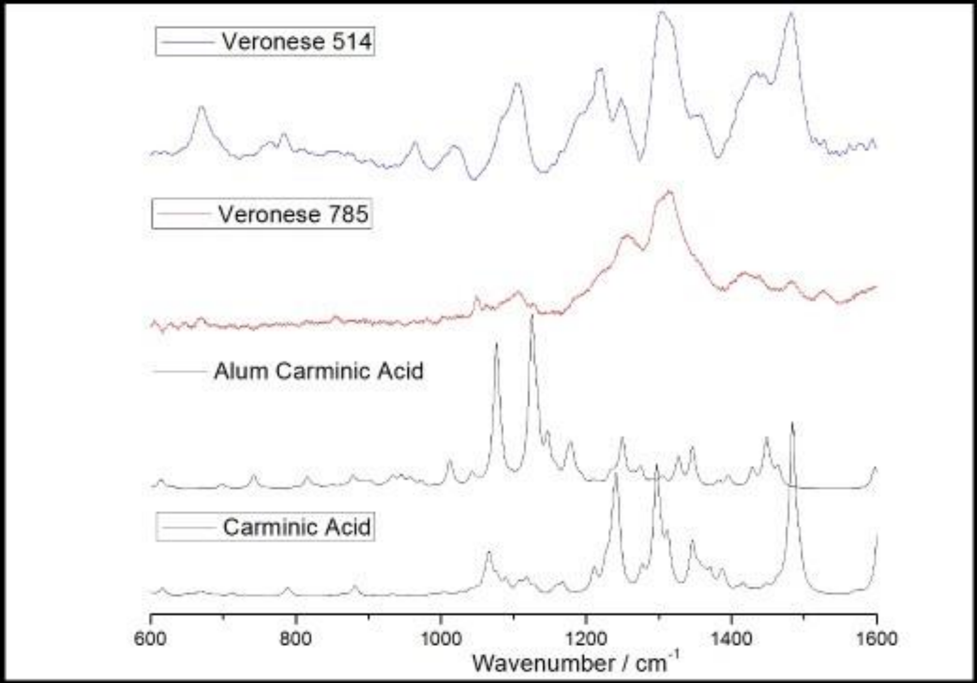


Veronese

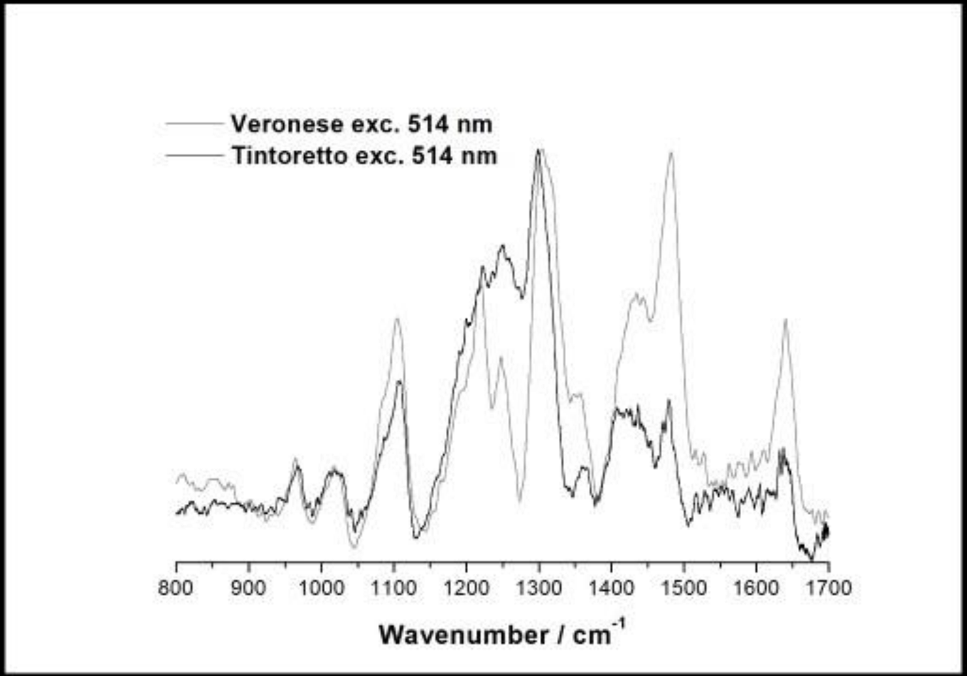
Carminic acid + Carmine lake







Spectra from Veronese vs. Tintoretto



World reds

Science in art conservation and education: the role of analysis in understanding and treating paintings




FONDATION BEYELER

Laser-Induced Fluorescence in Artwork Diagnostics: An Application in Pigment Analysis

DEMETRIOS ANGLOS,* MARIA SOLOMIDOU, IOANNA ZERGIOTI, VASSILIS ZAFIROPULOS, THEODORE G. PAPAZOGLOU, and COSTAS FOTAKIS

Foundation for Research and Technology–Hellas (FO.R.T.H.), Institute of Electronic Structure and Laser, Laser and Applications Division, P.O. Box 1527, GR 711 10 Heraklion, Greece (D.A., M.S., I.Z., V.Z., T.G.P., C.F.); and Department of Physics, University of Crete, Heraklion, Greece (M.S., C.F.)

The applicability of laser-induced fluorescence (LIF) spectroscopy as a nondestructive analytical technique for artwork diagnostics is investigated. In this work, LIF is employed in the examination of a set of cadmium sulfide- and cadmium selenide sulfide-based pigments in a series of oil painting test samples. Fluorescence spectra of the oil colors are recorded upon pulsed laser excitation at 532, 355 (Nd:YAG), and 248 nm (KrF excimer). The technique is shown to be suitable for differentiating among the various cadmium pigments used in this study and, furthermore, to be capable of identifying individual components in mixtures of these pigments on the basis of their characteristic fluorescence emission. Future prospects and the potential for the extension of LIF from a research laboratory technique into a conservator's tool for artwork diagnostics are discussed.

Index Headings: LIF; Artwork diagnostics; Oil colors; Cadmium pigments.

INTRODUCTION

Physical, chemical, and structural characterization of artworks, monuments, and antiquities is essential to the work of historians, archaeologists, art historians, artists, conservators, and restorers as it provides scientific information of artistic, cultural, and historical value. Establishment of reliable and efficient methodologies is thus most important for the systematic and informative analysis of works of art. Furthermore, development and use of techniques nondestructive to the artworks is highly desirable. To date, a wide variety of physicochemical analytical techniques have been employed to attack quite diverse and often complex problems in archaeology and art conservation.[1] Among them, most popular have been the spectroscopic techniques, mainly because of their high sensitivity and small sample quantity requirements.[2]

Modern laser-based techniques are currently under active investigation regarding their use in the field of artwork conservation and restoration both in cleaning and diagnostic applications.[3] The aim of our work is to investigate the applicability of laser-induced fluorescence (LIF) spectroscopy as a tool of painted artwork diagnostics. In this respect we present here preliminary results on the application of LIF in pigment analysis performed on test oil painting samples of cadmium based pigments, prepared in a way that closely simulates realistic cases. LIF is a versatile, nondestructive analytical technique; can be performed *in situ*— on the artwork itself; and provides information which can be directly related to the molecular structure of pigments or other components of paintings, both inorganic and organic. LIF has found numerous applications not only in basic research studies but also in biomedical diagnosis,[4] remote environmental monitoring,[5-7] and other fields. Despite this fact, the application of fluorescence spectroscopy in artwork analysis and diagnostics has been so far limited to the empirical examination of paintings with the naked eye or with photographic film under ultraviolet lamp illumination. The exception to this approach has been the work of de la Rie[8] and T. Miyoshi et al.,[9-11] who have investigated fluorescence properties of pigments, oils, and varnishes used in painting.

Received 15 March 1996; accepted 2 June 1996.
* Author to whom correspondence should be sent.

EXPERIMENTAL

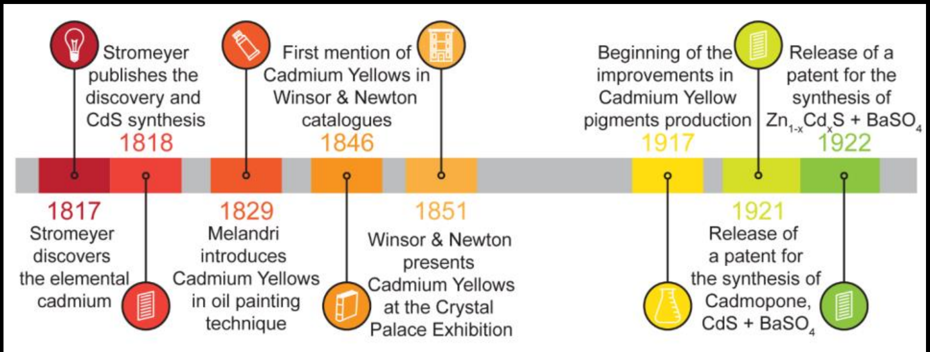
Test oil painting samples were prepared at the Conservation Department of the National Gallery of Athens (Greece) in the following way: Pigments in powder form (Kremer Pigmente, Old Holland) were mixed thoroughly with bleached linseed oil (Old Holland) in an agate mortar until they formed a homogeneous oil color paste of high pigment content. The oil colors were applied onto a gesso (calcium carbonate in animal glue) primed canvas panel, and the samples were allowed to dry naturally in the dark for a period of at least two weeks before any analysis was performed.

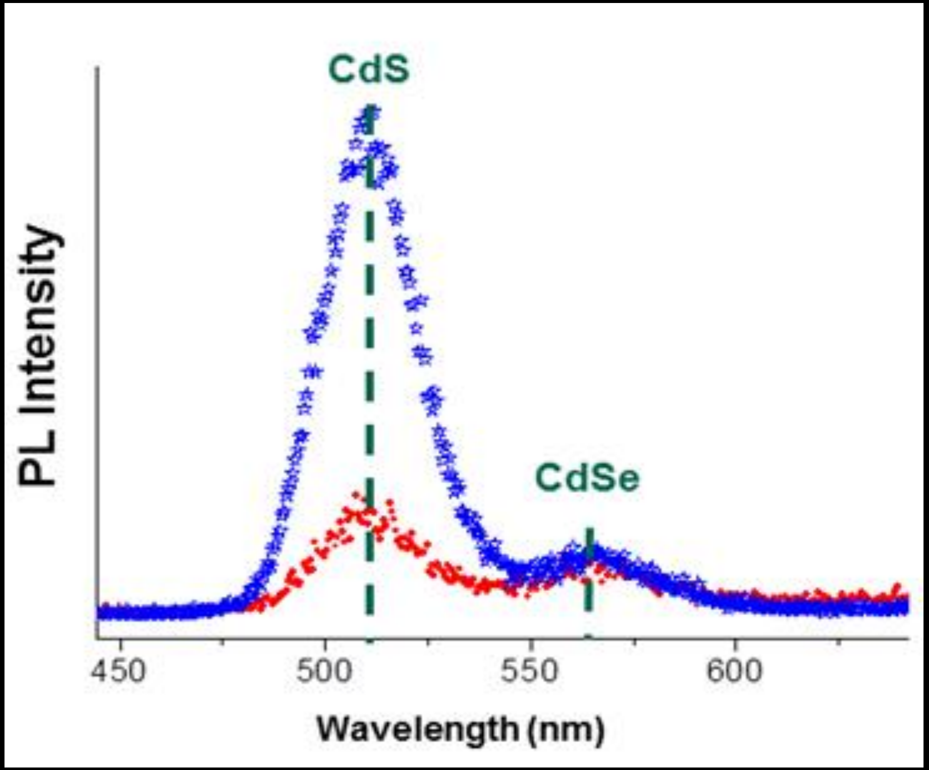
Fluorescence spectra were recorded on a laser fluorescence spectrophotometer. The basic components of the experimental setup are a frequency-doubled or -tripled nanosecond Q-switched Nd:YAG laser (Quantel, Brilliant, YG 881-20) or a KrF excimer laser (Lambda Physik, LPX 205SD), a 0.25-m grating spectrograph (PTI Model 01-001AD), an intensified photodiode array detector (EG&G PARC Model 1420UV), and an optical multichannel analyzer (OMA III system, EG&G PARC Model 1406).

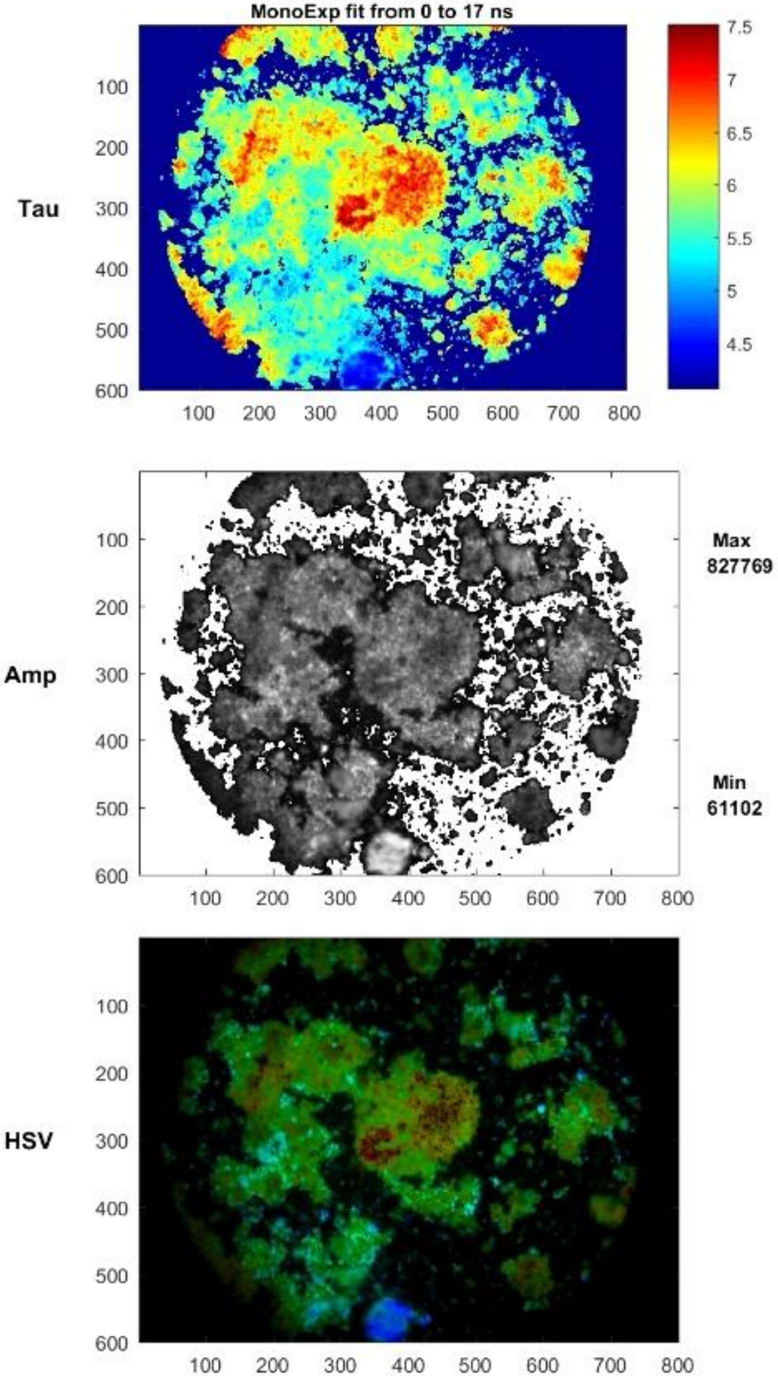
Briefly, the excitation laser at fluences of no more than 1 mJ/cm² illuminates the surface of the sample at 45° to the normal. The emitted fluorescence is collected with a fused-silica optical fiber (0.6-mm diameter) at 75° relative to the incident beam and analyzed by the spectrograph. The fluorescence spectrum is detected by the photodiode array and recorded on the OMA. With the use of a grating with 300 lines/mm, a spectral range of ~280 nm is covered at once. Wavelength calibration of the system is performed with a mercury lamp.

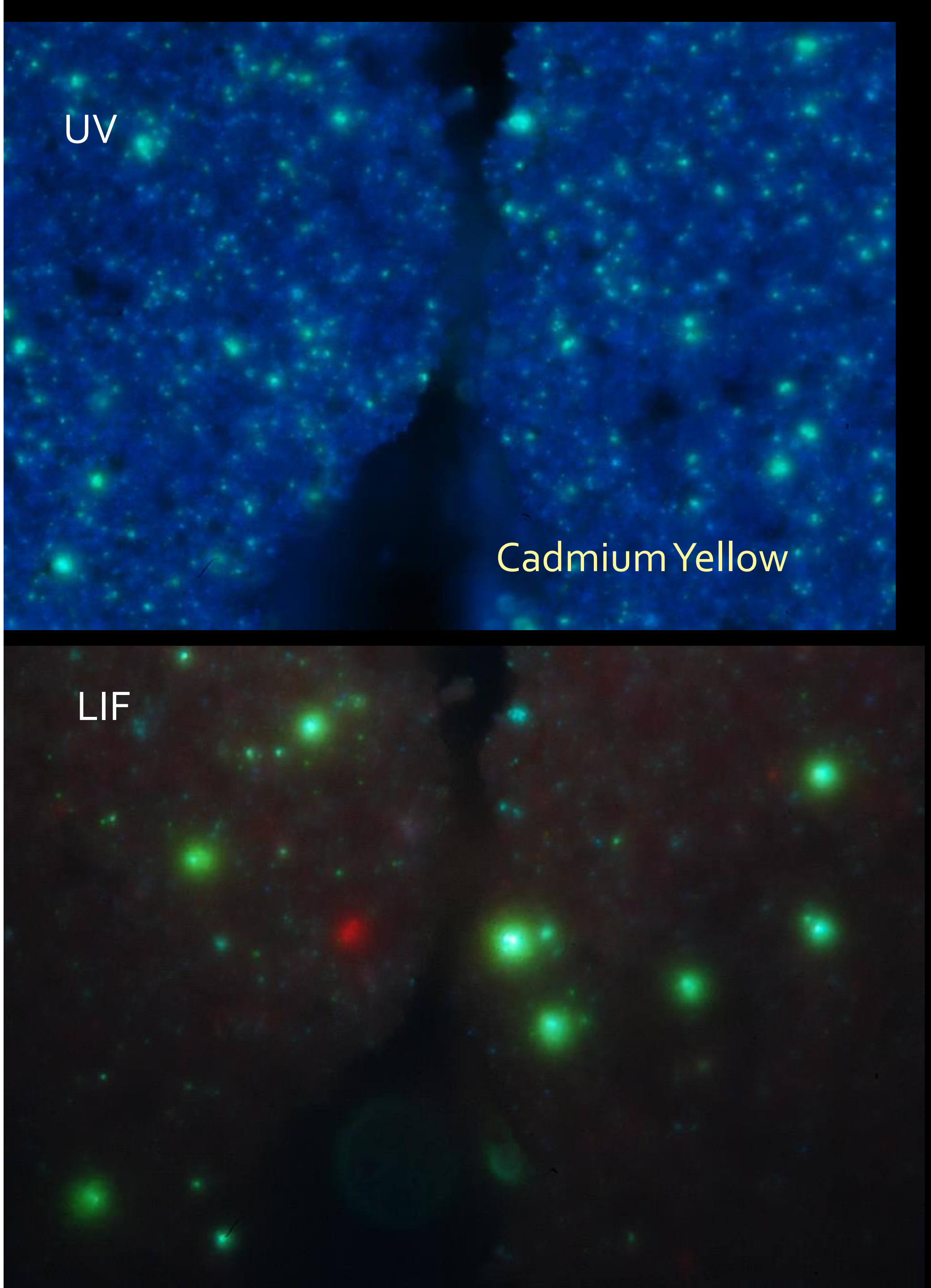
RESULTS AND DISCUSSION

A set of seven cadmium-based pigments with colors ranging from light yellow to deep red were studied (Table






MonoExp fit from 0 to 17 ns
Tau
7.5
7
6.5
6
5.5
5
4.5
Amp
Max
827769
Min
61102
HSV
100
200
300
400
500
600
700
800


UV
Cadmium Yellow
LIF

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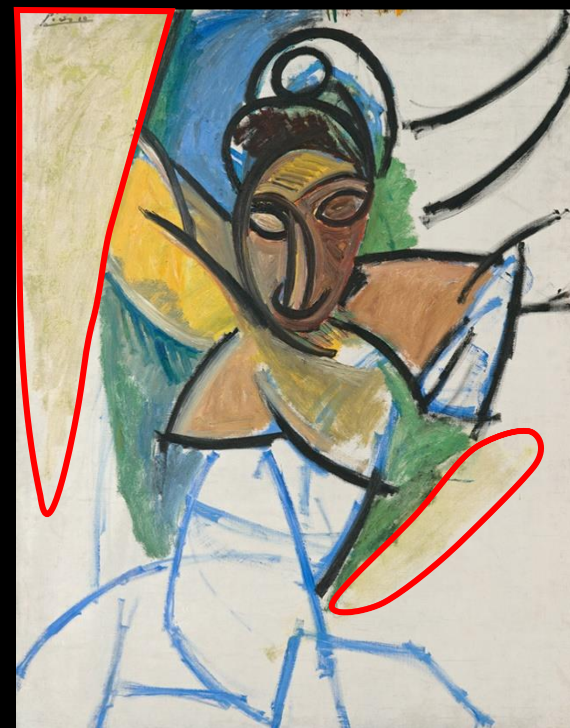
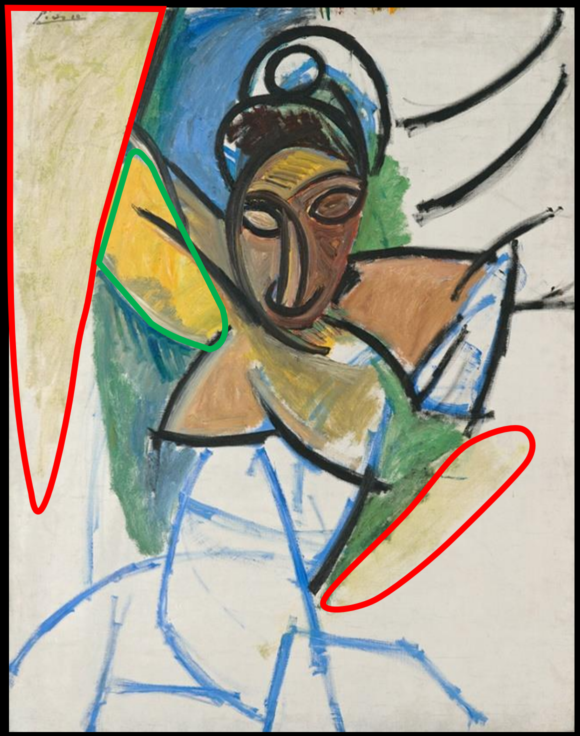
Picasso: Sketch for *Les Demoiselles d'Avignon*

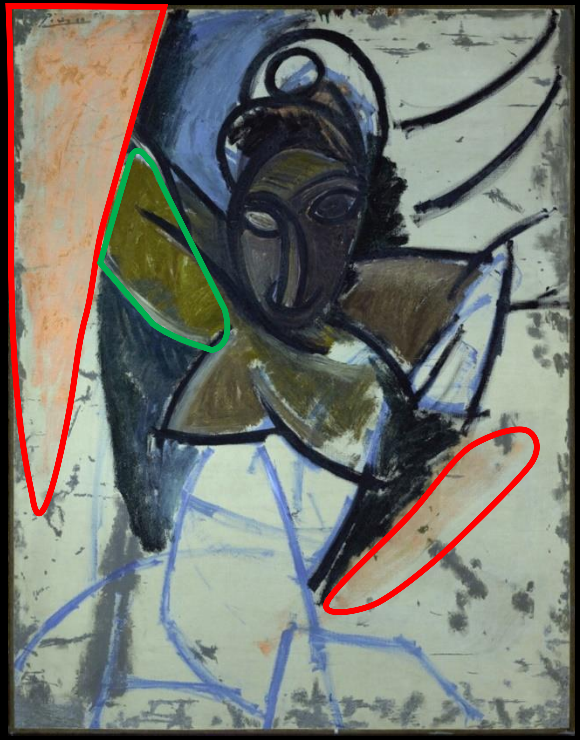
Old Ektachrome color slide from the Beyeler archives



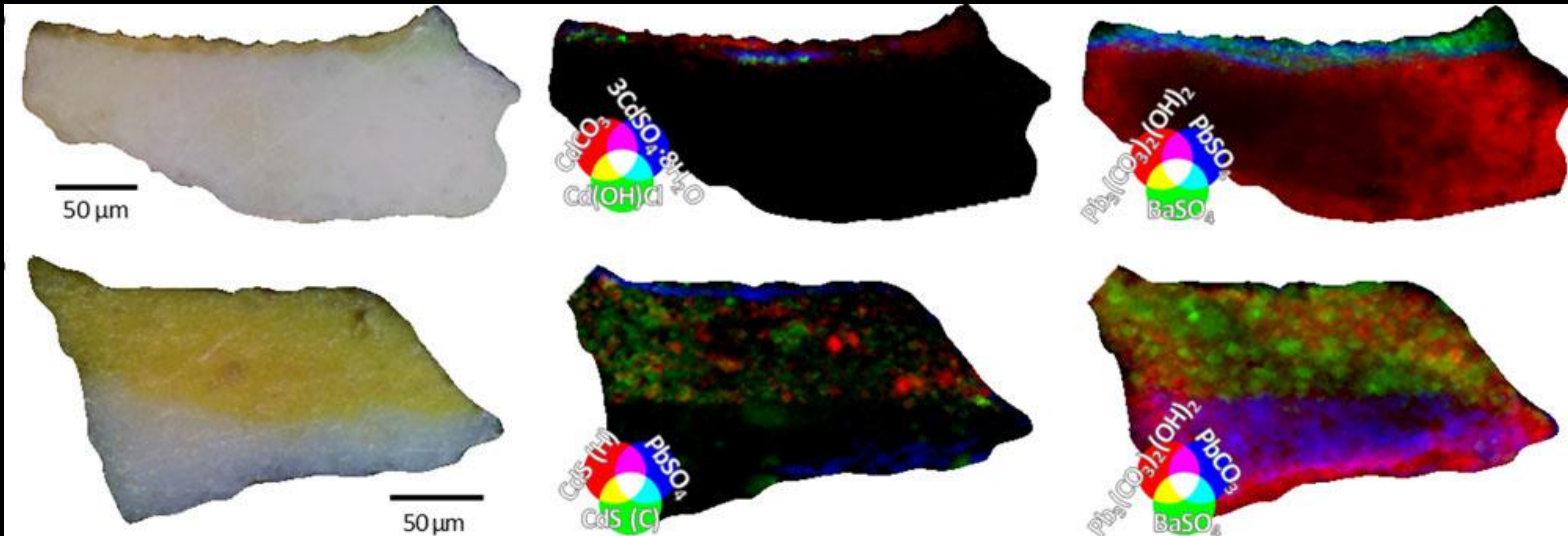
Recent photograpy

Fading and color alteration





Different photoluminescence emission of the altered yellow paint with respect to the preserved paint



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doi:10.1017/S1431927622000873

Science in art conservation and education: the role of analysis in understanding and treating paintings

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Iacopo Osticioli, CNR, Florence
Sharon Cather, Courtauld Institute of Art