

# Imaging spectroscopy for cultural heritage and conservation

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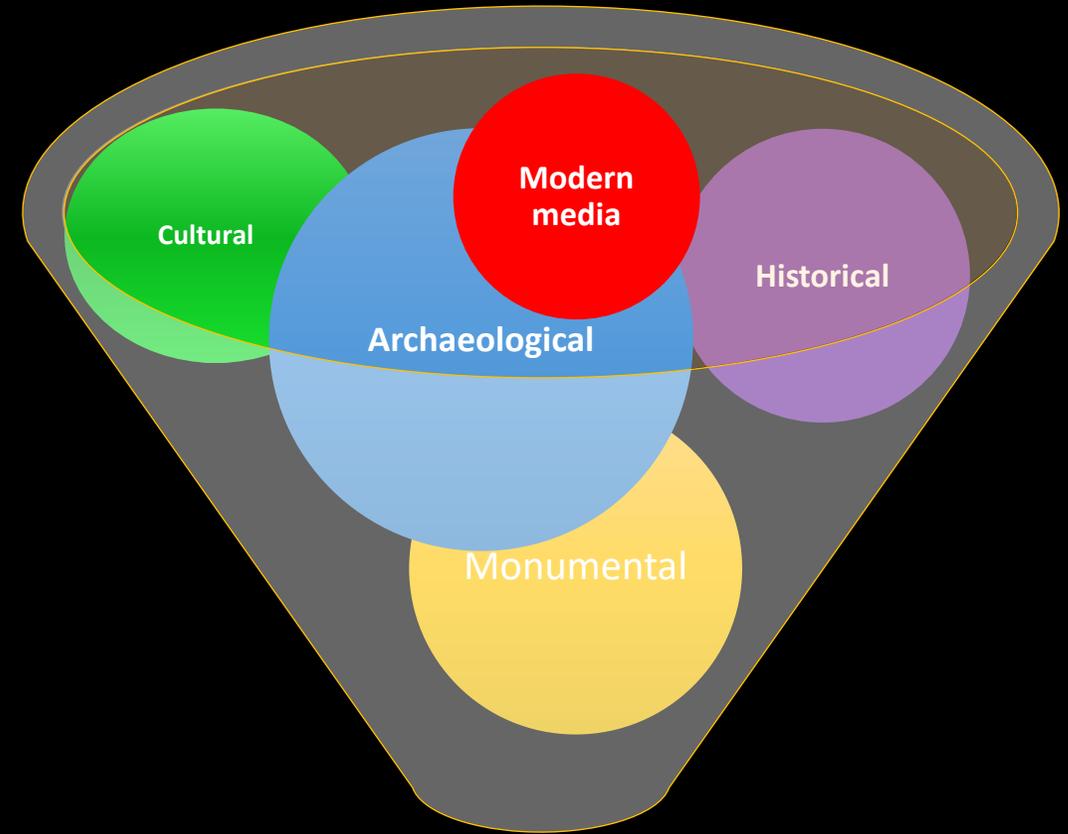
[radpour@udel.edu](mailto:radpour@udel.edu)

ELEG 404/604



# I. *Illuminating* Heritage <sup>1</sup>

- Understanding the artist's intent
  - The workshops in operation
    - Materials acquisition and trade
    - Knowledge transfer and mobility
- Connecting imagery to societal context
  - Understanding of the natural world (i.e. behavior of light / optics)



# I. *Illuminating Heritage* <sup>2</sup>

- Documentation and investigation
  - provides a history of the object
  - record new conservation interventions on the object
- Physical and chemical stability
  - diagnostics to inform condition
- New visualizations, i.e. accurate digital reconstructions (2D and 3D)

# I. Illuminating Heritage <sup>2</sup>

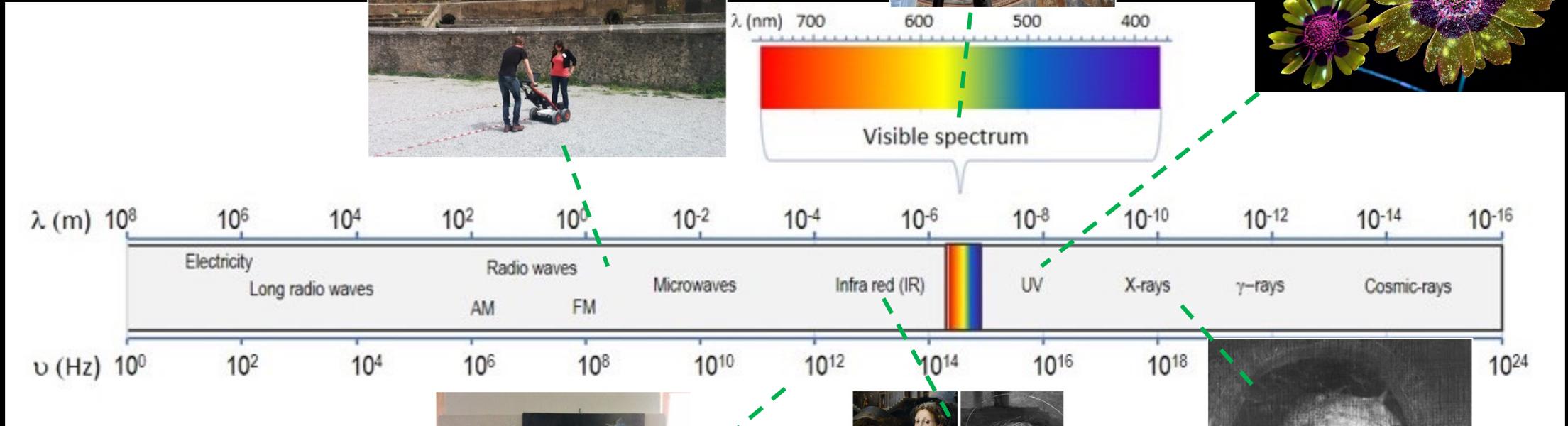
Ground Penetrating Radar (GPR)



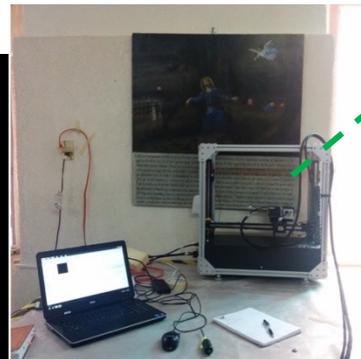
Reflectance imaging spectroscopy (RIS)



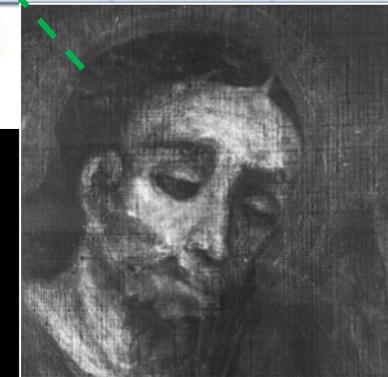
UV-induced visible fluorescence



Terahertz (THz) Time-Domain Imaging



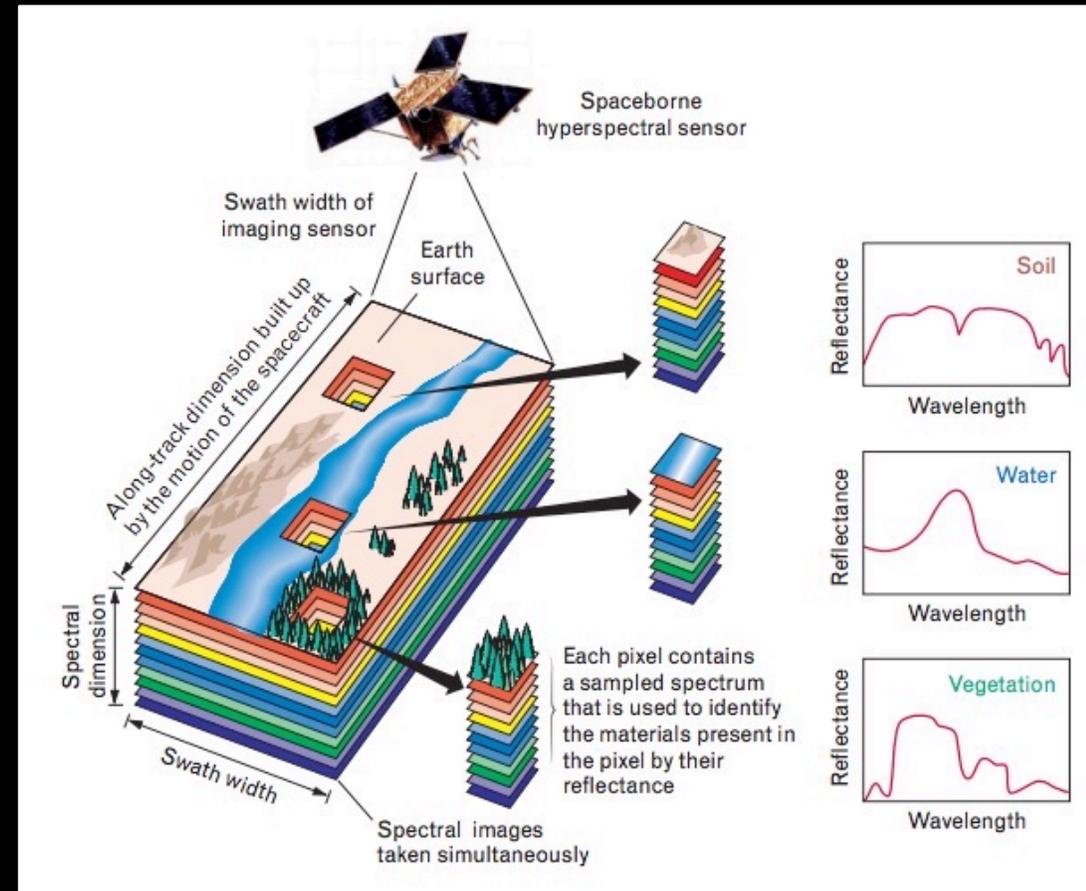
Infrared reflectography (IRR)



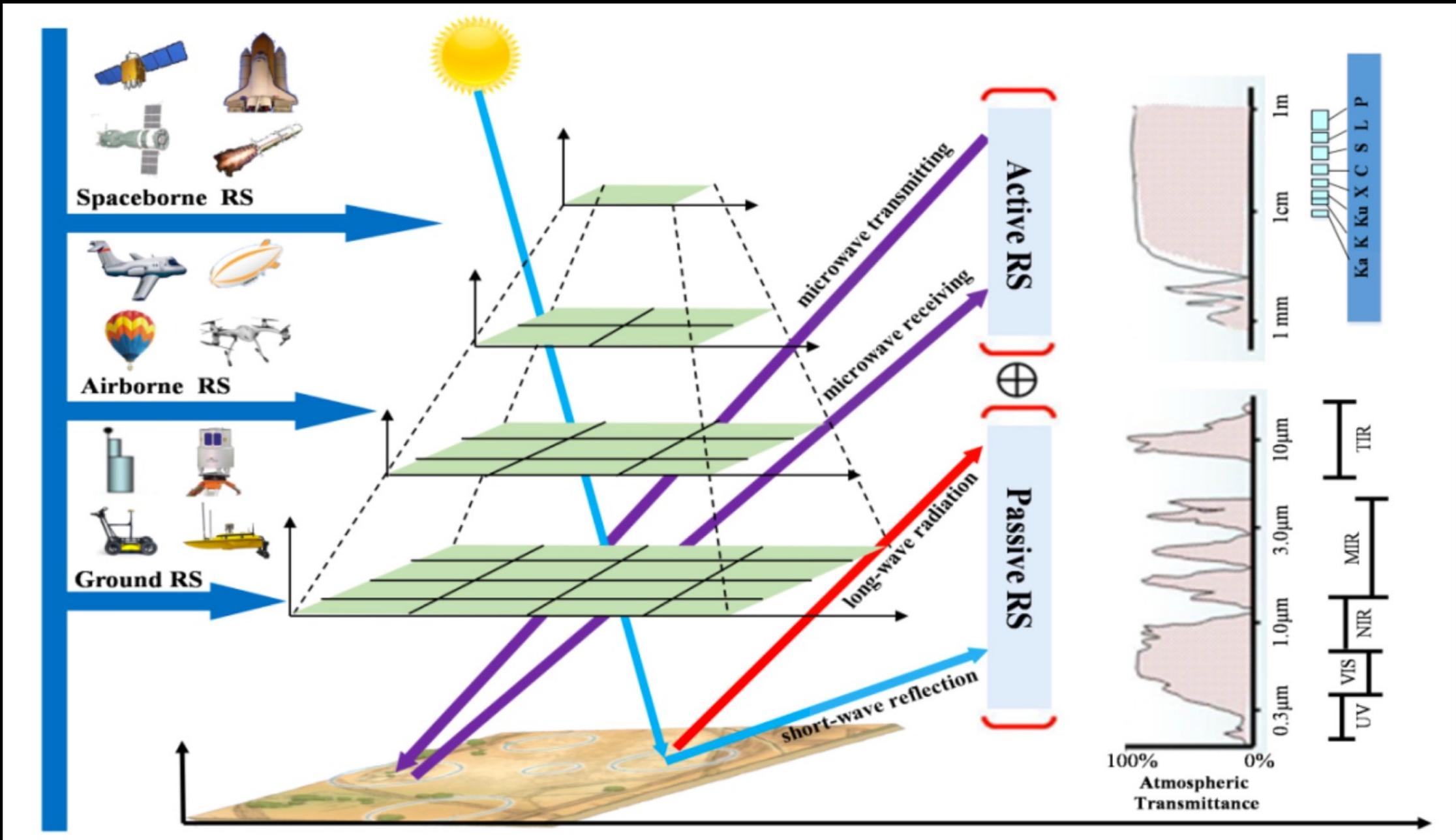
X-ray Radiography

# History of Remote Sensing (origin of HSI/MSI)

- Mid 19<sup>th</sup> century – first aerial photography
- 1960s – multi- and hyperspectral imaging spectrometers began dominating space and airborne land surveys
- Jet Propulsion Laboratory's (JPL) AVIRIS (Airborne Visual Infrared Imaging Spectrometer) revolutionized HSI applications in remote sensing (1984)



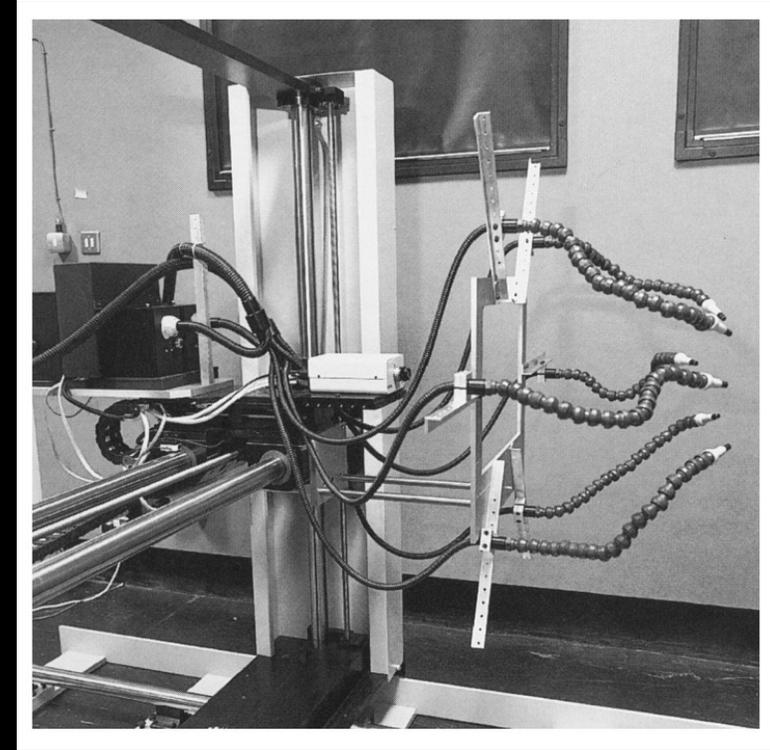
Gary A Shaw and Hsiao-Hua K Burke. Spectral imaging for remote sensing. Lincoln Laboratory Journal, 14(1):3–28, 2003



# Introducing spectral imaging in cultural heritage and conservation

1) The objective to acquire color accurate images of paintings with high resolution details

→ documentation

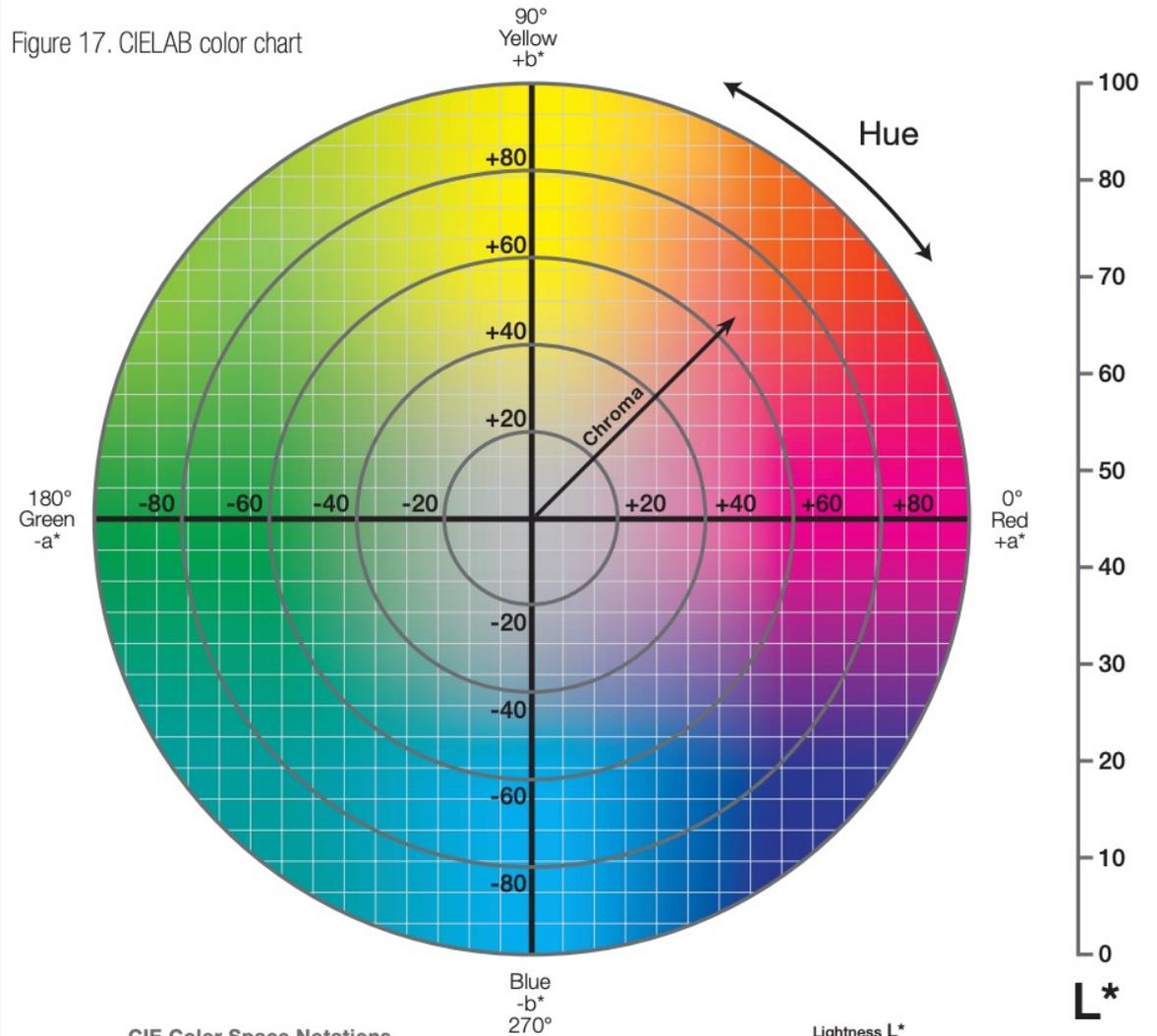


2<sup>nd</sup> generation camera of the VASARI project  
The National Gallery, London

# Accurate color information

- “A system of colorimetry is basically a ‘language’ with which an observer may describe a color unambiguously and uniquely to distinguish it from all others.”
  - [https://www.getty.edu/conservation/publications\\_resources/pdf\\_publications/pdf/color\\_science.pdf](https://www.getty.edu/conservation/publications_resources/pdf_publications/pdf/color_science.pdf)
- CIE systems
  - CIE 1976  $L^*a^*b^*$
  - [https://www.xrite.com/-/media/xrite/files/whitepaper\\_pdfs/I10-001\\_a\\_guide\\_to\\_understanding\\_color\\_communication/I10-001\\_understand\\_color\\_en.pdf](https://www.xrite.com/-/media/xrite/files/whitepaper_pdfs/I10-001_a_guide_to_understanding_color_communication/I10-001_understand_color_en.pdf)

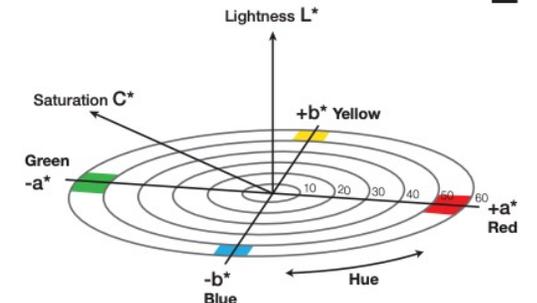
Figure 17. CIELAB color chart



## CIE Color Space Notations

- $\Delta L^*$  - difference in lightness/darkness value "+" = lighter "-" = darker
- $\Delta a^*$  - difference on red/green axis "+" = redder "-" = greener
- $\Delta b^*$  - difference on yellow/blue axis "+" = yellower "-" = bluer
- $\Delta C^*$  - difference in chroma "+" = brighter "-" = duller
- $\Delta H^*$  - difference in hue
- $\Delta E^*$  - total color difference value
- $\Delta E_{CMC}$  - total acceptable color difference value

$\Delta E_H$  1942 \*  $\Delta E_{ab}$  1976 \*  $\Delta E_{CMC}$  1984 \*  $\Delta E_{94}$  1992 \*  $\Delta E_{00}$  2000



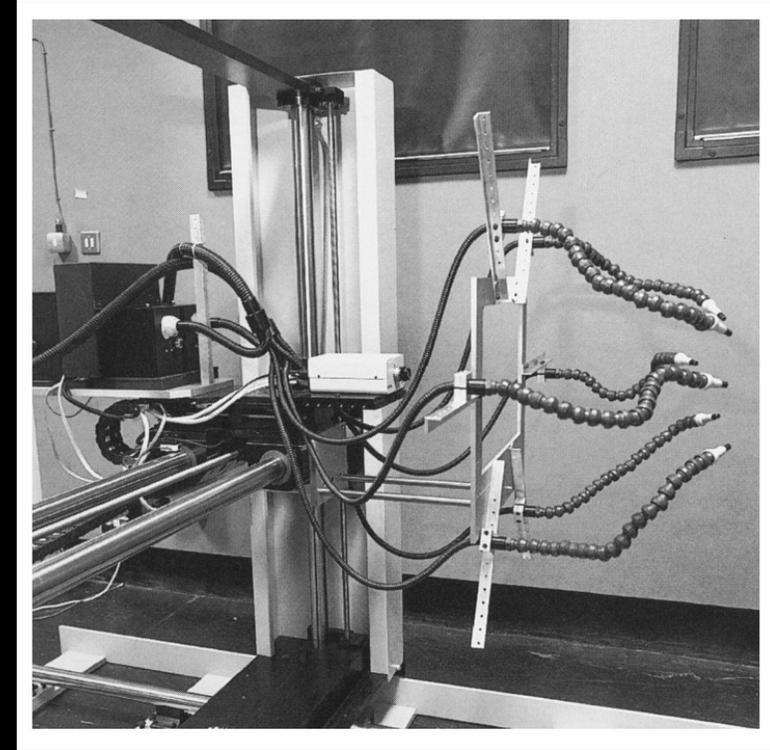
# Introducing spectral imaging in cultural heritage and conservation

1) The objective to acquire color accurate images of paintings with high resolution details

→ unbiased, accurate documentation

2) Exploration of image processing methods to extract new painting details through false color analysis (RGB photography, infrared reflectography, and X-ray radiography)

→ statistical analyses to discriminate between materials and identify differences between images



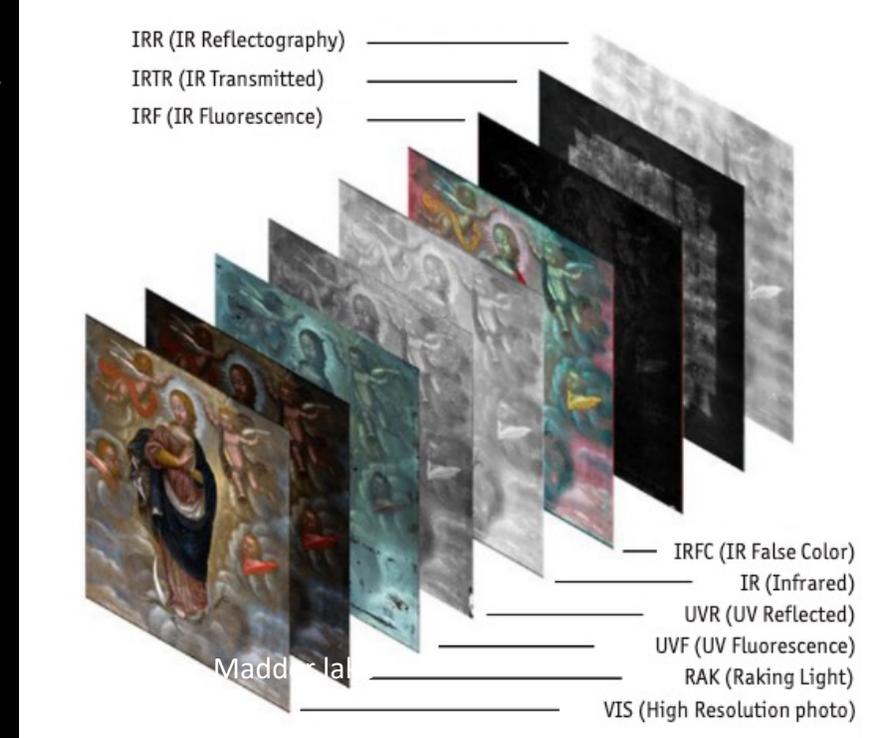
2<sup>nd</sup> generation camera of the VASARI project, The National Gallery, London (high resolution monochrome digital camera with filters)

Cosentino, Antonino. "A practical guide to panoramic multispectral imaging." *e-conservation Magazine* 25 (2013): 64-73.

# Terminology



- **Multiband imaging:** images captured in broad, wavelength bands using filters in front of a modified or monochrome camera
- **Multispectral imaging spectroscopy:** Spectral bands are broad (tens of nm) and few. Here, images are measured with respect to reference reflectance standards. Spectral signature is comprised of discrete points and non-contiguous
- **Imaging spectroscopy (IS):** image collection technique where hundreds of images are collected in narrow spectral bands, producing contiguous spectral profiles in each spatial pixel of the image scene.

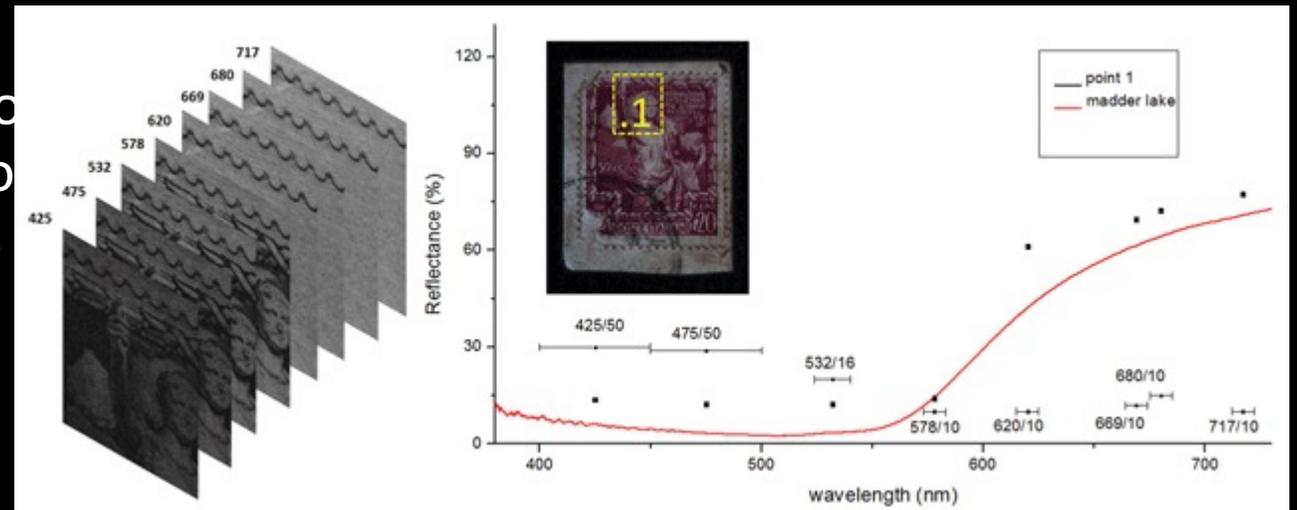
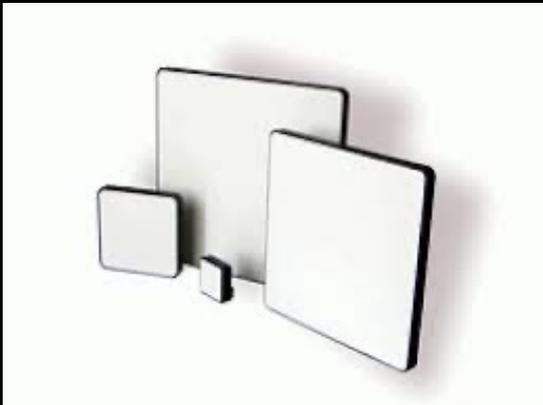
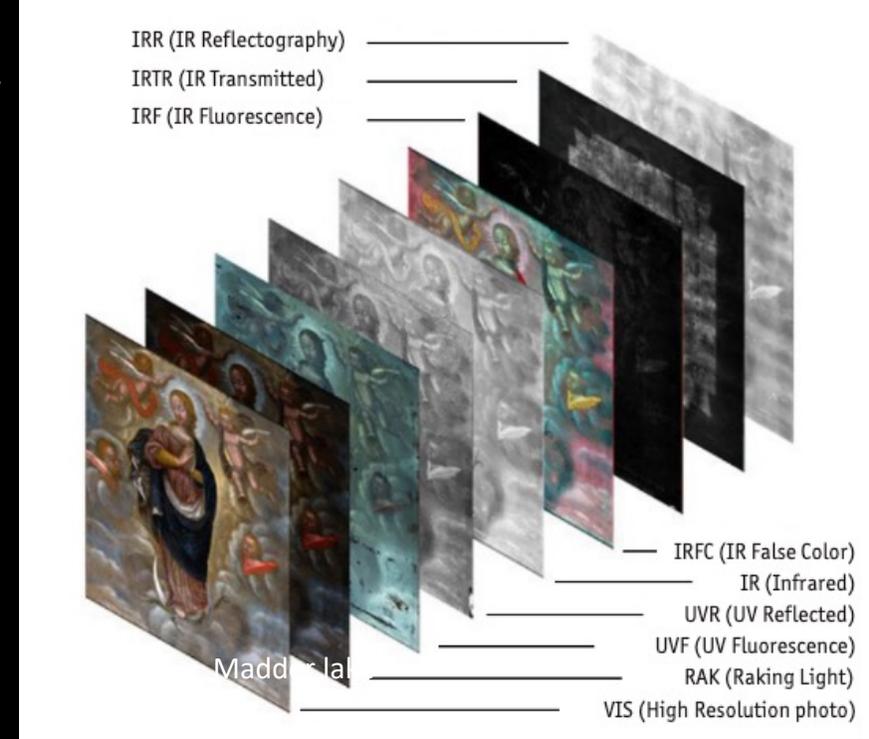


Cosentino, Antonino. "A practical guide to panoramic multispectral imaging." *e-conservation Magazine* 25 (2013): 64-73.

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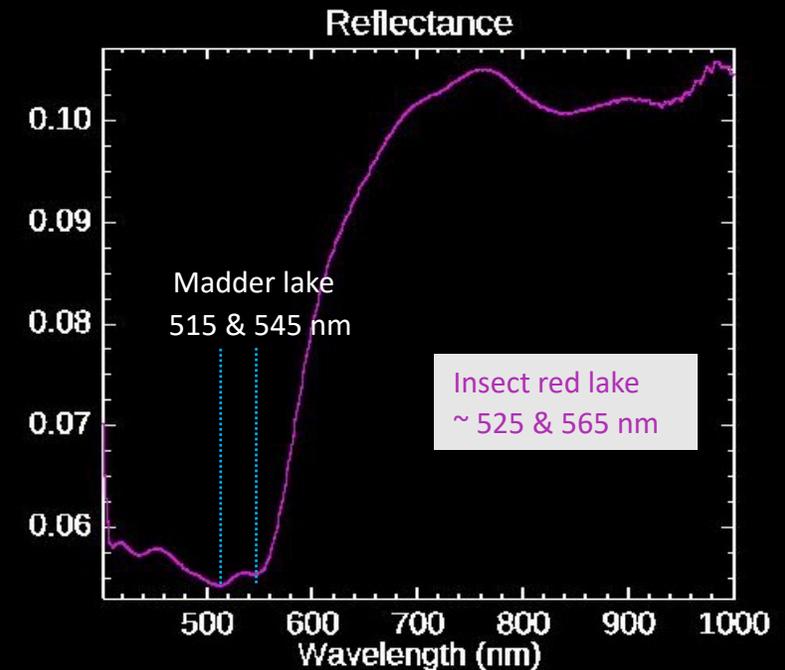


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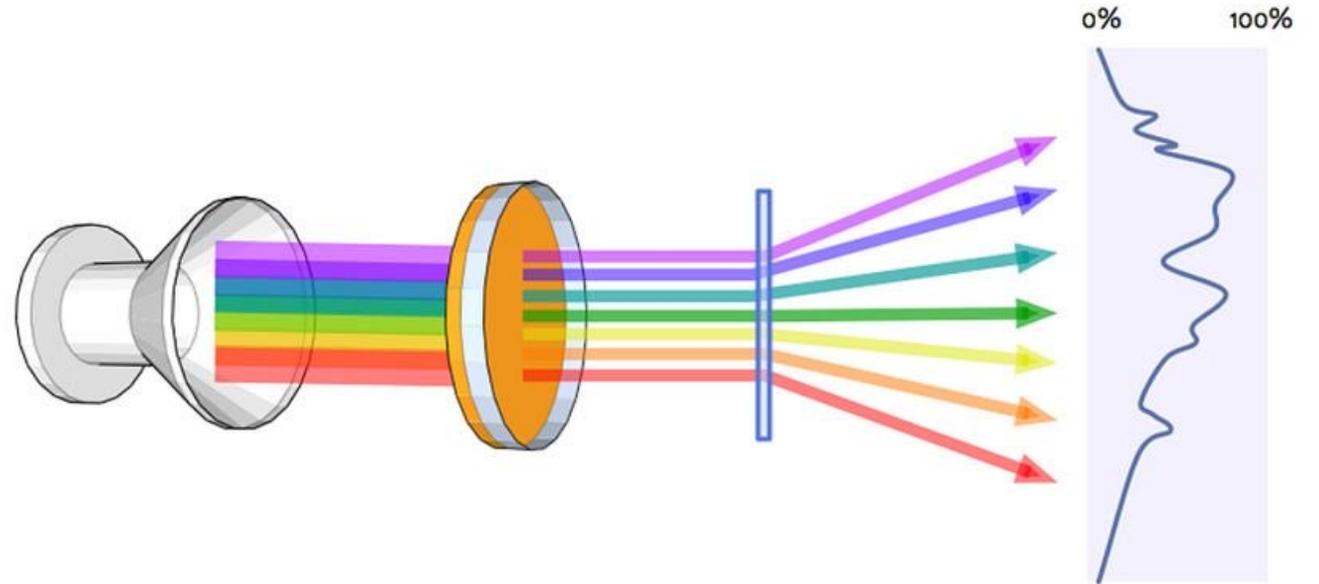
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- **Imaging spectroscopy (IS)**: image collection technique where hundreds of images are collected in narrow spectral bands, producing contiguous spectral profiles in each spatial pixel of the image scene.



# Imaging spectroscopy: the system

## Multiple band spectral and spatial data acquisition



1. A broad-spectrum light (halogen, incandescent) is shone through a sample

2. Some colors are absorbed more than others depending on its composition

3. Diffraction grating splits light into colors so they can be measured separately

**Table 1** Characteristics of multispectral and hyperspectral imaging systems used in conservation

<i>References</i>	<i>Detectors</i>	<i>Spectral range (nm)</i>	<i>Dispersing device / number of filters or bands</i>	<i>Applications</i>
50	Vidicon PbO-PbS	400–1000	Broadband filters	Paintings
12	CCD	400–2500	Optical filters	IR reflectography
51	Vidicon PbO-PbS PtSi Ge			
24, 52	Vidicon PbO-PbS	400–1600	Optical filters / 29	Paintings, pigments
53, 54	CCD	400–1000	Optical filters / 62, 14 LCTF / 15–20 bands	Rock art, pigments, inscriptions
43	CCD	400–1700	PGP / 256 bands	Semi-precious stones
55–57	CCD	650–1040	LCTF / 40 bands	Paintings, pigments
36, 58–60	CCD	380–1000	Optical filters / 33	Paintings, palimpsests, manuscripts, marble
61, 62	CCD	400–700	LCTF / 31 bands	Paintings, colour reproduction, metamerism
63	CCD Vidicon PbO-PbS InGaAs HgCdTe	800–2500	Cut-off filters	IR reflectography
64	CCD	400–700	Broadband filters	Gems, metamerism
65	CCD PtSi	450–1600	Optical filters / 8 VNIR, 3 SWIR	Paintings, pigments
66	Vidicon PbO-PbS	400–2200	Optical filters / 29	Drawings
67, 68	CCD	400–700 450–1000	Broadband filters / 7 Broadband filters / 12	Paintings (conservation, documentation, archiving)
69, 70	CCD	400–1000	Broadband filters / 13	Paintings (conservation, documentation, archiving)
71	CCD	400–1000	Interference filters / 13	Paintings, pigment identification
72	CCD	400–1000	Optical filters / 5	Paintings
73	CCD	400–700	LCTF / 31 bands	Paintings, documentation
74	CCD	380–1100	Tuneable light source	Documents, inks

## VNIR (400-1000 nm) Image sensor types:

- EMCCD
- sCMOS
- CMOS
- CCD

<https://www.e-consystems.com/blog/camera/technology/the-ultimate-image-sensor-guide-emccd-vs-scmos-vs-cmos-vs-ccd/>

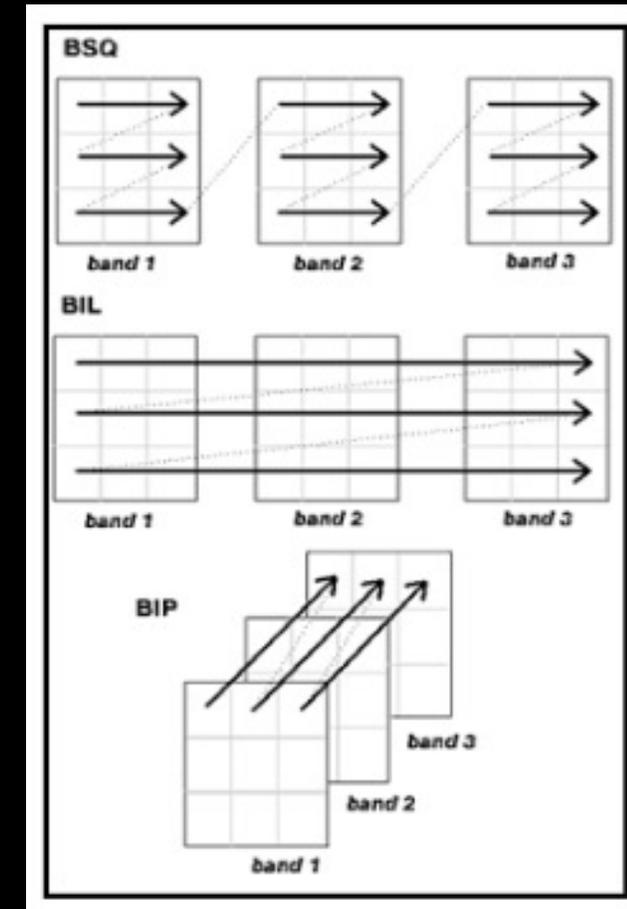
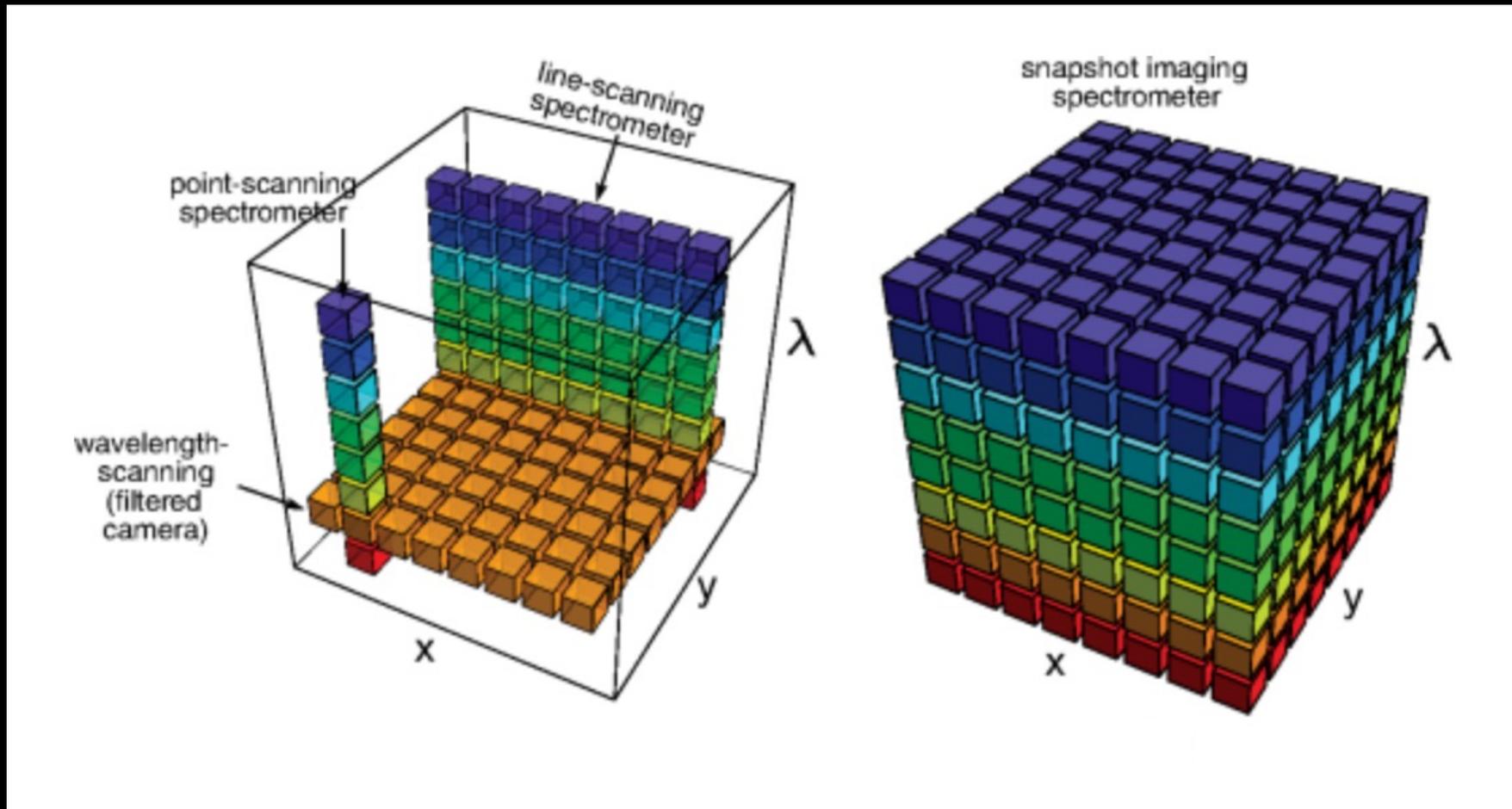
## SWIR (1000-2500 nm) Image sensor types:

- InGaAs
- Quantum dot
- Vidicon tubes (photoconductive layer)
- MCT

## Filters or dispersing components

Fischer, Christian, and Ioanna Kakoulli. "Multispectral and hyperspectral imaging technologies in conservation: current research and potential applications." *Studies in Conservation* 51.sup1 (2006): 3-16.

# Data collection and storage

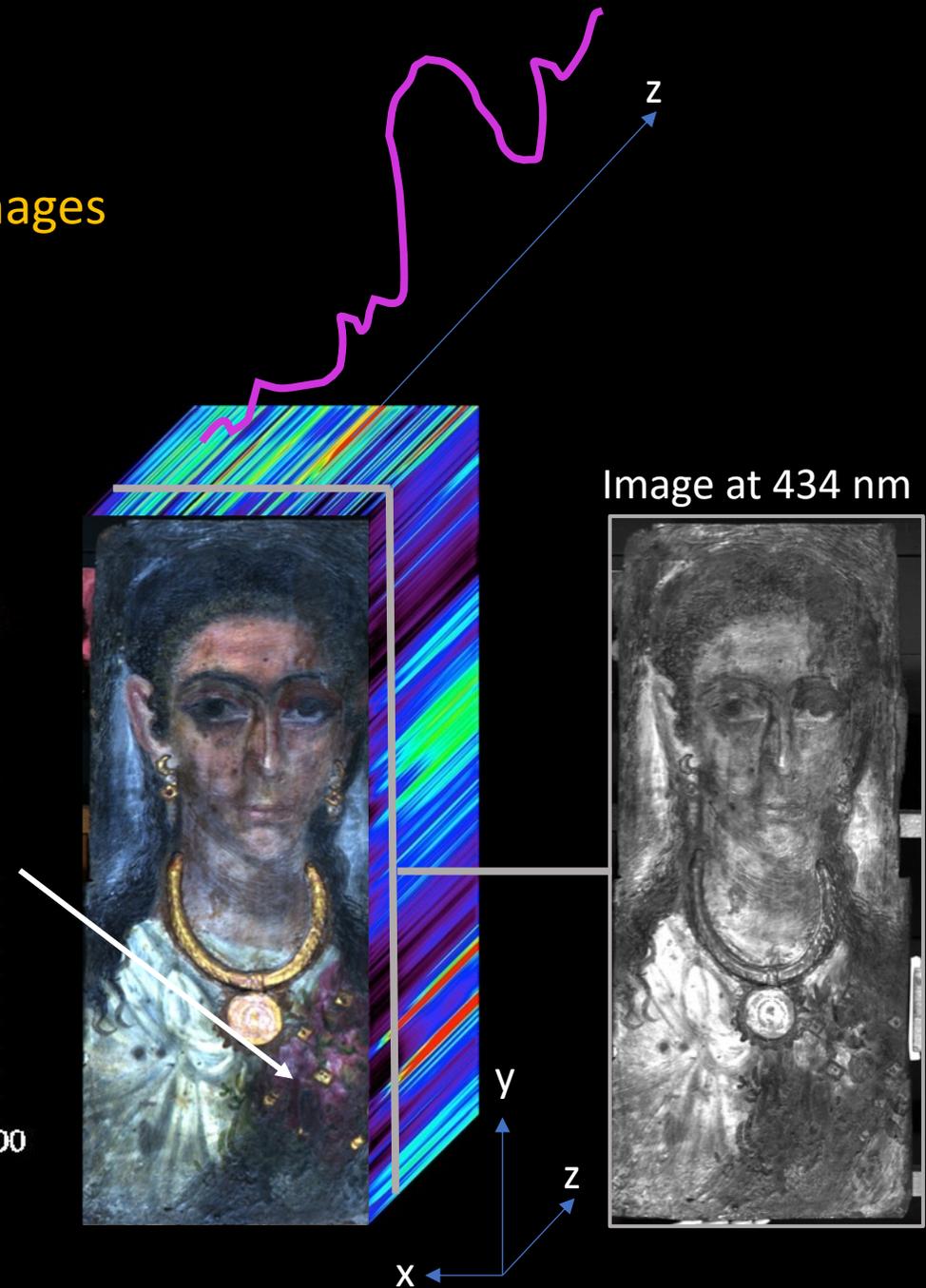
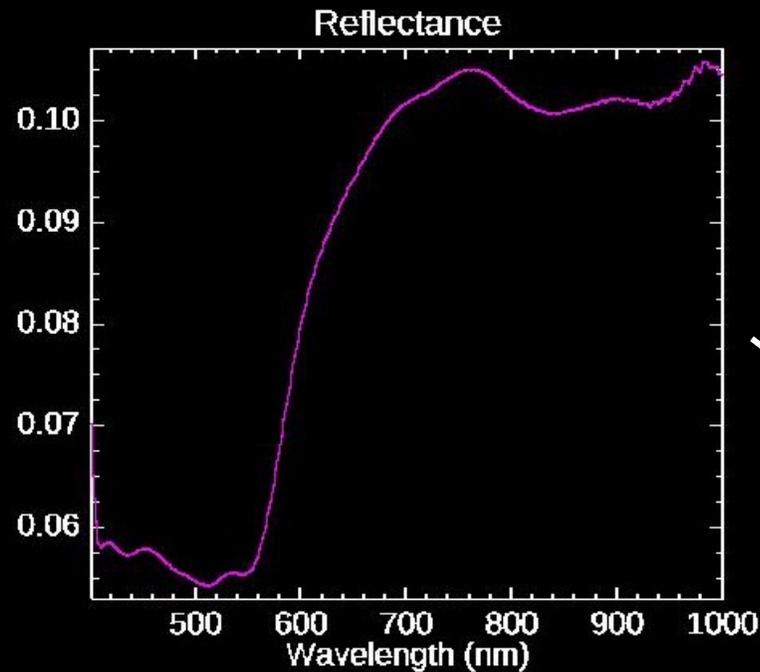


# Data Structure: 3D data cubes

Chemical data + images

Each pixel has a spectrum representing the interaction of light with the material at that point

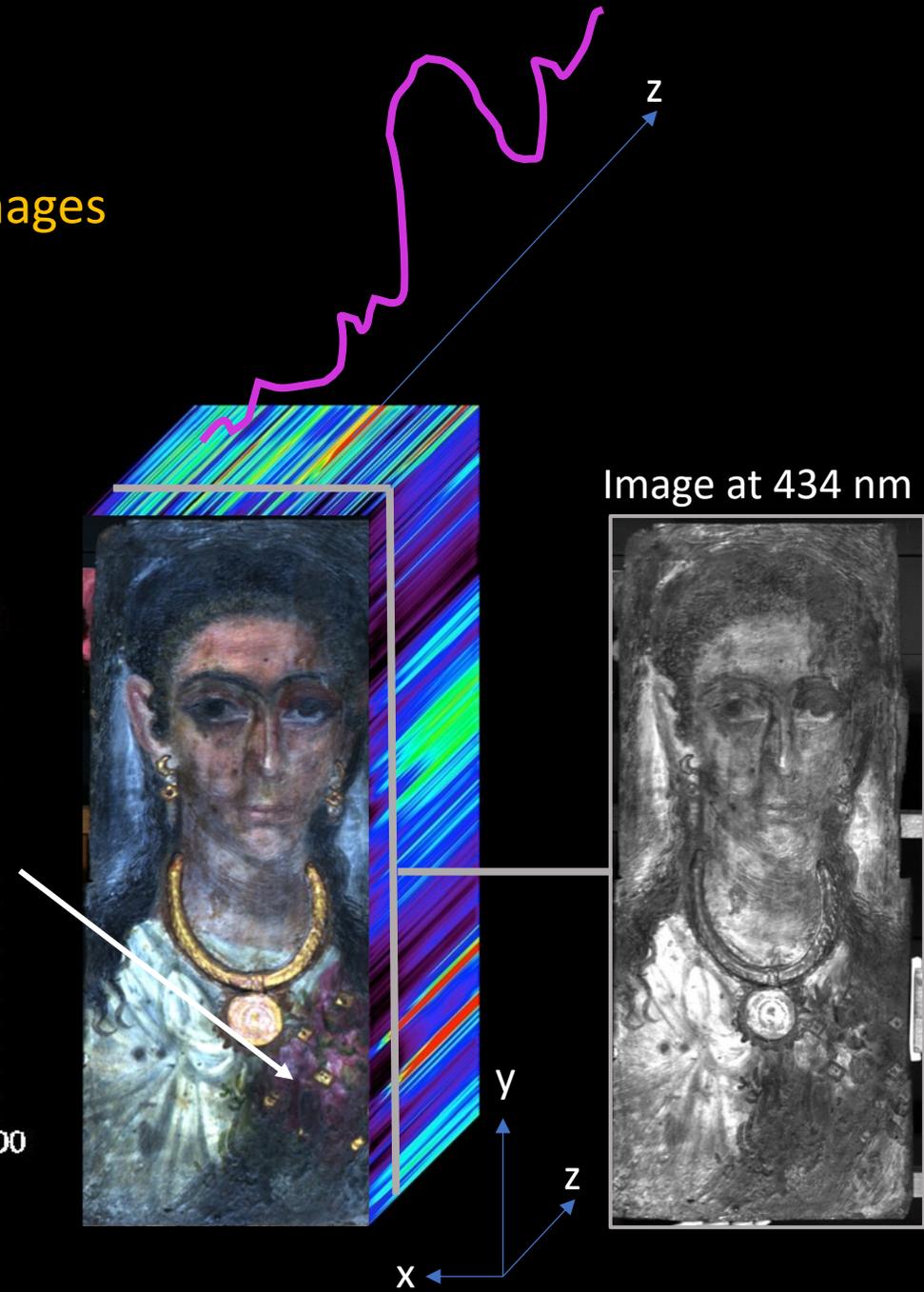
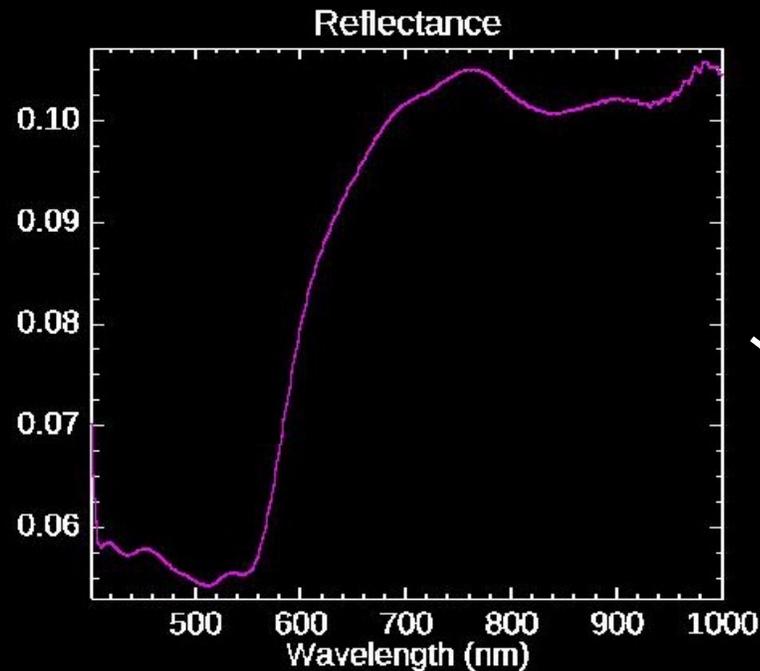
→ in reflectance mode, analysis follows principles of diffuse reflectance spectroscopy



# Data Structure: 3D data cubes

Chemical data + images

- Scanning (line scan or raster) produces an X-Y plane of pixels (spatial plane).
- The reflectance spectrum in each pixel forms the Z axis. This X-Y-Z structure produces **3D data cubes** of hyperspectral imaging data.
- → Images at a specific wavelength show how materials absorb/reflect at that wavelength.



# Imaging spectroscopy for analysis of paintings

Simultaneous spatial and chemical data collection  
→ hundreds of images + spectra

- Painting materials identification/characterization
  - Binders
  - Pigments
- Object condition and history
  - Degradation products
  - Alterations
  - Hidden depictions
- New object visualizations
  - Material maps
  - Color reconstructions
  - Revival of imagery

Delaney, John K., et al. "Macroscale multimodal imaging reveals ancient painting production technology and the vogue in Greco-Roman Egypt." *Scientific reports* 7.1 (2017): 1-12.

Binding media  
map of funerary  
portrait



Current condition of Van Gogh's *Field with Irises near Arles*

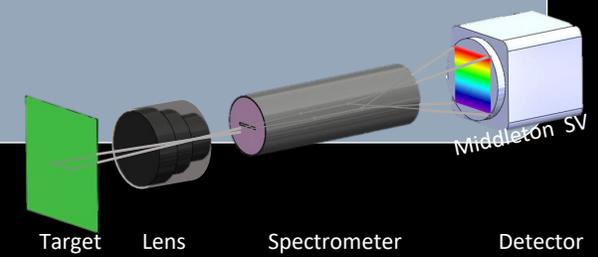
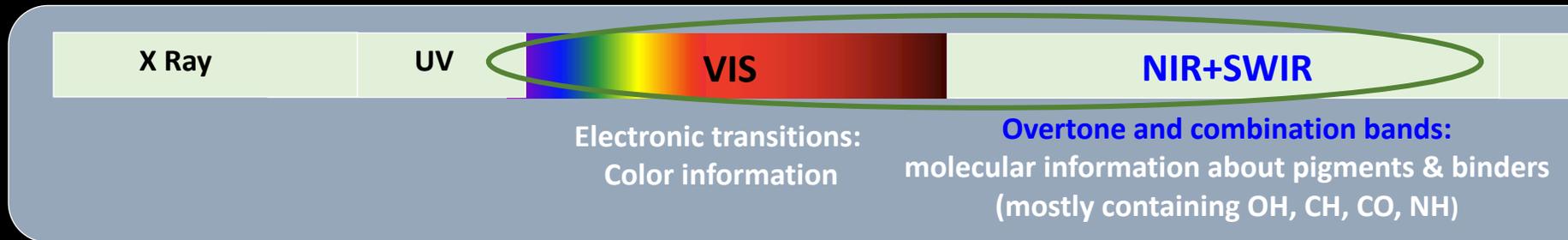
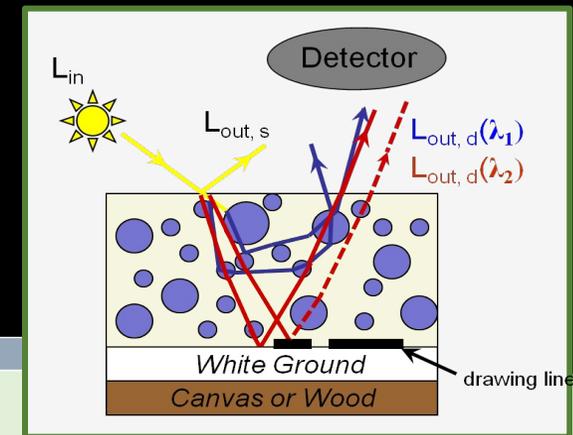


Digital reconstruction of Van Gogh's *Field with Irises near Arles*

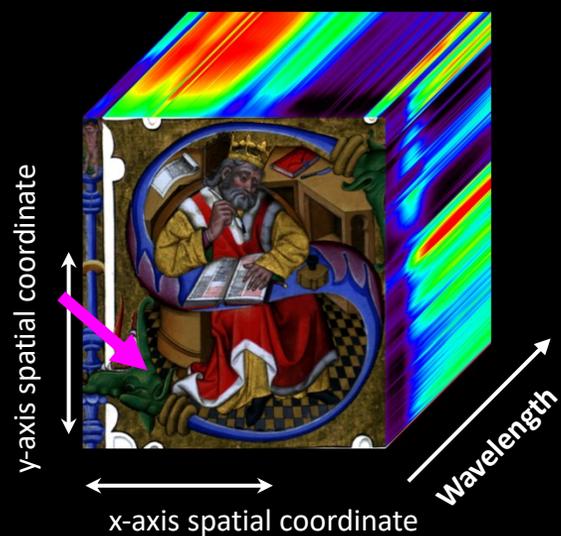
Kirchner, Eric, et al. "Digitally reconstructing Van Gogh's *Field with Irises near Arles* part 3: Determining the original colors." *Color Research & Application* 43.3 (2018): 311-327.

# Reflectance Imaging Spectroscopy (RIS)

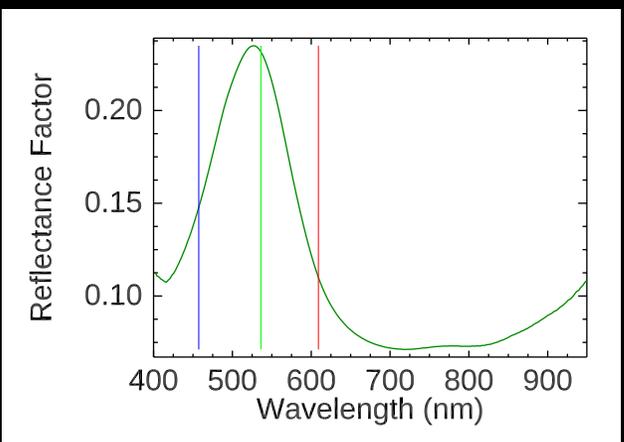
Diffuse reflectance spectroscopy (400 to 2500 nm) – *molecular information*



Example: Visible to Near-Infrared image cube  
400 - 950 nm (217 spectral bands)



Master of the Cypresses, "Initial S with King David as Scribe", 1964.8.1218  
Rosenwald Collection, NGA



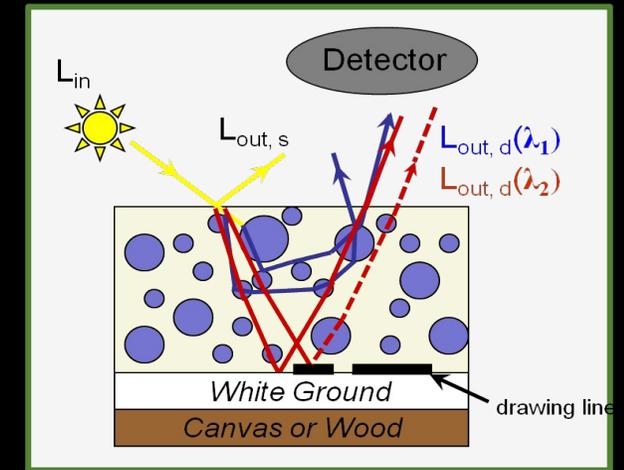
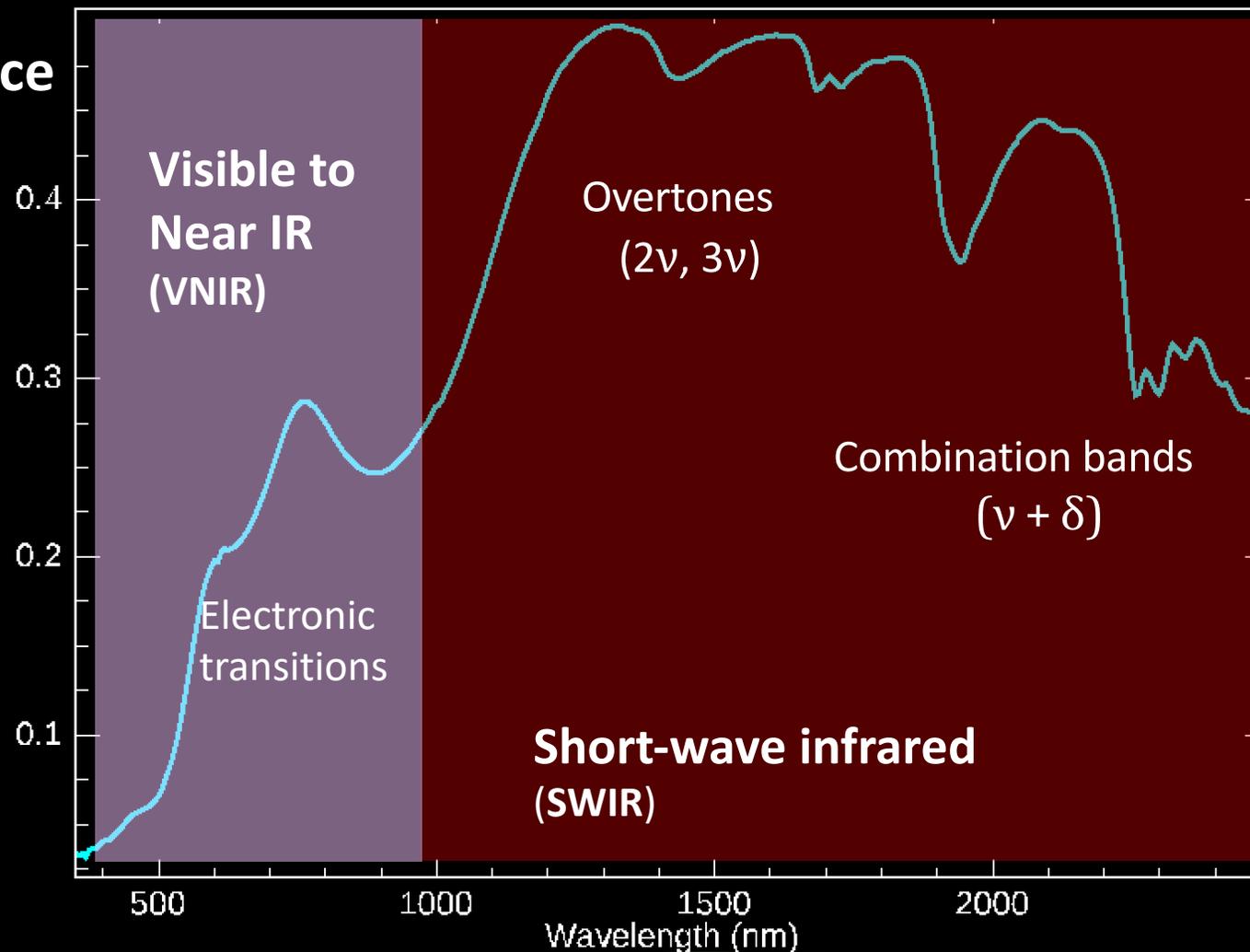
Find characteristic reflectance spectra (endmembers)

Map the spatial pixels with similar spectrum

*What materials make up characteristic reflectance spectrum?*

# Diffuse reflectance Spectroscopy

(400 to 2500 nm) *molecular information*



Stretching ( $\nu$ ) – change in length of a bond

Bending ( $\delta$ ) – change in angle between two bonds

X Ray

UV



VIS

NIR+SWIR

MID IR

Fundamental vibrations

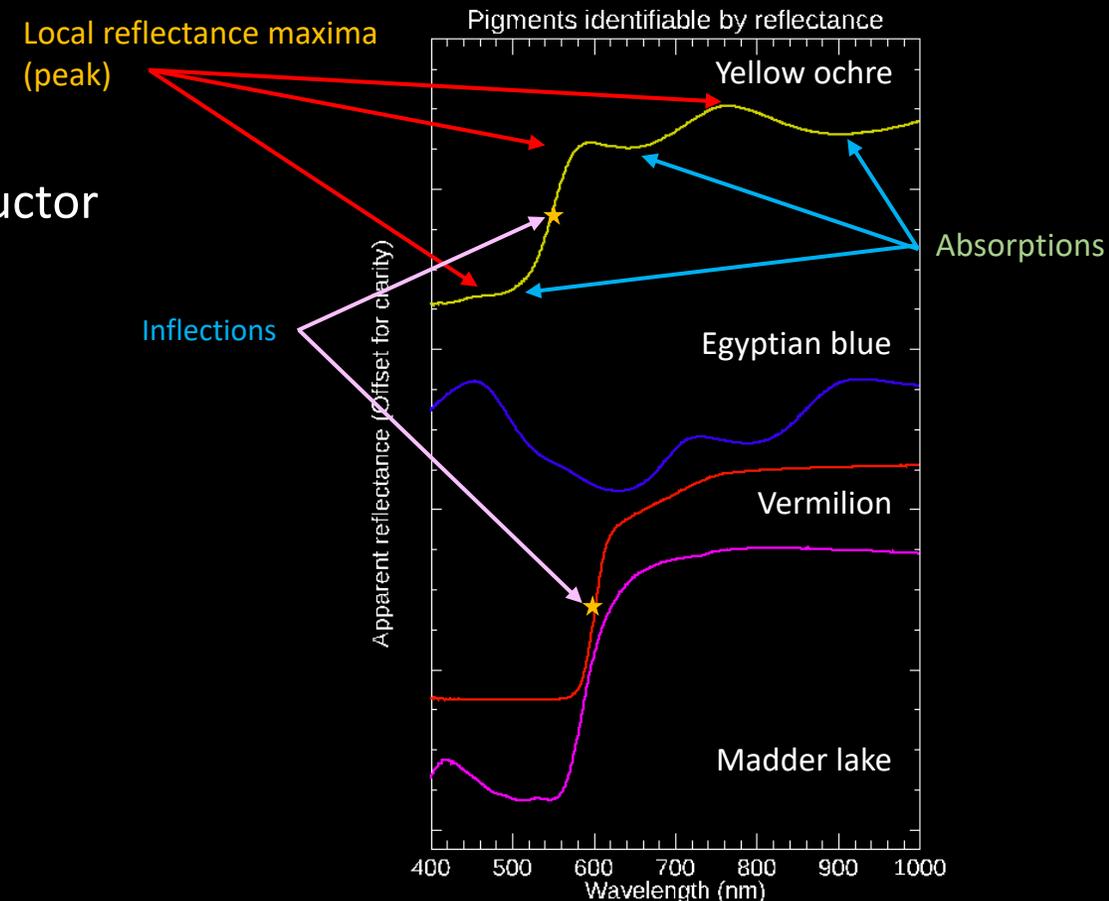
Electronic transitions:  
Color information

Overtone and combination bands:  
molecular information about pigments & binders  
(mostly containing OH, CH, CO, NH)

# Visible-to-near-infrared (VNIR, 400-1000 nm)

- Locations of peaks, absorptions, and inflections (which is a change in the slope of an increasing or decreasing curve) in the diffuse reflectance spectra correspond to electronic transitions

- Charge transfer (e.g. Fe ochres)
- d-d orbital transitions due to crystal field splitting
- Valence to conduction band transitions (semiconductor pigments)
- Delocalized molecular orbitals (lake pigments)



# Visible-to-near-infrared (VNIR, 400-1000 nm)

- Locations of peaks, absorptions, and inflections (which is a change in the slope of an increasing or decreasing curve) in the diffuse reflectance spectra correspond to electronic transitions
  - Charge transfer (e.g. Fe ochres)
  - d-d orbital transitions due to crystal field splitting
  - Valence to conduction band transitions (semiconductor pigments)
  - Delocalized molecular orbitals (lake pigments)

- Types of pigments reflectance spectroscopy can identify in the VNIR:

- Minerals
- Dye-based colorants (e.g. lakes)
- Semiconductor pigments
- Synthetic, inorganic/organic hybrid pigments

Madder lake



Cinnabar



Green earth



Malachite



Lapis Lazuli



Egyptian blue



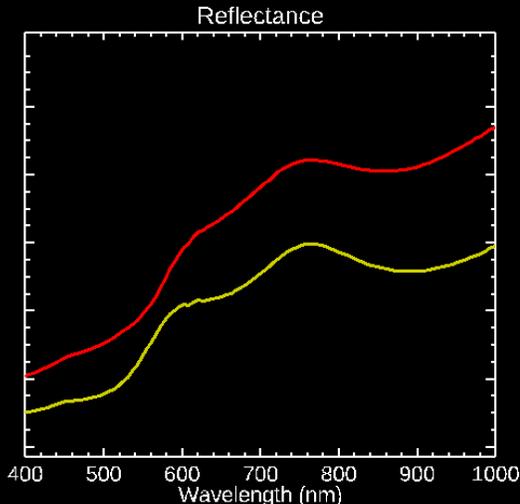
Red lead



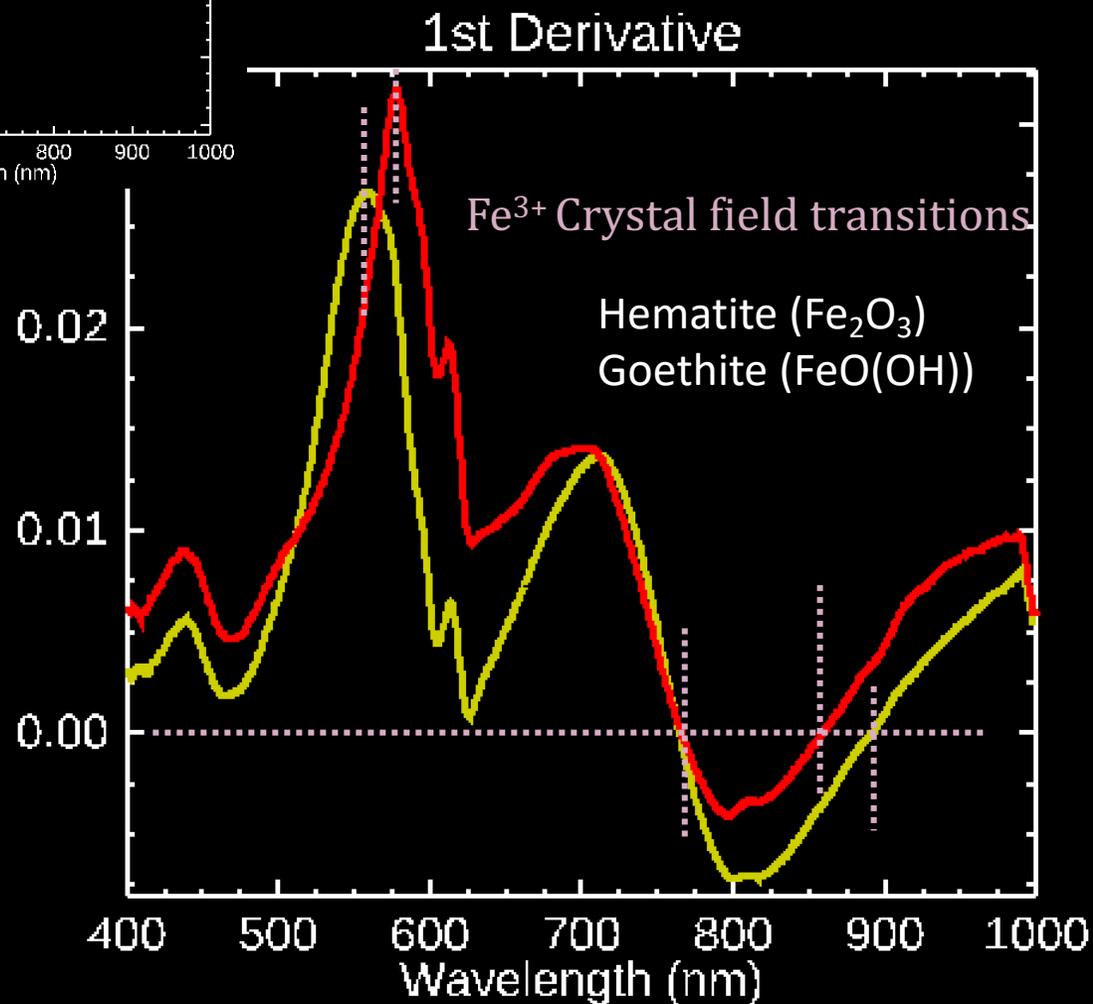
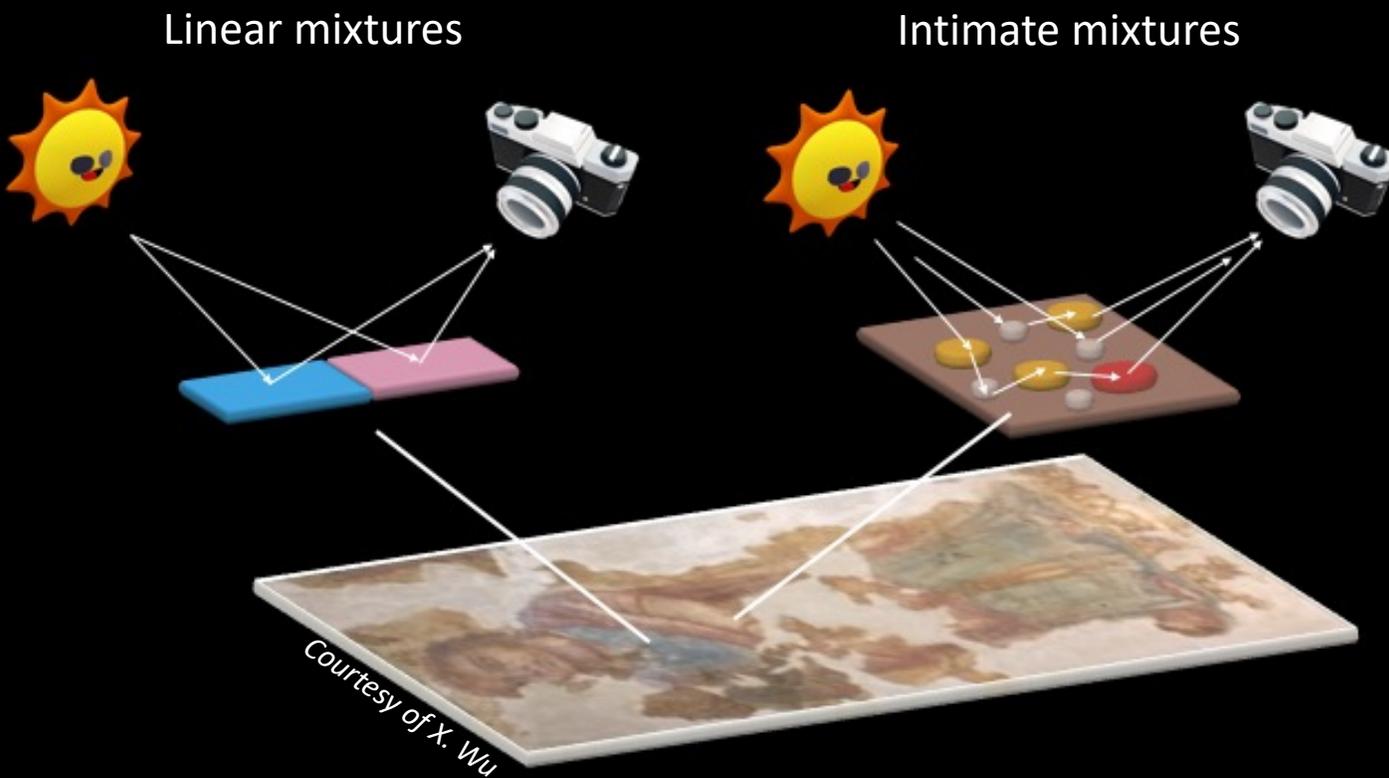
Ochres

# “Separation” of pigment mixtures

- Necessary to distinguish between similar yet different hues
- Mixed signals due to adjacent or layering of pigments



Derivative Spectroscopy ( $\frac{\partial R}{\partial \lambda}$ )  
→ extraction of unique endmembers with subtle differences in absorptions



# Reflectance Imaging Spectroscopy

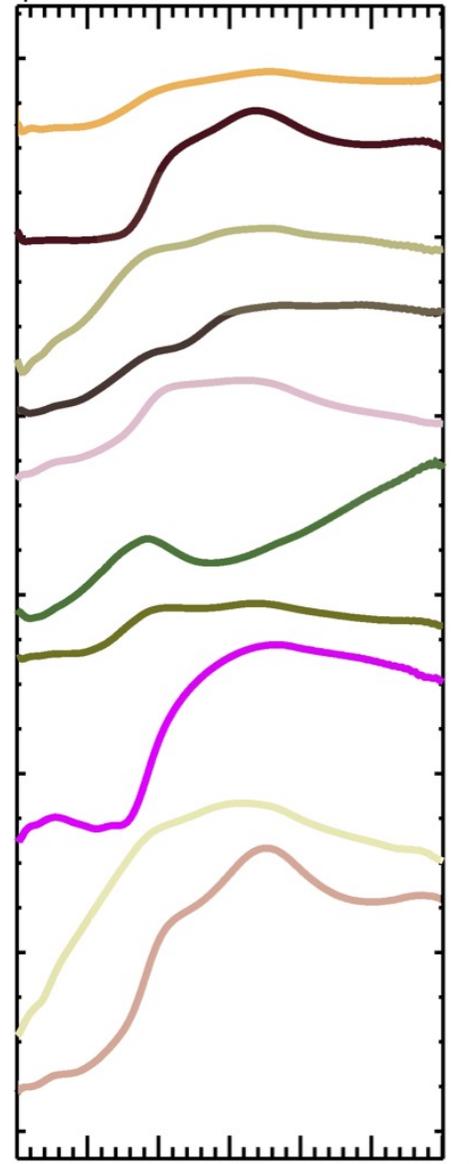
Portrait 32.4



Classification Map



Equivalent Reflectance Endmembers



Hematite (red ochre)  
-  $\text{Fe}_2\text{O}_3$

Lead white (cerussite)  
-  $\text{PbCO}_3$

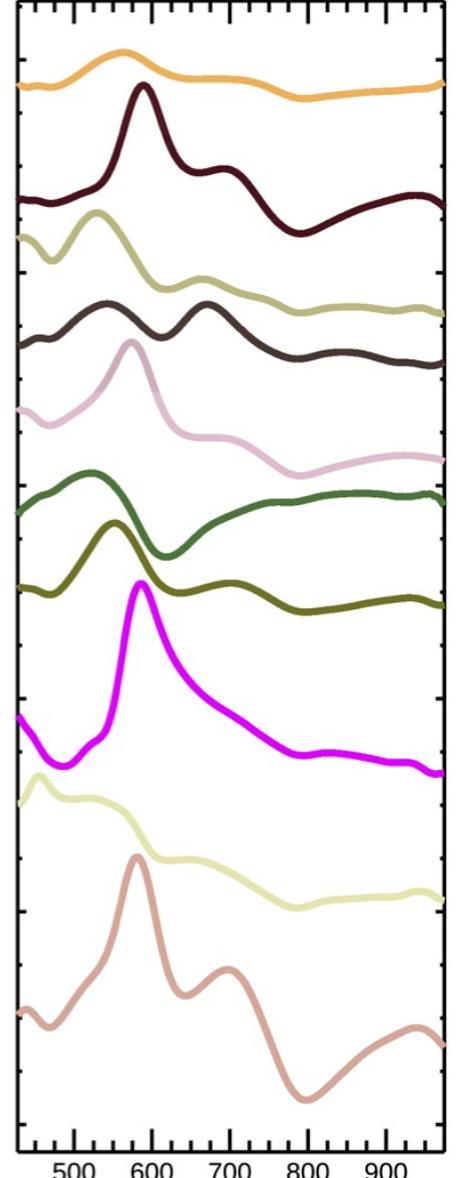
Copper carboxylate  
-  $\text{Cu}(\text{O}_2\text{CR})_2$

Madder lake  
- 1,2 & 1,2,4 HAQ  
(hydroxyanthraquinone)

Natrojarosite  
-  $\text{NaFe}^{3+}_3[(\text{SO}_4)_2(\text{OH})_6]$

Goethite (yellow ochre)  
-  $\text{FeO}(\text{OH})$

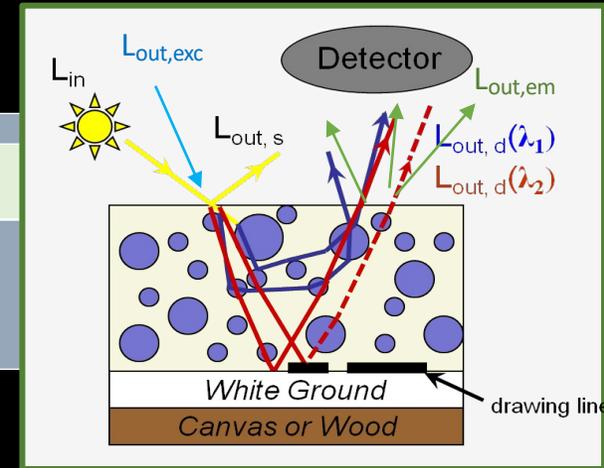
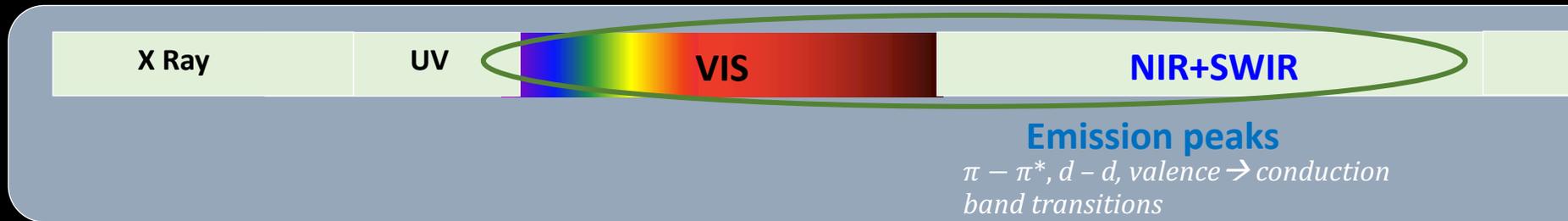
1st Derivative Endmembers



Radpour, Roxanne, et al. "Identification and mapping of ancient pigments in a Roman Egyptian funerary portrait by application of reflectance and luminescence imaging spectroscopy." *Heritage Science* 10.1 (2022): 1-16.

# Luminescence Imaging Spectroscopy

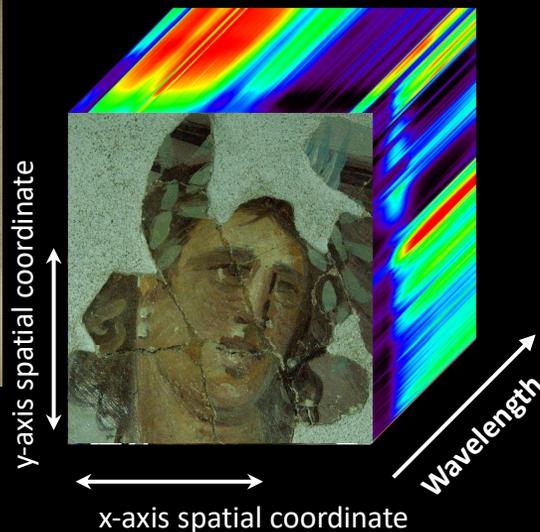
Fluorescence Spectroscopy (400 to 1000 nm) – *molecular information*



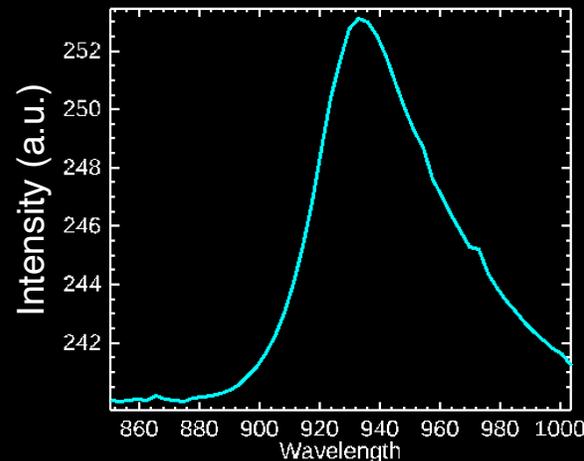
Example: Visible to Near-Infrared image cube  
 400 - 1000 nm (200 spectral bands)



Figurative painting from the House of Aion, Paphos, Cyprus (1<sup>st</sup> – 4<sup>th</sup> C AD)



Peak emission ~ 930 nm



Find characteristic reflectance spectra (endmembers)

Map the spatial pixels with similar spectrum!

*What materials exhibit this characteristic emission?*

Radpour, Roxanne. *Advanced imaging spectroscopy and chemical sensing in archaeometry and archaeological forensics*. University of California, Los Angeles, 2019.

# Luminescent ancient pigments

## Madder lake

(1,2 and 1,2,4 hydroxyanthraquinone (HAQ))

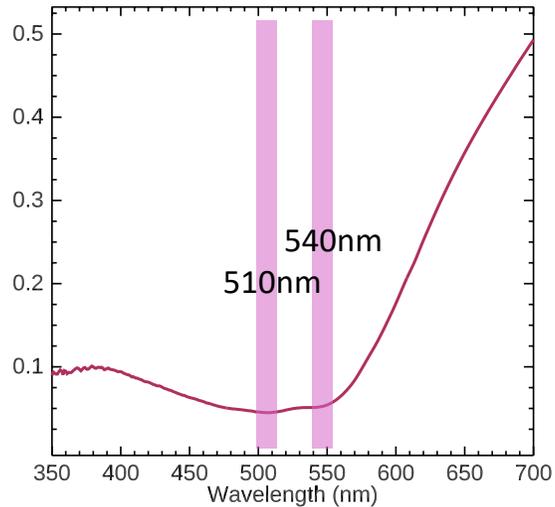
RGB (400 - 700 nm)



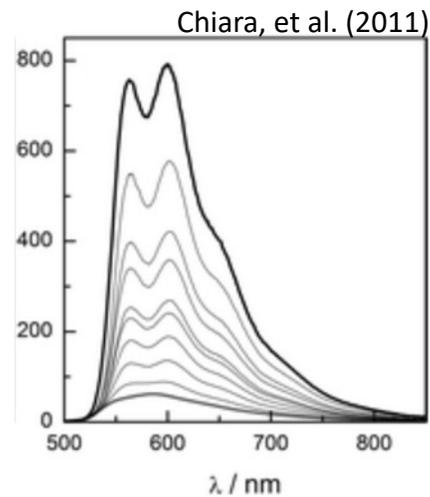
$\lambda_{ex\ max} = 515\ nm$   
 $\lambda_{em}: 580-700\ nm$

“Visible-induced visible”

Reflectance



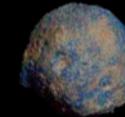
Photoluminescence



## Egyptian blue

( $CaCuSi_4O_{10}$ )

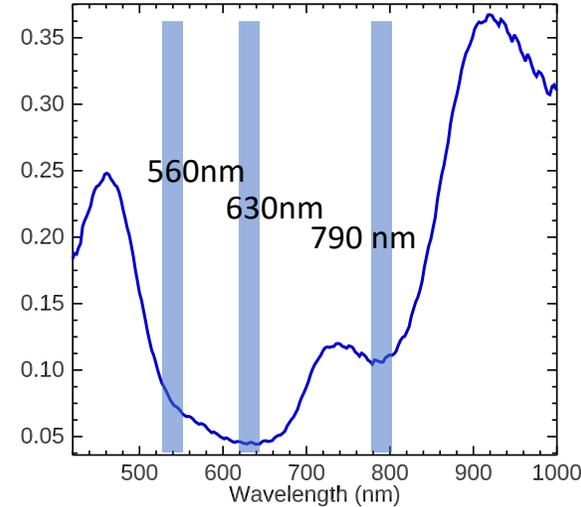
RGB (400 - 700 nm)



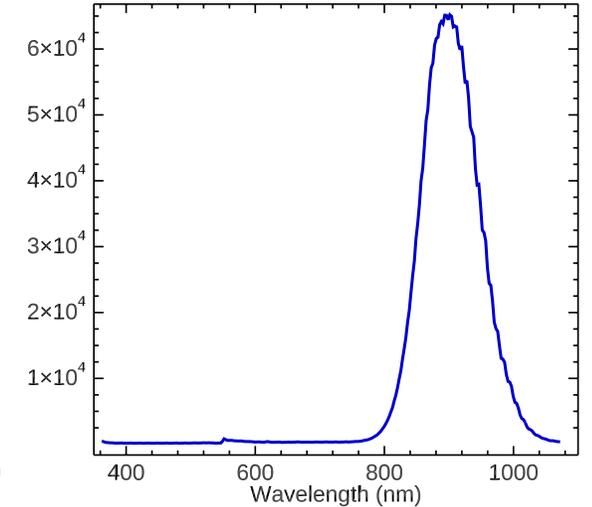
$\lambda_{ex, max} = 600\ nm$   
 $\lambda_{em}: 900-1000\ nm$

“Visible-induced near-IR”

Reflectance



Photoluminescence

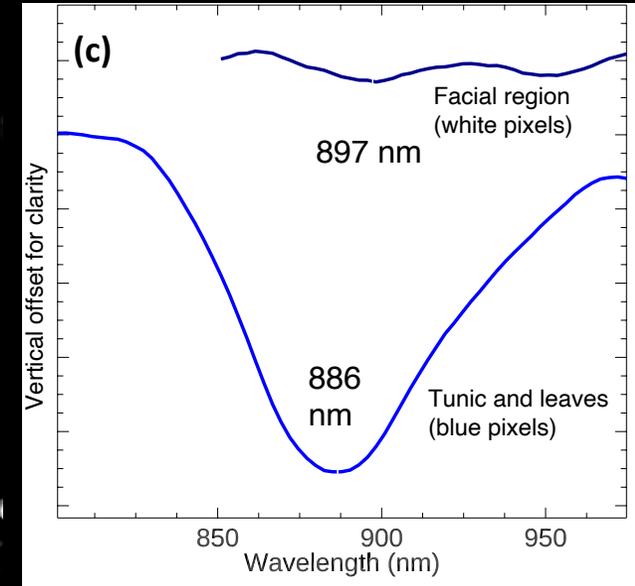
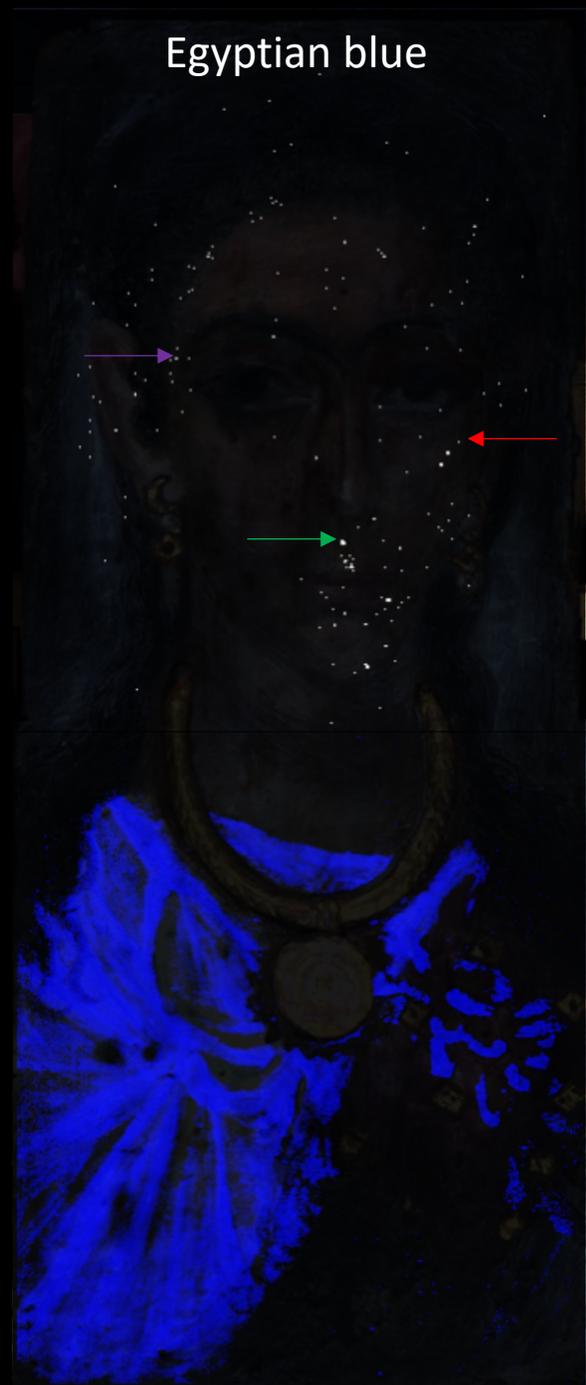
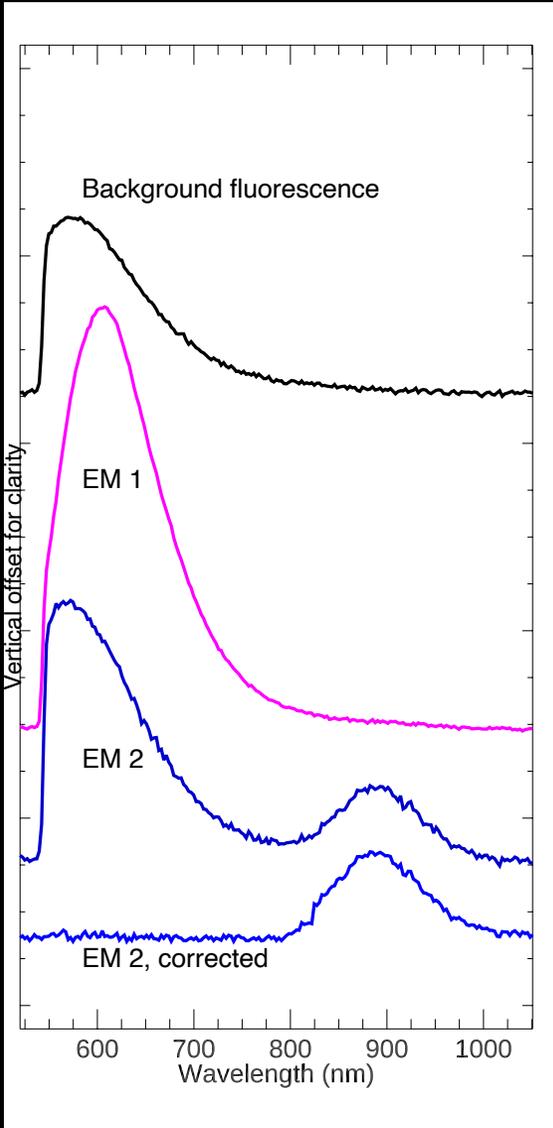


LIS endmembers  
→ linearly unmixed

Madder lake

Egyptian blue

2<sup>nd</sup> derivative  
LIS endmembers

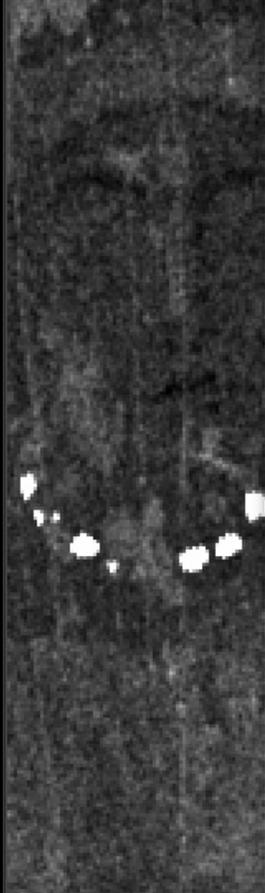
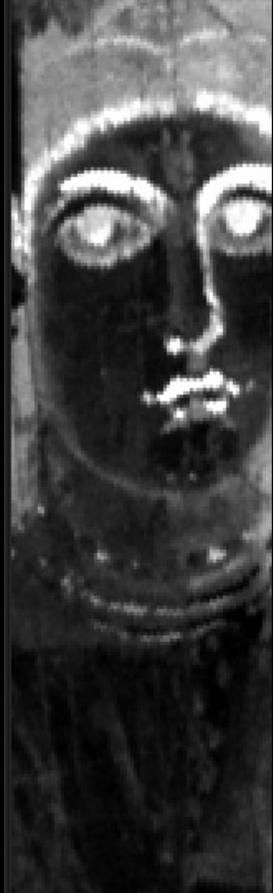
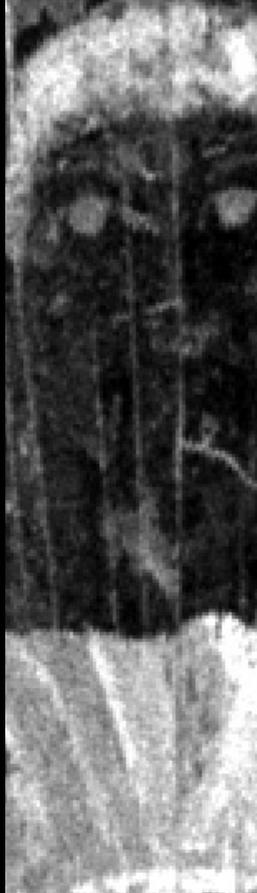


# Multi-modal imaging spectroscopy to reveal ancient painting production

Macroscale Scanning XRF (MA-XRF)

RIS

LIS

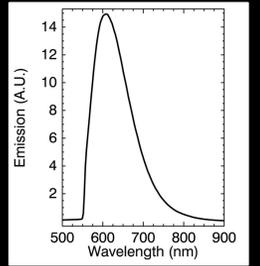
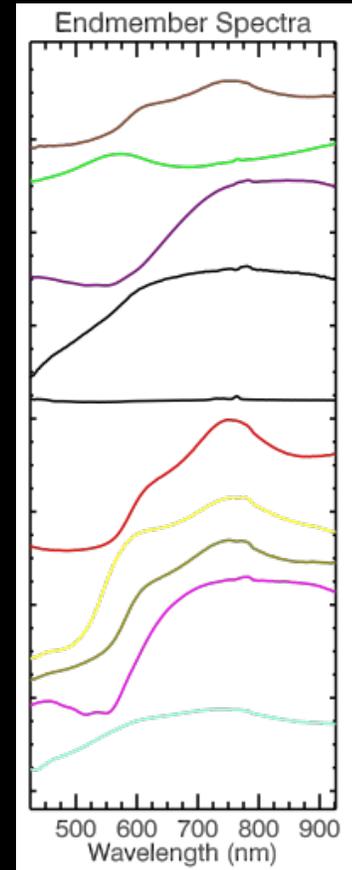


Ca

Fe

Cu

Pb



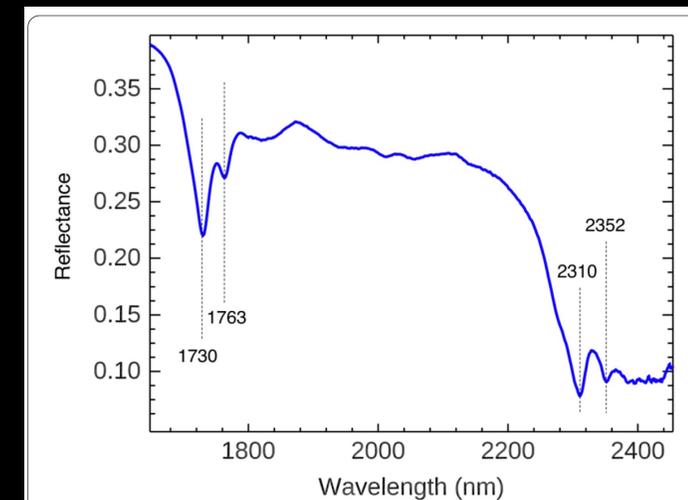
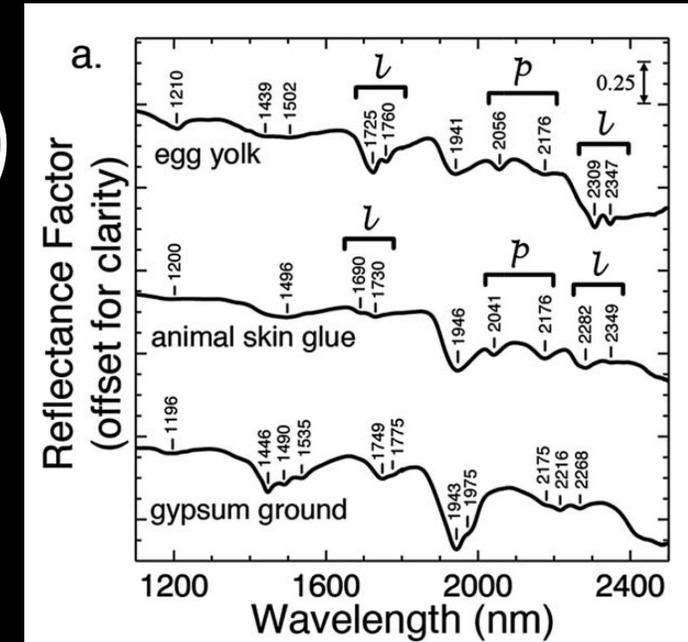
Delaney, J. K., Dooley, K. A., Radpour, R., & Kakoulli, I. (2017). Macroscale multimodal imaging reveals ancient painting production technology and the vogue in Greco-Roman Egypt. *Scientific reports*, 7(1), 15509.

# Short-Wave Infrared (1000 – 2500 nm)

- Pigments with unique SWIR signatures – e.g. azurite, malachite, green earths, cobalt-based pigments, lead white
- Binding media – e.g. tempera, animal skin glue, wax

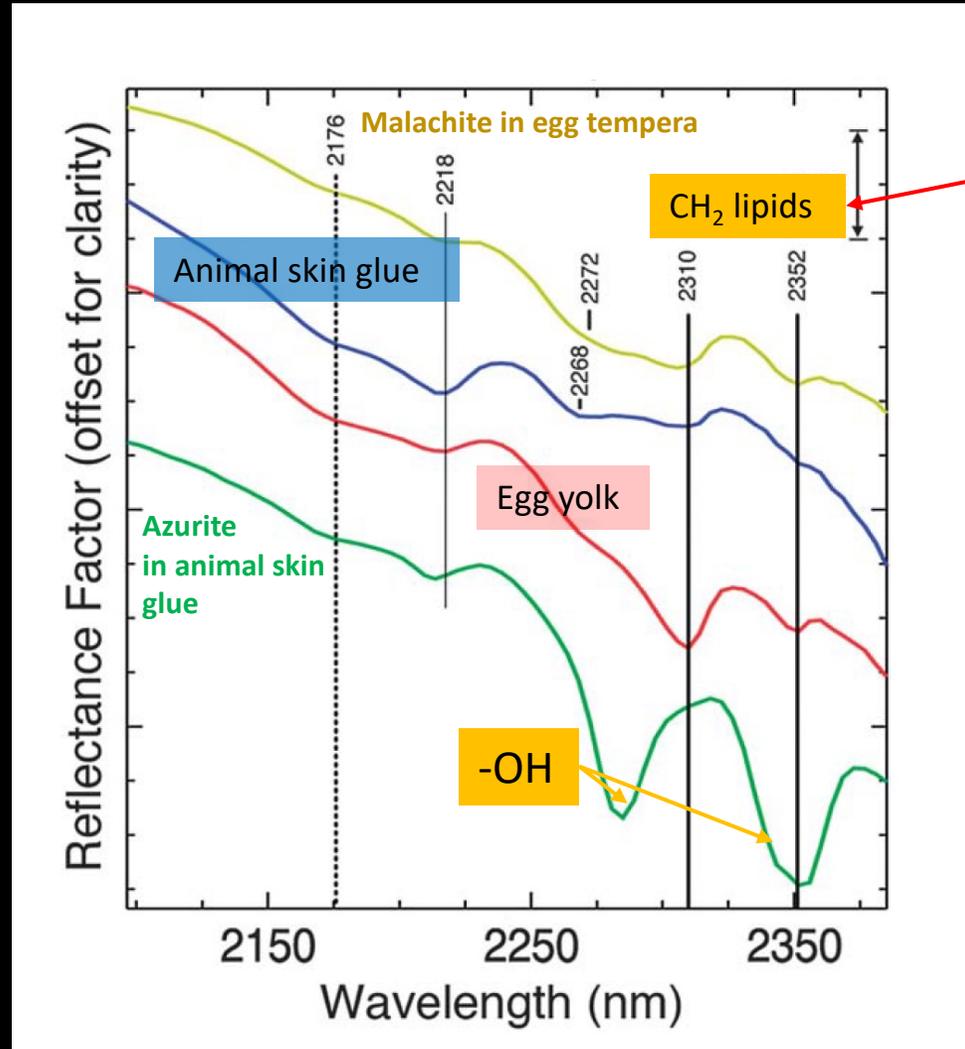
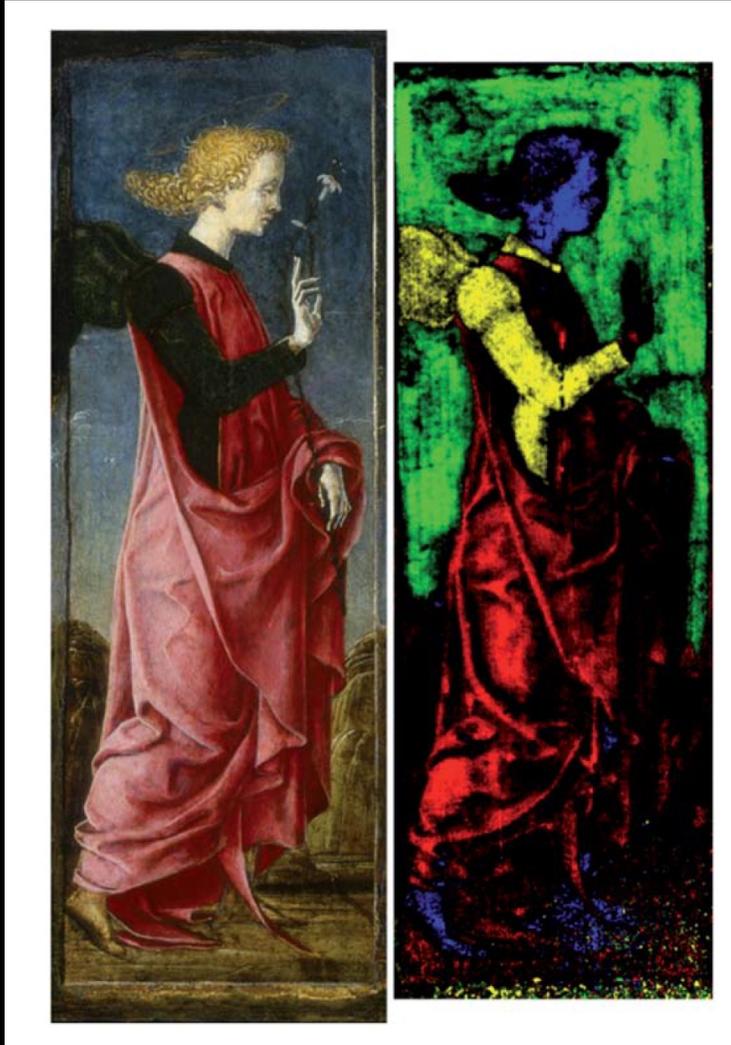
Dooley, Kathryn A., et al. "Mapping of egg yolk and animal skin glue paint binders in Early Renaissance paintings using near infrared reflectance imaging spectroscopy." *Analyst* 138.17 (2013): 4838-4848.

Radpour, Roxanne, et al. "Identification and mapping of ancient pigments in a Roman Egyptian funerary portrait by application of reflectance and luminescence imaging spectroscopy." *Heritage Science* 10.1 (2022): 1-16



**Fig. 3** Characteristic absorptions in the short-wave infrared at 1730, 1763, 2310, and 2352 due to CH<sub>2</sub> bending and stretching modes identify beeswax as the binding medium

# Binding media – animal skin glue and lipid-based materials (e.g. egg tempera, drying oils, wax)



Asymmetric/symmetric stretching and bending of  $\text{CH}_2$  ( $\nu + \delta$ )

2176 nm  
→ C = O + amide II ( $2\nu$ )

Dooley, Kathryn A., et al. "Mapping of egg yolk and animal skin glue paint binders in Early Renaissance paintings using near infrared reflectance imaging spectroscopy." *Analyst* 138.17 (2013): 4838-4848.

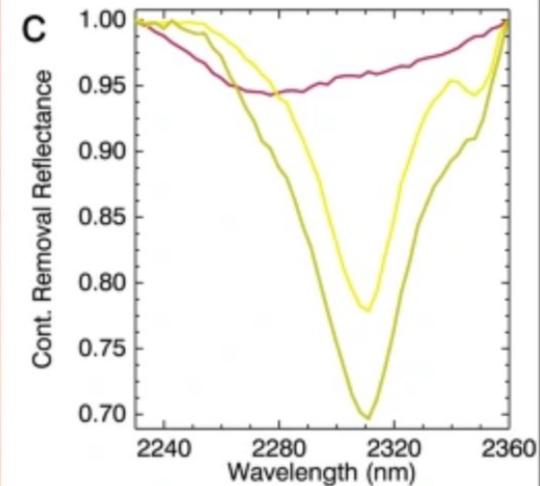
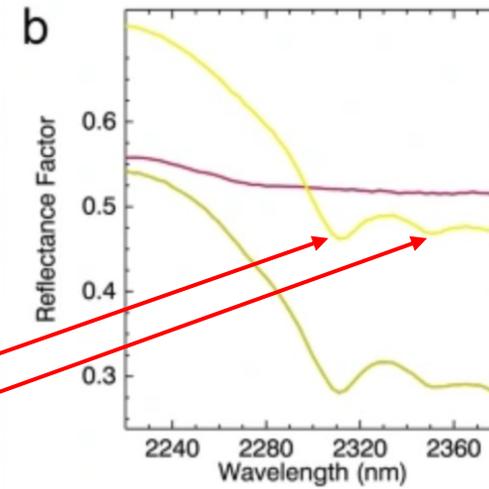
# Binding media

- Wax

~ 2312 nm and 2352 nm

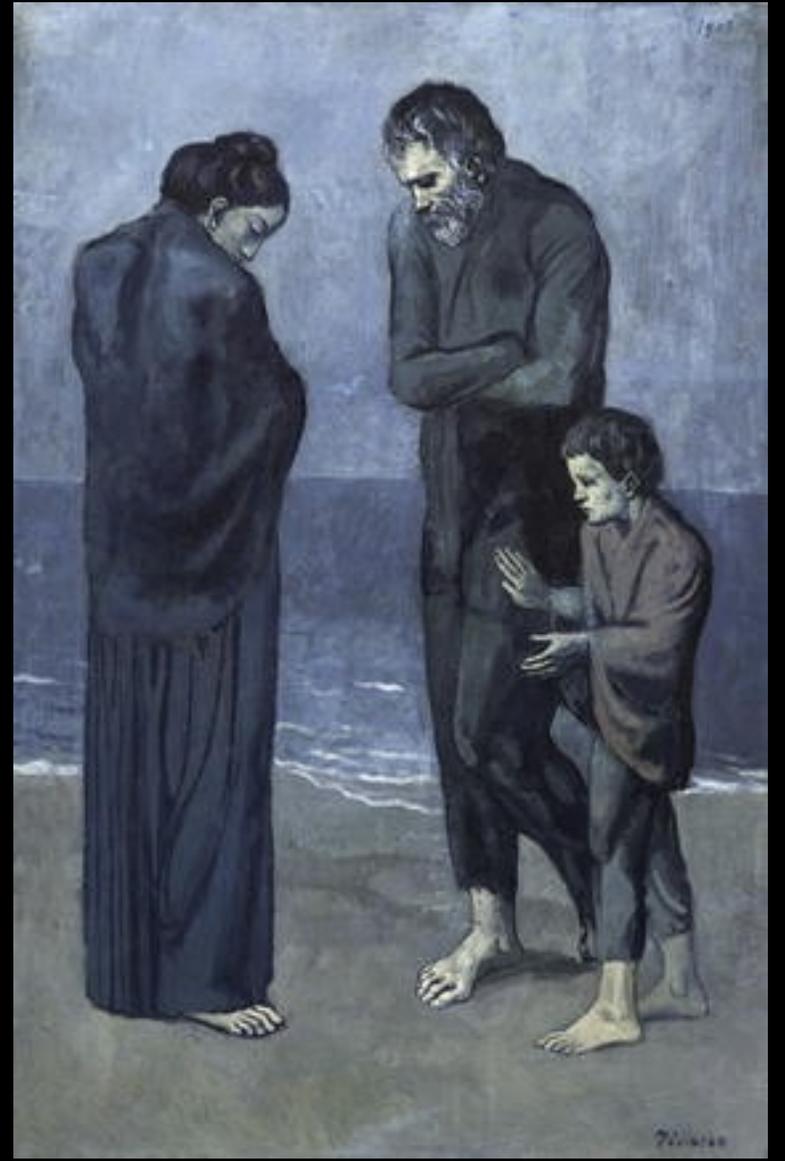
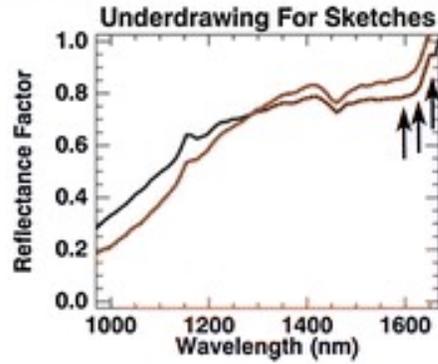
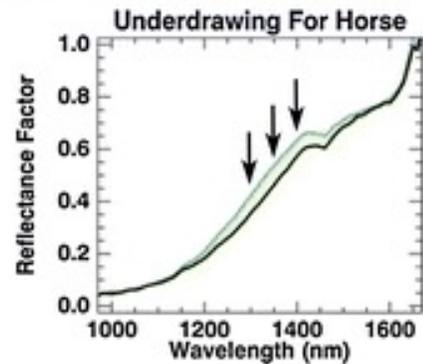
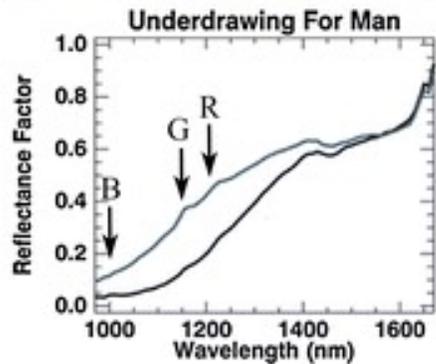
Asymmetric/symmetric stretching and bending of  $\text{CH}_2$  ( $\nu + \delta$ )

Note the slight shift in wavelength values from lipidic stretches in egg tempera



(a) Color image of the portrait; (b) reflectance spectral endmembers; (c) continuum removed endmembers which were used in the mapping; (d) chemical map of spectral signatures from endmembers in Fig. 3c.

# Search for underdrawings



Delaney, John K., et al. "Visible and infrared imaging spectroscopy of paintings and improved reflectography." *Heritage Science* 4 (2016): 1-10.

Picasso's *The Tragedy* (1903). Chester Dale collection, 1963.10.196, National Gallery of Art, Washington, DC

# Mapping Conservation Interventions



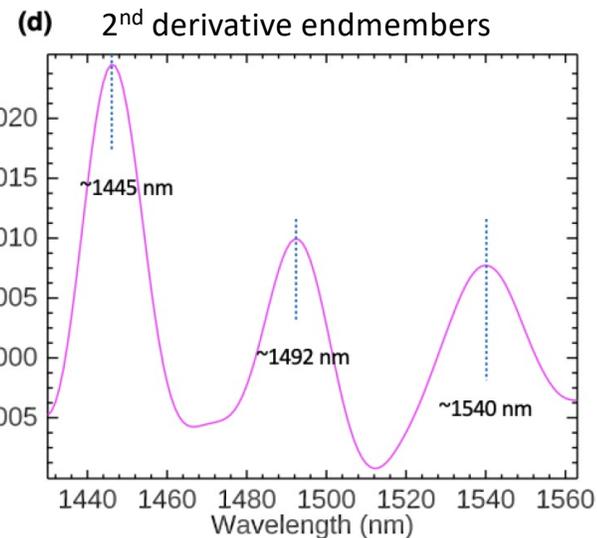
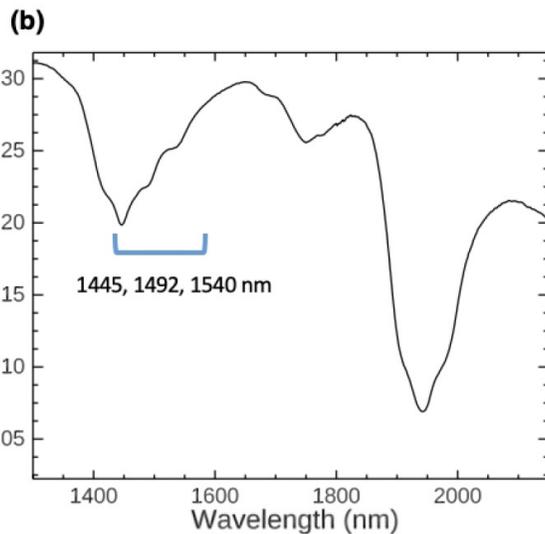
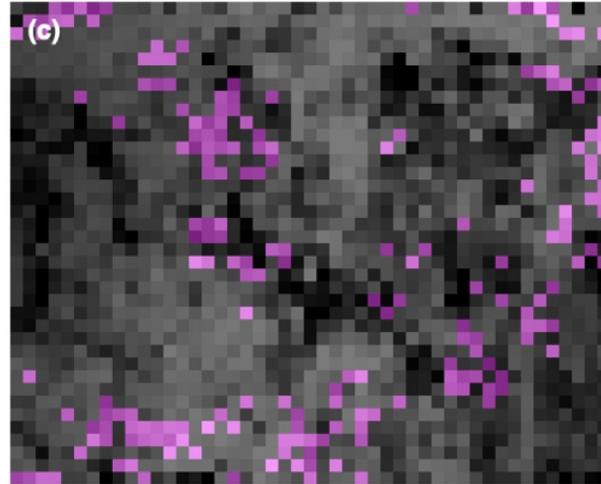
Color detail

Broadband IR reflectogram  
(1000-1700 nm)

IR False Color at 1650, 1400, and 1050 nm for RGB

# Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) mapping

→ Potential environmental monitoring tool



Characteristic triplet signature in the SWIR:

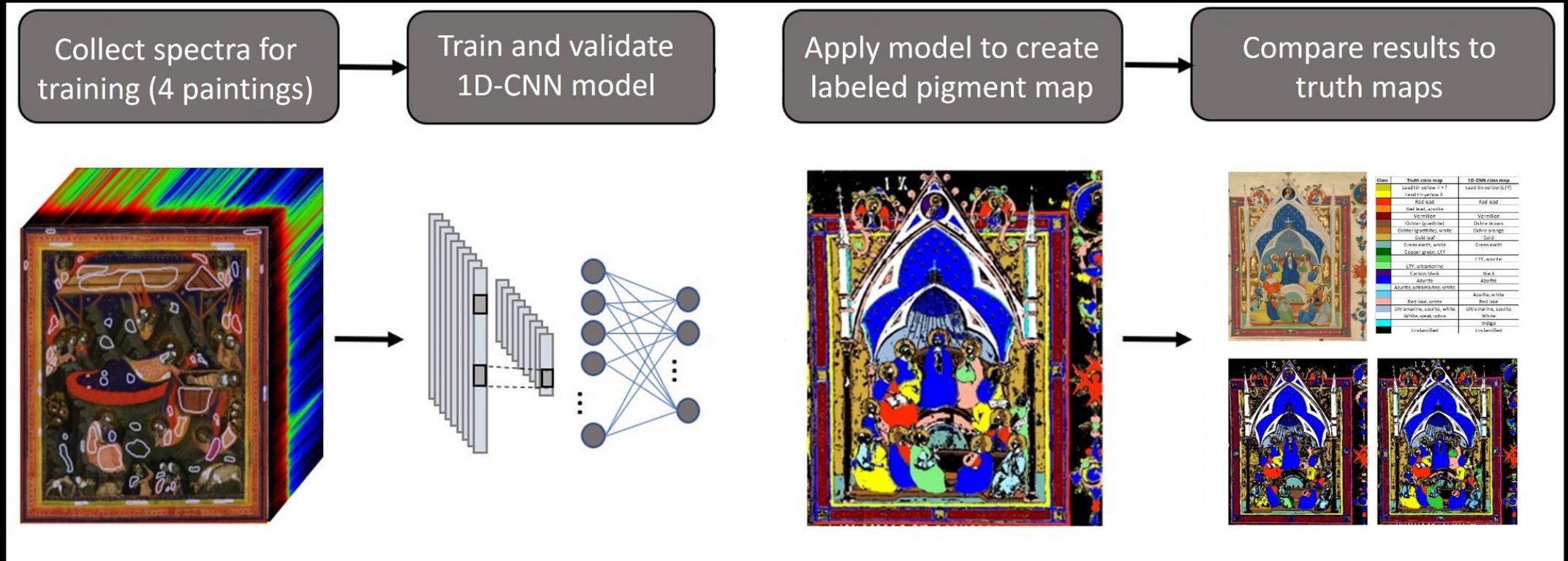
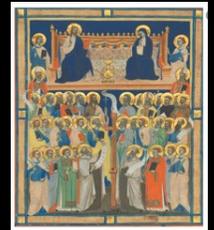
1<sup>st</sup> overtone vibrations of hydroxyl groups

Taking the 2<sup>nd</sup> derivative removes the continuum (overall background) and we can effectively map this triplet signature across the image scene.

# Motivation for new approaches to make labeled pigment maps

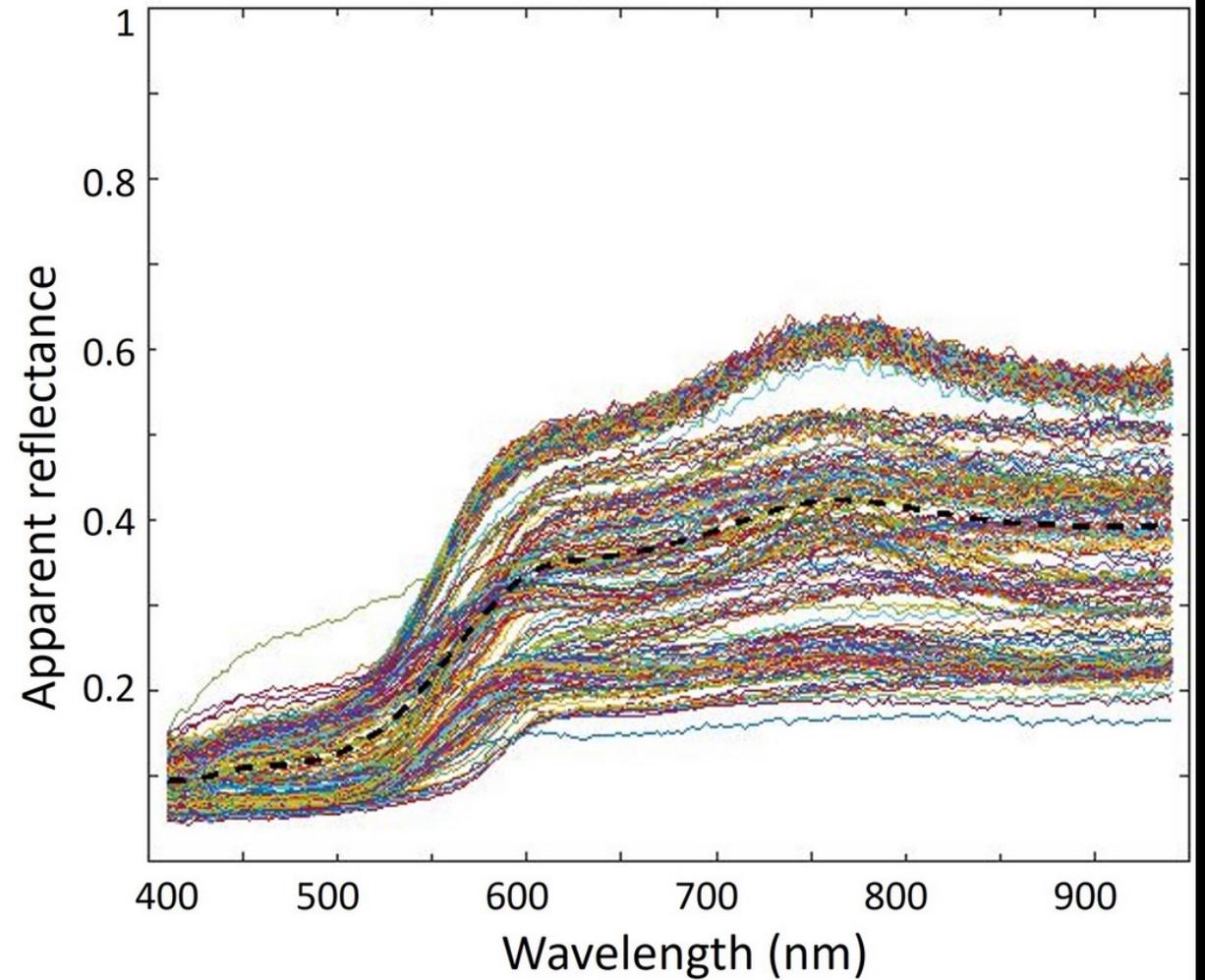
- Multivariate statistical methods are not robust or need too much manual intervention
  - *Days/weeks to analyze some paintings*
  - *Based on linear mixing model – not an accurate representation of paintings*
- Researchers have sought to use Kubelka Munk Theory to directly fit reflectance spectra from reflectance image cubes
  - *Needs large libraries of  $K$ ,  $S$  values and a priori knowledge of the paint layers*
- In Remote Sensing use of AI, more specifically Neural Networks (NN) have been used to solve non-linear spectral unmixing problems.
  - *Major challenge is training sets... paintings offer limited number of training sets, want thousands and have 10's of paintings*
- Objective: leverage the fact that a given artistic school often uses a consistent palette, with characteristic painting mixtures and paint layers
  - **Build a robust training library from a small number of paintings from such a school**

# “An alternative approach to mapping pigments in paintings with hyperspectral reflectance image cubes using artificial intelligence”



Used 4 illuminations to train the NN and 1 to test, all from the *Laudario of Sant' Agnese* (c. 1340)

“An alternative approach to mapping pigments in paintings with hyperspectral reflectance image cubes using artificial intelligence”



# “An alternative approach to mapping pigments in paintings with hyperspectral reflectance image cubes using artificial intelligence”



Class	Truth pigment map	1D-CNN pigment map
	Lead tin yellow II + ?	-
	Lead tin yellow II	Lead tin yellow (LTY)
	Red lead	Red lead
	Red lead, azurite	-
	Vermilion	Vermilion
	Ochre (goethite)	Ochre brown
	Ochre (goethite), white	Ochre orange
	Gold leaf	Gold
	Green earth, white	Green earth
	Copper green, LTY	-
	-	LTY, azurite
	LTY, ultramarine	-
	Carbon black	Black
	Azurite	Azurite
	Azurite, ultramarine, white	-
	-	Azurite, white
	Red lake, white	Red lake
	Ultramarine, azurite, white	Ultramarine, azurite
	White, weak ochre	White
	-	Indigo
	Unclassified	Unclassified

Labels