The “Scream” by Edvard Munch (1910): non invasive integrated spectroscopic investigations of the painting materials

L. Cartechini, F. Rosi, C. Grazia, L. Monico, A. Romani, R. Pereira de Freitas, C. Miliani

M. Godzimirska, E. Chan, G. Landro, E. S. Tveit, P. Pettersen, I.R.A. Sandu

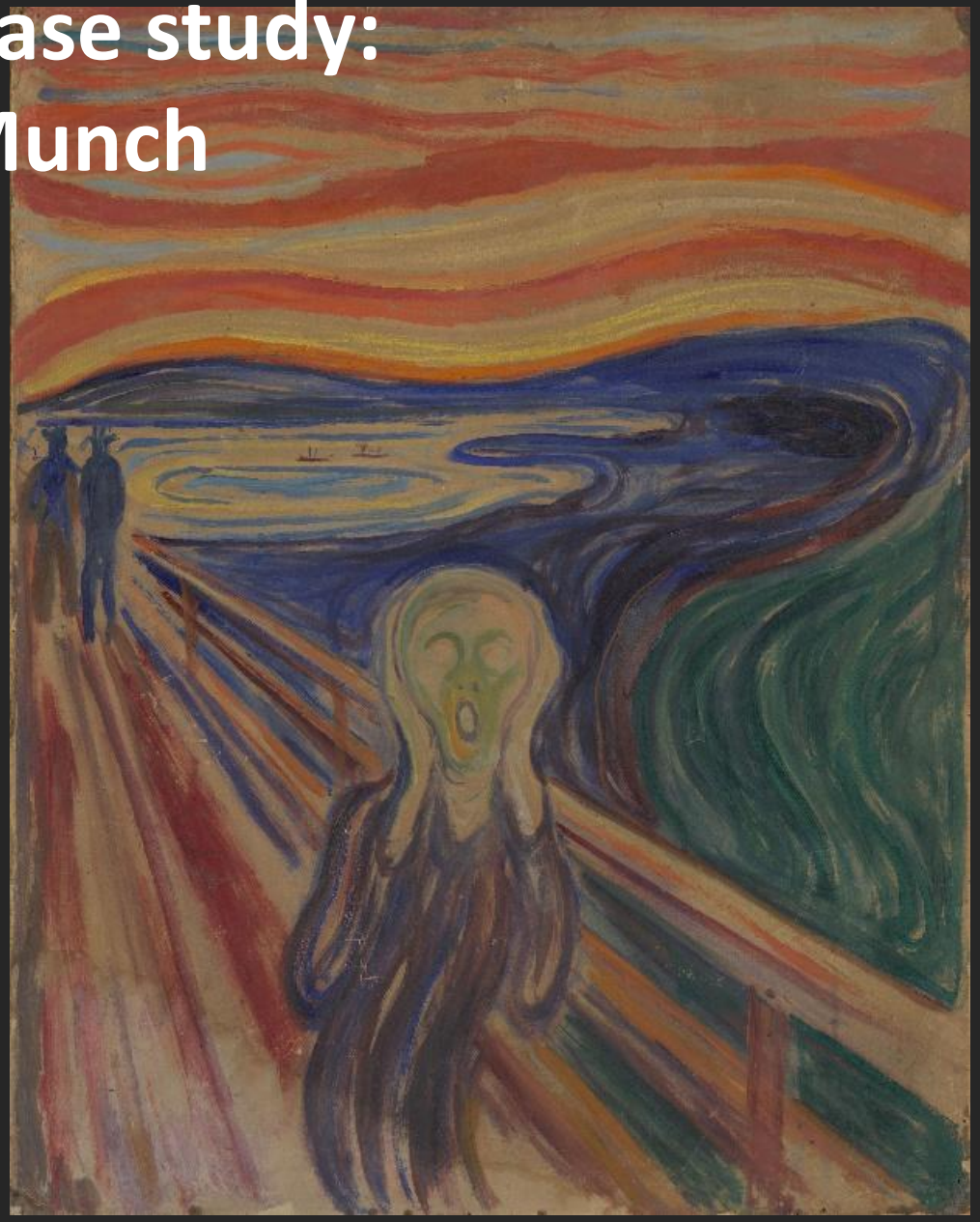
MUNCH
MUSEET

IPERION CH

MAXRF 2019 Catania, October 15-16,2018

An extraordinary case study: the Scream by E. Munch

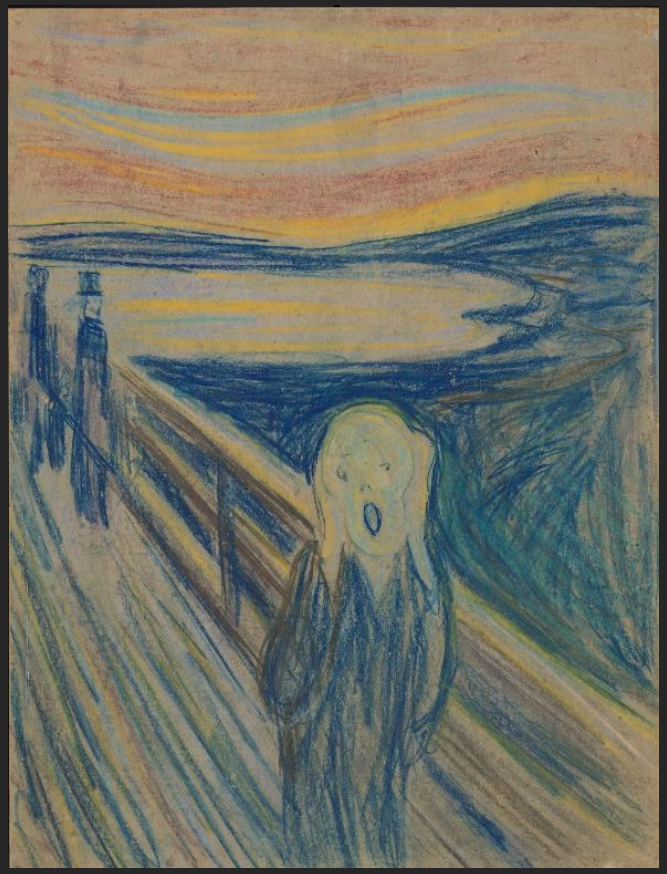
Edvard Munch (1863–1944)



The Scream (1910?) – The Munch Museum

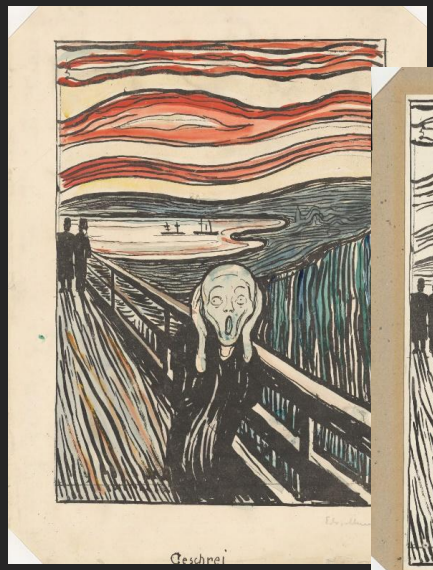
MUNCH
MUSEET

Prints and drawings



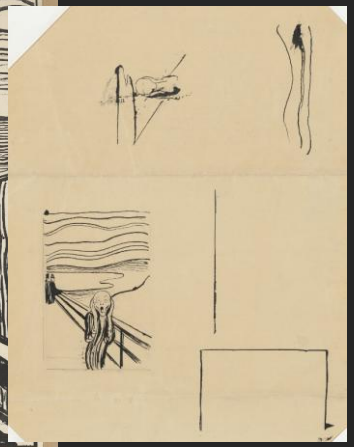
MM.M.00122b – Scream (1893), cryon/pastel drawing 74 x 56 cm

MM.T.02301 - Scream, 1910-1916, drawing



G0193-03 – Scream, 1895, print

G0193-01 - Scream, 1895, print



MM.T.00255 - Scream, 1895, drawing

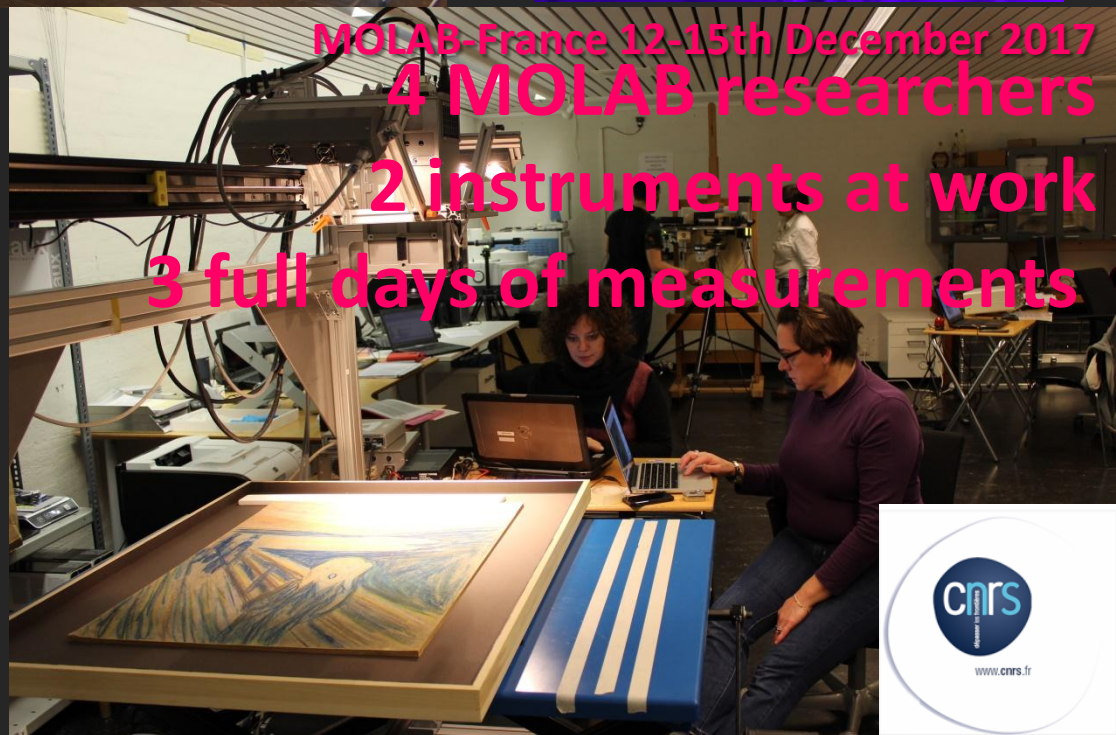
MOLAB-Italy 2nd-6th October 2017

8 MOLAB researchers

9 instruments at work

4 full days of measurements

MOLAB access proposal: Technical study of core art materials & techniques of SCREAM versions



MOLAB-France 12-15th December 2017

4 MOLAB researchers

2 instruments at work

3 full days of measurements

IPERION CH

www.iperionch.eu

www.cnrs.fr

MOLAB transnational access

the mobile laboratory for in situ non-invasive measurements for CH

Multi/Hyper spectral imaging

VIS-NIR multi spectral scanning
NIR hyper spectral imaging
VIS hyper spectral imaging
X-ray fluorescence scanning

2D/3D investigations

Optical Coherence Tomography
Confocal microscopy
Terahertz imaging
Digital holography
NMR-profiler

Point chemical analysis

X-ray fluorescence
Mid-FTIR
Near-FTIR
Raman
X-ray diffraction
UV-vis absorption
UV-vis fluorescence
Time resolved fluorimetry
NMR-relaxometry

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ITMC | RWTH AACHEN UNIVERSITY
FORTH Foundation for Research & Technology - Hellas

MOLAB transnational access

the mobile laboratory for in situ non-invasive measurements for CH

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Scanning MA-XRF

CRONO, XGLaB
Rh tube max power 50KV 200μA
130eV at MnKa @ 1Mcps Input Rate
Max Speed: 30 mm/s
0.5 mm, 1 mm and 2 mm collimators
Scan Area: 60x45cm
Z range: 7cm

XRF elemental maps produced by the PyMca and Datamuncher software packages.

R. Alberti, et al. X-ray Spectrom, 2017, doi 10.1002/xr s.2741

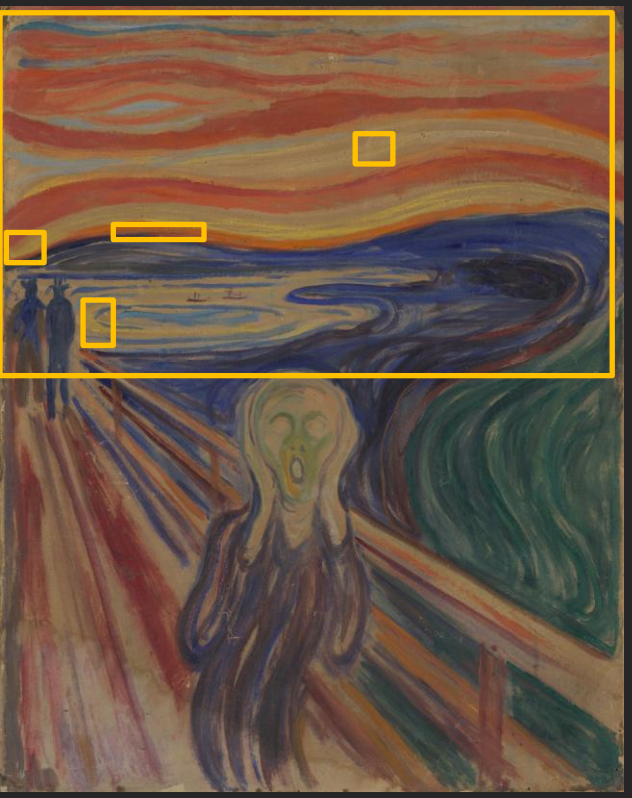
Vis-NIR and Fluorescence Hyperspectral Imaging

Spectral Coverage: 400-1000 nanometers
Spectral Resolution: 5 nanometer
Bands: 128
Dynamic Range: 12-bit
Pixels per frame: 696x520
Speed: 30 spatial lines per second, 23.2 seconds/cube (696 by 520 cube)
Focal Length: Configurable (based on lens used)

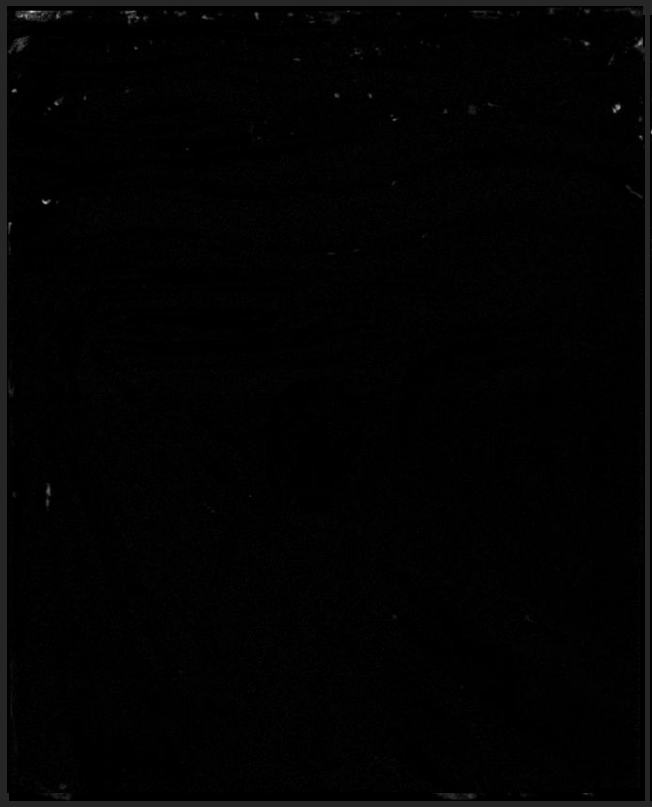
C. Grazia et al. in Conservation 360°, Vol. 1 "UV-Vis Fluorescence imaging techniques", (Eds. M. Picollo, M. Stols-Witlox and L. Fuster-López), accepted.

MA-XRF

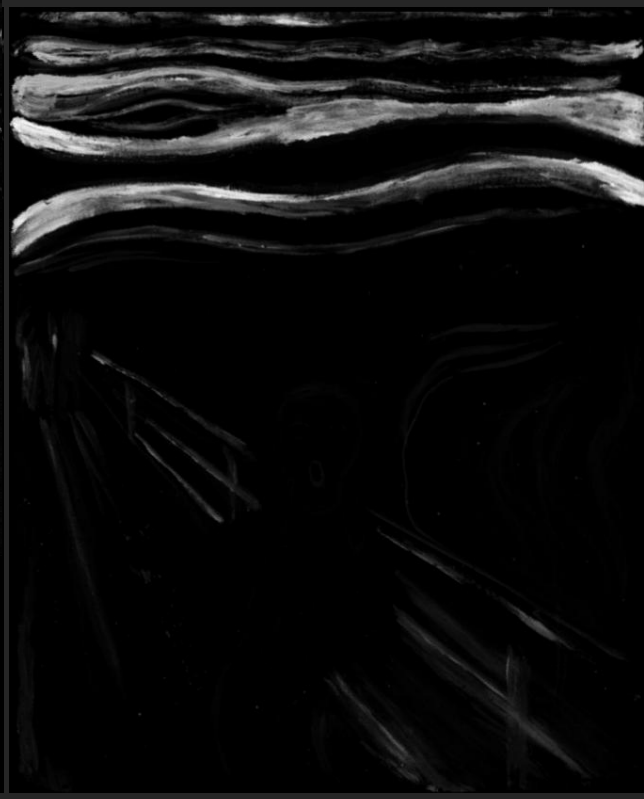
Red, orange and yellow hues



Se-K



Hg-L



Cadmium selenide (CdSe..?)

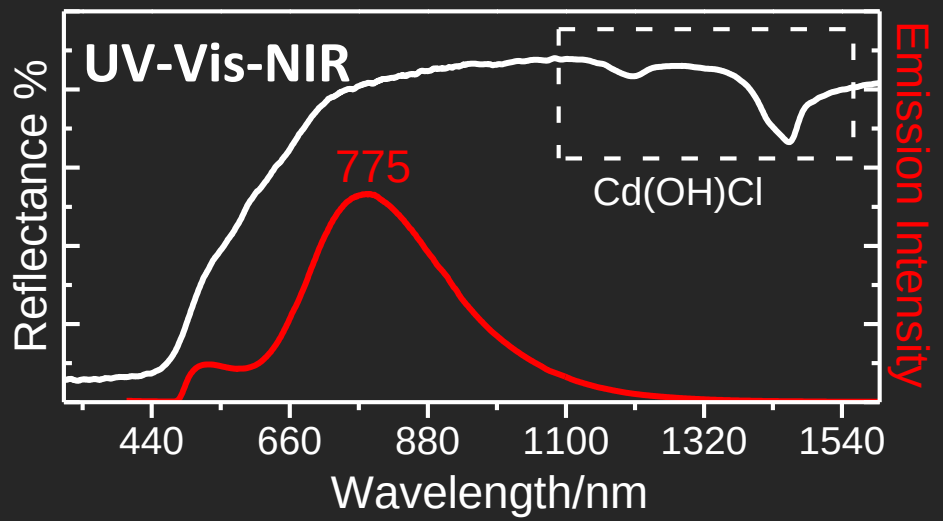
vermilion (HgS)

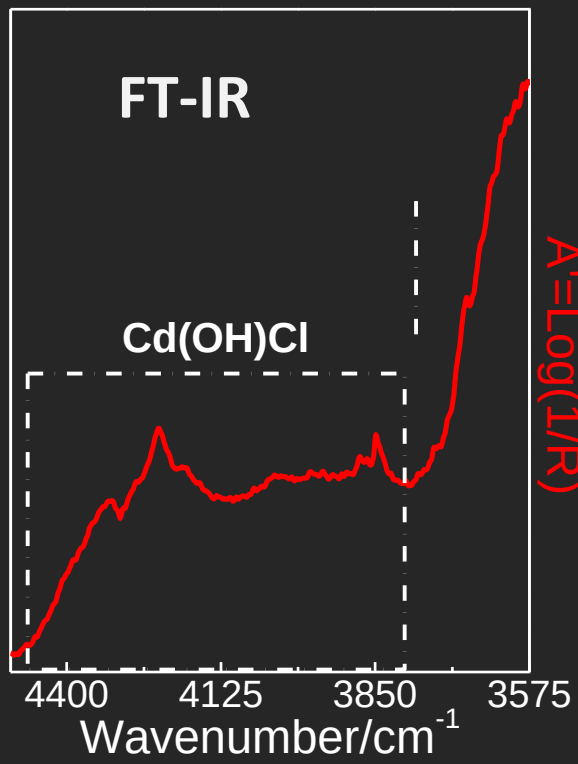
Secondary alteration in specific regions

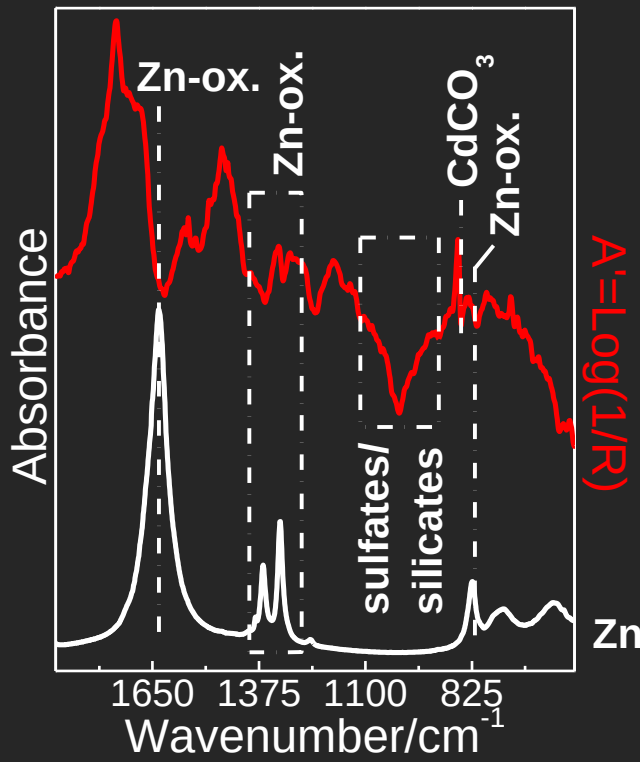
Retouchings?

Red, orange and yellow hues of the landscape

I. Yellow shades of the thick yellow paints in the sky and lake







-**Hexagonal CdS**-based yellow pigment characterized by a fluorescence band at 775nm

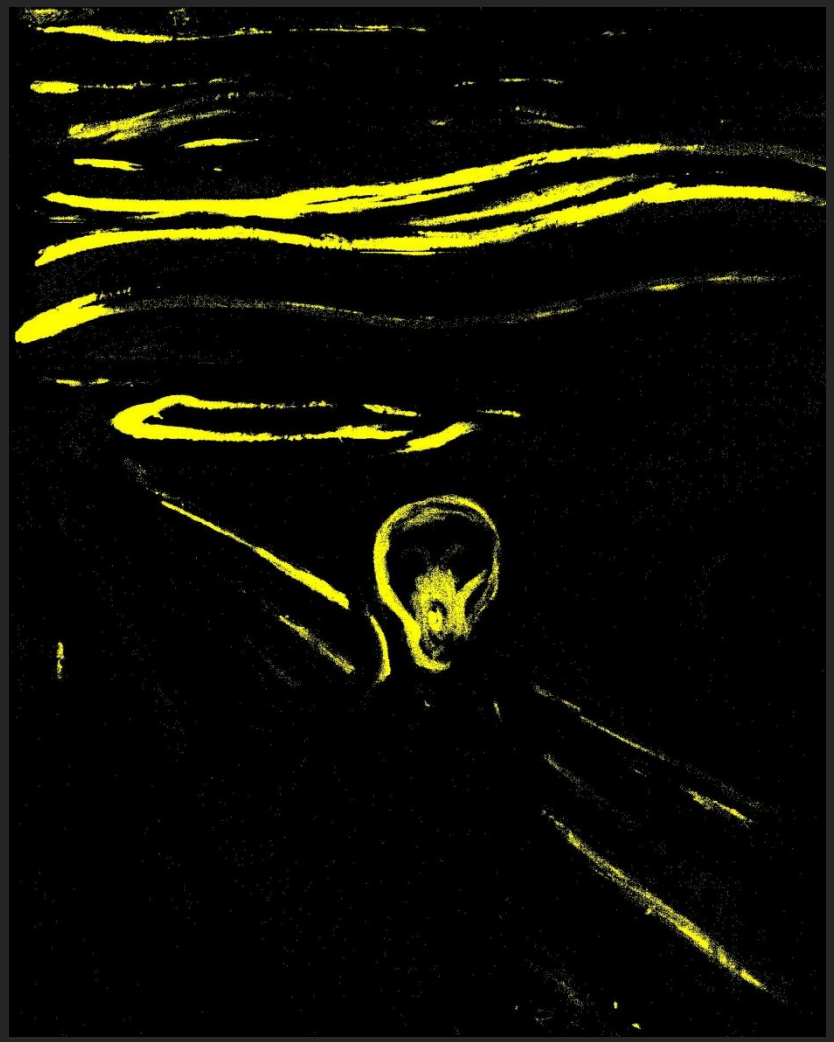
- identification of cadmium carbonate and zinc oxalates and Cd(OH)Cl by FT-IR & VIS-NIR

$ZnC_2O_4 \cdot 2H_2O$

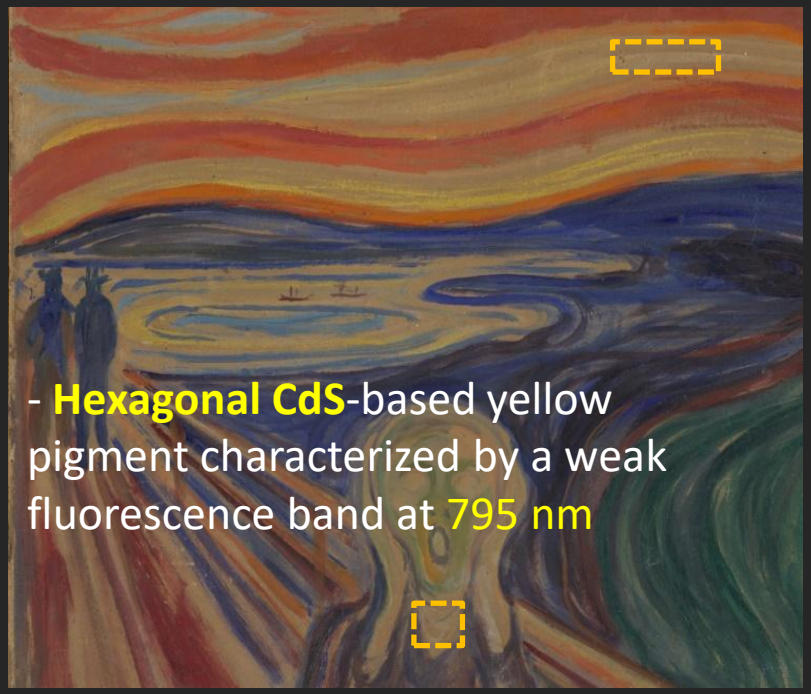
fluorescence hyper spectral imaging @ 775nm

Cd-L

CdS emission

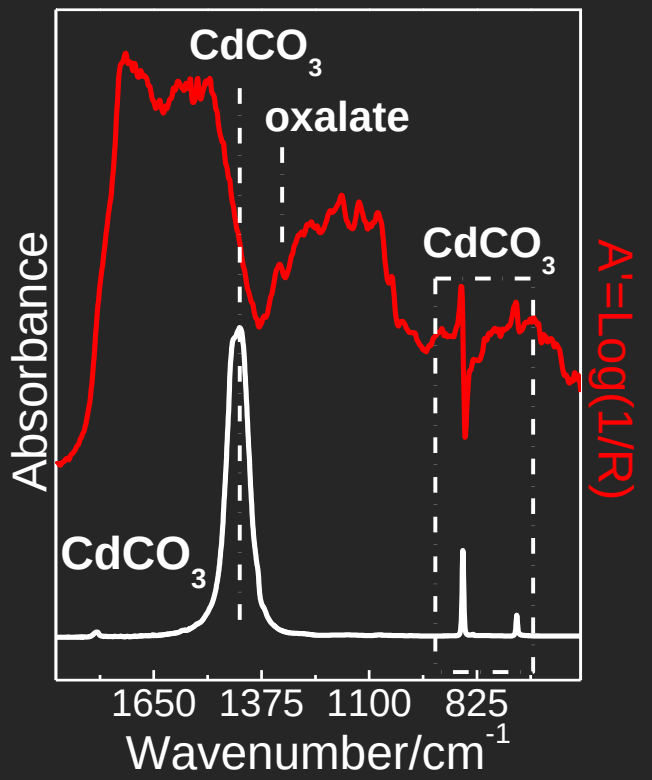


II. thin yellow/off-white paints on the sky and the neck

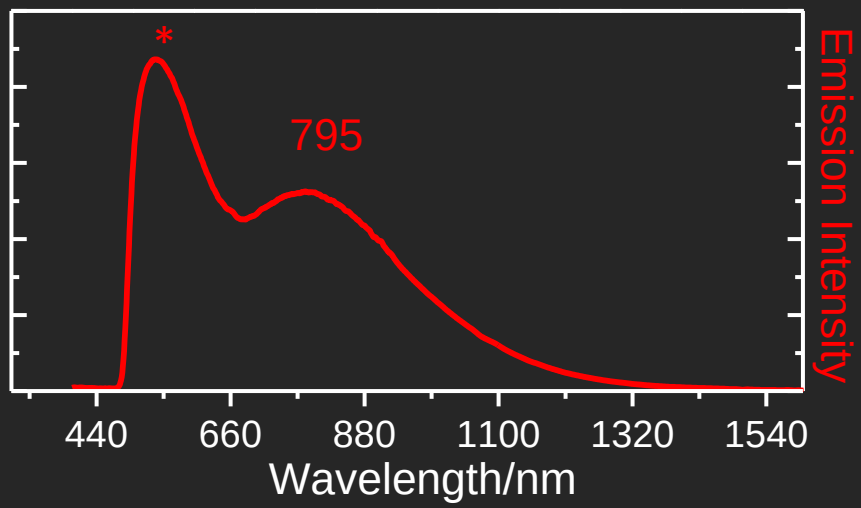


- **Hexagonal CdS**-based yellow pigment characterized by a weak fluorescence band at 795 nm

FT-IR

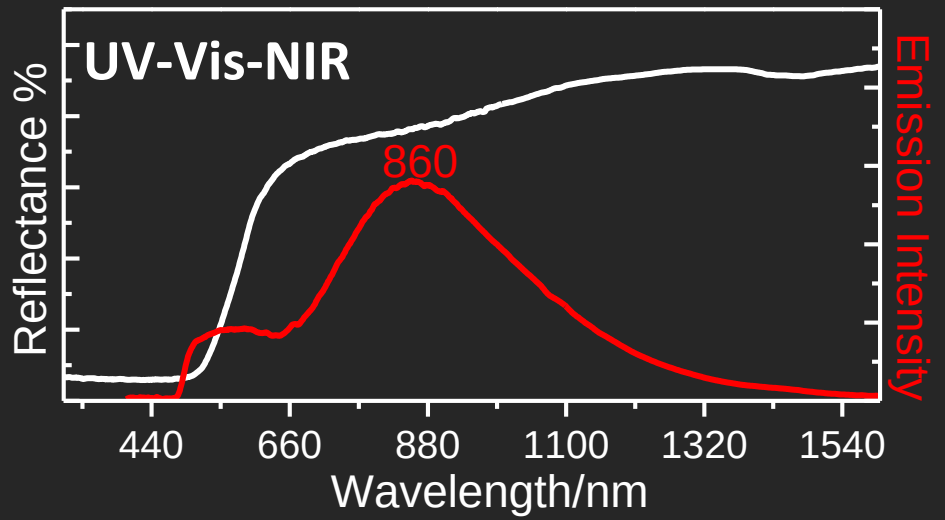


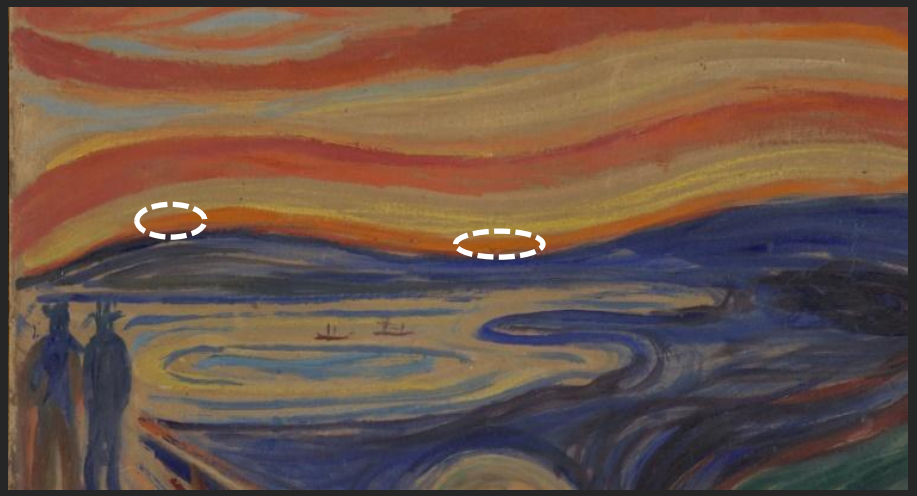
UV-Vis-NIR Fluorescence

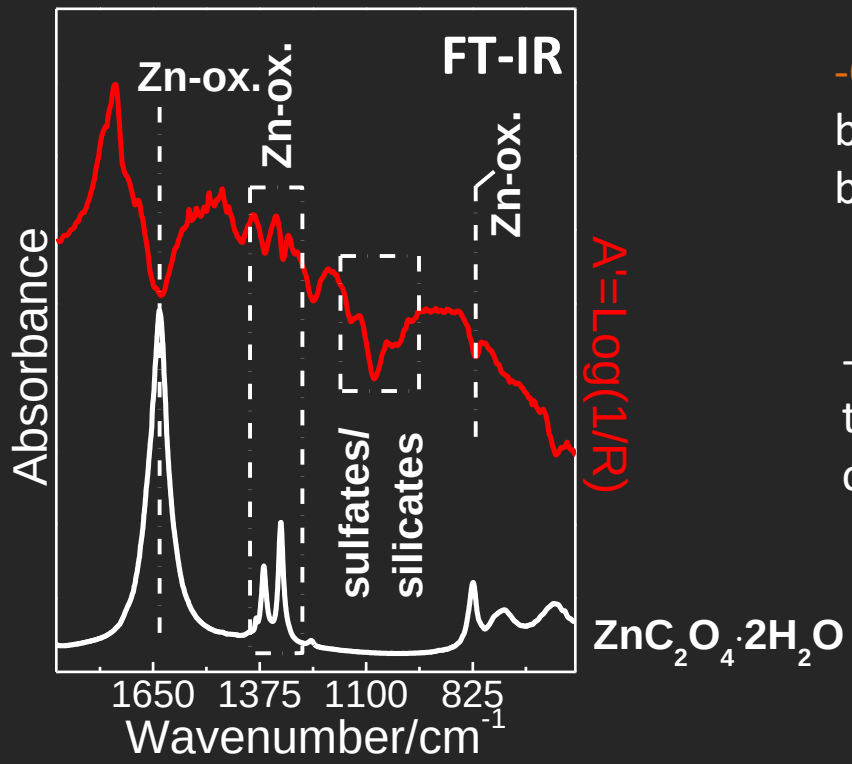


- identification of cadmium carbonate and oxalates by MIR spectroscopy

III. Orange hues of the sky





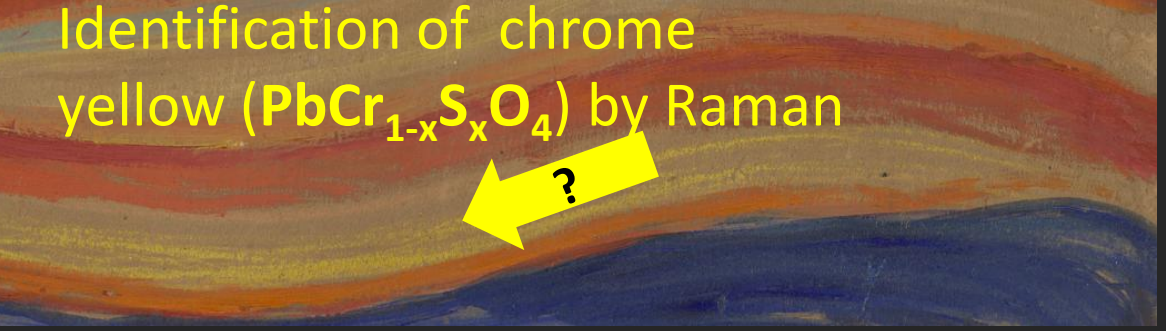


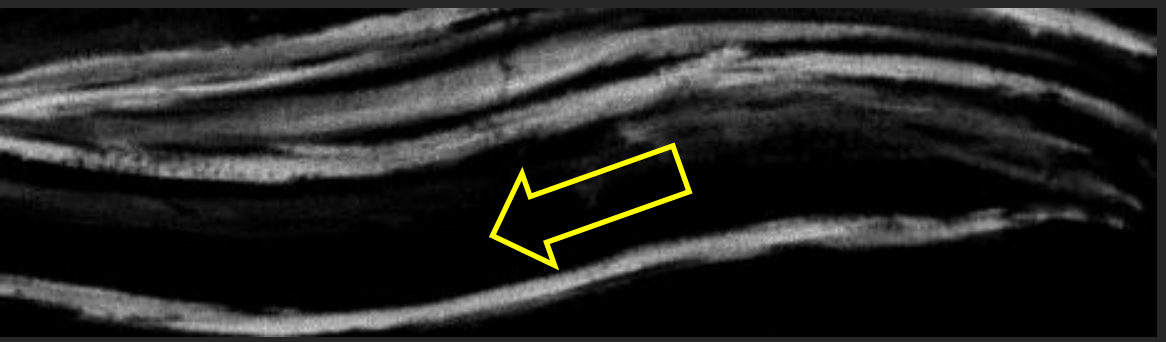
$ZnC_2O_4 \cdot 2H_2O$

-**Cubic+Hexagonal CdS**-based pigment characterized by a fluorescence band at 860 nm and reflectance band with inflection point at about **530** nm.

- identification of zinc oxalates (signals more intense than in the yellow tones. No presence of cadmium carbonate and Cd(OH)Cl in this area.

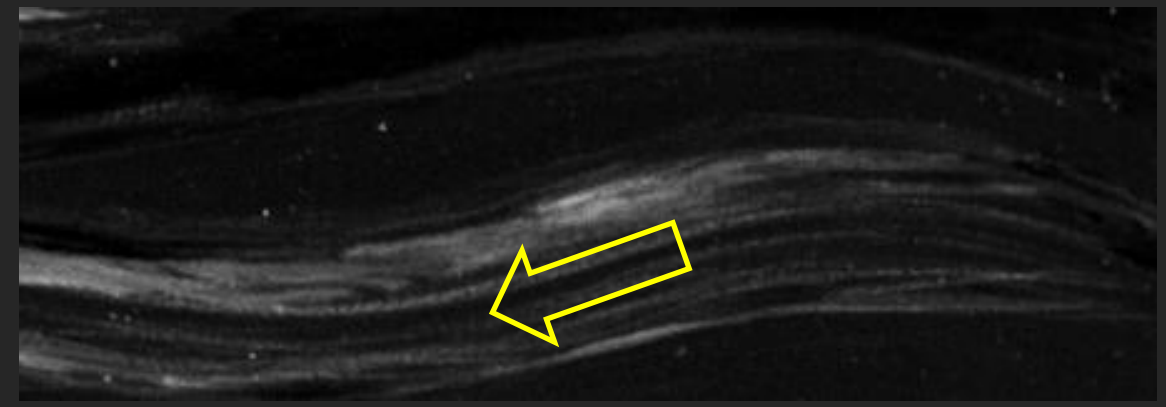
Identification of chrome yellow ($PbCr_{1-x}S_xO_4$) by Raman





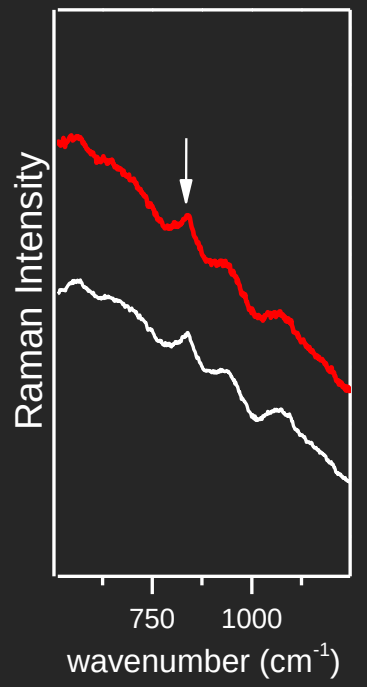
Cd-L

Cr-K



Pb-L

yellow strokes that do not show up in the Cd-L map

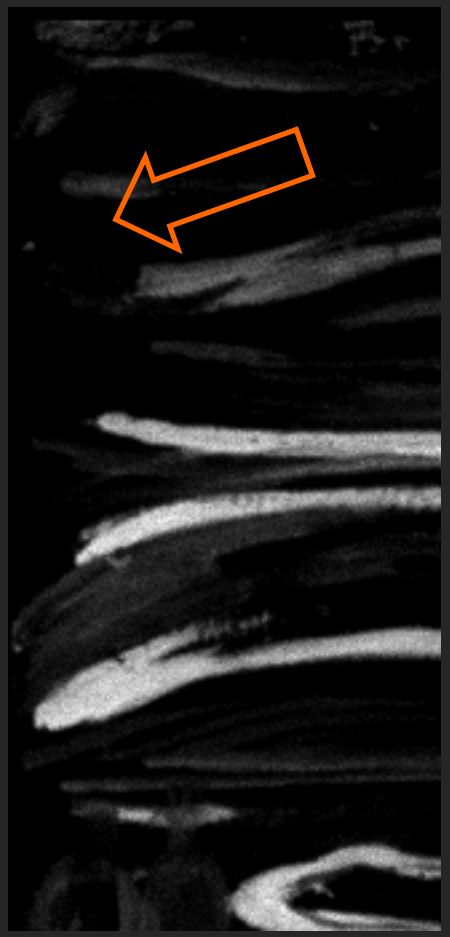


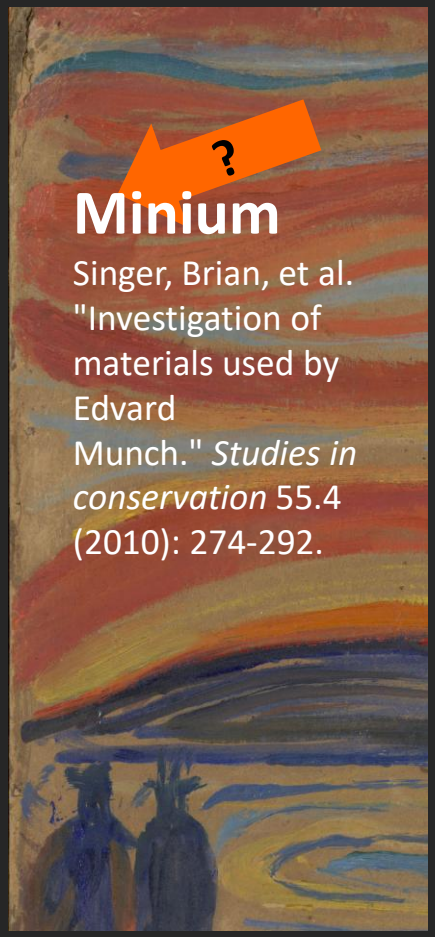
but in the maps of Pb-L and Cr-K

Cd-L

Hg-L

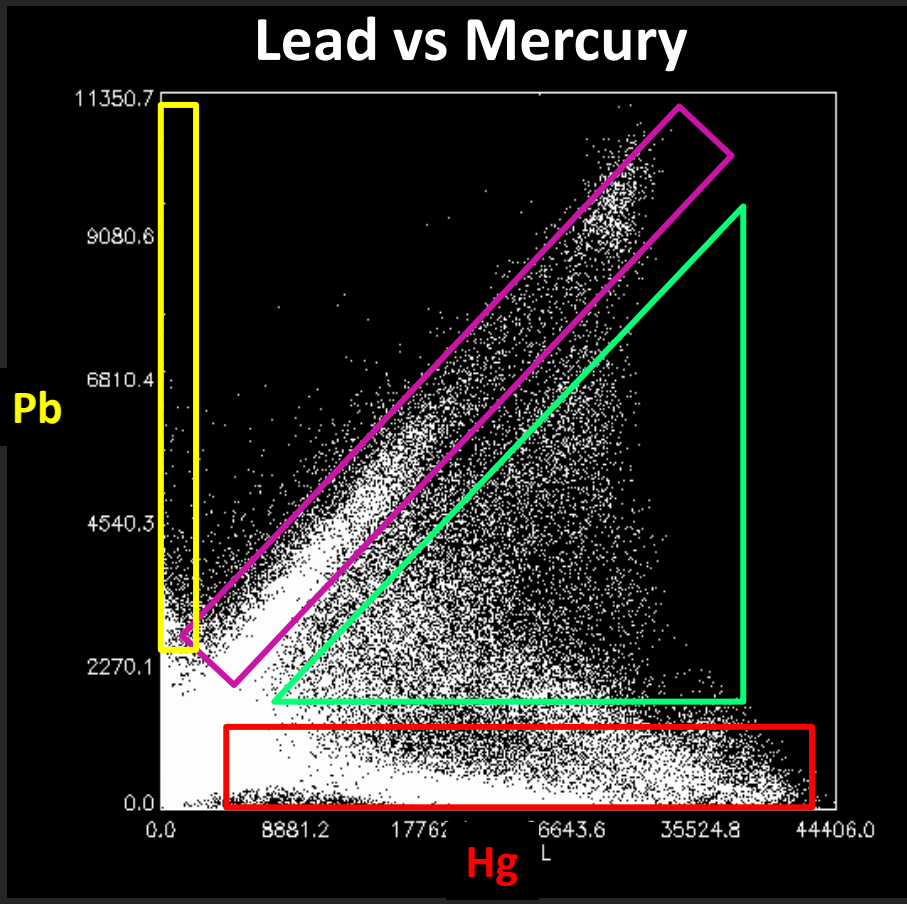
Pb-L





orange strokes that do not show up in the Cd-L map but in the maps of Pb-L and Hg-L.

Correlation plot



Pb without Hg: lead chromate

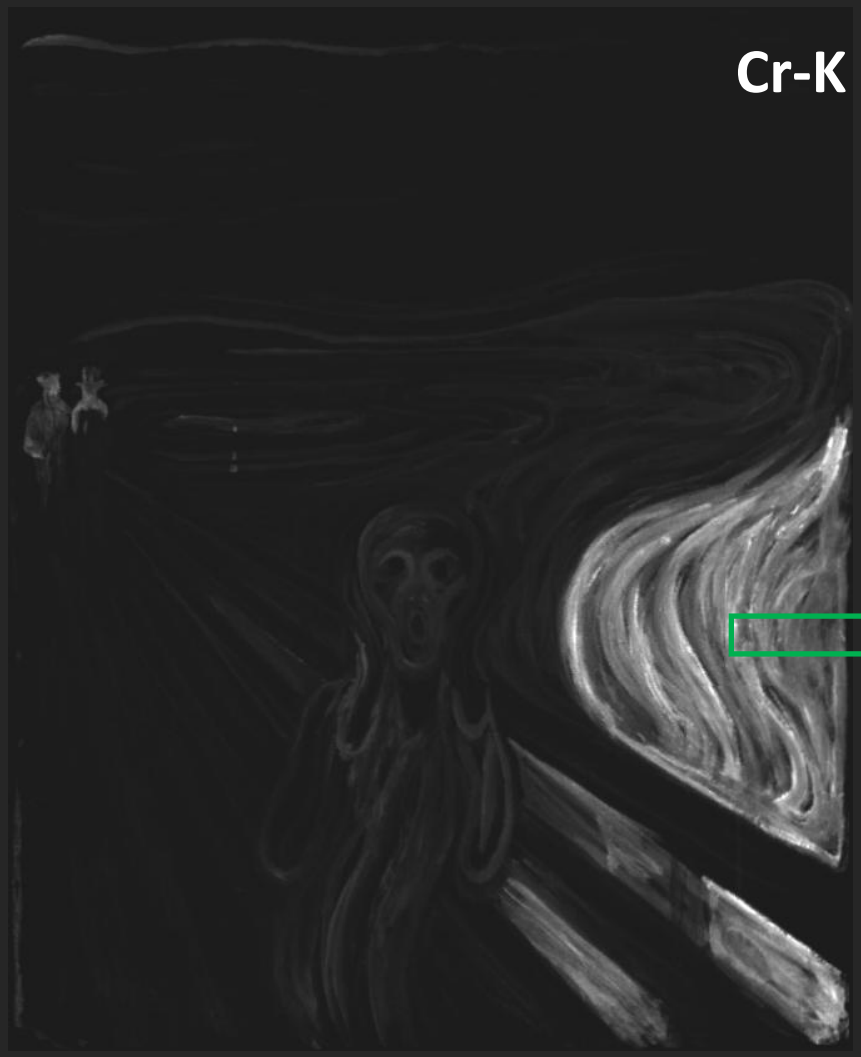
Hg without Pb: HgS

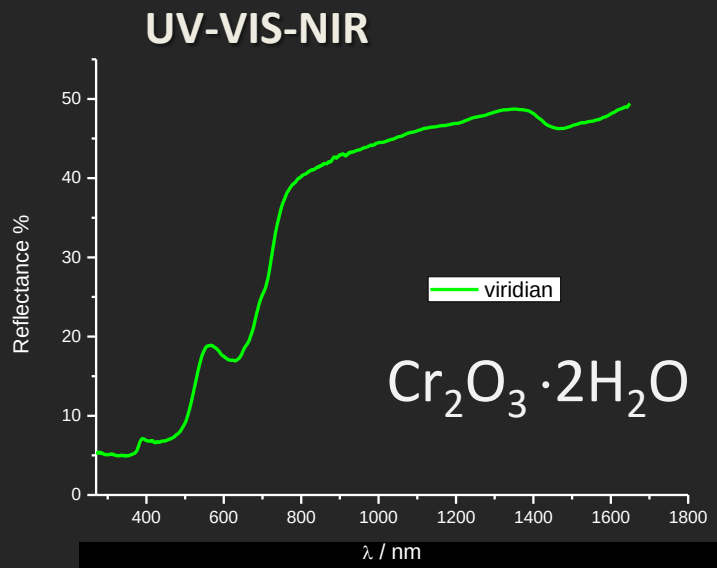
Correlated Pb/Hg =intentional pigment mixture or tube formulation

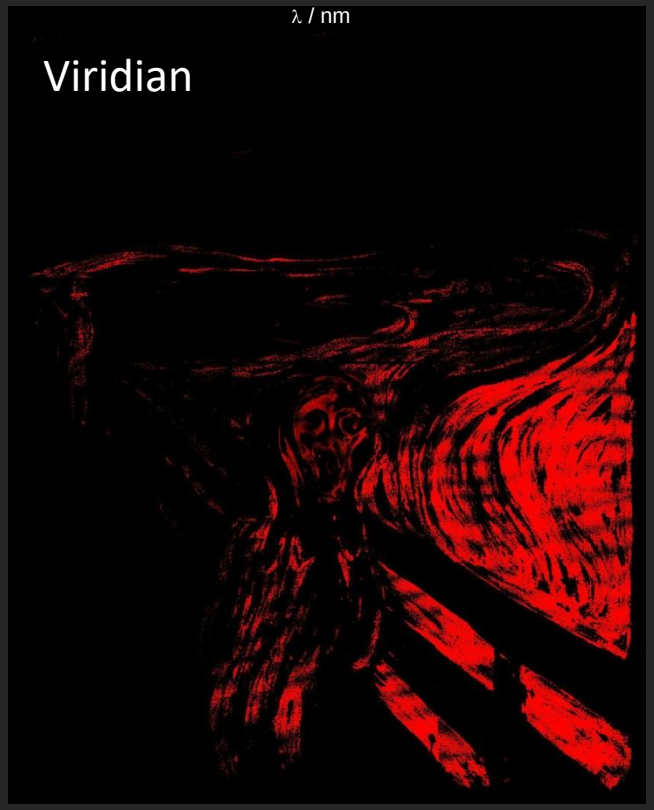
Uncorrelated Hg/Pb

Other pigments

Cr-based green

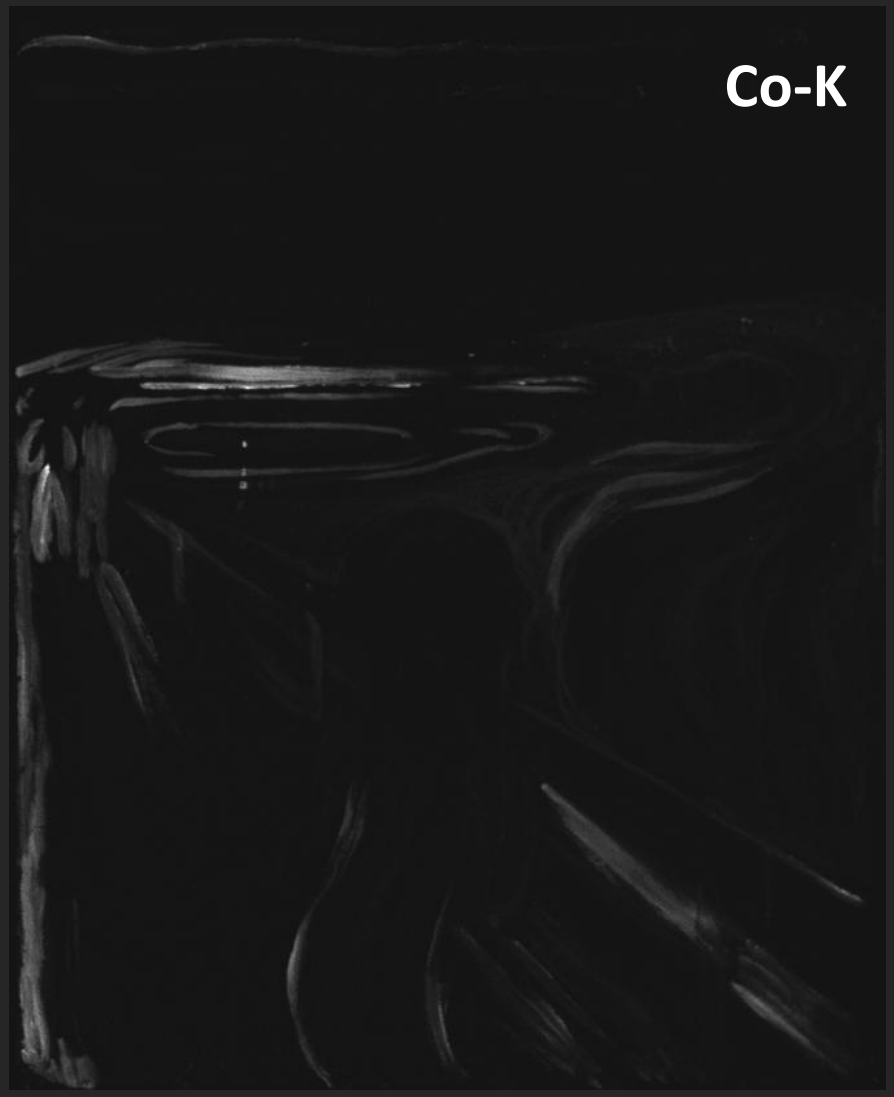


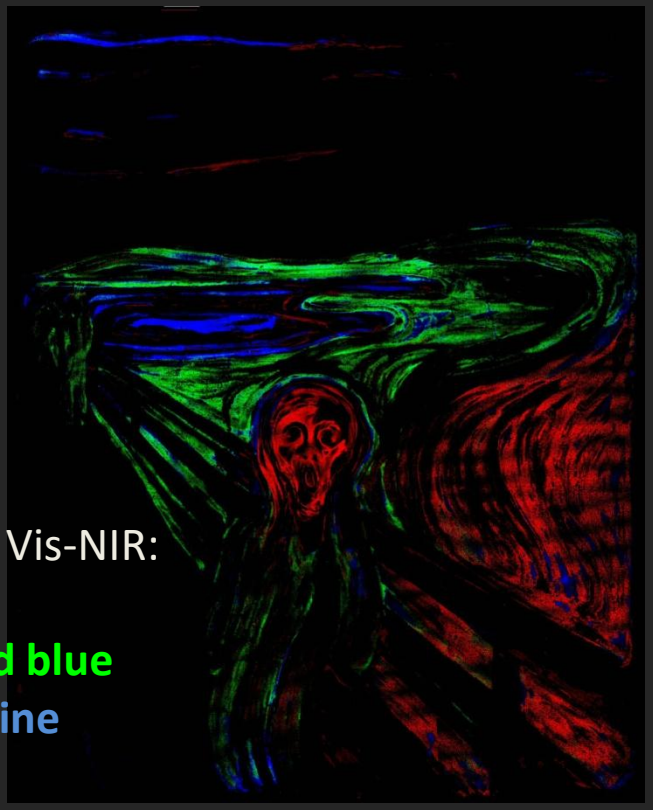




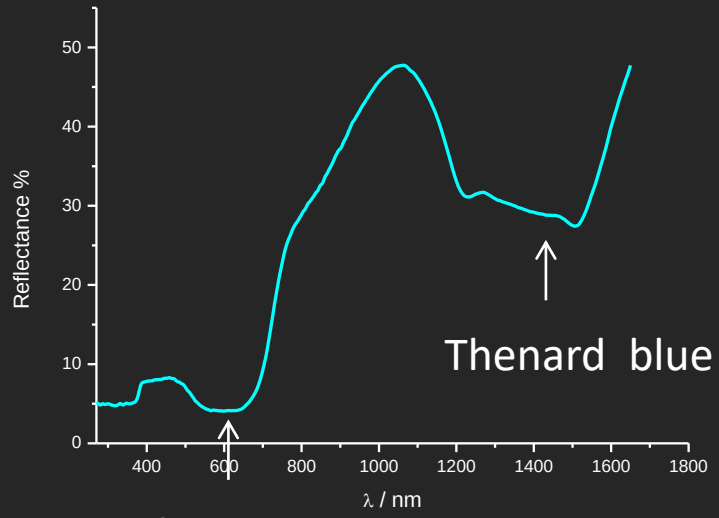
VIS-NIR hyperspectral imaging

Blue areas



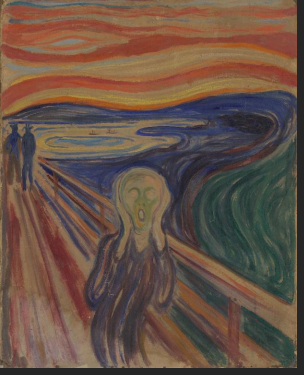


Hyperspectral Vis-NIR:
red: viridian,
green:Thenard blue
blue:ultramarine



Material identification summary

	support	Yellow/ Orange	Red	blue	green	white	Alteration products/ synthesis residuals
The Scream (MM)	Ca,Ba,Zn (low counts) Kaolin	CdS : ▪Hexagonal type 1 ▪Hexagonal type2 ▪cubic/hexagonal $PbCr_{1-x}S_xO_4$	HgS Organic lakes (antraquinone type) Minium	Thenard Blue ($CoO \cdot nAl_2O_3$) Ultramarine ($Na_{8-x}[AlSiO_4]_6[S_3,S_2]_{2-x}$)	Viridian ($Cr_2O_3 \cdot 2H_2O$)	ZnO	Zn Oxalates $CdCO_3$ Cd(OH)Cl



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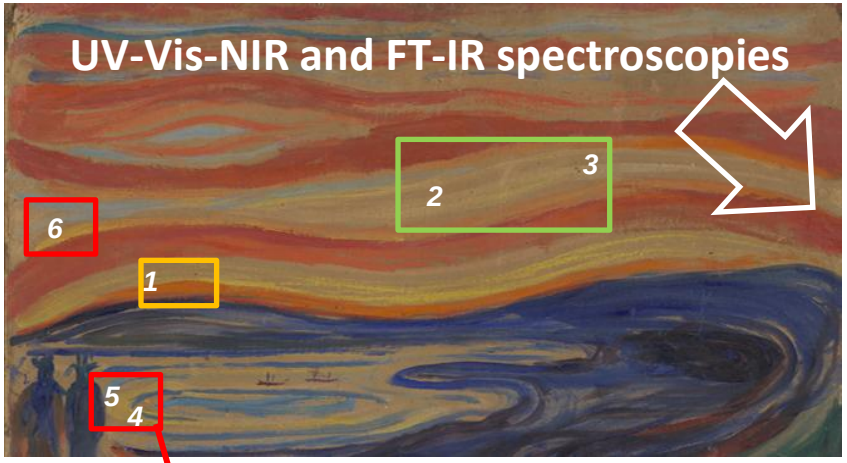
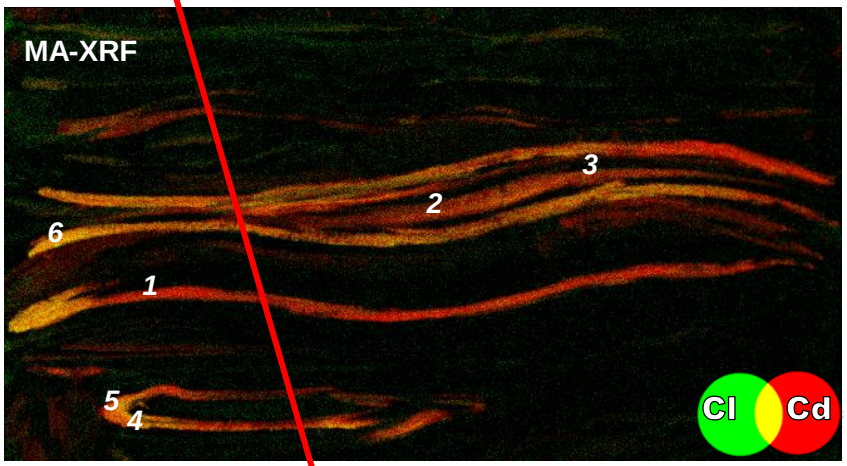
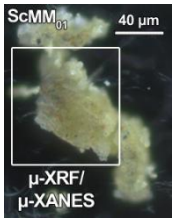
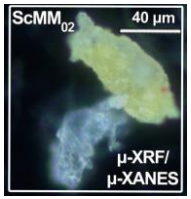
Body of knowledge useful for…



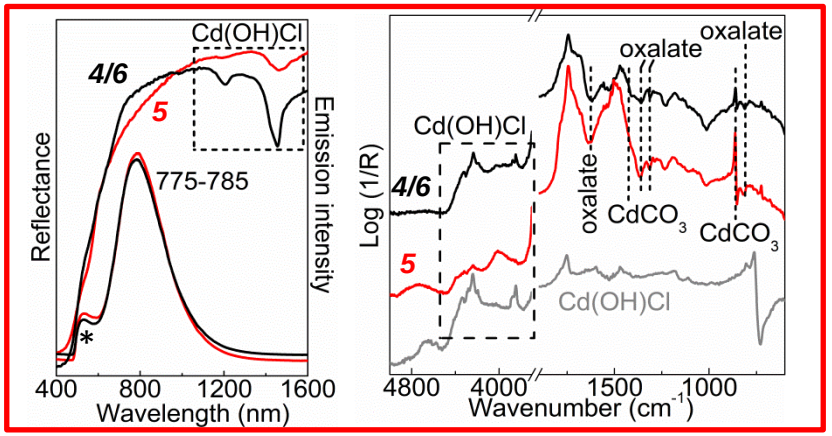


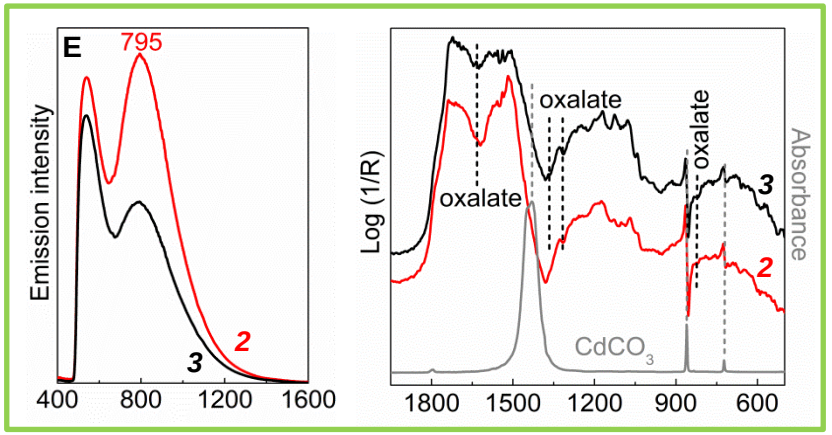




Probing the chemistry of CdS paints in *The Scream* by *in situ* non-invasive spectroscopies and synchrotron radiation X-ray techniques

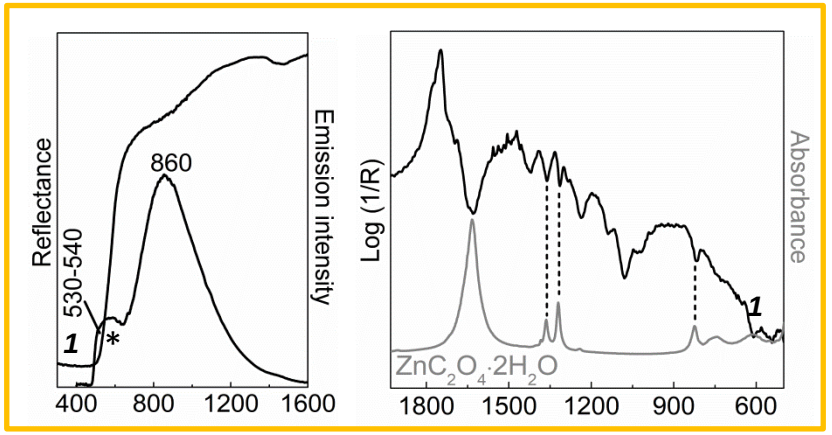
Letizia Monico et al. Science Advances, in publication





Hexagonal CdS

mixture of hexagonal and cubic CdS



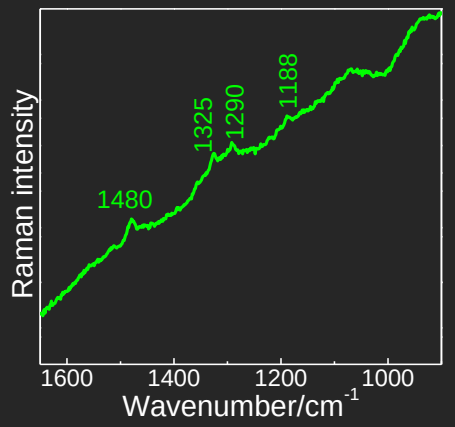
Thank you for your attention

laura.cartechini@cnr.it

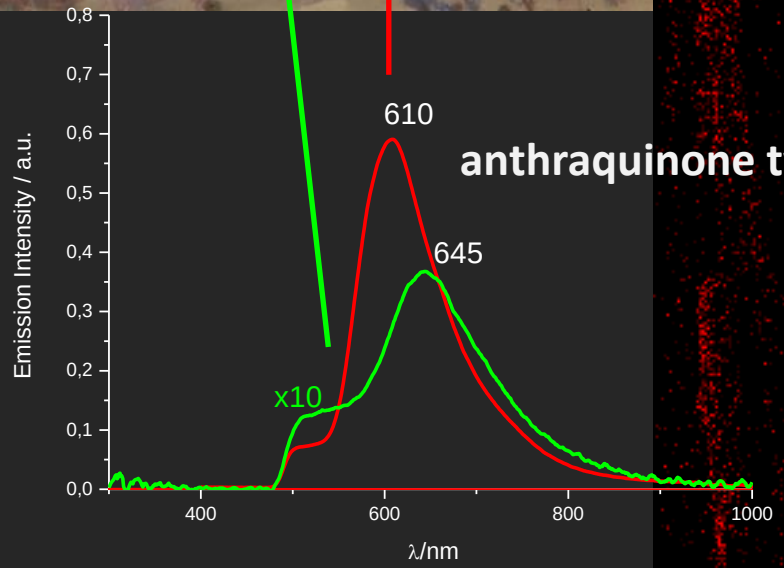
Special thanks to the MOLAB team:
Brenda Doherty, Francesca Rosi, Letizia Monico, Costanza Miliani,
Chiara Grazia, Aldo Romani, David Buti, Renato Pereira de Freitas

IPERION CH

Red strokes that do not show up in the elemental maps of Pb-Cd-Hg_L. P-rich



P-K



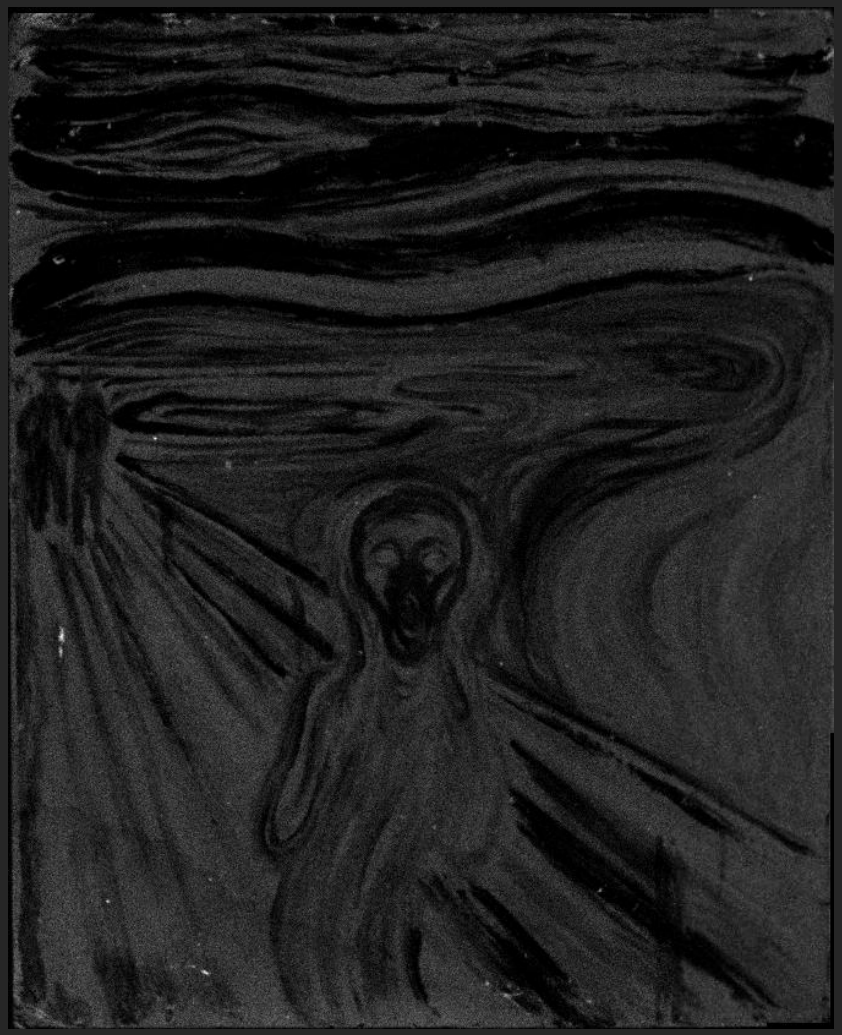
anthraquinone type

Cardboard - MM version

Pb-L

Lead = cardboard + paint

Ba-L



Barium = cardboard + retouchings

Cardboard - MM version

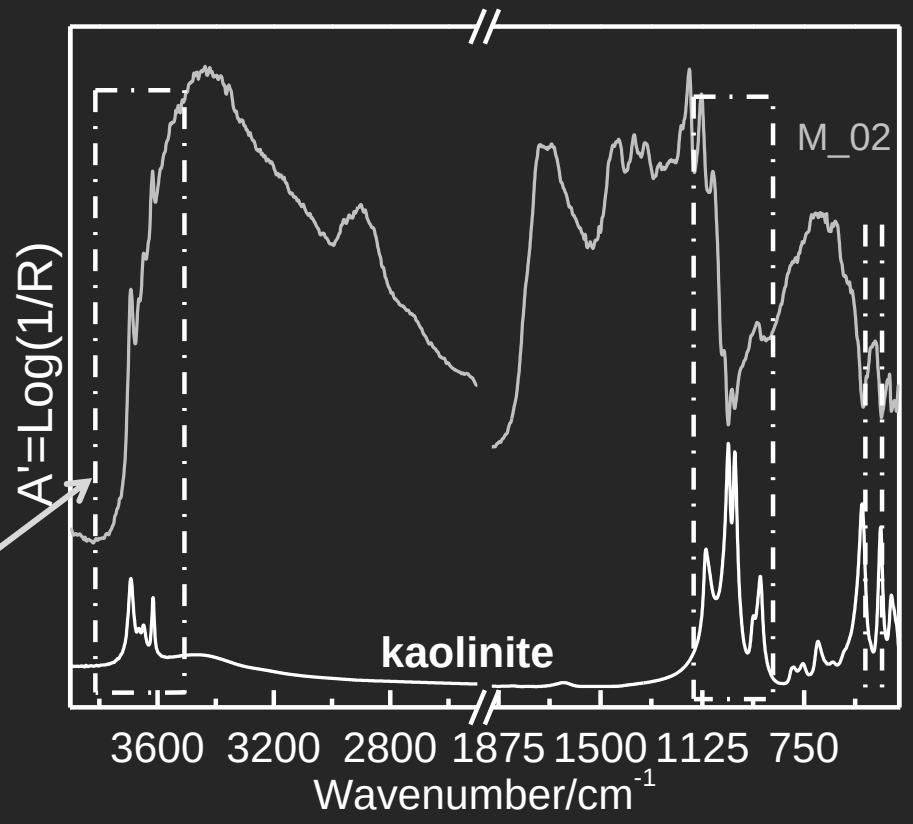
Ca-K

Fe-K

Calcium = cardboard + retouchings/stains

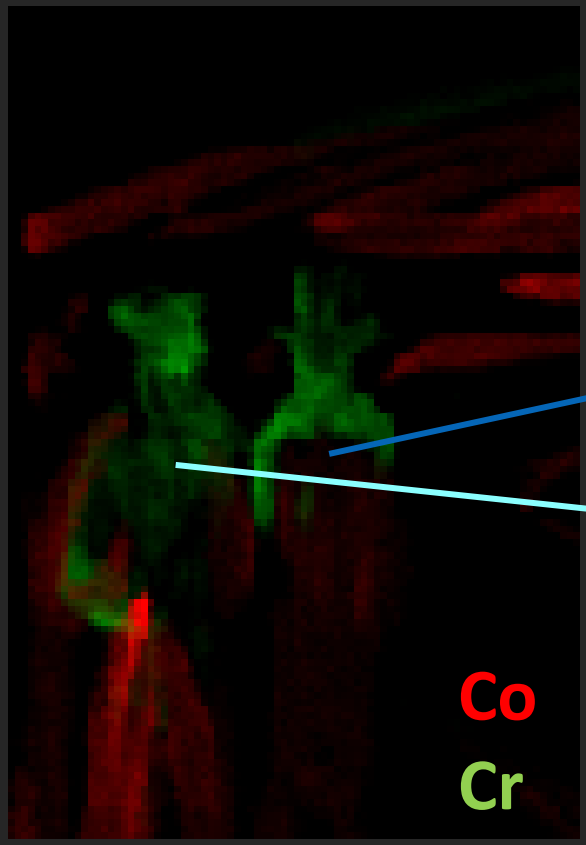
Iron = cardboard + retouchings/drippings

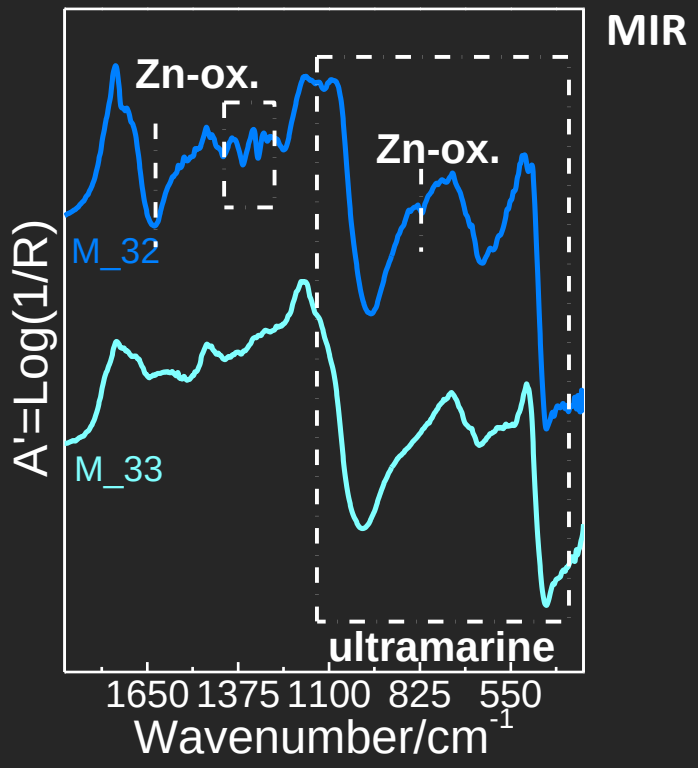
Cardboard



MIR : kaolinite

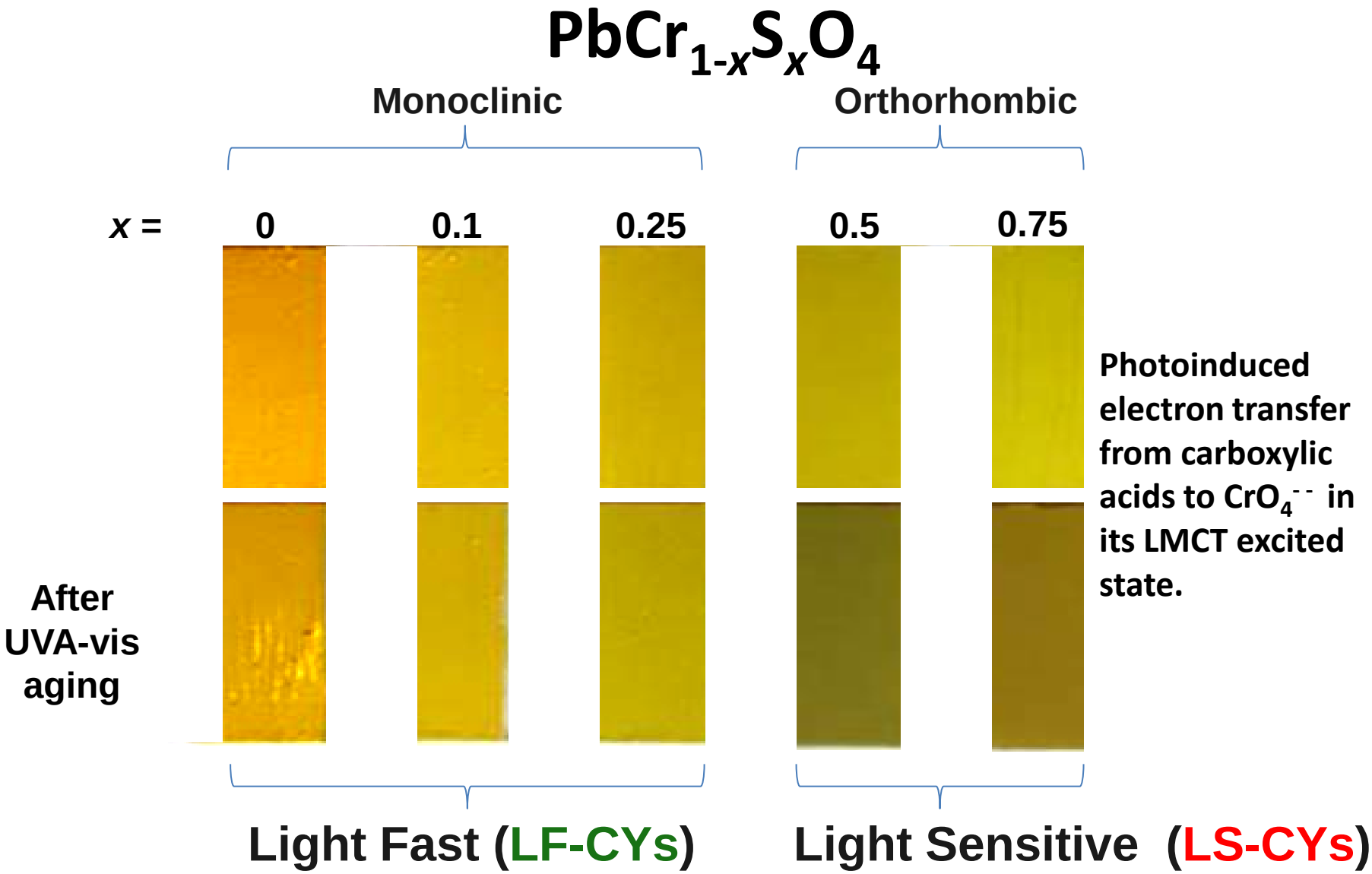
Complex blue paints





-identification of **ultramarine** in both areas;
-Only in M32: additional presence of zinc oxalates
- Presence of **Thenard blue** confirmed by UV-Vis-NIR spectroscopy

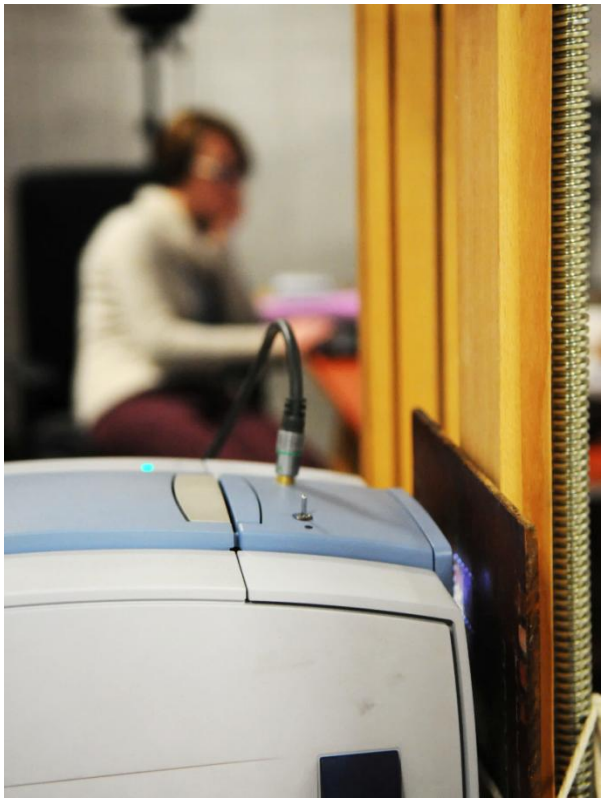
CY: structure, color & lightfastness



Mid-FTIR system used for monitoring of cleaning

The portable ALPHA (Bruker) spectrometer
– technical data:

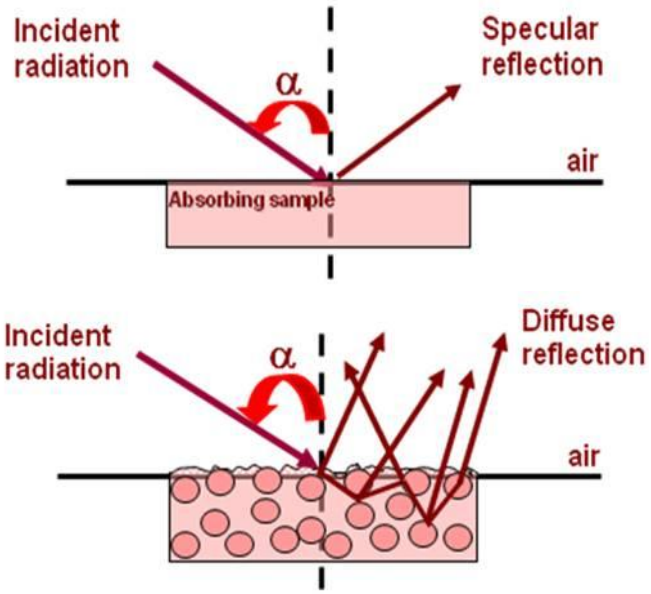
- Infrared source and a Globar DLaTGS detector
- Exploits a range from 7500 cm^{-1} to 375 cm^{-1}
- Spectral resolution of 4 cm^{-1}
- Spatial resolution of about 25 mm^2
  (5 mm spot)
- Distance to the object: 1 cm



Measurements were performed by an external reflectance module with an optical layout of 22°/22°. Pseudo-absorption spectra [log(1/R); R = reflectance] were acquired using by averaging of 186 spectral scans. Spectra from a gold flat mirror were used as background.

REFLECTION FTIR SPECTROSCOPY

- specificity for organic, inorganic and organometallic compounds
- High sensitivity for surface molecular properties
- Non-invasive, portable, fast and reliable

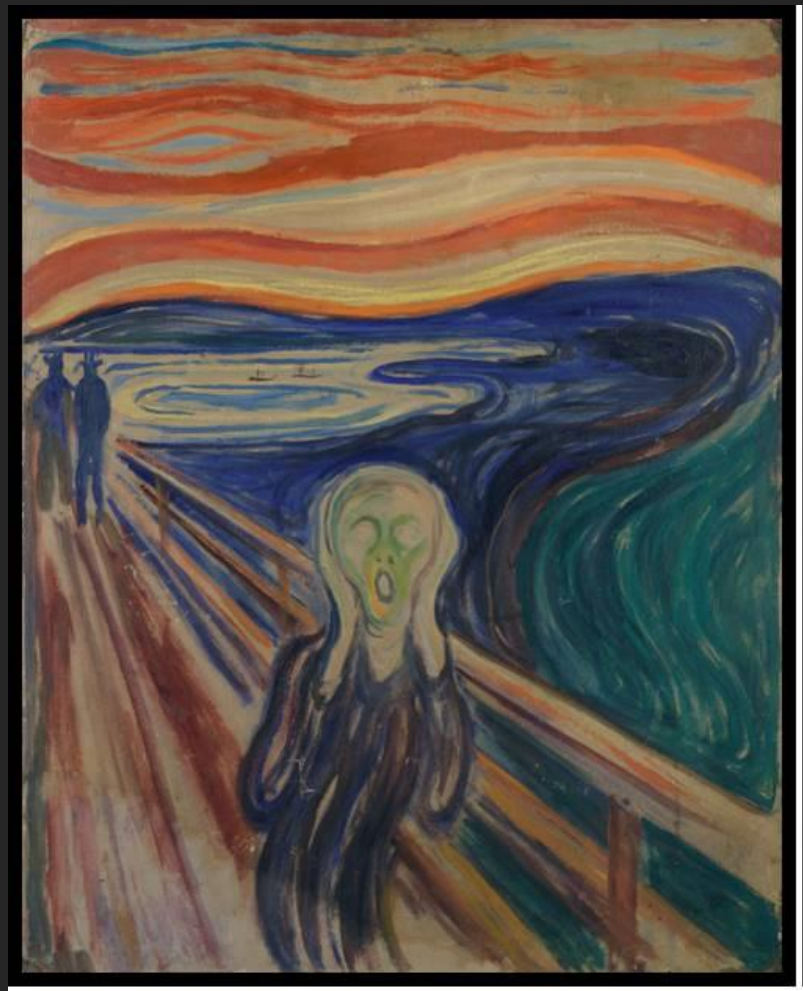


DISTORTION OF SPECTRAL FEATURES:

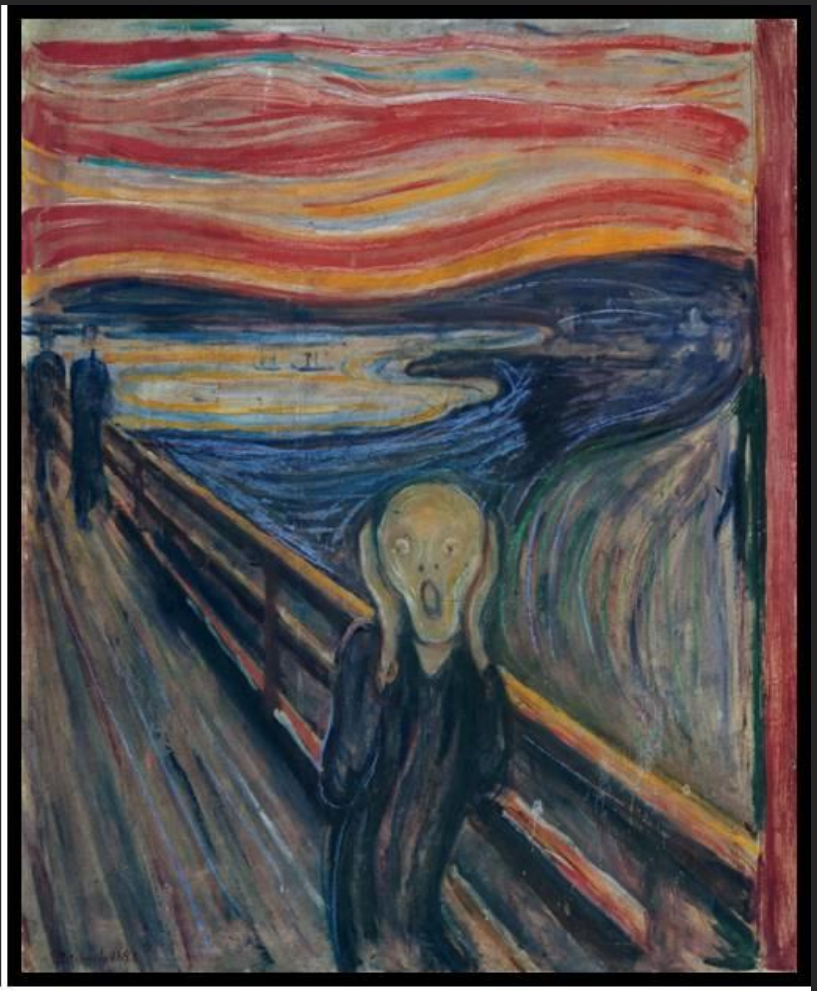
-INVERSION OF BANDS

- DERIVATIVE SHAPES

- CHANGES OF RELATIVE INTENSITY



MM Scream c. 1910
Tempera and oil on cardboard

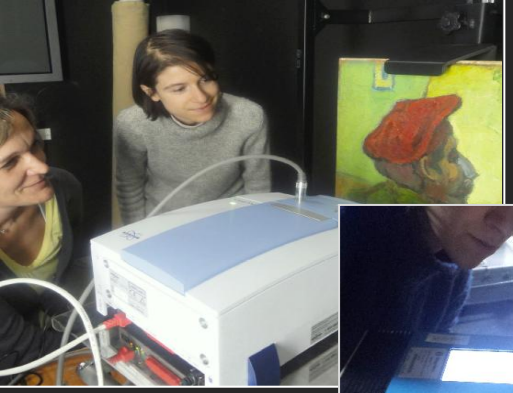


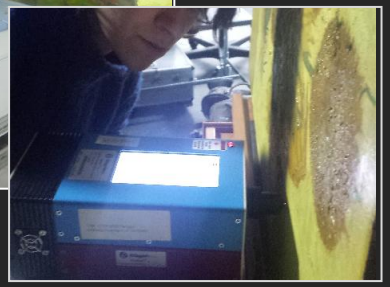
NM Scream 1893
Tempera and crayon on cardboard

CONCLUSIONS

	Support	Yellow/ Orange	Red/ Brown	Blue	Green	White	Alteration products/ synthesis residuals
MM version	Ca,Ba,Zn (low counts) Kaolin	CdS : ▪Hexagonal type 1 ▪Hexagonal type2 ▪Cubic/hexagonal $PbCr_{1-x}S_xO_4$	HgS Organic lakes (antraquinone type) Minium?	Thenard Blue Ultramarine	Viridian	ZnO	Zn Oxalates $CdCO_3$ Cd(OH)Cl
NM version	Fe	CdS Cr yellow	HgS Fe + Mn	Prussian blue? Not identified (No Cobalt blue)	Cr based green	Lithopone? ZnO? Lead white?	

POINT ANALYSES





Portable FT-IR ALPHA spectrometer by Bruker
-spectral range: 7400-345cm^{-1}
-spectral resolution 4 cm^{-1}

Portable Raman Xantus-2 spectrometer by Rigaku
-laser excitation at 785 nm
-spectral resolution 7-10 cm^{-1}

UV-Vis-NIR Absorption and Fluorescence Spectrometer
-deuterium-halogen lamp source
-absorption and emission measurements
-spectral range: 300nm -1100nm

Fluorescence Lifetime Spectrometer
-pulsed laser sources (375nm and 650nm picosecond scale)
-single photon counting
-minimum area: 12 mm^2 (spatial resolution)
-time resolution: 100 picoseconds