From X-ray to radio wave: the multi-technique diagnostic of the European mobile laboratory MOLAB

Aldo Romani

Excellence Centre SMAArt (Scientific Methodologies applied to Archaeology and Art)
c/o Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia,
Via Elce di Sotto, 8, 06123, Perugia, Italy;

aldo.romani@unipg.it

FP6

2004 – 2009 Eu-ARTECH - http://www.eu-artech.org/ Access, Research and Technology for the conservation of the European Cultural Heritage; coordinated by UNIPG

B.G. Brunetti

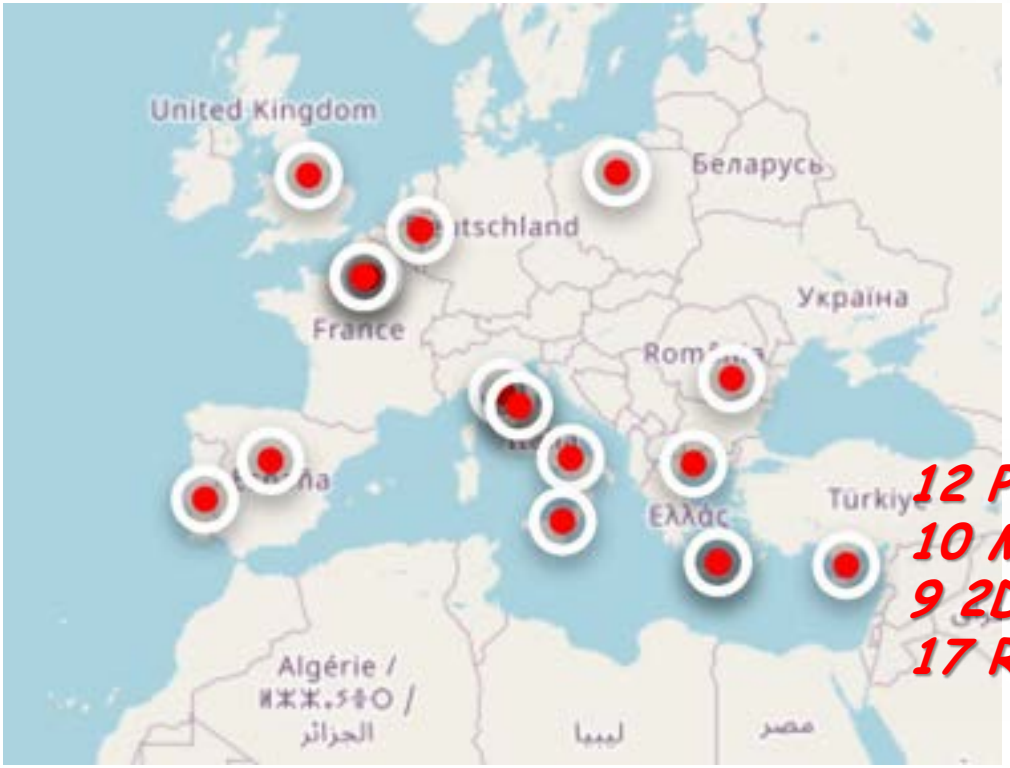
A. Sgamellotti

MOLAB®

Access activity

Ten portable instruments, XRF, FTIR, UV-VIS, Raman, etc. (7 UNIPG, 2 CNR, 1 OPD) for in-situ not invasive diagnostic on Cultural Heritage

2019 – 2024 Integrated Platform for the European Research Infrastructure ON Heritage Science http://www.iperionhs.eu/ coordinated by CNR



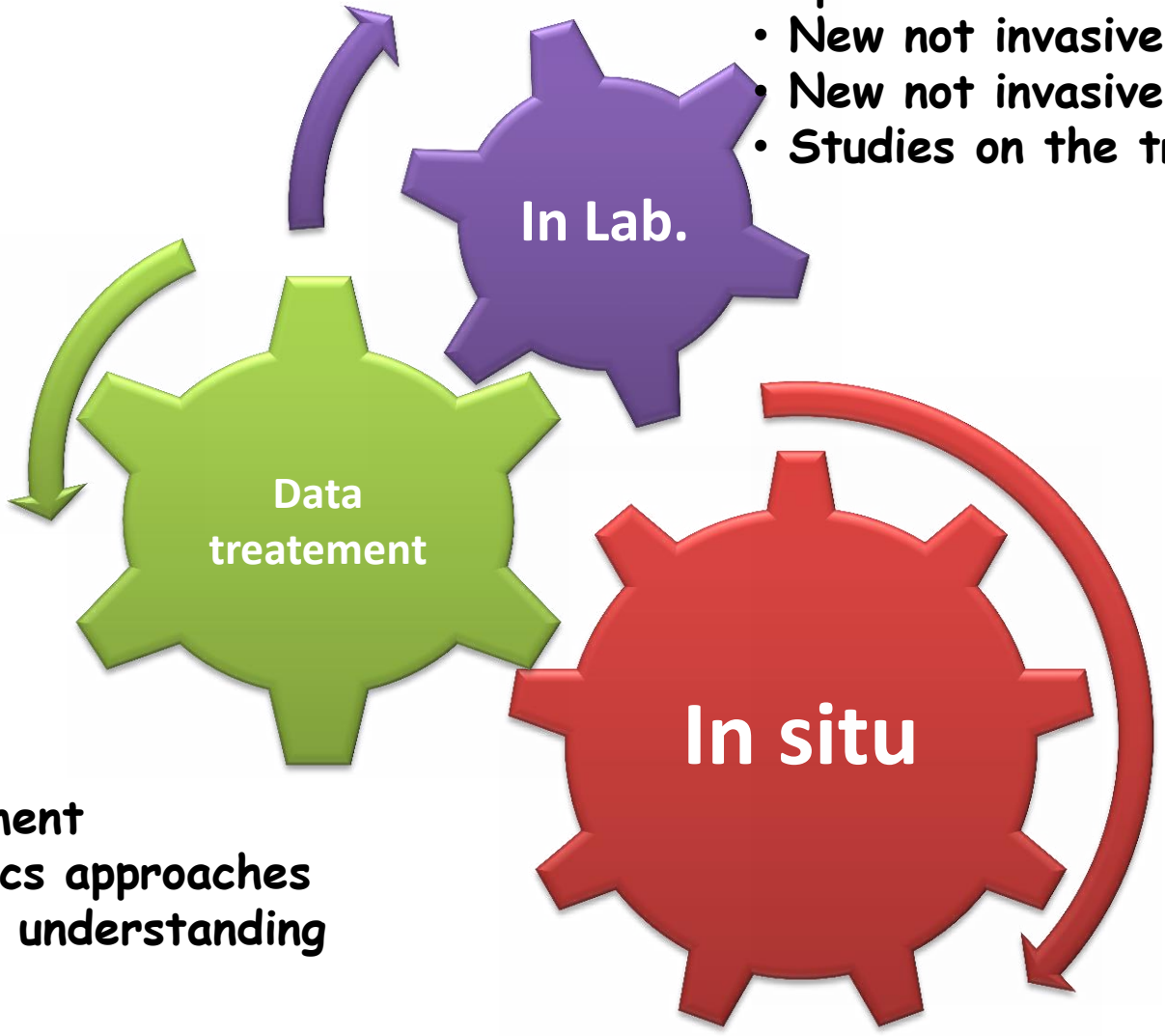
E-RIHS
EUROPEAN RESEARCH INFRASTRUCTURE FOR HERITAGE SCIENCE

16 research units from da 10 European countries, providing **48 portable instruments**

12 Point analysis
10 Multi/Hyper spectral imaging/mapping
9 2D/3D analysis
17 Remote sensing

MOLAB *modus operandi*

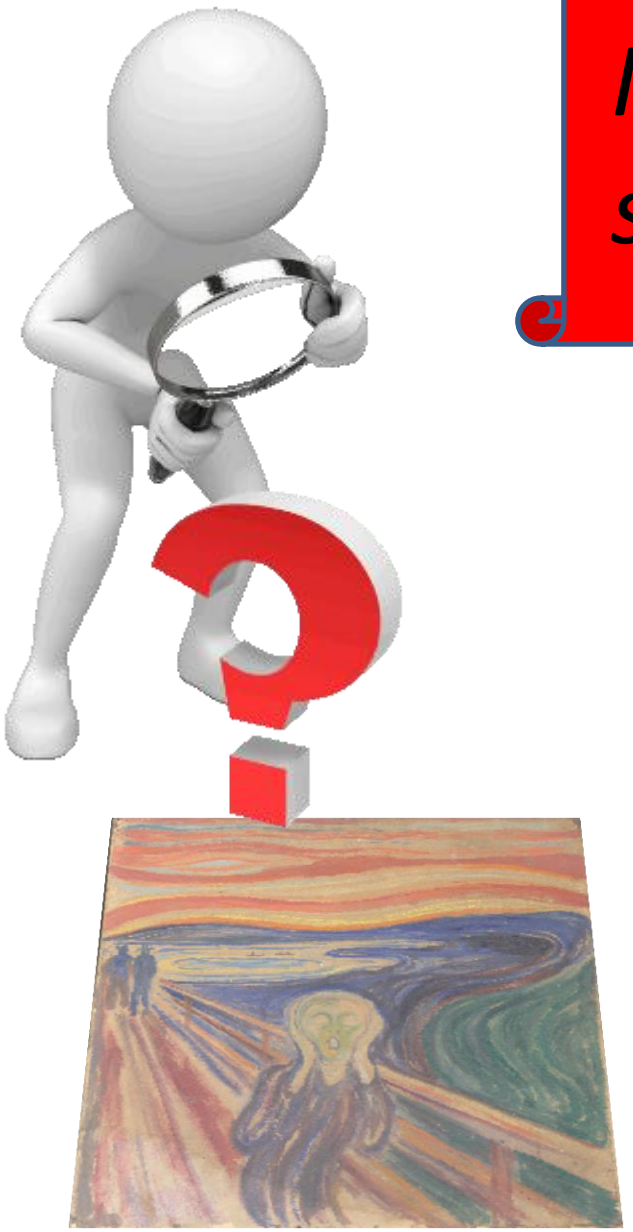
- Spectral database
- New not invasive methods
- New not invasive techniques
- Studies on the transformations



- Data treatment
- Chemometrics approaches
- Mechanisms understanding

In Lab

In situ




The Book of Kells
Trinity College Library Dublin

Matthew

Matthew_58_I_2v

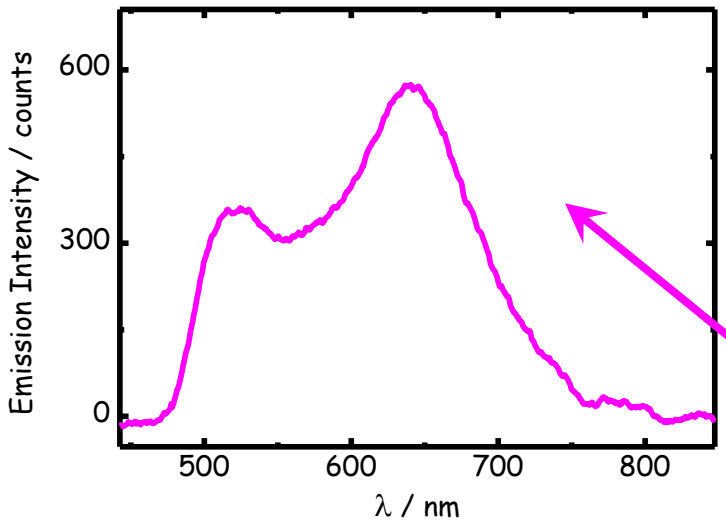
Matthew_58_I_7v

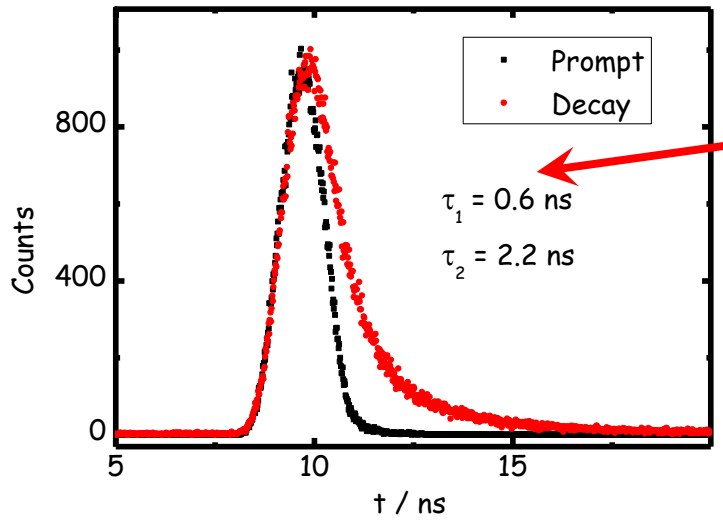
Matthew_58_I_114r

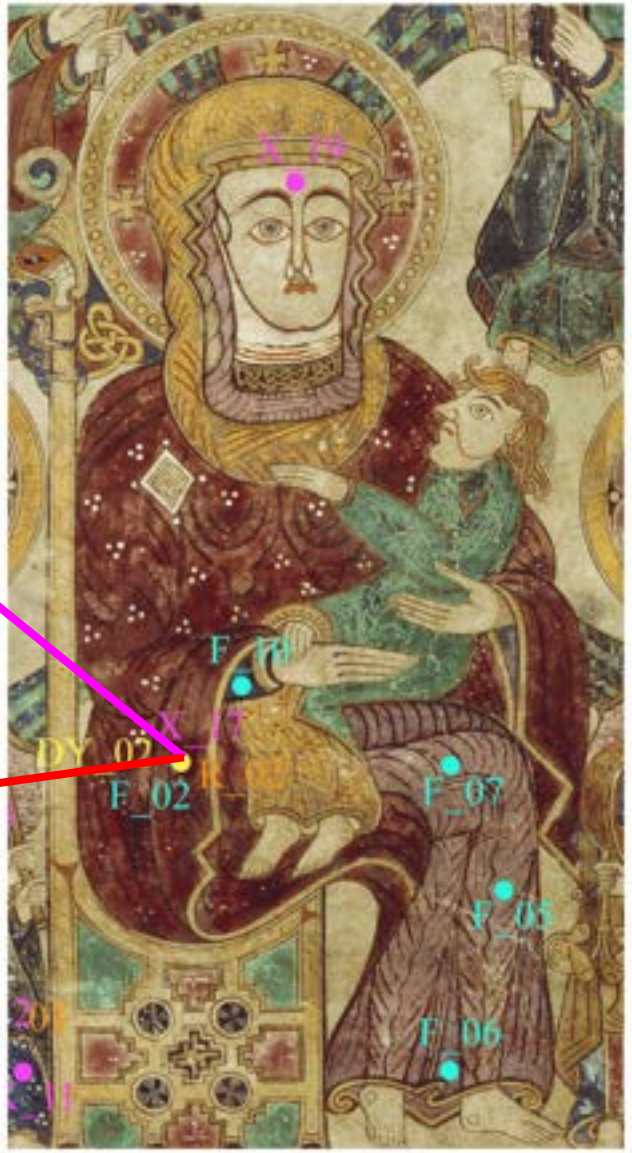

Centro di Eccellenza
SMAArt
Università degli Studi di Perugia

SCITEC

Orcein

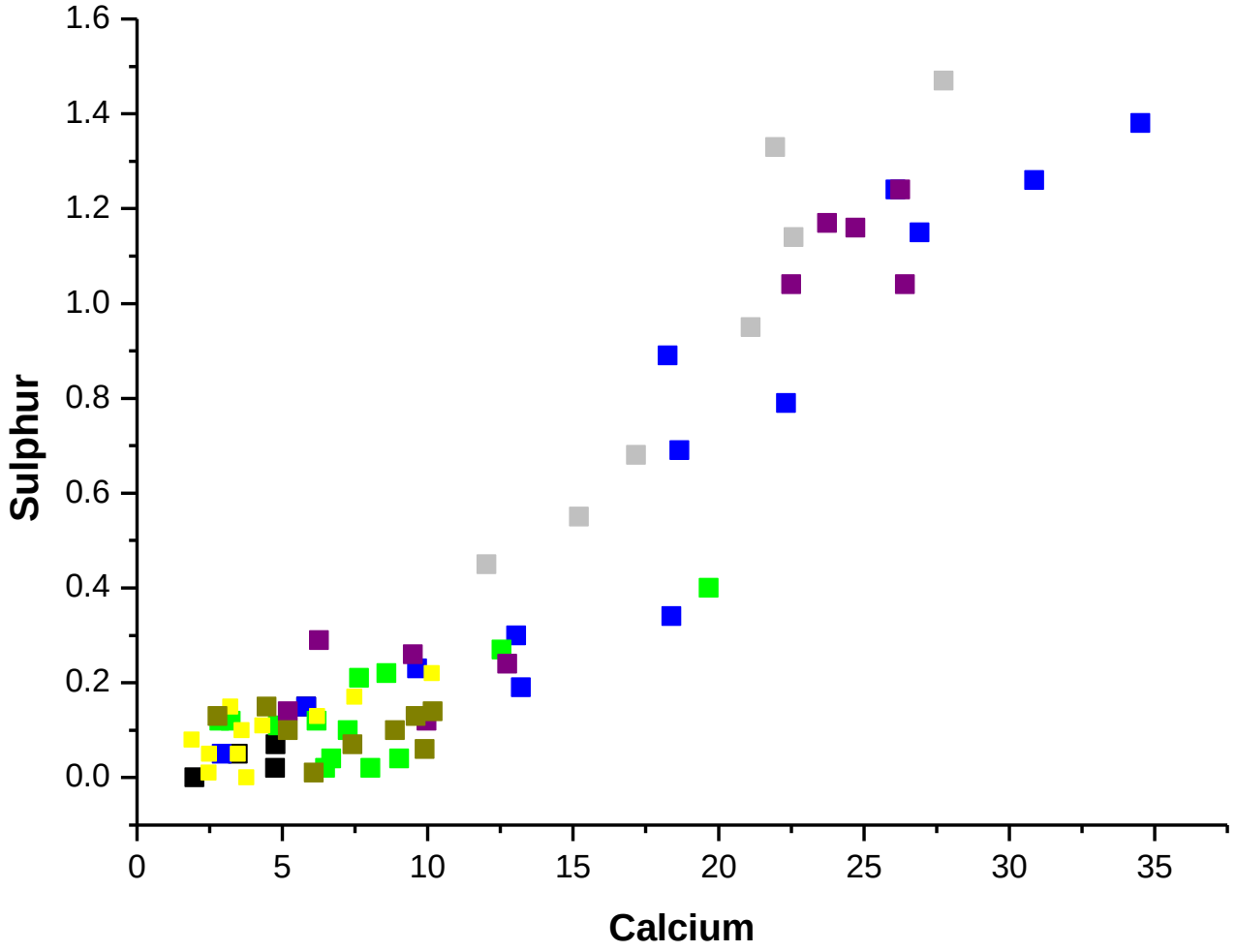




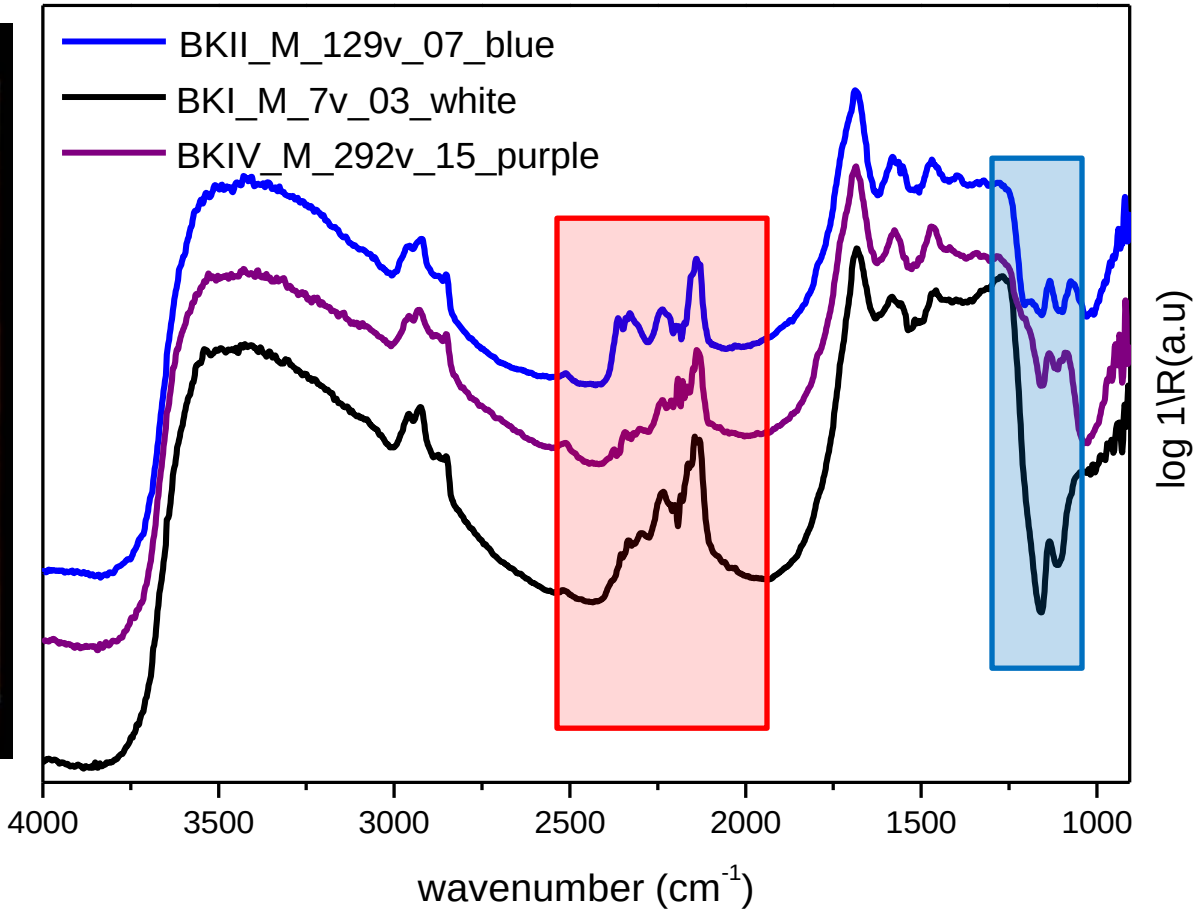


A. Romani, C. Clementi, C. Miliani, G. Favaro, Acc. Chem. Res., 43(6), (2010) 837

XRF: Calcium *vs.* Sulphur



Infrared spectra highlight the presence of calcium sulphate (ν_3 SO_4^- at 1140 cm^{-1}) in blu, violet and white zones of all the four books



The spectral region between 2000-2500 cm^{-1} shows characteristics of the specific crystalline phases oc calcium sulphate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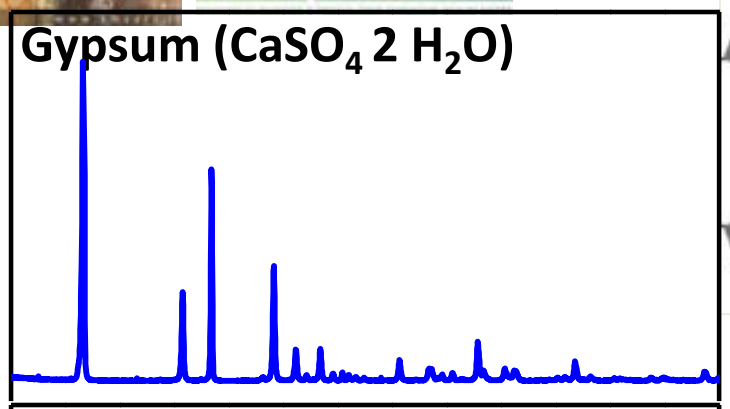
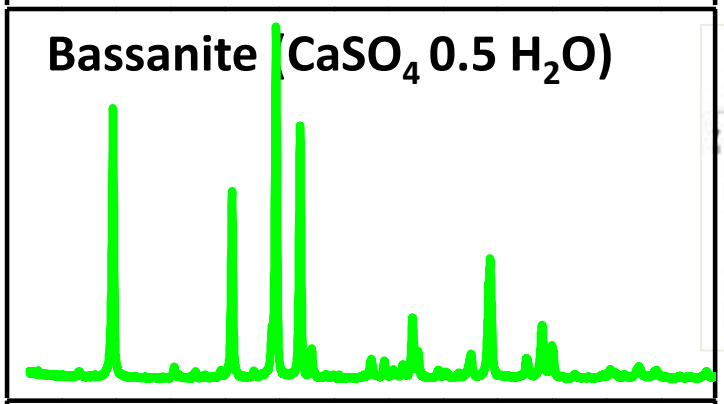
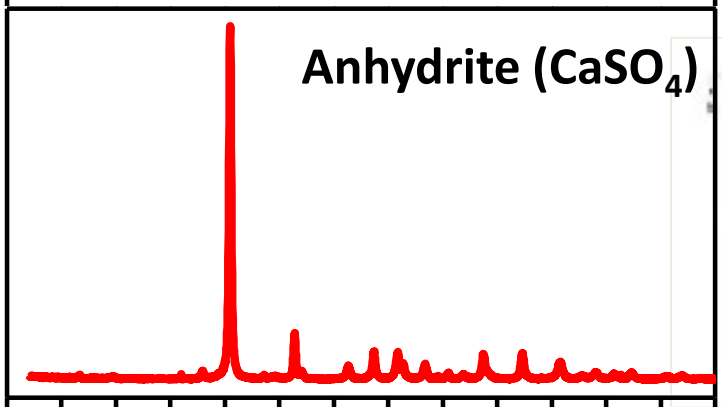
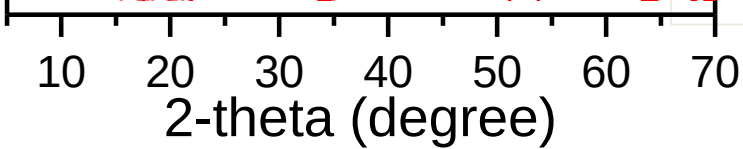
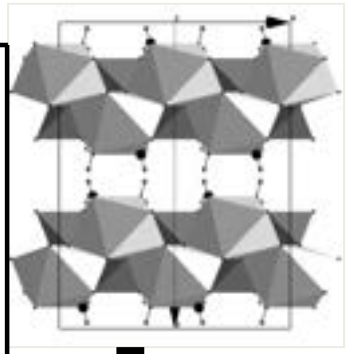

Gypsum (CaSO4 2 H2O)

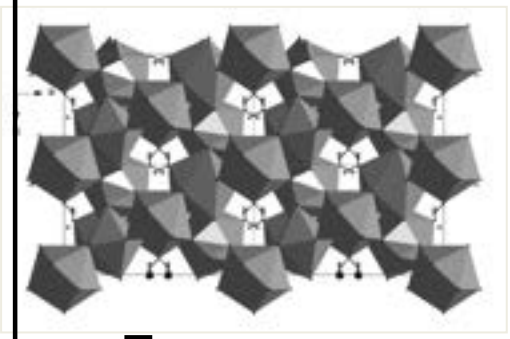

Bassanite (CaSO4 0.5 H2O)


Anhydrite (CaSO4)

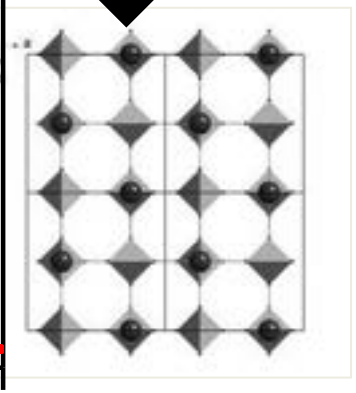

10
20
30
40
50
60
70
2-theta (degree)

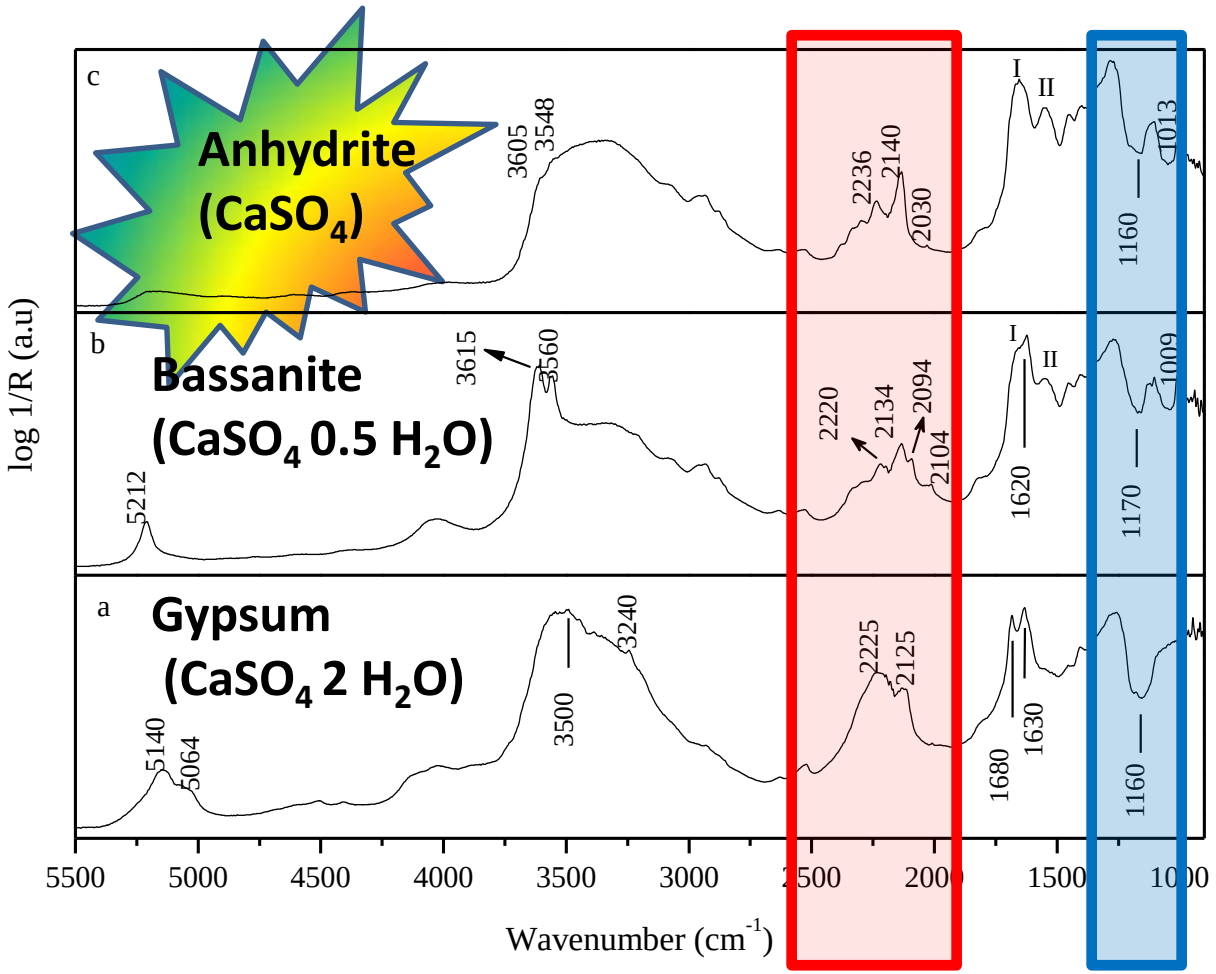


135°C



400°C





MID-FT-IR spectra of pictorial replicas prepared with gypsum, bassanite and anhydrite

B. Doherty, A. Daveri, C. Clementi, A. Romani, S. Bioletti, B. Brunetti, A. Sgamellotti, C.Miliani, *Spectrochimica Acta A, 115 (2013) 330–336*

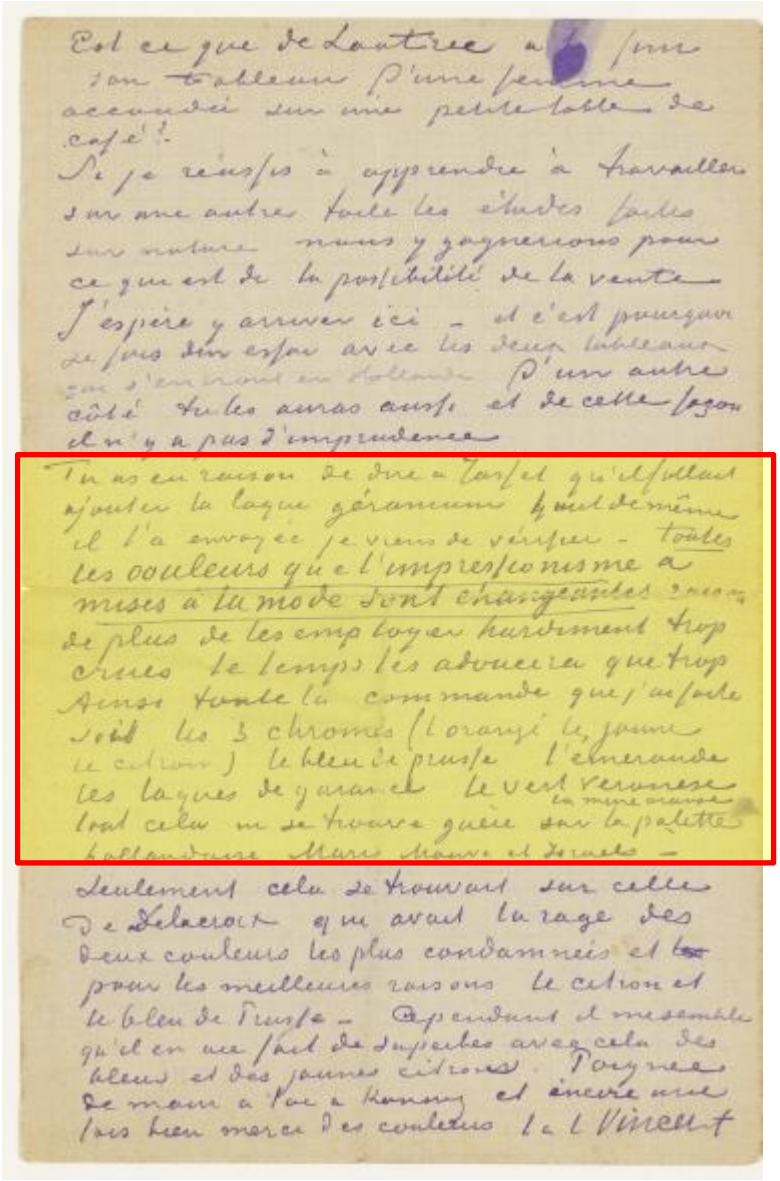
A technical in situ examination of paintings by Vincent van Gogh: focus on the alteration of chrome yellow paints

VAN GOGH MUSEUM
AMSTERDAM

Low photochemical stability and tendency to lose original brilliance.

Sunflowers, repetition of the 4th version (yellow background), Van Gogh Museum, Amsterdam, NL.

What is the alteration mechanism?
What are the factors that induce the darkening?

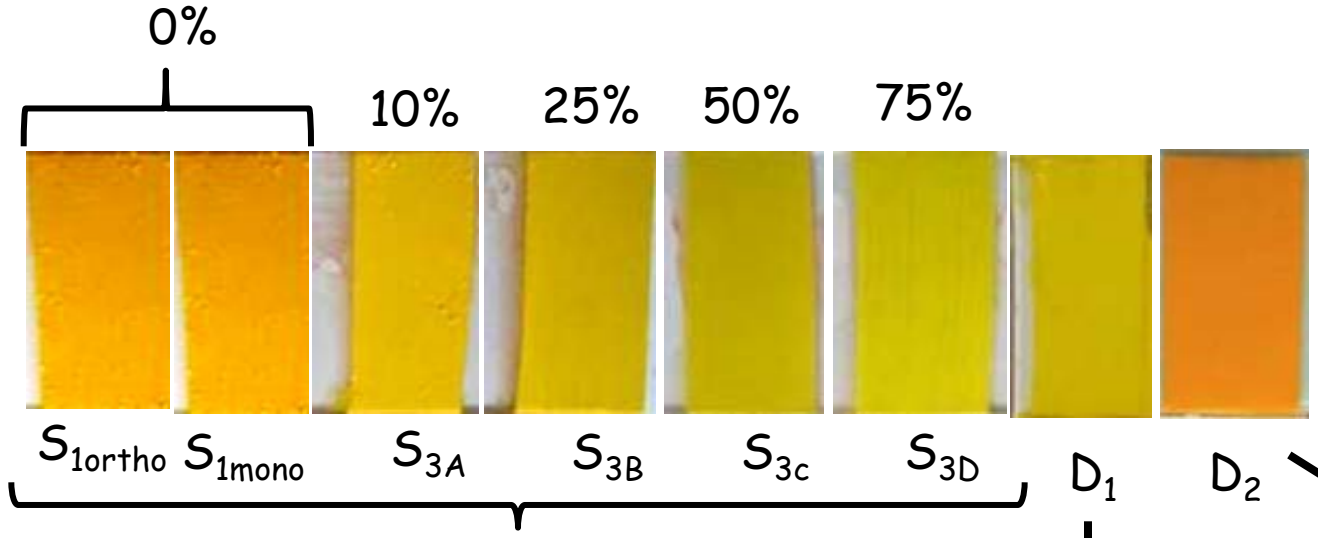


Van Gogh was already aware of the instability of the chrome yellow pigments.

"[…] You were right to tell Tasset that the geranium lake should be included after all, he sent it, I've just checked — **all the colors that Impressionism has made fashionable are unstable**, all the more reason boldly to use them too raw, time will only soften them too much. So the whole order I made up, in other words the **3 chromes (the orange, the yellow, the lemon)** the Prussian blue, the emerald, the madder lakes, the Veronese green, the orange lead, all of that is hardly found in the Dutch palette, Maris, Mauve and Israëls. […]"

(letter n. 595, to Theo van Gogh. Arles, 11 April 1888)

Pictorial linseed oil reproductions containing chrome yellows with different composition



Synthesized in lab

$PbCrO_4$ +$PbSO_4$(1:2)

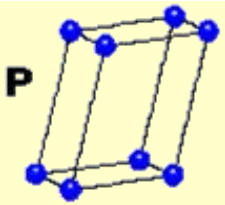
Commercial pigment (CIBA, BASF)

MONOCLINIC

$a \neq b \neq c$

$\alpha = \gamma = 90°$

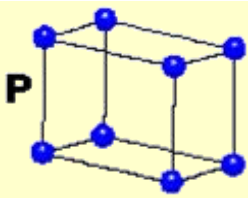
$\beta \neq 120°$



ORTHORHOMBIC

$a \neq b \neq c$

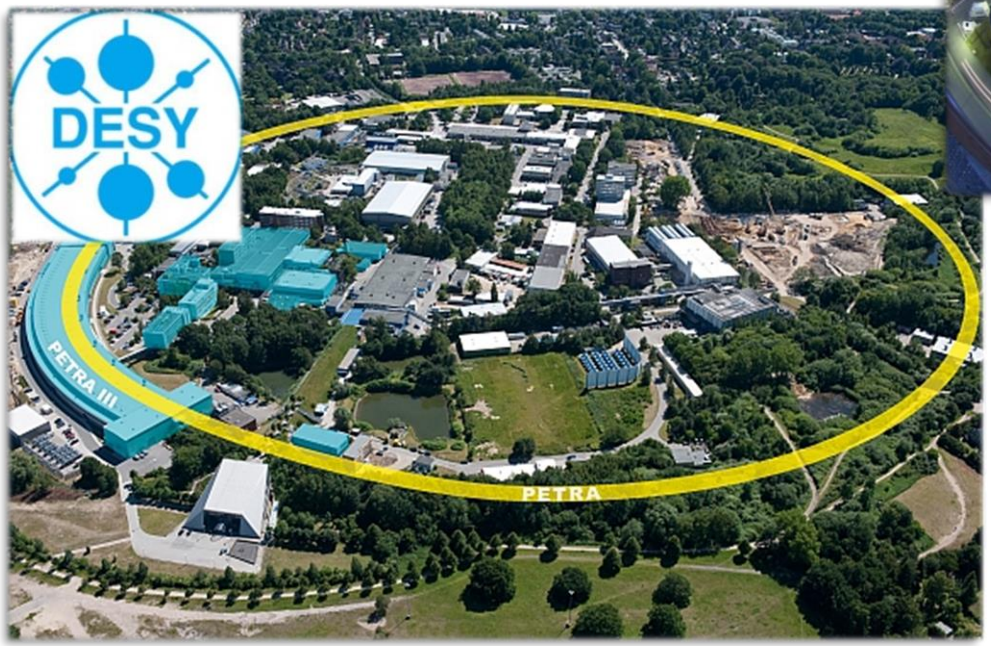
$\alpha = \beta = \gamma = 90°$



Photochemical ageing:
SOLARBOX 1500e
800 hours, T= 50-60 °C

European Synchrotron Radiation Facility

Grenoble (F)



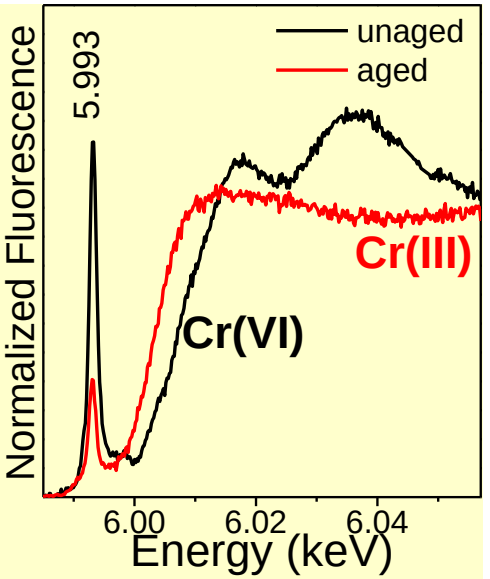
Deutsches Elektronen-Synchrotron

Hamburg (D)

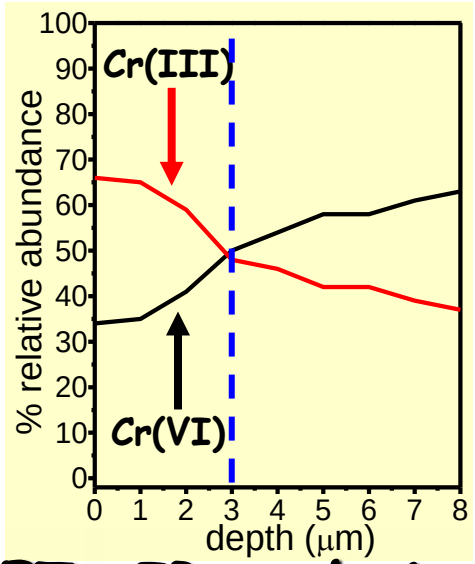
micro-mapping with XANES, XRF, XRD,…

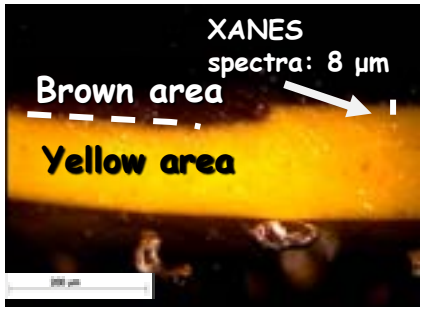
Alteration: chrome VI to chrome III reduction

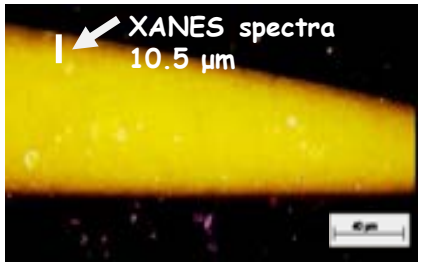
Sample A S_{3D} (75% SO_4^{2-})

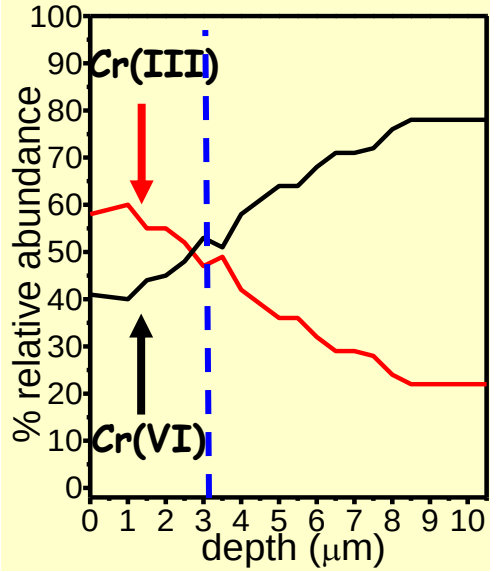


UVA-visible light , 800 h, T~ 55°C









FT- IR analysis : degradation products identification → **Organo-metalic compounds**

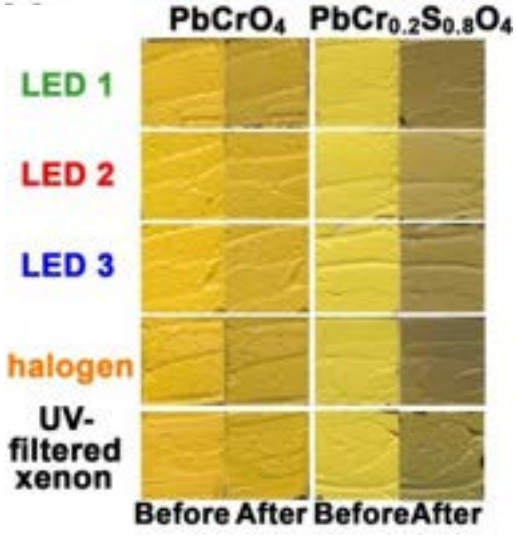
→ **Amorphous Cr(III) oxide**

L. Monico et al., *Analytical Chemistry*, 83 (2011) 1214-1223 DOI: 10.1021/ac102424h

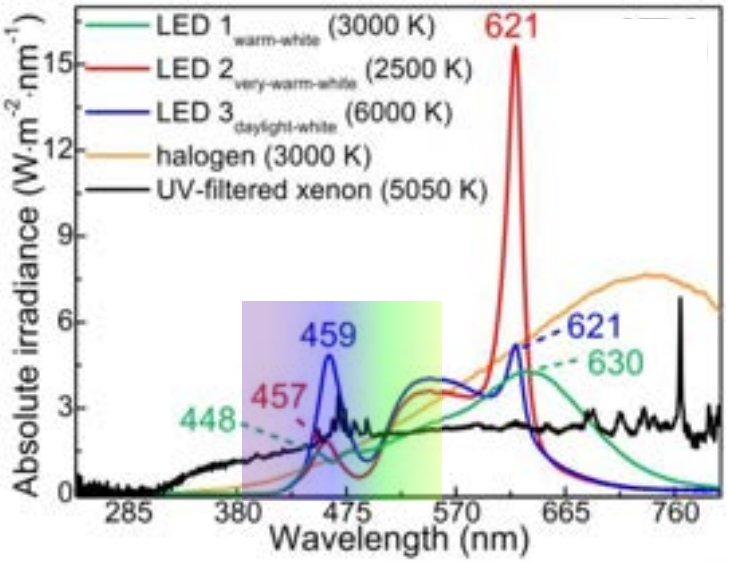
L. Monico et al., *Analytical Chemistry*, 83 (2011) 1224-1231 DOI: 10.1021/ac1025122

Aging experiments with commercial white sources

Aging of a series of oil paints containing the lightfast monoclinic $PbCrO_4$ and the light-sensitive $PbCr_{0.2}S_{0.8}O_4$



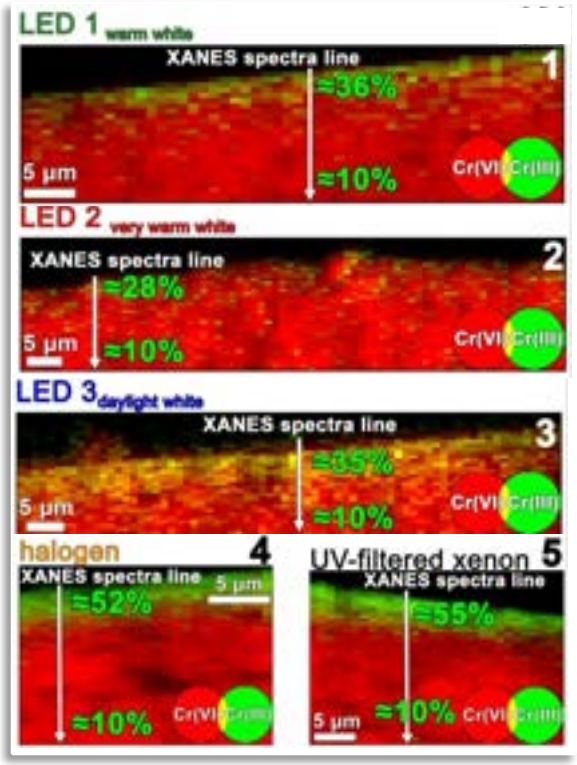
The darkening of the paint surface depends on the employed illumination device

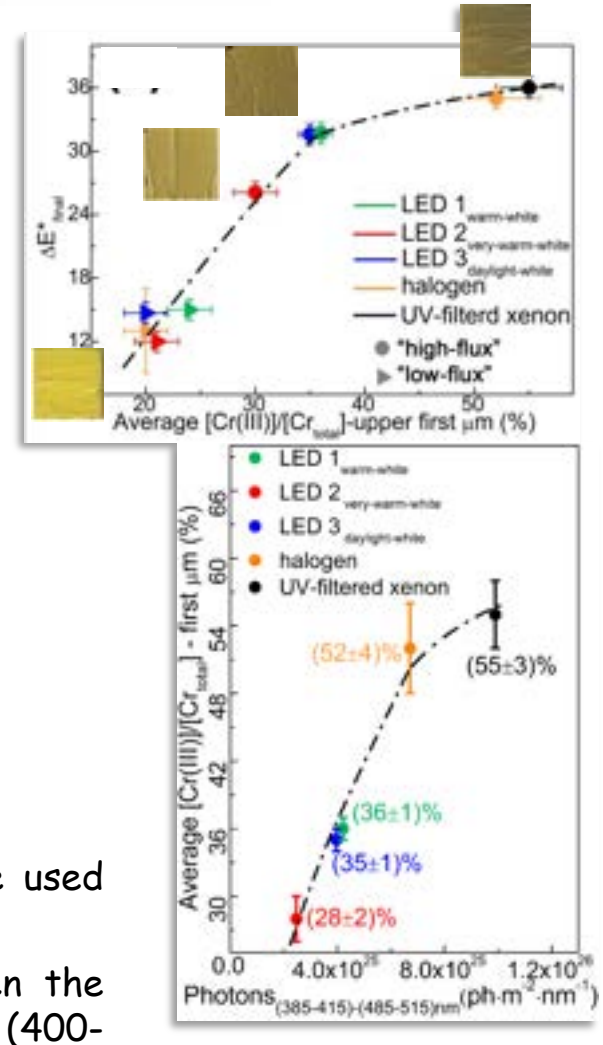


Different emission of the lamps in the region around the maximium absorption of the pigment

SR μ-XANES/XRF & colorimetric analysis

light-sensitive $PbCr_{0.2}S_{0.8}O_4$

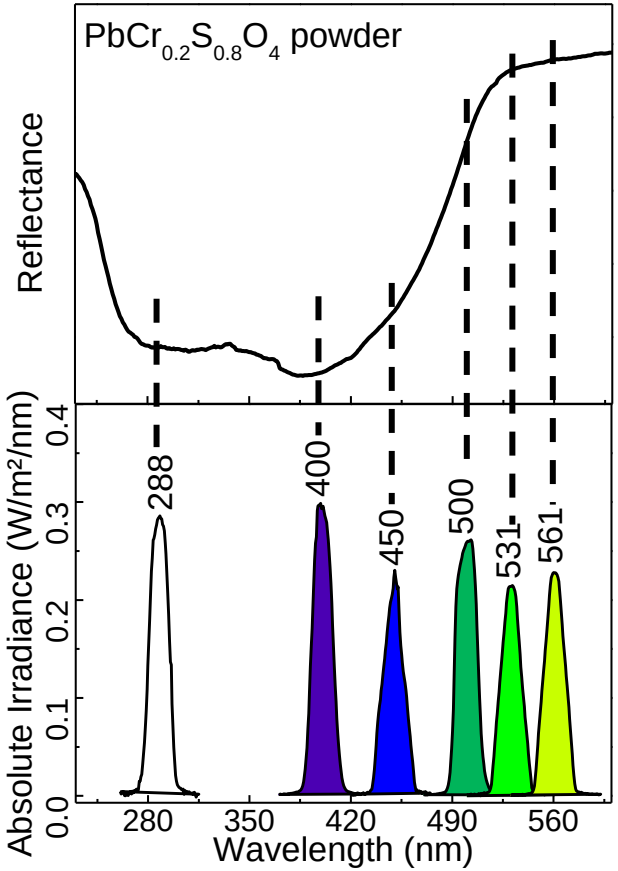




lightfast $PbCrO_4$: ~10-15% of Cr(III), irrespective of the used lamp.

light-sensitive $PbCr_{0.2}S_{0.8}O_4$: positive correlation between the Cr(III) and the ΔE*/amount of violet-blue-green radiation (400-530 nm) emitted by the source.

Exposure of $PbCr_{0.2}S_{0.8}O_4$ to monochromatic lights

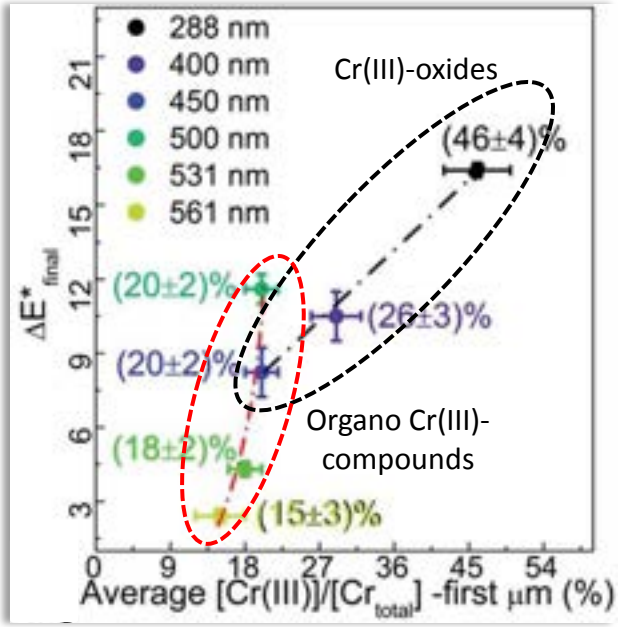


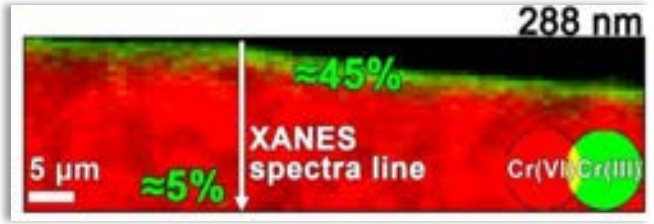
Study of the darkening response of the light-sensitive chrome yellow pigment toward exposure to selected wavelengths.

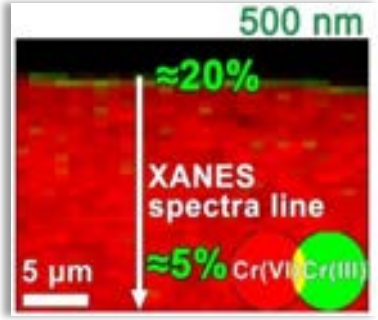
The wavelengths employed for the aging experiments were selected on the basis of the UV-Vis spectrum of the $PbCr_{0.2}S_{0.8}O_4$ powder.

SR μ-XANES/XRF & colorimetric analysis

Confirmation of the effects of the violet-blue-green light



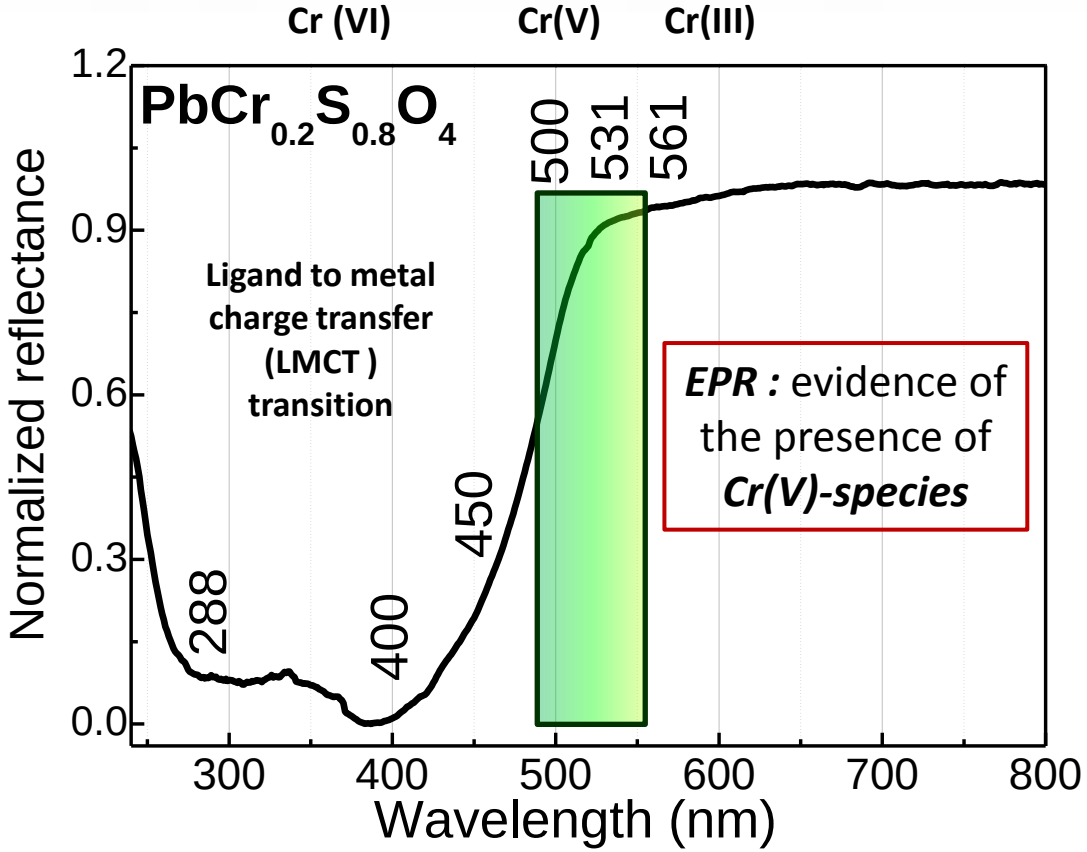




The Cr(III)-amount depends on the wavelength.

Two different positive correlations: indication of the formation of various Cr(III)-compounds.

Why is S-rich CY vulnerable to green radiation?



Cr(VI) is thermally reduced to Cr(V) by radicals produced during oil drying.

Cr(V) is stabilized by the ligands of the oil medium.

L. Monico et al., *J. Anal. At. Spectrom.*, 30 (2015) 1500-1510 DOI: 10.1039/c5ja00091b

Multi/Hyper spectral imaging

VIS hyper spectral imaging
NIR hyper spectral imaging
SWIR hyper spectral imaging
X-ray fluorescence mapping

painting technique

underdrawing

underpaints

Point chemical analysis

X-ray fluorescence
Mid-FTIR
Near-FTIR
Raman
X-ray diffraction
UV-Vis absorption
UV-Vis fluorescence

pigments and dyes

organic components

alteration products

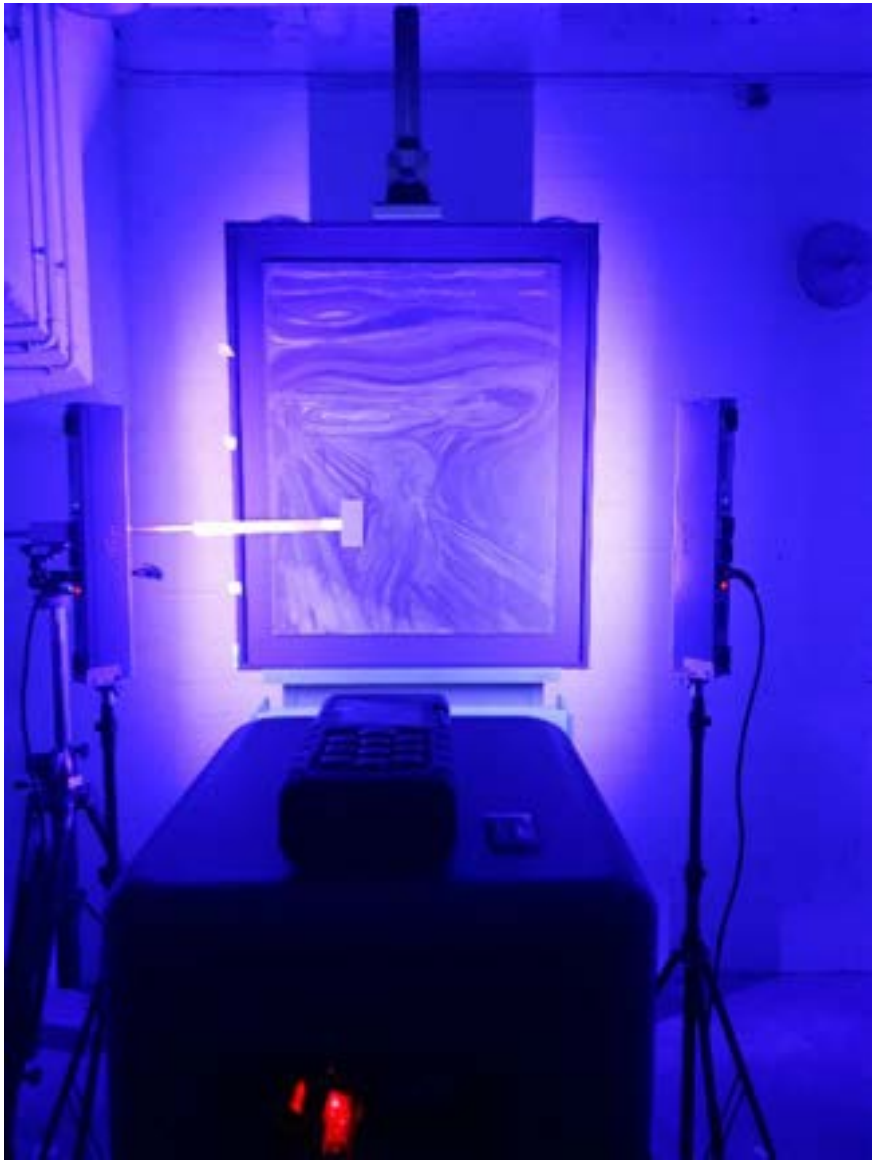
conservation treatments

MOLAB @ Munch Museum

MUNCH
MUSEET

Fluorescence Hyperspectral Imaging

X-ray fluorescence mapping



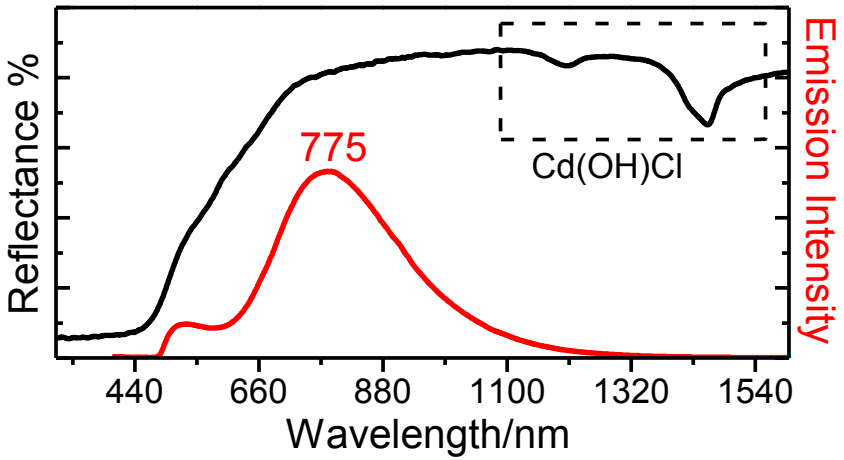
XRF Cd-L mapping

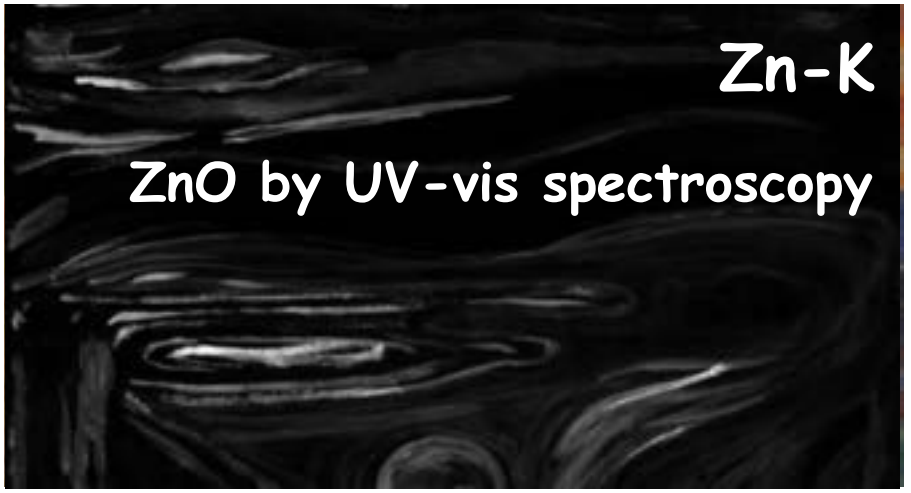
fluorescence hyper spectral imaging @ 775nm

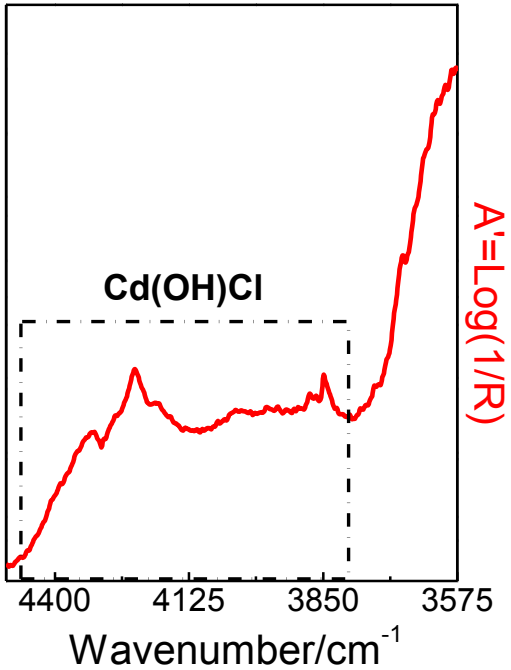
Cd-L

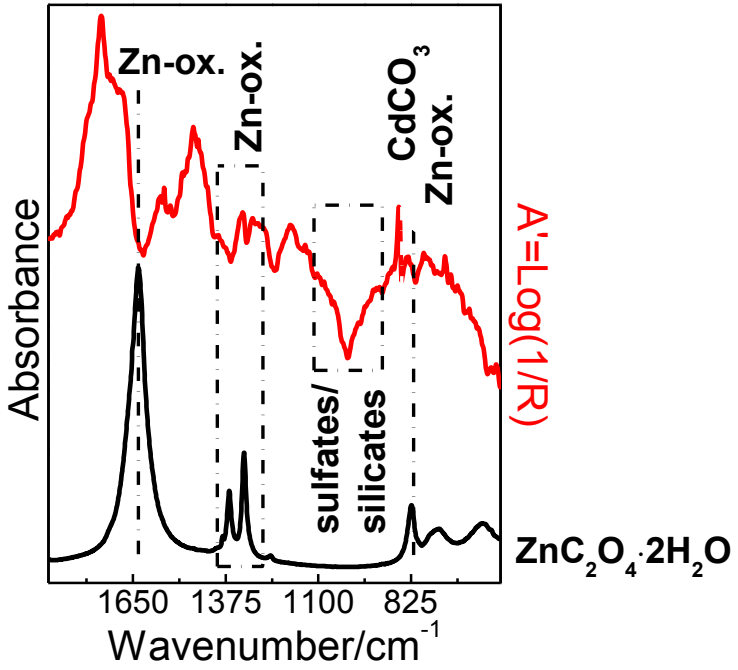
CdS emission

Yellow shades of the sky and lake





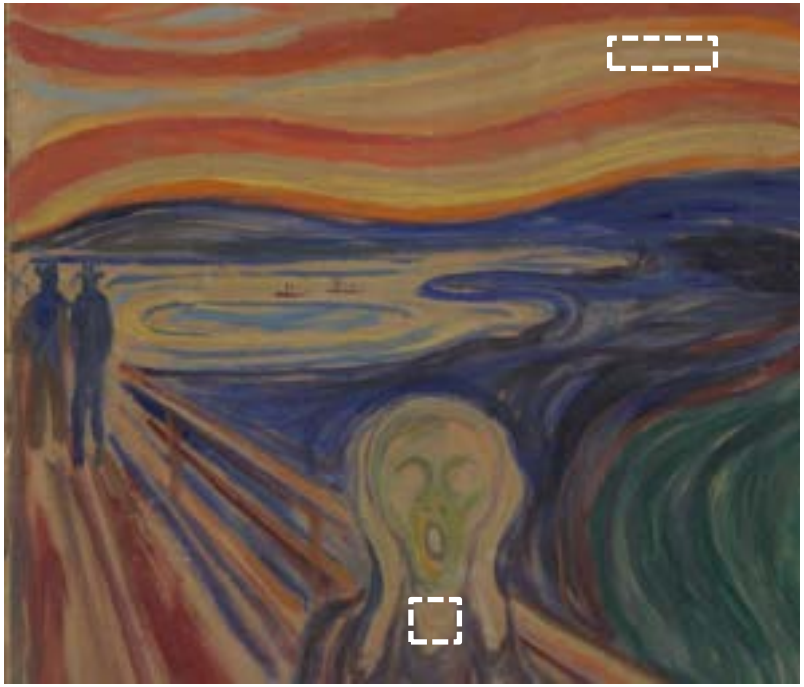




-**Hexagonal CdS**-based yellow pigment characterized by a fluorescence band at 775nm

- identification of cadmium carbonate and zinc oxalates and *Cd(OH)Cl* by MIR

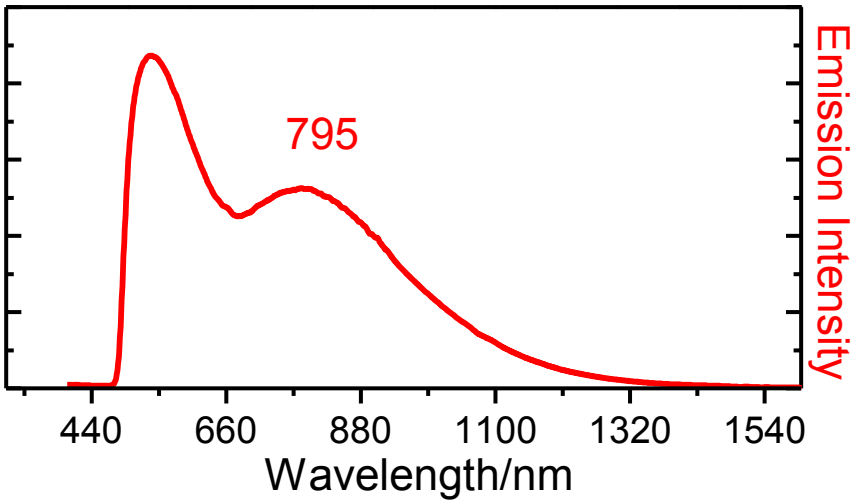
yellow areas: sky and neck of the man



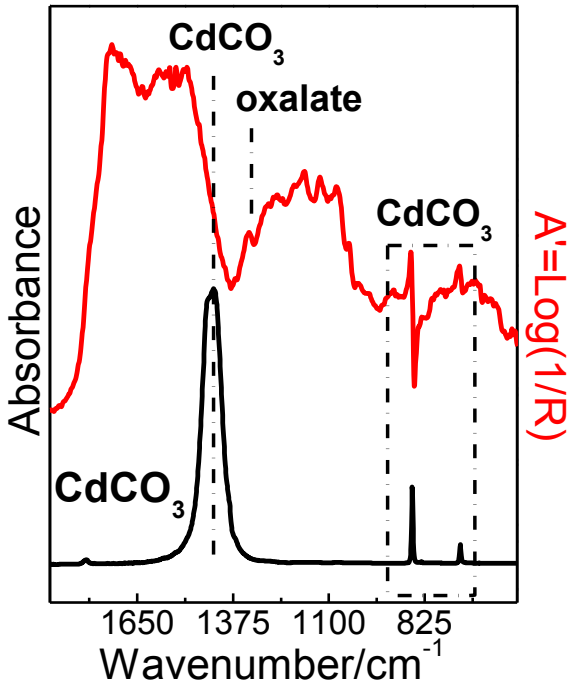
- **Hexagonal CdS**-based yellow pigment characterized by a weak fluorescence band at 795 nm

- identification of cadmium carbonate and oxalates by MIR spectroscopy

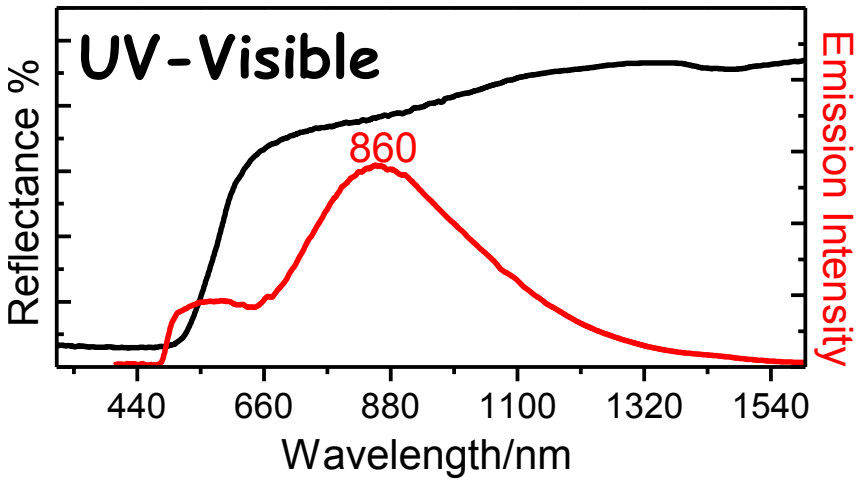
UV-vis Fluorescence

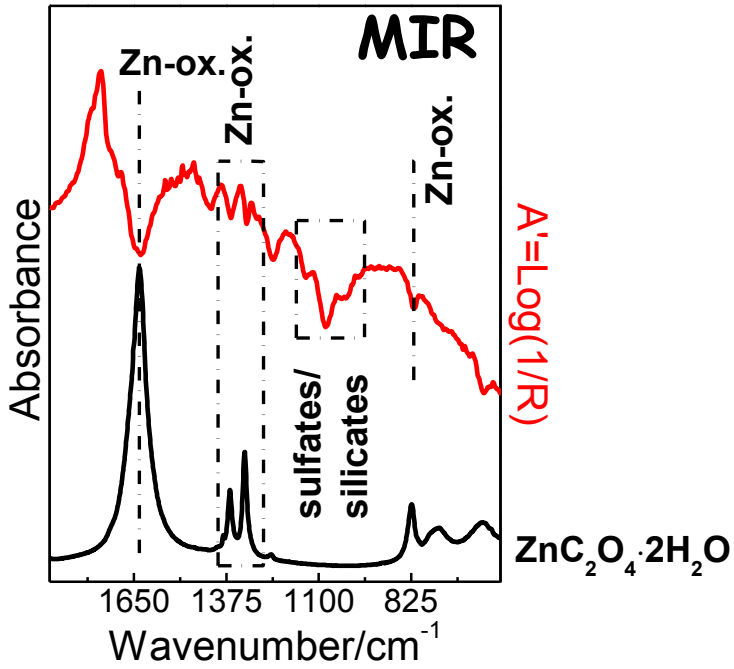


MIR



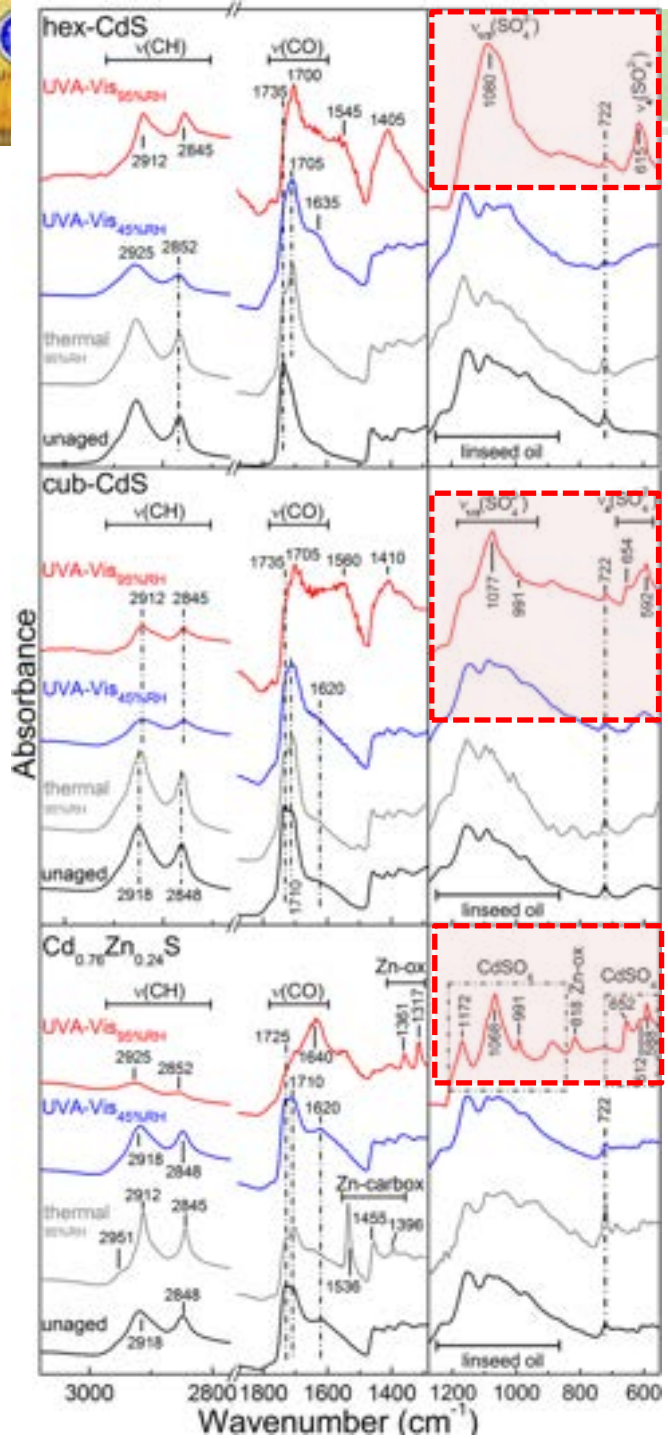
Orange hues of the sky





-**Cubic+Hexagonal** **CdS**-based pigment characterized by a fluorescence band at 860 nm and reflectance band with inflection point at about **530** nm.
-Second inflection point at **590** nm indicating a red pigment (HgS)

- identification of zinc oxalates (signals more intense than in the yellow tones) and sulfates and/or silicates by MIR spectroscopy. No presence of cadmium carbonate and Cd(OH)Cl in this area.



Cadmium sulphate and organo-metallic compounds

No changes

Oxalates

Cadmium sulphate and organo-metallic compounds

No changes

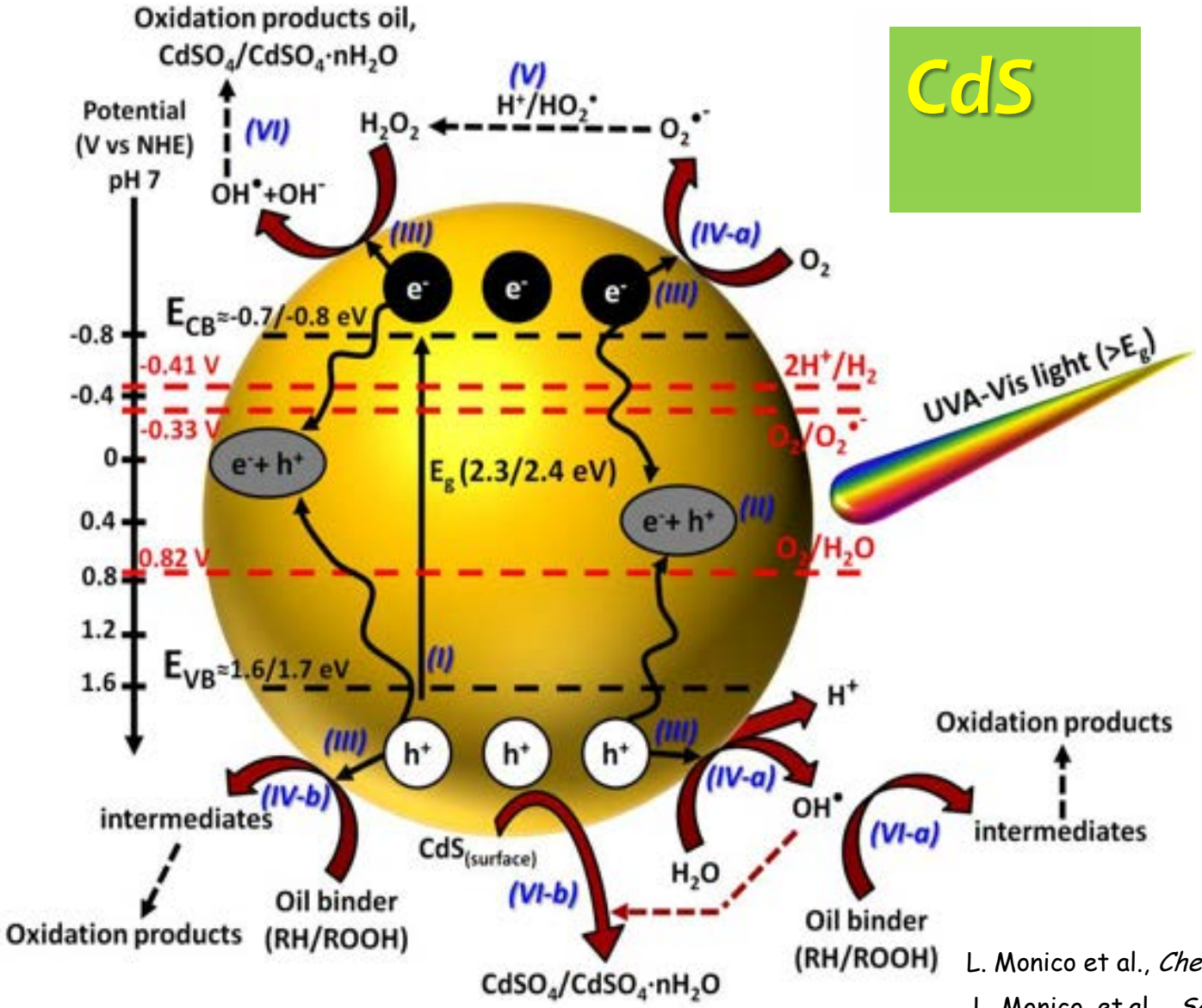
Oxalates

Cadmium sulphate and Zinc oxalates

No changes

Zinc carboxilates

CdS



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Thank You!