The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

Synchrotron radiation (SR)-based X-ray spectromicroscopy for the study of the alteration process of artists' pigments

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OUTLINES

- Introduction: SR-based X-ray spectromicroscopic methods for the study of the chromatic alteration of painting materials

- The fading of cadmium yellows

- The discoloration of smalt and the fading of Prussian blue

- The darkening of vermilion

- The fading of red lead

Analytical investigations of art objects

➢ Art objects: heterogeneous and composite systems, in the most of cases composed of multi layers, whose thickness can achieve values down to the sub-micrometers

➢ Main aims of the analytical investigations are:

a) Determination of the composition, structure, morphology and physico-chemical properties of the constitutive materials → Assessment of the provenance, manufacture procedures and, in some cases, authenticity of the object under investigation.

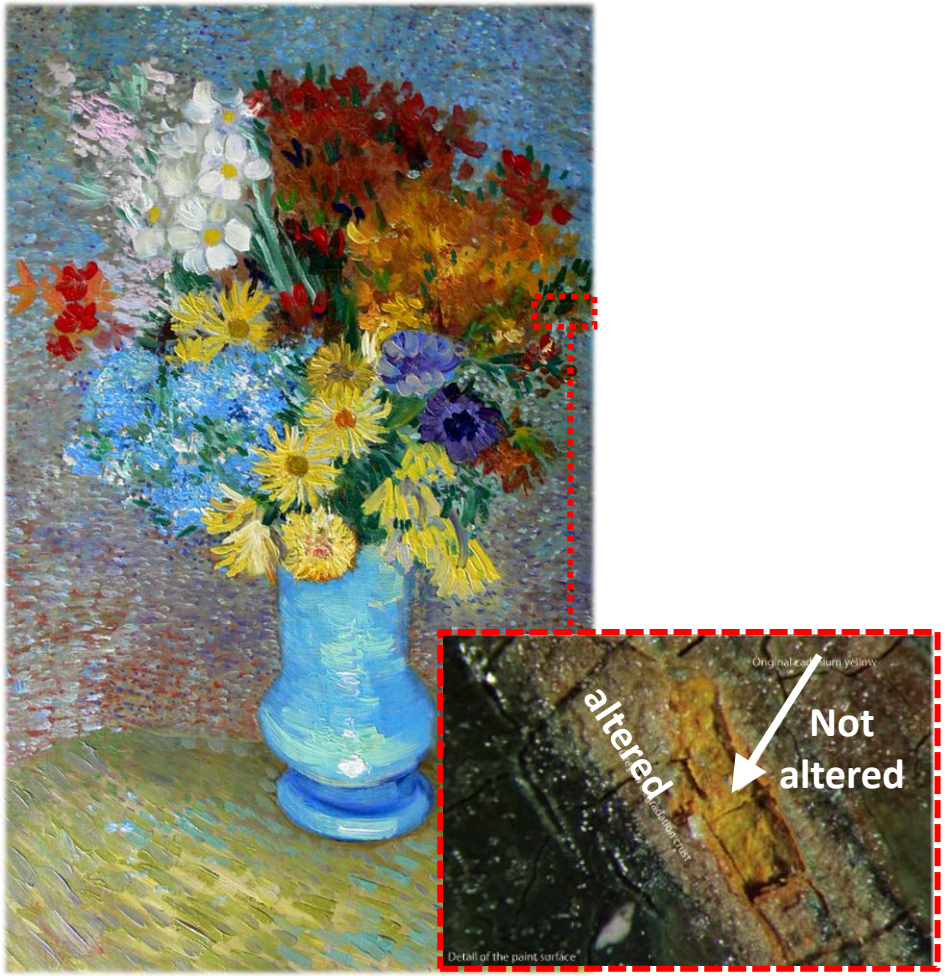
b) Identification of the causes of deterioration of the constitutive materials →

➢ Development of strategies for slowing down the alteration processes.

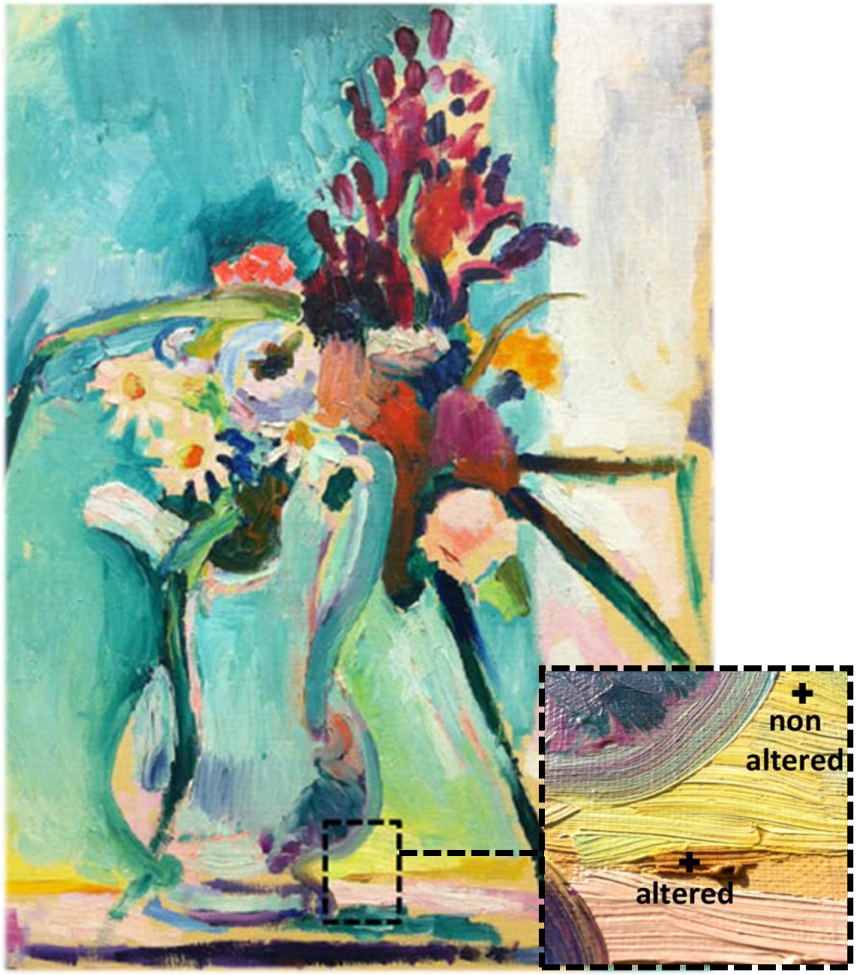
➢ Optimization of the conservation and/or restoration practices for the long-term storage of art objects.

Chromatic alteration on paintings: yellow pigments

Fading of cadmium yellow



Flowers in a blue vase (1887, Vincent van Gogh; Kröller-Müller Museum, Otterlo, NL).[(a)]



Flower Piece (1906, Henri Matisse; The Barnes Foundation, Philadelphia, USA).[(b)]

[(a)] G. Van der Snickt *et al.,* Anal. Chem. 84 (2012) 10221-10228. [(b)] E. Pouyet *et al.,* Appl. Phys. A: Mater. Sci. Process. (2015) DOI: 10.1007/s00339-015-9239-4.

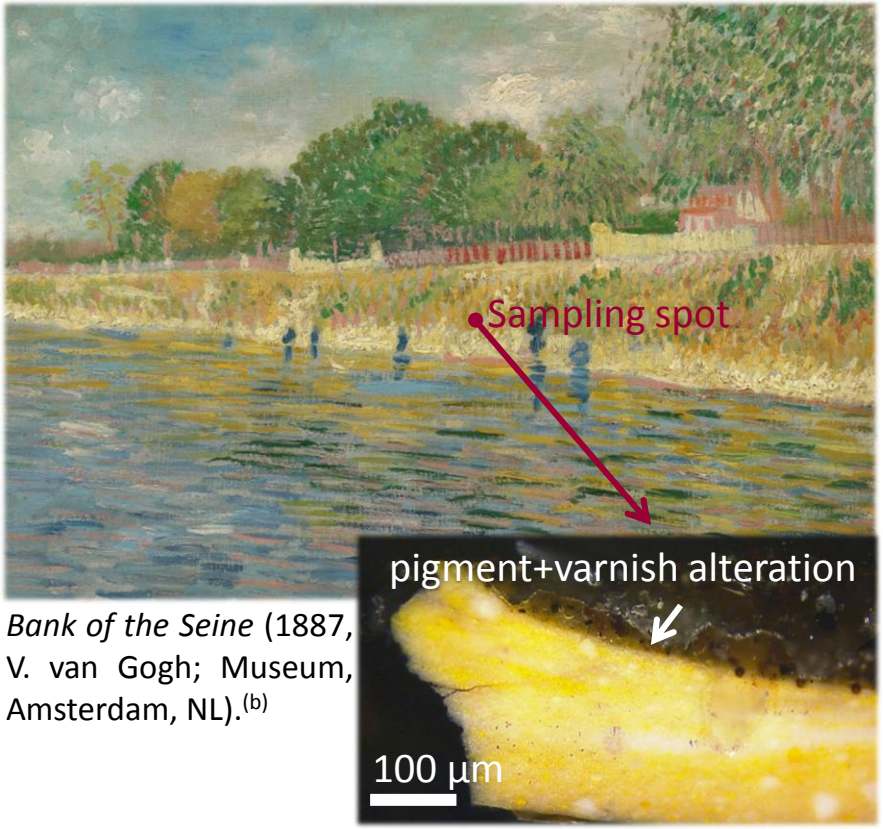
Chromatic alteration on paintings: yellow pigments

Darkening of zinc yellow

A Sunday on La Grande Jatte – 1884 (Georges Seurat; Helen Birch Bartlett Memorial Collection, The Art Institute of Chicago; USA).

photomicrograph from the juncture between shadowed and sunlit grass in the middle ground at far right[(a)]

Darkening of chrome yellow

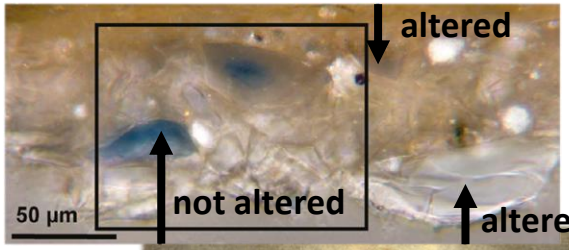


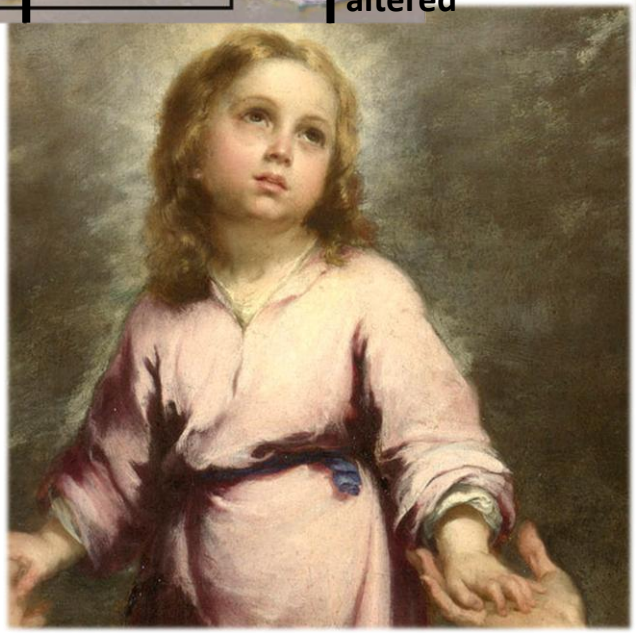
Bank of the Seine (1887, V. van Gogh; Museum, Amsterdam, NL).[(b)]

[(a)] L. Zanella *et al.,* J. Anal. Atom. Spectrom. 26 (2011) 1090-1097; F. Casadio *et al.,* Anal Bioanal Chem 399 (2011) 2909-2920. [(b)] L. Monico *et al.,* Anal. Chem. 83 (2011) 1224-1231; L. Monico *et al.,* Anal. Chem. 86 (2014) 10804-10811.

Chromatic alteration on paintings: blue pigments

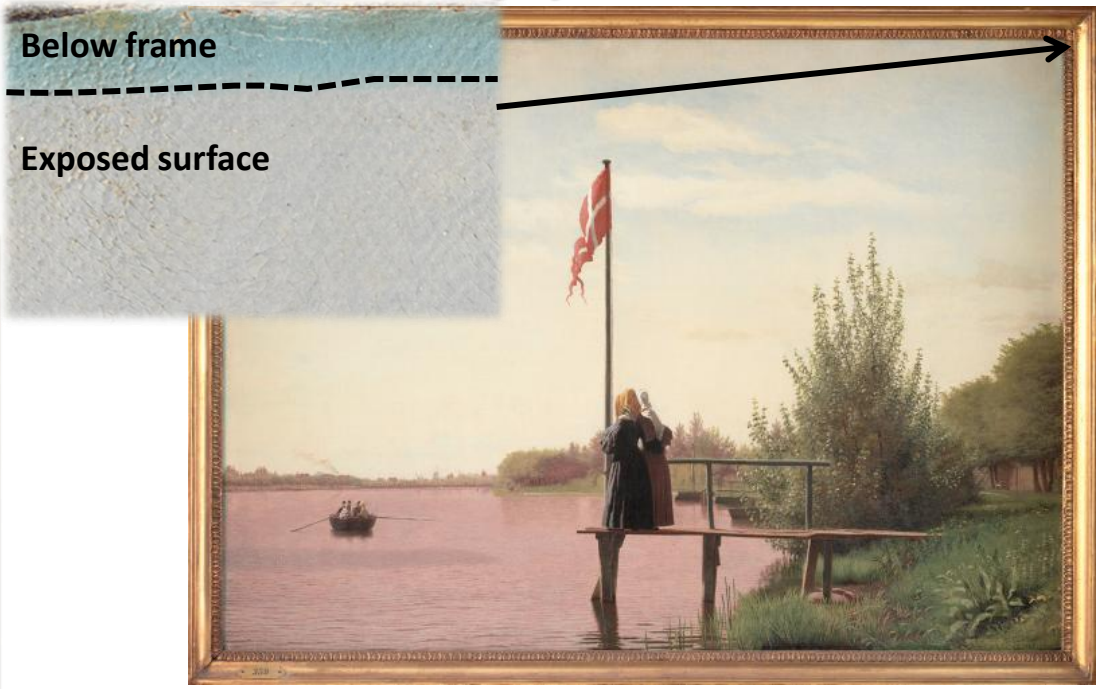
Smalt discoloration





Detail of *The Heavenly and Earthly Trinities* (*ca.* 1675-82, Bartolomé Esteban Murillo; The National Gallery, London, UK).[a]

Fading of Prussian Blue

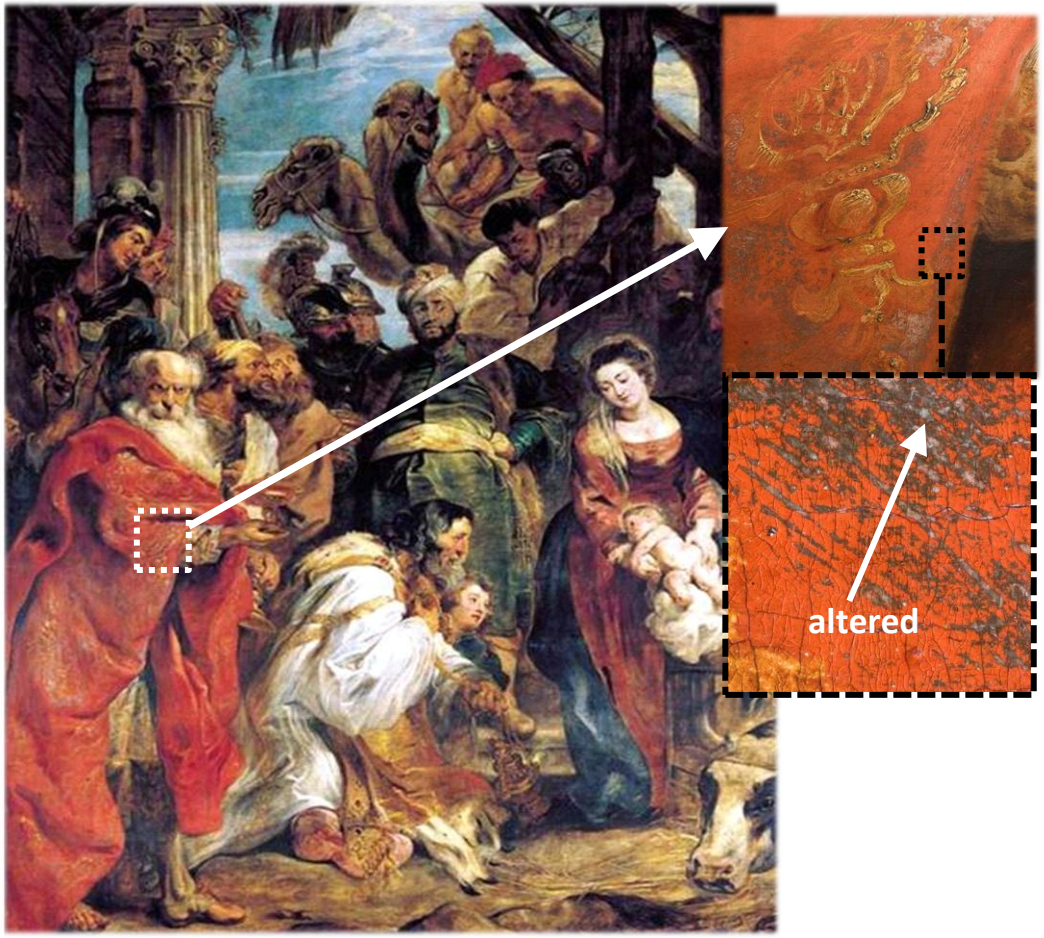


View of Lake Sortedam from Dosseringen Looking Towards the Suburb Nørrebro outside Copenhagen (1838, Christen Købke; Statens Museum for Kunst, Copenhagen, DK).[b]

[a] L. Robinet *et al.,* Anal. Chem. 83 (2011) 5145–5152. [b] A. Vila *et al.,* in: "Science and Art: The Painted Surface" (Eds: A. Sgamellotti, B. G. Brunetti, C. Miliani), The Royal Society of Chemistry, London, 2014, pp. 354-372.

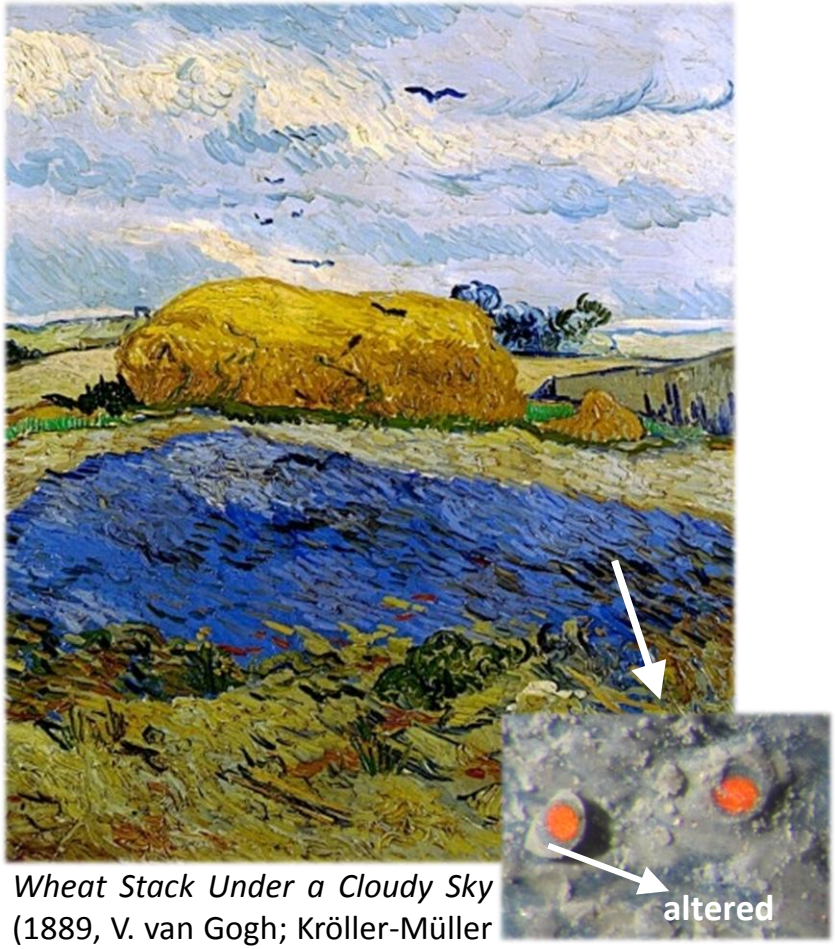
Chromatic alteration on paintings: red pigments

Darkening of vermilion



The Adoration of the Magi (1624, Peter Paul Rubens; Koninklijk Museum voor Schone Kunsten, Antwerp, BE).[a]

Fading of red lead



Wheat Stack Under a Cloudy Sky (1889, V. van Gogh; Kröller-Müller Museum, Otterlo, NL). [b]

[a] M. Radepont *et al.,* J. Anal. Atom. Spectrom. 26 (2011) 959-968. [b] F. Vanmeert *et al.,* Angew. Chem. Int. Edit. 127 (2015) 3678-3681.

SR-based X-ray spectromicroscopies on paintings

➢ ***SR-based experiments:*** possibility of mapping/imaging mode analysis at high lateral spatial resolution (down to the sub-micrometer scale) and reduced dwell times (less than 1 second) with highly brilliant and collimated X-ray micro-beams.

➢ The X-ray analysis more frequently employed for the study of the alteration process of painting materials are the following:

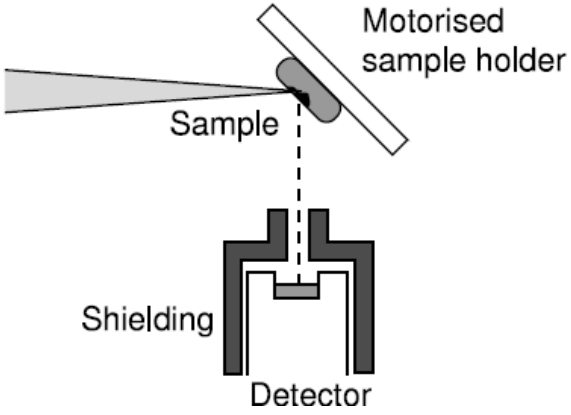
a) **micro-X-ray fluorescence (μ-XRF)** for elemental microanalysis down to the sub-ppm level.

b) **micro-X-ray absorption spectroscopy (μ-XAS)** for probing the local chemical state (oxidation state, coordination numbers, site symmetry and distortion, specific bond distances) of selected (trace) constituents; it can be equally applied on amorphous or crystalline materials.

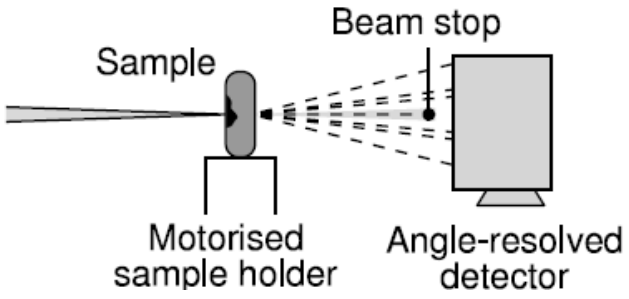
c) **micro-X-ray diffraction (μ-XRD)** for obtaining long range order information about the presence and nature of crystalline phases.

Experimental set-up*

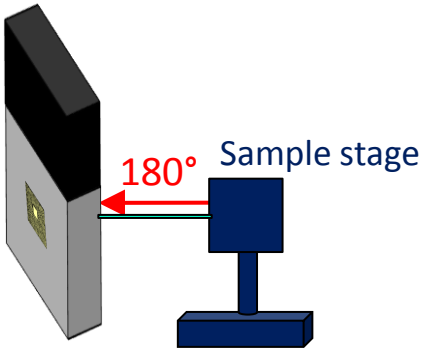
Scanning-mode. Sequential collection of spectra from adjacent regions of a sample obtained by moving each region into the photon beam. The beam is focalized by means of Kirkpatrick-Baez (KB) mirrors or Fresnel zone plates (FZP).



µ-XRF/XANES in XRF mode (concentrated or thick samples)



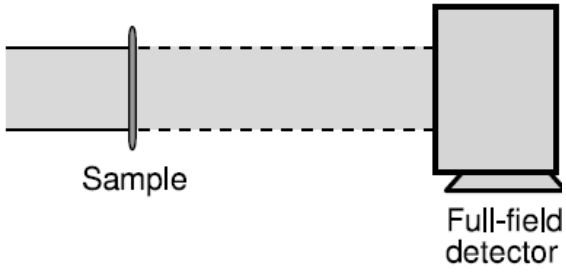
µ-XRD in transmission mode



Fast Maia X-ray detector (P06-DESY and XFM-AS)

µ-XRF/XANES in XRF mode

Full Field-mode. An image of the sample is focused onto an array detector where the signal coming from each region of the sample is measured at each pixel.

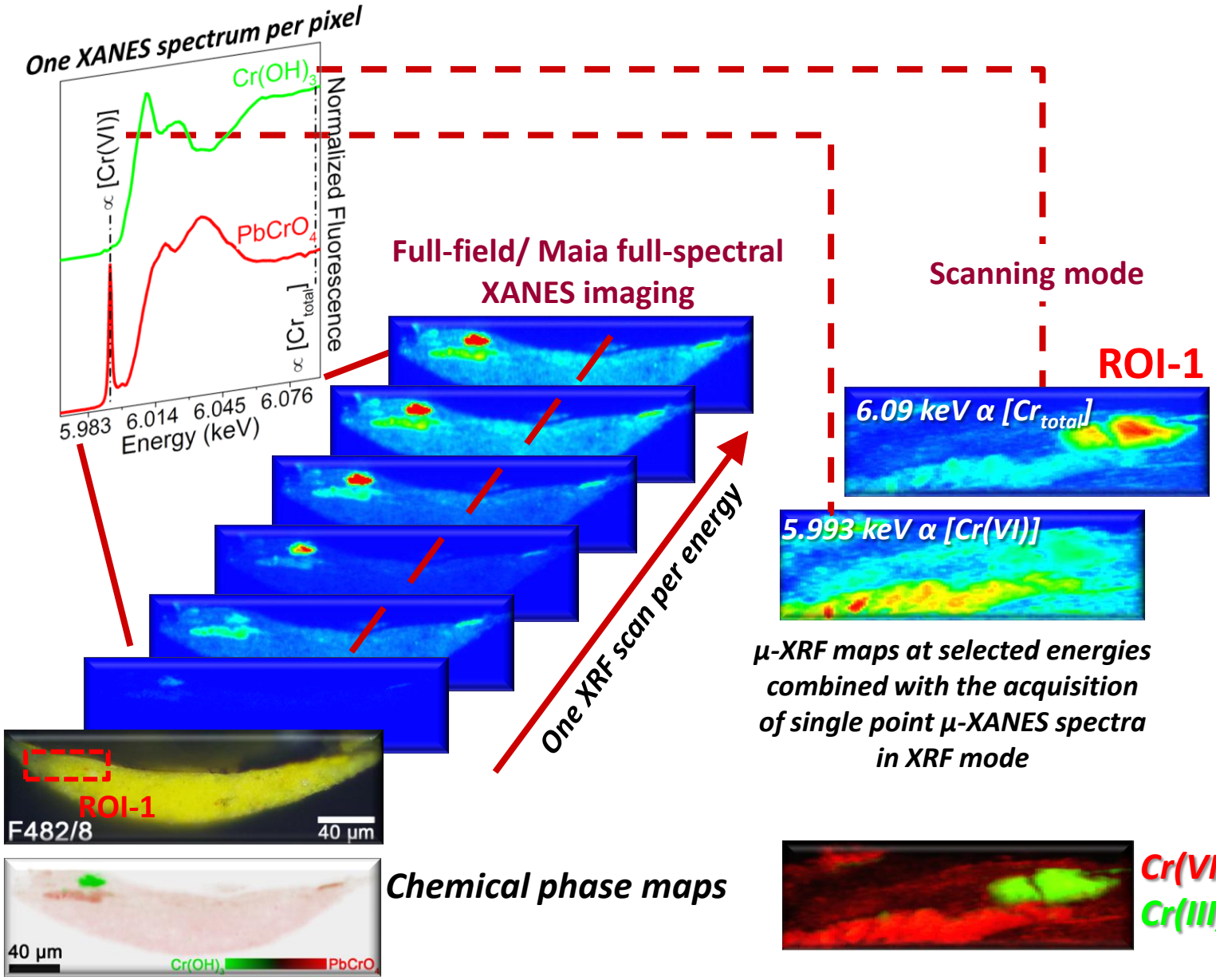


Faster measurements (shorter time exposure, decrease of the probability of beam-damage)

Possibility of XANES imaging

* L. Bertrand *et al.,* Physics Reports 519 (2012) 51–96; C. G. Ryan *et al.,* J. Phys.: Conf. Ser. 499 (2014) 012002.

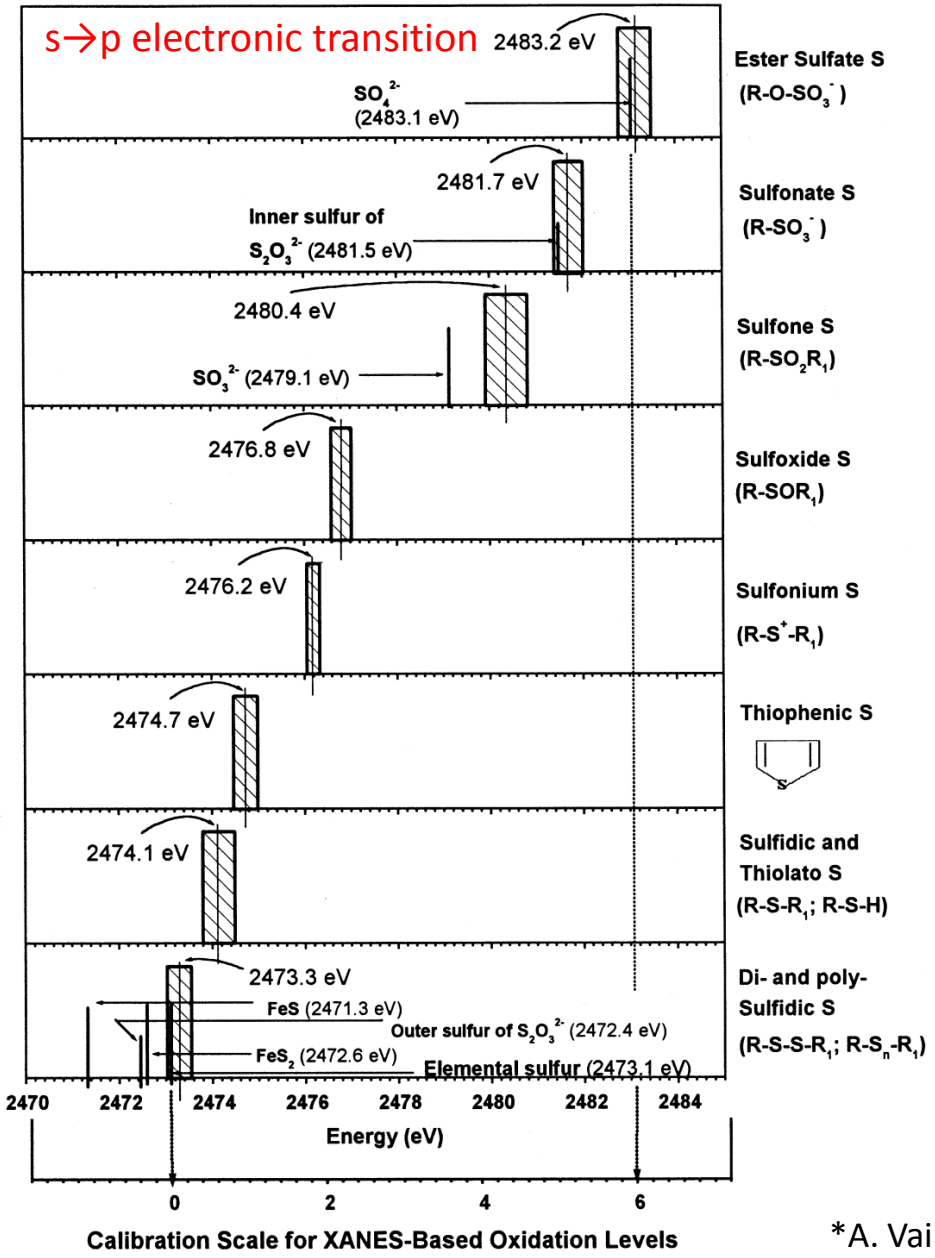
Chemical speciation experiments



Fading of cadmium yellow (CdS)

XANES, XRF and XRD analysis for the determination of the alteration process and identification of the alteration products

S K-edge XANES profiles*



- Suitable for clearly distinguishing sulfur-based compounds with different oxidation states.
- The position of the peak energy changes for different types of sulfur functional groups.

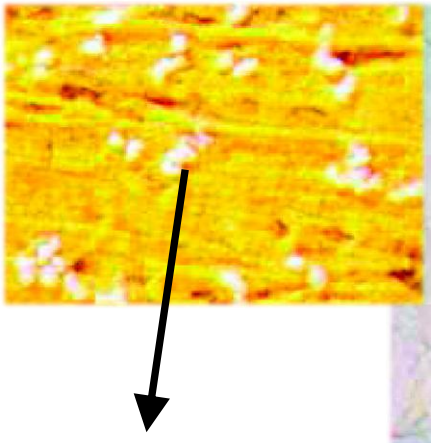
*A. Vairavamurthy, Spectrochimica Acta Part A 54 (1998) 2009–2017

Still Life with Cabbage (ca. 1921, James Ensor)

Characterization of a Degraded Cadmium Yellow (CdS) Pigment in an Oil Painting by Means of Synchrotron Radiation Based X-ray Techniques

Geert Van der Snickt,[†] Joris Dik,[‡] Marine Cotte,[§,∥] Koen Janssens,[*,†] Jakub Jaroszewicz,[†] Wout De Nolf,[†] Jasper Groenewegen,[‡] and Luuk Van der Loeff[⊥]

Anal. Chem. 2009, *81*, 2600–2610

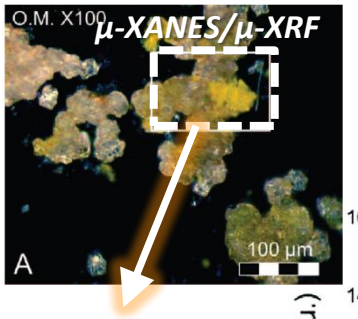


White globules at the exposed yellow paint surface

Why the yellow cadmium sulfide is became white?

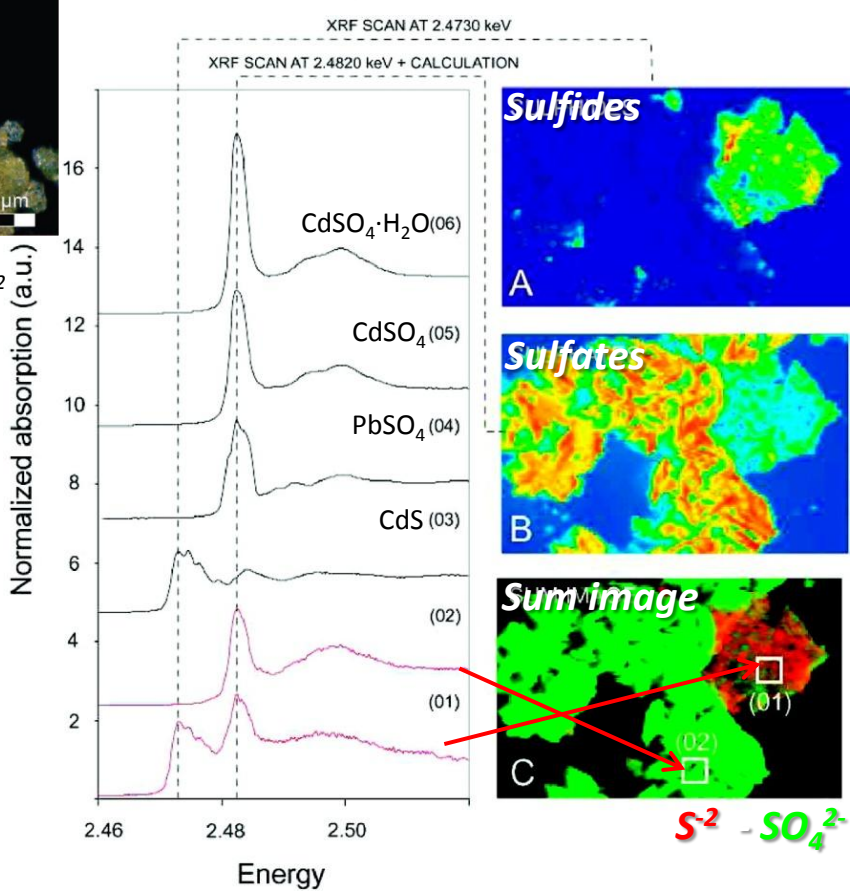
White globules: S K-/Cd L_{III}-edges μ-XANES/ μ-XRF

ID21 beamline (ESRF, Grenoble, FR)
Scanning mode analysis with a focused beam of 0.9×0.3 μm²
HPGe solid-state energy-dispersive detector

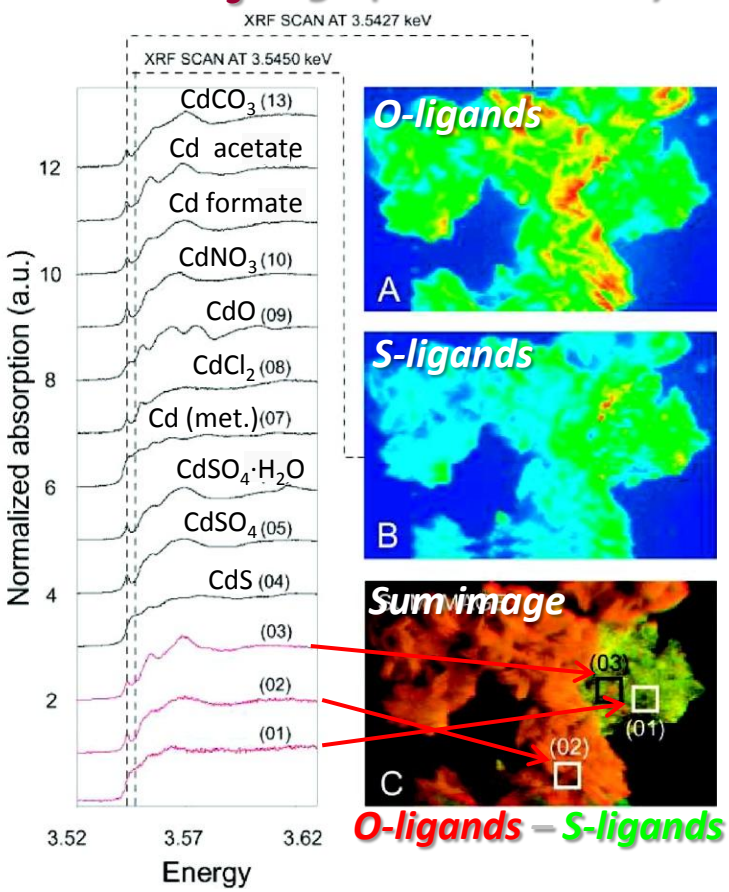


Map size: 144×91 *μm²*
step size: 1×1 μm²

S K-edge (2.46-2.53 keV)



Cd L_3-edge (3.52-3.65 keV)

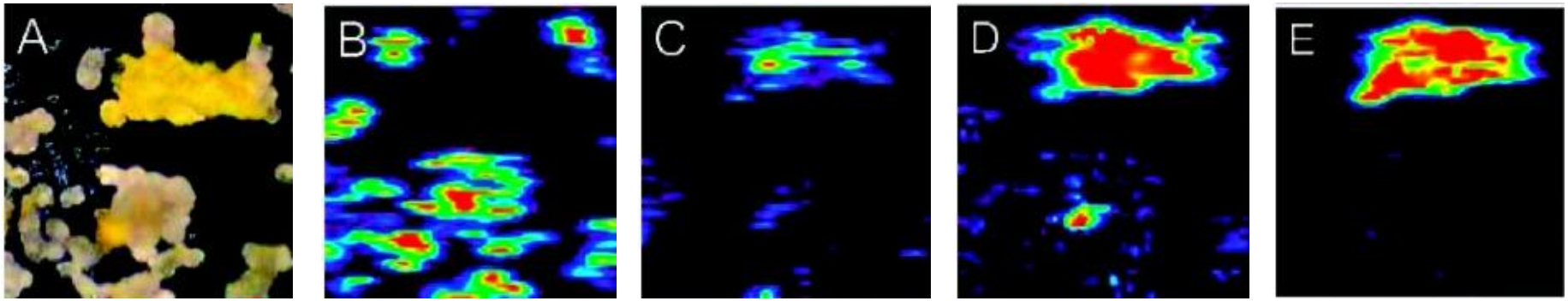


Clear evidence that the formation of the globules resulted from an oxidation process in which the original **CdS was oxidized to $CdSO_4$**

White globules: μ-XRD (transmission mode)

ID18F beamline (ESRF, Grenoble, FR)
Energy: 28 keV
Beam size (h×v): 22.7×1.7 μm^2
Detector: 2k×2k MarCCD camera (78×78 μm^2 pixel size)

Map size: 300×300 μm^2; step size: 6×6 μm^2



Optical micrograph	$CdSO_4 \cdot H_2O$	$CdCO_3$	CdS (hexagonal)	$PbSO_4$
	↓	↓	↓	↓
	CdS oxidization product (not clear identification by XANES)	Residue of the raw material or adulterant	Original pigment	Unclear origin (intentionally added to the paint? Contaminant? originally present as $PbCO_3$?)

➢ Additional presence of **ammonium cadmium sulfate** in another position in the white/transparent areas (unclear origin: possibly due to the cleaning of the paint surface with diluted ammonia)

Proposed alteration pathways of cadmium yellow

$$CdS + 2\ O_2 + H_2O \rightarrow CdSO_4 \cdot H_2O$$

Flowers in a blue vase (1887, Vincent van Gogh)

analytical chemistry

Anal. Chem. 2012, 84, 10221−10228 Article

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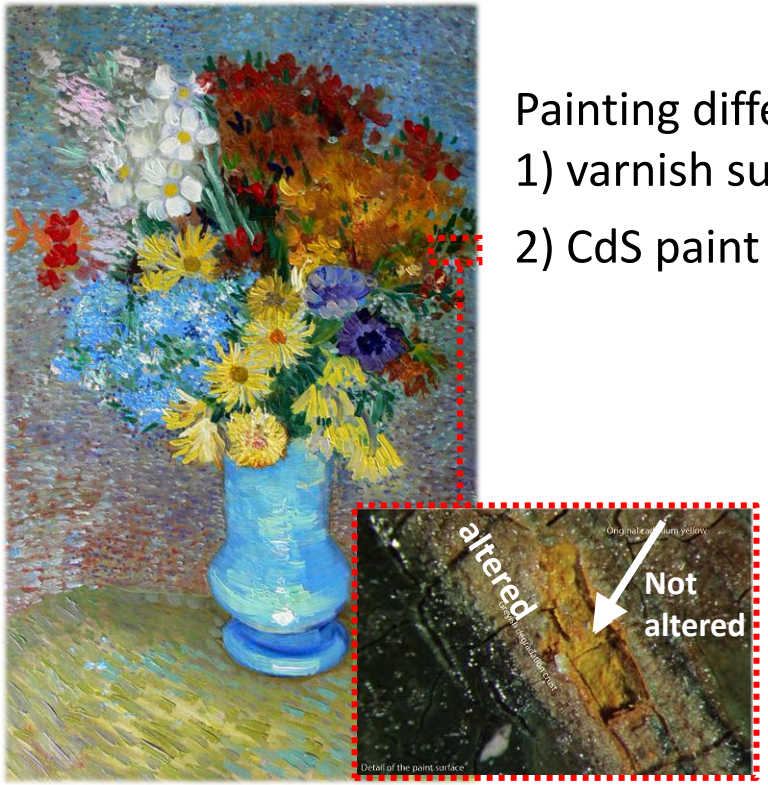
Combined use of Synchrotron Radiation Based Micro-X-ray Fluorescence, Micro-X-ray Diffraction, Micro-X-ray Absorption Near-Edge, and Micro-Fourier Transform Infrared Spectroscopies for Revealing an Alternative Degradation Pathway of the Pigment Cadmium Yellow in a Painting by Van Gogh

Geert Van der Snickt,*[,⊤] Koen Janssens,[⊤] Joris Dik,[‡] Wout De Nolf,[⊤] Frederik Vanmeert,[⊤] Jacub Jaroszewicz,[†] Marine Cotte,[§,∥] Gerald Falkenberg,[⊥] and Luuk Van der Loeff[¶∥]

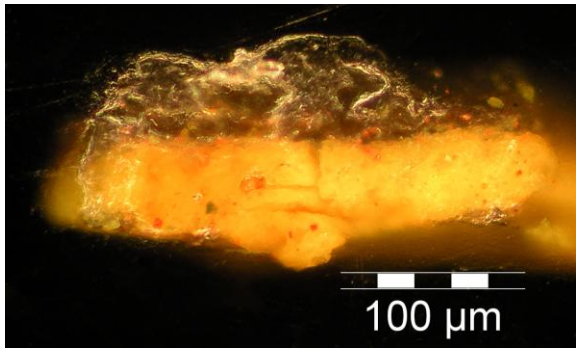


Painting different from the Ensor case:

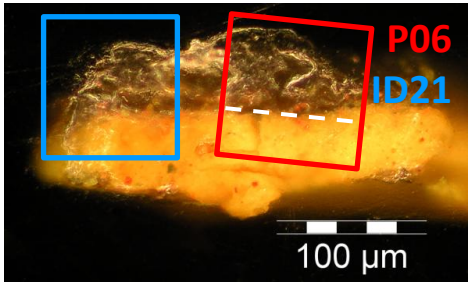
1) varnish superimposed onto the degraded paint surface.

2) CdS paint area entirely covered with an opaque crust.

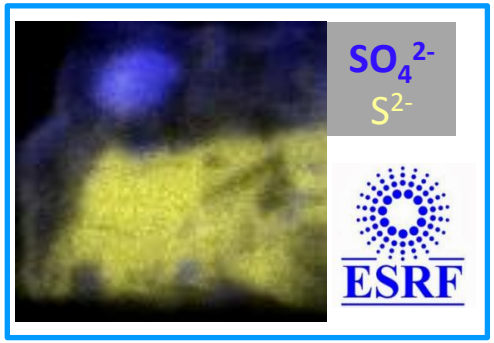
S K-edge μ-XANES/μ-XRF and μ-XRD analysis on cross-sectioned micro-samples



S K-edge μ-XANES/μ-XRF and μ-XRD

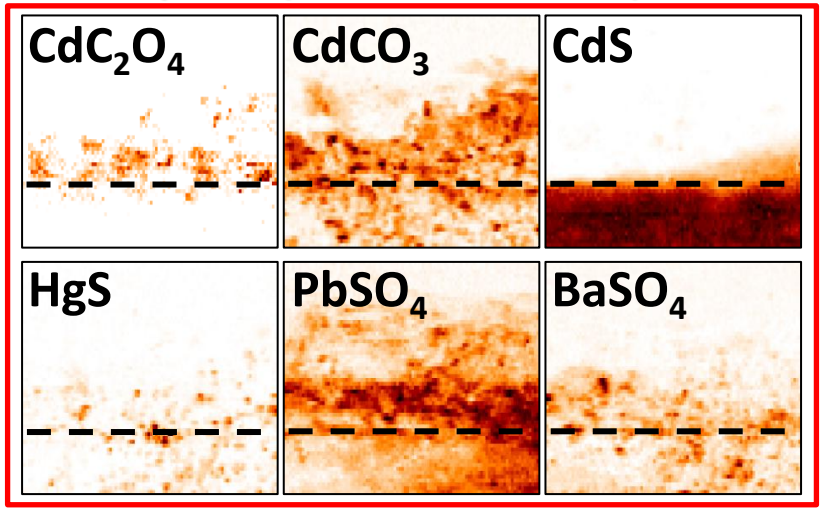


S K-edge μ-XANES/μ-XRF



ID21 beamline (ESRF, Grenoble, FR)
Map size: 100×100 μm²
Step size: 1×1 μm²
Energy: 2.473 keV (S^{2-}); 2.482 keV (SO_4^{2-})
Beam size: 0.9×0.3 μm²
HPGe solid-state energy-dispersive detector

μ-XRD (transmission mode)



P06 beamline (DESY, Hamburg, DE)
Map size: 100×90 μm²
Step size: 1×1.5 μm²
Energy: 18 keV
Beam size: 1.6×0.6 μm²
Detector: 2k×2k MarCCD camera (78×78 μm² pixel size)

DESY

Proposed alteration pathways in presence of varnish

varnish

Alteration product ← $C_2O_4^{2-}$ Pb^{2+} → driers

STEP I

Not crystalline

$CdS + 2\,O_2 \rightarrow \mathbf{CdSO_4} \rightarrow Cd^{2+} + SO_4^{2-}$

Before applying varnish
(as for the Ensor case)

↓ ↓

$Cd\,C_2O_4$ **$PbSO_4$**

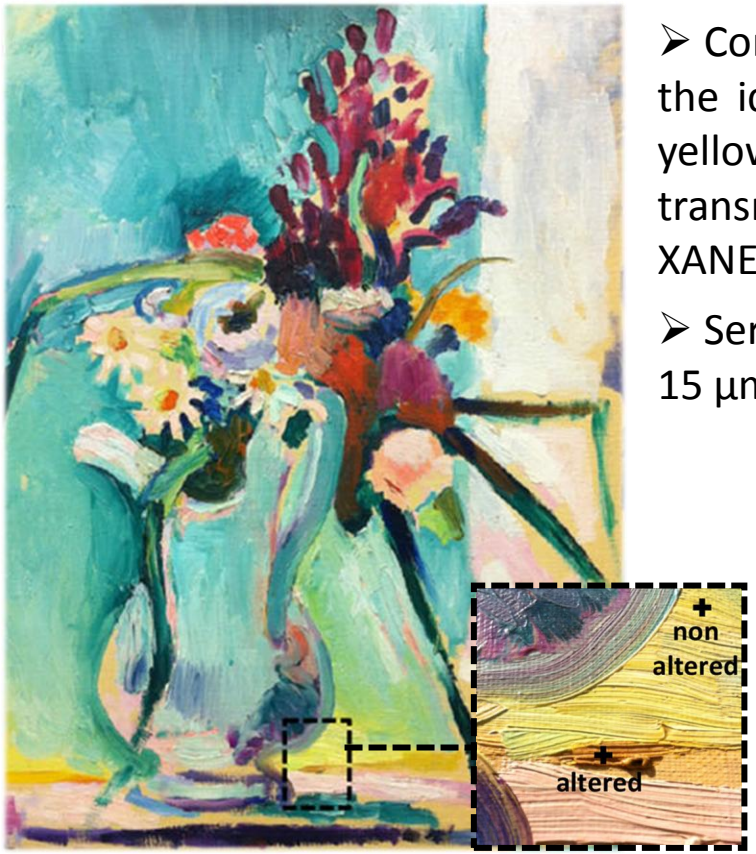
The Joy of Life/Flower Piece (1905-06, Henry Matisse)

Appl. Phys. A
DOI 10.1007/s00339-015-9239-4

Applied Physics A
Materials Science & Processing

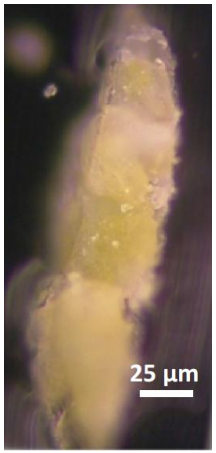
2D X-ray and FTIR micro-analysis of the degradation of cadmium yellow pigment in paintings of Henri Matisse

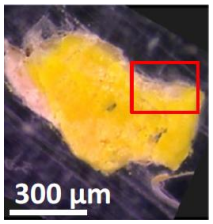
E. Pouyet[1,2] · M. Cotte[1,3] · B. Fayard[1] · M. Salomé[1] · F. Meirer[4] · A. Mehta[5] · E. S. Uffelman[6] · A. Hull[7] · F. Vanmeert[8] · J. Kieffer[1] · M. Burghammer[1] · K. Janssens[8] · F. Sette[1] · J. Mass[9]



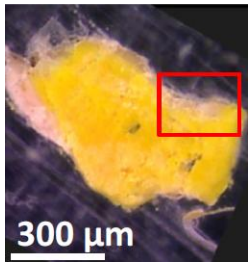
Flower Piece (1906, Henri Matisse; The Barnes Foundation, Philadelphia, USA).

- Combination of two dimensional X-ray techniques for the identification of the alteration products of cadmium yellow: µ-XRD (ID13-ESRF and P06-DESY), Full-field transmission mode XANES imaging and scanning mode µ-XANES/µ-XRF at the S K-, Cl K- and Cd L_3-edges (ID21-ESRF).
- Series of samples analyzed as thin sections of about 10-15 µm thickness

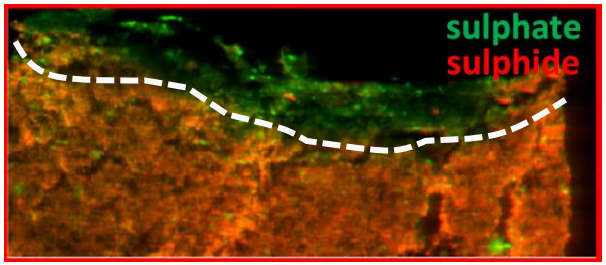




S K-edge μ-XRF, Cd-L_3 edge XANES imaging, μ-XRD



Optical micrograph

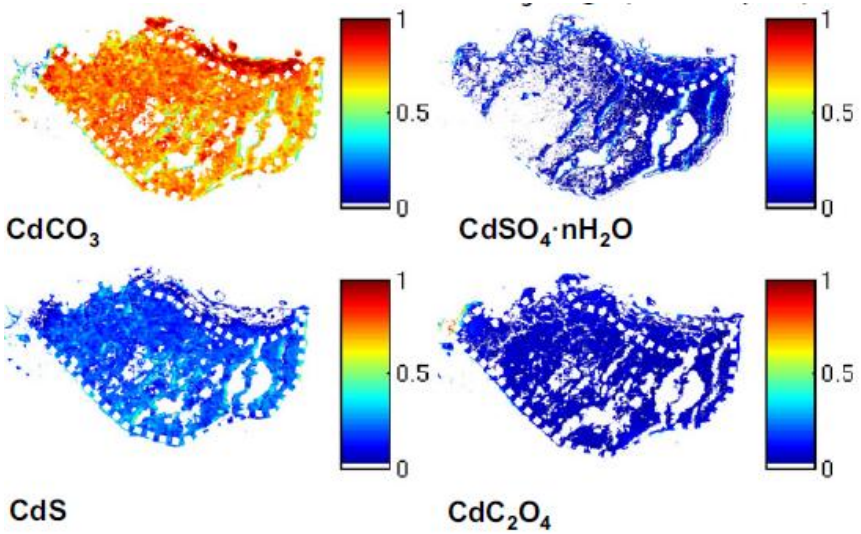


Sulfur chemical state maps (ID21-ESRF)
(scanning mode; step size: 2×2 μm²)

White degraded area:
mainly composed of CdC_2O_4, $CdSO_4 \cdot nH_2O$ and $CdCO_3$ (degradation products of the orginal CdS pigment)

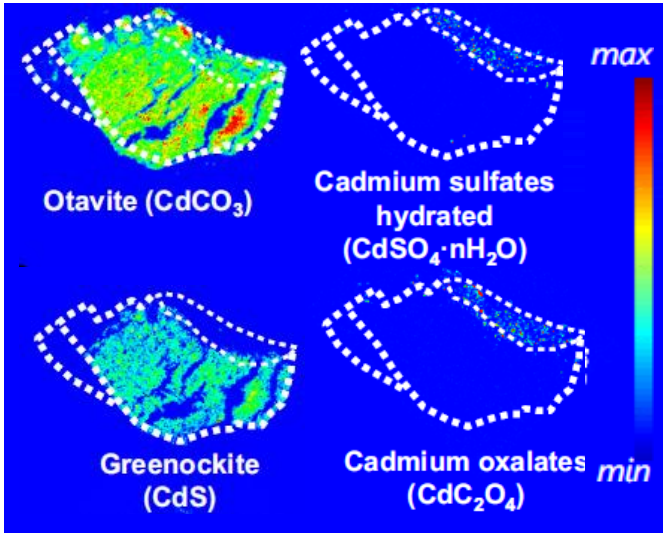
Distribution of difference Cd-based phases

Full field mode Cd L_3-edge XANES imaging (ID21-ESRF)



Distributions obtained by linear combination fitting of the Cd L_3-edge full field stack (step size: 0.7×0.7 μm²) using the XANES spectra of different Cd-reference compounds.

Transmission mode μ-XRD (ID13-ESRF)



energy: 18 keV; step size: 2×2 μm²

Alteration of blue pigments

Co K- and Fe K-edges XAS analysis for the study of the discoloration of Smalt and fading of Prussian blue

Smalt discoloration

➢ ***Smalt*** : blue pigment commonly used by artists between the 16th and 18th centuries. It is a potash glass in which the color stems from cobalt ions in the divalent oxidation state.

➢XAS investigations of micro-samples taken from paintings and artificially aged model samples have established the alteration mechanism of this pigment.

analytical chemistry

Anal. Chem. 2011, 83, 5145–5152 ARTICLE

pubs.acs.org/ac

Investigation of the Discoloration of Smalt Pigment in Historic Paintings by Micro-X-ray Absorption Spectroscopy at the Co K-Edge

Laurianne Robinet,*,† Marika Spring,‡ Sandrine Pagès-Camagna,§ Delphine Vantelon,∥ and Nicolas Trcera∥

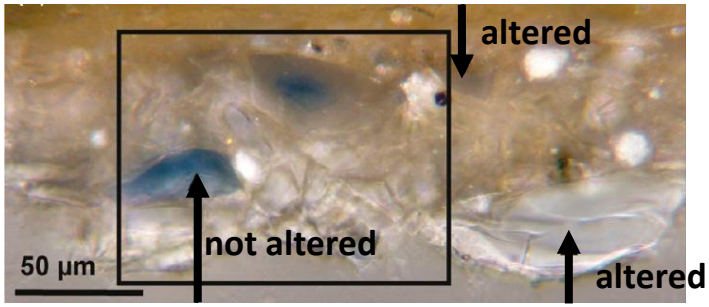
JAAS *J. Anal. At. Spectrom.*, 2012, **27**, 1941–1948

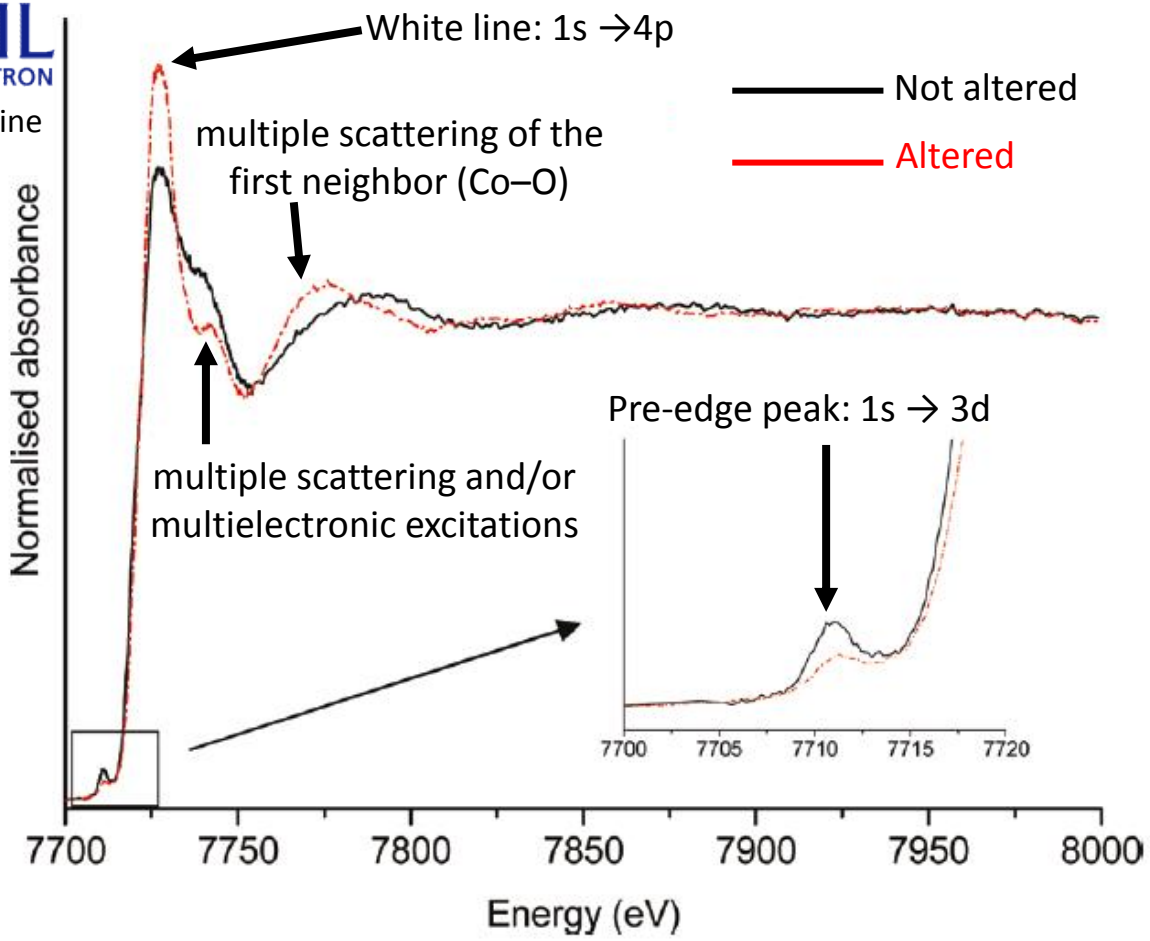
Discoloration of the smalt pigment: experimental studies and *ab initio* calculations†

Ilaria Cianchetta,[a] Ivan Colantoni,[b] Fabio Talarico,*[c] Francesco d'Acapito,[d] Angela Trapananti,[d] Chiara Maurizio,[e] Simona Fantacci[f] and Ivan Davoli[b]

Co K-edge XAS analysis*

LUCIA beamline





➢ ***Discoloration*** due to a change in the local environment of Co^{2+} from tetrahedral (blue) to octahedral (pink) while the leaching of K^{+} takes place.

The process does not involve modifications of the oxidation state of the cobalt ion.

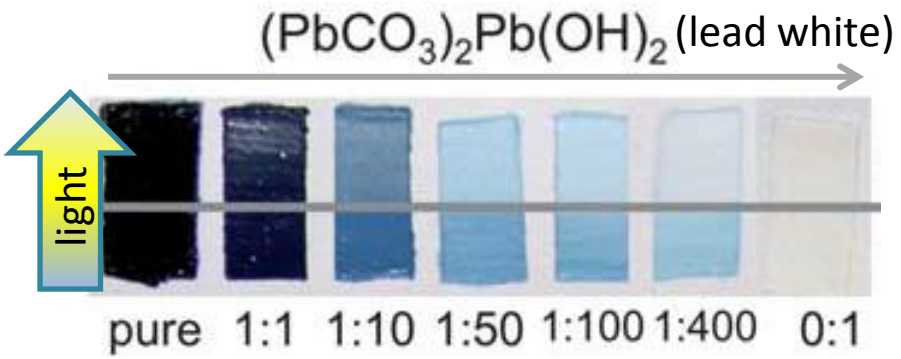
*Figures re-adapted from L. Robinet *et al.,* Anal. Chem. 83 (2011) 5145–5152.

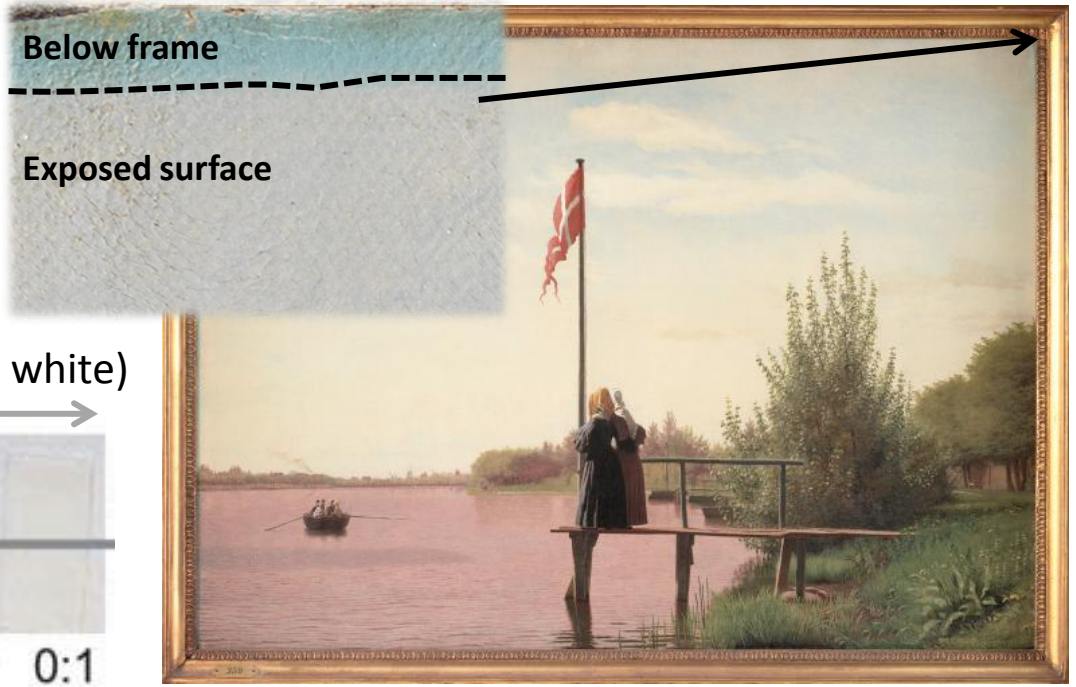
Fading of Prussian blue

➢ ***Prussian blue:*** discovered at the beginning of 18th century and of composition $MFe^{III}[Fe^{II}(CN)_6]\cdot xH_2O$ (with M= K^+, NH_4^+ or Na^+). The intense blue color arises from an intervalent electron transfer between the Fe(II) and Fe(III) oxidation states when light is absorbed at about 700 nm.

➢ Artificially aged model samples before and after light exposure have been investigated using a combination of Fe K-edge XAS analysis and iron-57 Mössbauer spectroscopy for the understanding of the alteration mechanism of this pigment.[(a)]

Artificially aged oil paint models

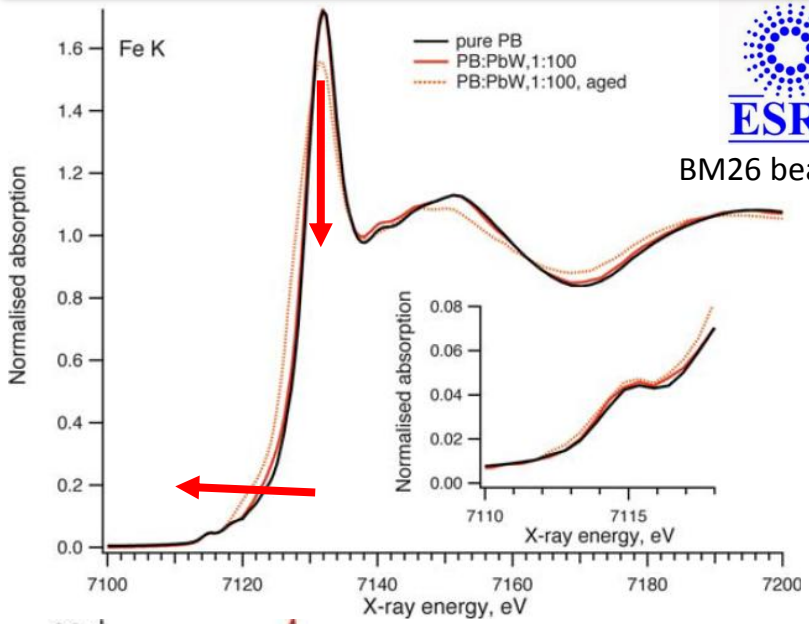




View of Lake Sortedam from Dosseringen Looking Towards the Suburb Nørrebro outside Copenhagen (1838, Christen Købke; Statens Museum for Kunst, Copenhagen, DK).[(b)]

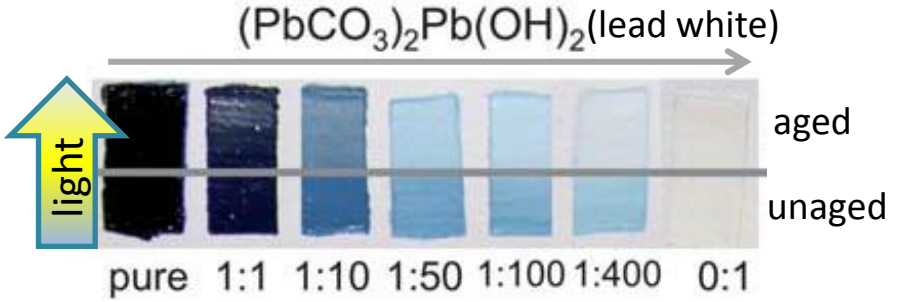
[(a)] L. Samain et *al.,* J. Anal. At. Spectrom. 26 (2011) 930-941; L. Samain *et al.,* J. Anal. At. Spectrom. 28 (2013) 524–535.
[(b)] A. Vila *et al.,* in: "Science and Art: The Painted Surface" (Eds: A. Sgamellotti, B. G. Brunetti, C. Miliani), The Royal Society of Chemistry, London, 2014, pp. 354-372.

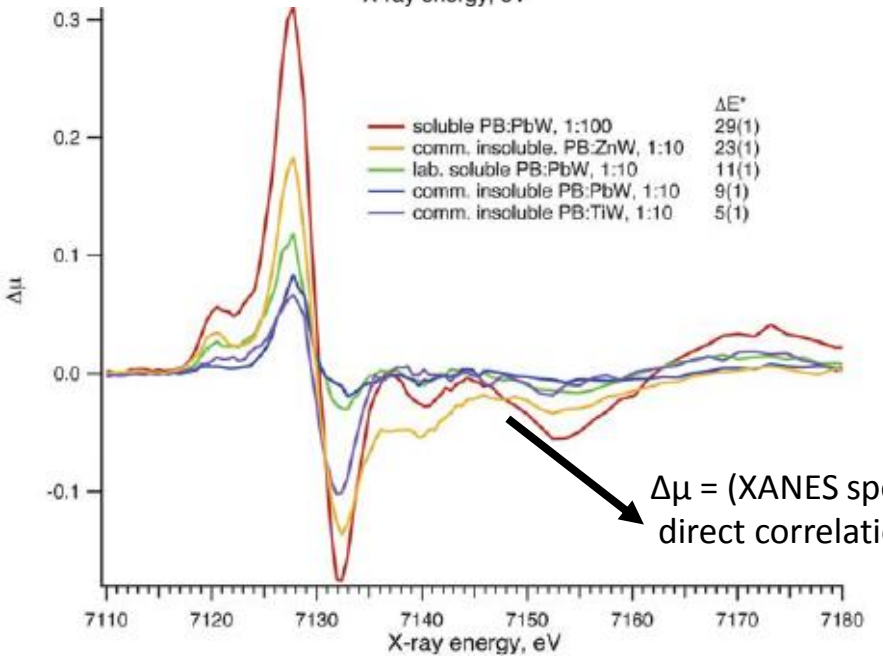
Fe K-edge XAS analysis*



ESRF

BM26 beamline





- ***Fading*** due to a Fe(III)→Fe(II) reduction (in the XAS spectrum: decreasing of the intensity of the white line and shift of the absorption edge towards lower energies).
- Disruption of the intervalent electron transfer Fe(II)-C-Fe(III).
- Decrease in the Fe coordination number in the second and third shell that lead to a weakening of the intervalent Fe(II)/Fe(III) charge transfer.
- The fading is influenced by the nature and amount of the white pigment.

$\Delta\mu$ = (XANES spectrum$_{unaged}$-XANES spectrum$_{aged}$): direct correlation with the total colour change (ΔE^*)

* L. Samain et *al.,* J. Anal. At. Spectrom. 26 (2011) 930-941.

Alteration of red pigments

2D μ-XRD mapping and 2D μ-XRD tomography for the determination of the degradation process and identification of the alteration products of vermilion and red lead

Darkening of vermilion (HgS)

JAAS *J. Anal. At. Spectrom.*, 2011, **26**, 959–968

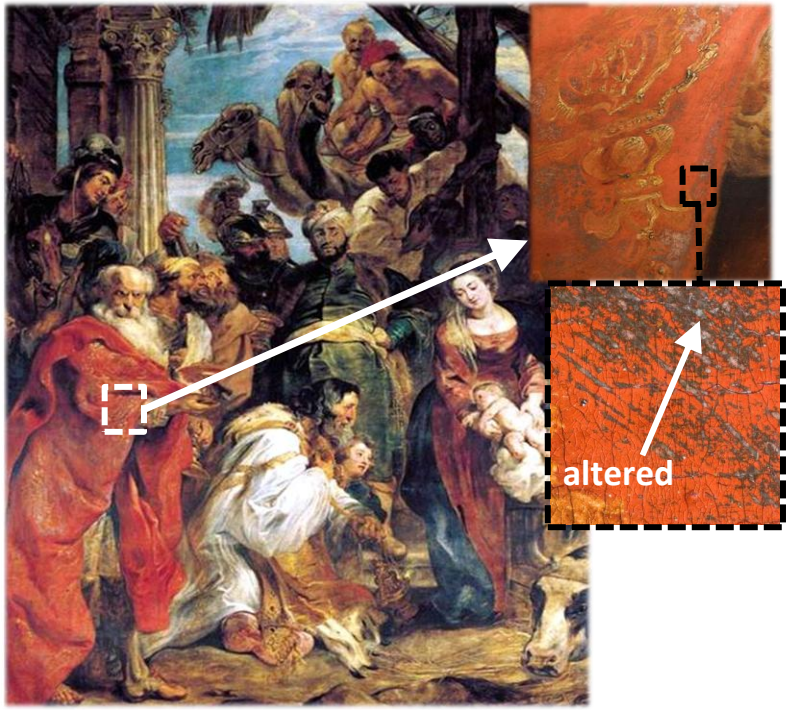
The use of microscopic X-ray diffraction for the study of HgS and its degradation products corderoite (α-$Hg_3S_2Cl_2$), kenhsuite (γ-$Hg_3S_2Cl_2$) and calomel (Hg_2Cl_2) in historical paintings†

Marie Radepont,[*ab] Wout de Nolf,[a] Koen Janssens,[a] Geert Van der Snickt,[a] Yvan Coquinot,[b] Lizet Klaassen[d] and Marine Cotte[bc]

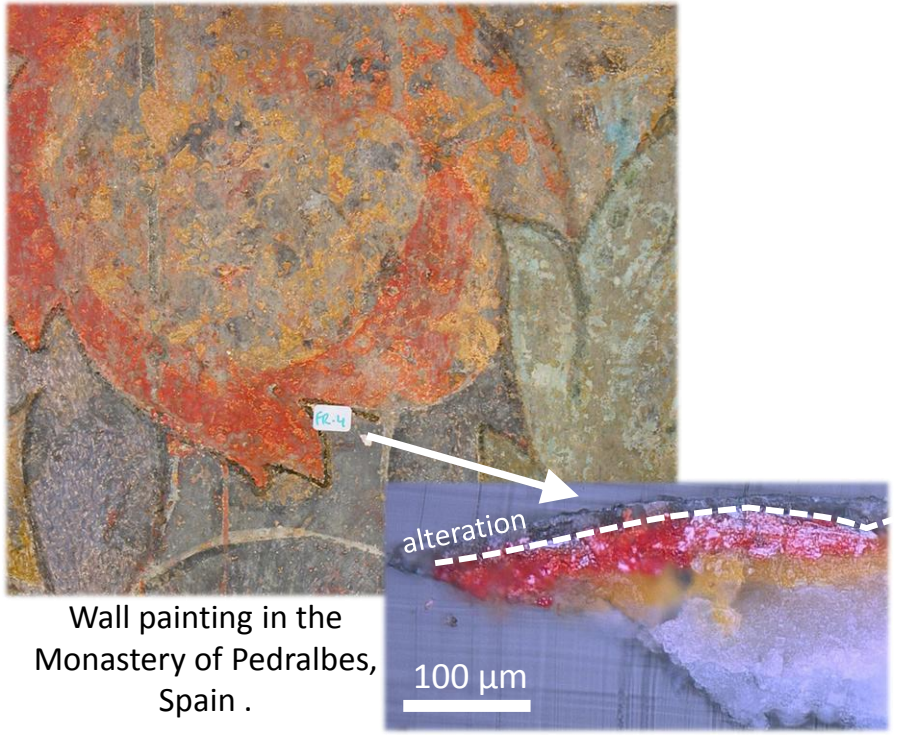
PRL **111**, 208302 (2013) PHYSICAL REVIEW LETTERS

Casting Light on the Darkening of Colors in Historical Paintings

F. Da Pieve,[1,2,*] C. Hogan,[3,4] D. Lamoen,[2] J. Verbeeck,[2] F. Vanmeert,[5] M. Radepont,[5] M. Cotte,[6] K. Janssens,[5] X. Gonze,[7] and G. Van Tendeloo[2]

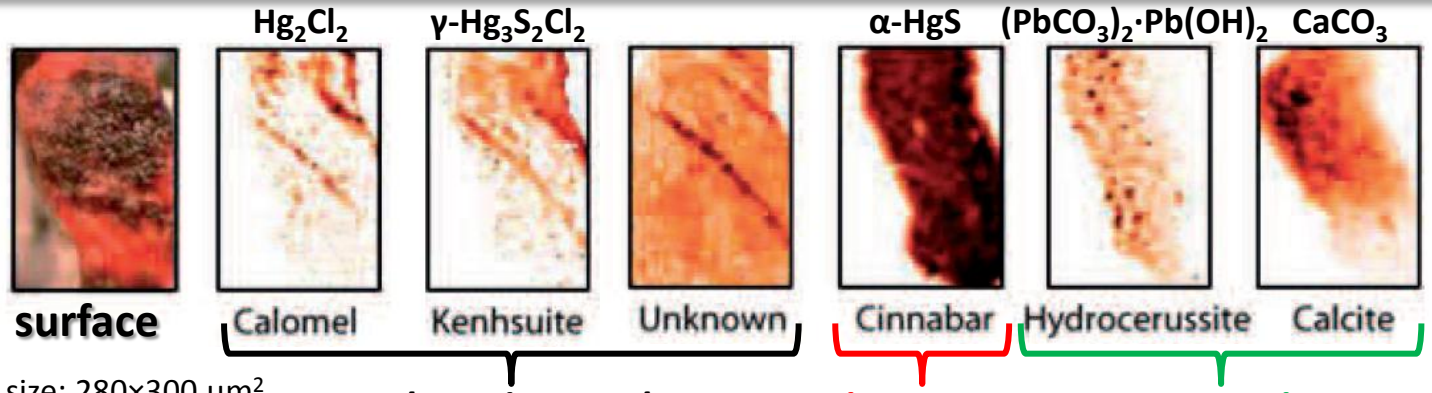


The Adoration of the Magi (1624, P. P. Rubens; Koninklijk Museum voor Schone Kunsten, Antwerp, BE).



Wall painting in the Monastery of Pedralbes, Spain .

The Adoration of the Magi (1624, P.P. Rubens): μ-XRD*



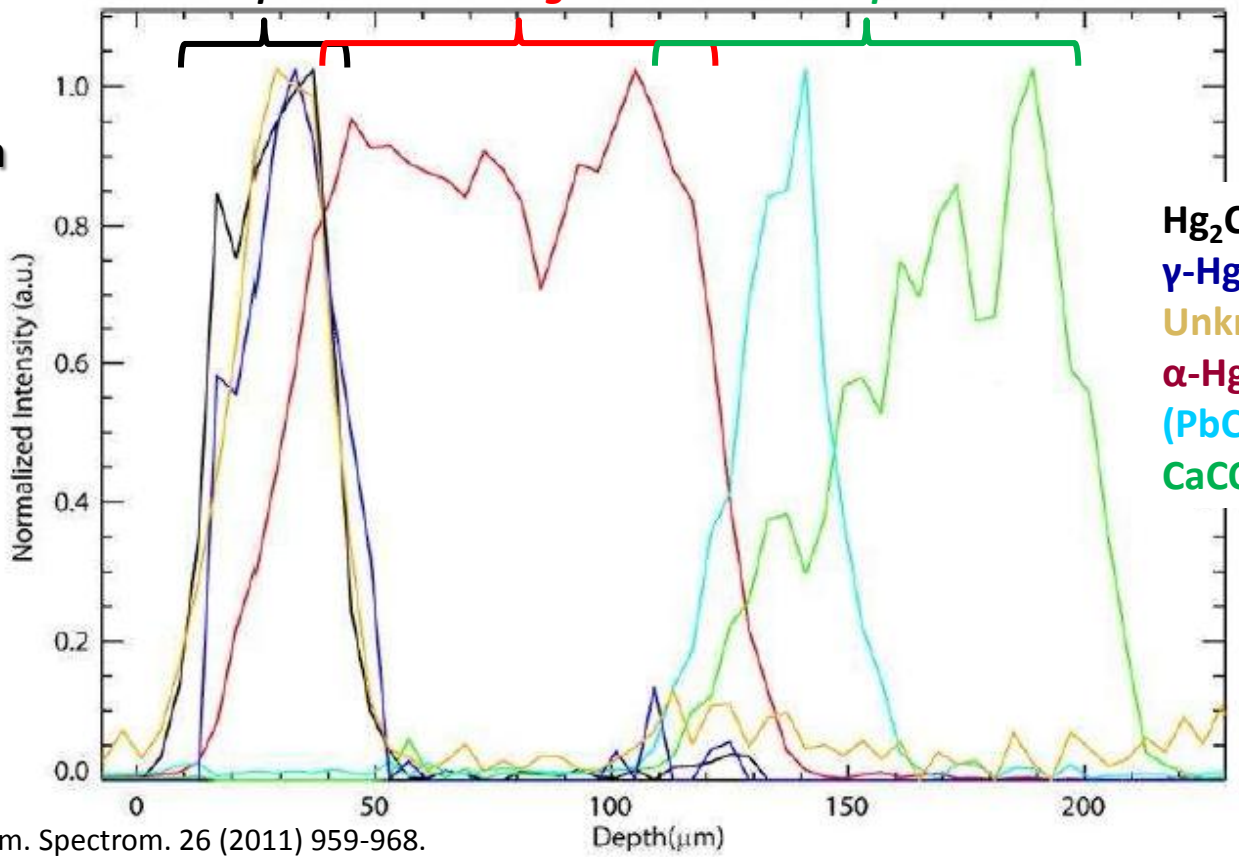
ESRF

ID18F beamline
Energy: 28 keV
Beam size (h×v): 5.3×1.8 μm²

Map size: 280×300 μm².

Alteration products *Pigment* *Preparation*

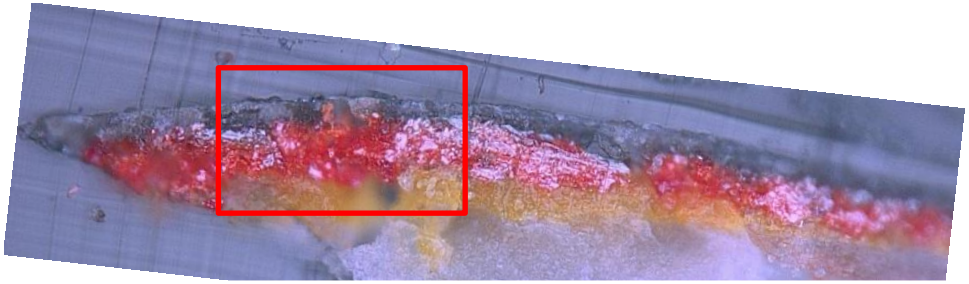
Cross-section

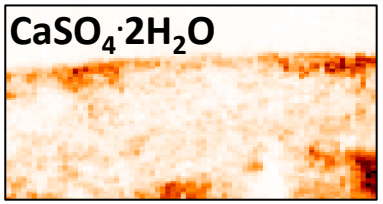


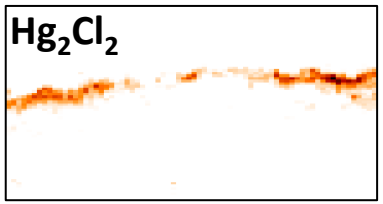
Hg_2Cl_2
γ-$Hg_3S_2Cl_2$
Unknown
α-HgS
$(PbCO_3)_2 \cdot Pb(OH)_2$
$CaCO_3$

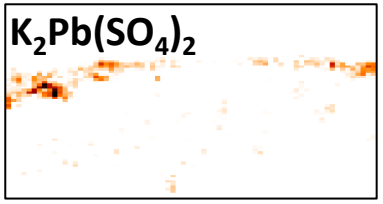
* M. Radepont *et al.,* J. Anal. Atom. Spectrom. 26 (2011) 959-968.

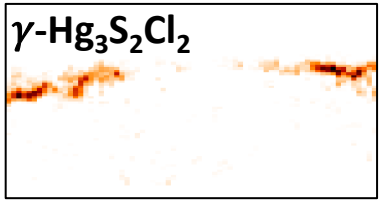
Monastery of Pedralbes, Spain: μ-XRD[a]

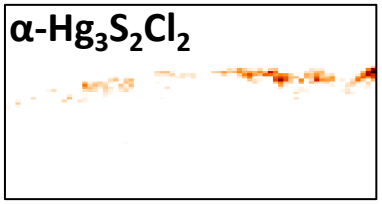


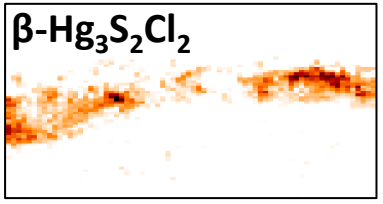


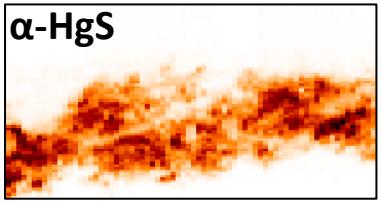


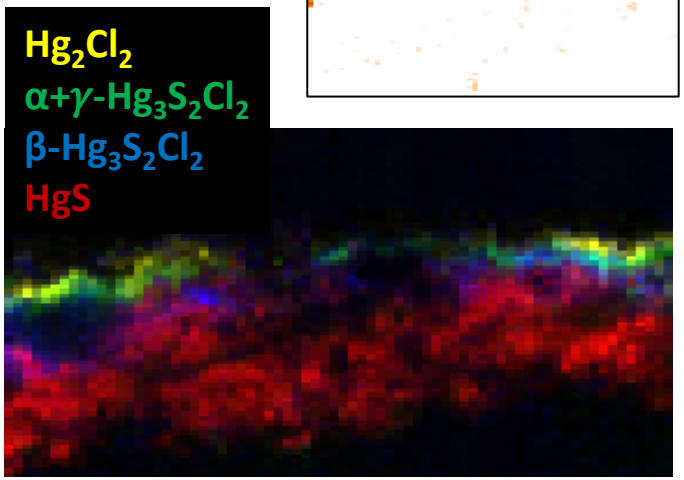












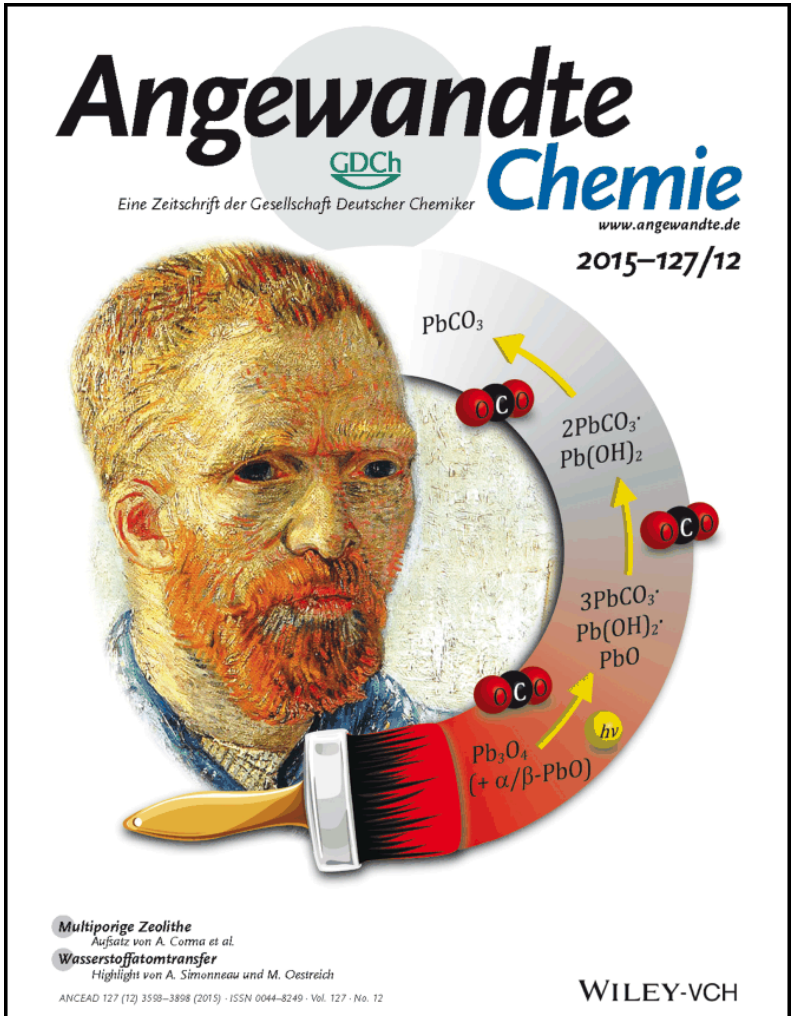
P06 beamline (DESY, Hamburg, DE)
Map size (h×v): 144×74 μm²
Step size (h×v): 2×1 μm²
Energy: 18 keV
Exposure time: 1s
Beam size: 1.6×0.6 μm²
Detector: 2k×2k MarCCD camera (78×78 μm² pixel size)

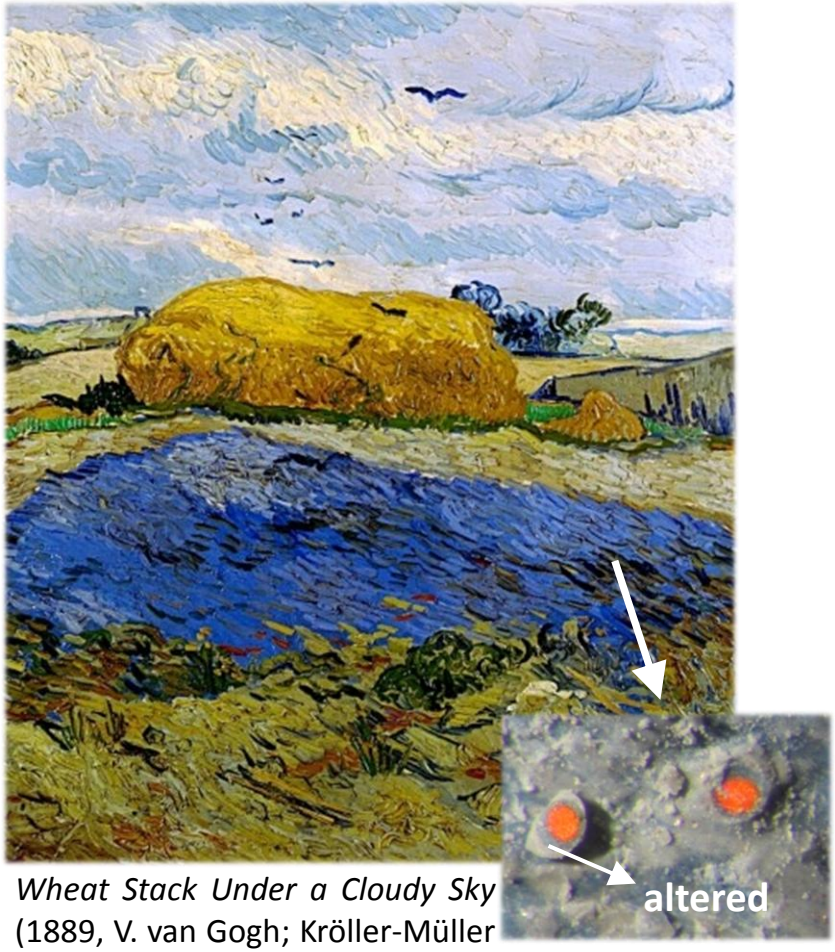
Darkening alteration pathway

$$Hg(II)S \xrightarrow[+\,Cl^-\ +UV]{+\,O_2} \beta\text{-}Hg_3S_2Cl_2 \rightarrow \gamma\text{-}Hg_3S_2Cl_2 + \alpha\text{-}Hg_3S_2Cl_2 \xrightarrow[+\,Cl^-]{+\,O_2} \underbrace{SO_4^{=} + Hg(I)_2Cl_2 \rightarrow Hg^0}_{\text{Electrochemical methods}^{(b)}}$$

[a] F. Da Pieve *et al.*, PRL 111(2013) 208302. [b] W. Anaf *et al.*, Angew. Chem. Int. Edit. 125 (2013) 12800-12803.

Fading of Red lead (Pb_3O_4)



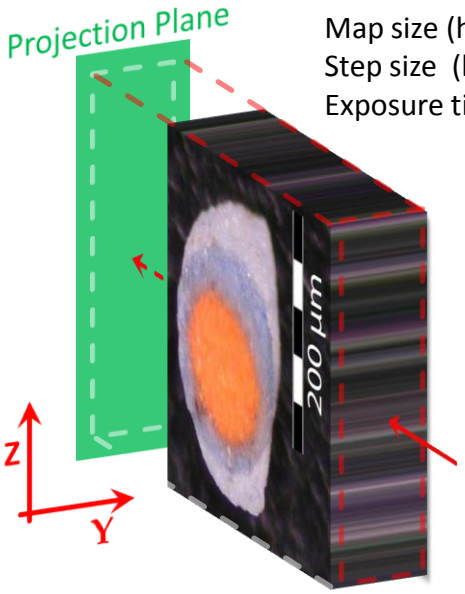


Wheat Stack Under a Cloudy Sky (1889, V. van Gogh; Kröller-Müller Museum, Otterlo, NL).

Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting**

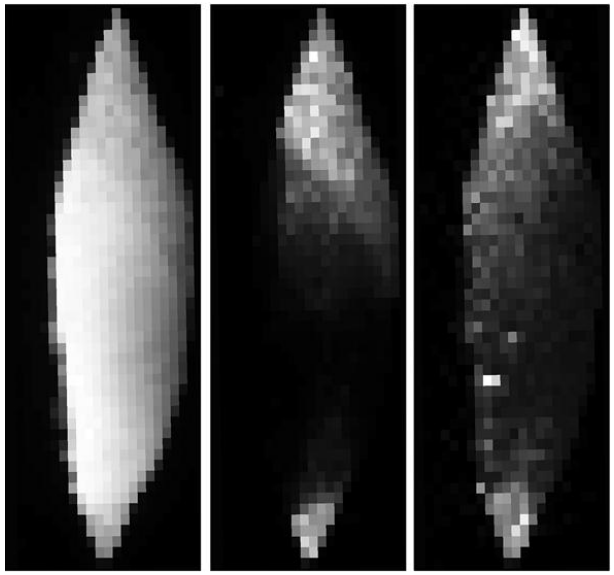
*Frederik Vanmeert, Geert Van der Snickt, and Koen Janssens** Angew. Chem. 2015, 127, 3678–3681

2D μ-XRD mapping



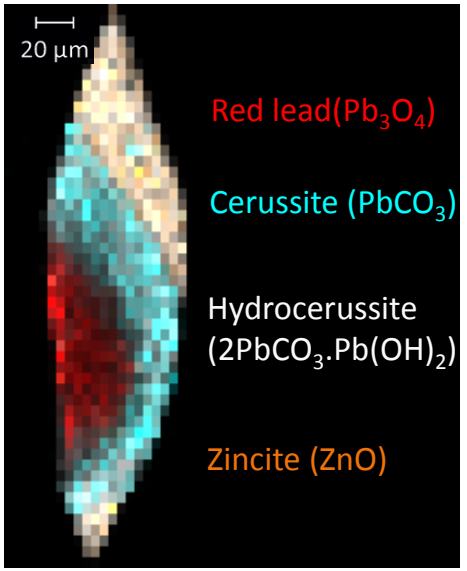
Map size (h×v): 80×255 μm²
Step size (h×v): 4×5 μm²
Exposure time: 1 s

μ-XRF

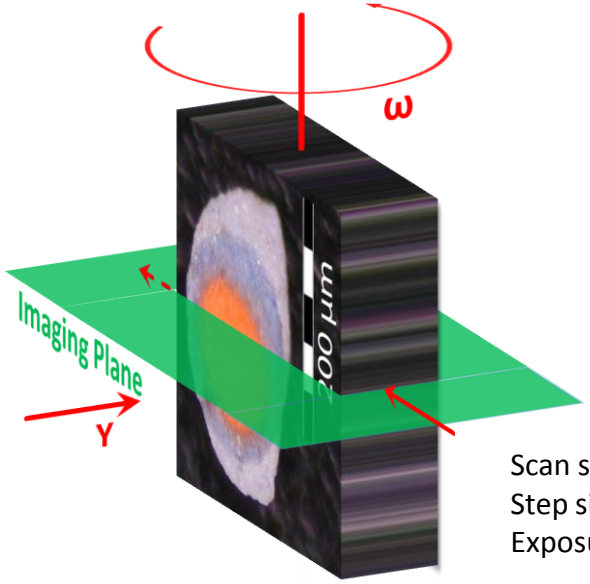


Pb-L Zn-K Co-K

μ-XRD

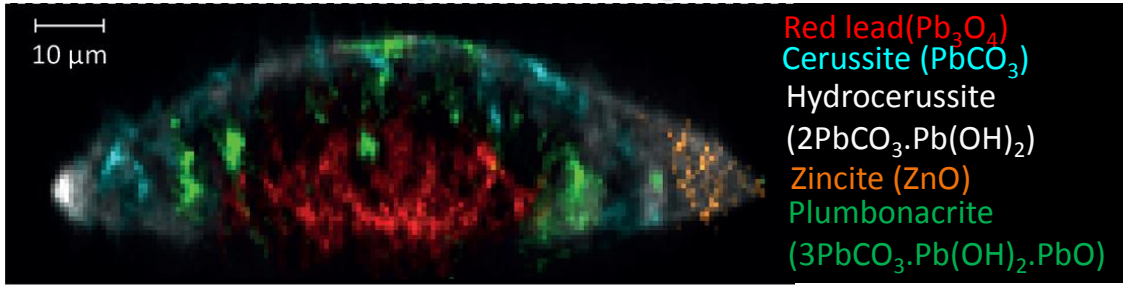


2D μ-XRD tomography



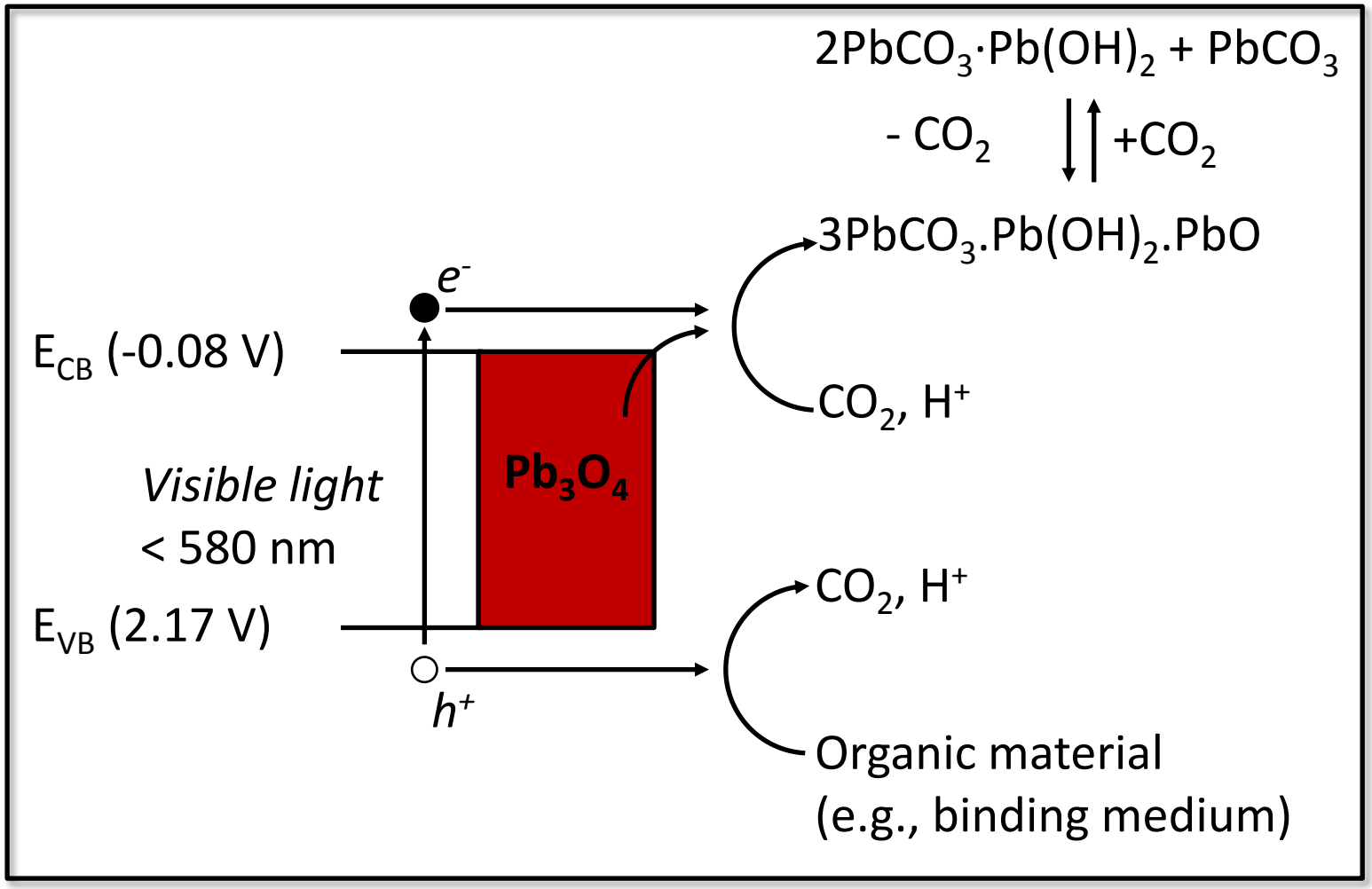
Scan size (trans × rot): 181 μm×180°
Step size (trans × rot): 1 μm×2°
Exposure time: 1 s

2D μ-XRD tomogram



Plumbonacrite: intermediate degradation product formed during the whitening of Pb_3O_4

Photo-degradation of Pb_3O_4: proposed pathway



Conclusions

- SR-based X-ray imaging techniques: relevant analytical tool for the study of structured and heterogeneous arrangements as occurring in painting materials.
- Micrometric/sub-micromteric probes are essential for the discriminative study of each layer.
- The combination of μ-XRF, μ-XANES and μ-XRD offers a powerful tool for the precise analysis on the nature and distribution of the constitutive materials and of the alteration products.
- The major advantage of μ-XANES is the possibility to specifically study the chemical environment of a particular element, even diluted in a complex mixture and both in crystalline and amorphous materials.
- μ-XRD is accurate for the identification of mineral compounds but these need to be crystalline.
- Vibrational spectroscopic methods (*i.e.,* FTIR, Raman – with SR or traditional sources) are also often used for studying the alteration of pigments due to their suitability in providing complementary/additional information about the nature of the organic binder and on the nature of organic/inorganic alteration compounds.
- An accurate preparation of samples is necessary.