# The Degradation Mechanisms of Matisse and van Gogh's Pigments – Probing Photo-oxidation Reactions at the Nanoscale


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**Matisse's *Le Bonheur de vivre (The Joy of Life, 1905-6)***

**the single most consequential early modern painting**

**many of Picasso's works competitive response**

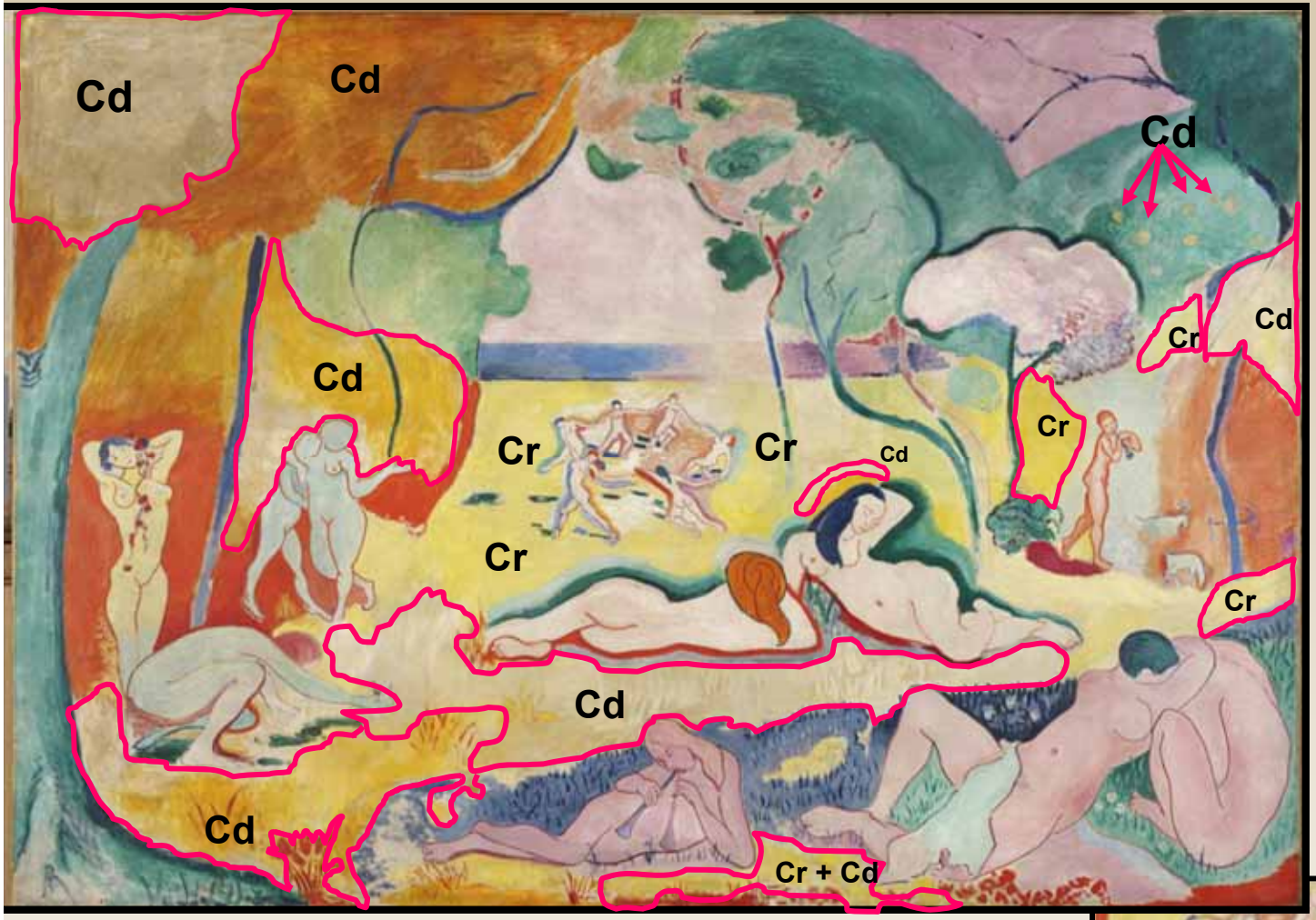
**four versions - yellows fading, darkening, spalling in Barnes version**

**mottled surface - tan, ochre hues**

**S. F. MOMA final oil sketch (1905-6)**

**Severe degradation of yellow paint – fading, flaking, spalling**

# Handheld XRF Survey Overview

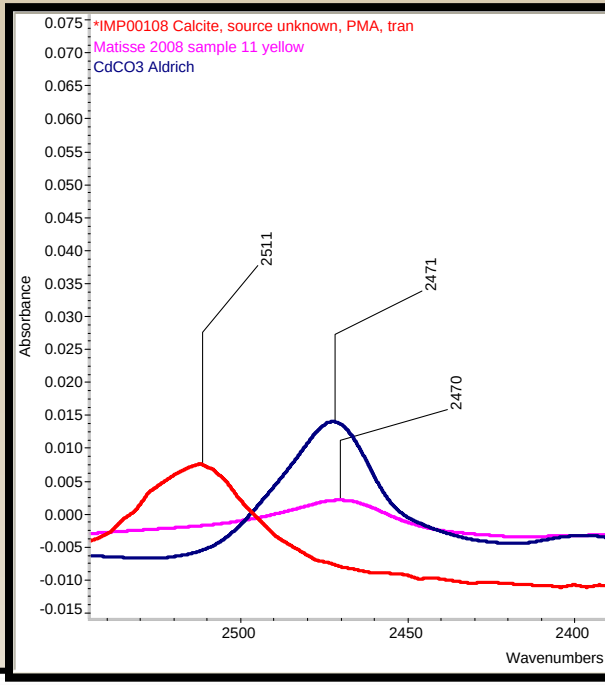


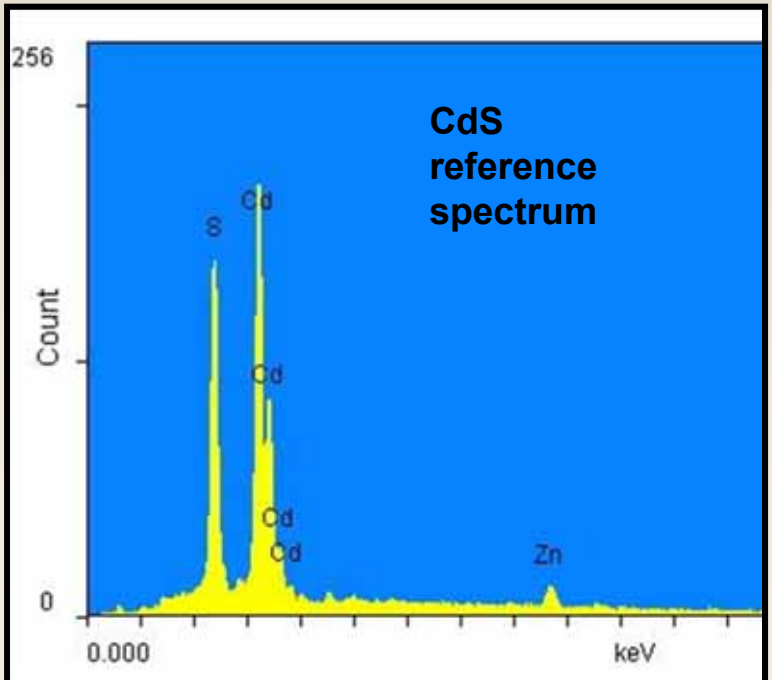

**Degradation confined to Cd yellows**

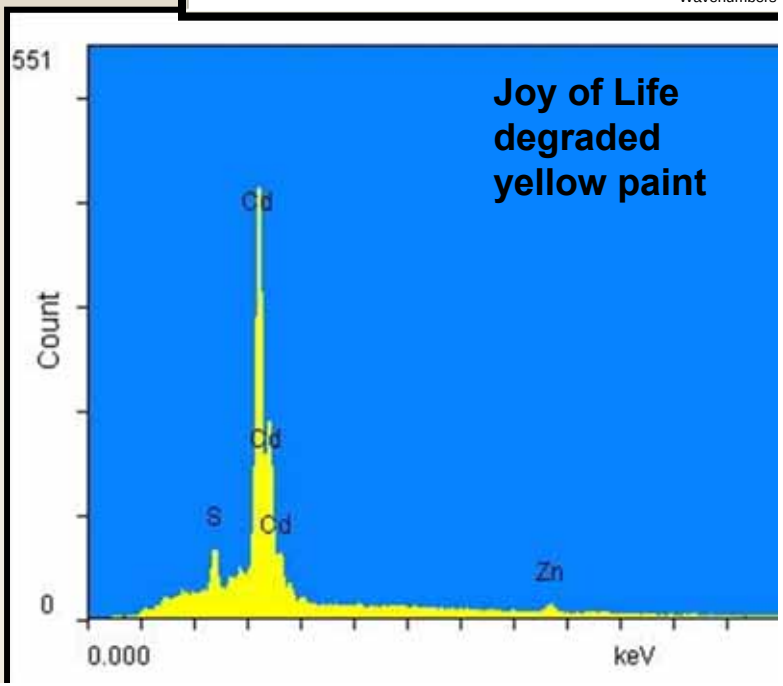
**CdS-based pigments**

# Elemental and Molecular Analysis Degraded Yellows – Confirm CdS?

- **SEM-EDS**
  - **Stoichiometry incorrect**
  - CdS no longer major Cd phase
- **X-Ray Diffraction**
  - **$CdCO_3$ only**
  - No CdS powder pattern
    α-CdS (greenockite), β-CdS (hawleyite)
  - **CdS, if present, is amorphous or nanocrystalline**
- **FTIR**
  - **$CdCO_3$**



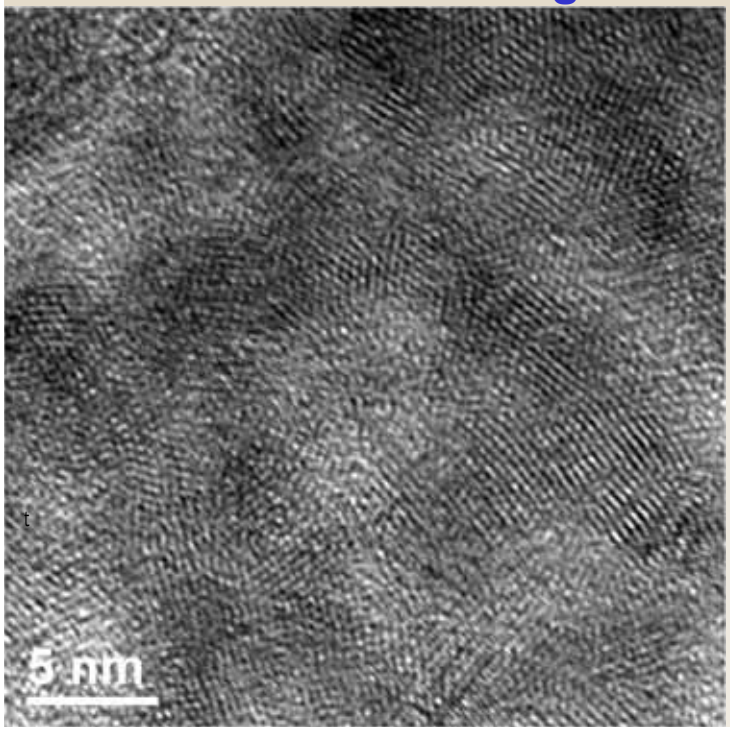




**(B. Berrie, G. Gates, M. Palmer NGA)**

# Synthesis of CdS Using Period Recipes for Matisse Paint Replication

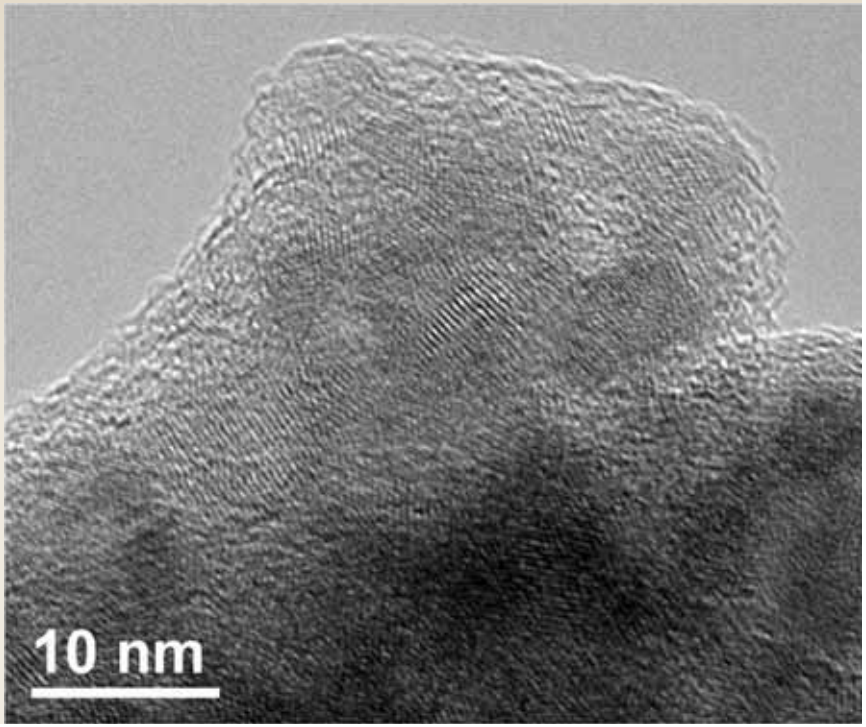
- **XRD, HR-TEM used to monitor**

1. **Amorphous CdS**
   - **$CdO + H_2S \longrightarrow CdS + H_2O$**
   - Translucent ivory solid
   - **Would not have been used as a yellow pigment**
2. **Nanocrystalline CdS**
   - **$CdSO_4.8H_20 + Na_2S.9H_2O \xrightarrow{50°C} CdS + Na_2SO_4$**
   - **Yellow-orange solid - 2.9 nm crystallite size**



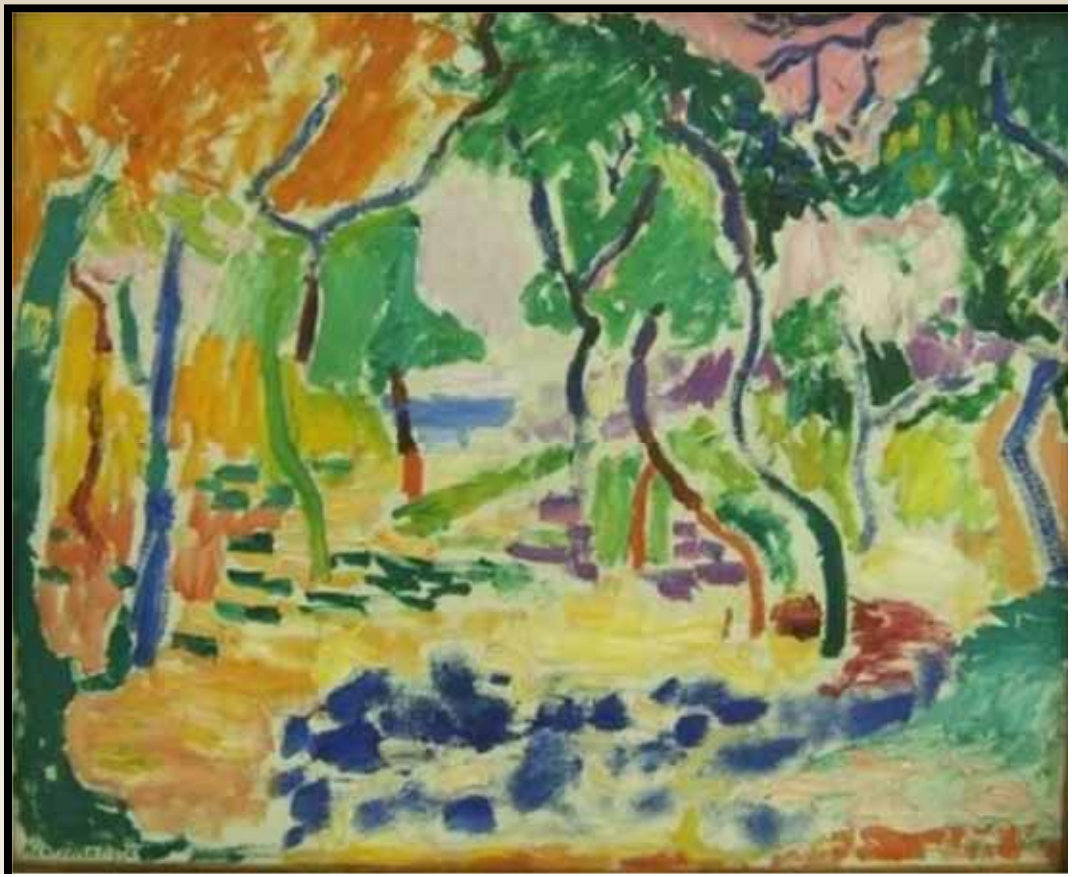

No calcination step in turn of 20th c.

caused later reactivity



## One Explanation for $CdCO_3$: Photo-Oxidative Degradation of CdS

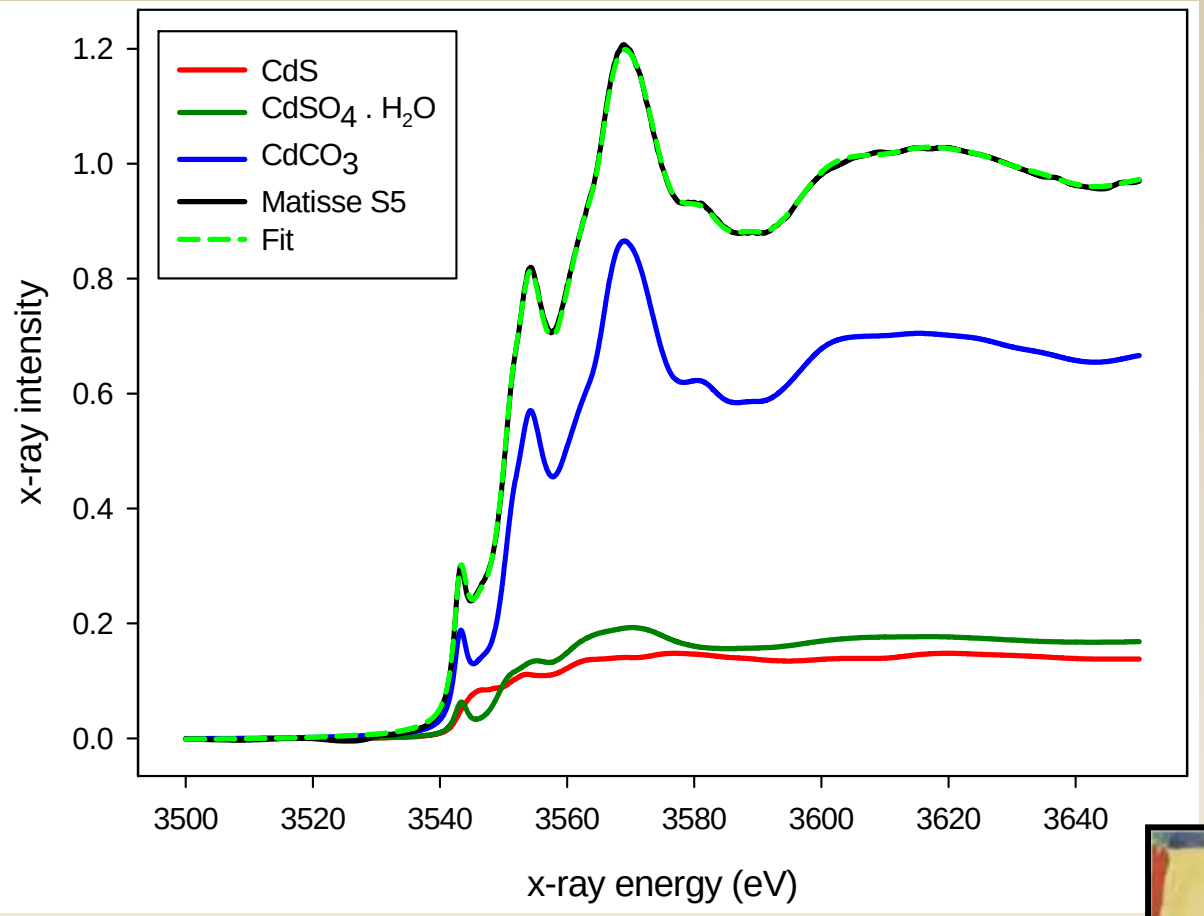
- **When photon E incident light ≈ band gap (2.42 eV, 512 nm)**
  - $CdS + h\nu = CdS + e^- + h^+$
  - $CdS + 2h^+ = \mathbf{Cd^{2+}} + S(s)$
  - $CdS + 2O_2 = Cd^{2+} + \mathbf{SO_4^{2-}}$
  - $Cd^{2+} + SO_4^{2-} = \mathbf{CdSO_4}$
  - $CdS + 1.5\ O_2 = \mathbf{CdO} + SO_2$
  - $CdO + CO_2 = \mathbf{CdCO_3}$



Landscape at Collioure/Study for *Le Bonheur de vivre* (1905)
Statens Museum for Kunst
Copenhagen

# Cd L Edge XANES Data

**10 micron beam size**




**Best fit local composition:**

**68.6 % $CdCO_3$**
**14.2 % CdS**
**17.1 % $CdSO_4.nH_2O$**

**Consistent with XRD, FTIR**

**$CdSO_4.nH_2O$ makes proposed photo-oxidation mechanism more likely**

**opportunity to re-evaluate scholarship of iconic work**

**"…the dirty yellow ground is for the most part patchily scrubbed in…"**

*Matisse and the Subject of Modernism*, Alastair Wright, 2004

**Georges Seurat *A Sunday on La Grande Jatte* (1884) The Art Institute of Chicago (Casadio et al.)**

*First Campaign*: May 1884 - March 1885
*Second Campaign*: October 1885 - March 1886
*Third Campaign*: 1888/1889

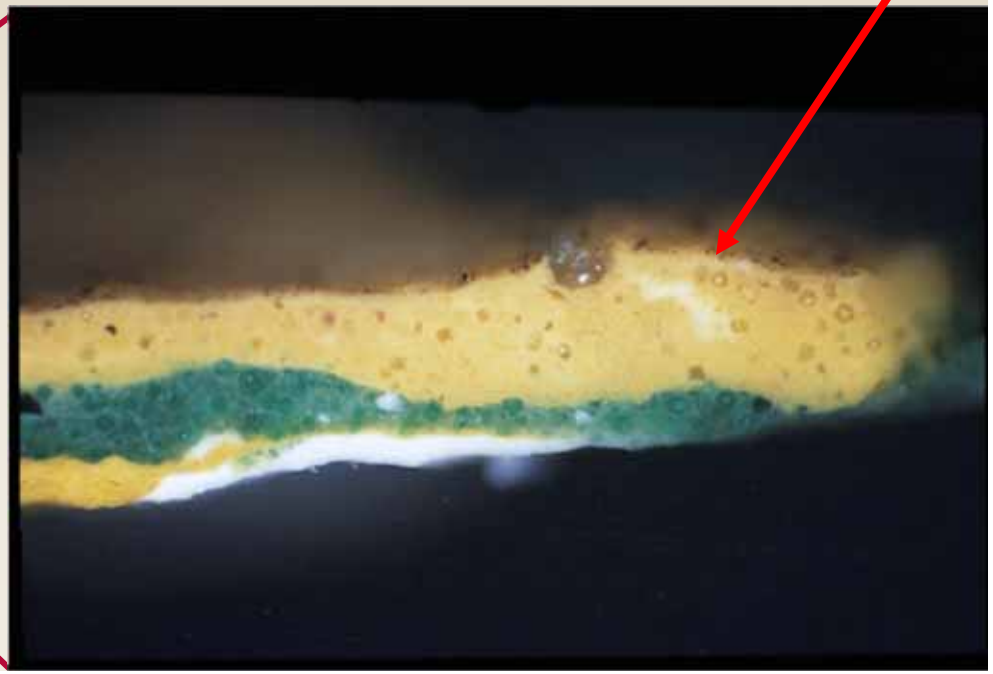
L. Zanella et al., "The Darkening of zinc yellow: XANES speciation of chromium in artist's paints after light and chemical exposures", **J. Anal.At. Spectrom.** 26 (2011) 1090-1097.

- **zinc yellow ($K_2O*4ZnCrO_4*3H_2O$)**
- bright greenish-yellow
- upon manufacture

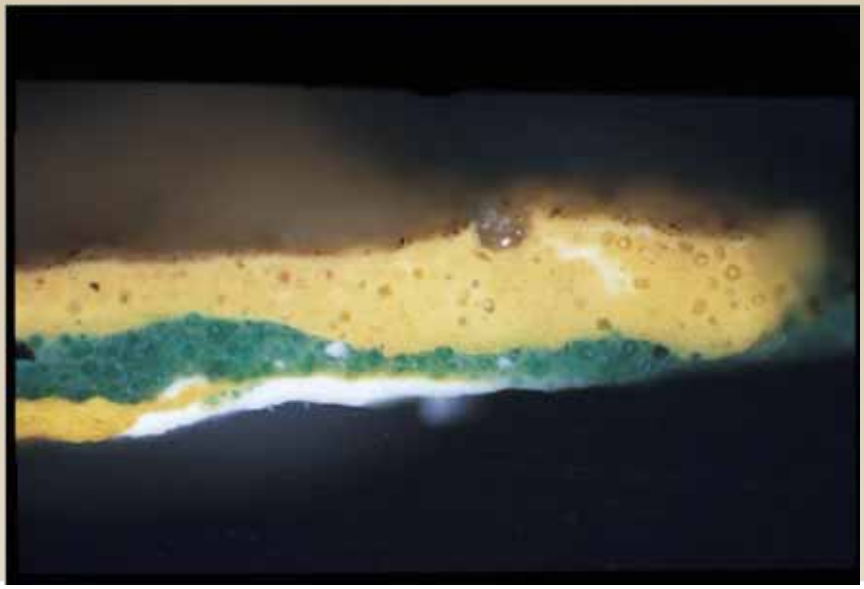
•darkens rapidly to dull, ochre yellow hue

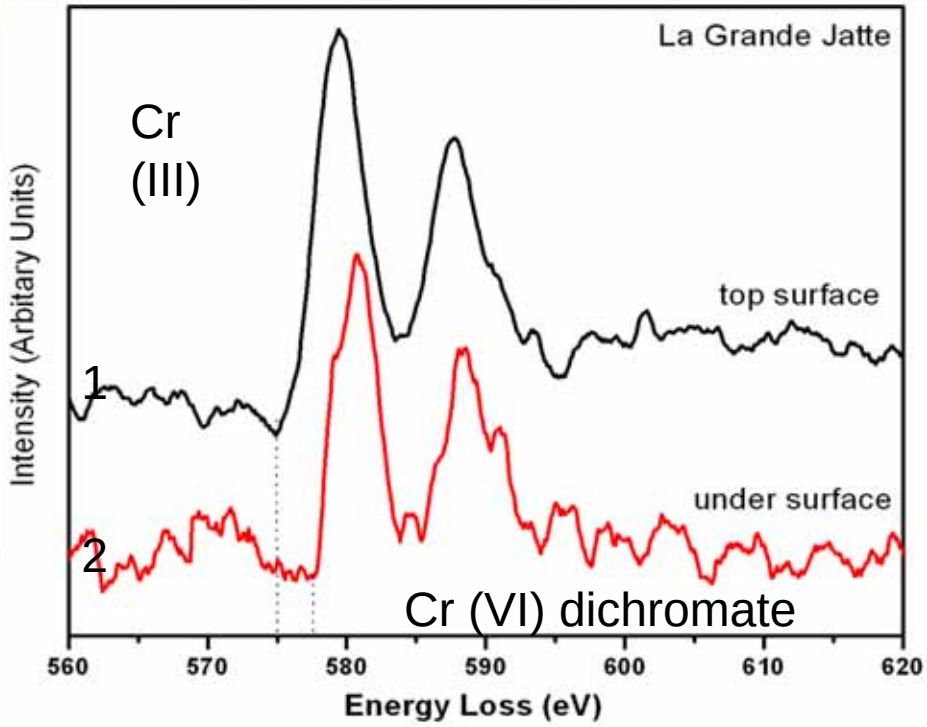
- photochemical reduction of chromates?

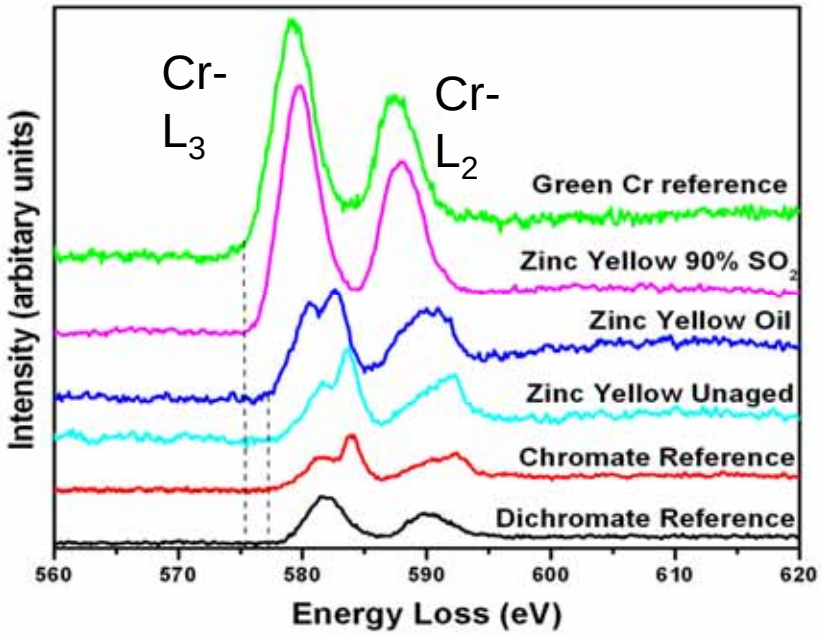
- greenish color of zinc yellow due to transformation of chromate ($CrO_4^{2-}$) into chromium oxide ($Cr_2O_3$)?



# Cr EELS on Altered Zinc Yellow from La Grande Jatte






Cr (III)

Cr (VI)

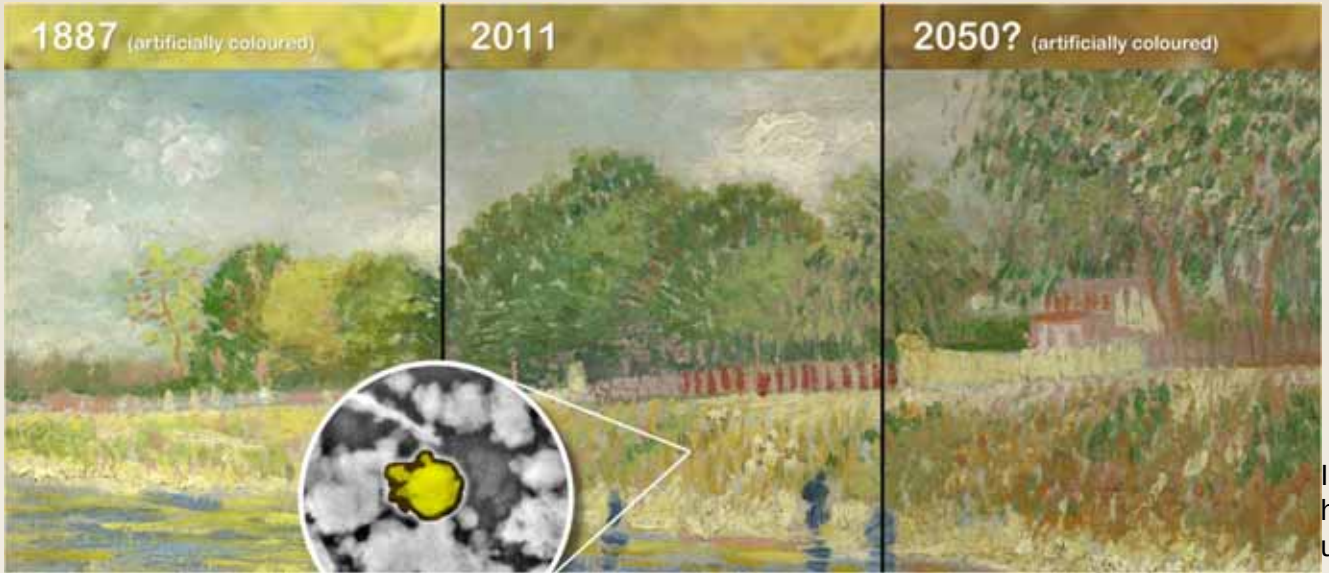
PRESENT STATE

AFTER DIGITAL REJUVENATION

**$PbCrO_4$ photo-reduction in works by van Gogh**

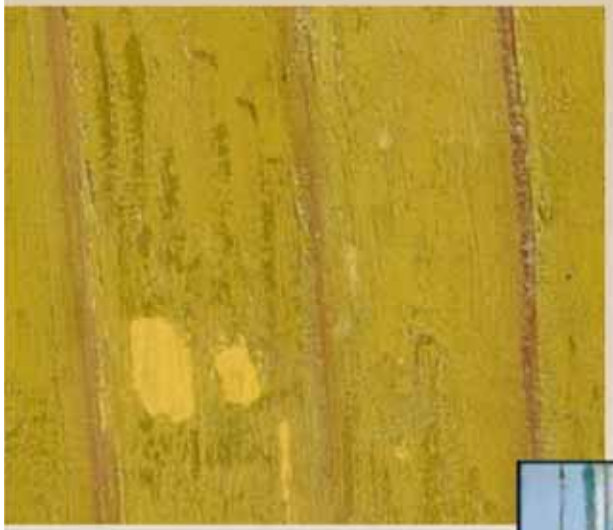
*Bank of the Seine* (V. Van Gogh, 1887)

J. Dik, Koen Janssens, *et al.*




Images from: http://www.vangogh.ua.ac.be/

*The Bedroom* (October 1888)
when the artist was living in the Yellow House in Arles



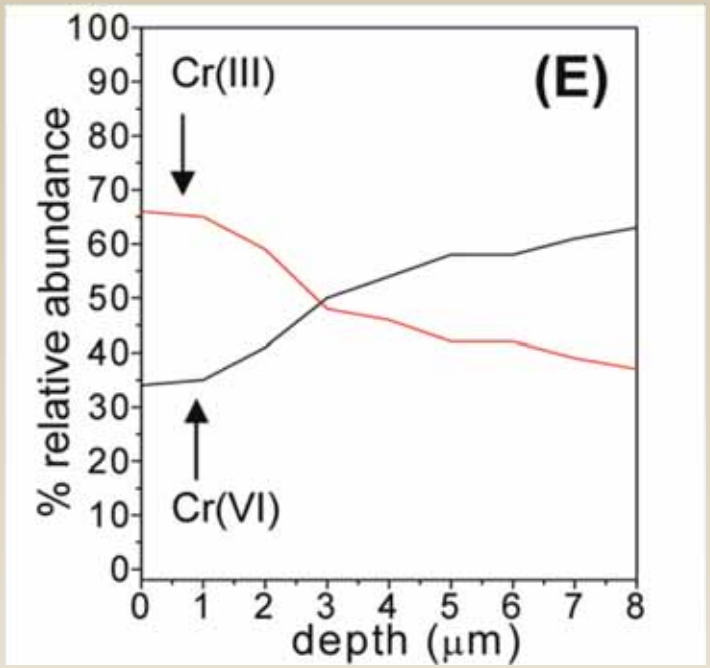
**Photomicrographs of altered $PbCrO_4$ (chrome yellow) paint**

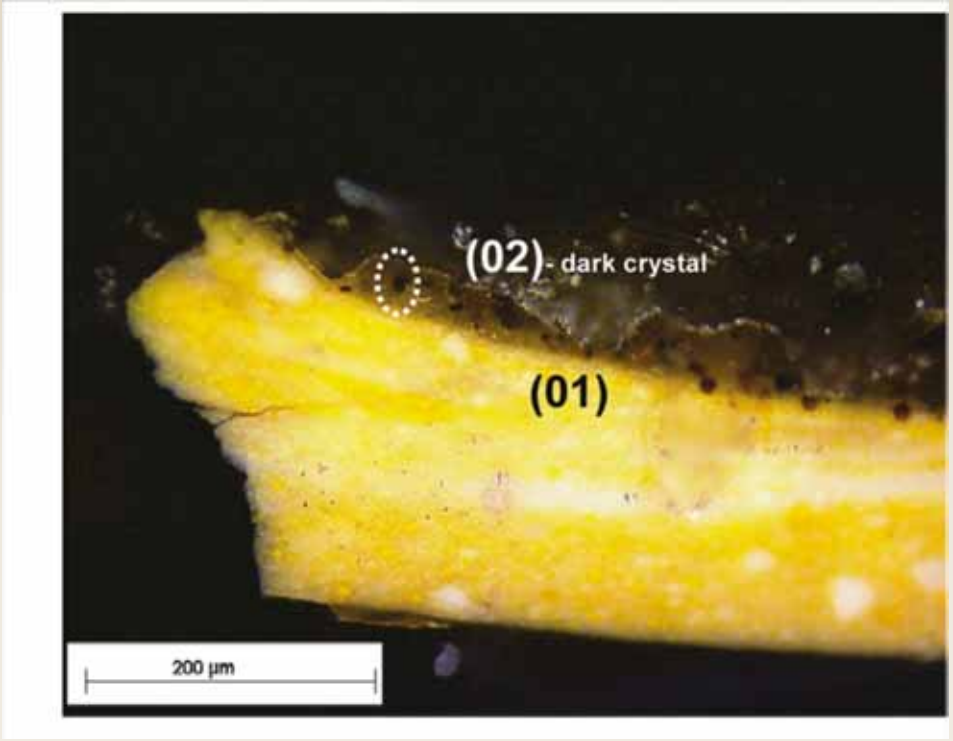
**Alteration layer less than 3 μm thick**

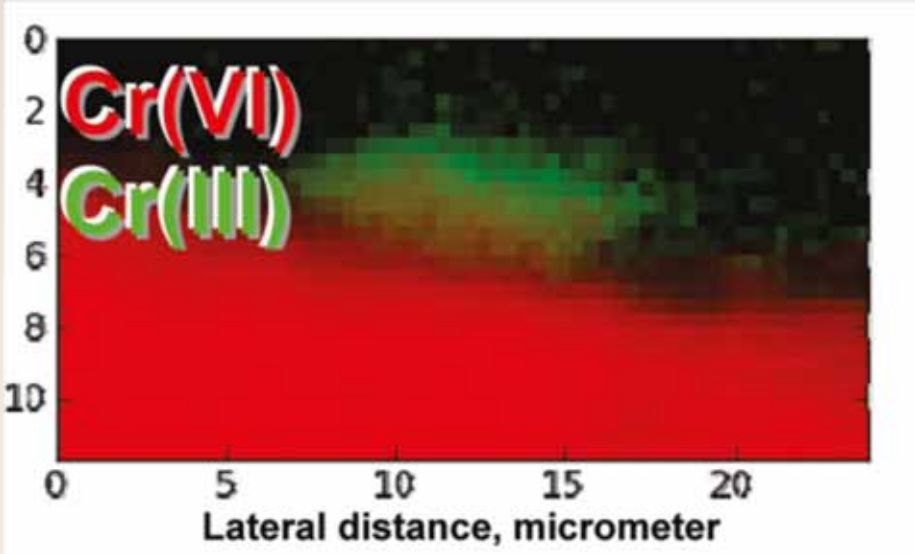
http://www.vangogh.ua.ac.be/

# μXANES Mapping

*"Degradation Process of Lead Chromate in Paintings by Vincent van Gogh Studied by Means of Synchrotron X-ray Spectromicroscopy and Related Methods. 2. Original Paint Layer Samples",by* Letizia Monico et al.,***Analytical Chemistry***83 (2011) 1224-1231,



# Proposed ERL or USR Experiments – Diffraction Limited Hard X-Ray Source

- **Objective: identification of *incipient* photodegradation in Impressionist and Early Modern paintings**

- **Alteration occurring in the top nanometers of paint layers**
  - **Damage visible/disfiguring when 1- 3 μm of photodegradation reached**
- Allows preventive conservation methods before damage is visible
  - Argon-filled cases
  - Controlled light levels
  - RH control

- Speciation of paint surfaces as a function of depth:
  - **CdS photo-oxidation reactions**
  - $CdSO_4.nH_2O$
  - CdO
  - $CdCl_2$ – leftover starting reagent decreased band gap
  - $Cd(OH)_2$
  - $CdCO_3$
  - **$PbCrO_4$ and $K_2O*4ZnCrO_4*3H_2O$ photoreduction**
  - $Cr_2O_3$
  - $PbCrO_4$
  - $K_2O*4ZnCrO_4*3H_2O$

# Experiments for Determining Speciation as a Function of Depth or Photoaging for Model Systems

## Applications of nanoscale x-ray probes

- **nanoXANES – speciation mapping in paint cross-sections**
  - **"screen" painting collections for evidence of incipient photodegradation**
  - **MOMA, Getty, Barnes, MMA, Whitney, Art Institute of Chicago, National Gallery**
- **Confocal nanoXANES – on intact paintings**
  - **Directly probe within and beneath painting's photodegraded "skin"**
  - **Unmounted paint flakes**
    - **Avoid solubility issues**
- **Time-resolved XANES on artificially aging model samples**
- **Time-resolved XRD on artificially aging samples**

**Spatially resolved 3D micro-XANES by a confocal detection scheme**
Geert Silversmit, Bart Vekemans, Sergey Nikitenko, Sylvia Schmitz, Tom Schoonjans, Frank E. Brenker and Laszlo Vincze
***Phys. Chem. Chem. Phys.***, 2010, **12**, 5653-5659

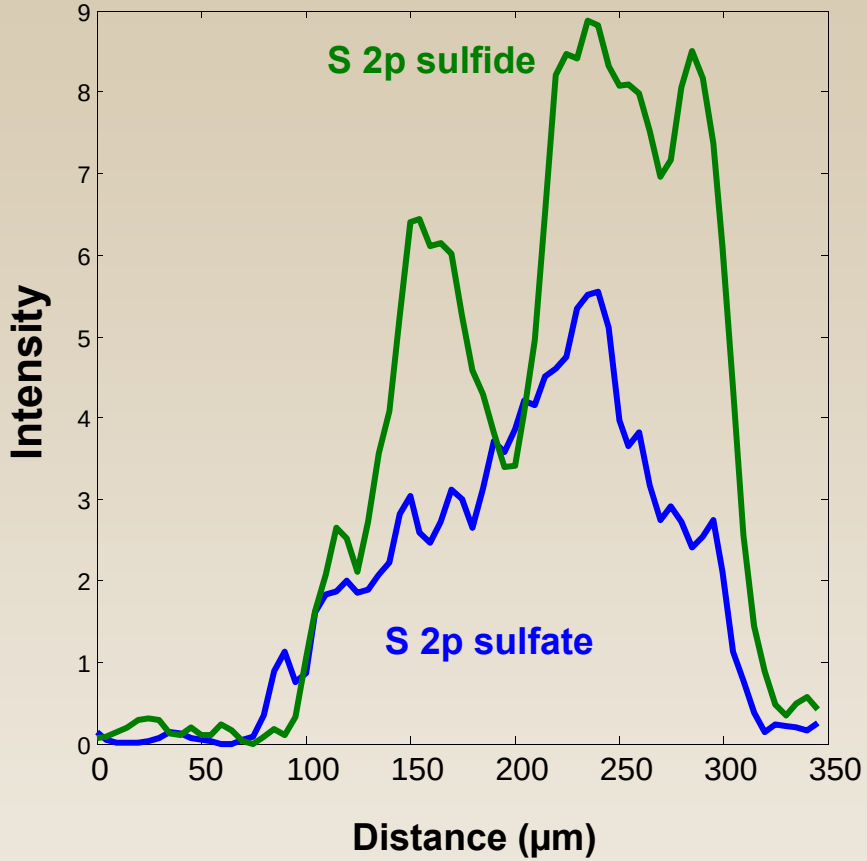
**18.5 x 12.0 x 10.0 $\mu m^3$ at the Cu K-edge**

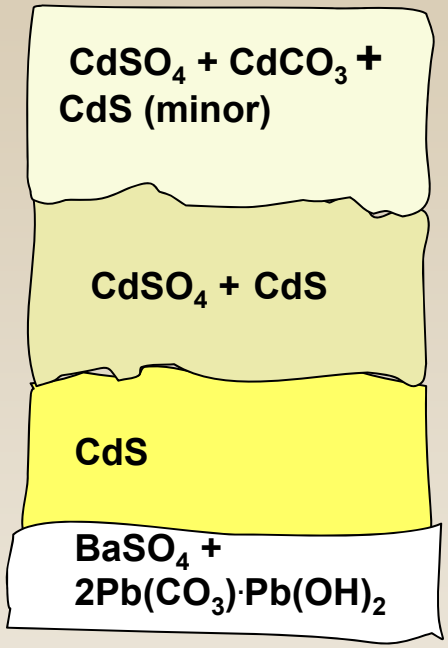
# Why Pigment Alteration Problems Require Resolution Beyond Microbeams (limitations of cross-sections):

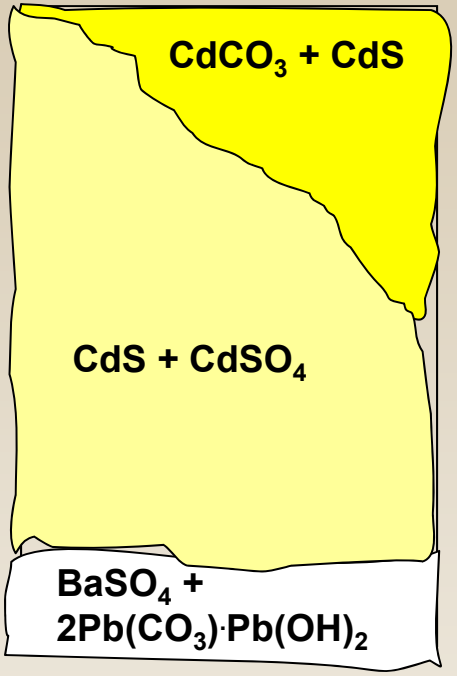
## XPS $S^{2-}$ and $SO_4^{2-}$ Concentrations

## Cross Section Line Scan - 10 micron steps

### S 2p line scans




$SO_4^{2-}$ peaks in center of x-section

$CdCO_3$ dominates surface chemistry

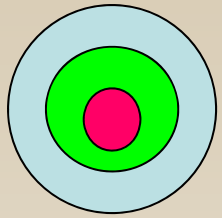
phase distribution does not fit photo-oxidation model proposed – solubility and transport phenomena reflected instead?

# "Coring" of Individual Pigment Particles

**Objective: Photodegradation mechanisms obtained**

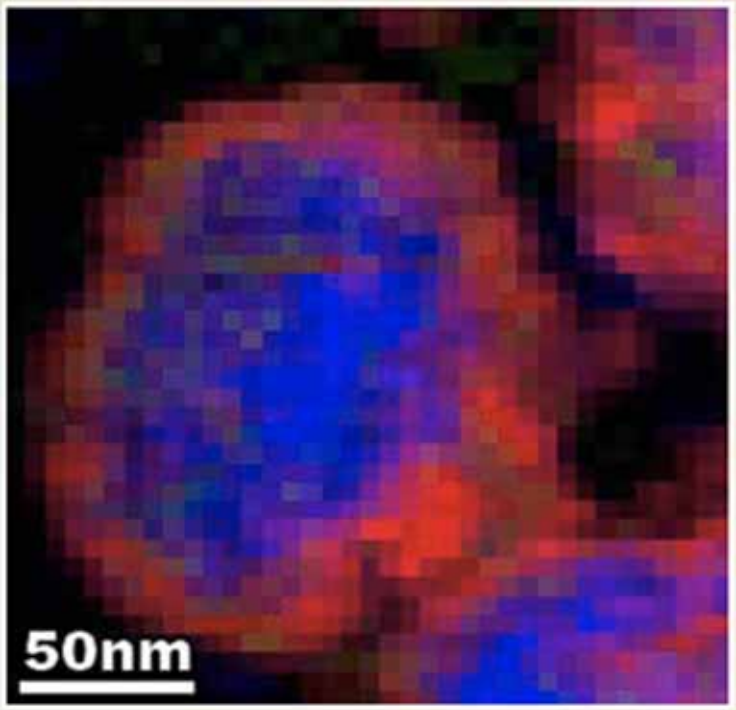
- **impact of transport phenomena eliminated**
- **impact of solubility phenomena eliminated**

**CdS pigment particle size – 1-20 μm**



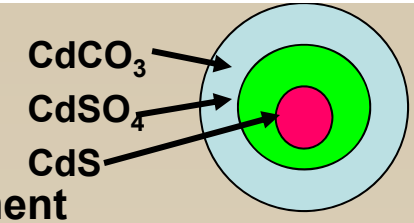
**STEM/EELS map of chromium oxide ($Cr_2O_3$) from one of the grains of $PbCrO_4$ inside the brown alteration layer**

**newly formed Cr(III) compound - a nanometers-thin coating of the pigment particles**



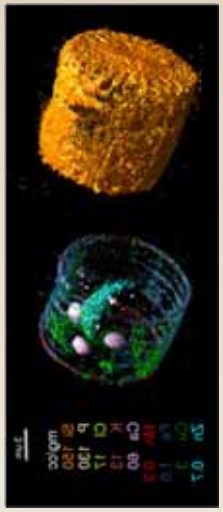

*"Degradation Process of Lead Chromate in Paintings by Vincent van Gogh Studied by Means of Synchrotron X-ray Spectromicroscopy and Related Methods. 1. Artificially Aged Model Samples",*
*by* Letizia Monico, Geert Van der Snickt, Koen Janssens, Wout De Nolf, Costanza Miliani, Johan Verbeeck, He Tian, Haiyan Tan, Joris Dik, Marie Radepont, and Marine Cotte,
***Analytical Chemistry***
83 (2011) 1214-1224

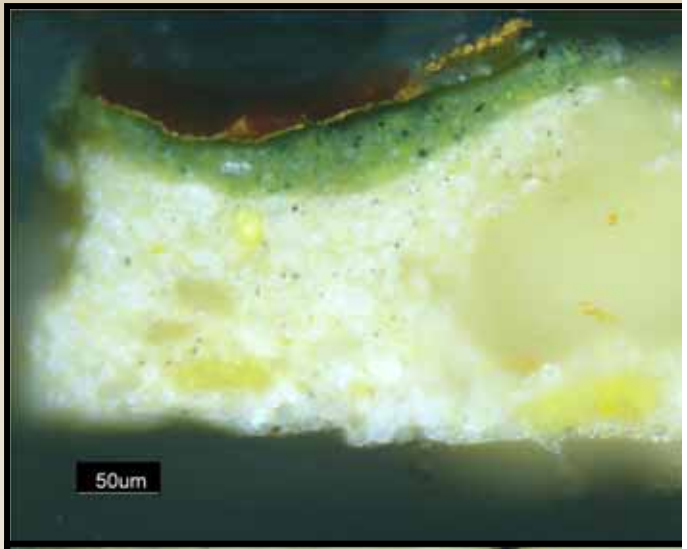
# nanoXRF Experiments




- **Cd/S as a function of depth in pigment particles**
  - **traditional geometry for paint cross-sections**
  - **photoaged model systems**
  - **microsamples removed from paintings**
  - **confocal or conventional geometry for "XRF tomography"**

Trends in hard X-ray fluorescence mapping: environmental applications in the age of fast detectors, E. Lombi et al., **Analytical and Bioanalytical Chemistry**, 400(6) 1637-1644, JUN 2011

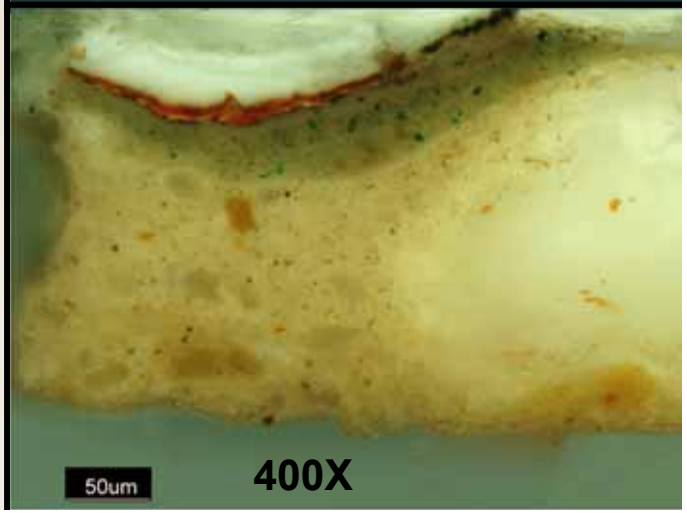





- **confocal geometry for intact paintings**

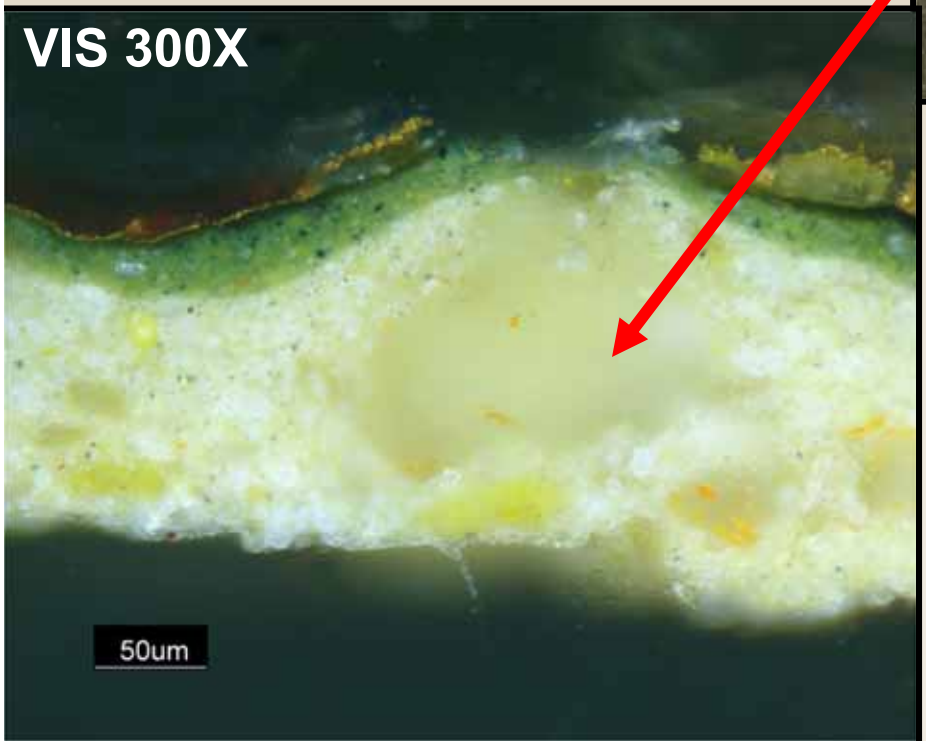
## nanoTomography Experiments

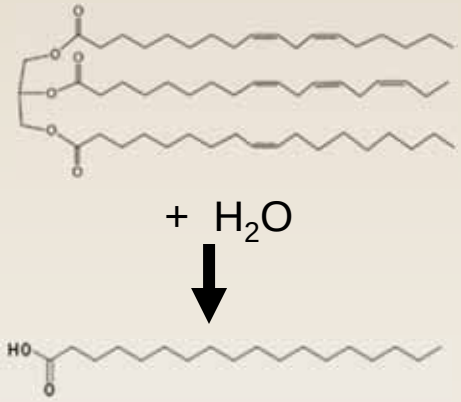
- **nanoscale x-ray tomography of paint cross-sections**
- **imaging of alteration zones, reaction zones**
- **imaging of materials migrating through cross-sections (J. Boon μm length scale)**
- **growth of lead carboxylate aggregates**
- **growth of new phases inside aggregates ($Pb_3O_4$)**



# Lead Soap Aggregates

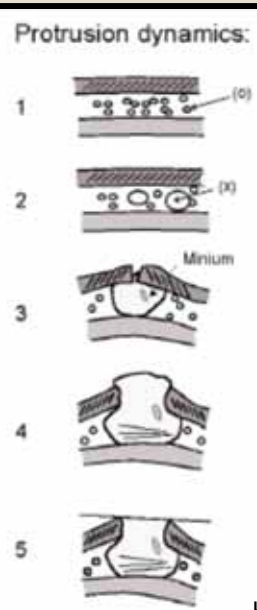
- **lead pigments react with free fatty acids in drying oil**
  - **Form lead carboxylate salts/soaps**
- **phase separate from rest of layer**
- **Creates pebbly surface**
- **pinpoint paint losses**
- **monitor formation by nanoscale x-ray scattering?**




Free fatty acids come from hydrolysis of paint layers

Slow formation and aggregation by controlling R.H.

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