Physics, Chemistry and Biology in Art Conservation

Dani Arias-Rotondo

MacMillan Group Meeting
May 6, 2020

(dedicated to my Mom, who wishes I was an artist instead)

Art Conservation and Cultural Heritage

What are “Works of Art”?

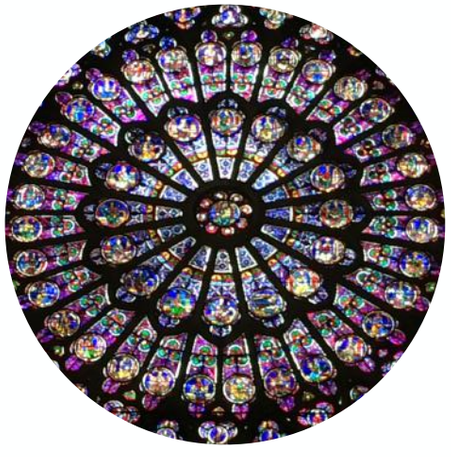
paintings

sculptures

frescoes

buildings

textiles



stained glass

Large variety of materials and techniques employed: ***art conservation is a multidisciplinary scientific endeavor***

https://commons.wikimedia.org

Physics, Chemistry and Biology in Art Conservation

Presentation Outline

Introduction

- Motivation
- Relevant Questions

Understanding the Past

- Analytical Techniques
- X-ray Spectroscopy
- Case Studies: Vermilion Photodarkening

Towards the Future

- Cleaning Works of Art
- Case Studies: Microorganisms for Biocleaning

From Craft to Science

Until the Nineteenth Century

Art conservation was carried out by artisans, taught as an apprenticeship

Late 19th century – Early 20th century

***1880** – First Museum Laboratory opened (State Museum in Berlin)*

***1919** – British Museum opened its laboratory for Research in Conservation*

finding and training scientists to work on art conservation was still a challenge

In the United States

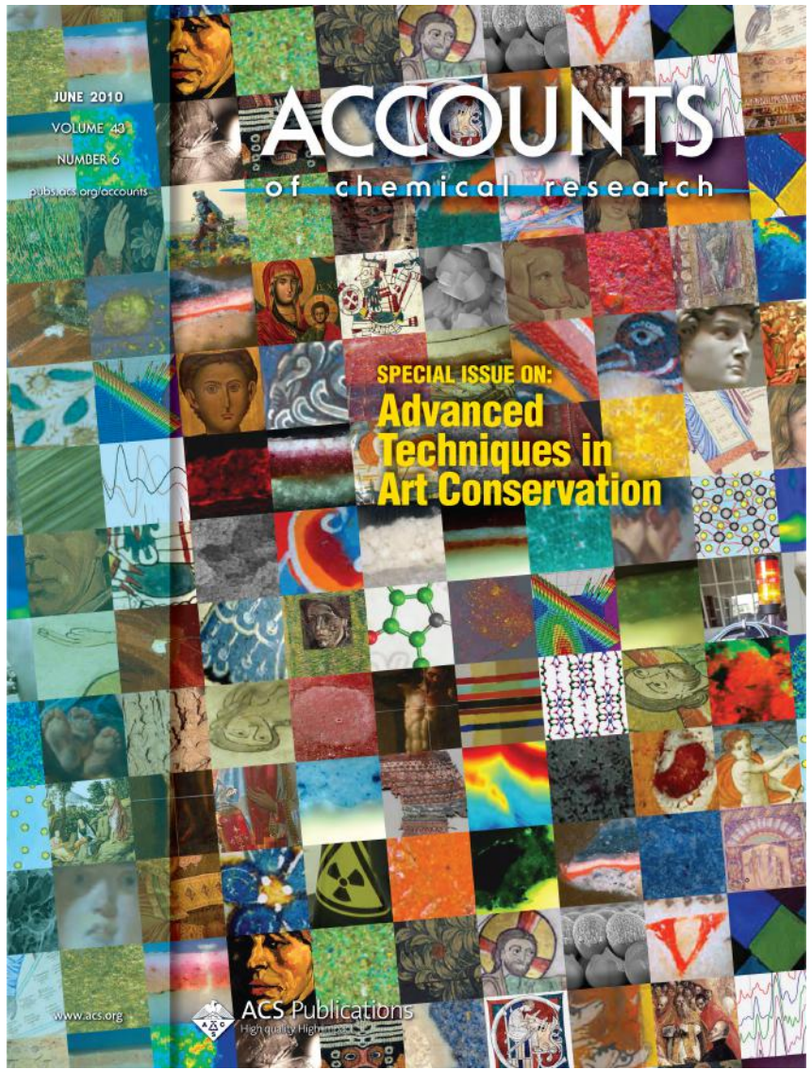
***late 1950s** – Fogg Museum (Harvard) ceased to accept apprentices*

***1960** – The Conservation Center of the Institute of Fine Arts (NYU) opened*

oldest degree-granting conservation program in North America

https://www.nyu.edu/gsas/dept/fineart/conservation/history.htm
Gettens, R. *Science* **1961**, *133*, 1212.

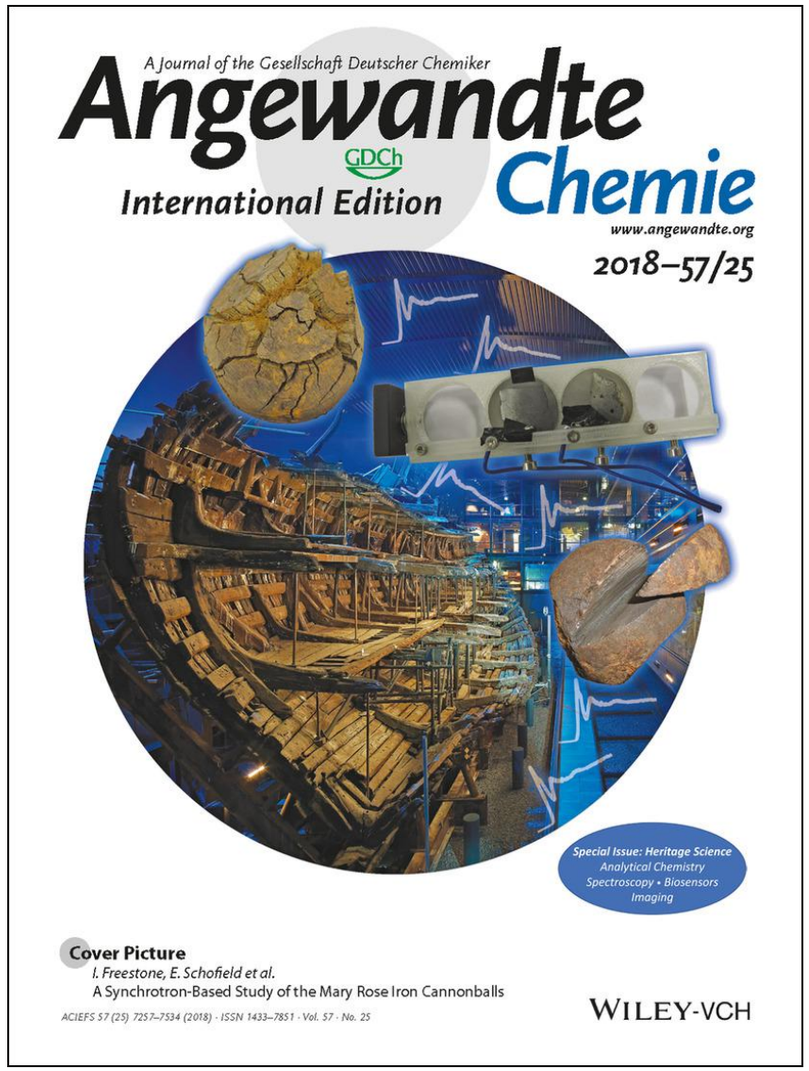
From Craft to Science



Volume 43, Issue 6 – 2010

Special Issue

Advanced Techniques in Art Conservation



Volume 57, Issue 25 – 2018

Special Issue

Heritage Science

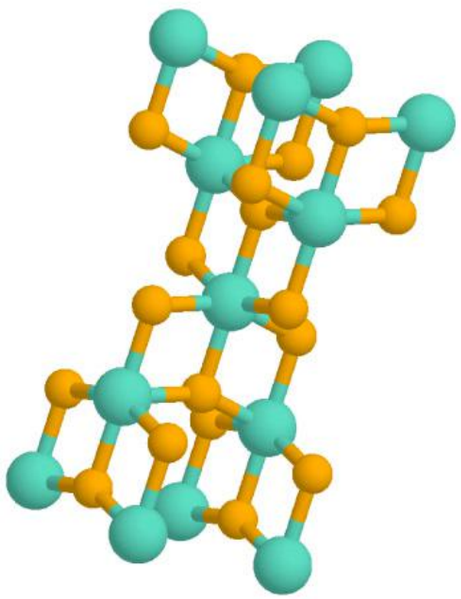
What Questions are Relevant for Art Conservation?

A Better Understanding of the Past

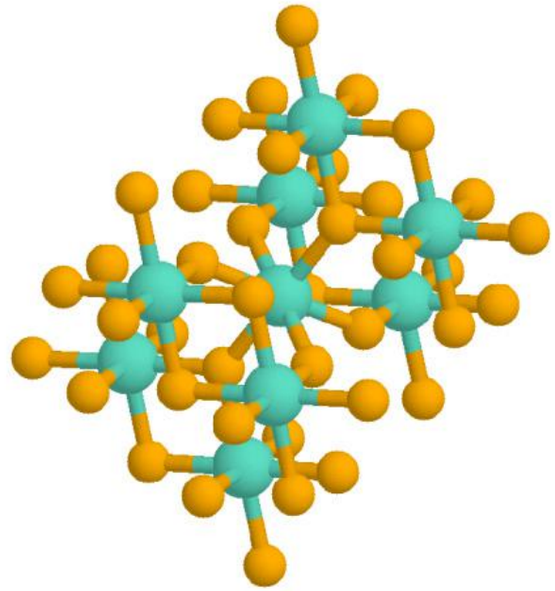
- Choice of ingredients
- Manufacturing processes
- Geographical origin

Artifacts may be dated and/or authenticated

synthetic white pigments in modern paintings: TiO_2



anatase (~1920)



rutile (~1940)

Cotte, M. et al. *J. Anal. At. Spectrom.* **2008**, *23*, 820.
Cotte, M. et al. *Acc. Chem. Res.* **2010**, *43*, 705.

What Questions are Relevant for Art Conservation?

A Better Understanding of the Past

- Choice of ingredients
- Manufacturing processes
- Geographical origin

Artifacts may be dated and/or authenticated

A Well-Founded Prediction of the Future

- Alteration due to external factors
- Effect of past treatments
- Inherent decay processes

Improve restoration and conservation techniques

This combined approach is key to successfully preserve cultural heritage

Cotte, M. et al. *J. Anal. At. Spectrom.* **2008**, *23*, 820.
Cotte, M. et al. *Acc. Chem. Res.* **2010**, *43*, 705.

What Questions are Relevant for Art Conservation?

This combined approach is key to successfully preserve cultural heritage

https://www.nytimes.com/2012/08/24/world/europe/botched-restoration-of-ecce-homo-fresco-shocks-spain.html

Analytical Techniques in Art Conservation

Works of Art

unique and irreplaceable

non-destructive techniques

microsampling

complex and heterogenous

high sensitivity

spatial resolution

Such artifacts are better studied using a combination of techniques

AFM *GC-MS* *UV-vis*

optical microscopy *SIMS* *Raman* *ion chromatography*

TGA *DSC* *SEM-EDX*

FTIR ***XRD*** ***XAS*** ***XRF***

greatly enhanced by synchrotron radiation

Giovanni Brunetti, B. et al. *Acc. Chem. Res.* **2010**, *43*, 693.

Synchrotron Radiation (SR)-Based Techniques

Advantages of Synchrotron Radiation

- higher sensitivity
- minimal sample preparation
- micro-to-submicroscale

European Synchrotron Radiation Facility

Grenoble (France)

https://www.esrf.eu/about

Cotte, M. et al. *Acc. Chem. Res.* **2010**, *43*, 705.

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European Synchrotron Radiation Facility

Grenoble (France)

ID21 beamline

~25% beamtime

Cultural Heritage applications

Cotte, M. et al. *J. Anal. At. Spectrom.* **2017**, *32*, 477.

https://www.esrf.eu/about

Cotte, M. et al. *Acc. Chem. Res.* **2010**, *43*, 705.

Synchrotron Radiation (SR)-Based Techniques

Advantages of Synchrotron Radiation

- higher sensitivity
- minimal sample preparation
- micro-to-submicroscale

μ-FTIR

functional groups

μ-XRD

phase identification

structural information

μ-XAS (absorption)

amorphous or crystalline materials

XANES

oxidation states

chemical speciation

EXAFS

bond distances

coordination numbers

μ-XRF (fluorescence)

low detection limits

elemental maps

Cotte, M. et al. *J. Anal. At. Spectrom.* **2017**, *32*, 477.
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Vermilion

The Most Widely Used Red Pigment Around the World

Vermilion (pigment)

- Deep red hue
- Good covering
- Compatible with numerous media (dying oils, egg tempera, true fresco)

Wall painting from the Villa of P. Fannius Synistor at Boscoreale,
ca. 50–40 B.C. Roman, Late Republic. Fresco
The Metropolitan Museum of Art

Funerary Mask, A.D. 900–1100. Peru.
Gold, silver-copper overlays, cinnabar,
The Metropolitan Museum of Art

https://www.metmuseum.org/blogs/collection-insights/2018/cinnabar-vermilion

Vermilion

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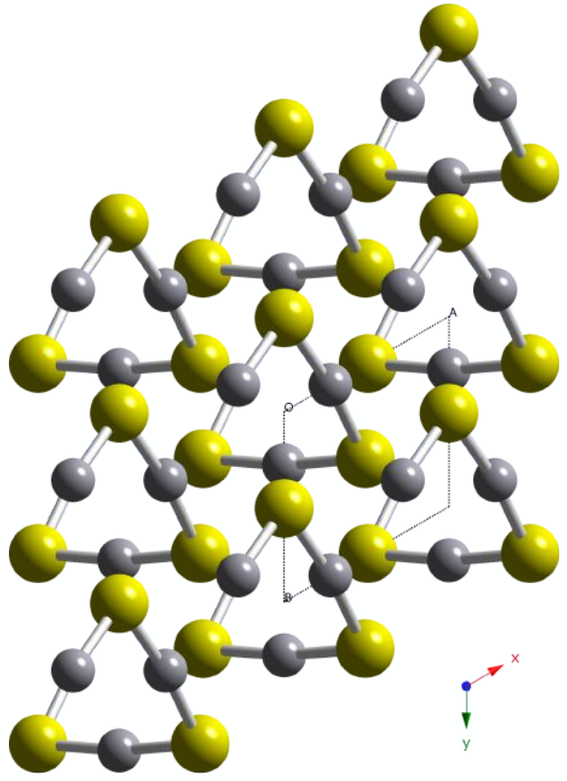
The Mineral

- Most common mercury ore
- Mined since 10,000 B.C.
- α-HgS (cinnabar structure)



Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.
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Vermilion is photosensitive in the presence of halogens ⟹ **it darkens over time**

Understanding the degradation processes informs conservation efforts

Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.

https://www.metmuseum.org/blogs/collection-insights/2018/cinnabar-vermilion

The Monastery of Pedralbes in Barcelona

Vermilion in Gothic Architecture

Founded in 1326 by Queen Elisenda de Montcada and her husband King James II

https://monestirpedralbes.barcelona/ca/monestir/lespai/claustre

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Vermilion in Gothic Architecture

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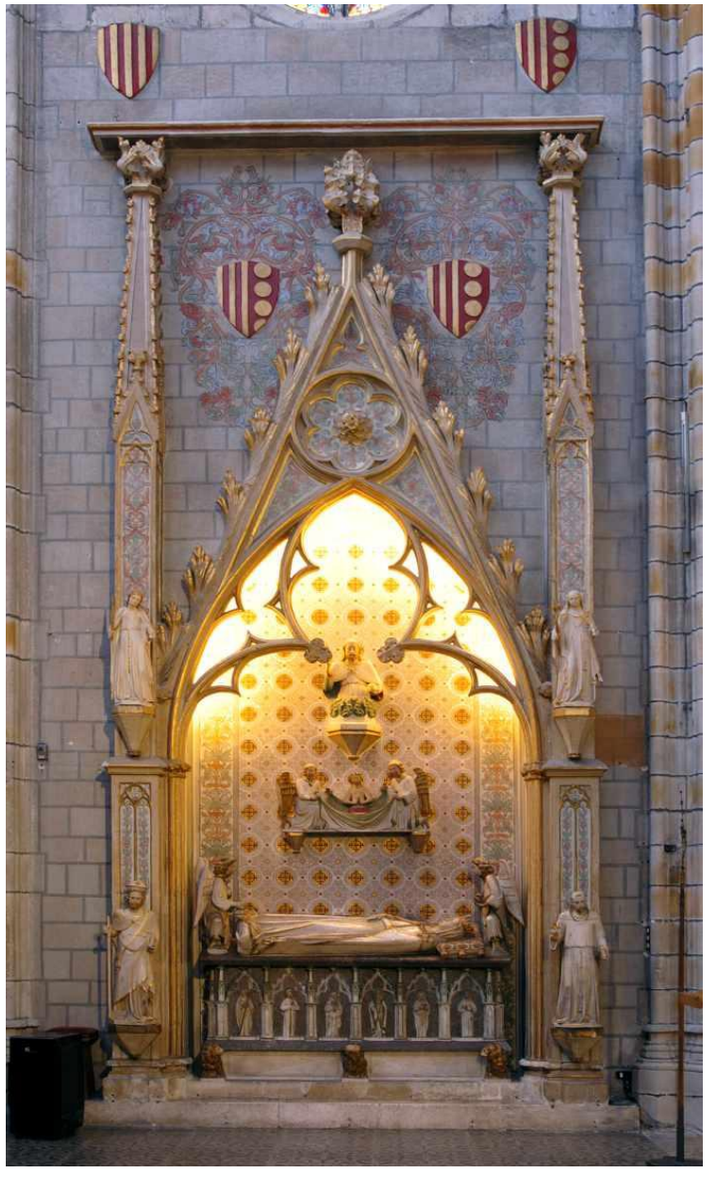

Queen Elisenda's Tomb

Polychromic flowered decoration using vermilion

The walls were covered with plaster (gypsum) at a later time

The plaster was later removed, damaging the original painting

Restoration project began in 2007

https://monestirpedralbes.barcelona/es/monasterio/espacio/sepulcro_de_reina

Cotte, M. et al. *J. Anal. At. Spectrom.* **2008**, *23*, 820.

The Monastery of Pedralbes in Barcelona

Vermilion in Gothic Architecture

- Goal: Identify Original Materials and Decomposition Products

Cinnabar identified using SEM-EDX

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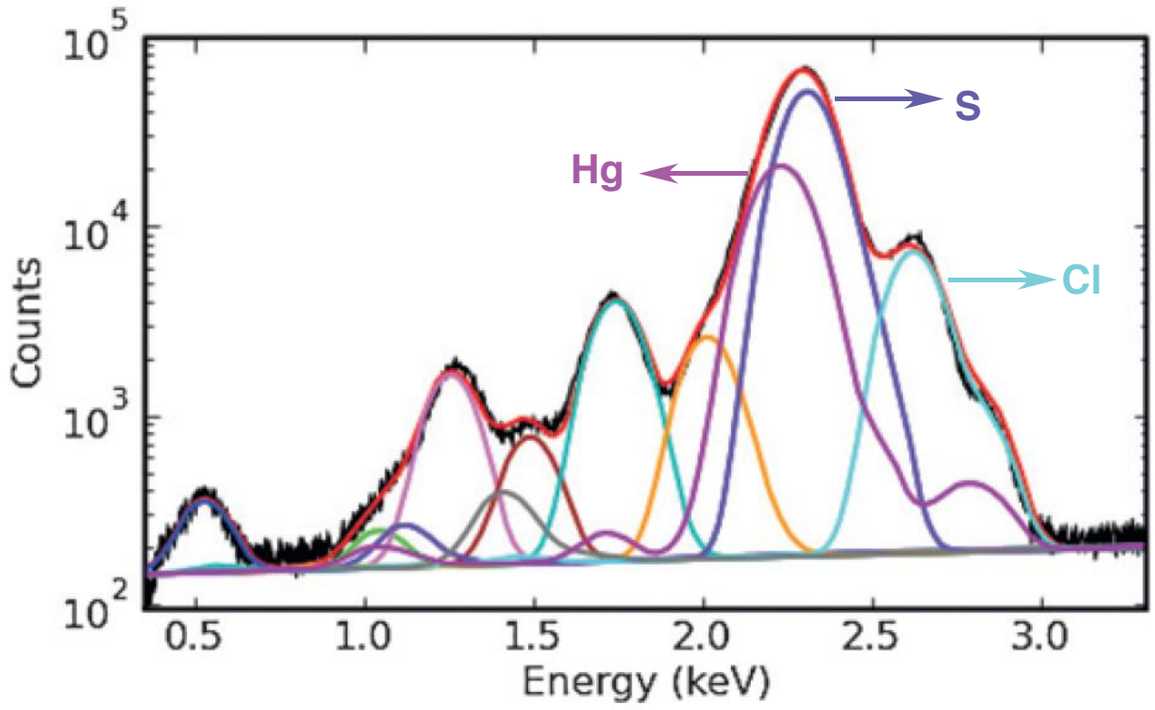


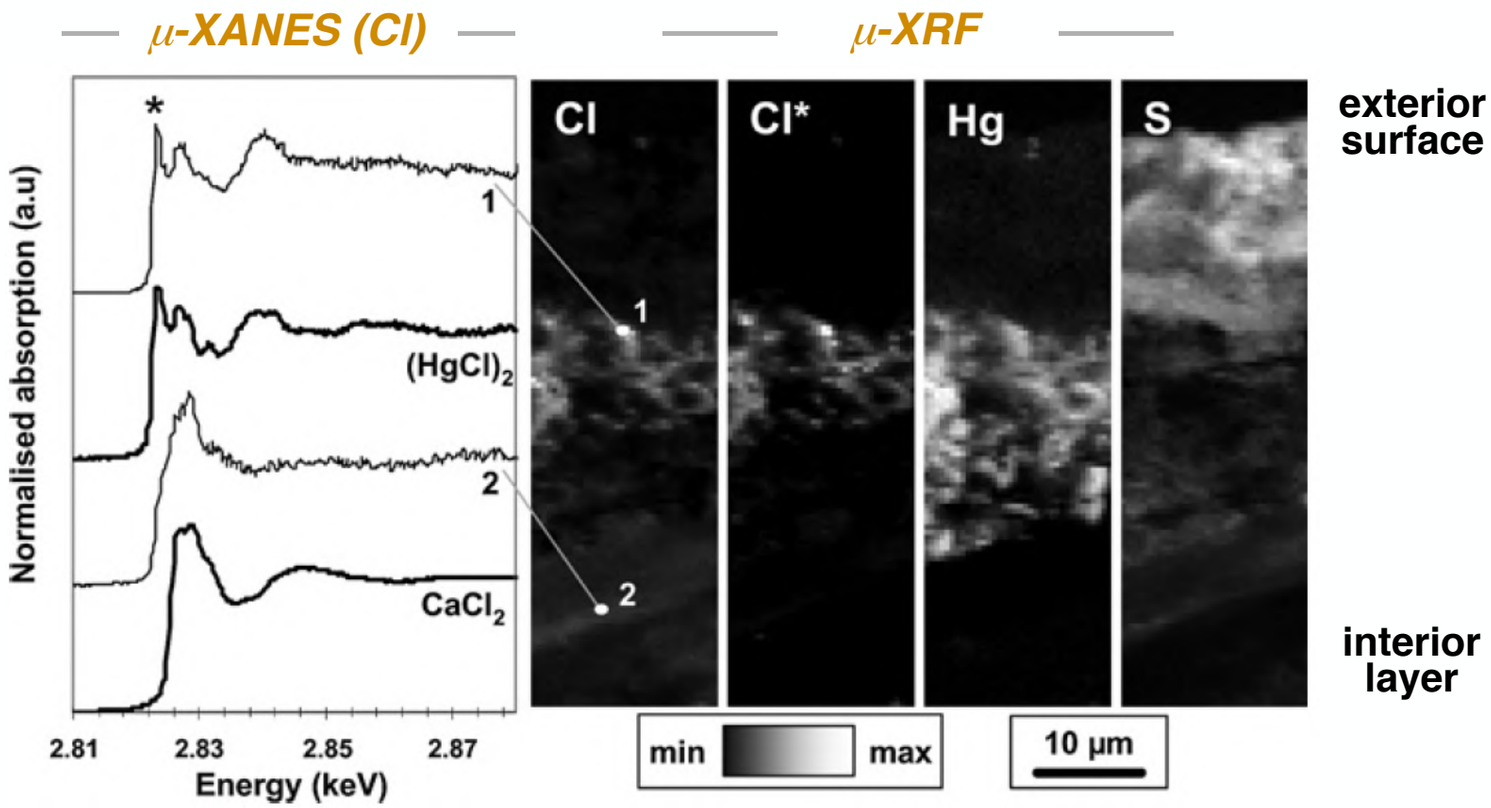
Main elements not always co-located

Cotte, M. et al. *J. Anal. At. Spectrom.* **2008**, *23*, 820.

The Monastery of Pedralbes in Barcelona

Vermilion in Gothic Architecture

- Three elements of interest: Hg, S, and Cl – μ-XANES and μ-XRF to distinguish co-location and bonding



- Cl is only bonded to Hg on the surface of the grains
- S and Cl are mainly separated

Cotte, M. et al. *J. Anal. At. Spectrom.* **2008**, *23*, 820.

The Monastery of Pedralbes in Barcelona

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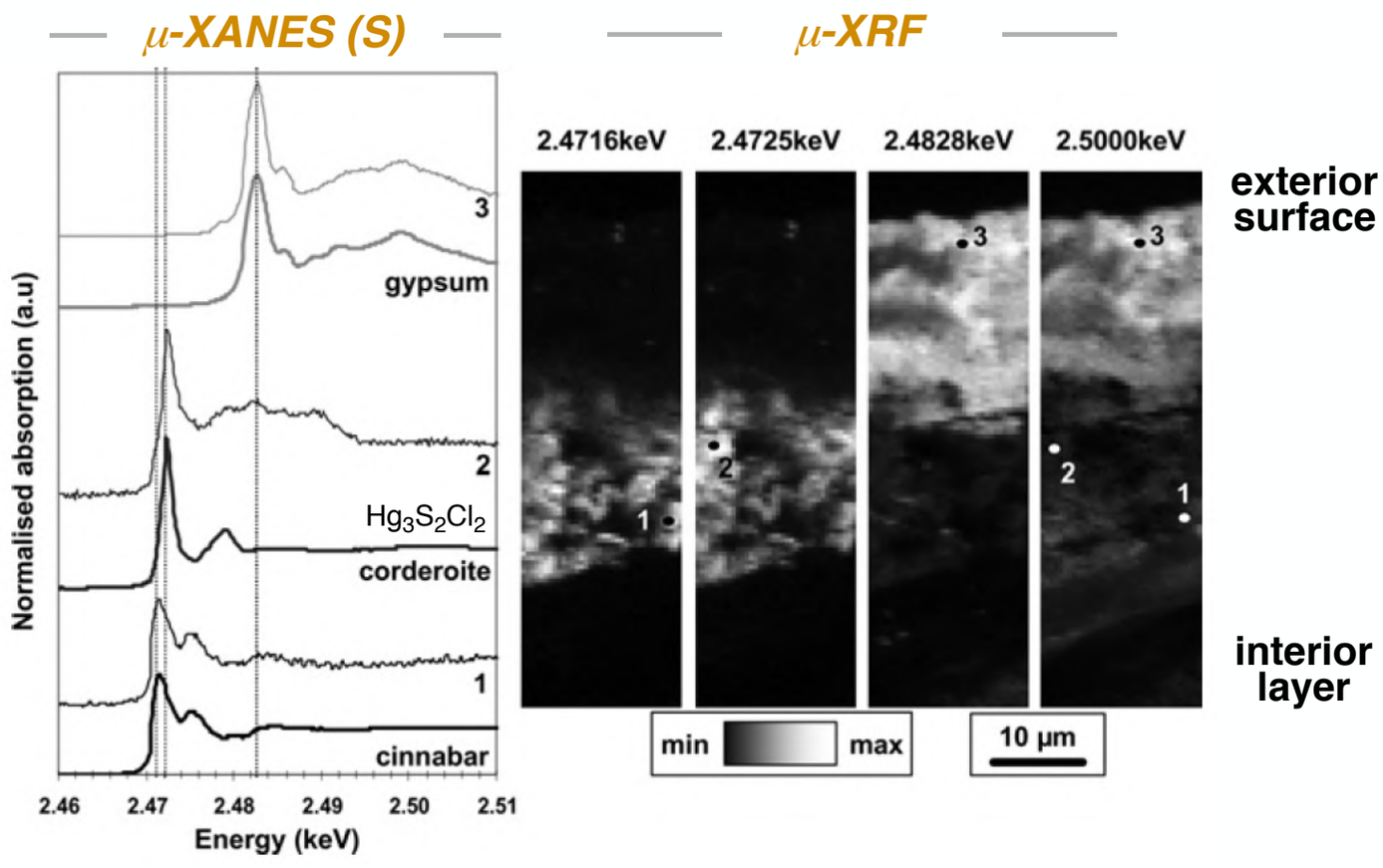


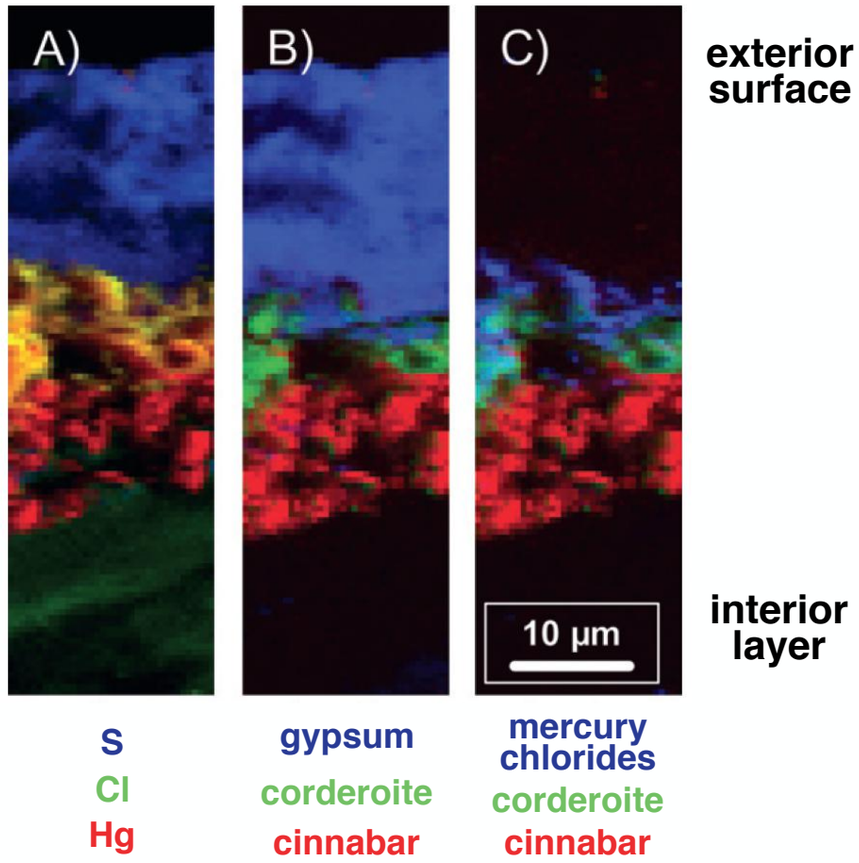
- Three main S-containing species, forming separate layers

Cotte, M. et al. *J. Anal. At. Spectrom.* **2008**, *23*, 820.

The Monastery of Pedralbes in Barcelona

Vermilion in Gothic Architecture

- From cinnabar to calomel – what is the role of chlorine?



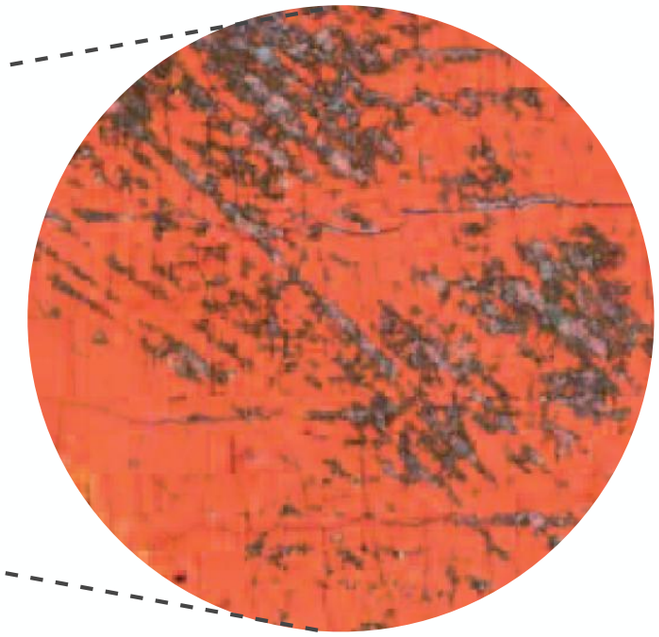
Layered structure suggests chlorine "digests" cinnabar from the top down

Cotte, M. et al. *J. Anal. At. Spectrom.* **2008**, *23*, 820.

Aging of Cinnabar: Paintings vs. Laboratory Samples

original paint samples

P. P. Rubens (1577-1640)
The Adoration of the Magi (1624), oil on canvas
Royal Museum of Fine Arts Antwerp



white crystals observed
on top of the darkened sections

Radepont, M. et al. *J. Anal. At. Spectrom.* **2011**, *26*, 959.

Aging of Cinnabar: Paintings vs. Laboratory Samples

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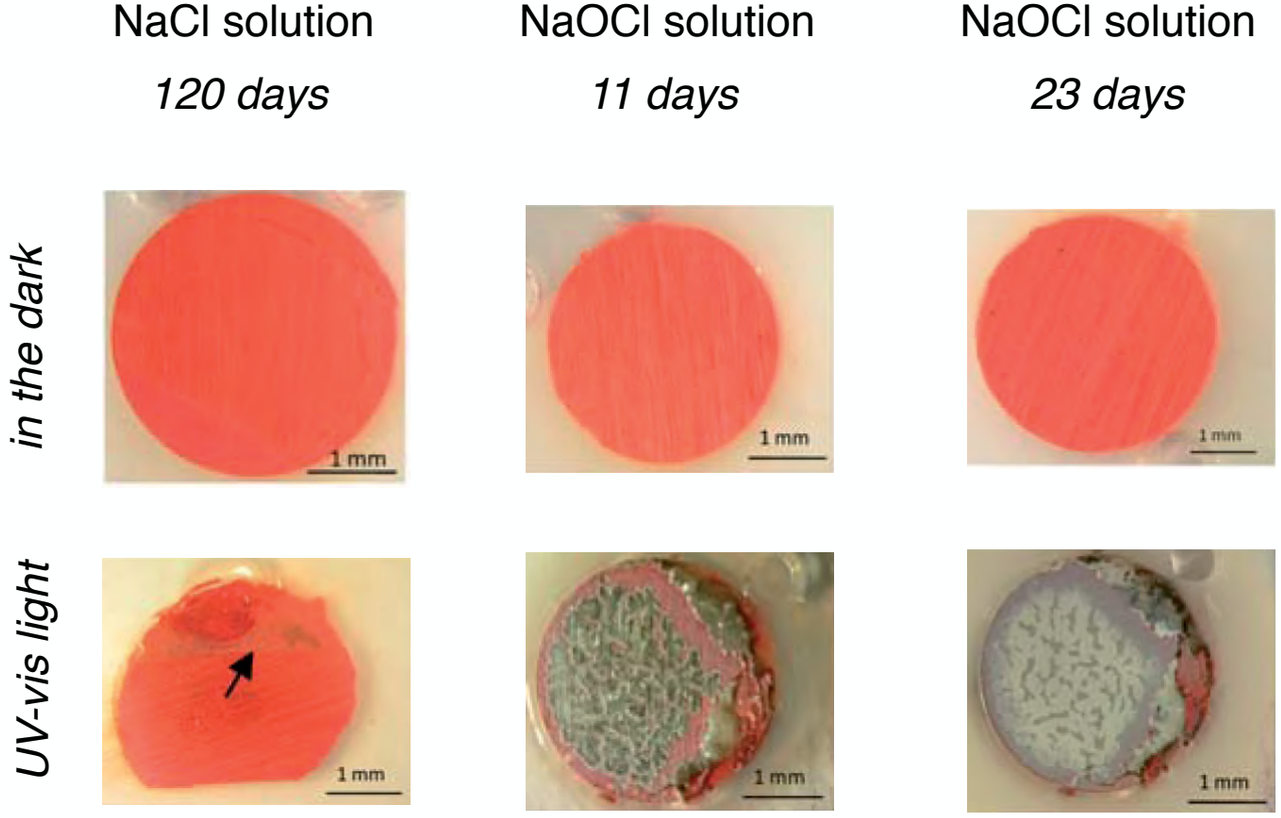
laboratory samples: α-HgS



Radepont, M. et al. *J. Anal. At. Spectrom.* **2011**, *26*, 959.

Aging of Cinnabar: Paintings vs. Laboratory Samples

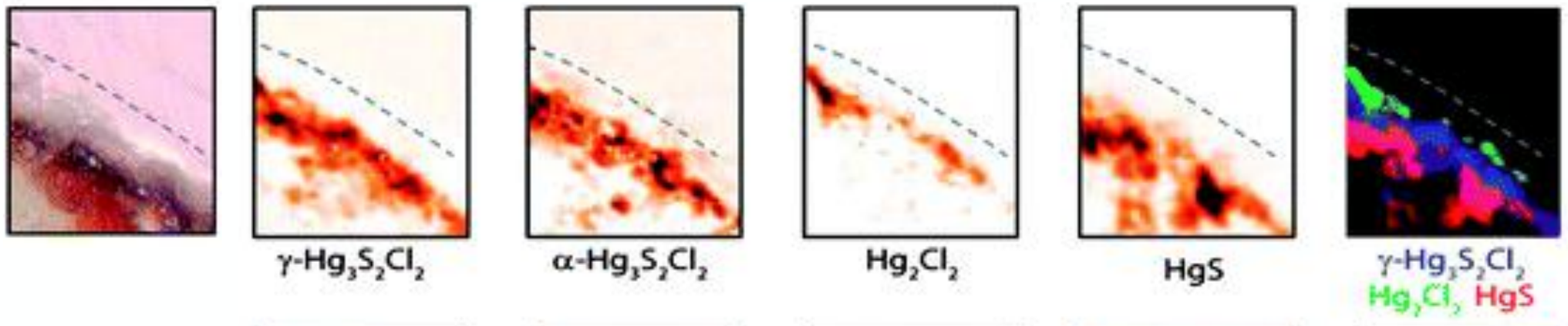
samples	***methods***	***identified compounds***		
artificially aged HgS	lab μ-XRD SR μ-XRD	α-HgS	α-$Hg_3S_2Cl_2$	Hg_2Cl_2
Adoration of the Magi	μ-XRF/μ-XANES SR μ-XRD	α-HgS	γ-$Hg_3S_2Cl_2$	Hg_2Cl_2
Pedralbes Monastery	μ-XRF/μ-XANES SR μ-XRD	α-HgS	α-$Hg_3S_2Cl_2$ γ-$Hg_3S_2Cl_2$	Hg_2Cl_2

Corderoite (α-$Hg_3S_2Cl_2$; purple-gray) and calomel (Hg_2Cl_2; white) responsible for color changes

Radepont, M. et al. *J. Anal. At. Spectrom.* **2011**, *26*, 959.

Aging of Cinnabar: Paintings vs. Laboratory Samples

- Pedralbes Monastery – μ-XRD results



possible decomposition mechanism

$$\alpha\text{-HgS} \rightleftharpoons \gamma\text{-}Hg_3S_2Cl_2 \rightleftharpoons \alpha\text{-}Hg_3S_2Cl_2 \rightleftharpoons Hg_2Cl_2$$

Radepont, M. et al. *J. Anal. At. Spectrom.* **2011**, *26*, 959.

Ab-Initio Treatment of Vermilion Photodarkening

Vermilion photodarkening is a widespread phenomenon

Photodegradation products have been identified, but mechanism is unclear

Understanding these processes helps develop conservation strategies

Novel approach

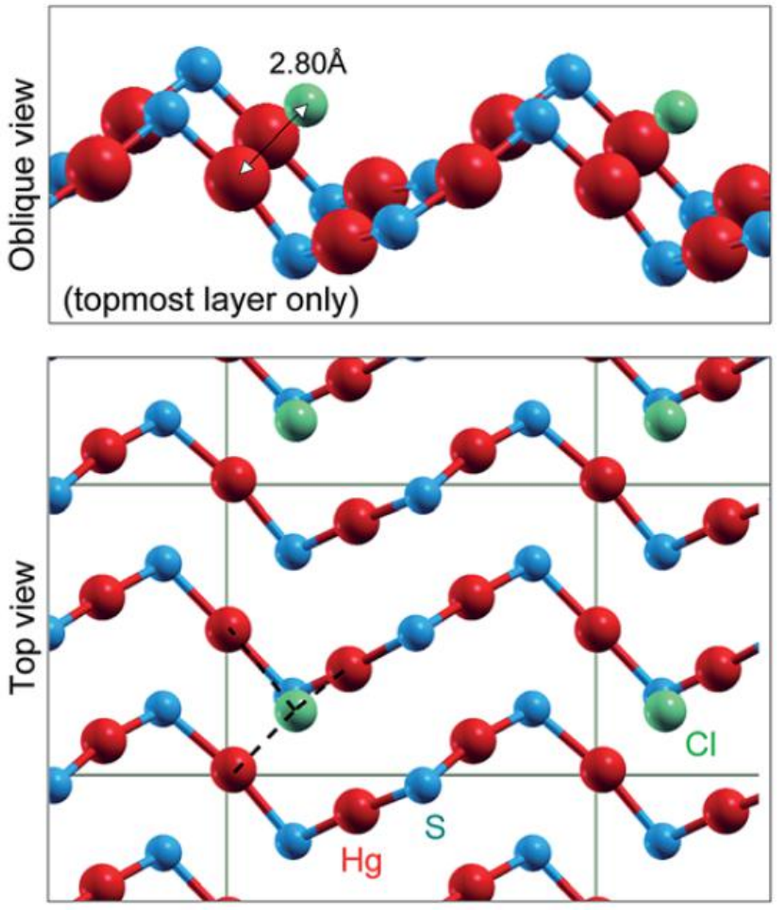
DFT + TD-DFT to interpret
previously reported experimental results

Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.

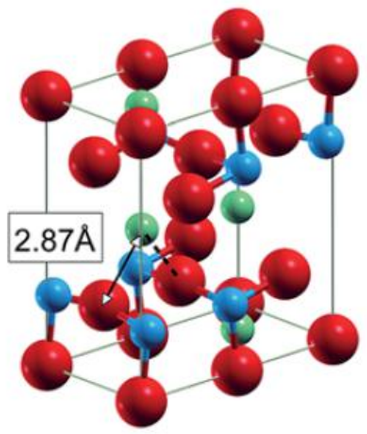
Ab-Initio Treatment of Vermilion Photodarkening

The Effect of Chloride

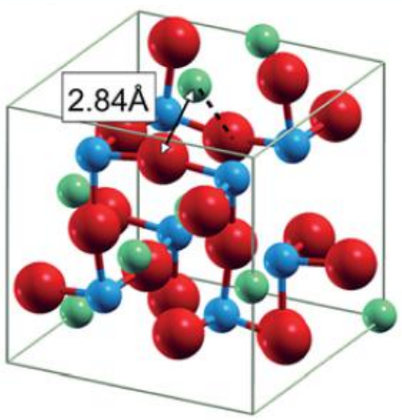
Cl adsorption on cinnabar (modeled)



α-$Hg_3S_2Cl_2$



γ-$Hg_3S_2Cl_2$



chlorine bonding environment is similar in all three lattices

Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.

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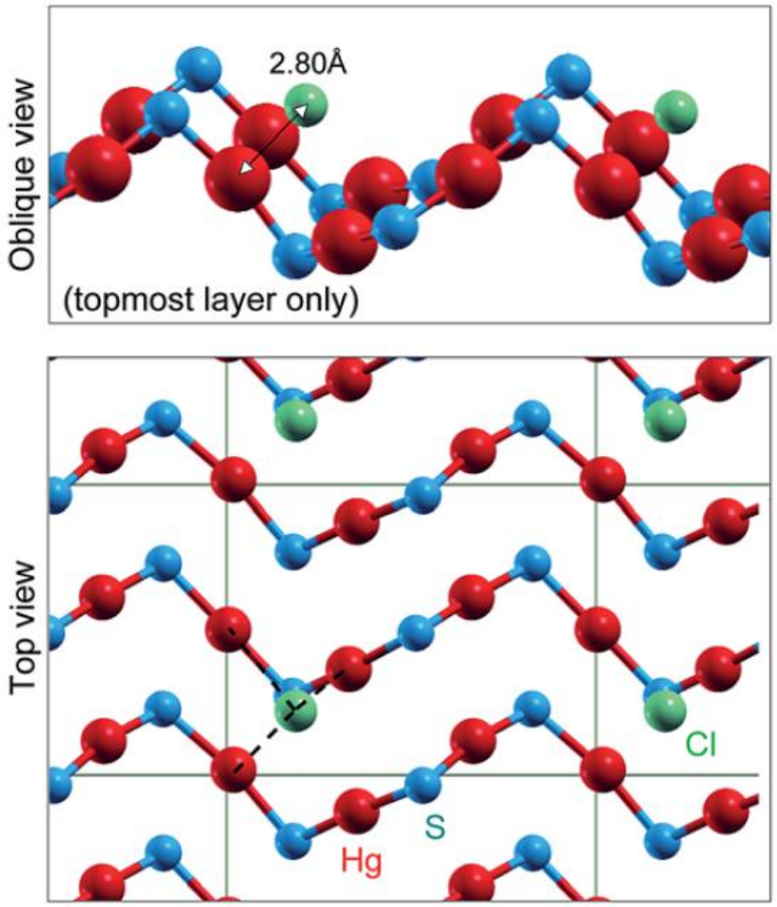
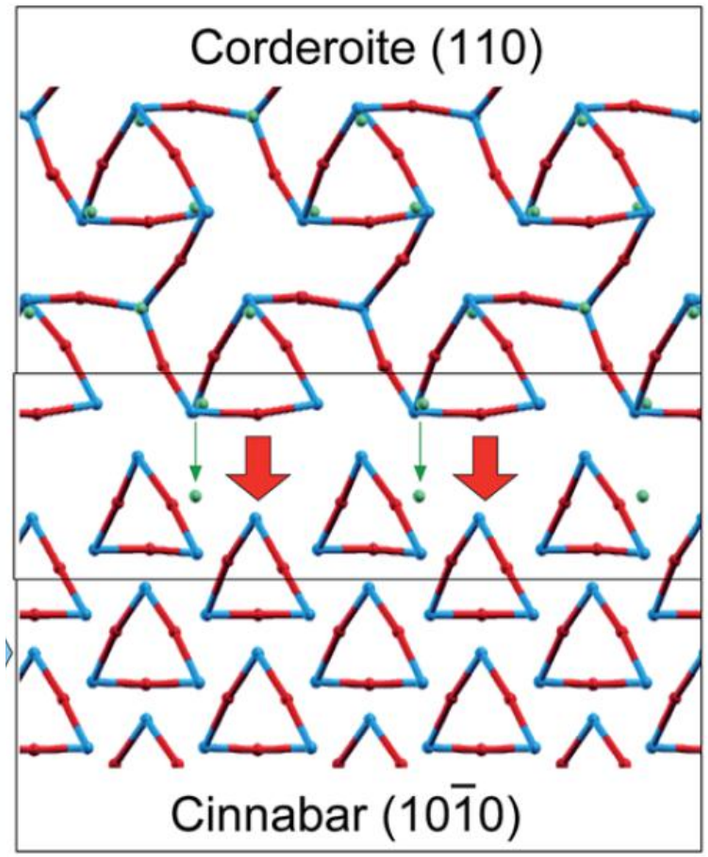


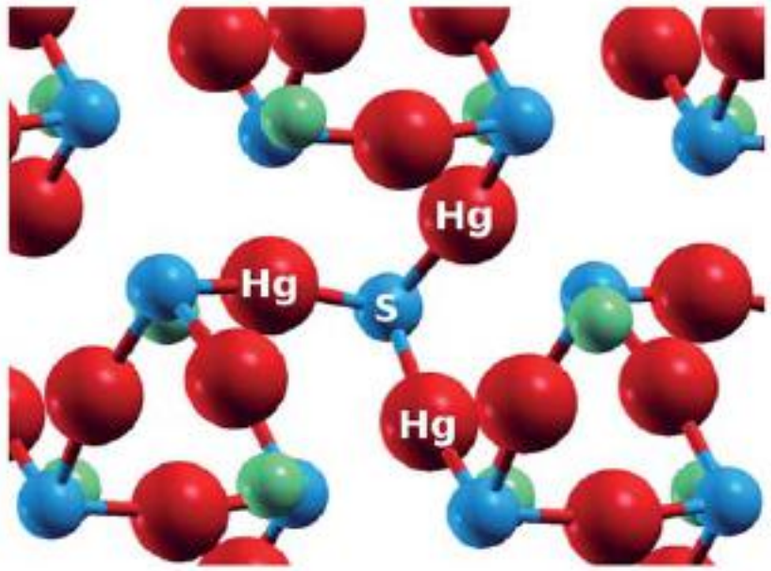


closer lattice match between HgS and α-$Hg_3S_2Cl_2$ → ***α-$Hg_3S_2Cl_2$ is the main product***

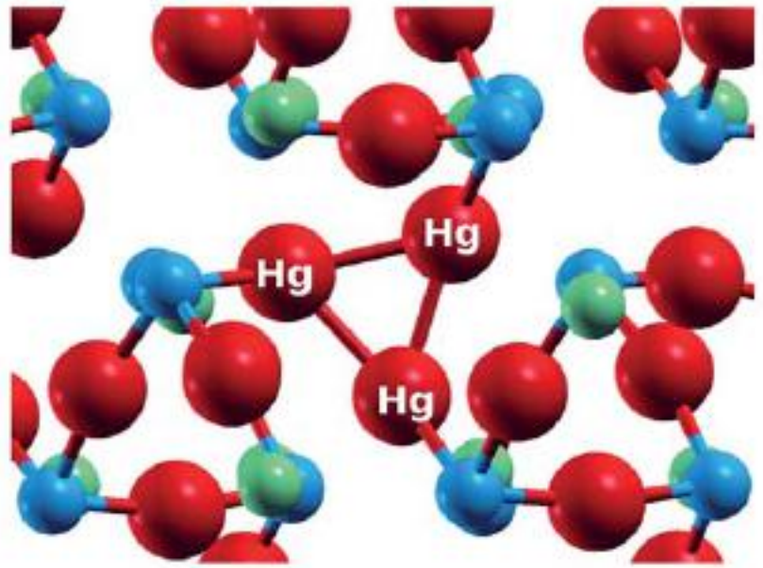
Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.

Ab-Initio Treatment of Vermilion Photodarkening

The Role of Defects



Pure α-$Hg_3S_2Cl_2$



Defective α-$Hg_3S_2Cl_2$

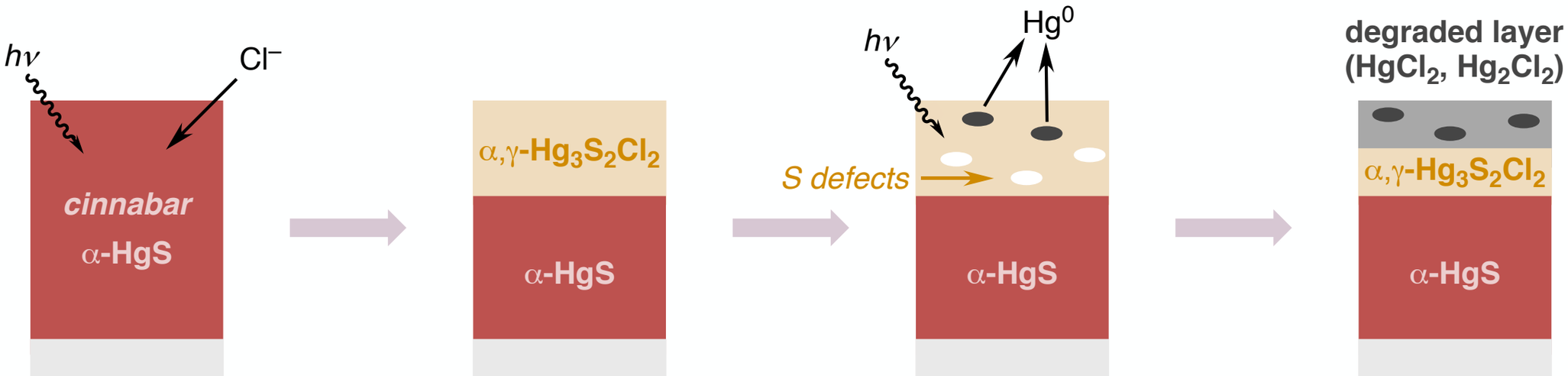
$$\{Hg_3^{4+}\} \xrightarrow{h\nu} Hg^0 + Hg_2Cl_2$$

Photoexcited Hg_3 units are Jahn-Teller distorted and disproportionate releasing Hg atoms

Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.

Ab-Initio Treatment of Vermilion Photodarkening

Proposed Mechanism



defect-mediated photolysis

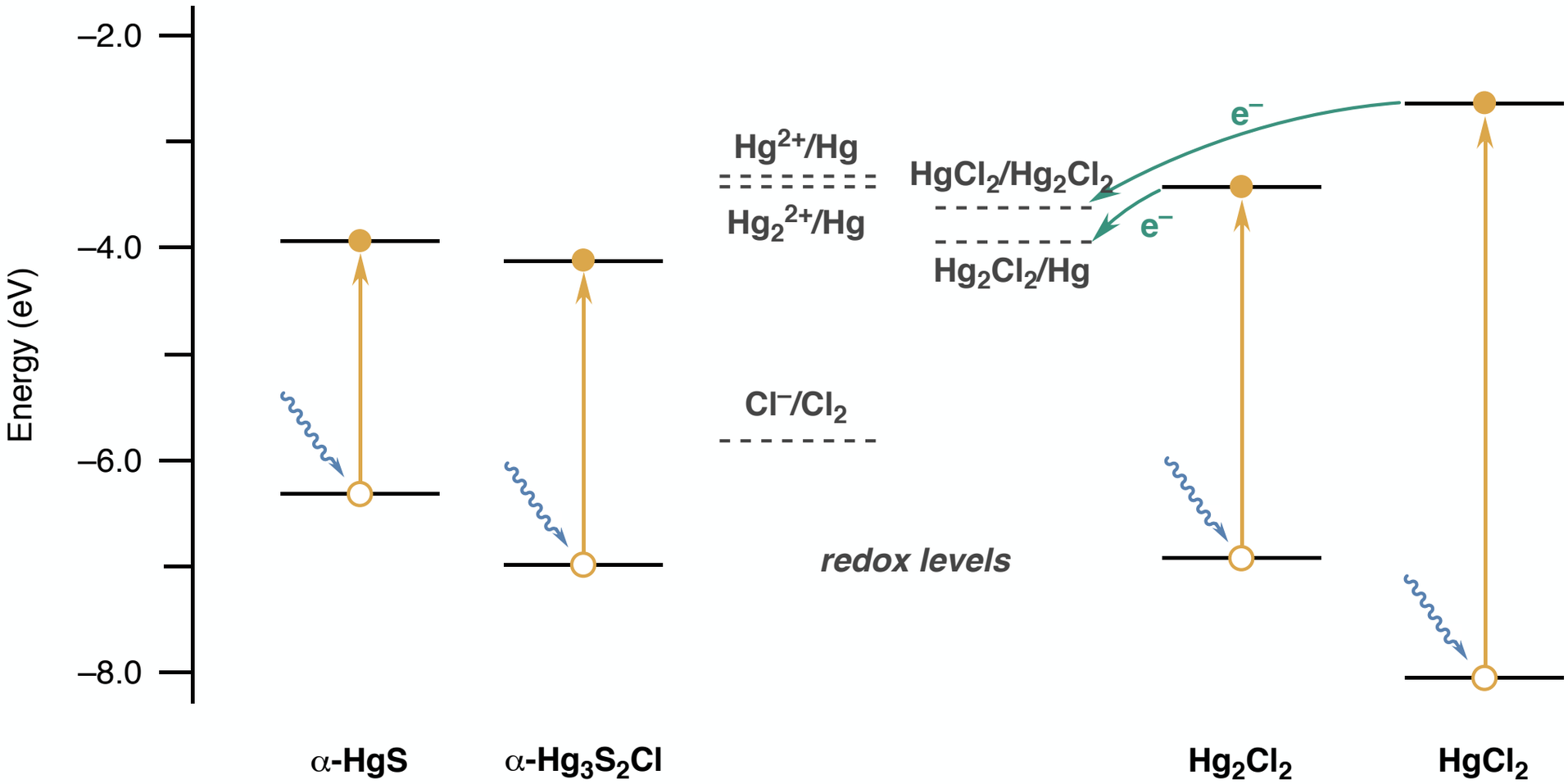
- Elemental Hg is responsible for darkened areas
- Hg_2Cl_2 (and $HgCl_2$) result in white streaks

Do other factors contribute to the degradation of the chlorides?

Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.

Ab-Initio Treatment of Vermilion Photodarkening

Photoinduced Electron Transfer as a Degradation Mechanism



Electron transfer is more favorable for $HgCl_2$ than Hg_2Cl_2

Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.

Ab-Initio Treatment of Vermilion Photodarkening

Conclusions and Outlook

*“Our study thus implies that, while works of art such as outdoor mural paintings can hardly be protected, degradation of indoor paintings in museums can be avoided with continuous control of the **humidity and chloride levels** in the air and by using **below-gap illumination** of the paintworks.”*

Hogan, C.; Da Pieve, F. *J. Anal. At. Spectrom.* **2015**, *30*, 588.

A Scientific Approach to Cleaning Works of Art

Ideal Cleaning Agents

selectively remove deposits and deteriorated varnish

do not affect underlying paint layers

are completely removed with no damage to the artwork

Chelazzi, D. et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 7296.
Carretti, E. et al. *Acc. Chem. Res.* **2010**, *43*, 751.

Biotechnology in Art Conservation

traditional: "wet" solvents

may dissolve the painting

toxic to the operator

hazardous waste generated

alternative: enzymes or microorganisms

highly selective

nonpathogenic microorganisms

main degradation products are CO_2 and H_2O

enzymes

target a single linkage

high cost

trained operators

microorganisms

remove resistant or complex materials

lower cost

easier application

P. Stutzeri
Picture courtesy of Dr. Rich Davis

Ranalli, G. et al. *J. Appl. Microbiol.* **2019**, *126*, 1785.

Biorestoration of Frescoes

Camposanto Monumentale di Pisa (Italy)

The cemetery was bombed during WWII

Frescoes detached from the walls for safekeeping

Hydrophobic behavior due to protein polymerization

Previous restoration using traditional methods

https://www.opapisa.it/en/multimedia/photo-gallery/

Ranalli, G. et al. *J. Appl. Microbiol.* **2018**, *125*, 800.

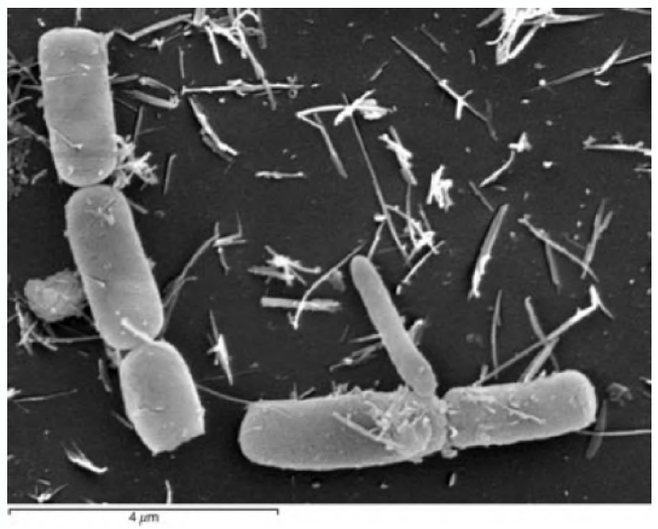
Biorestoration of Frescoes

Removal of Old Glue and Gauze

Aged animal glue had become resistant to solvents

Pseudomonas grown using animal glue as complex organic matter

P. stutzeri selected



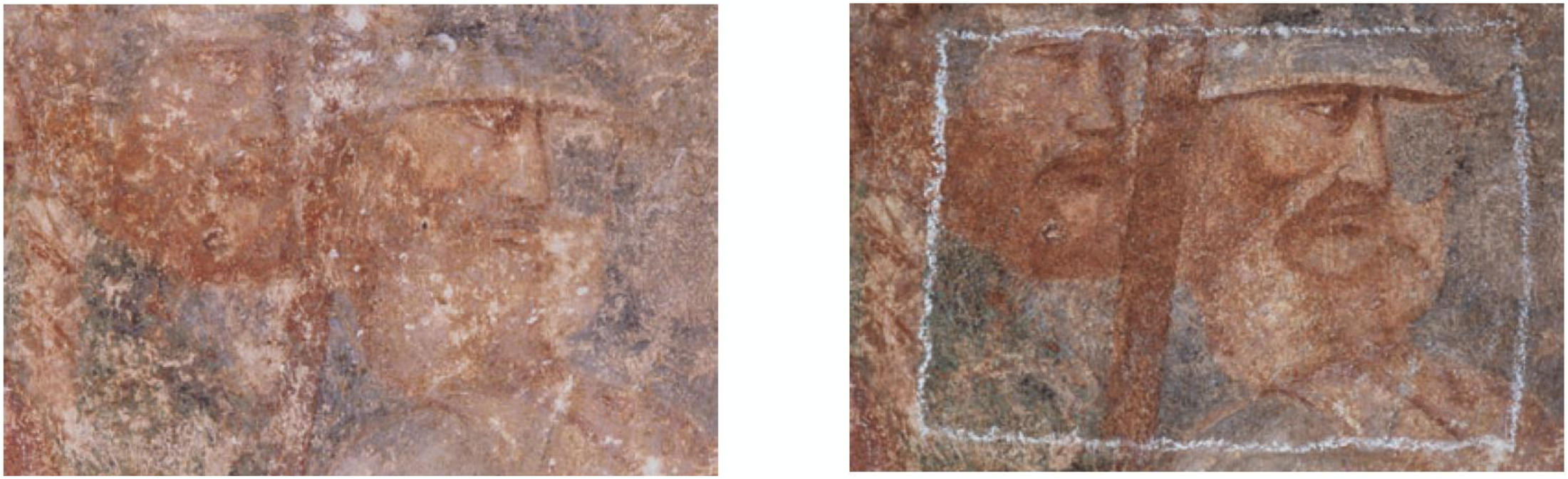
Effectiveness depended on thickness of glue layer: longer application times damaged the painting

first stage	***second stage***	***after treatment***
removal of glue and gauze using *P. stutzeri*	proteases to remove leftover glue	carefully remove bacteria check for bacterial growth

Ranalli, G. et al. *J. Appl. Microbiol.* **2005**, *98*, 73.

Biorestoration of Frescoes

Removal of Old Glue and Gauze



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Bioremoval of a Sulfate Layer from a Marble Artifact

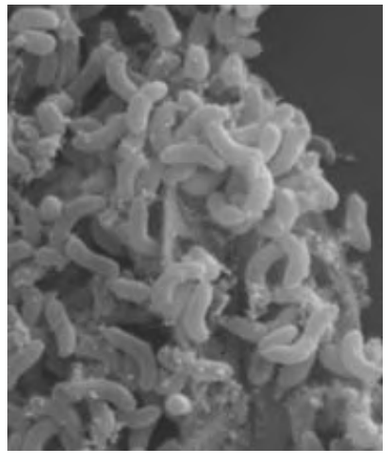
Eternal Father in the Act of Blessing

Regional Gallery of Palazzo Abatellis (Palermo, Italy)

Polychrome marble bas-relief from the 15th century

"Black sulfate" crust ($CaSO_4$ with coal and silicates)

Desulfovibrio vulgaris



- anaerobic, sulfur-reducing bacteria
- found in soil, fresh and salt water

$$6\ CaSO_4 + 4\ H_2O + 6\ CO_2 \longrightarrow 6\ CaCO_3 + 4\ H_2S + 2\ S + 11\ O_2$$

Martino, M. et al. *Conserv. Sci. Cult. Her.* **2015**, *15*, 235.

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Polychrome marble bas-relief from the 15th century

"Black sulfate" crust ($CaSO_4$ with coal and silicates)

Desulfovibrio vulgaris

Cells immobilized in Carbogel (polyacrylic acid)

Successful removal confirmed by XRF

Desired cleaning obtained after three applications

Martino, M. et al. *Conserv. Sci. Cult. Her.* **2015**, *15*, 235.

Physics, Chemistry and Biology in Art Conservation

Presentation Outline

Introduction

- Motivation
- Relevant Questions

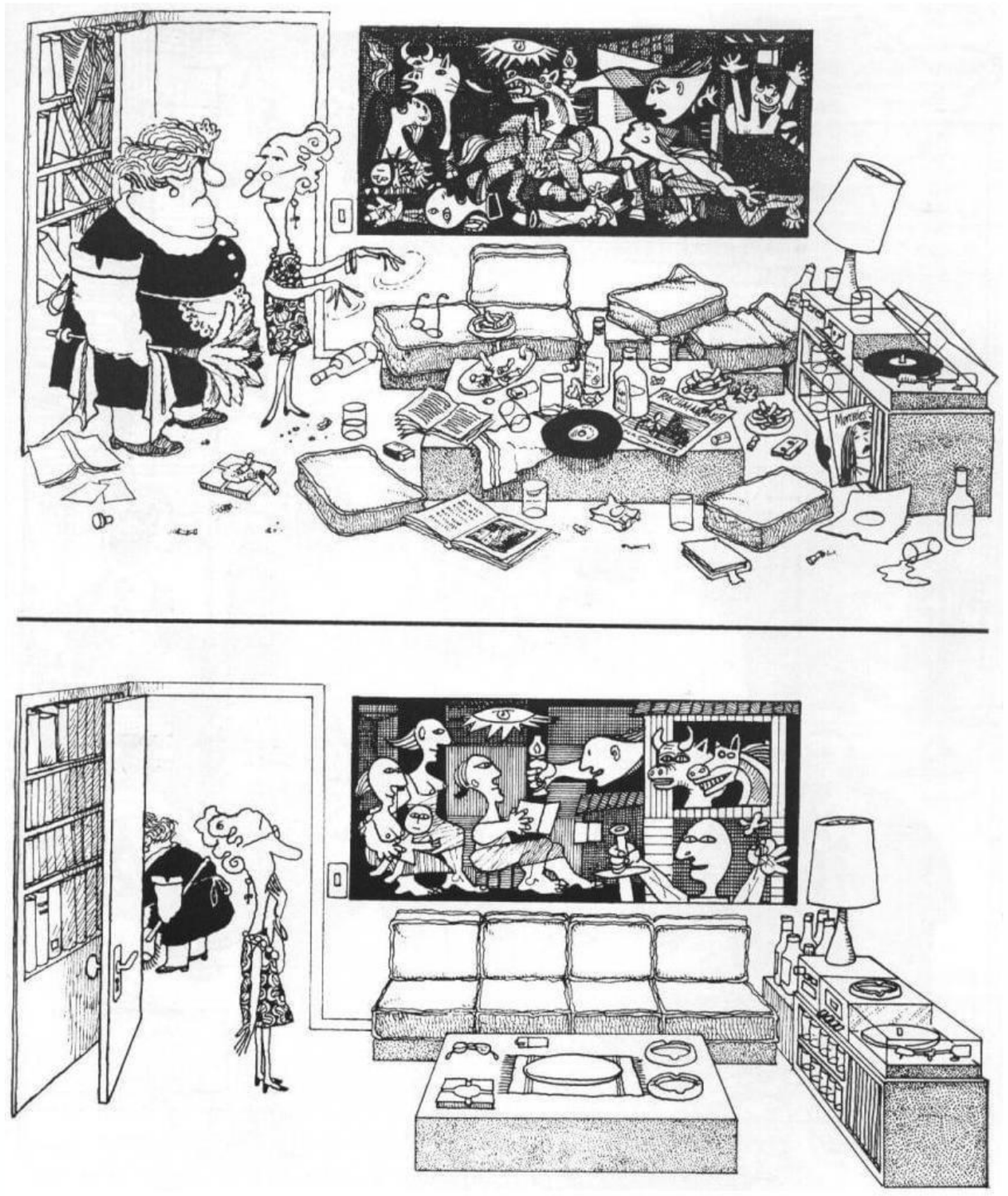
Understanding the Past

- Analytical Techniques
- X-ray Spectroscopy
- Case Studies: Vermilion Photodarkening

Towards the Future

- Cleaning Works of Art
- Case Studies: Microorganisms for Biocleaning

Thank You!



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