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”?

Large variety of materials and techniques employed: *art conservation is a multidisciplinary scientific endeavor*
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: TiO₂

anatase (~1920)  rutile (~1940)

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*

What Questions are Relevant for Art Conservation?

This combined approach is key to successfully preserve cultural heritage

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
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

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

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*ID21 beamline*

~25% beamtime

*Cultural Heritage applications*

https://www.esrf.eu/about
Synchrotron Radiation (SR)-Based Techniques

Advantages of Synchrotron Radiation
- higher sensitivity
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- \(\mu\)-FTIR
  - functional groups

- \(\mu\)-XAS (absorption)
  - amorphous or crystalline materials
- XANES
  - oxidation states
  - chemical speciation
- EXAFS
  - bond distances
  - coordination numbers

- \(\mu\)-XRD
  - phase identification
  - structural information

- \(\mu\)-XRF (fluorescence)
  - low detection limits
  - elemental maps

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

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The Mineral
- Most common mercury ore
- Mined since 10,000 B.C.
- \( \alpha \)-HgS (cinnabar structure)

Vermilion
The Most Widely Used Red Pigment Around the World

Vermilion (pigment)
- Deep red hue
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Vermilion is photosensitive in the presence of halogens ➔ it darkens over time

Understanding the degradation processes informs conservation efforts

The Monastery of Pedralbes in Barcelona
Vermilion in Gothic Architecture

Founded in 1326 by Queen Elisenda de Montcada and her husband King James II
The Monastery of Pedralbes in Barcelona
Vermilion in Gothic Architecture

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

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
The Monastery of Pedralbes in Barcelona

Vermilion in Gothic Architecture

- Goal: Identify Original Materials and Decomposition Products

Cinnabar identified using SEM-EDX

The Monastery of Pedralbes in Barcelona
Vermilion in Gothic Architecture

Goal: Identify Original Materials and Decomposition Products

Cinnabar identified using SEM-EDX

Main elements not always co-located

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

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

Three main S-containing species, forming separate layers.
From cinnabar to calomel – what is the role of chlorine?

Layered structure suggests chlorine “digests” cinnabar from the top down.

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

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

laboratory samples: $\alpha$-HgS

- NaCl solution 120 days
- NaOCl solution 11 days
- NaOCl solution 23 days

in the dark

UV-vis light

### Aging of Cinnabar: Paintings vs. Laboratory Samples

<table>
<thead>
<tr>
<th><strong>samples</strong></th>
<th><strong>methods</strong></th>
<th><strong>identified compounds</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>artificially aged HgS</td>
<td>lab µ-XRD, SR µ-XRD</td>
<td>α-HgS, α-Hg$_3$S$_2$Cl$_2$, HgCl$_2$</td>
</tr>
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<td>Adoration of the Magi</td>
<td>µ-XRF/µ-XANES, SR µ-XRD</td>
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<td>µ-XRF/µ-XANES, SR µ-XRD</td>
<td>α-HgS, α-Hg$_3$S$_2$Cl$_2$, γ-Hg$_3$S$_2$Cl$_2$, HgCl$_2$</td>
</tr>
</tbody>
</table>

Corderoite ($\alpha$-Hg$_3$S$_2$Cl$_2$; purple-gray) and calomel (Hg$_2$Cl$_2$; white) responsible for color changes.

Aging of Cinnabar: Paintings vs. Laboratory Samples

Pedralbes Monastery – µ-XRD results

possible decomposition mechanism

$$\alpha\text{-HgS} \rightleftharpoons \gamma\text{-Hg}_3\text{S}_2\text{Cl}_2 \rightleftharpoons \alpha\text{-Hg}_3\text{S}_2\text{Cl}_2 \rightleftharpoons \text{Hg}_2\text{Cl}_2$$

**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.

chlorine bonding environment is similar in all three lattices
Ab-Initio Treatment of Vermilion Photodarkening
The Effect of Chloride

Closer lattice match between HgS and $\alpha$-Hg$_3$S$_2$Cl$_2$  $\rightarrow$ $\alpha$-Hg$_3$S$_2$Cl$_2$ is the main product

Ab-Initio Treatment of Vermilion Photodarkening
The Role of Defects

Pure $\alpha$-Hg$_3$S$_2$Cl$_2$
Defective $\alpha$-Hg$_3$S$_2$Cl$_2$

{Hg$_3$}$^{4+}$ → $\text{Hg}^0 + \text{Hg}_2\text{Cl}_2$

*Photoexcited Hg$_3$ units are Jahn-Teller distorted and disproportionate releasing Hg atoms*

Ab-Initio Treatment of Vermillion Photodarkening

Proposed Mechanism

Elemental Hg is responsible for darkened areas

Hg₂Cl₂ (and HgCl₂) result in white streaks

Do other factors contribute to the degradation of the chlorides?

Ab-Initio Treatment of Vermilion Photodarkening
Photoinduced Electron Transfer as a Degradation Mechanism

Electron transfer is more favorable for HgCl₂ than Hg₂Cl₂
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.”
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  - Motivation
  - Relevant Questions

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Towards the Future
  - Cleaning Works of Art
  - Case Studies: Microorganisms for Biocleaning
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

**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 \( H_2O \)

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**enzymes**
- target a single linkage
- high cost
- trained operators

**microorganisms**
- remove resistant or complex materials
- lower cost
- easier application

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P. Stutzeri
Picture courtesy of Dr. Rich Davis

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/
**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.

- **First stage**: removal of glue and gauze using *P. stutzeri*.
- **Second stage**: proteases to remove leftover glue.
- **After treatment**: carefully remove bacteria, check for bacterial growth.

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

Biorestoration of Frescoes
Removal of Old Glue and Gauze

**first stage**
removal of glue and gauze
using *P. stutzeri*

**second stage**
proteases to remove leftover glue

carefully remove bacteria
check for bacterial growth

---

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

\[6 \text{CaSO}_4 + 4 \text{H}_2\text{O} + 6 \text{CO}_2 \rightarrow 6 \text{CaCO}_3 + 4 \text{H}_2\text{S} + 2 \text{S} + 11 \text{O}_2\]

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

Cells immobilized in Carbogel (polyacrylic acid)

Successful removal confirmed by XRF

Desired cleaning obtained after three applications

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Presentation Outline

- Introduction
  - Motivation
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- Towards the Future
  - Cleaning Works of Art
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Thank You!

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