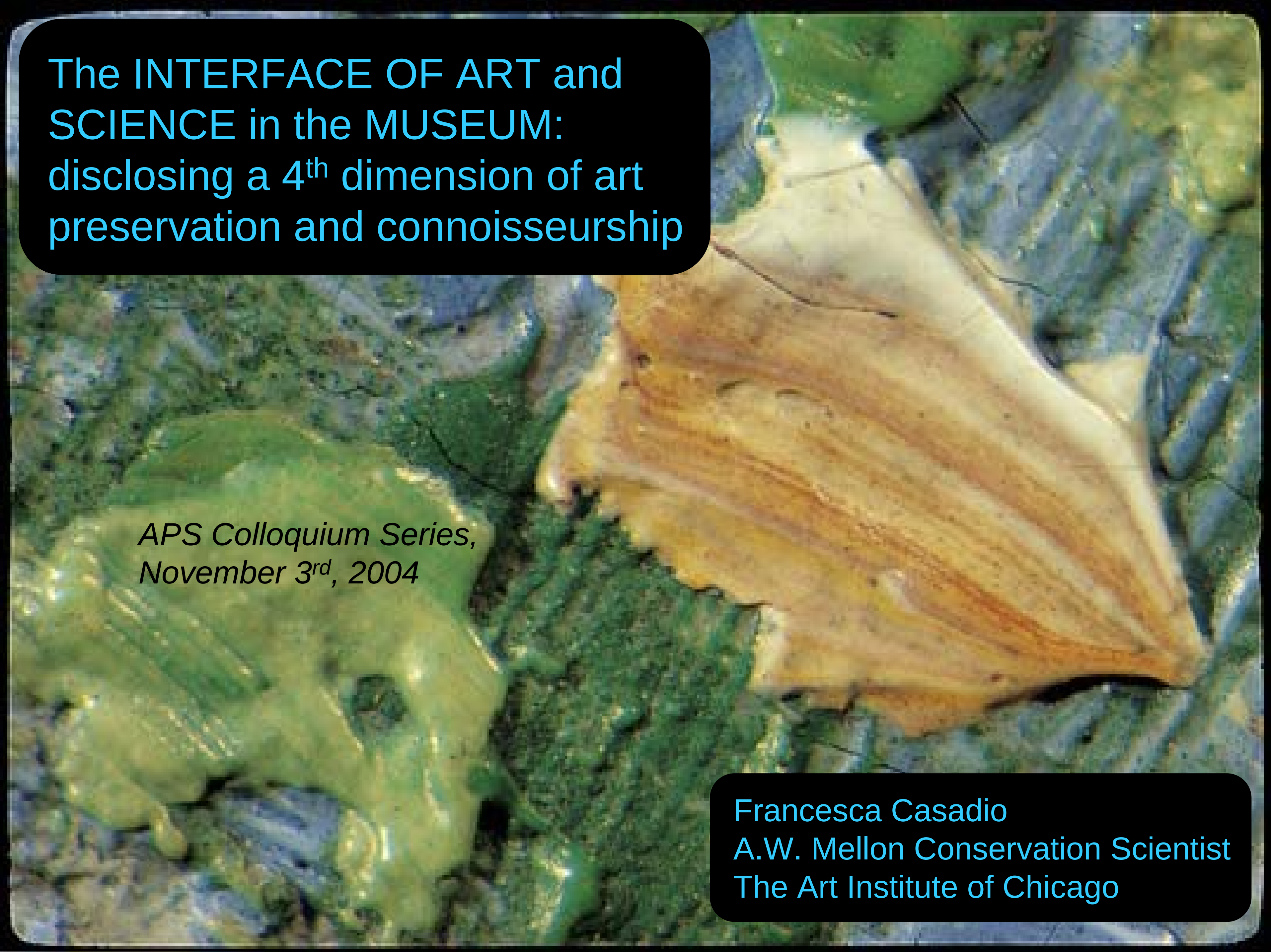


The INTERFACE OF ART and SCIENCE in the MUSEUM: disclosing a 4th dimension of art preservation and connoisseurship

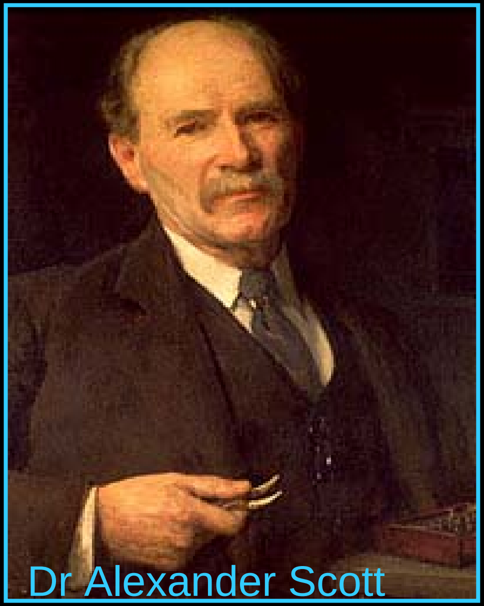
APS Colloquium Series,
November 3rd, 2004

Francesca Casadio
A.W. Mellon Conservation Scientist
The Art Institute of Chicago

SUMMARY

- What is a Conservation scientist?
- Other laboratories in the US and Europe
- The Conservation Science Initiative at the ART INSTITUTE of Chicago: plans for the scientific laboratory and future research
- Applications of analytical instrumental techniques to the analysis, preservation and understanding of works of art: past experiences, recent advances and future directions.

THE ROLE OF A CONSERVATION SCIENTIST



THE BRITISH MUSEUM:

among the first museums to recognise that in-house scientific expertise was essential for the care and interpretation of its collections: Research Laboratory founded in **1920**.

LOUVRE, PARIS (C2RMF):

the laboratories were founded in **1932**

NATIONAL GALLERY LONDON:

appointed a Scientific Adviser in **1934**, who carried out pioneering work in X-Ray photography of pictures and established a Physics Laboratory at the Gallery. In **1947**, a Chemical Laboratory was established.

in Europe

STRAUS CENTER FOR CONSERVATION : 2

Established in **1928** by Edward Forbes.

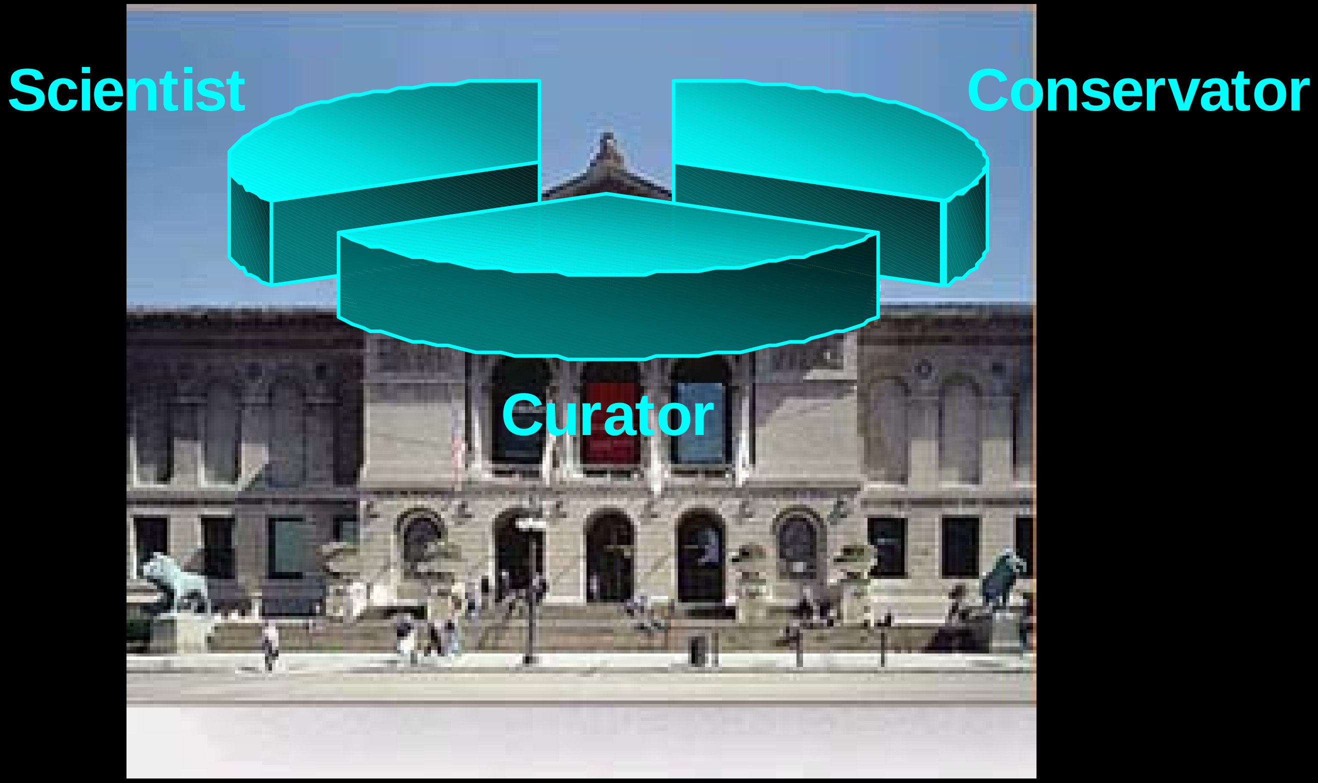
GCI:	**25 scientists**
SCMRE:	**11**
NGA, MET:	**<10**
MFA:	**1 +1/2**
MOMA :	**1**
LACMA:	**2**
Philadelphia Museum of Art:	**2**
Detroit Institute of Art:	**2**
The Walters Art Museum	**1**

in USA

In July 2003, the Art Institute of **Chicago** has announced the award of a **$2.75 million grant from the Andrew W. Mellon Foundation**.

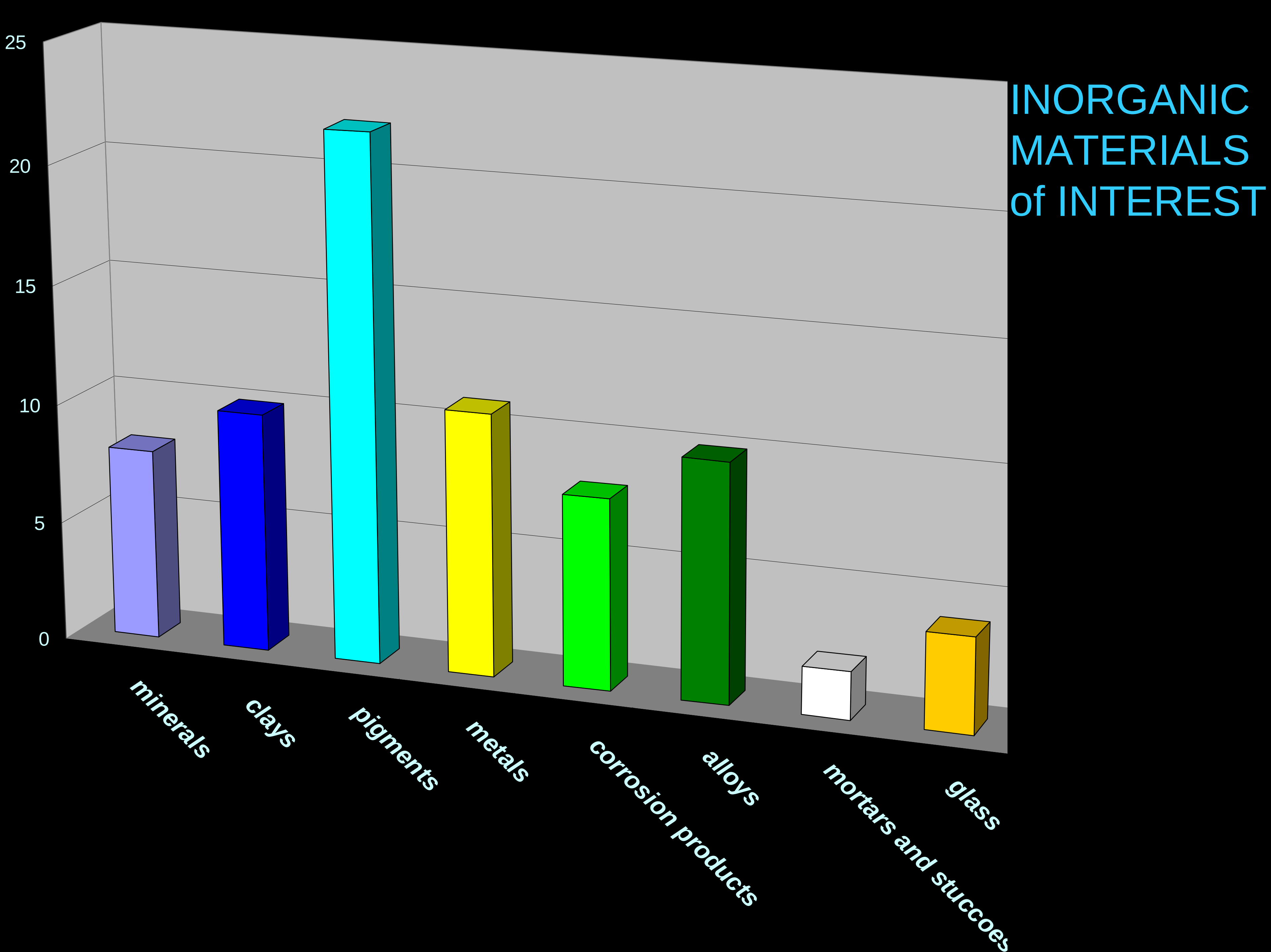
Endowment of a new Conservation Scientist position, within the museum's Department of Conservation

Provide funds for use over a five-year period to purchase analytical instruments, establish and operate a scientific laboratory for analysis and conduct research on the museum's collection.

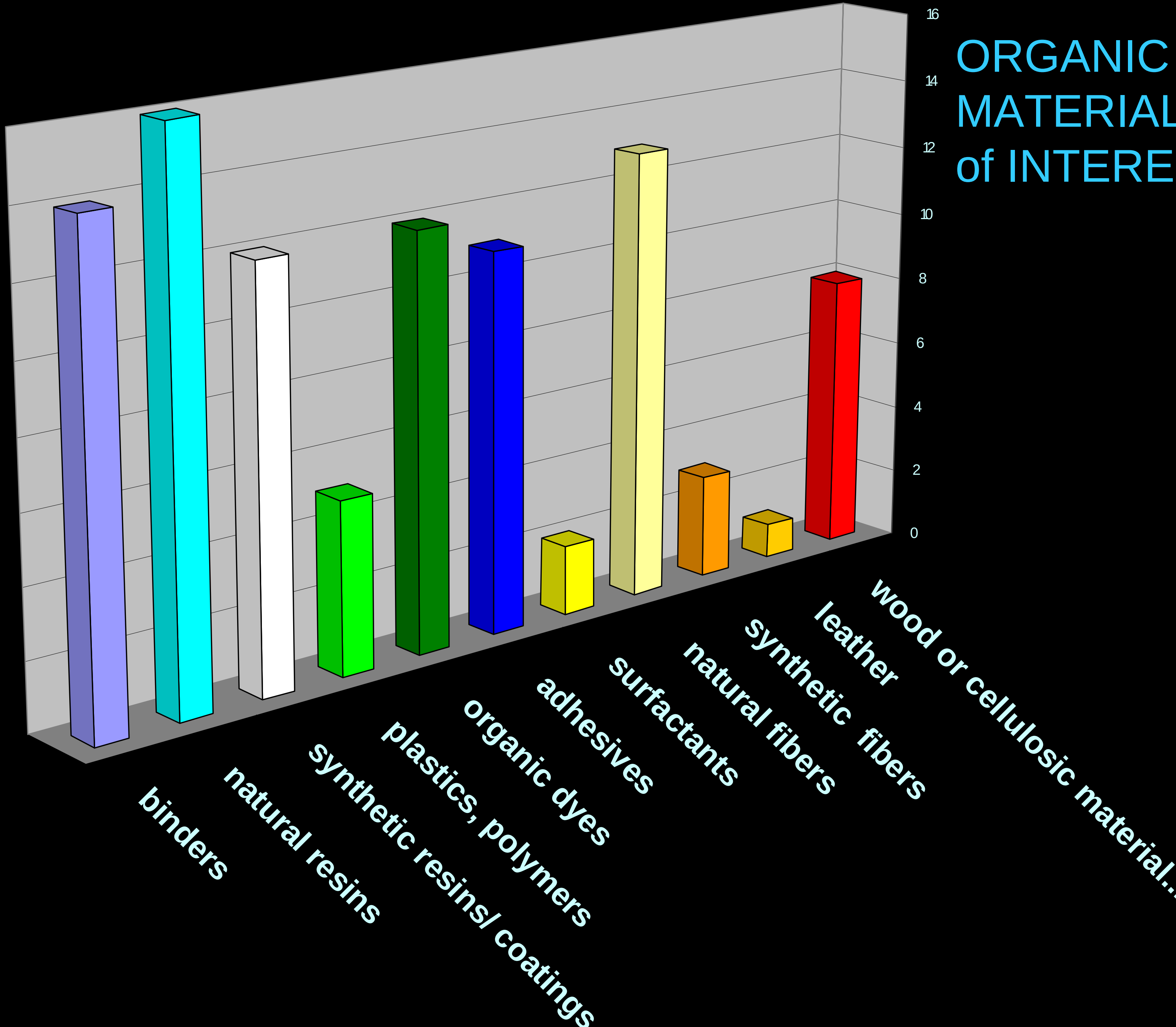

Scientist
Conservator
Curator

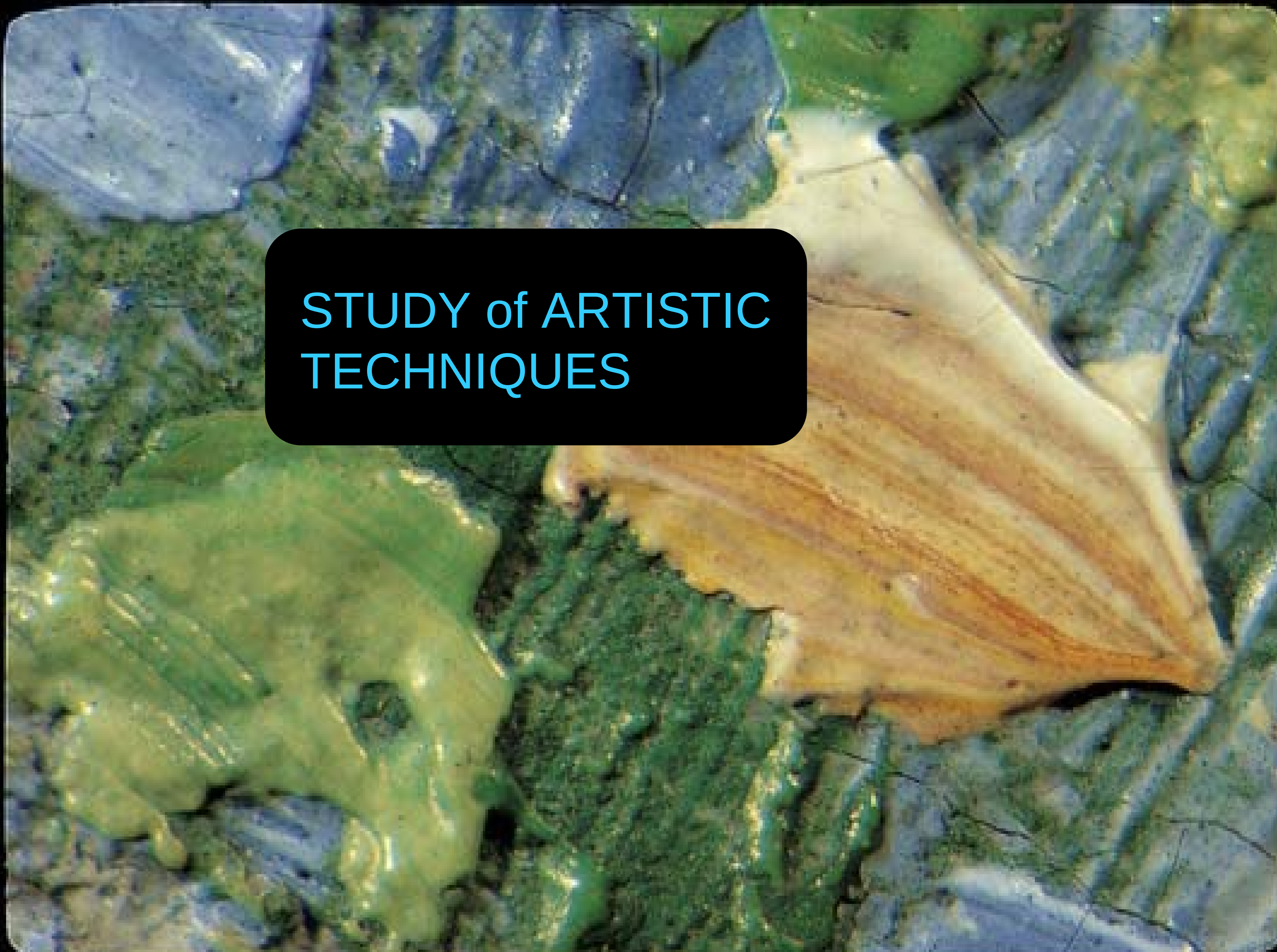

African & American Indian
American
Ancient
Architecture
Armor
Asian
Contemporary
European Decorative


European Painting
Photography
Prints & Drawings
Textiles

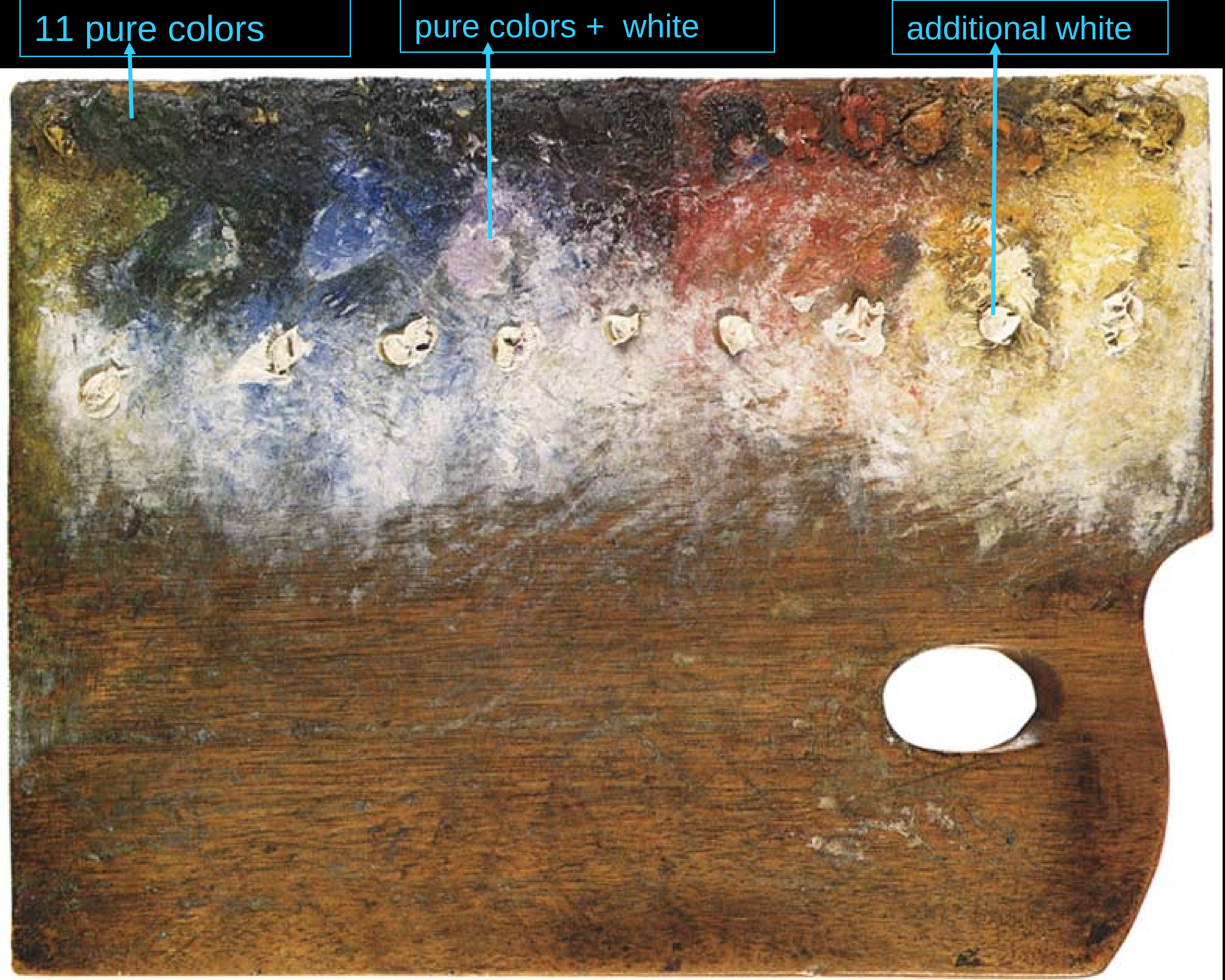

INORGANIC MATERIALS of INTEREST
25
20
15
10
5
0
minerals
clays
pigments
metals
corrosion products
alloys
mortars and stuccoes
glass

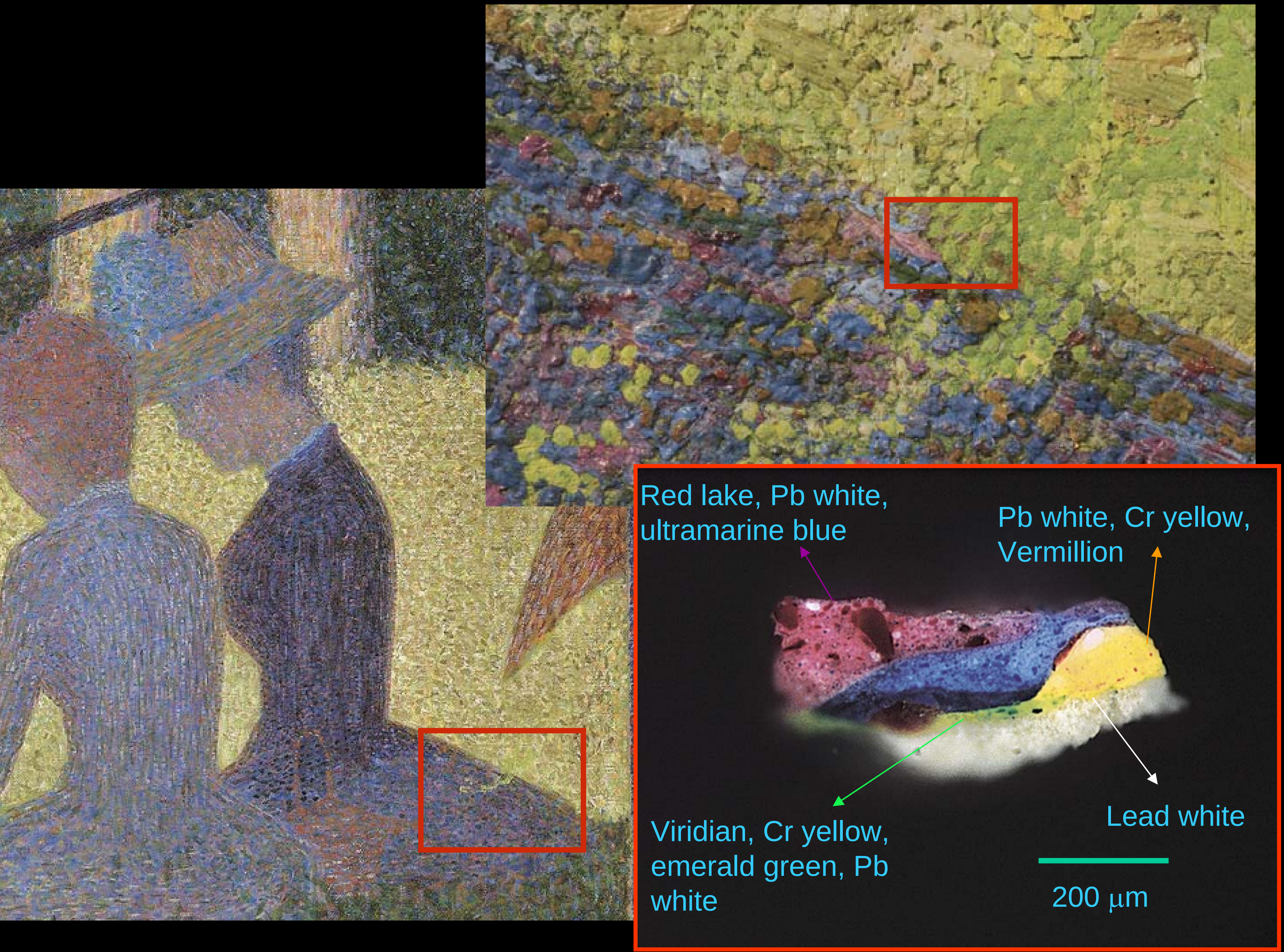
ORGANIC MATERIALS of INTEREST

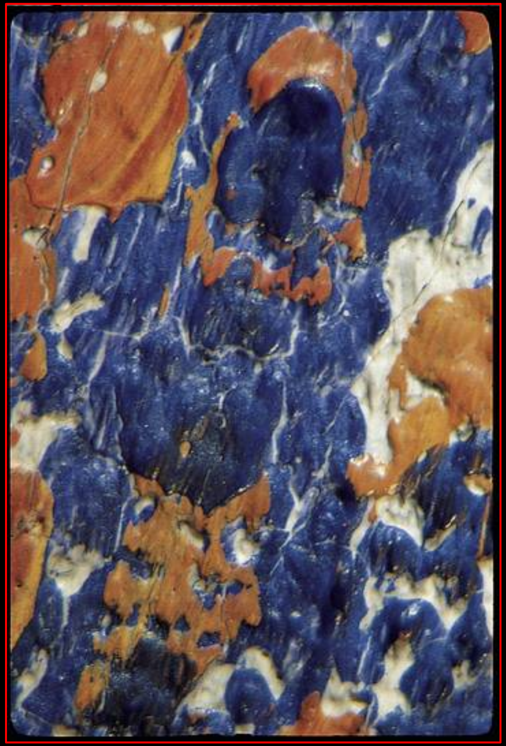


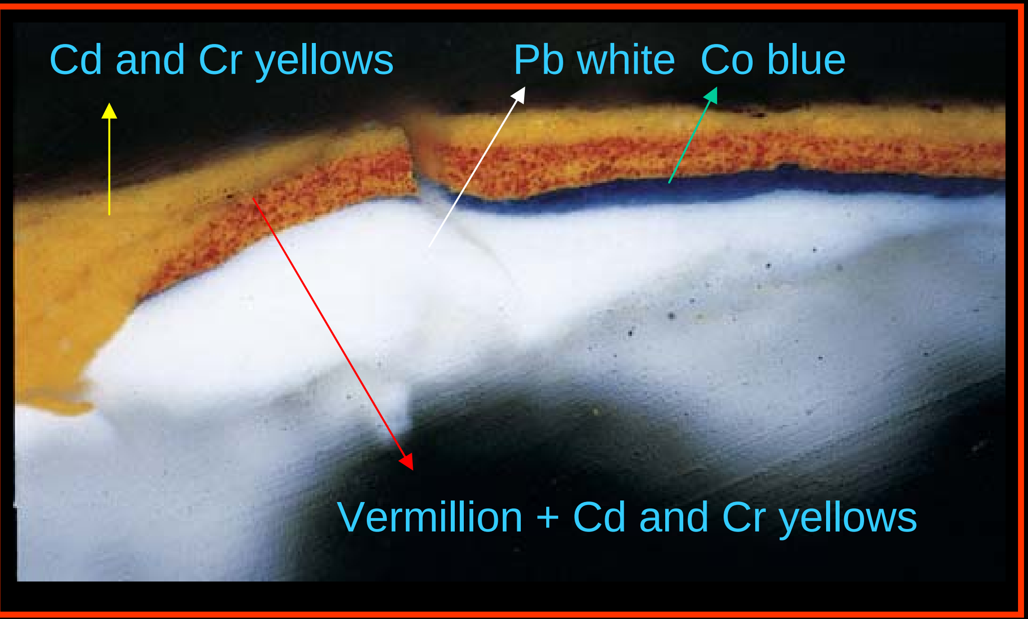

STUDY of ARTISTIC
TECHNIQUES

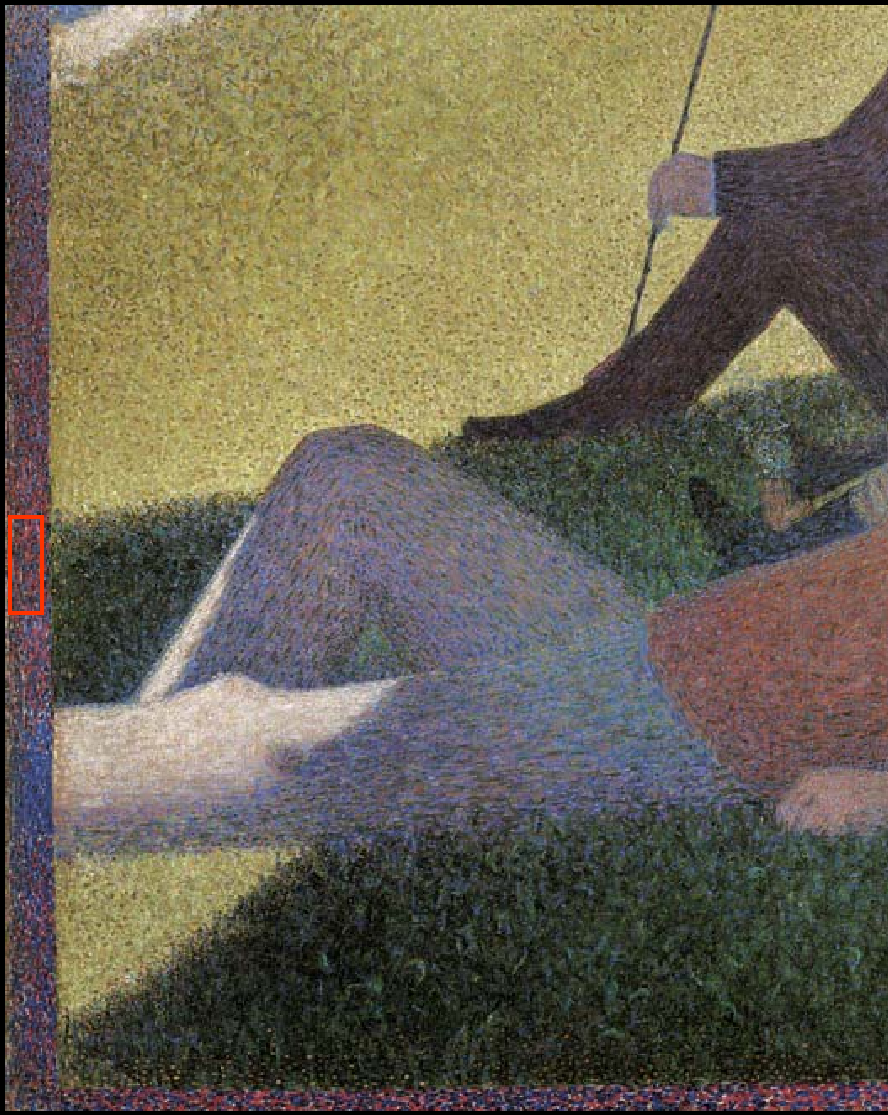
Artists’ methods

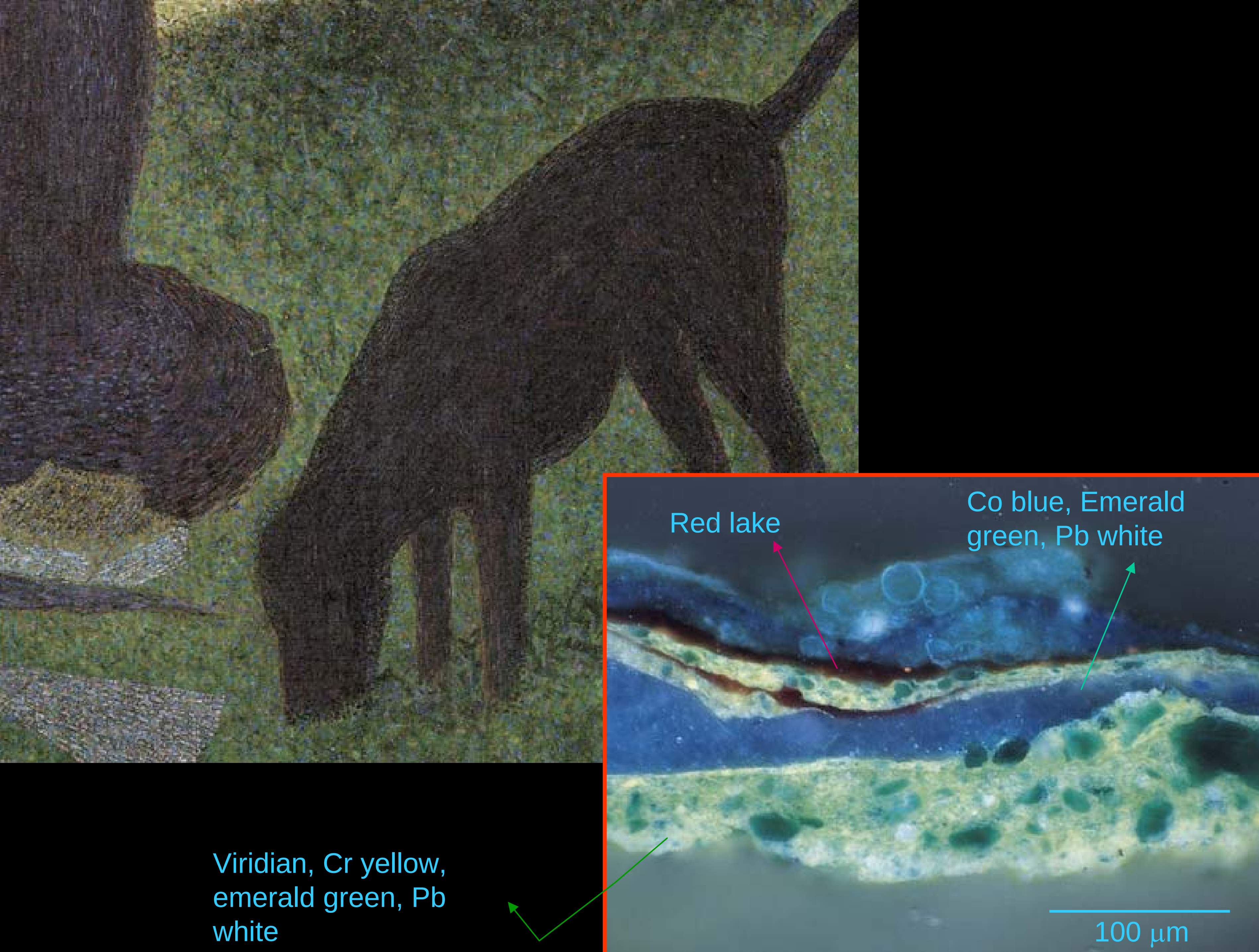

11 pure colors
pure colors + white
additional white


Red lake, Pb white, ultramarine blue
Pb white, Cr yellow, Vermillion
Viridian, Cr yellow, emerald green, Pb white
Lead white
200 μm



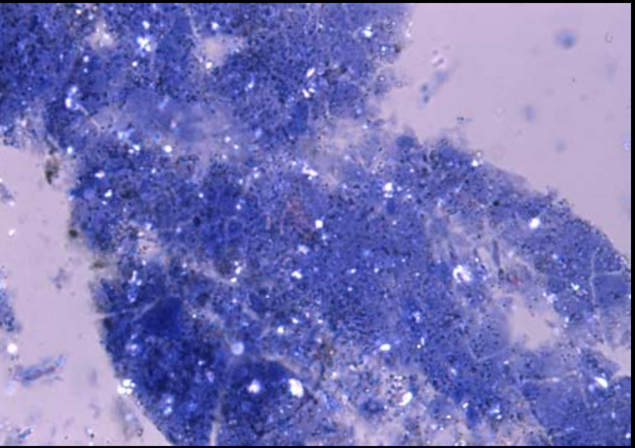

Cd and Cr yellows
Pb white
Co blue
Vermillion + Cd and Cr yellows




Red lake
Co blue, Emerald green, Pb white
Viridian, Cr yellow, emerald green, Pb white
100 μm

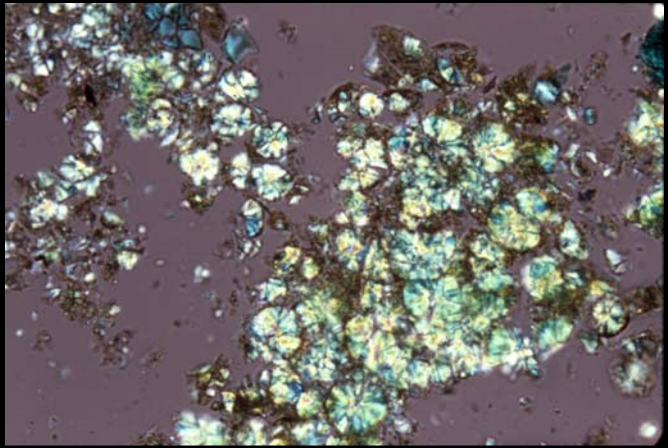
$CoO*Al_2O_3$

Cobalt blue



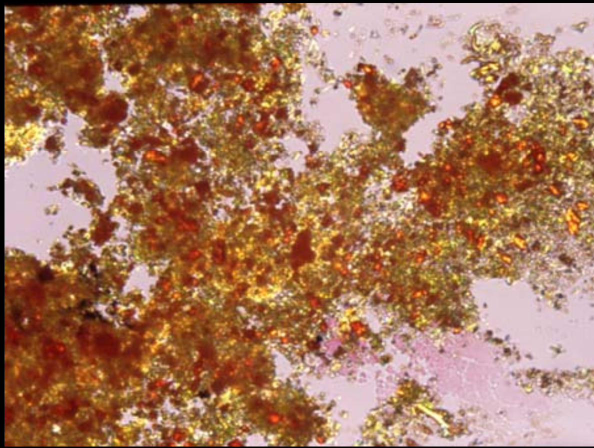
$Cu(C_2H_3O_2)_2*3Cu(AsO_2)_2$

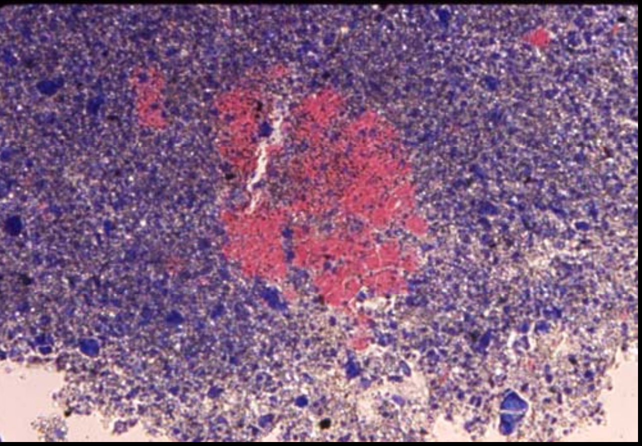
Emerald green



$PbCrO_4$, HgS

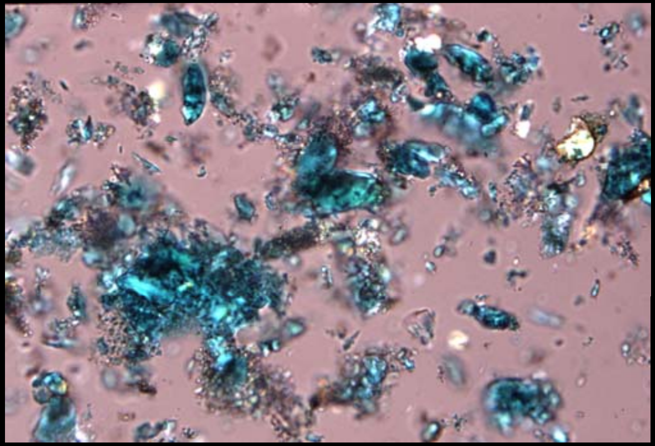
Chrome yellow and Vermilion





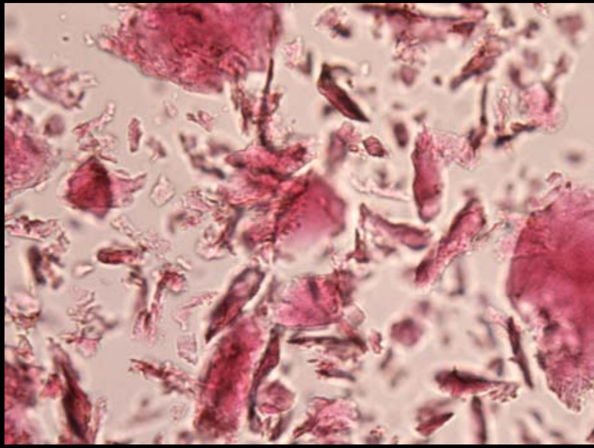
Ultramarine blue and Red lake

$Na_{6-10}Al_6Si_6O_{24}S_{2-4}$

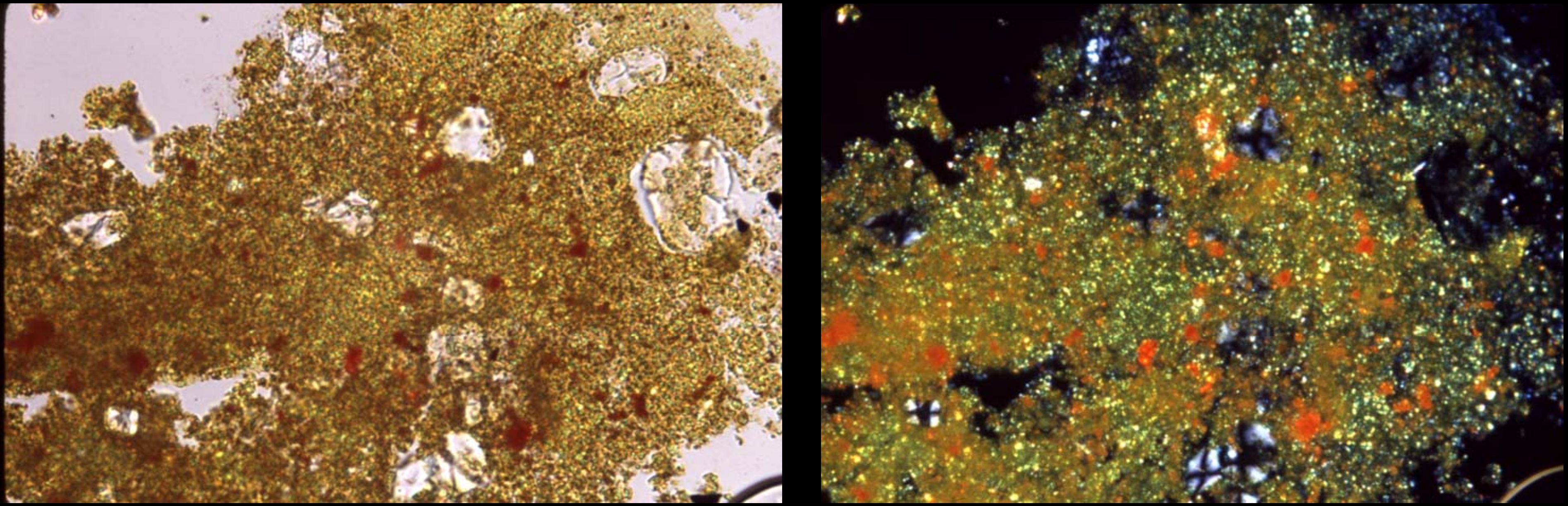


Viridian green

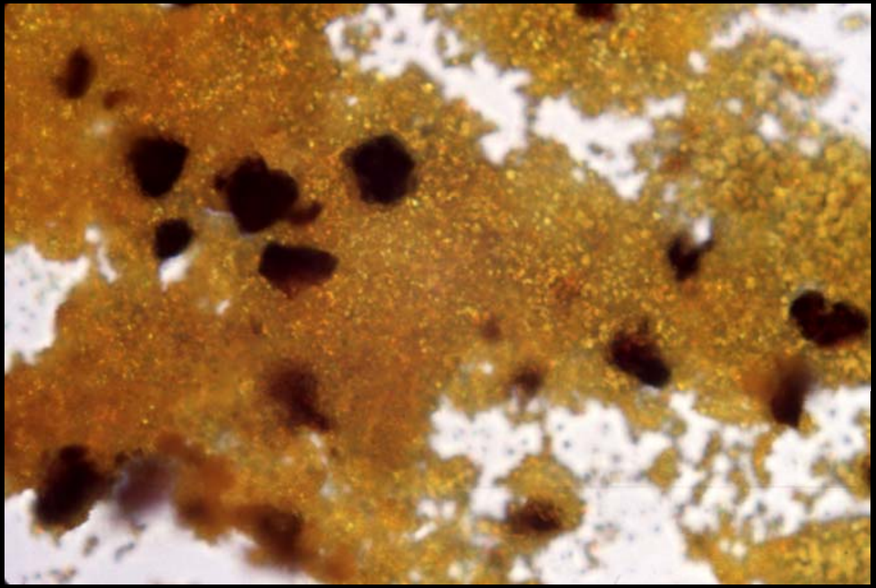
$Cr_2O_3*2H_2O$



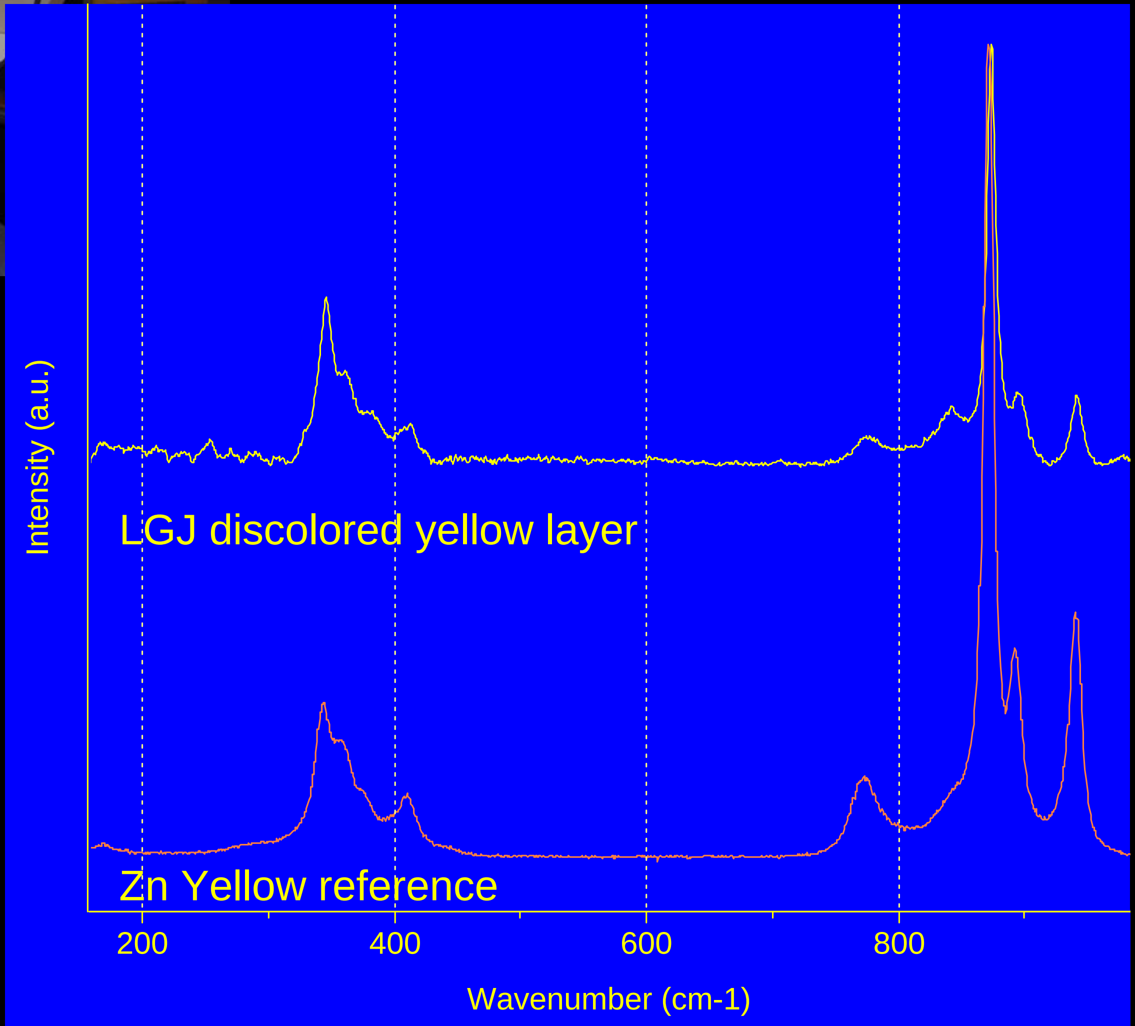
Red lake



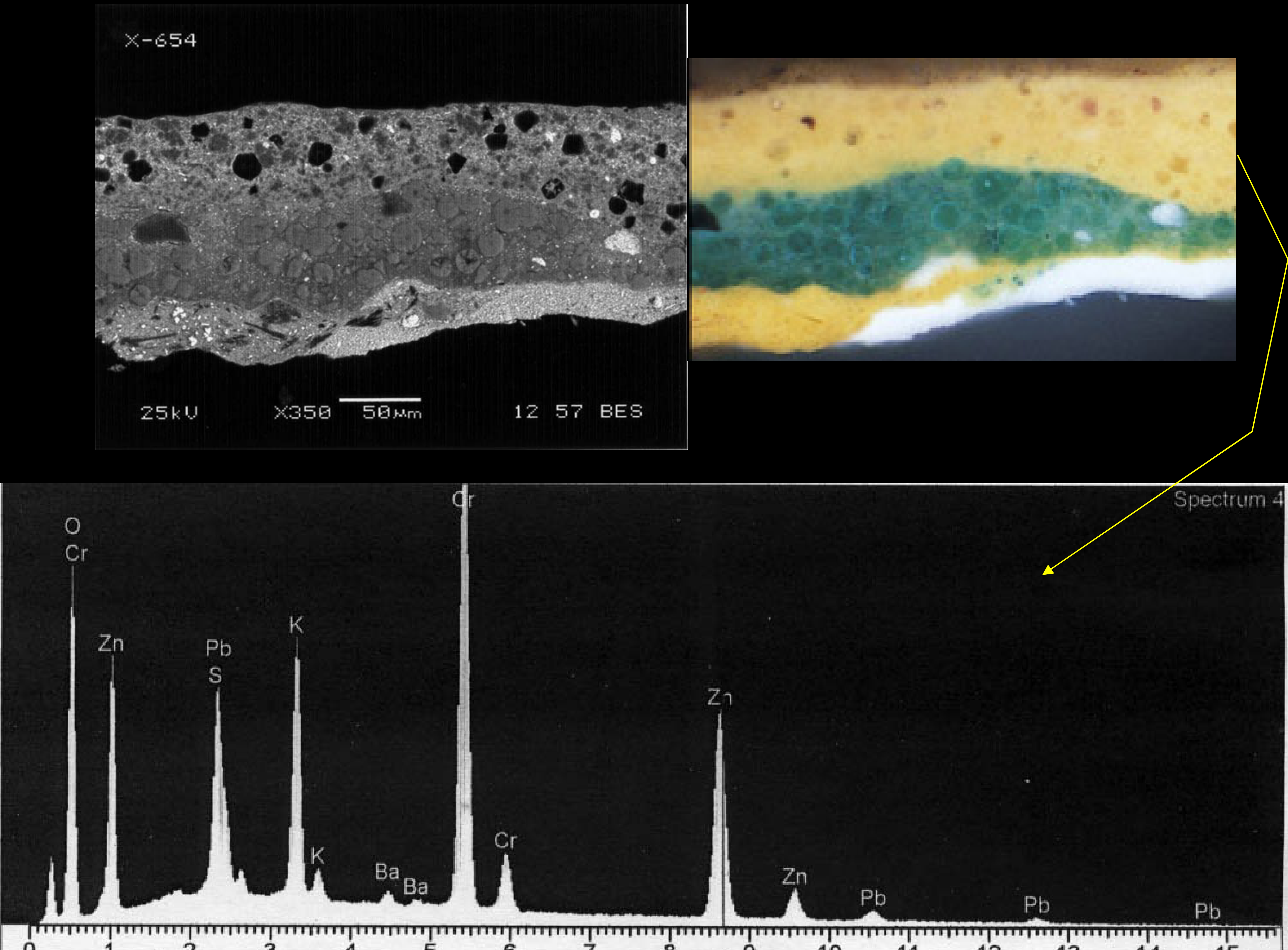
Zinc yellow ($K_2O*4ZnCrO_4*3H_2O$), Vermilion and Starch



Iodine test for starch



Intensity (a.u.)
LGJ discolored yellow layer
Zn Yellow reference
200
400
600
800
Wavenumber (cm-1)


X-654
25kV
X350
50µm
12 57 BES
Spectrum 4
O
Cr
Zn
Pb
S
K
K
Ba
Ba
Cr
Cr
Zn
Zn
Pb
Pb
Pb

MATERIALS OF LA GRANDE JATTE

Examination campaigns: 1957; 1982; 2003.

- **SUPPORT**: Special, oversized canvas, commercially pre-primed with a thin layer of lead white tinted to a neutral off-white tone. Coarsely woven canvas + thin ground = grainy surface
- **BINDER**: Linseed oil (heat bodied). Use of starch as a thickener
- **PIGMENTS**:

  FIRST CAMPAIGN: mixtures of 5-6 pigments. Ex. Brown tone: burnt Sienna, Fe Oxide yellow, ultramarine blue, organic red lake, vermilion, lead white, some black.

  SECOND CAMPAIGN: simpler mixtures (optical combination on the retina, minimally on the palette). Mostly yellow + orange dots, with complementary blue shade. Effect of reflected solar light portrayed as circular bright dots

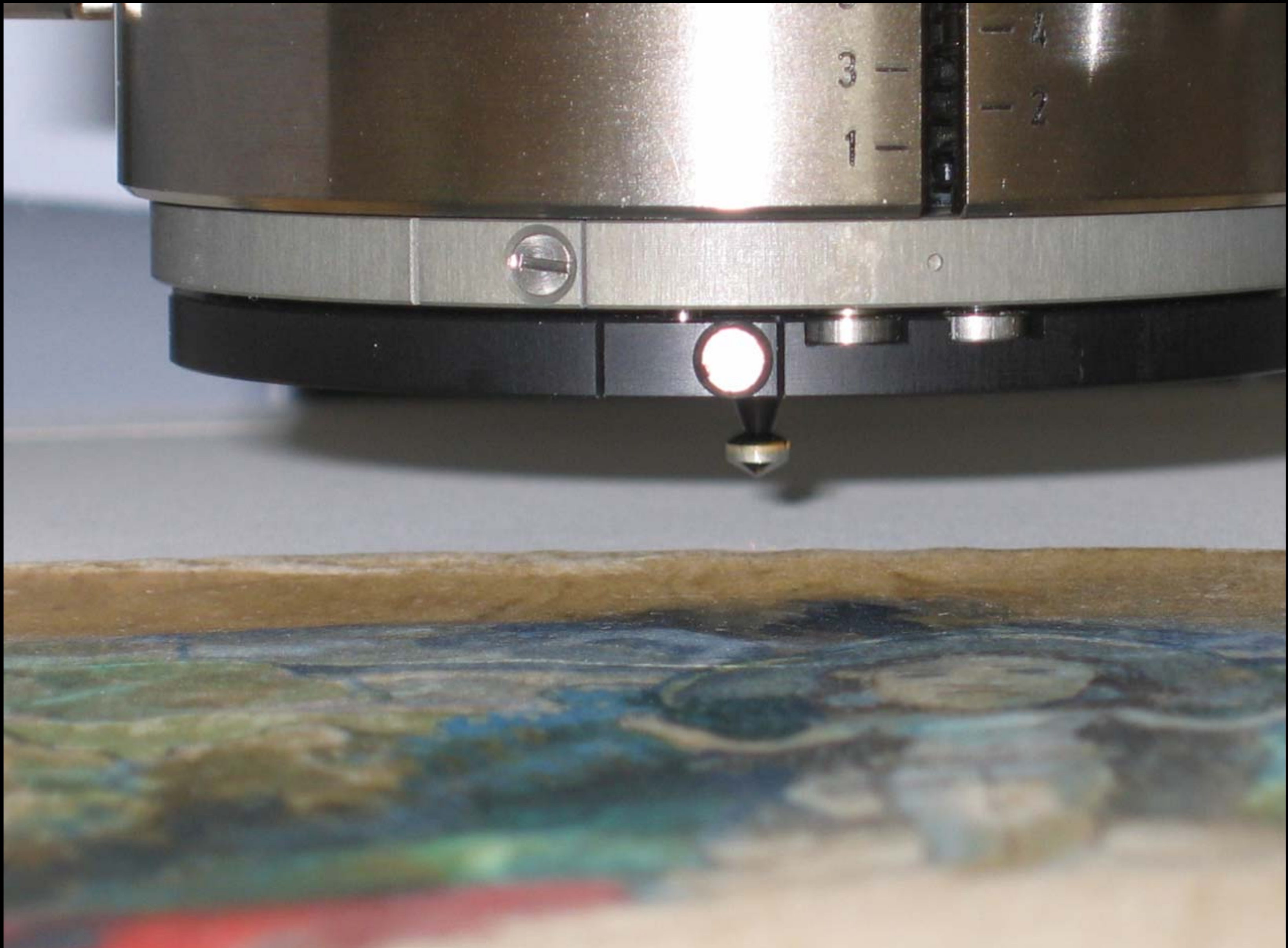
  THIRD CAMPAIGN: single colours.(predominatly blue & red, + orange and yellow, on lead white support)

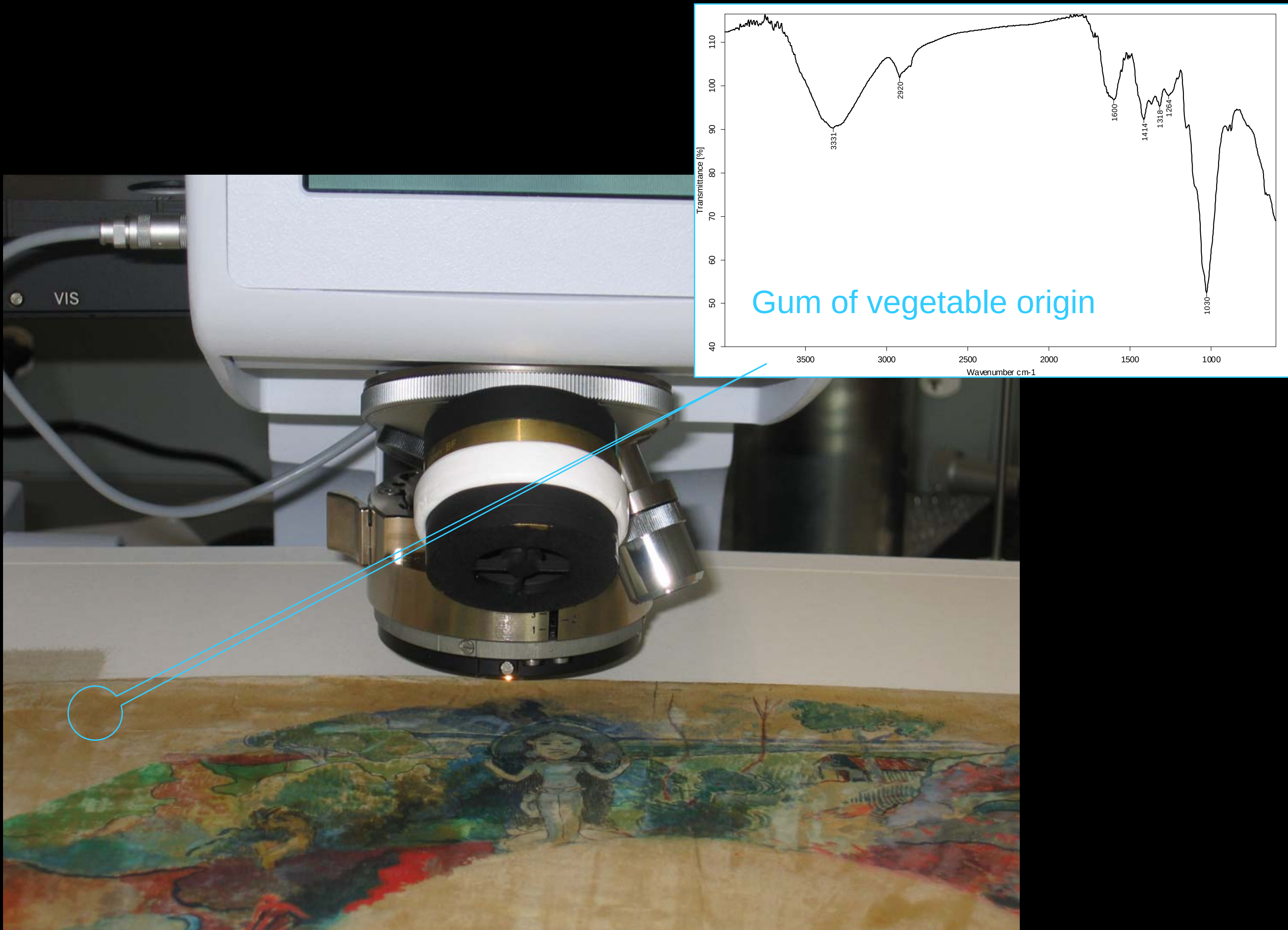
- **VARNISHES**: None.

	Stage 1 (1884-85)	Stage 2 (1885-86)	Stage 3 (borders> 1889)
Vermilion (mercuric sulfide)	●	●	●
Organic Red Lake (unidentified)	●	●	●
Burnt Sienna (calcined iron oxide)	●		
Iron Oxide Yellow (hydrated iron oxide)	●		
Chrome Yellow (lead chromate)	●	●	●
Chrome Orange (basic lead chromate)			●
Zinc Yellow (zinc potassium chromate)		●	
Cadmium yellow (Cadmium sulfide)	●	●	●
Viridian (hydrous chromium oxide)	●	●	
Emerald Green (copper acetoarsenite)	●	●	
Ultramarine Blue (sodium aluminium sulfo-silicate)	●	●	
Cobalt Blue (cobalt aluminate)	●	●	●
Lead White (basic lead carbonate)	●	●	●
Charcoal or Bone Black	●		

P. Gauguin, Tahitian Landscape: Design for a Fan, 1900-1903

watercolor and gouache over graphite on support prepared by pasting three sheets of Japanese paper to a single sheet of wove, Western paper





Gum of vegetable origin
Transmittance [%]
Wavenumber cm-1
110
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
3331
2920
1600
1414
1318
1264
1030
VIS

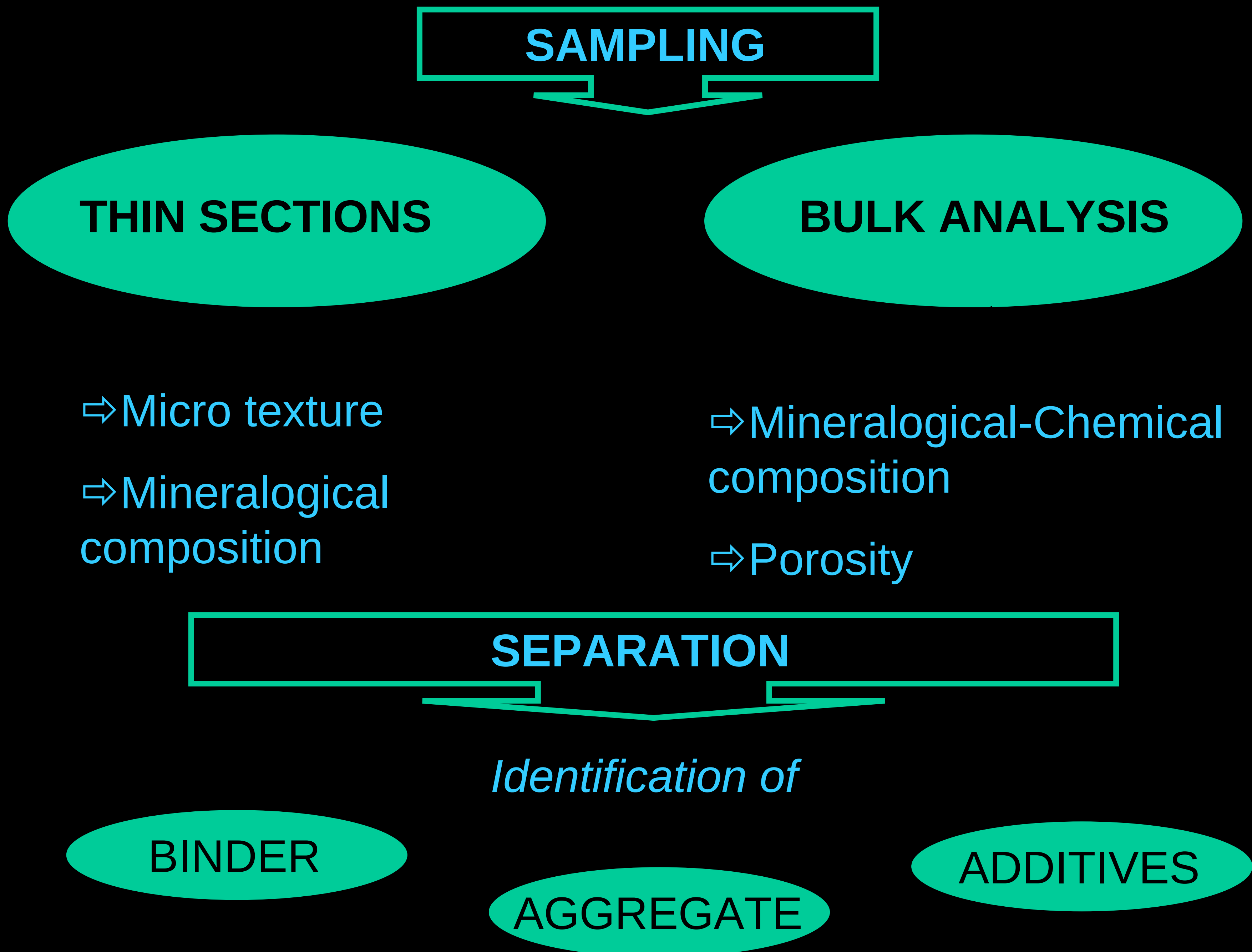
SCIENTIFIC INVESTIGATION of MORTARS

Answers questions related to:

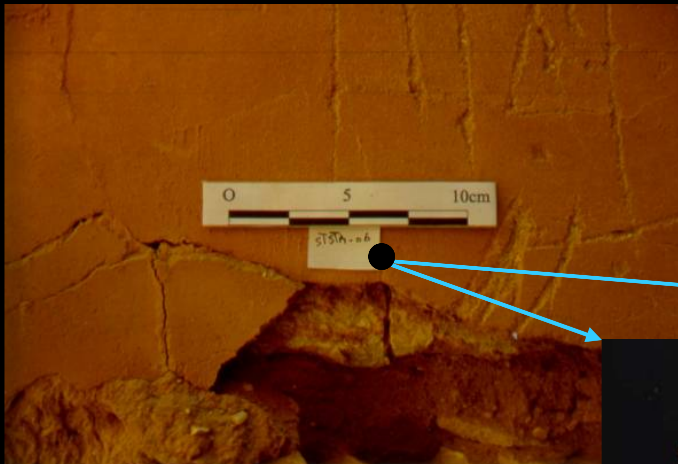
- RESTORATION
- CONSERVATION
- TECHNOLOGY and RELATIVE DATING

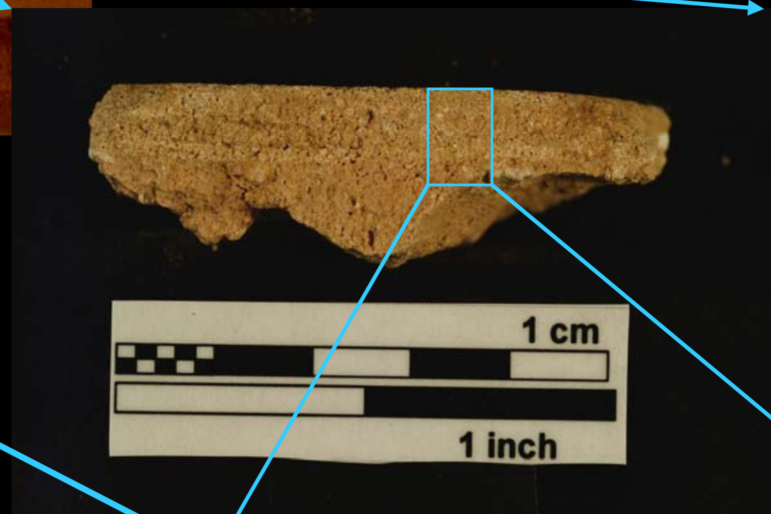
CONSERVATION

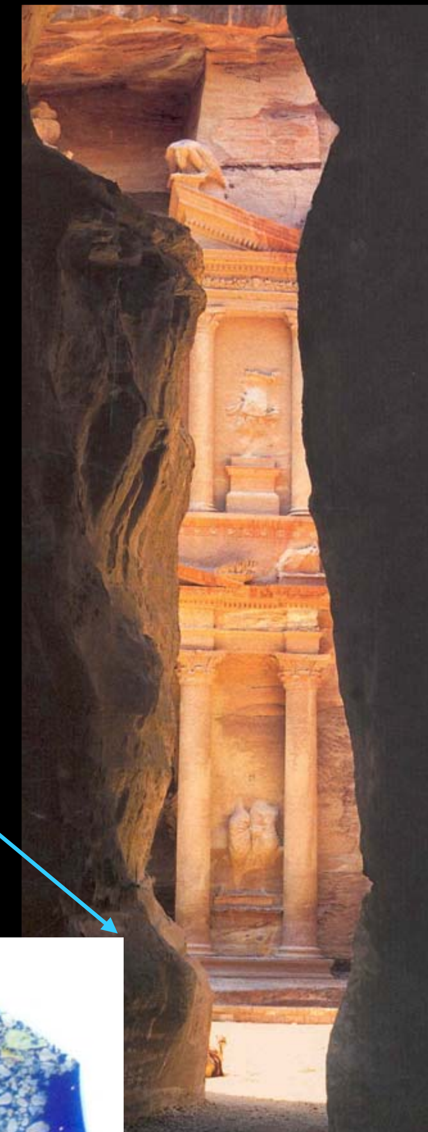
- Insufficient cohesion
- Lack of adhesion
- Type of aggregate
- B/A values
- Porosity
- Mortar’s mixing ratios
- Salt contamination
- Changes due to previous treatments

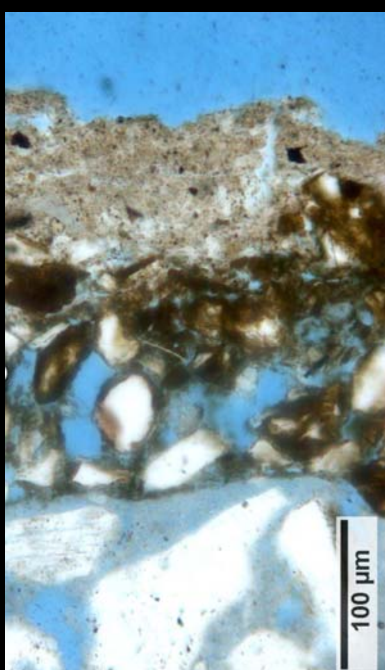

SAMPLING
THIN SECTIONS
BULK ANALYSIS
⇨Micro texture
⇨Mineralogical composition
⇨Mineralogical-Chemical composition
⇨Porosity
SEPARATION
Identification of
BINDER
AGGREGATE
ADDITIVES

Painted plaster (Petra, Jordan, III cent. B.C.)





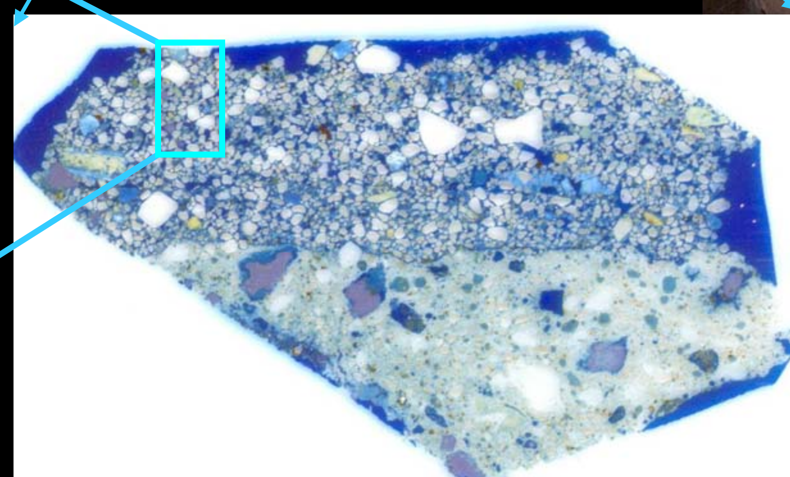




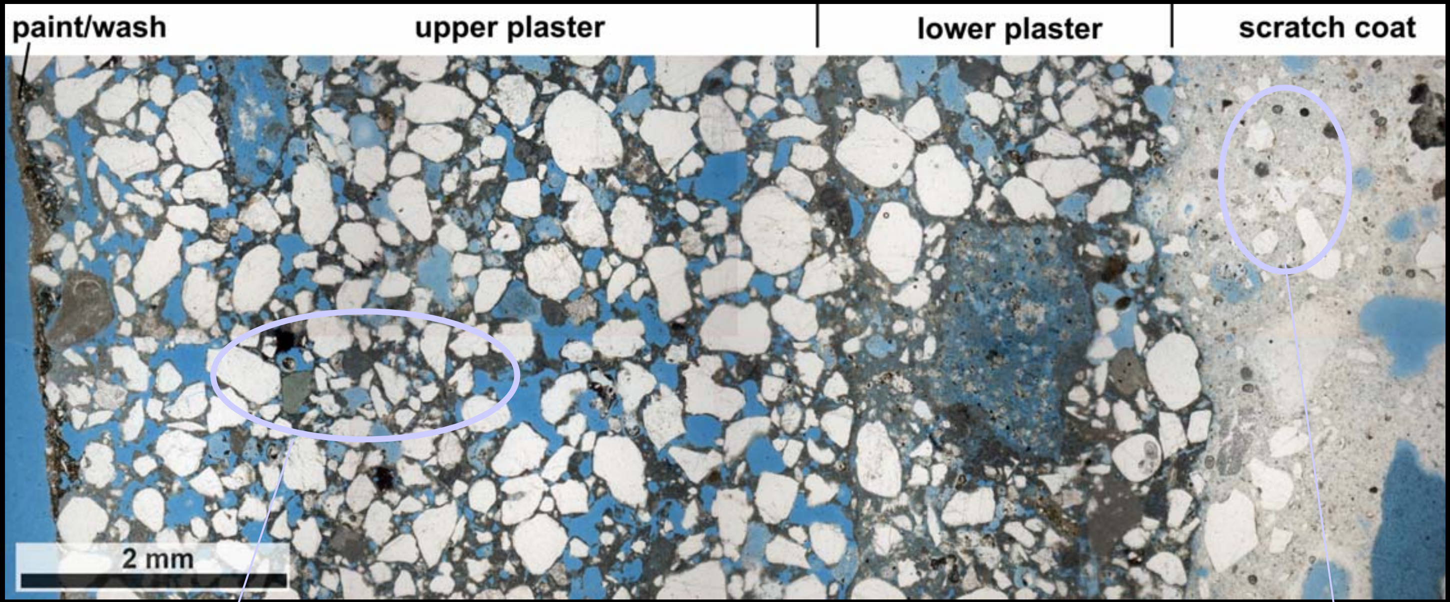
paint

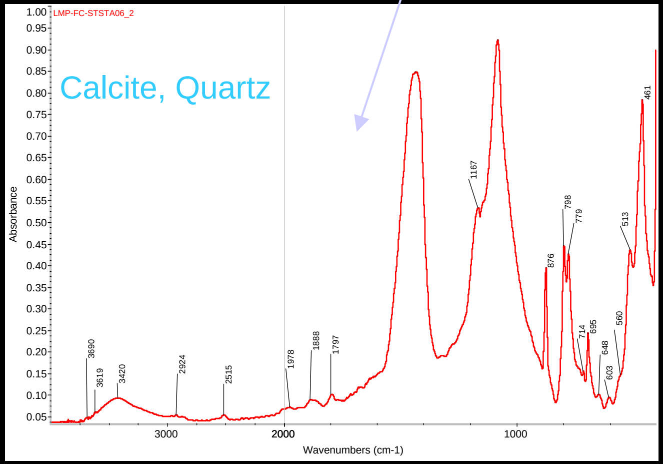
ground

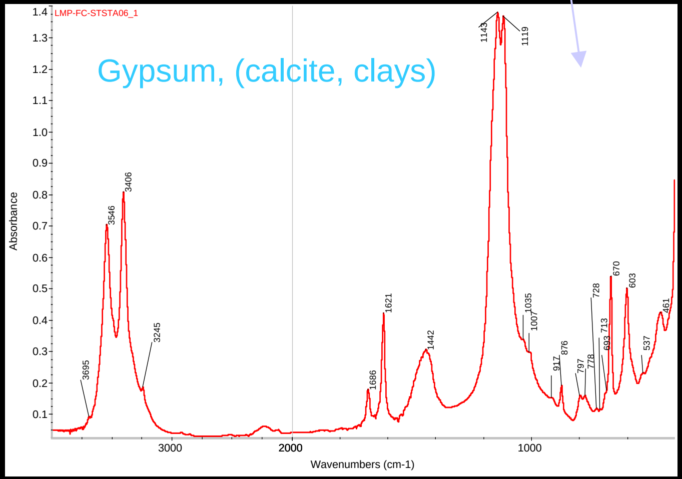
plaster



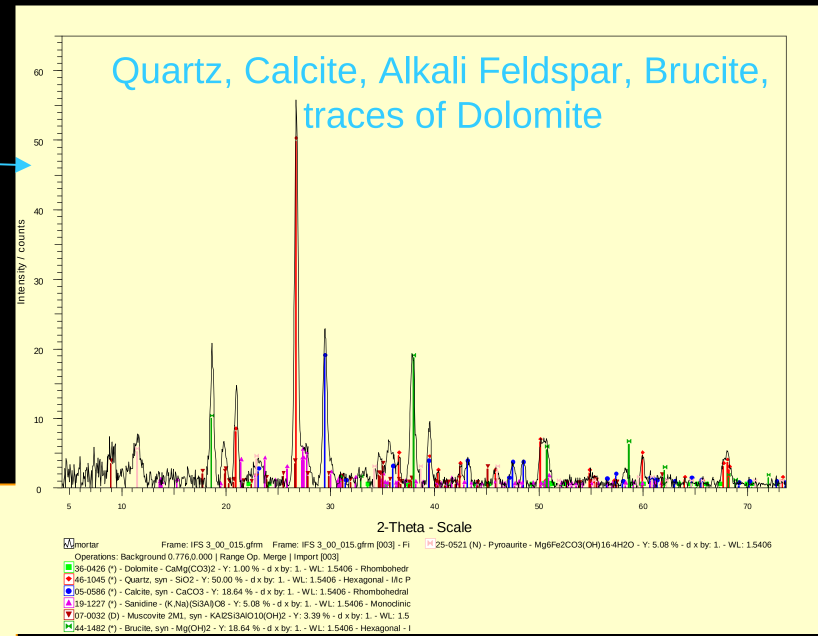
DIFFERENT CHEMICAL COMPOSITION



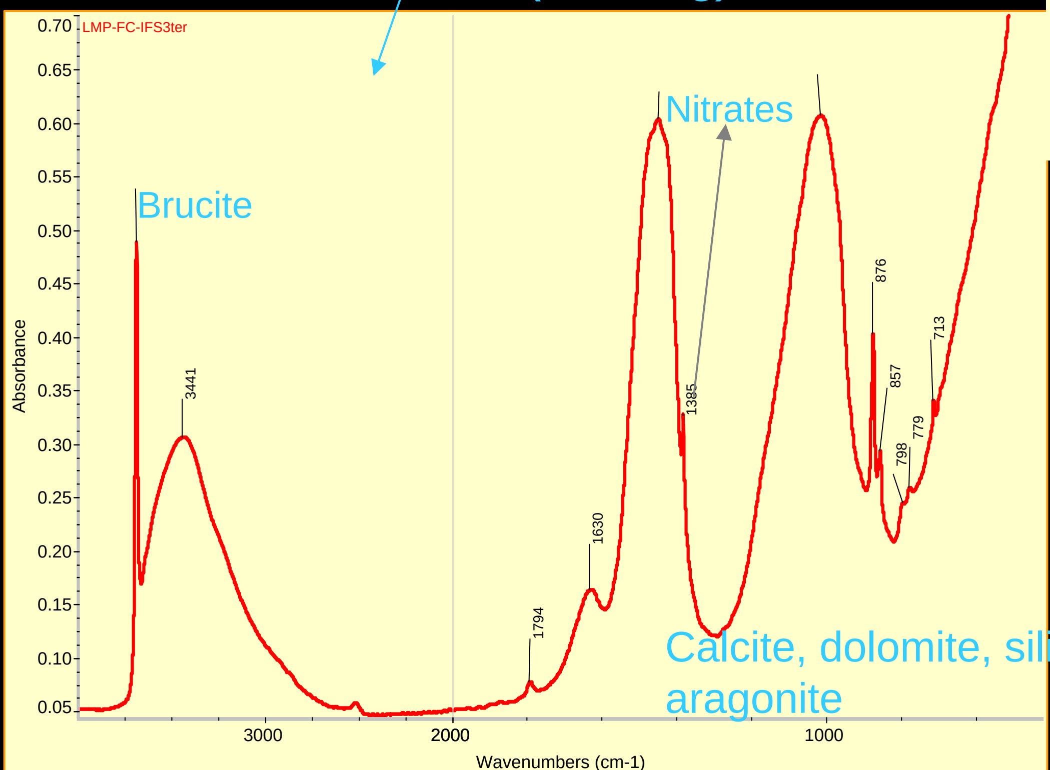




COMPLEMENTARITY of TECHNIQUES



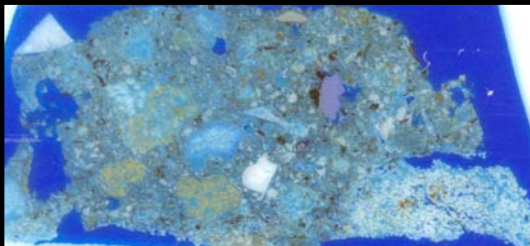
Trier, Roman Thermes (flooring)



BULK XRD

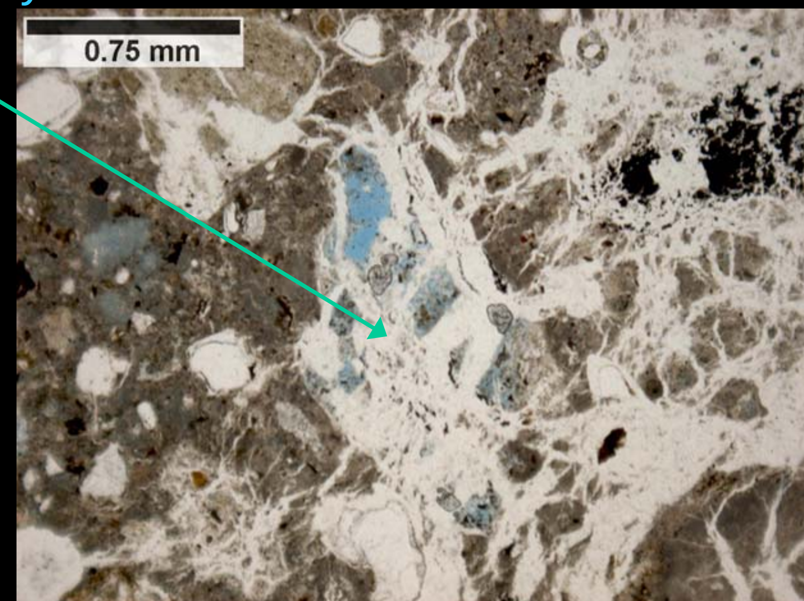
BULK FTIR

LOCALIZATION of INFORMATION



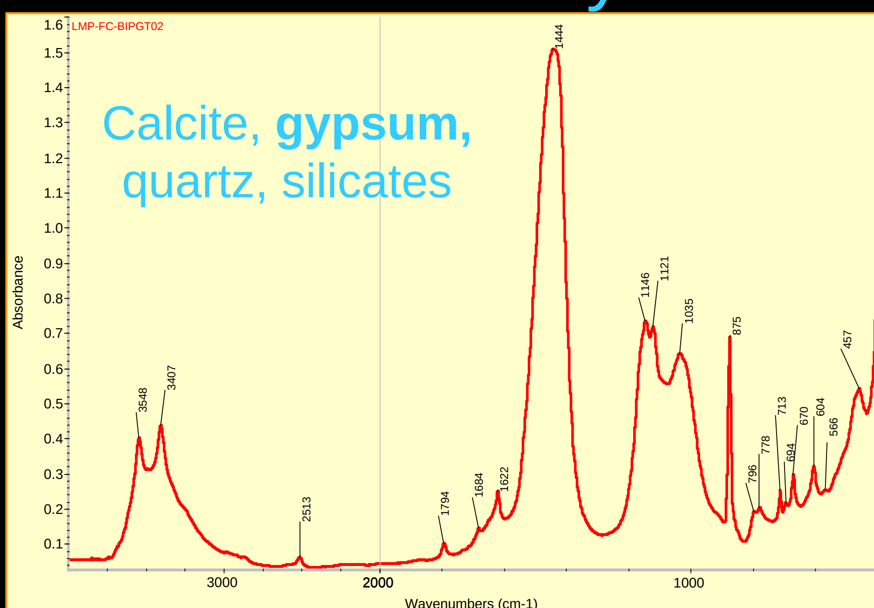
Petra, Great Temple
Binding mortar

Secondary precipitation of **gypsum** filling cracks and air voids completely



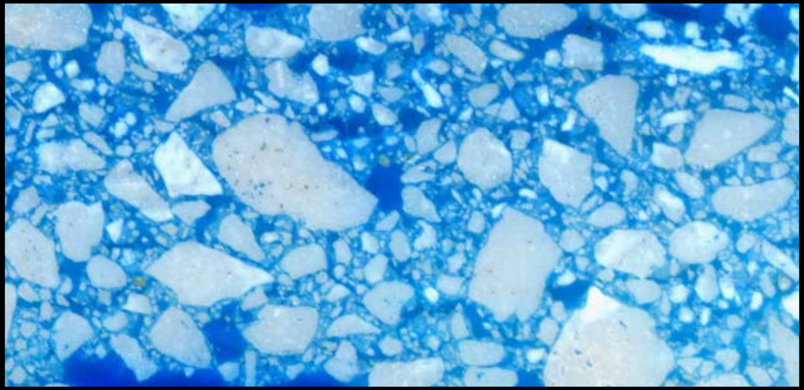
PLM- pinpointing the information

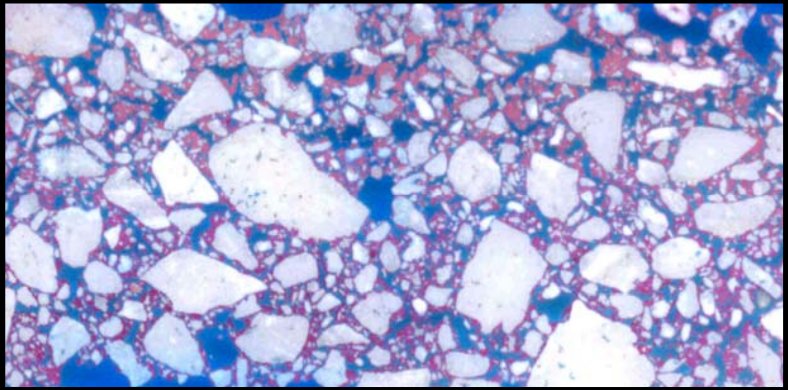
FTIR- Bulk analysis

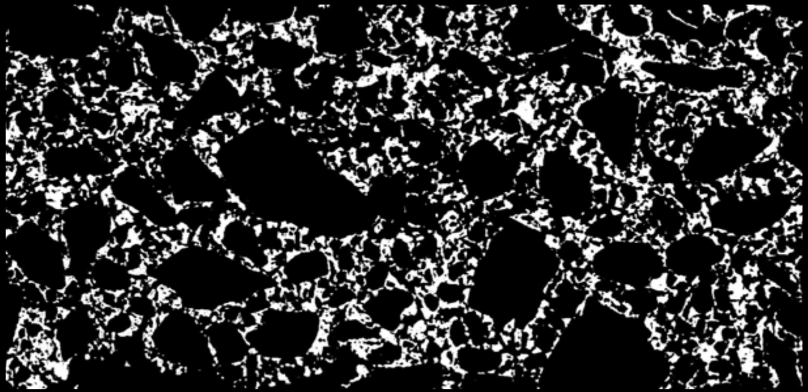


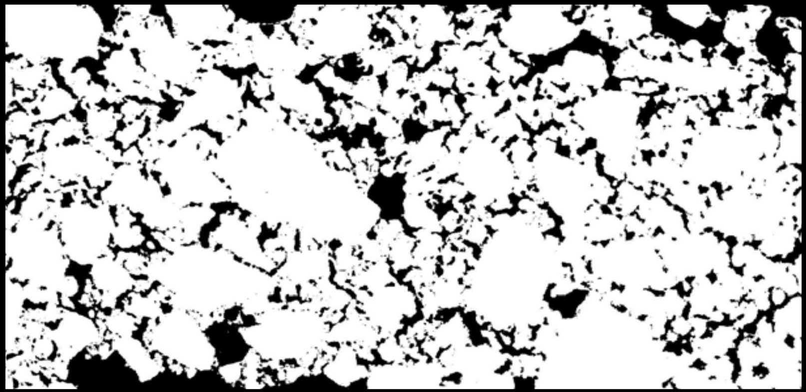
Mortar's component	Colormod				Image Pro Plus
	% area mes.1	% area mes.2	% area mes.3	Avg	% area
Binder	22.40	24.65	25.28	24.11	16.47
Pores and other resin filled zones	29.17	22.50	18.52	23.4	23.73
Aggregate	47.73	52.07	52.67	50.82	59.8

B/A mass ratio1: 9









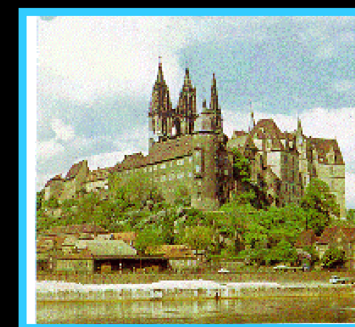
AUTHENTICATION AND DATING

Decoration of Meissen Porcelain:

Raman Microspectroscopy as an aid for Authentication and Dating

CHRONOLOGY

- **June 1710** Opening of the Royal-Polish-Electoral-Saxonian Porcelain Manufactory of Meissen (on the Albrechtsburg-castle). Discovery of porcelain by Johann Friedrich Böttger and Walther von Tschirnhaus under the auspices of August the Strong .



- **1861-1864** Removal from the Albrechtsburg to new location in the Triebisch valley of Meissen

- **from 1918 to today** Staatliche Porzellan-Manufaktur Meissen GmbH (100% shares Saxony)

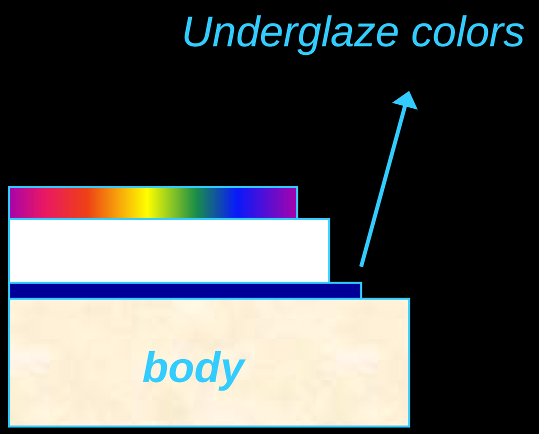






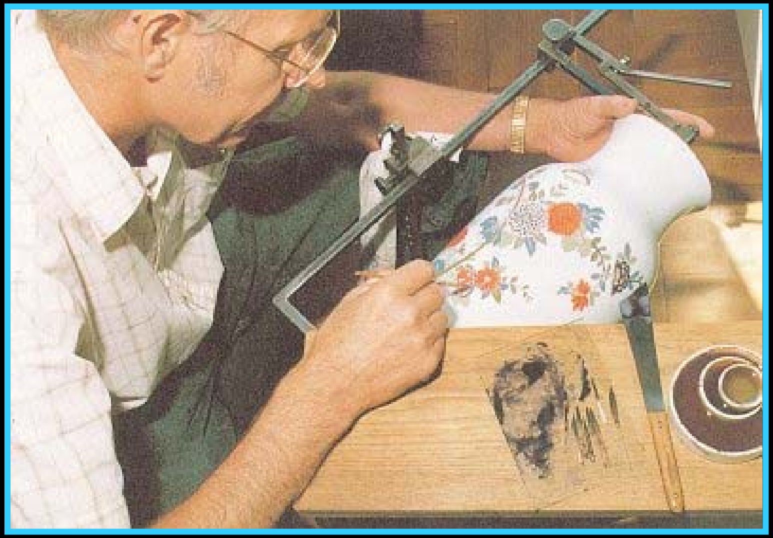
STRUCTURE

- Painting layers applied on white enamel
- Overglaze paint colours fired at low temperature.
- Thickness of paint = 10-50 μm
- Thickness of glaze = 100-200 μm
- **Microstructure** ➡ ceramics
- **Nanostructure** ➡ enamels and glazes (size of crystalline pigments dispersed in glassy host coatings must be close to 100 nm or less to obtain a high gloss glaze).



Initially:

- white porcelain
- unfired colours
- restricted range of fired overglaze enamels (blue, gold, red, purple)



THE COLOR OF OVERGLAZE ENAMELS

BLUE

<u>Co</u> based ➡ **<u>Zinc oxide</u>** used ***after 1760***

YELLOW

Naples Yellow **(Sb)**
➡ **Uranium** or **Va oxide** used in the ***19th century***

GREEN

Cu as base ***until 1802*** ➡ **Cr**

RAMAN MICROPROBE

- **Jobin Yvon Horiba Labram 300 confocal Raman microscope**

  with Andor multichannel air cooled open electrode charge-coupled device (CCD) detector (1024x256), holographic notch filter, and two dispersive gratings (950 and 1800 grooves/mm).

- **BXFM open microscope frame (Olympus)**

  50x long working distance objective

- **Kr ion laser (l_0= 514.5 nm)**, He-Ne laser (l_0=**632.8 nm**), or a solid state diode laser (l_0=785 nm)

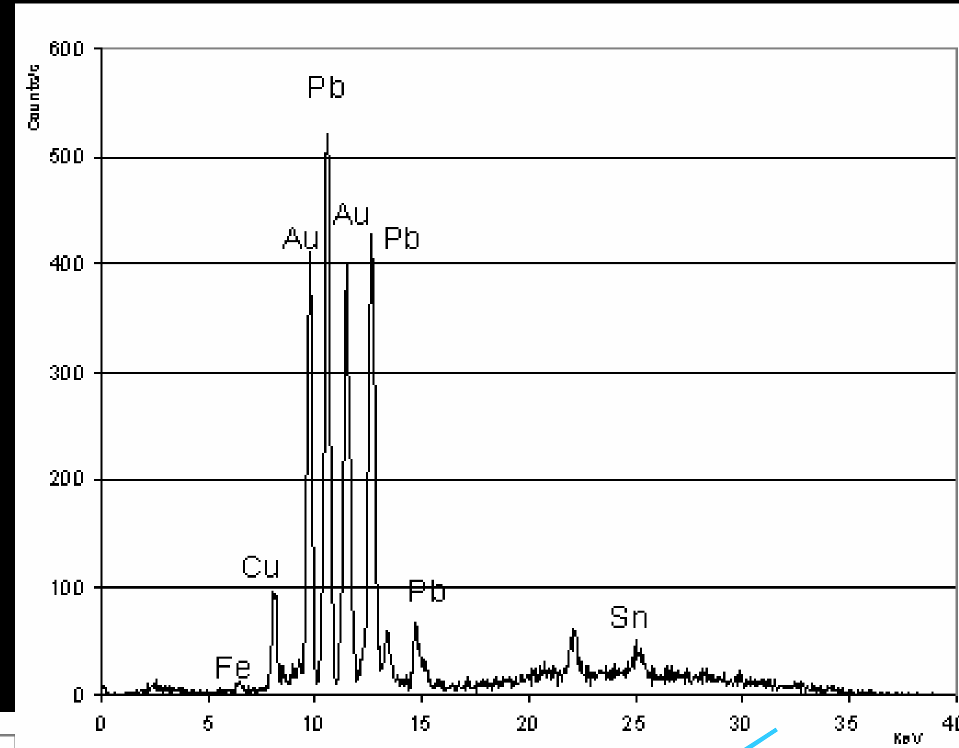
- **Neutral density filters**

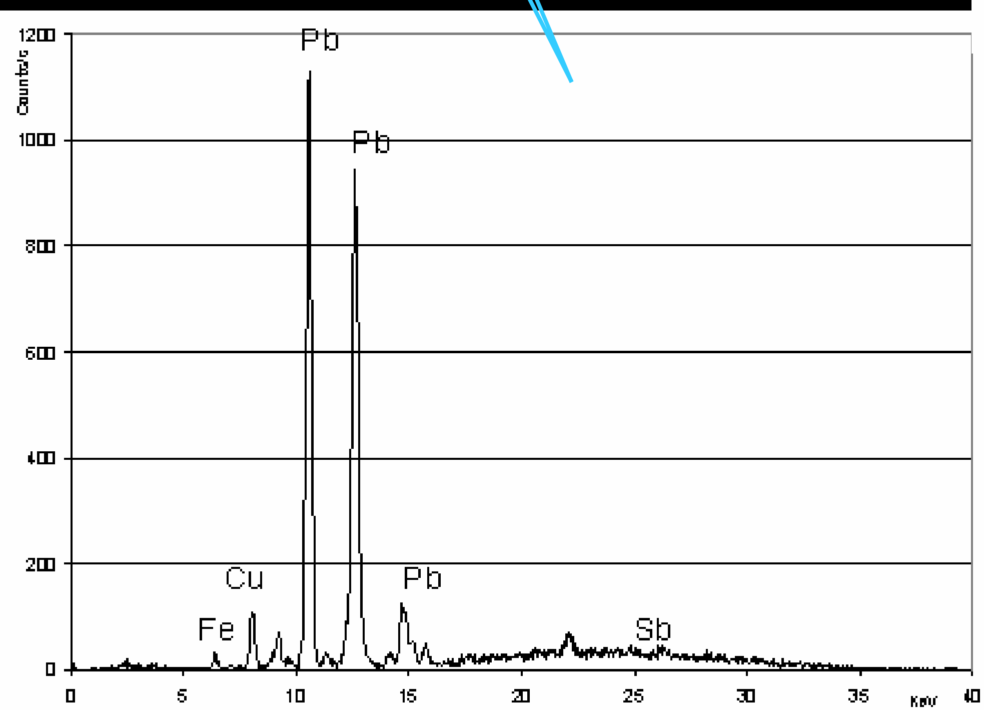
  Scans: **10 sec. → 6 minutes**

XRF SPECTROMETER

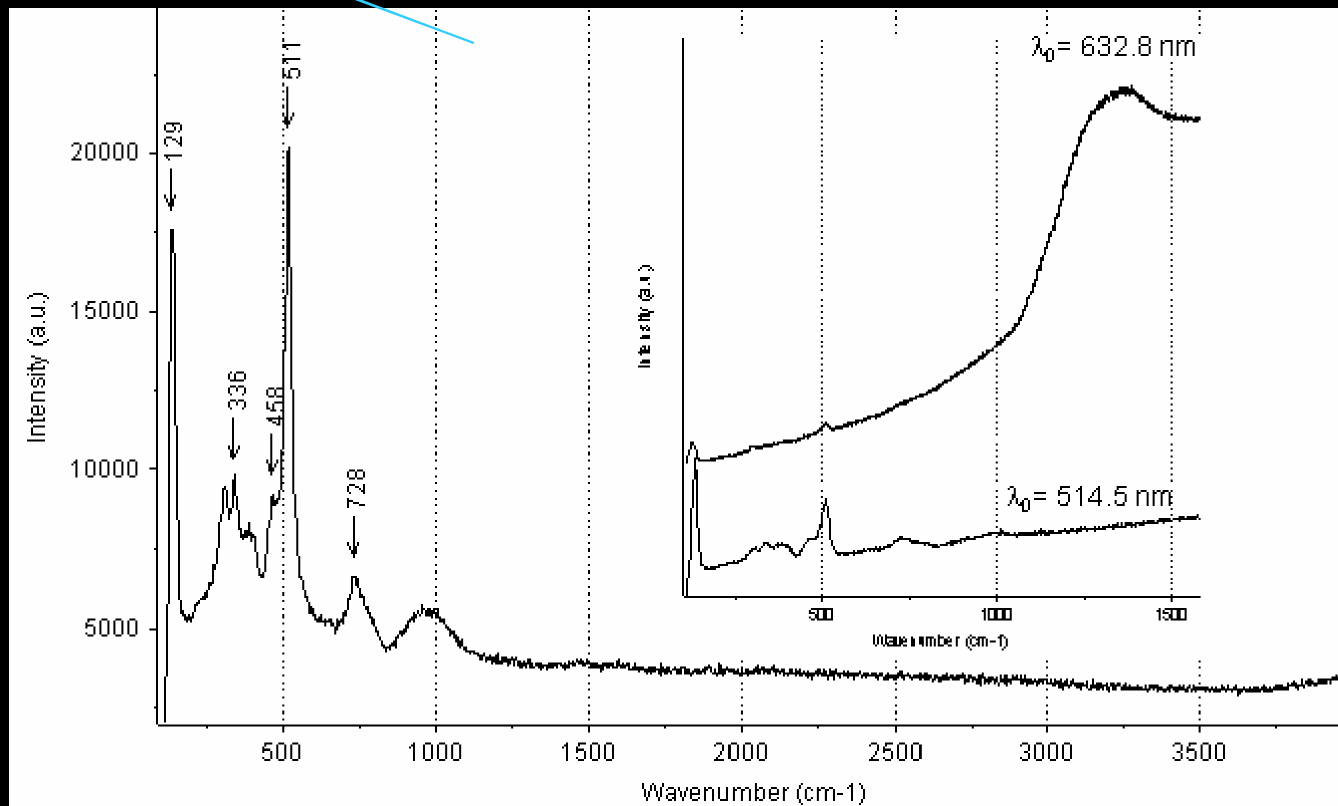
- Keymaster TRACeR III portable XRF spectrometer with X-ray tube (Re target)

- Acquisition times: 60 → 120 seconds

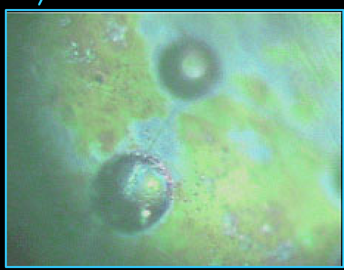

Counts/s
Pb
Au
Au
Pb
Cu
Pb
Fe
Sn
0
100
200
300
400
500
600
0
5
10
15
20
25
30
35
KeV

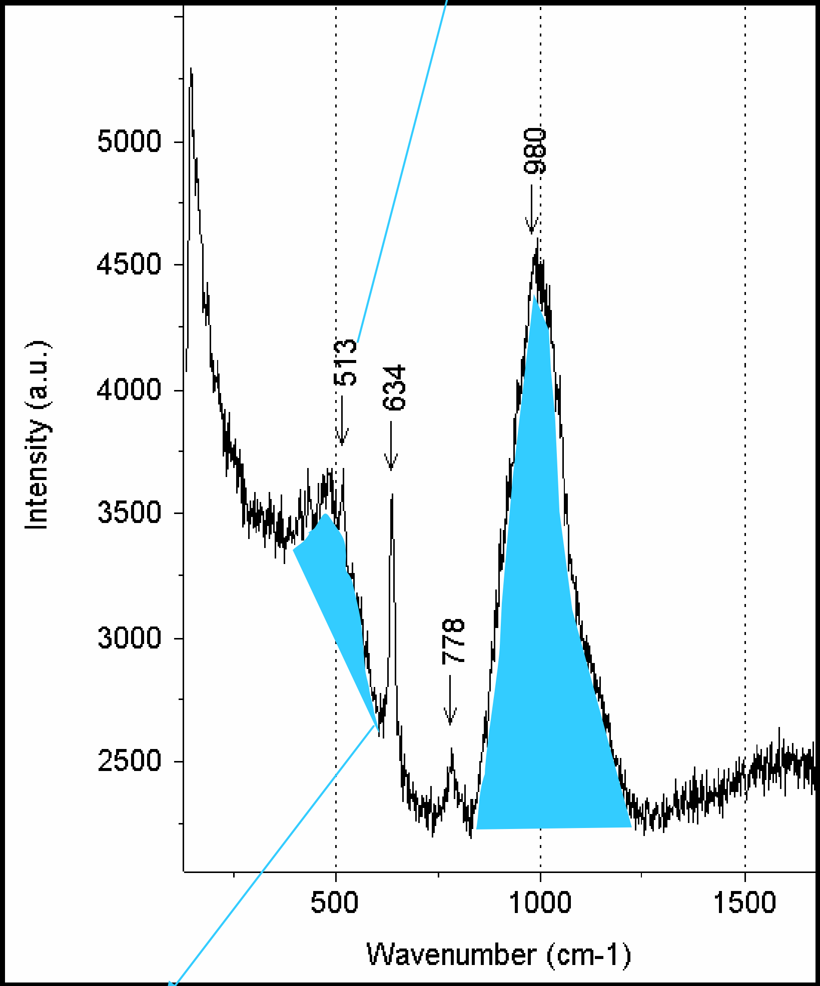

Counts/s
Pb
Pb
Cu
Pb
Fe
Sb
0
200
400
600
800
1000
1200
0
5
10
15
20
25
30
35
40
KeV

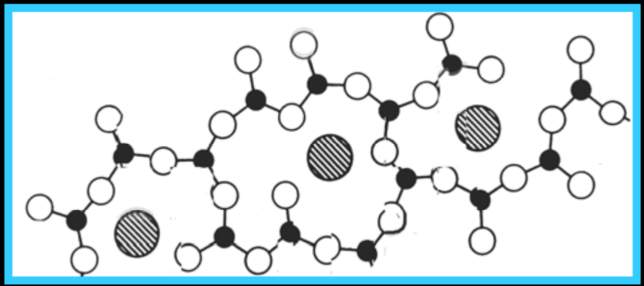
Naples Yellow ($Pb_2Sb_2O_7$)

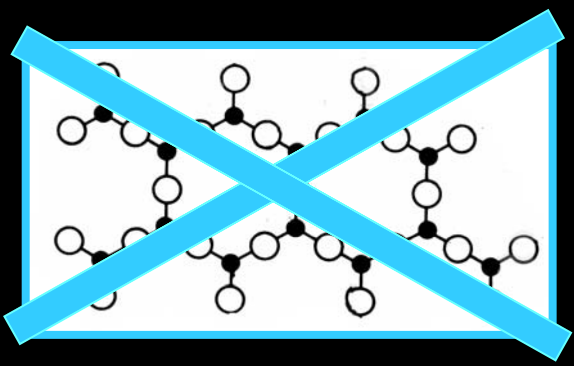


Incompletely reacted feldspar grains in medium T fired glaze (510 cm^{-1})

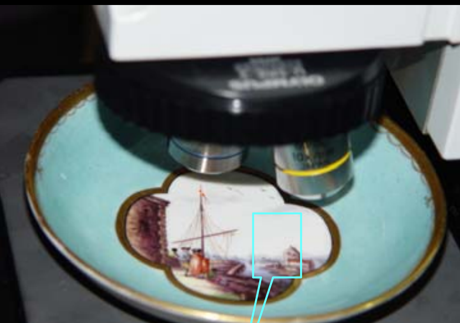


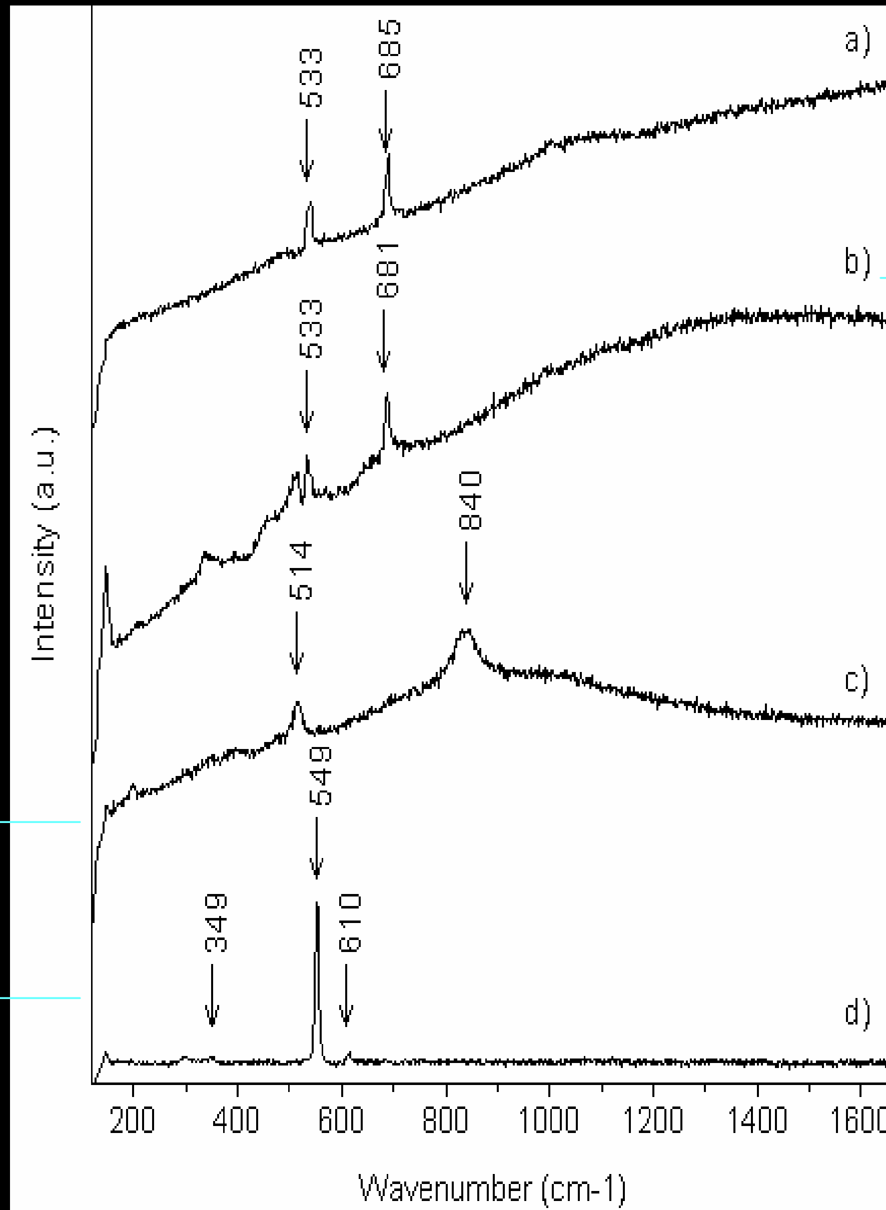






Cassiterite (SnO_2 <u>634</u>, 475 cm^{-1})



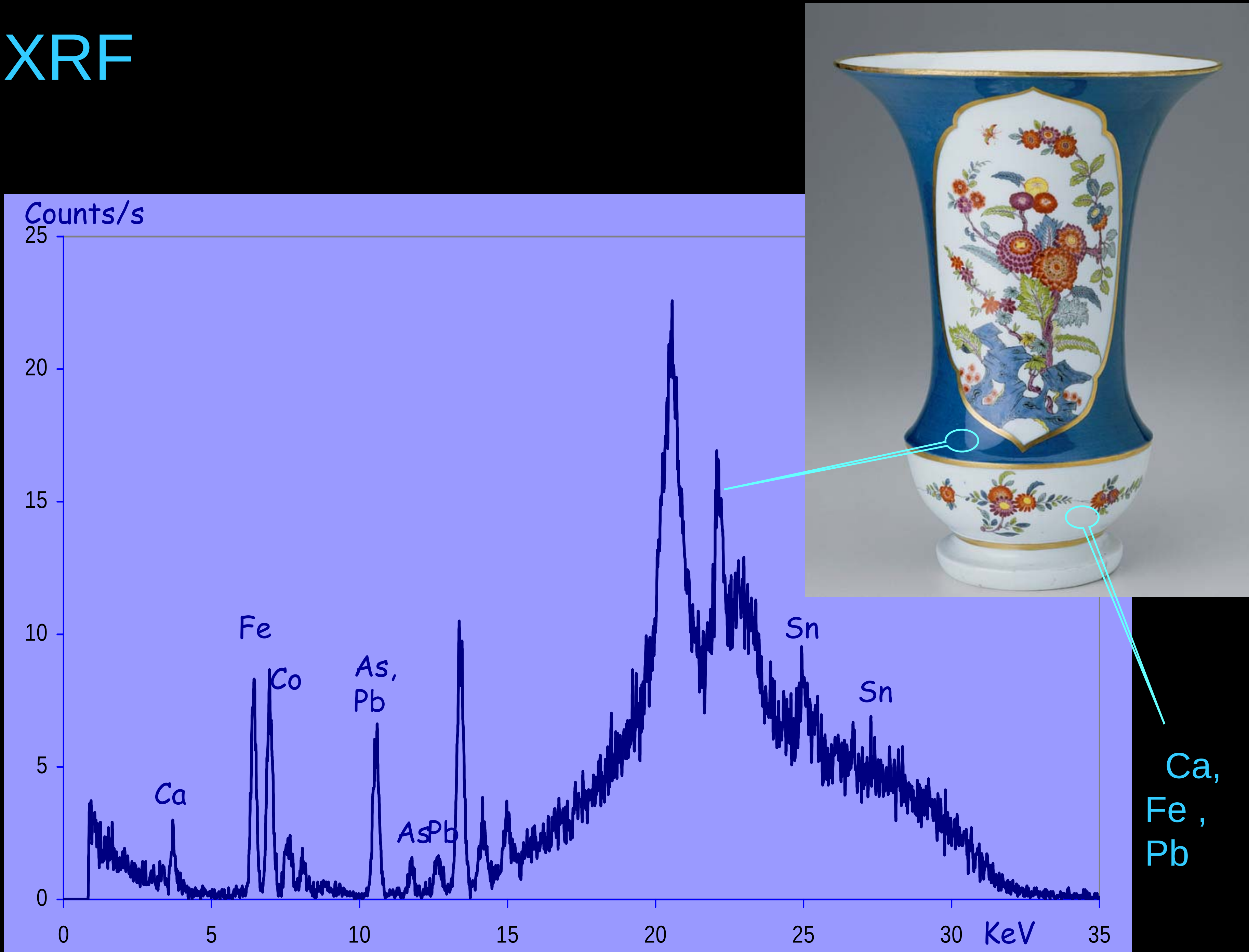


Naples yellow + Co and/or Cr-rich, spinel like phase

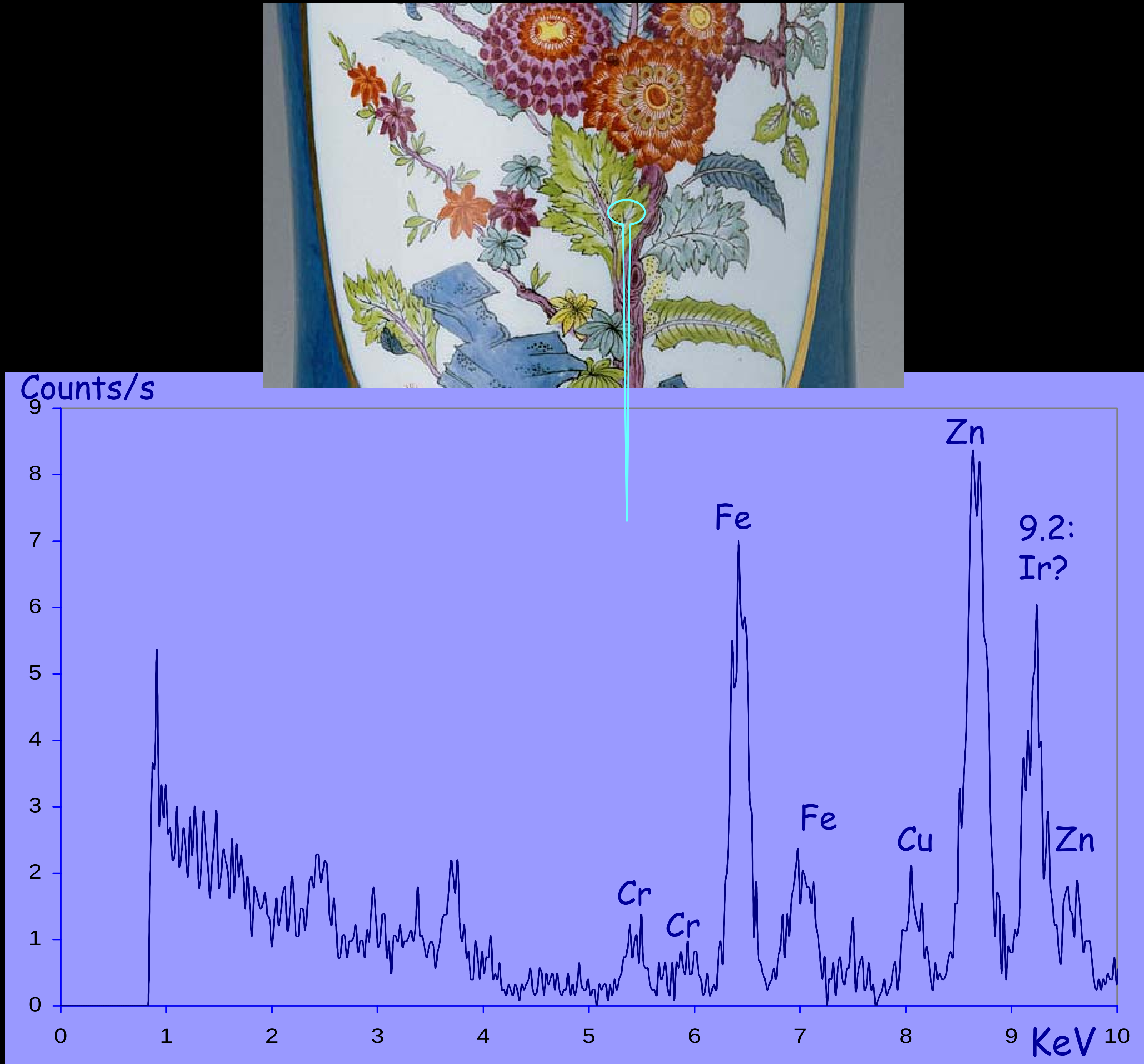
Uvarovite garnet (Victoria green, $Ca_3Cr_2(SiO_4)_3$

Chromium oxide Cr_2O_3

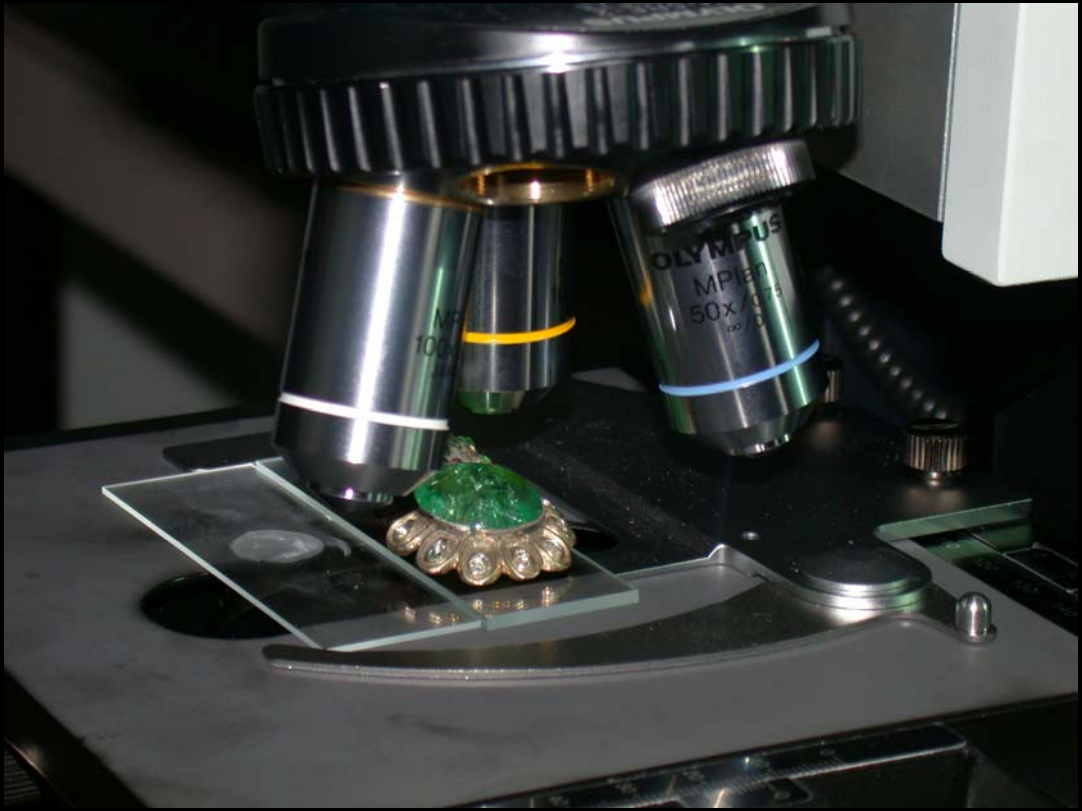
XRF



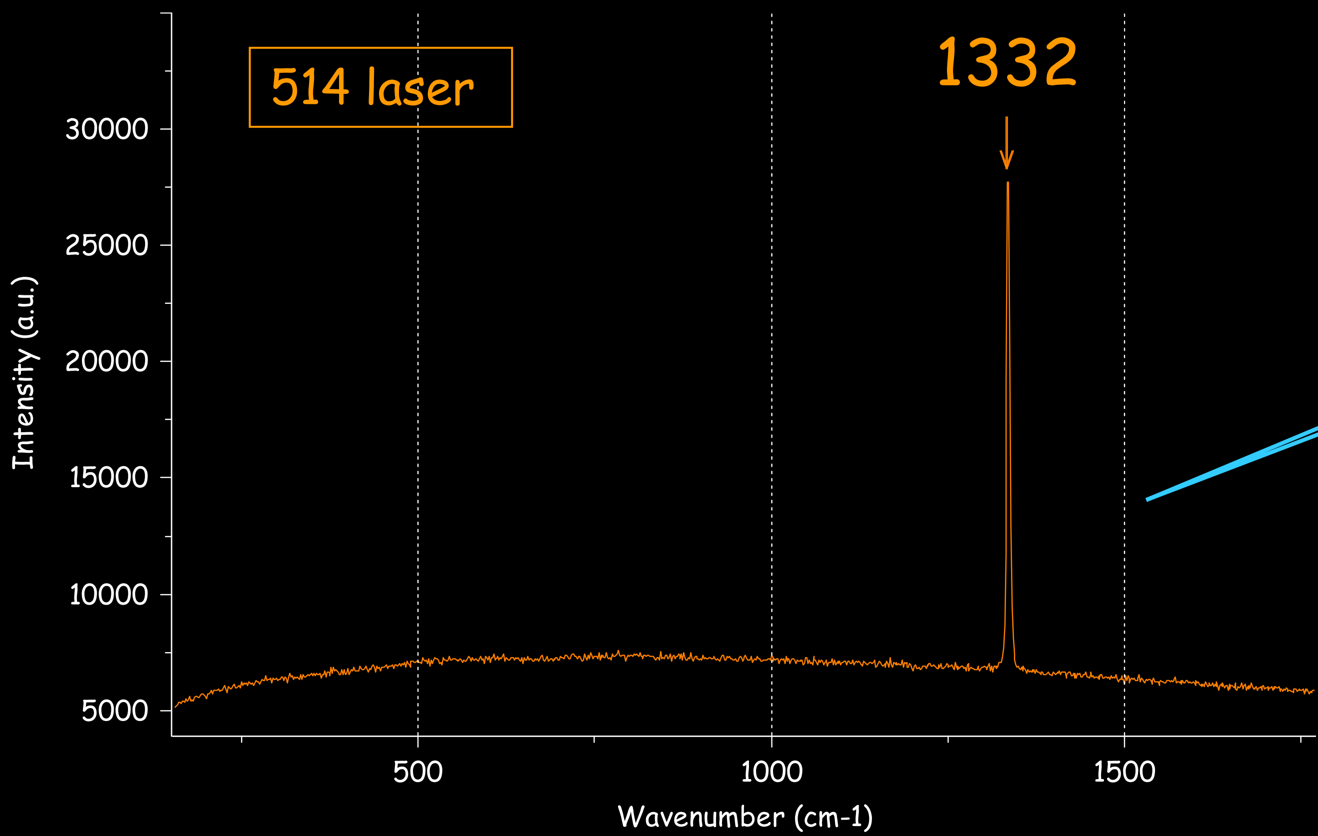
Counts/s
25
20
15
10
5
0
0
5
10
15
20
25
30
35
KeV
Ca
Fe
Co
As,
Pb
As
Pb
Sn
Sn
Ca,
Fe ,
Pb

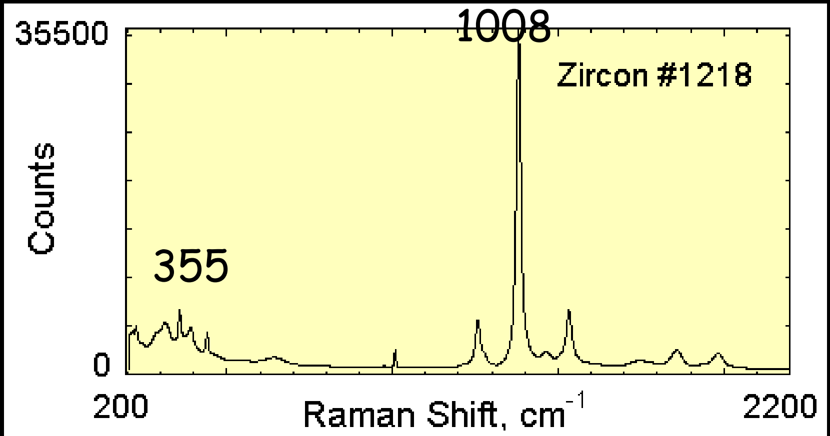

Counts/s
9
8
7
6
5
4
3
2
1
0
0
1
2
3
4
5
6
7
8
9
10
KeV
Fe
Zn
9.2:
Ir?
Fe
Cu
Zn
Cr
Cr

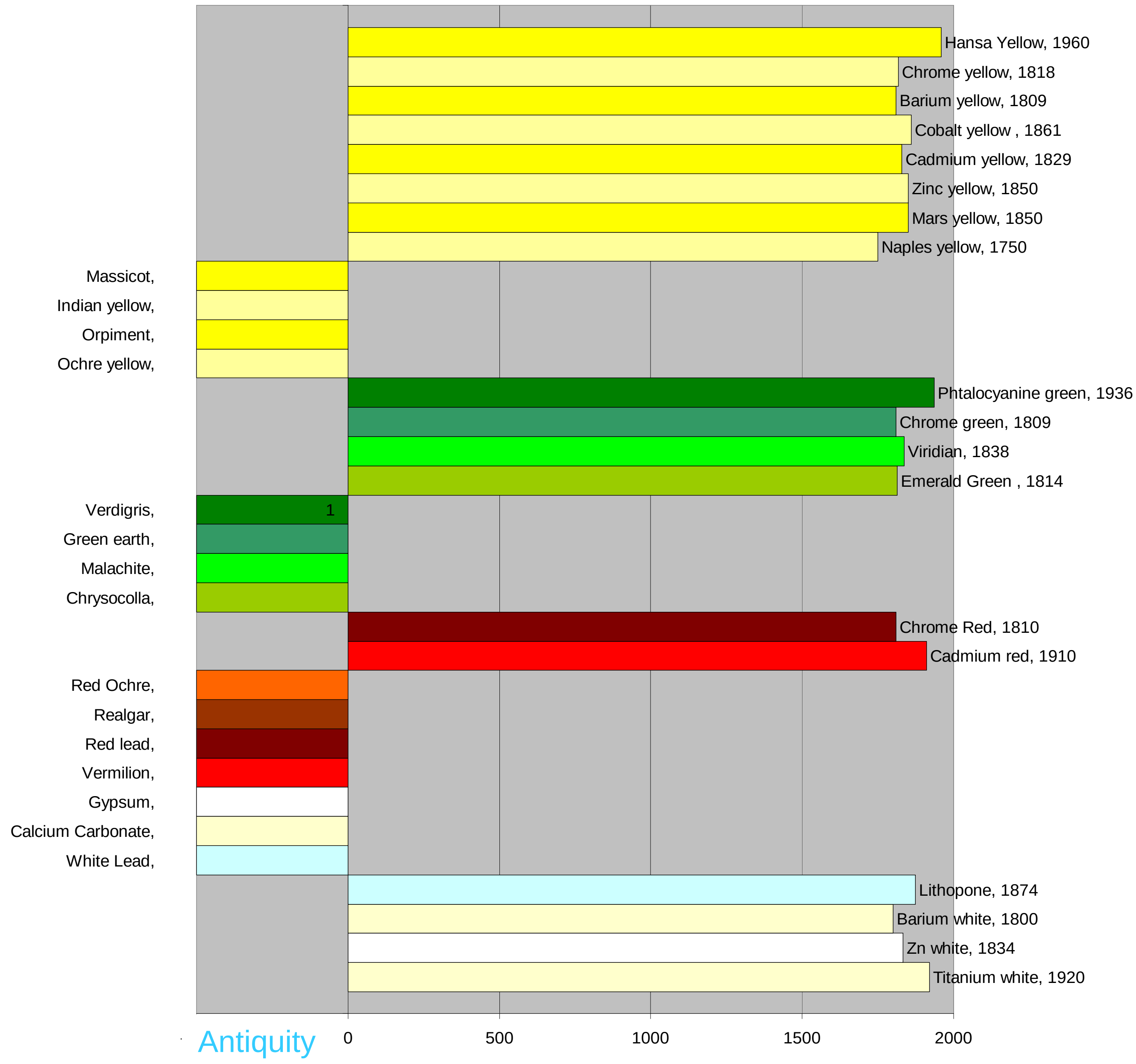
AUTHENTICATION: GEMS



Ottoman turkish Sword - blade inscribed 1099 Hejira [A.D. 1867]


514 laser
1332
30000
25000
20000
15000
10000
5000
500
1000
1500
Intensity (a.u.)
Wavenumber (cm-1)

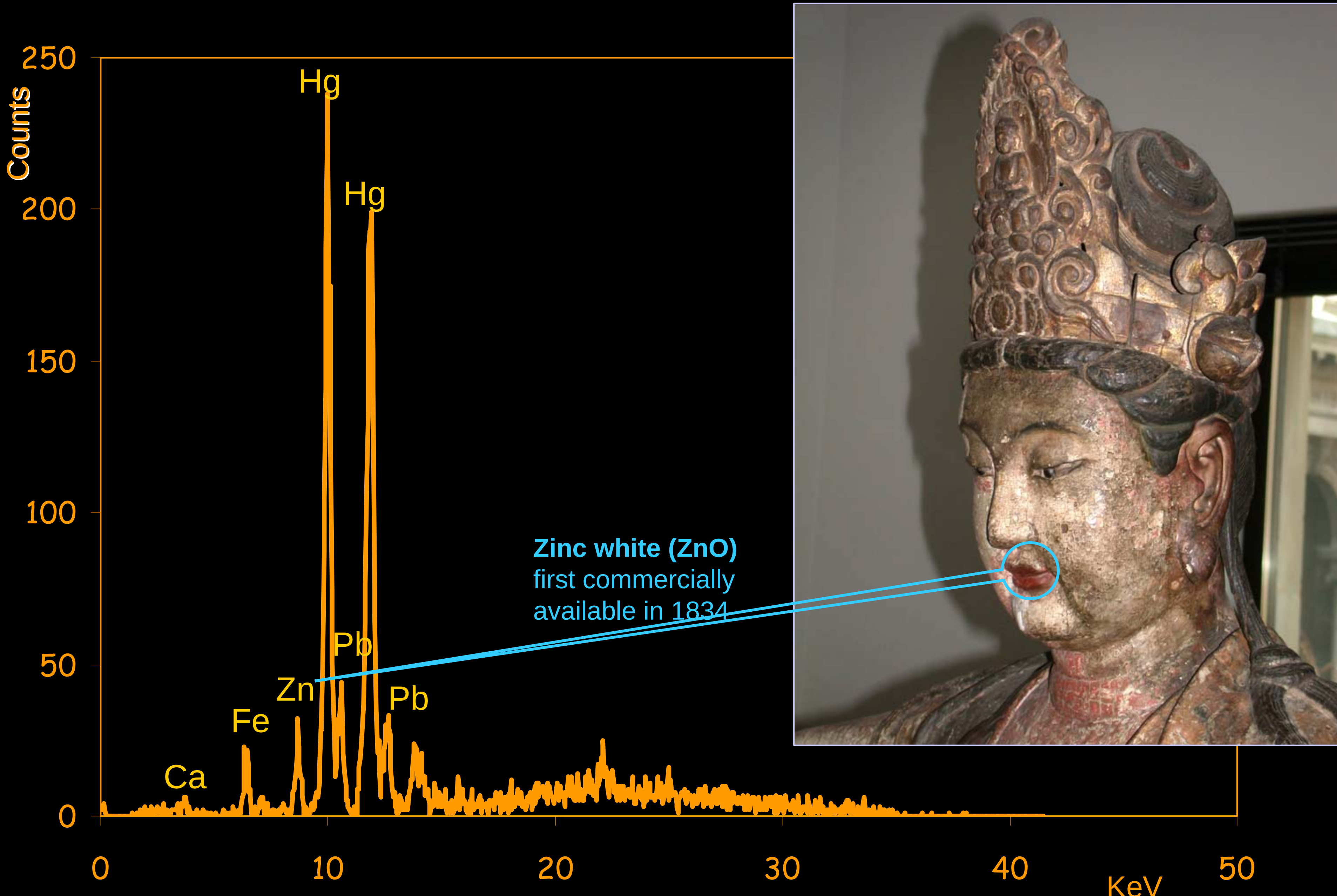

35500
1008
Zircon #1218
Counts
355
0
200
Raman Shift, cm-1
2200



Hansa Yellow, 1960
Chrome yellow, 1818
Barium yellow, 1809
Cobalt yellow , 1861
Cadmium yellow, 1829
Zinc yellow, 1850
Mars yellow, 1850
Naples yellow, 1750
Massicot,
Indian yellow,
Orpiment,
Ochre yellow,
Phtalocyanine green, 1936
Chrome green, 1809
Viridian, 1838
Emerald Green , 1814
Verdigris,
1
Green earth,
Malachite,
Chrysocolla,
Chrome Red, 1810
Cadmium red, 1910
Red Ochre,
Realgar,
Red lead,
Vermilion,
Gypsum,
Calcium Carbonate,
White Lead,
Lithopone, 1874
Barium white, 1800
Zn white, 1834
Titanium white, 1920
Antiquity
0
500
1000
1500
2000

ASIAN ART

Anonymous, Chinese Seated Guanyin Song dynasty (960-1279)



Fe is detected also in exposed wood substrate

THE ADSORPTION OF DYES ON CLAYS: INVESTIGATION OF COLOR FABRICATION TECHNOLOGY OF ANCIENT PRE-COLUMBIAN CULTURES

TRADITIONAL ARTISTS PIGMENTS:

THE COLOR BLUE in the WESTERN COUNTRIES

Egyptian Blue (cuprorivaite) $CaOCuO_4SiO_2$
(III millennium BC to IV-VII C AD)

$CaCO_3$, SiO_2 $CuCO_3$
Na_2CO_3, oxidating atmosphere, 800-940ºC

Vitruvius: sand, Cu scrapings and natrum

Ultramarine Blue Na_{6}-$_{10}Al_6Si_6O_{24}S_{2-4}$
(natural XI c AD- XIX C AD; artificial 1826- today)

Azurite $2CuCO_3$* $Cu(OH)_2$
(antiquity – XIX C AD)

Indigo (antiquity)

Smalt K-Co-Al-Silicate
(XVI C AD – XIX C AD)

Prussian Blue $Fe_4[Fe(CN)_6]_3$*14-16 H_2O
(1704-today)

MAYA BLUE PIGMENT

- Pigment of extraordinary durability (unaffected by attack with acids HCl, HNO_3, alkalis, organic solvents, oxidants, reducing agents, moderate heat) and richness of color.

- Used since the Maya Classic Period –VII cent. A.D.

- “Rediscovered” by western researchers in 1931.

- Composition a mystery until 1960.

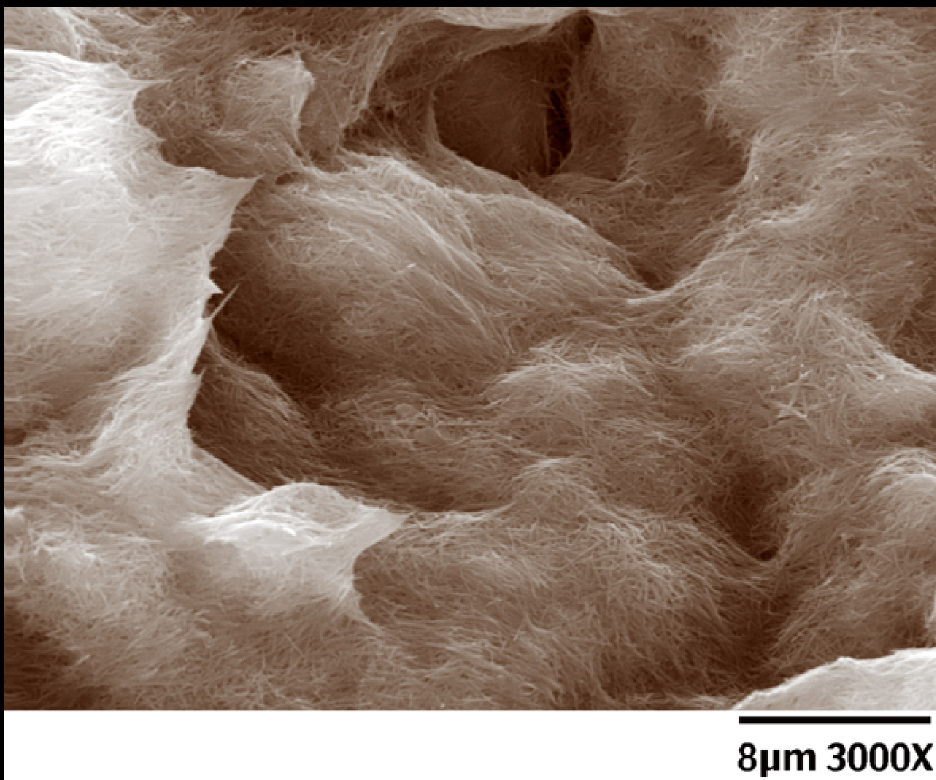
PALYGORSKITE

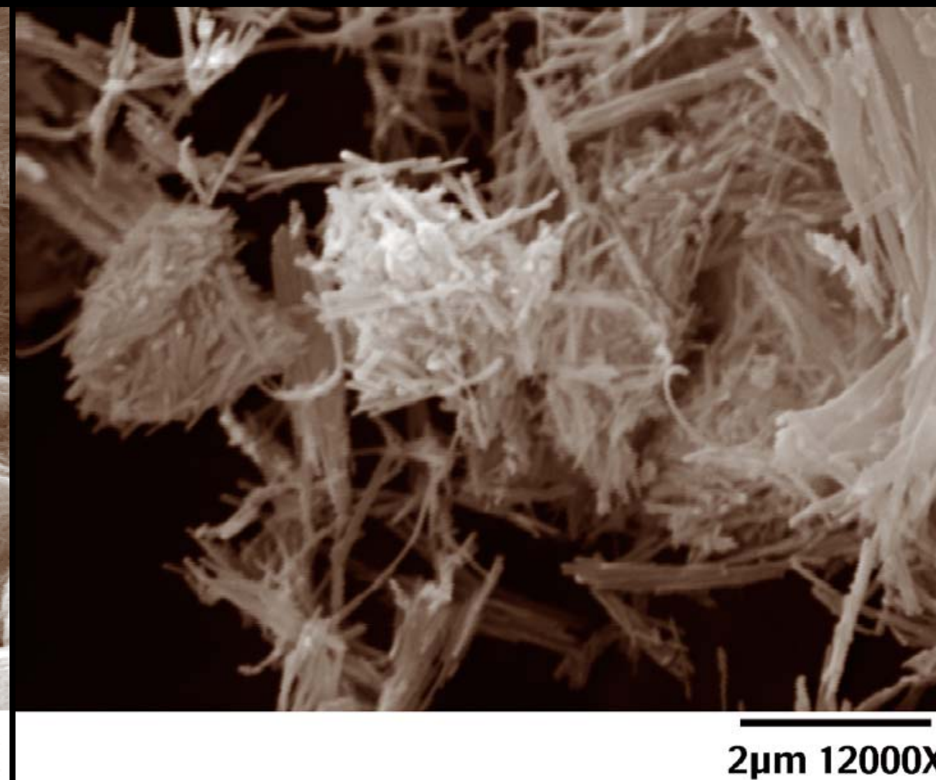
• Mg rich dioctahedral clay, with fibrous morphology

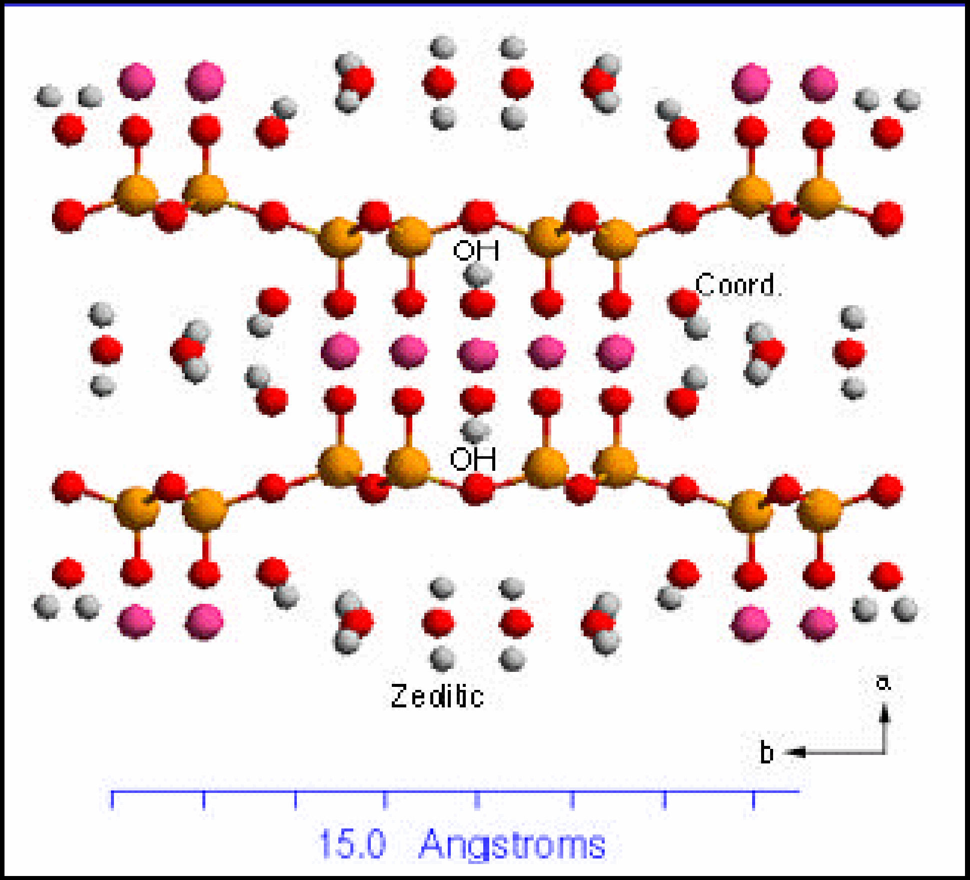
•[ideal composition $(Mg, Al)_4 (Si)_8 (O, OH, H_2O)_{24} \bullet nH_2O$]

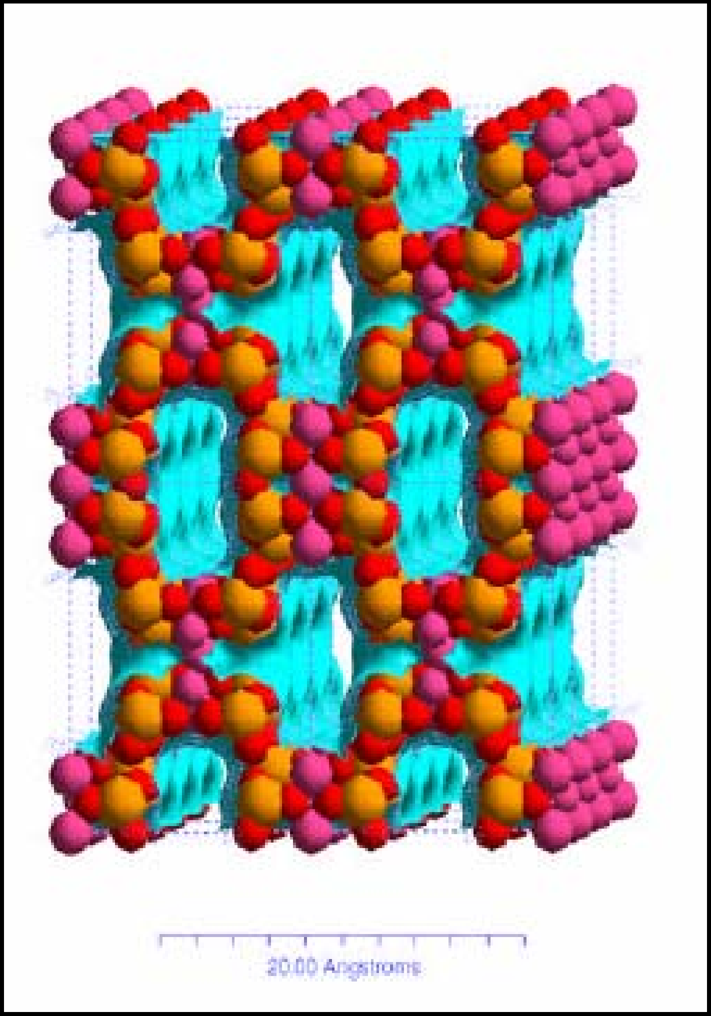
• It contains continual tetrahedral layers of SiO_4, with discontinuous octahedral layers of $(Mg, Al) O_6$.

• The apexes of the tetrahedra point alternatively upwards and downwards every two chains, causing the structure to be crossed by zeolitic-like channels along c.

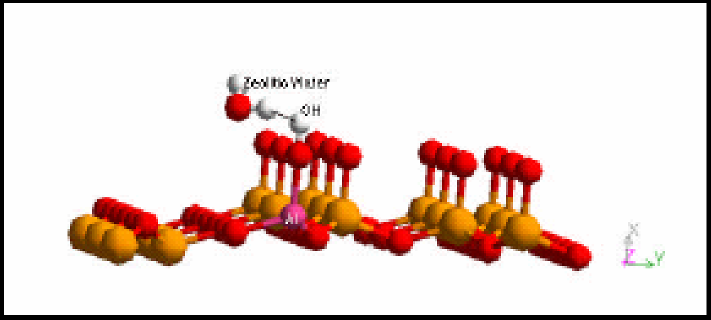

8µm 3000X


2µm 12000X





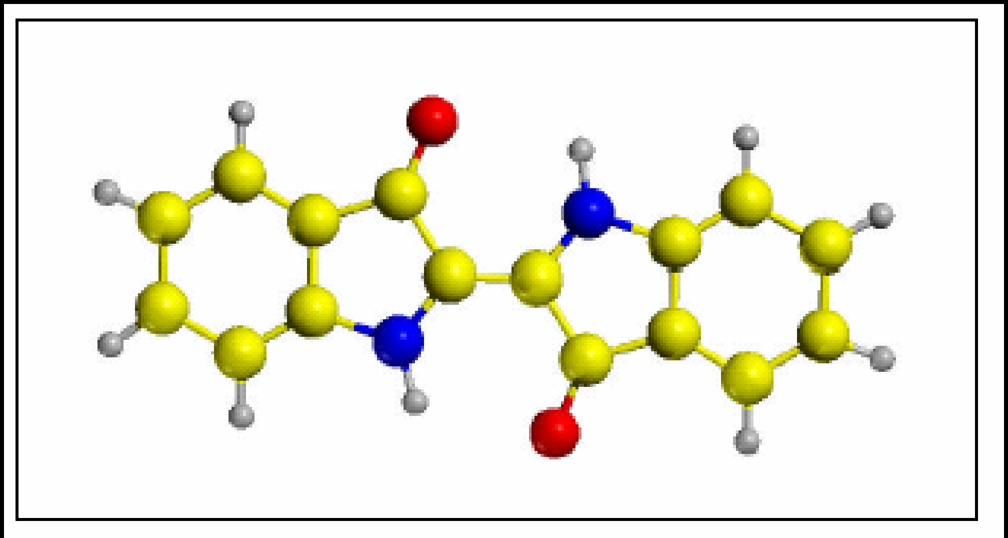
Channels: 7.3 Angstrom

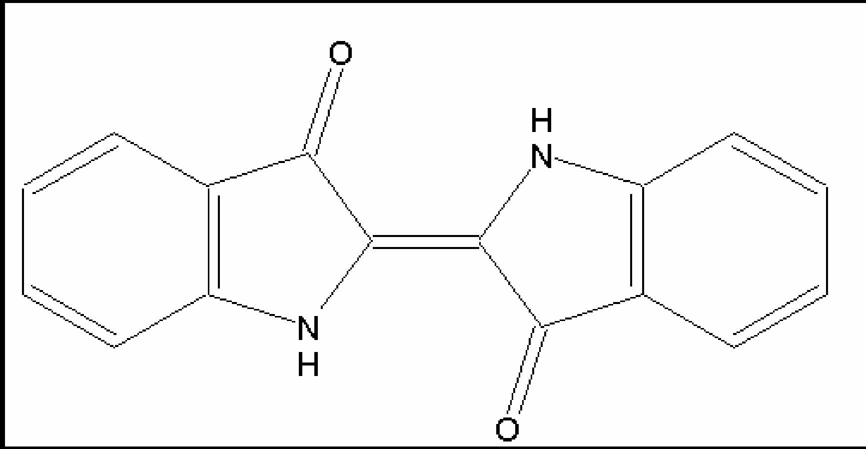


- 3 types of adsorbed water molecules:
- **physisorbed** water, on surface of every fiber
- **zeolitic water** (weakly bound, in channels and grooves)
- **structural water** (tightly bound, completing coordination of Al and Mg cations)

+ structural hydroxyl groups (Mg-OH and Al-OH)

IDIGO DYE





Indigo molecule: approx. 4.8 Angstrom wide

PREPARATION

in antiquity:

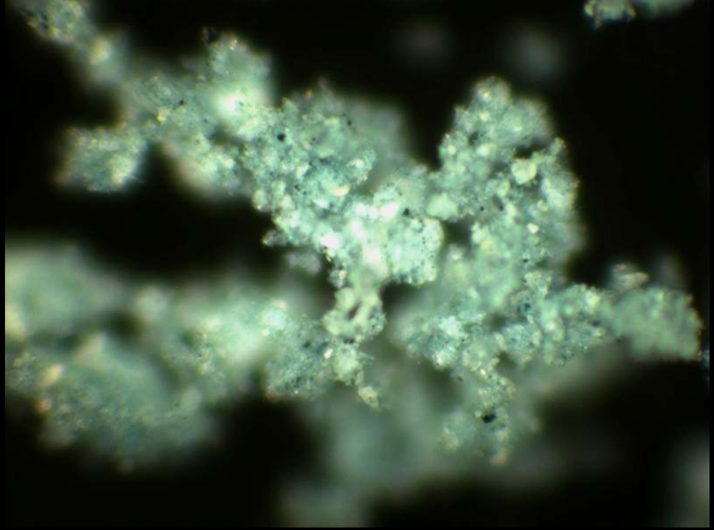
•Ferment Anil Plant

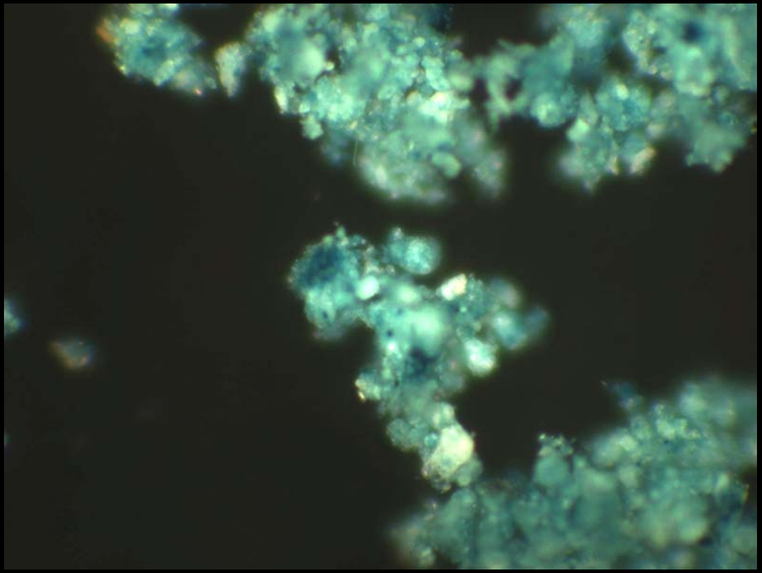
• Extract Indigo

• Convert to leuco-indigo

• Mix with Clay and **Heat** ~3 days

@120ºC

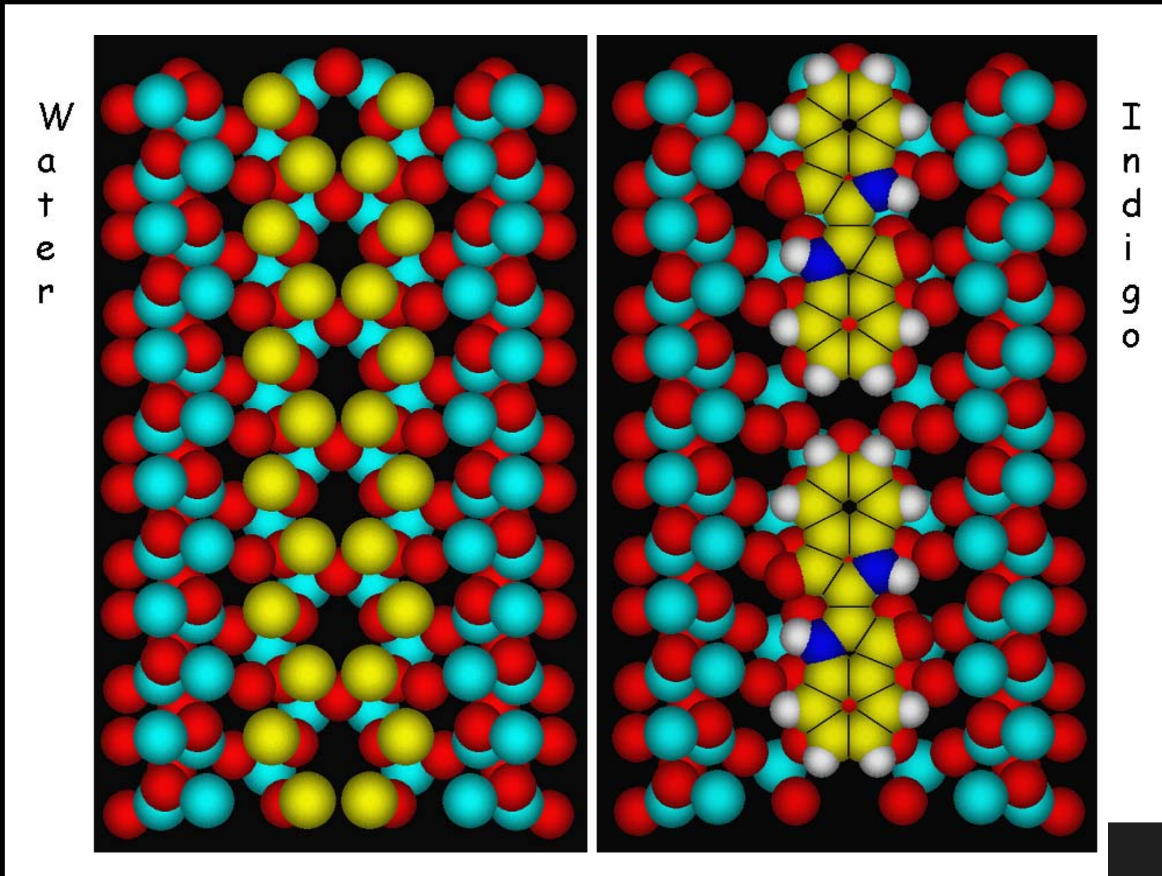


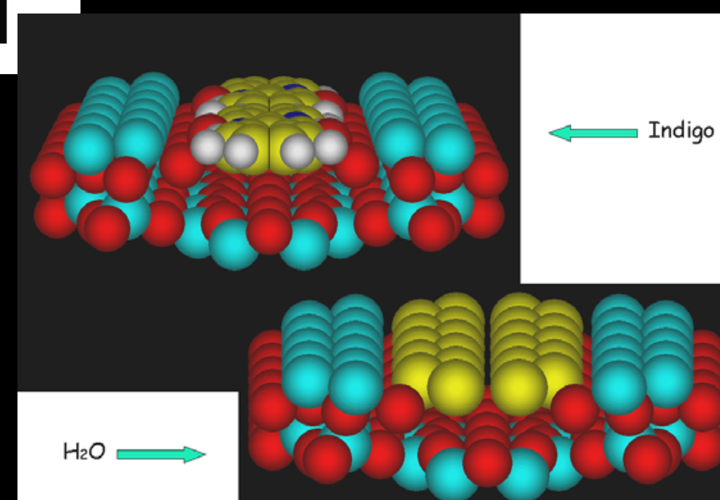


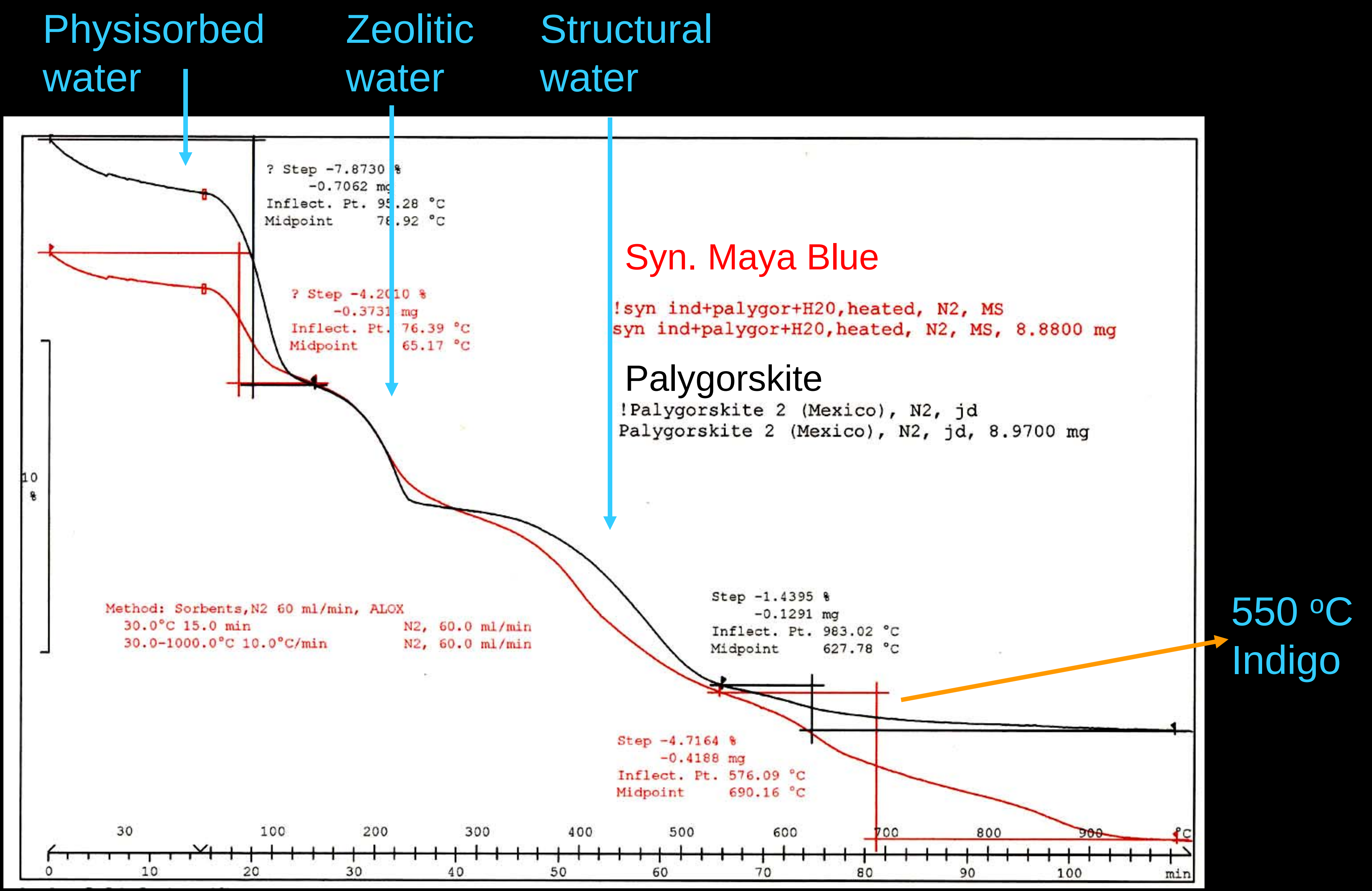
Alternative route (simpler):

• Indigo blended with clay, heated at T> 120ºC for several hours

W% of indigo in Maya Blue: 0.1-2%


Water
Indigo


Indigo
H2O



Indigo alone sublimates at 300°C and decomposes at 380°C

QUESTIONS:

PIGMENT STABILITY?

NATURE OF INTERACTION?

Adsorption of indigo:

exothermic (-37 kJ/mol) on dehydrated Palygorskite

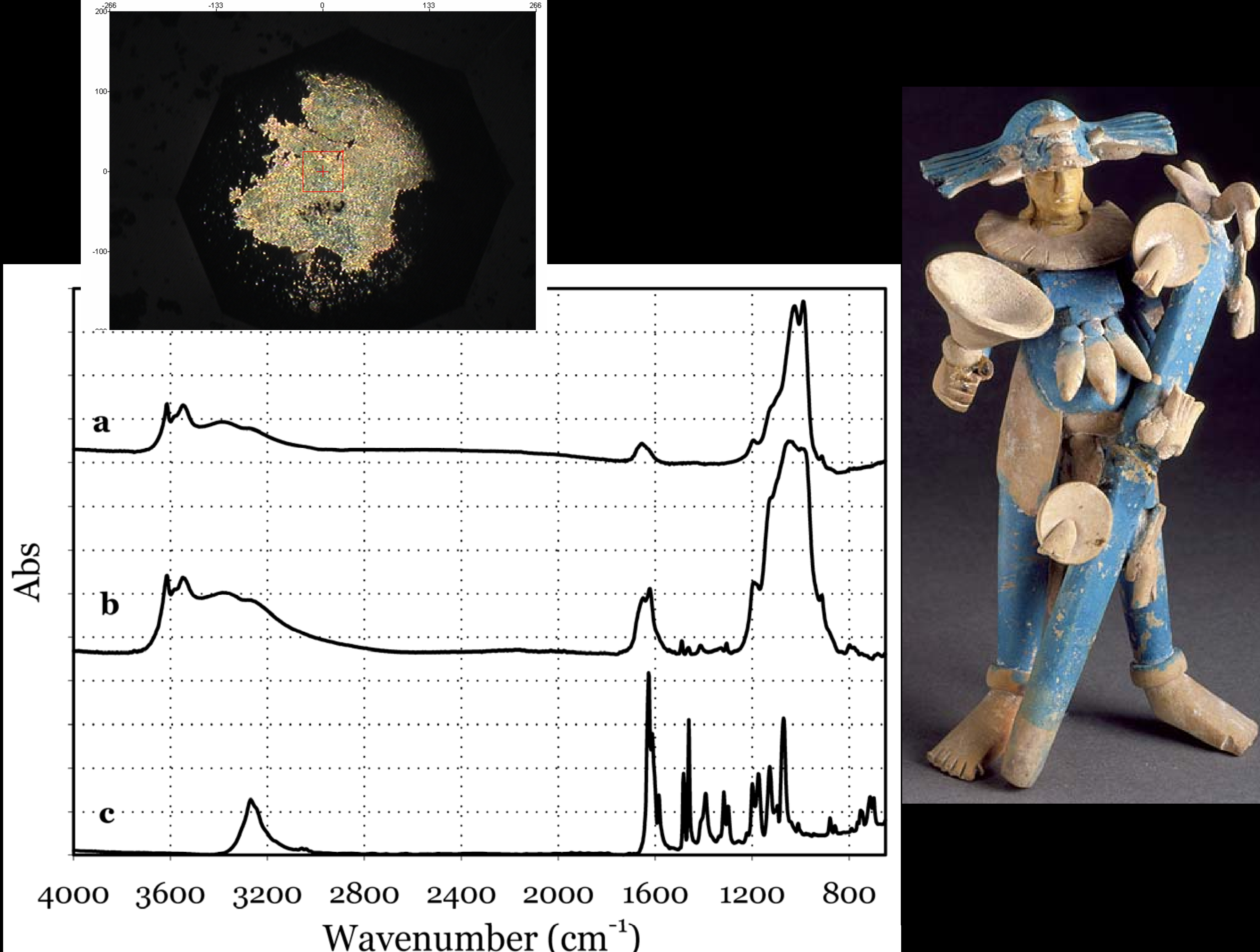
Endothermic (152 kJ/mol) on hydrated Palygorskite

MOLECULAR MODELING

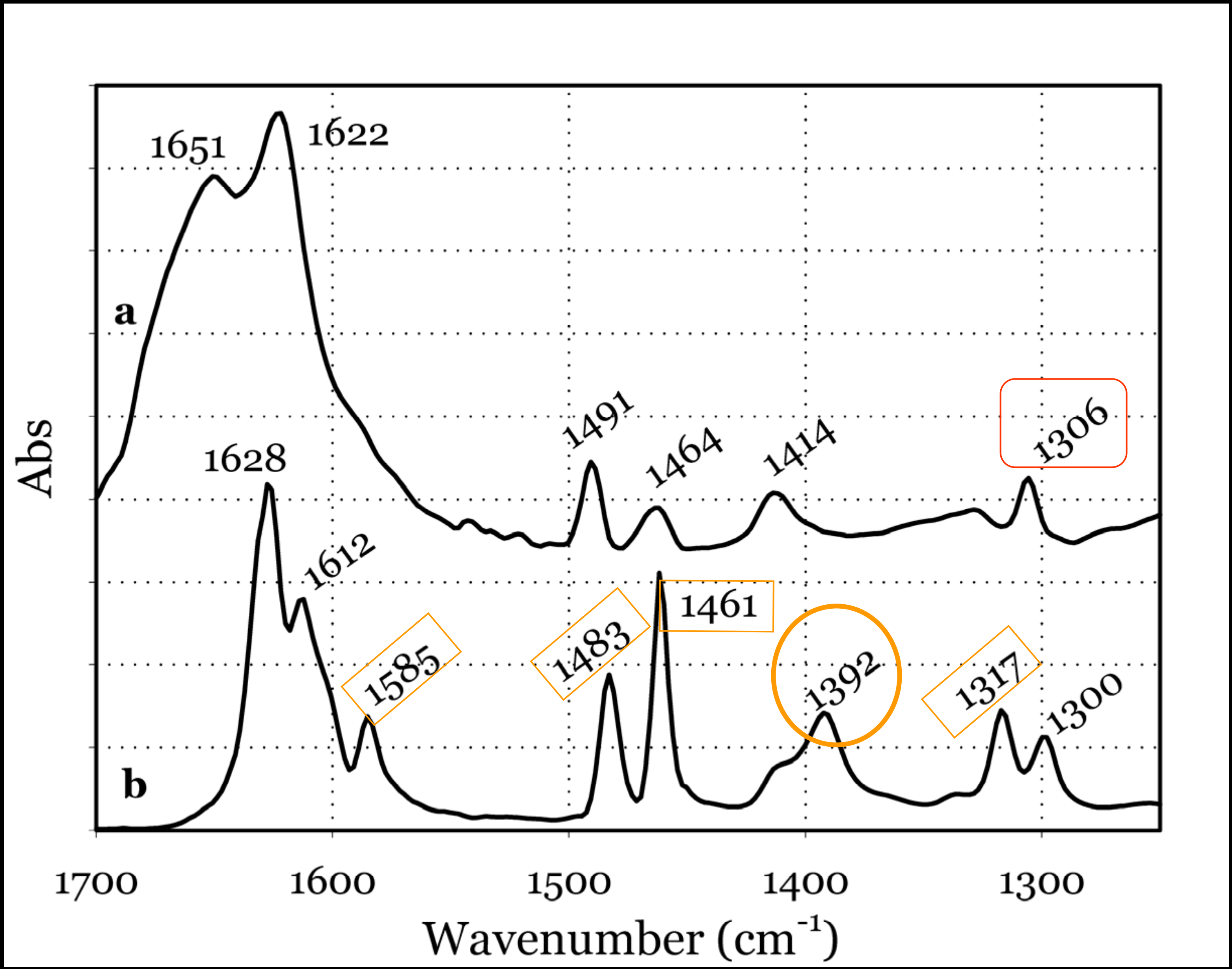
Short H-bonds between indigo carbonyl group and structural water. No such interaction observed for NH

Stability : Chelating effect ? 2 H bonds need to be broken simultaneously.

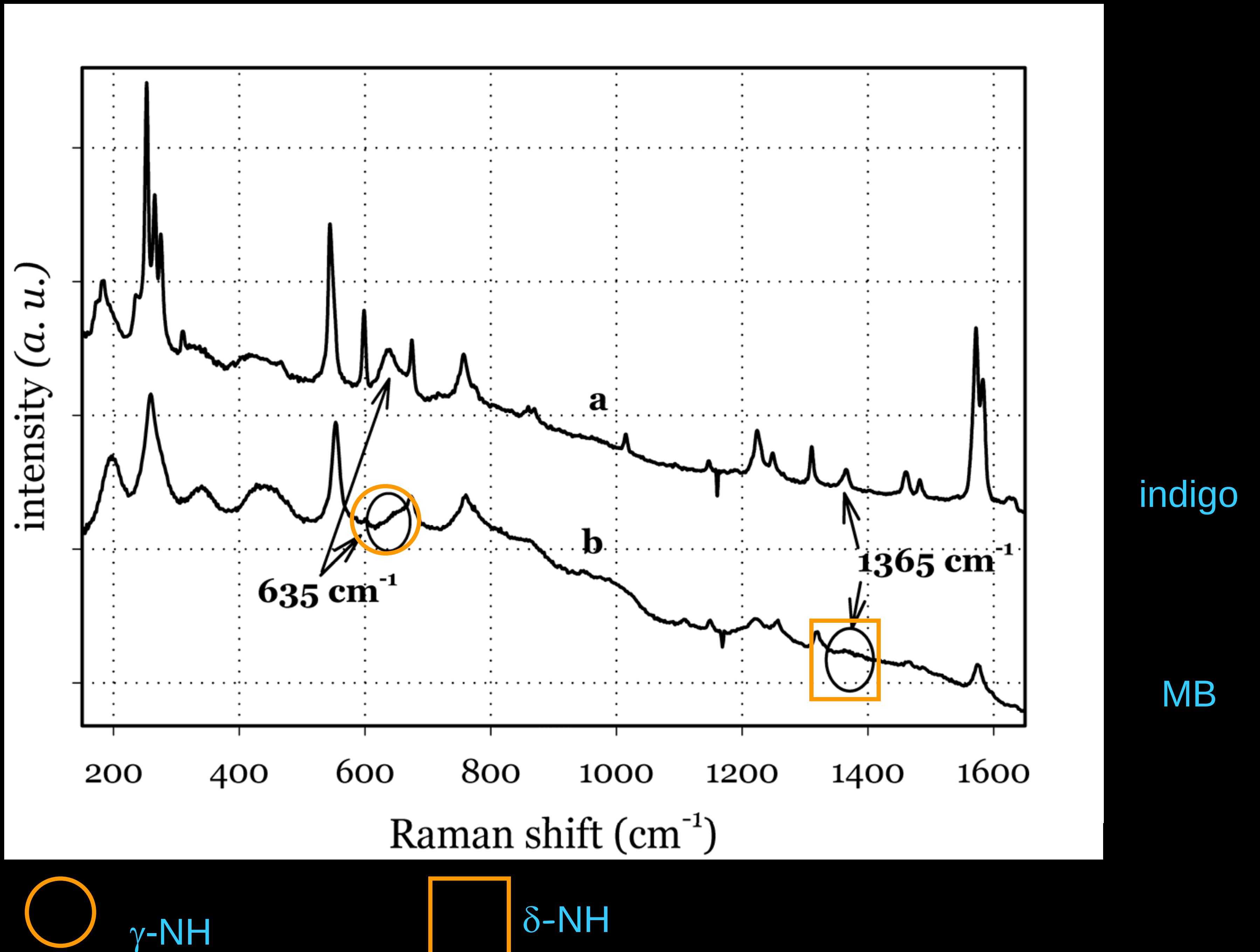
Steric effect of the groove?

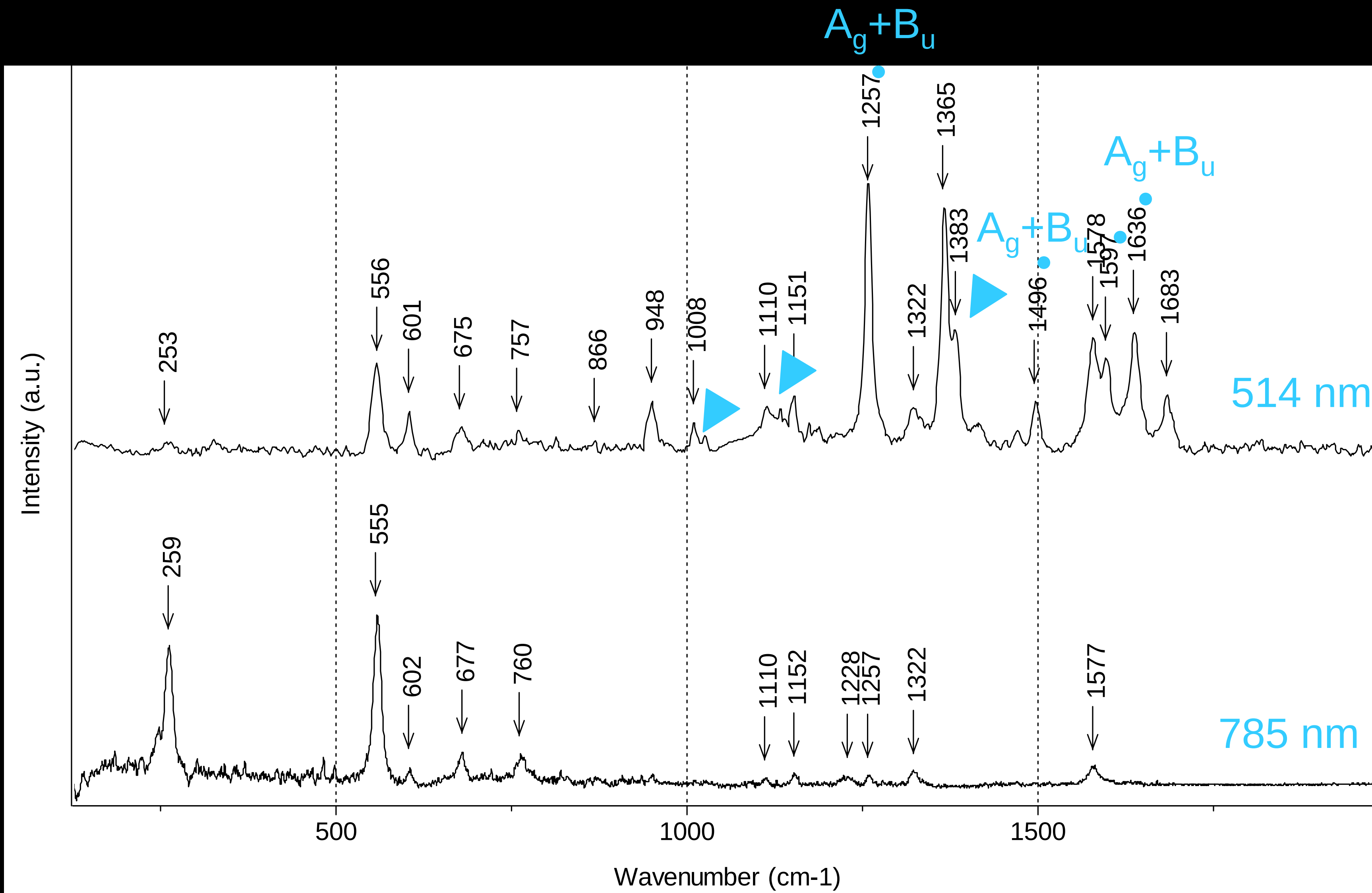


-266
-133
0
133
266
200
100
0
-100
Abs
a
b
c
4000
3600
3200
2800
2400
2000
1600
1200
800
Wavenumber (cm-1)

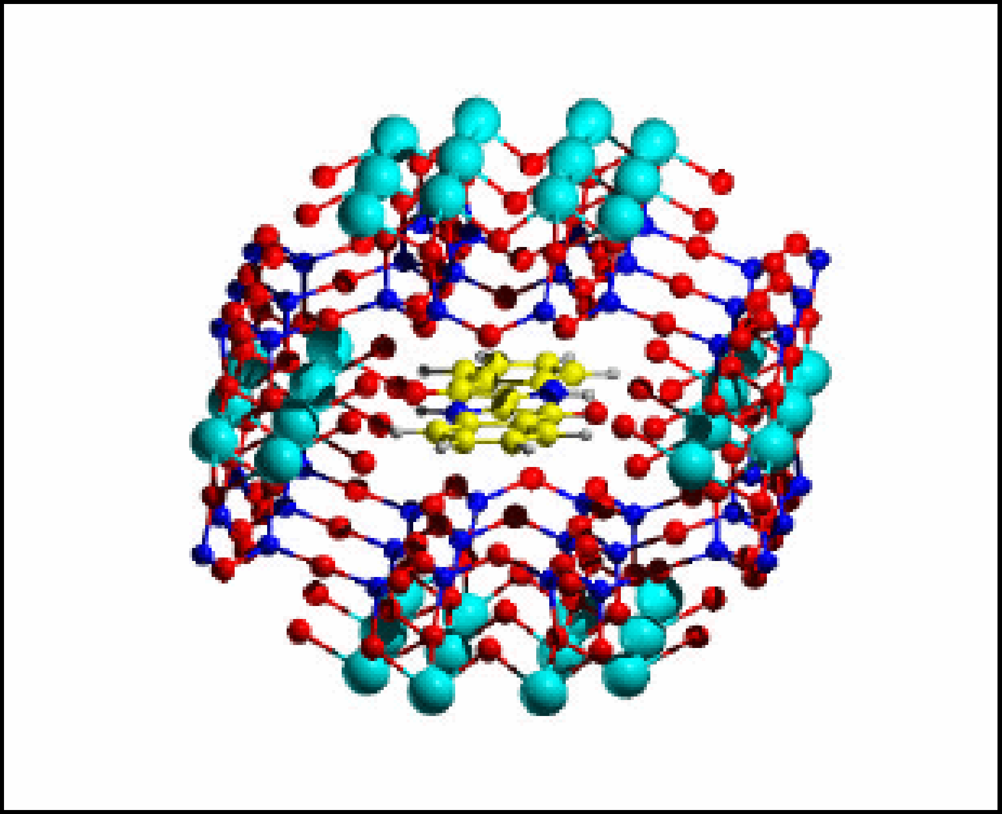


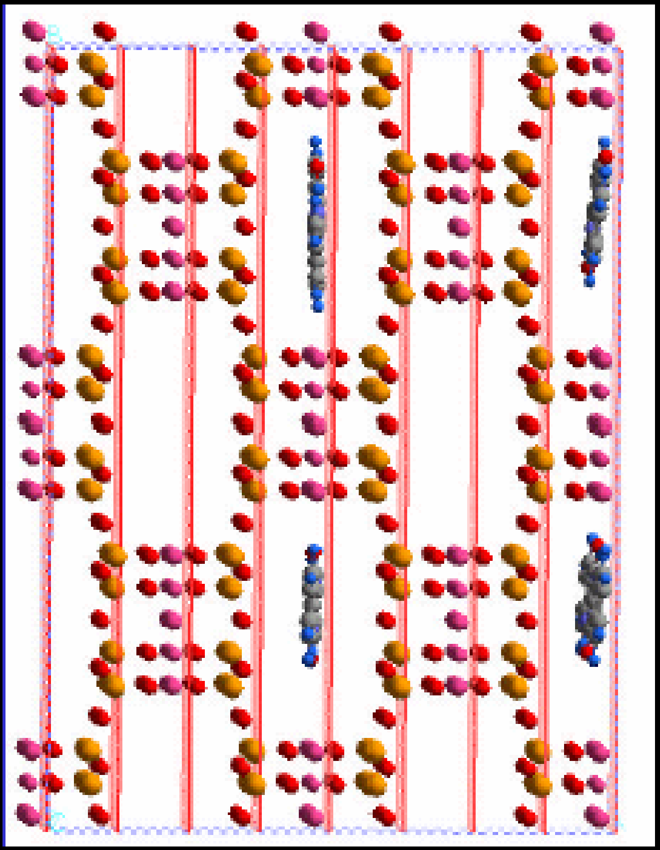
Benzene ring CC vibrations δ-NH IR forbidden A_g symmetry becomes IR active!


intensity (a. u.)
Raman shift (cm⁻¹)
200
400
600
800
1000
1200
1400
1600
a
b
635 cm⁻¹
1365 cm⁻¹
indigo
MB
γ-NH
δ-NH



▶ inactive Raman modes (B_u symmetry): 1017, 1128, 1383 cm^{-1}





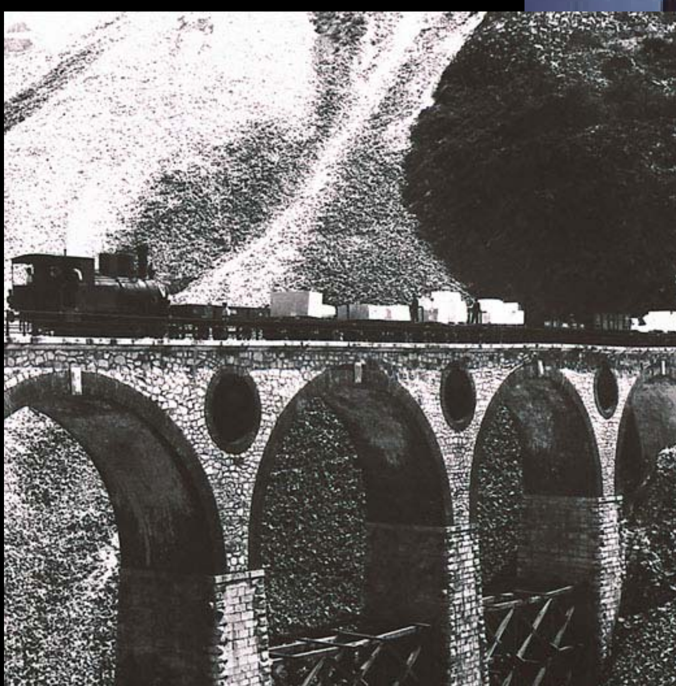
DEVELOPMENTS OF FINE-TUNED CONSERVATION STRATEGIES

MICHELANGELO’S DAVID

Commissioned by the Opera del Duomo of Florence in 1501

Michelangelo started work on his David at 26

Sculpted on a marble block partially worked by Agostino di Duccio in the XIV century



- September 8, 1504 positioned in Piazza della Signoria
- The image of David the victor became the emblem of Republican victory in Florence
- 1873 during celebration of 4 centuries form the birth of Michelangelo, the statue is transferred to the Accademia di Belle Arti, for preservation reasons.

“WHOEVER CONTEMPLATES IT HAS SEEN ALL THE SCULPTURE HE NEEDS TO SEE” (G.VASARI)

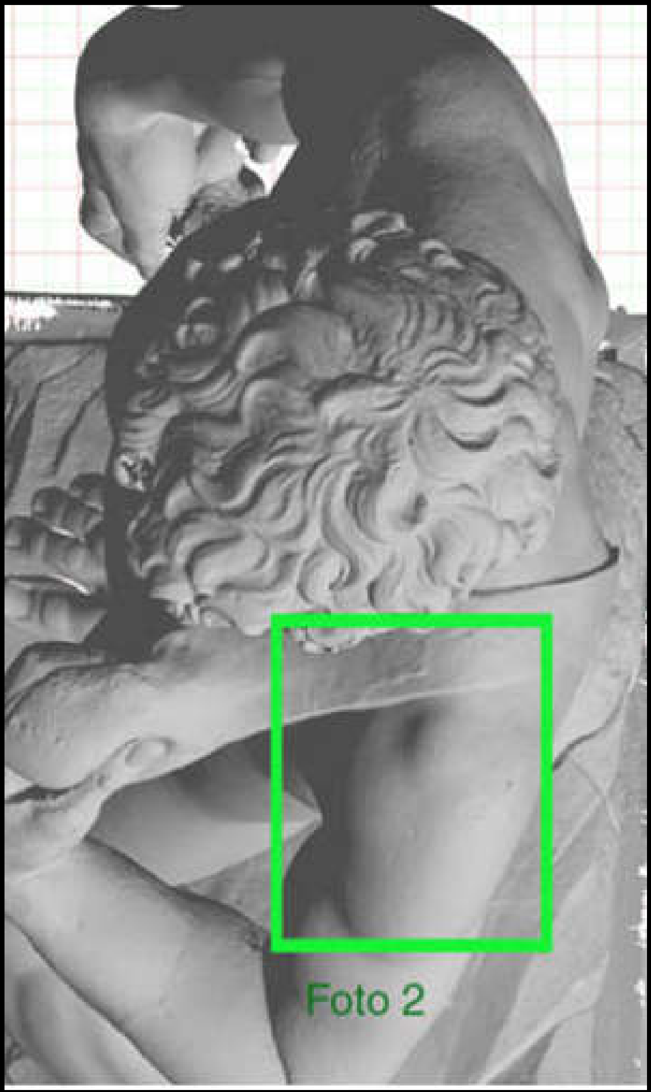
- •1512: base struck by lightning
- •1527: left arm broken into pieces during popular upheaval against the Medicis in Florence
- •1808-1815: encaustic treatment, to protect from environmental weathering
- •1815: Stefano Ricci riconstruct the middle finger of the right hand
- •1843: Aristodemo Costoli cleans it with HCl solution and reconstruct the little toe of the right foot (operation repeated in 1851)
- •1847: Clemente Papi takes a mould of the sculpture
- •1991: the vandal Pietro Cannata destroys with a hammer the tip of the second toe of the left foot (reintegrated by the OPD)

16 September 2002: Conservation work begins (the statue has not been touched since 1873)

Project totally financed by the not-for-profit Dutch foundation, Ars Longa Stichting (€ 165.000,00)

The Friends of Florence Foundation covered the costs of the diagnostic and monitoring programs

Project conducted in close cooperation with the Opificio delle Pietre Dure, along with the Consiglio Nazionale delle Ricerche, the Politecnico di Milano and the Universities of Catania, Lecce and Perugia.



3D digital rendering of statue (project Digital Michelangelo, Prof. M. Levoy, Stanford University- 1999 with laser scanner Cyberware)

Diagnostic program and monitoring

AFTER CONSERVATION

Microclimate (at heavy visitors' flux – 1 year)

•RH (at three hights)

•T (environmental and in contact)

•Particle deposition rate, size and morphology (fibers from public)

•Quali-quantitative analysis of gaseous pollutants of significance for conservation of marble (SO_x and NO_x)

BEFORE, UPON COMPLETION AND AFTER CONSERVATION

•UV photography and FLIM imaging

•Representative areas chosen (10 areas, different heights, different inclinations)

•Colorimetric measurements

•Measurement of superficial morphology (laser profilometry)

•Thermography

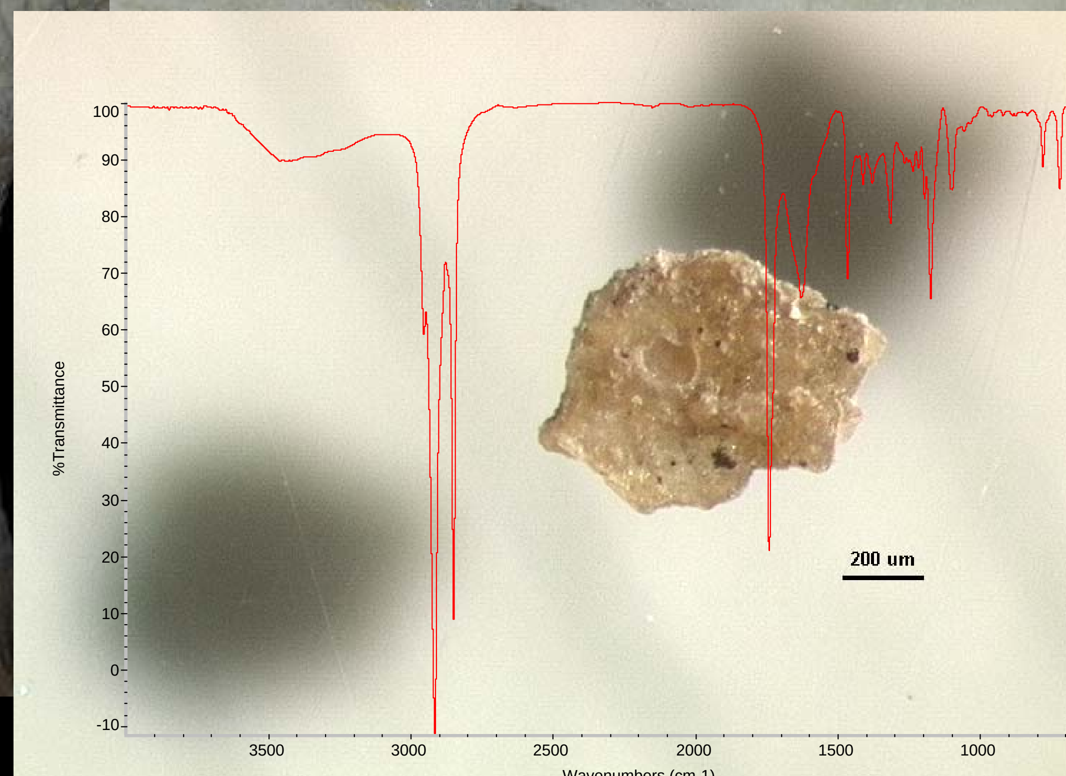
•Particle chemical composition

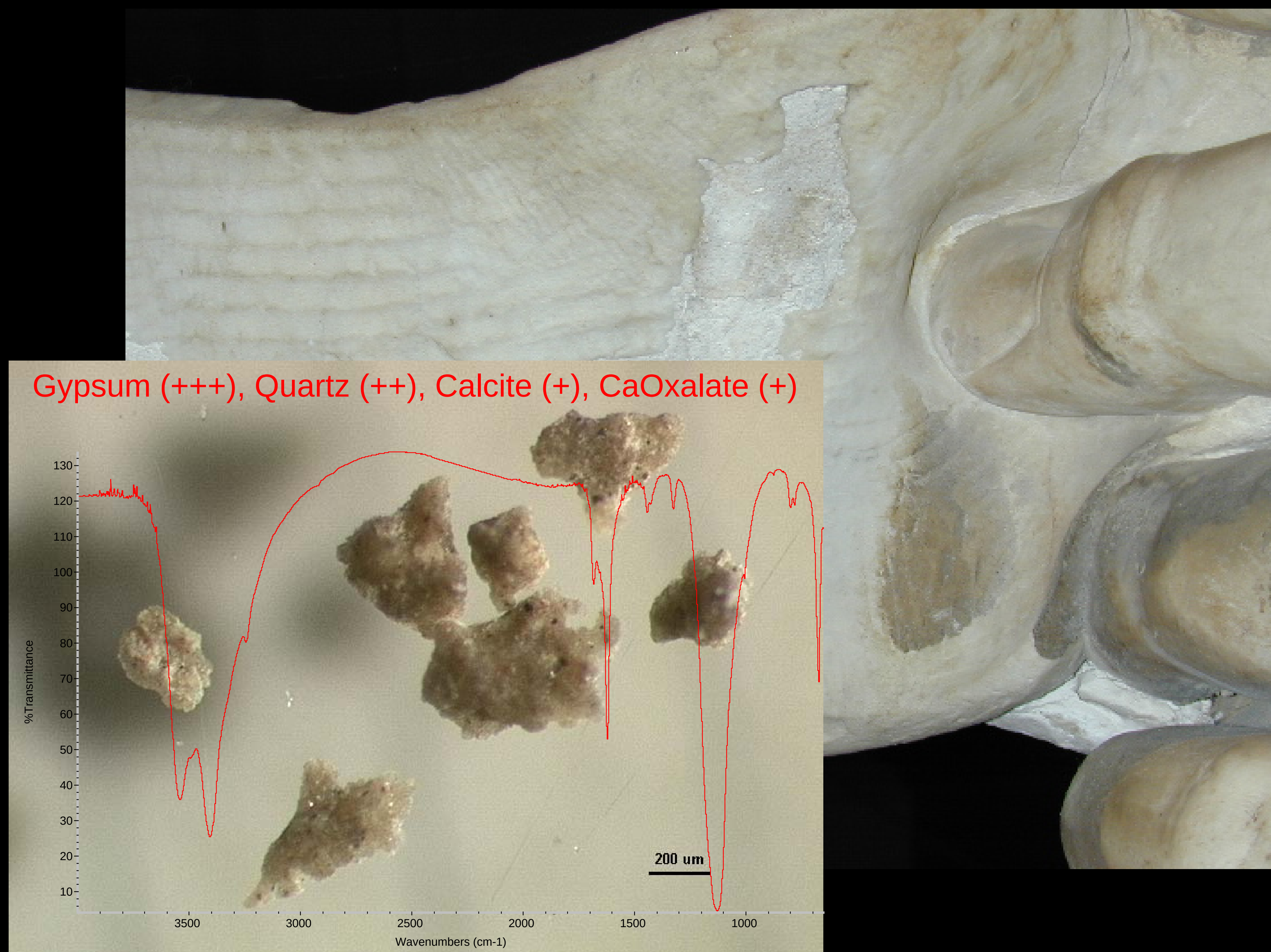
XRF mapping of S

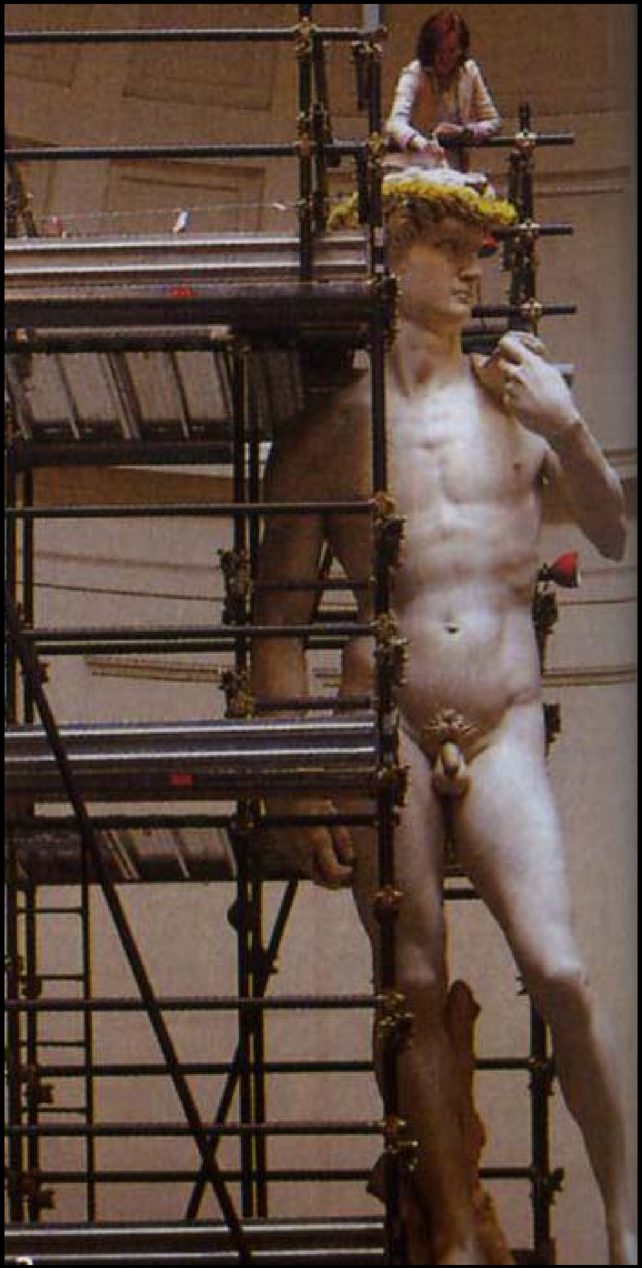
•Fiber-optic (1000-4000 cm^{-1}) portable FTIR analysis of superficial deposits and contaminants

•Mineralogical and petrographical analysis of the marble and isotopic provenancing (C, O), porosimetry

Micro-sampling

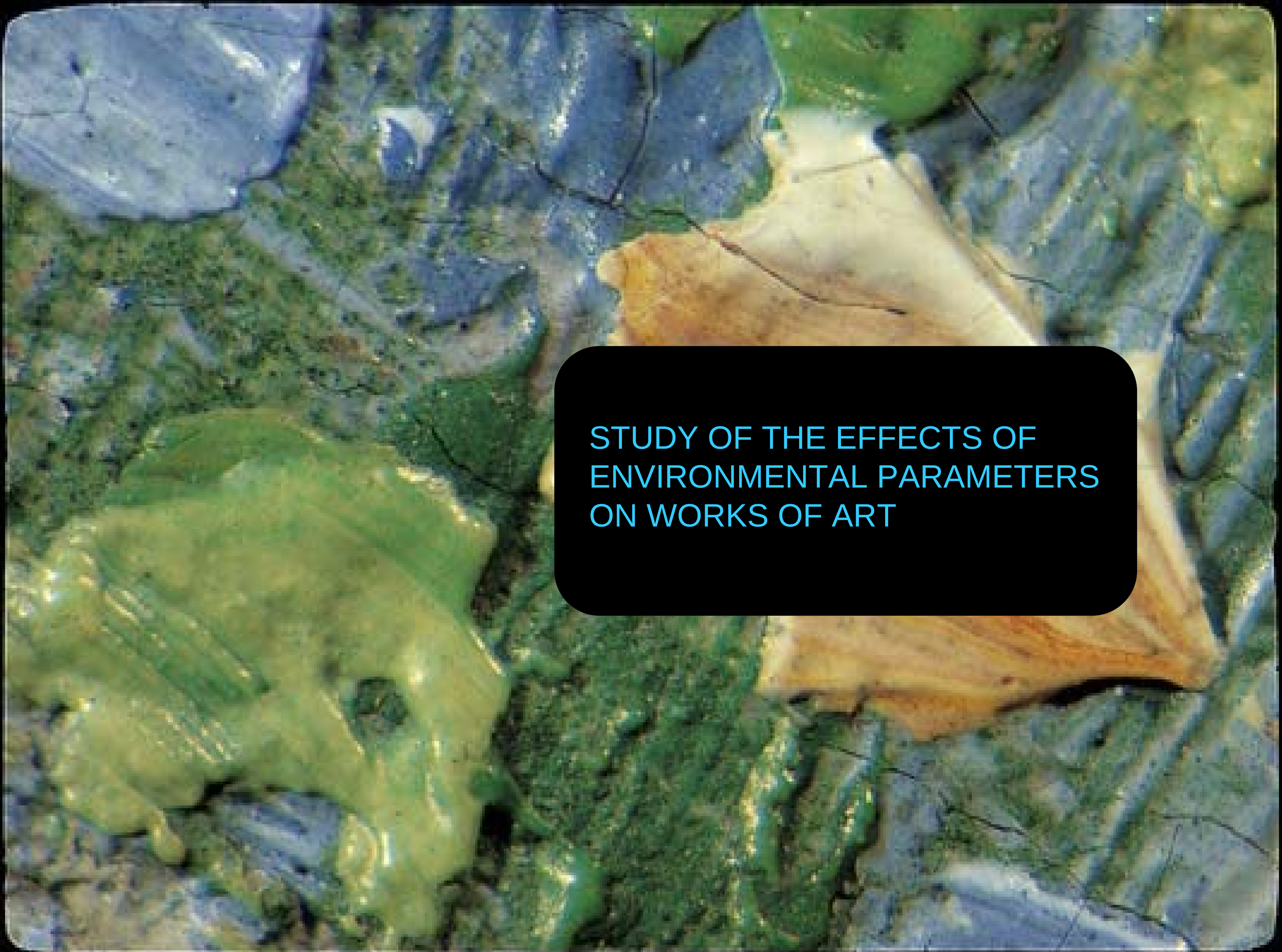

%Transmittance
100
90
80
70
60
50
40
30
20
10
0
-10
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
200 um


Gypsum (+++), Quartz (++), Calcite (+), CaOxalate (+)
%Transmittance
130
120
110
100
90
80
70
60
50
40
30
20
10
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
200 um



Development of a conservation strategy:

- Brushing with soft brushes
- Application of poultices of attapulgite and distilled water
- Localized cleaning with solvents and cotton swabs



STUDY OF THE EFFECTS OF ENVIRONMENTAL PARAMETERS ON WORKS OF ART

Materials used for display, packing and storage ⇨ aesthetic concerns/ protection of artefacts from the outside environment,

Acetic acid, methanol, formic acid, formaldehyde and methyl acetate (wood)

S-containing gases (dyes, wool, leather)

Acetic acid (cellulose acetate fibres)

HCl (PVCs)

Solvents, additives and plasticizers (paints, glues, plastics)

testing for potential atmospheric corrosiveness should be performed prior to use in proximity of works of art.

Oddy test

•Metal coupons (generally lead, copper and silver) are suspended in an air tight
•reaction vessel where the material to be tested is also present + measured volume of distilled water (100% RH).

•The vessel is placed in an oven at 60ºC for 28 days

•Metal coupons are checked for evidence of corrosion and declared suitable, unsuitable or recommended for temporary usage only.

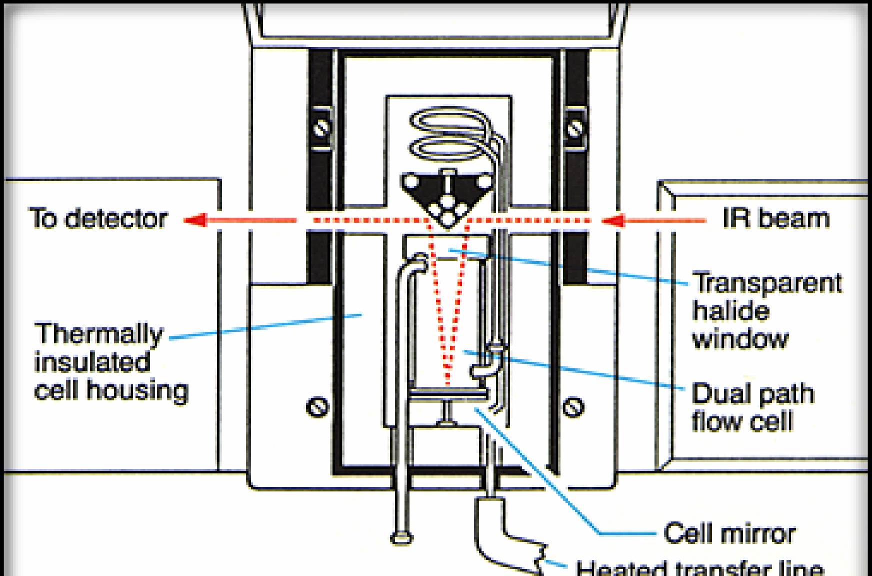
TG/FTIR method:

•5 to 15 mg of sample

•He flux of 60 ml/min.

•FTIR sample chamber, with heated gas cell (set to 230 ^{o}C to prevent condensation of the gases) and coupled to TGA via heated transfer line (220 ^{o}C).

•Temperature ramping profile: 10^{o}C/min up to 120^{o}C (equilibrating at 120^{o}C for 10 minutes); then 10^{o}C/min up to 250^{o}C



TGA interface components

Oddy Test results: Wood MDF

NOT recommended for use in cases with metals

Recommended for other artifacts

COPPER - Covered area stayed light in color with slight rainbowing. Uncovered area darkened slightly. Darkening on one edge of sample.

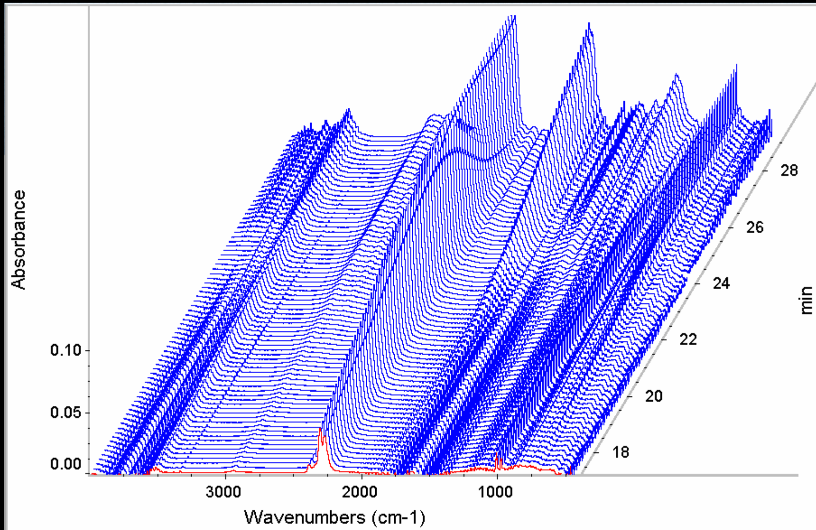
-
NO REACTION

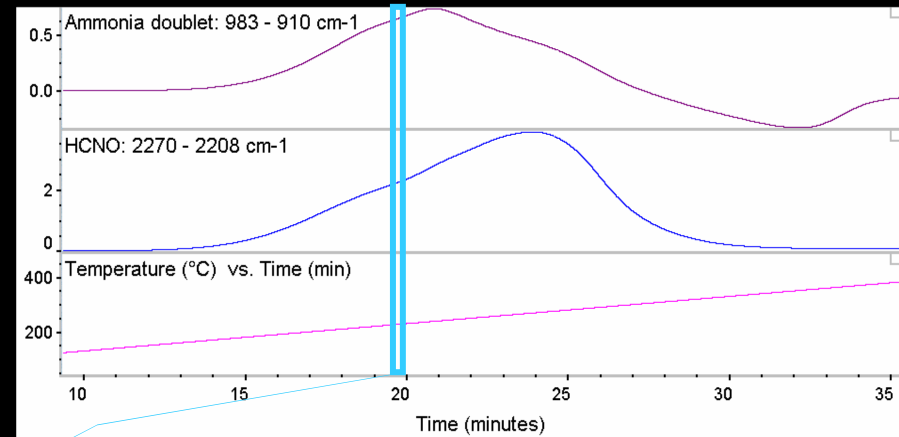
SILVER - Slight darkening of area under sample both from end grain and flat surface.

+
SLIGHTLY CORROSIVE

LEAD - Light layer of white corrosion on test side overall., starting to creep along side edges to back .

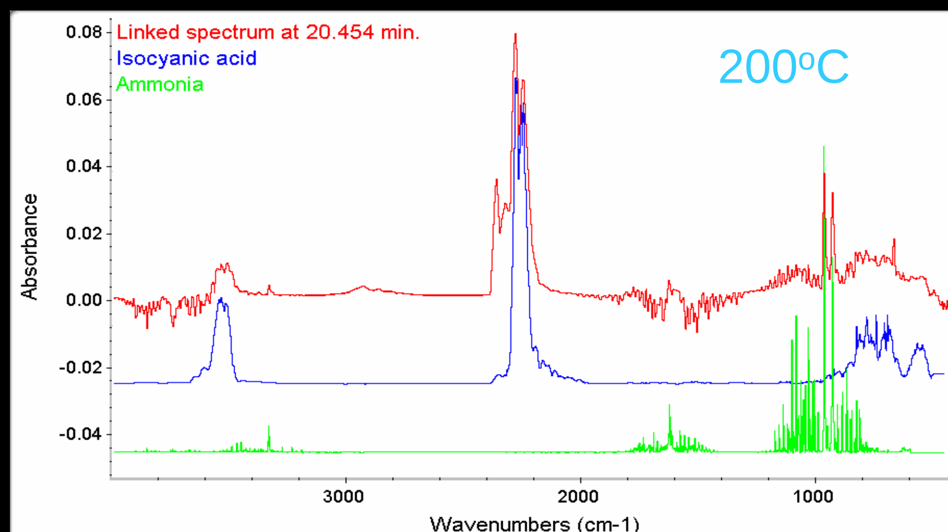
+
SLIGHTLY CORROSIVE





Waterfall plot of evolved gases during central portion of T ramp

Profiles of Abs of selected marker bands vs time for Ammonia and Isocyanic acid



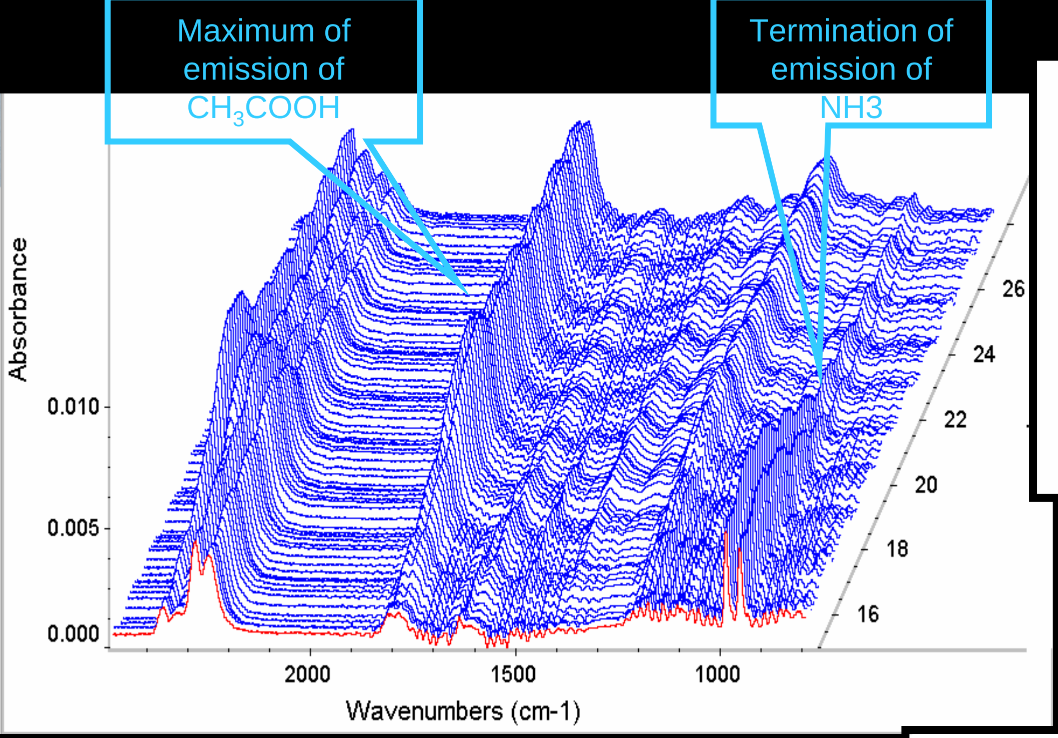
TG-FTIR results: the wood sample outgases NH_3 and HNCO; at the end of the temperature ramp no noticeable change is observed on the sample.

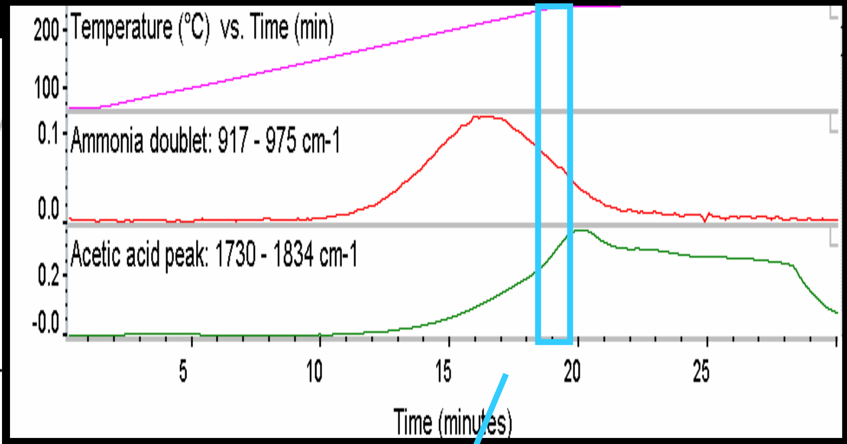
Oddy Test results: velvet

NOT recommended for use in cases with metals

Recommended for other artifacts

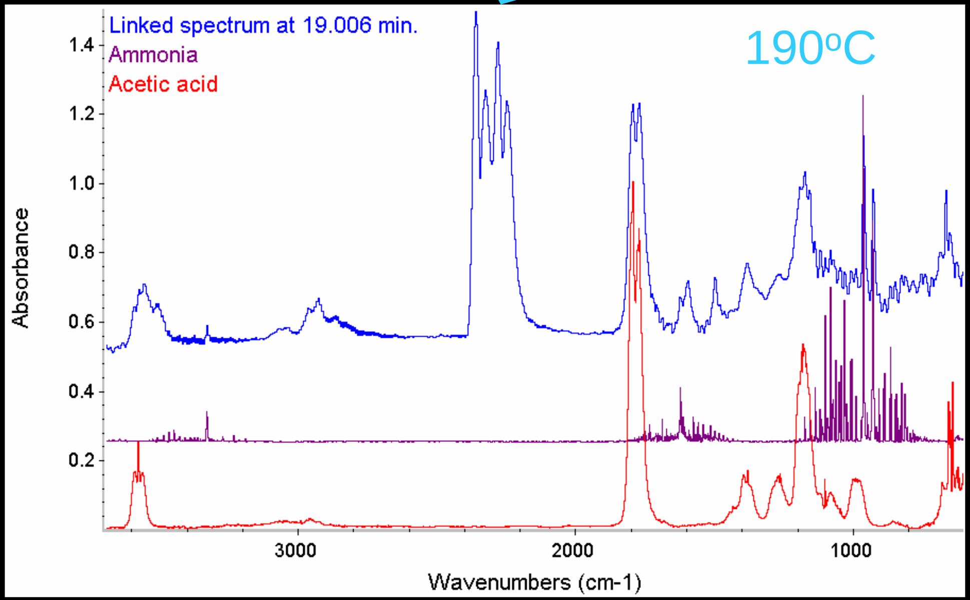
COPPER - darkened around edges; dark pink striations	+ SLIGHTLY CORROSIVE
SILVER - slight haze at edges	+ SLIGHTLY CORROSIVE
LEAD - no noticeable change	- NO REACTION



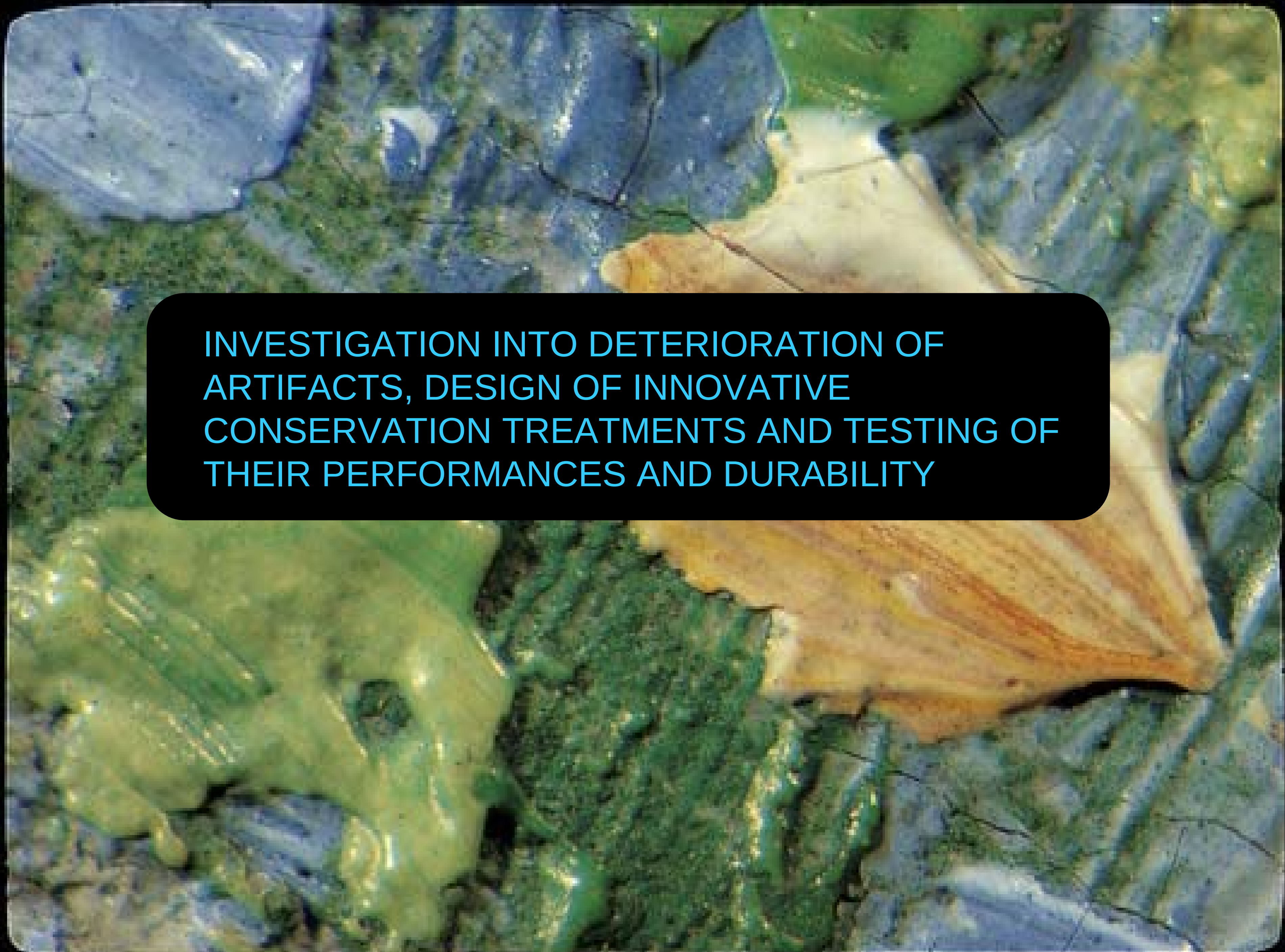


Profiles of Abs of selected marker bands vs time for Ammonia and Acetic acid.

Waterfall plot of evolved gases during central portion of Tramp

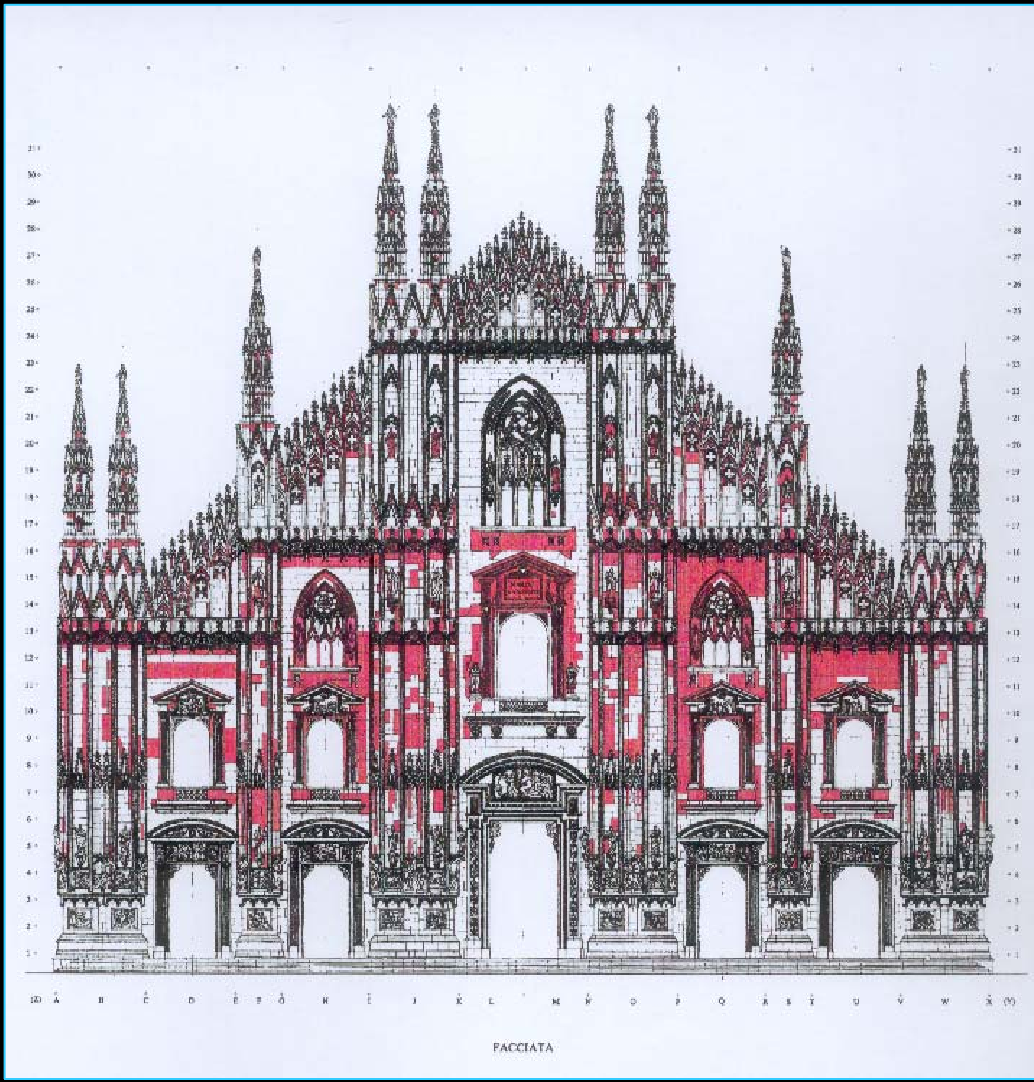


TG-FTIR results: the velvet sample outgases NH_3 and CH_3COOH


INVESTIGATION INTO DETERIORATION OF ARTIFACTS, DESIGN OF INNOVATIVE CONSERVATION TREATMENTS AND TESTING OF THEIR PERFORMANCES AND DURABILITY

CONDITION SURVEY

Mapping of various forms of weathering and alteration



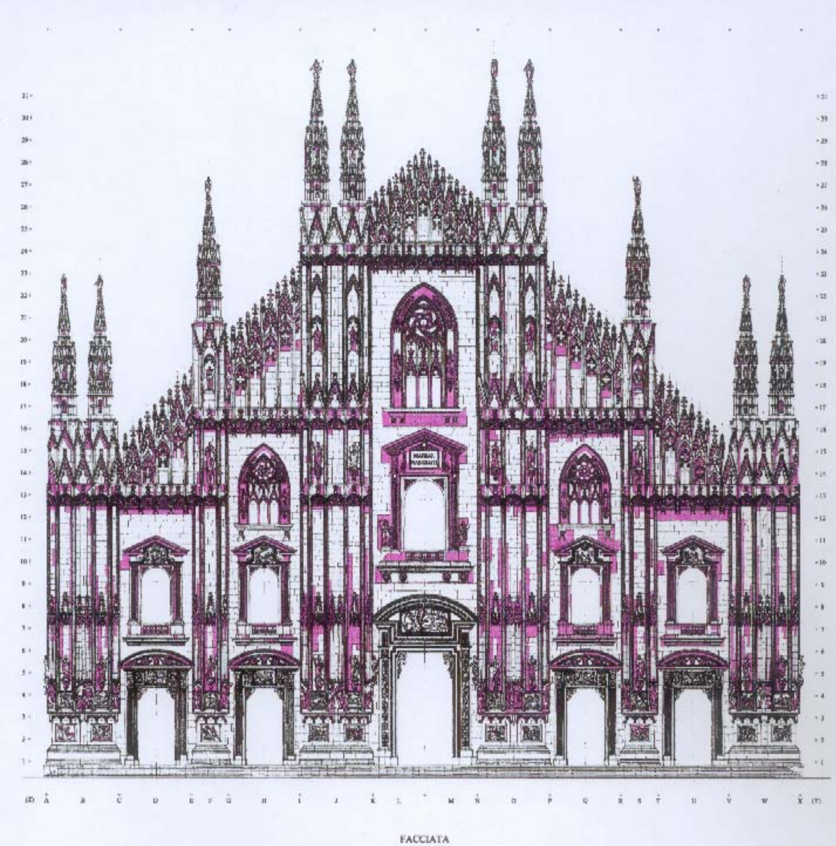
SELECTIVE SAMPLING

LABORATORY ANALYSIS

CHEMICAL AND MORPHOLOGICAL CHARACERIZATION OF FORMS OF DECAY

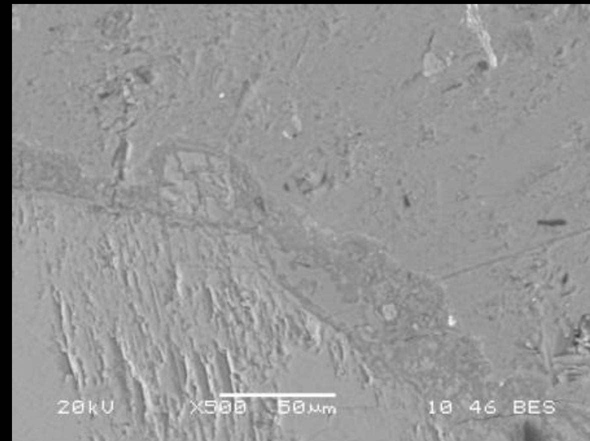
GEOREFERENTIATION OF DATA

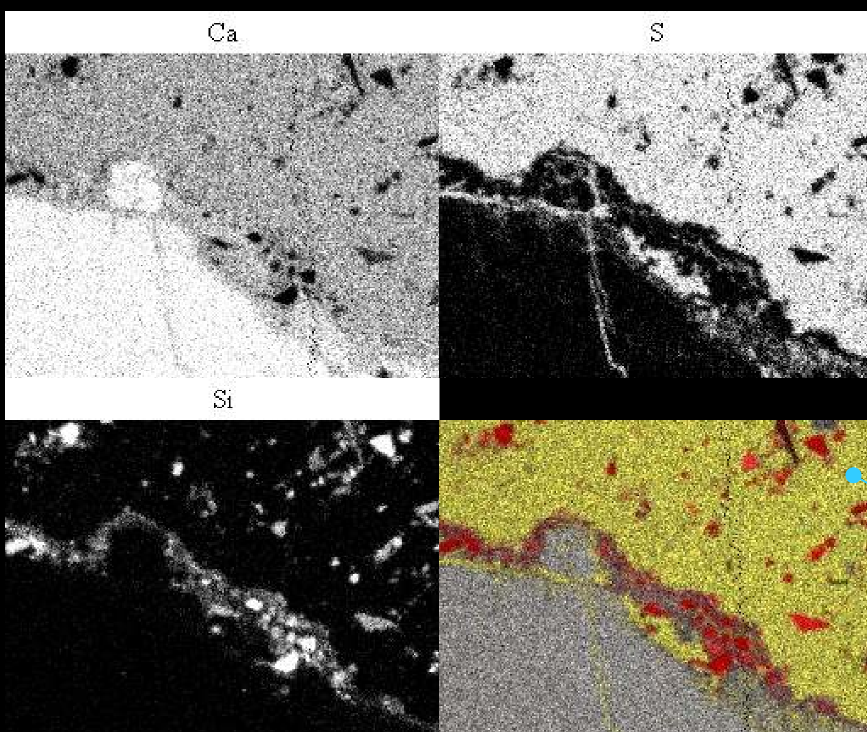
EVALUATION OF DIFFUSION OF PHENOMENA


FACCIATA


500 um

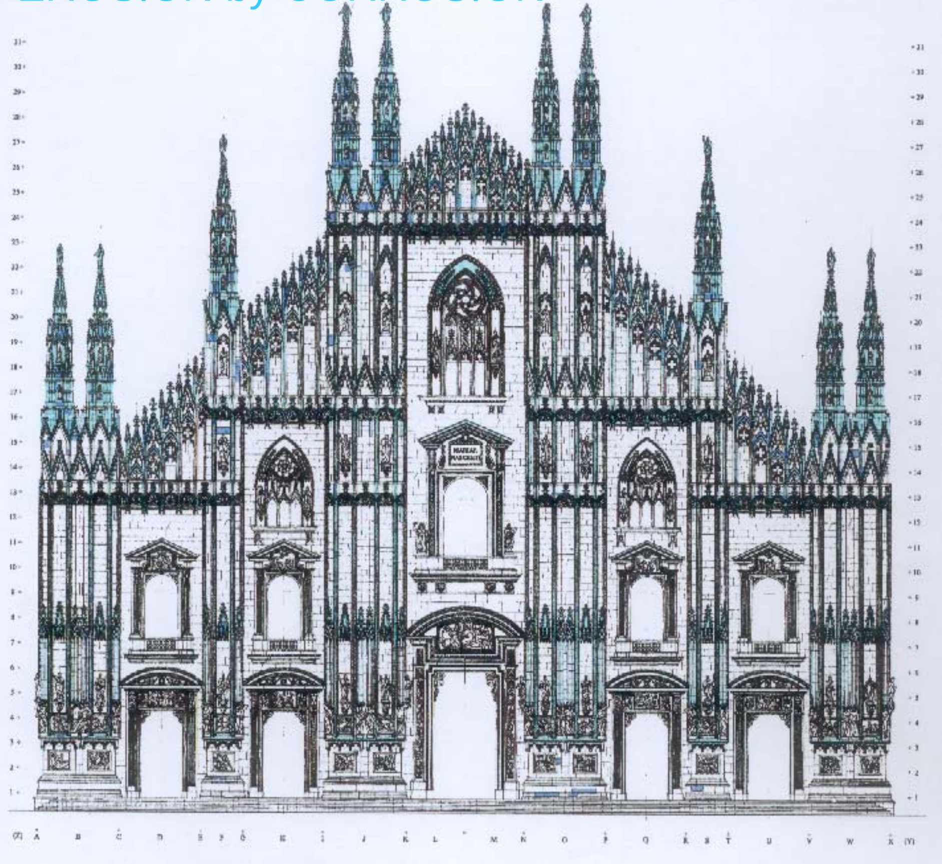
1 mm

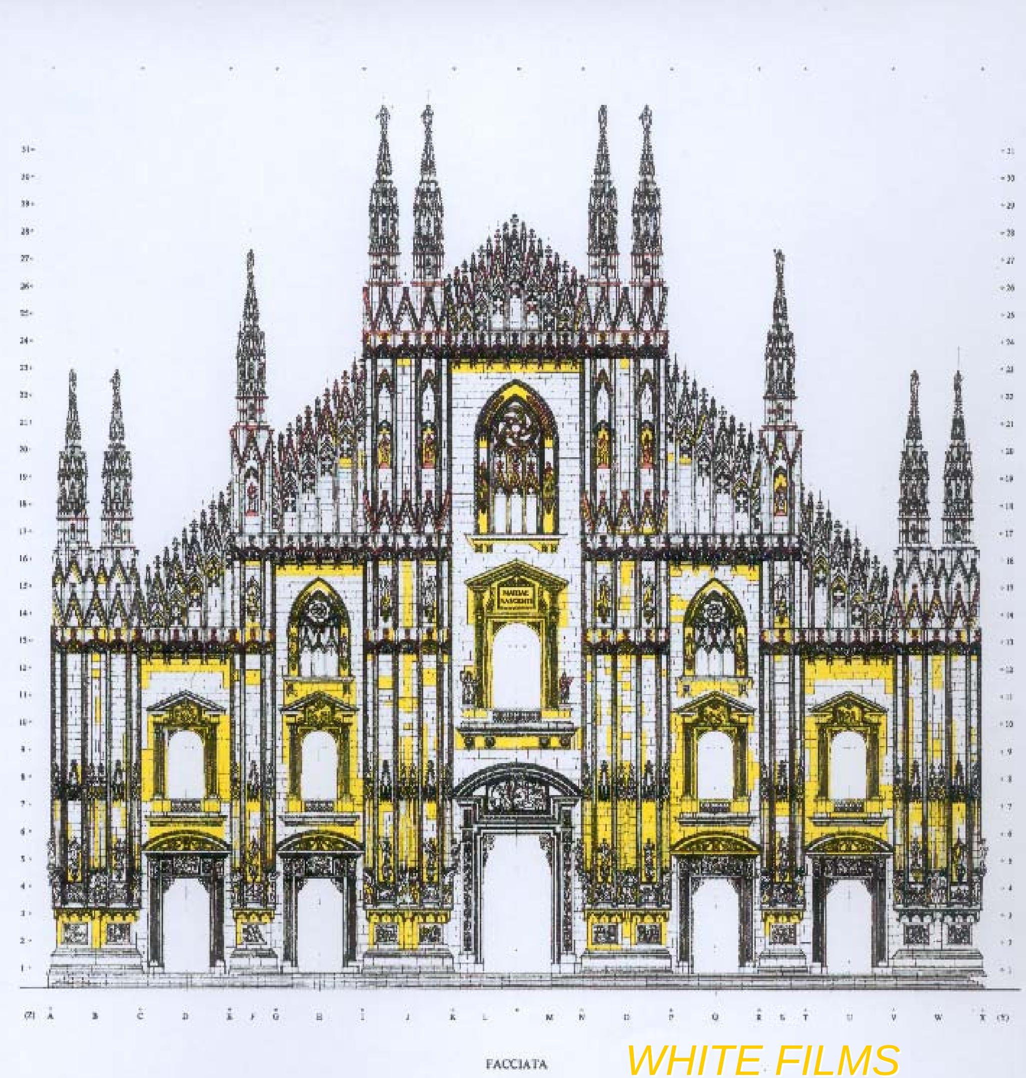




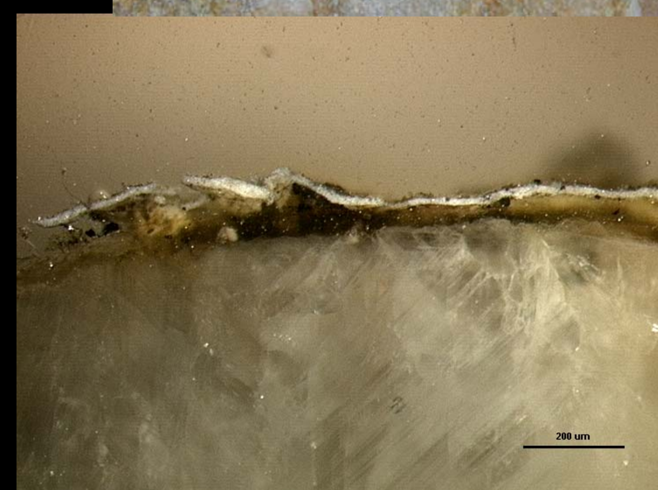
False colors superposition of EDX maps: Si (red), Ca (white), S (yellow).

EROSION by CORROSION

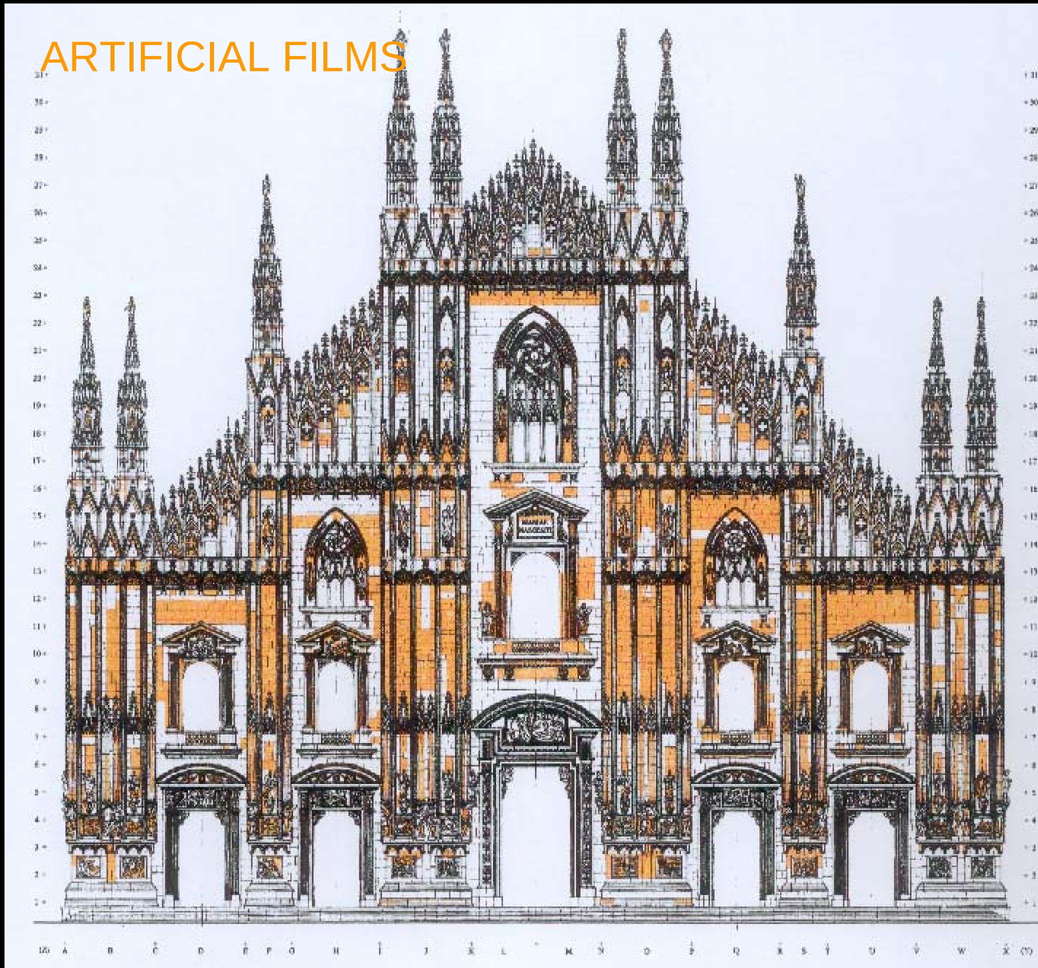


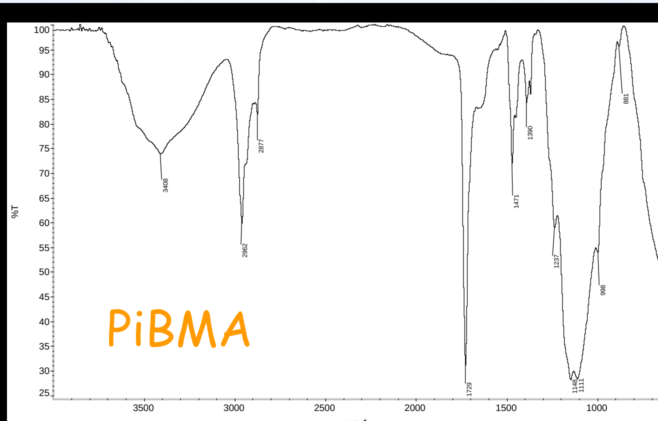

FACCIATA
WHITE FILMS

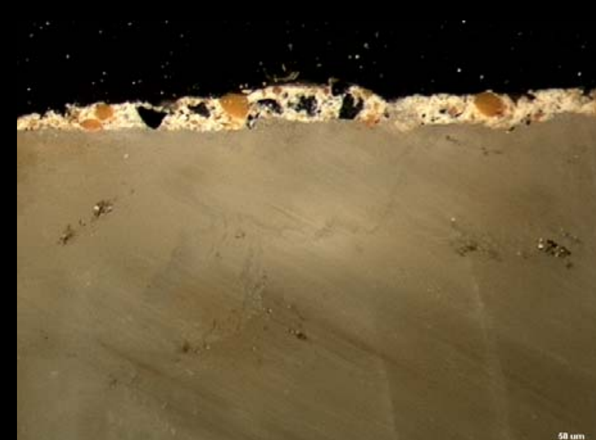

MA

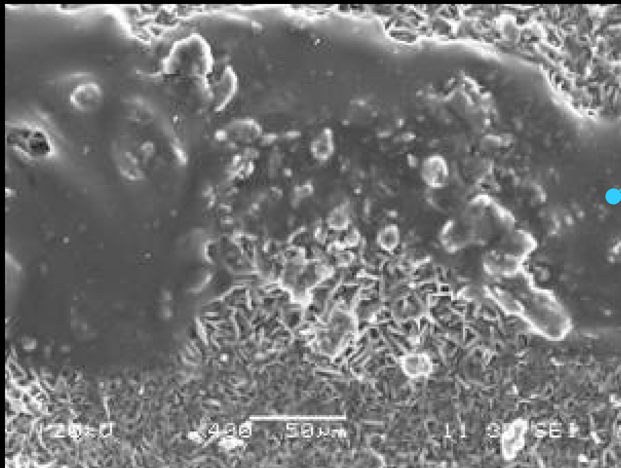

200 um


ARTIFICIAL FILMS

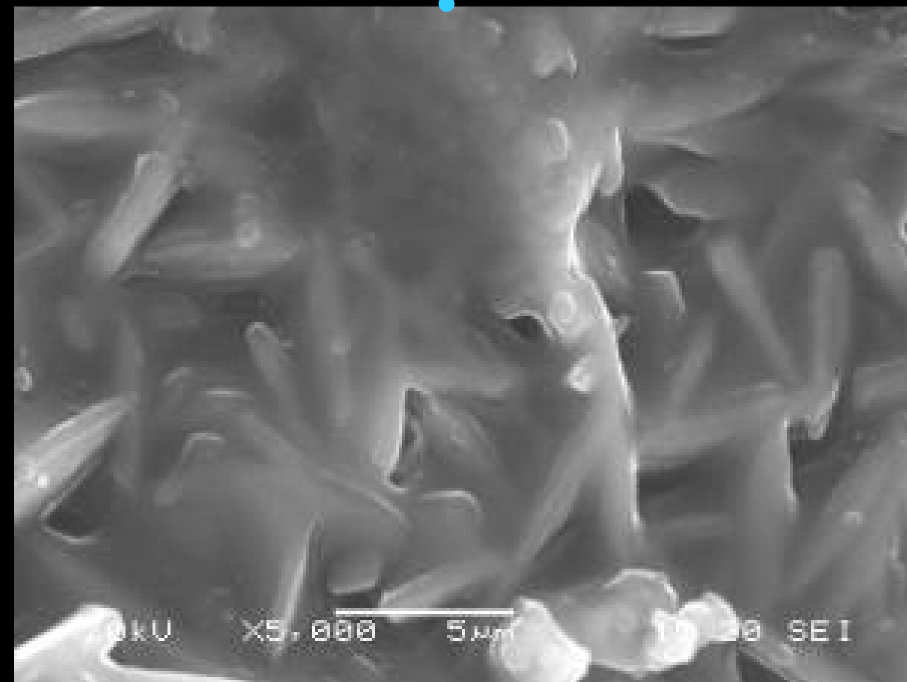






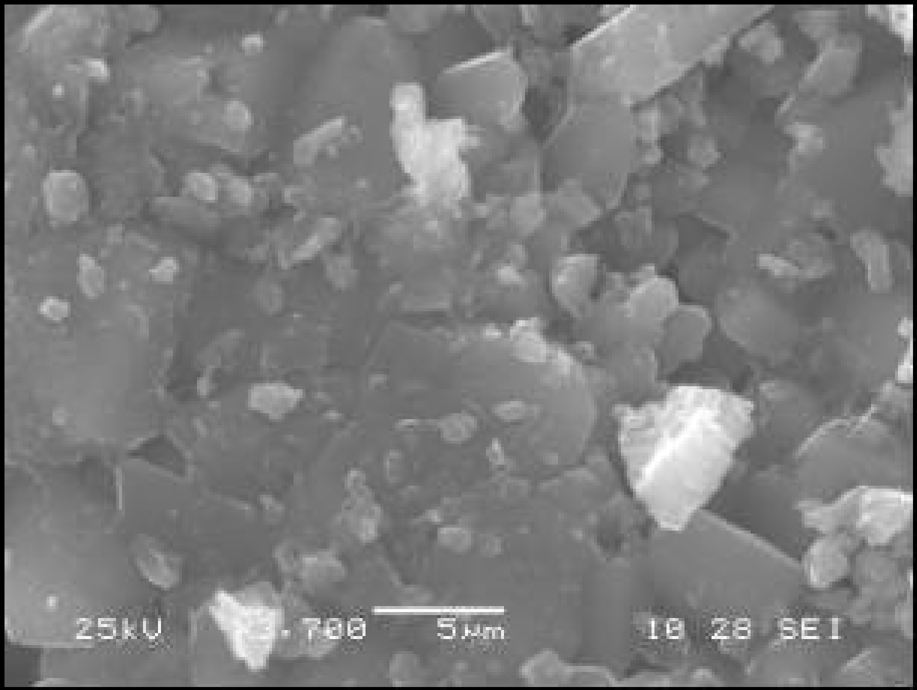


Resin covering underlaying gypsum crystals

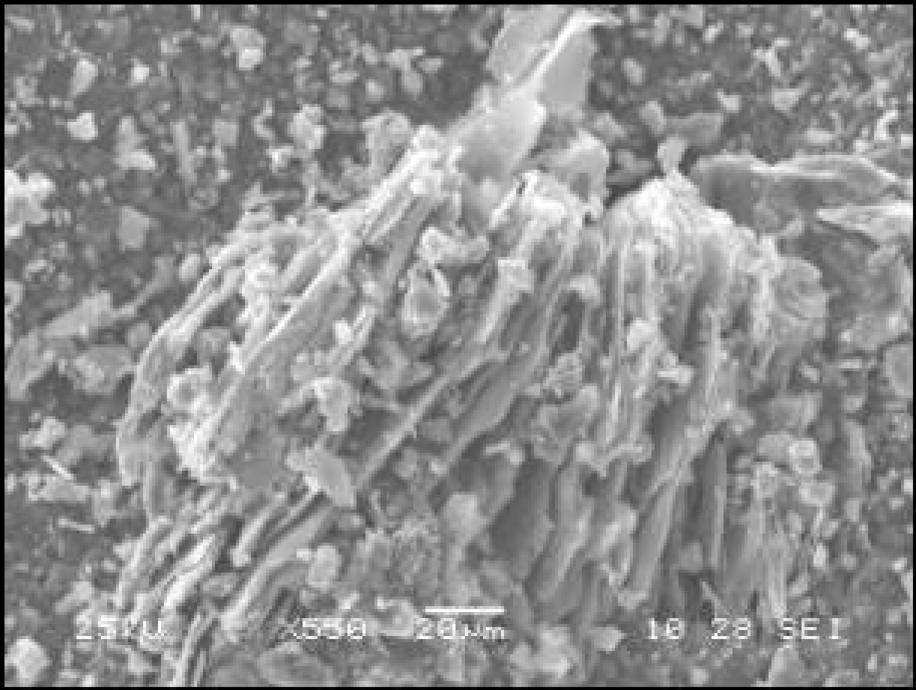


Resin film fractured by gypsum crystals' growth

SEM: MORPHOLOGICAL OBSERVATION



The gypsum is in a thick impasto with resinous materials



Accretion of gypsum crystals perforating the resinous film

Surface treatments applied in the past on stone materials

Classical Antiquity

PITCH
PLASTER
BEESWAX
OILS

Middle Ages and Renaissance

PLASTER
NATURAL RESINS
BEESWAX
OILS

Modern Times

OILS
WAXES
VARIOUS RECIPES (pig's skin, eggs white)
SILICATES and FLUOSILICATES

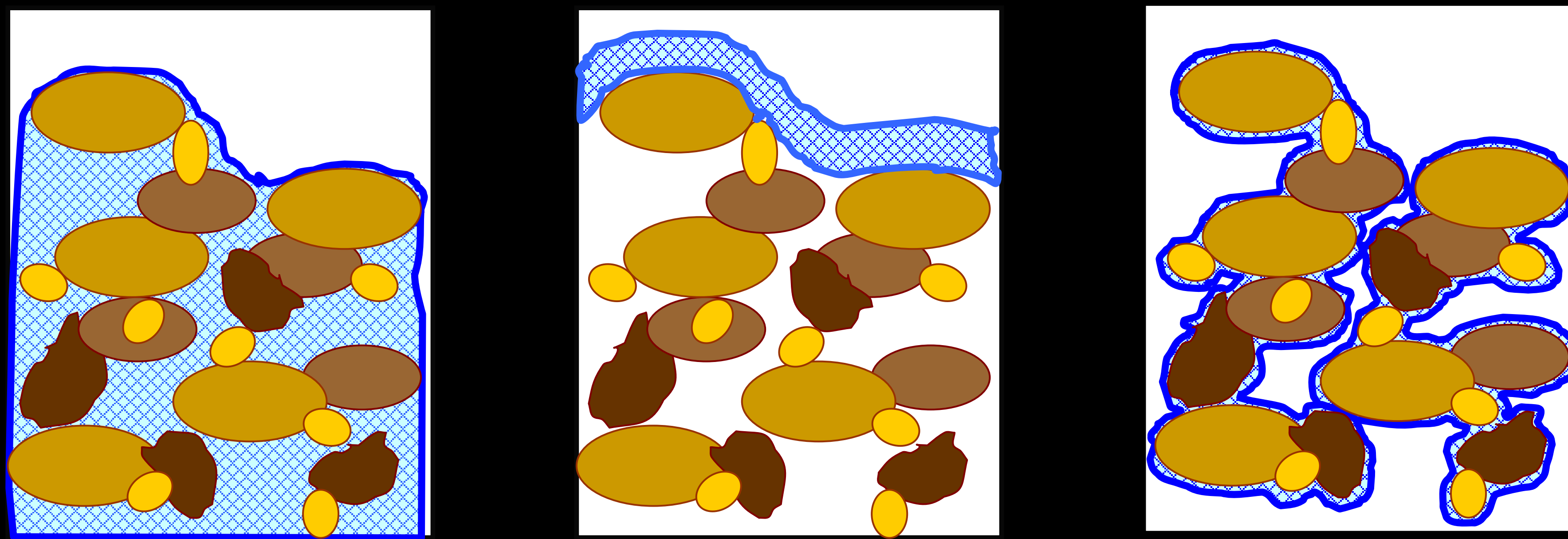
POLYMERS

SILICONES
- silanes,
- siloxanes
- alkylalkoxysilanes
- polysiloxanes

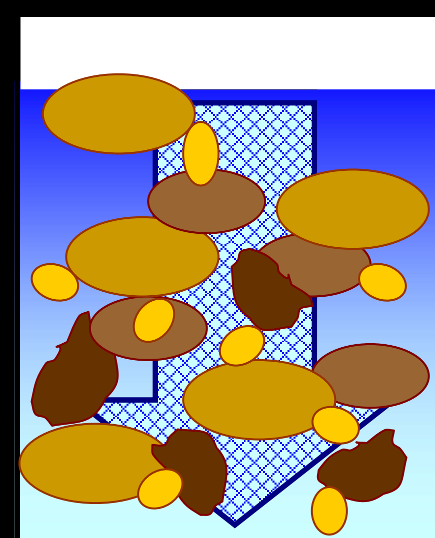
FLUORINATED
- perfluoropolyethers
- polyfluorourethanes
- fluoroelastomers
- polyfluoroolephines
- fluorinated acrylics

ACRYLICS
- polyacrylates
- polymethacrylates
- acrylate/methacrylate copolymers

distribution



penetration depth

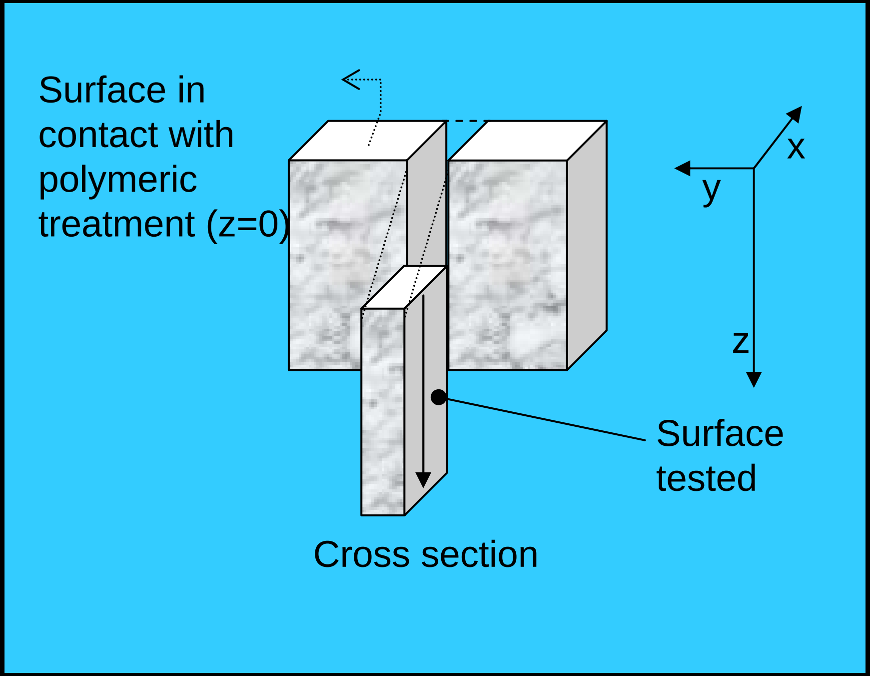


ANALYTICAL STRATEGY

Study of stone/polymer system by direct methods of analysis

- No indirect detection of products.
- No solvent extraction.
- Reduced manipulation of samples.

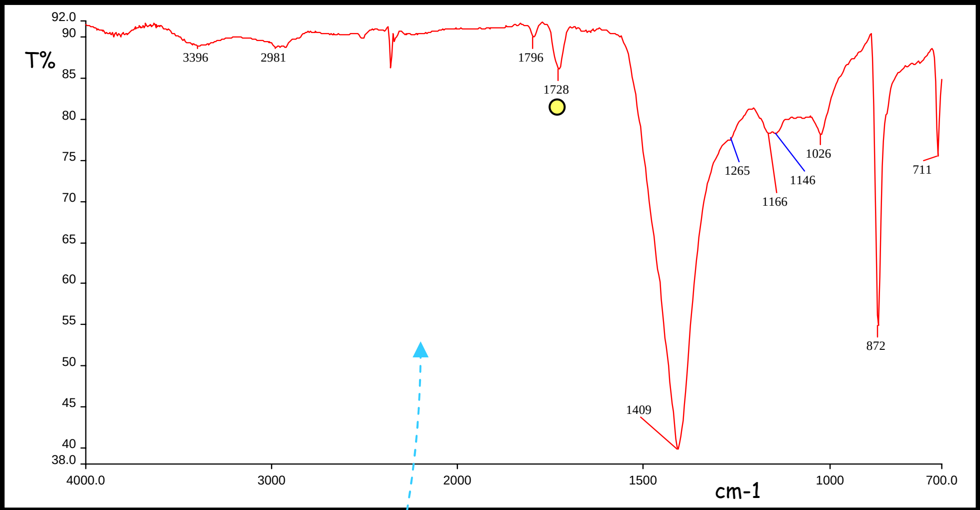
Micro-ATR spectroscopy

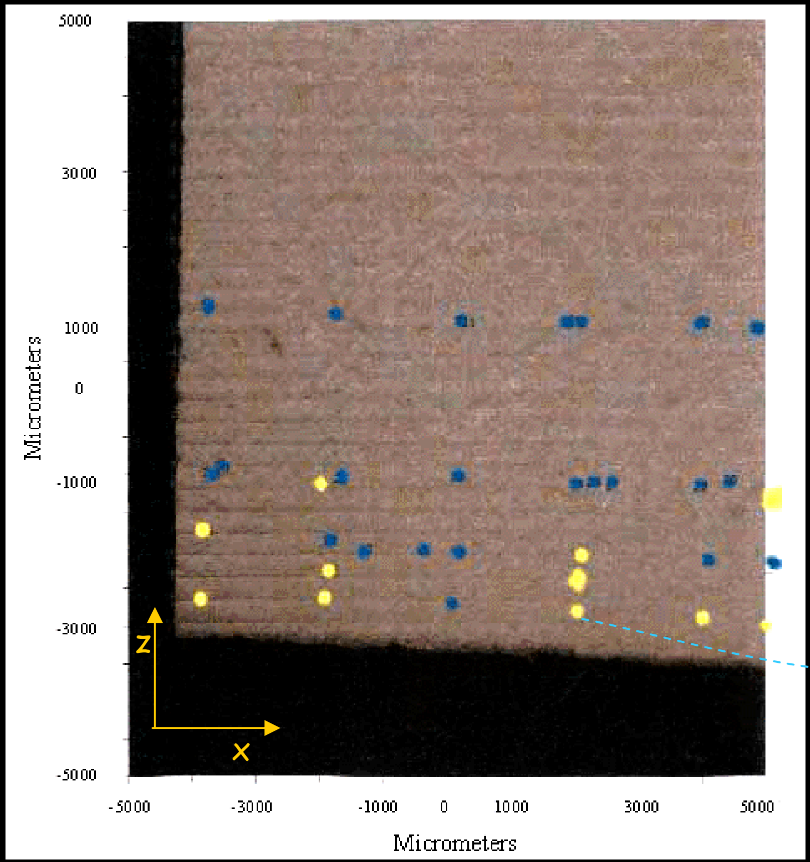


Limestone (25-35% total open porosity)

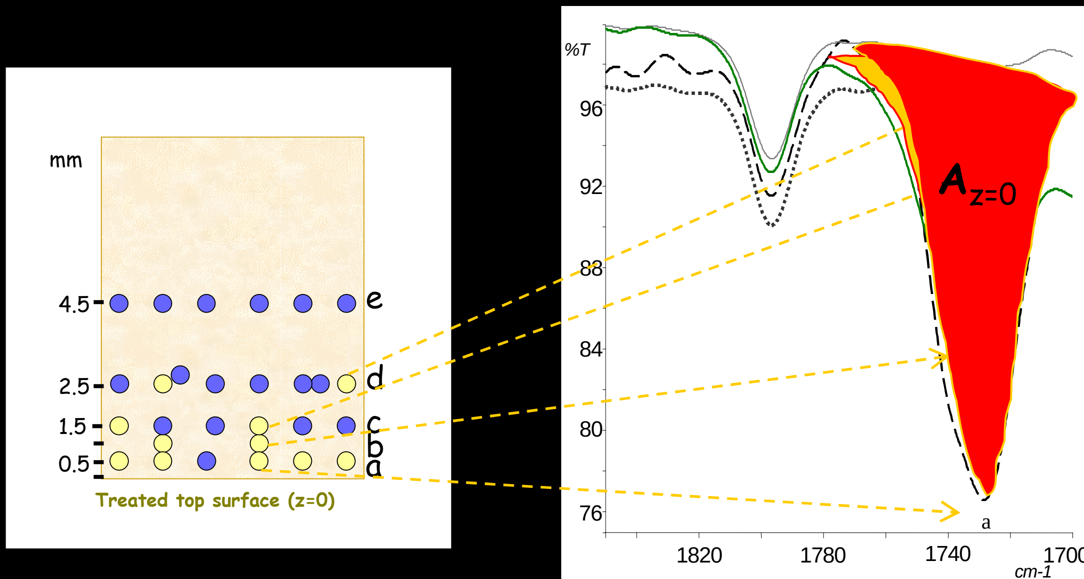
PARALOID B72
(poly-EMA/MA)

1726 cm^{-1} : $\nu_{C=O}$





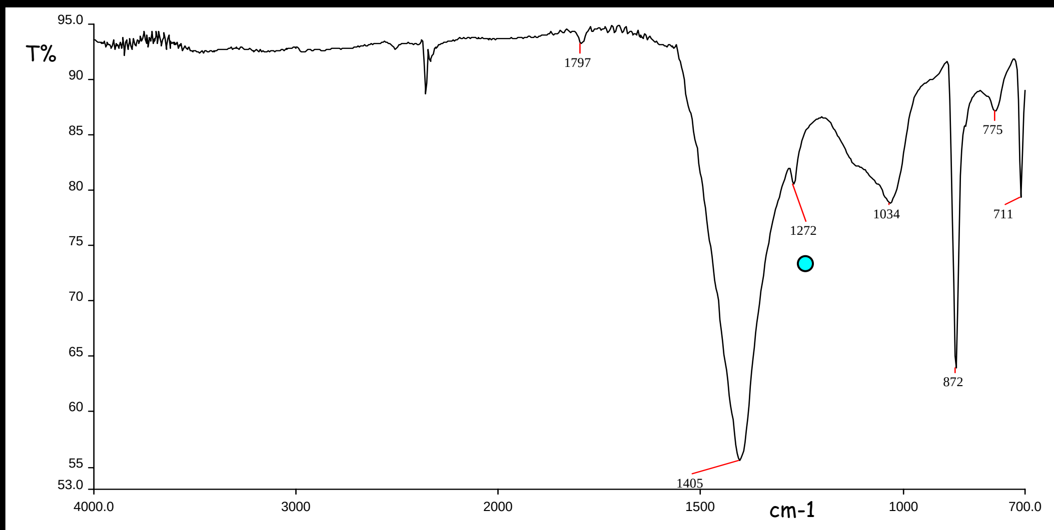
PARALOID B72



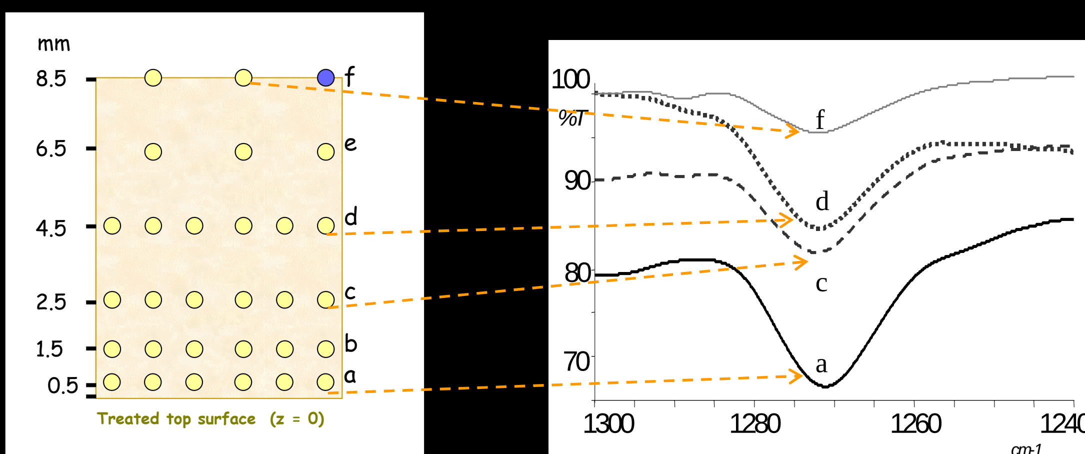
$$\frac{A_{z=n}}{A_{z=0}} = \%$$

Distance from surface (mm)	Polymer’s dose
z = 0	100%
z = 0.5	64.1%
z = 1	8.3%
z = 1.5	13.9%
z = 2.5	10.1%

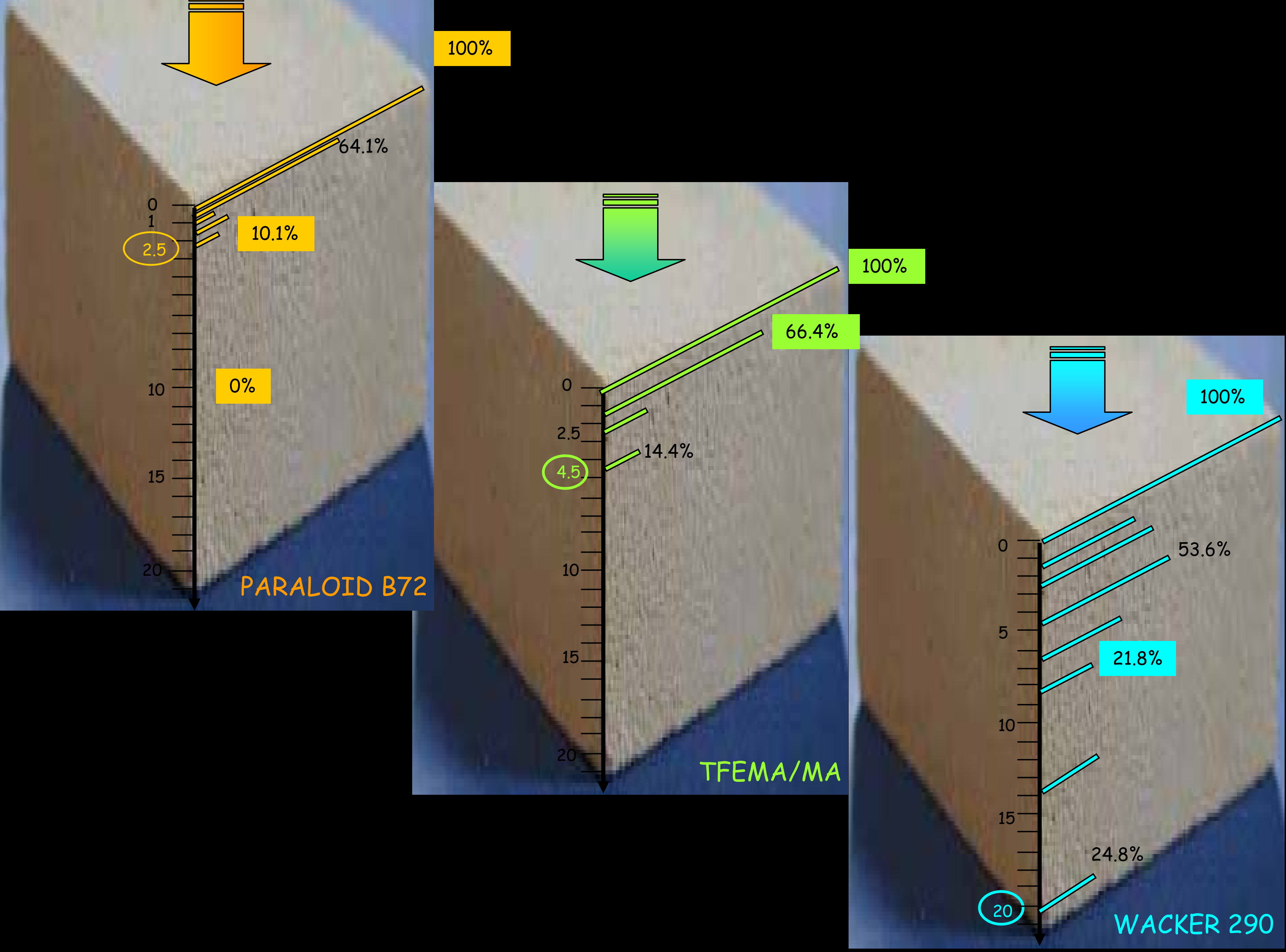
WACKER 290
(from oligomeric alkylalkoxysiloxanes)



ν Si-C of $-SiCH_3-$: 1270 cm^{-1}

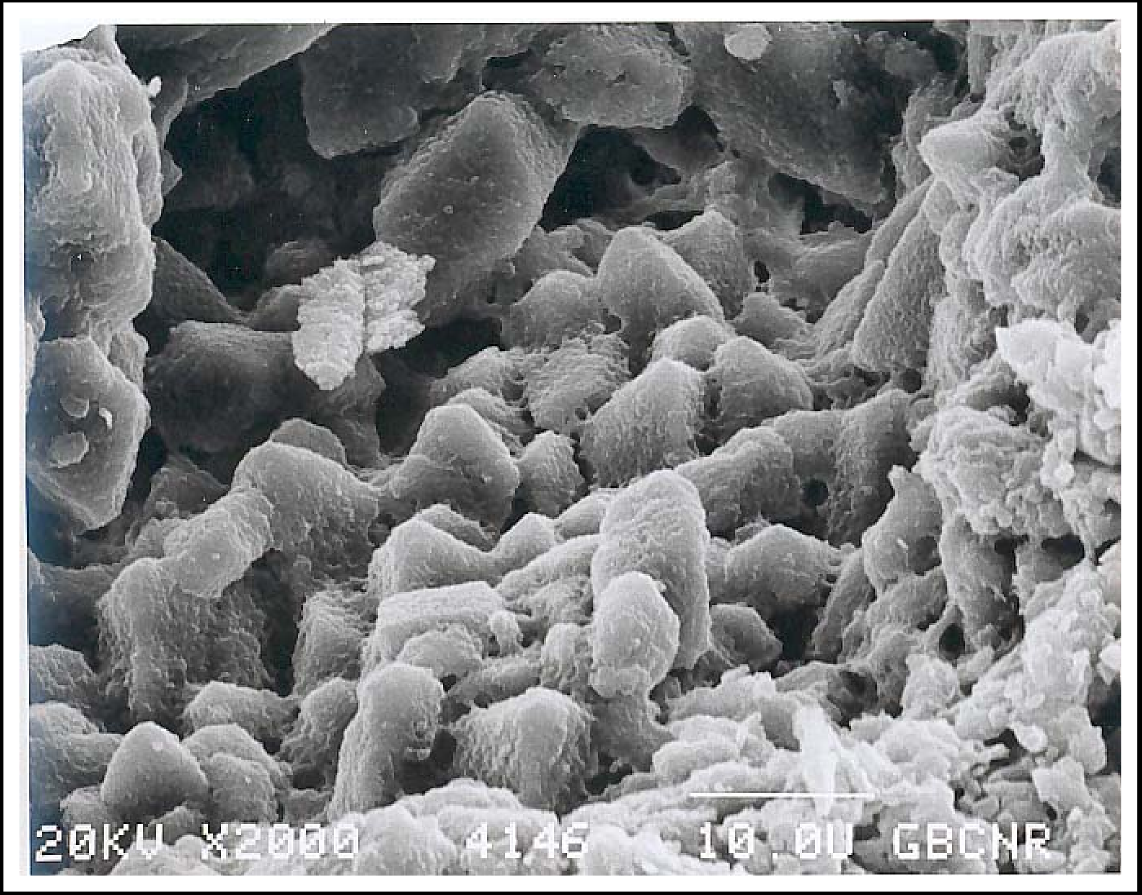


Distance from surface (mm)	Polymer's dose
z = 0.5	100%
z = 1.5	38.7%
z = 2.5	47.1%
z = 4.5	53.6%
z = 6.5	33.2%
z = 8.5	21.8%
z = 20	24.8%



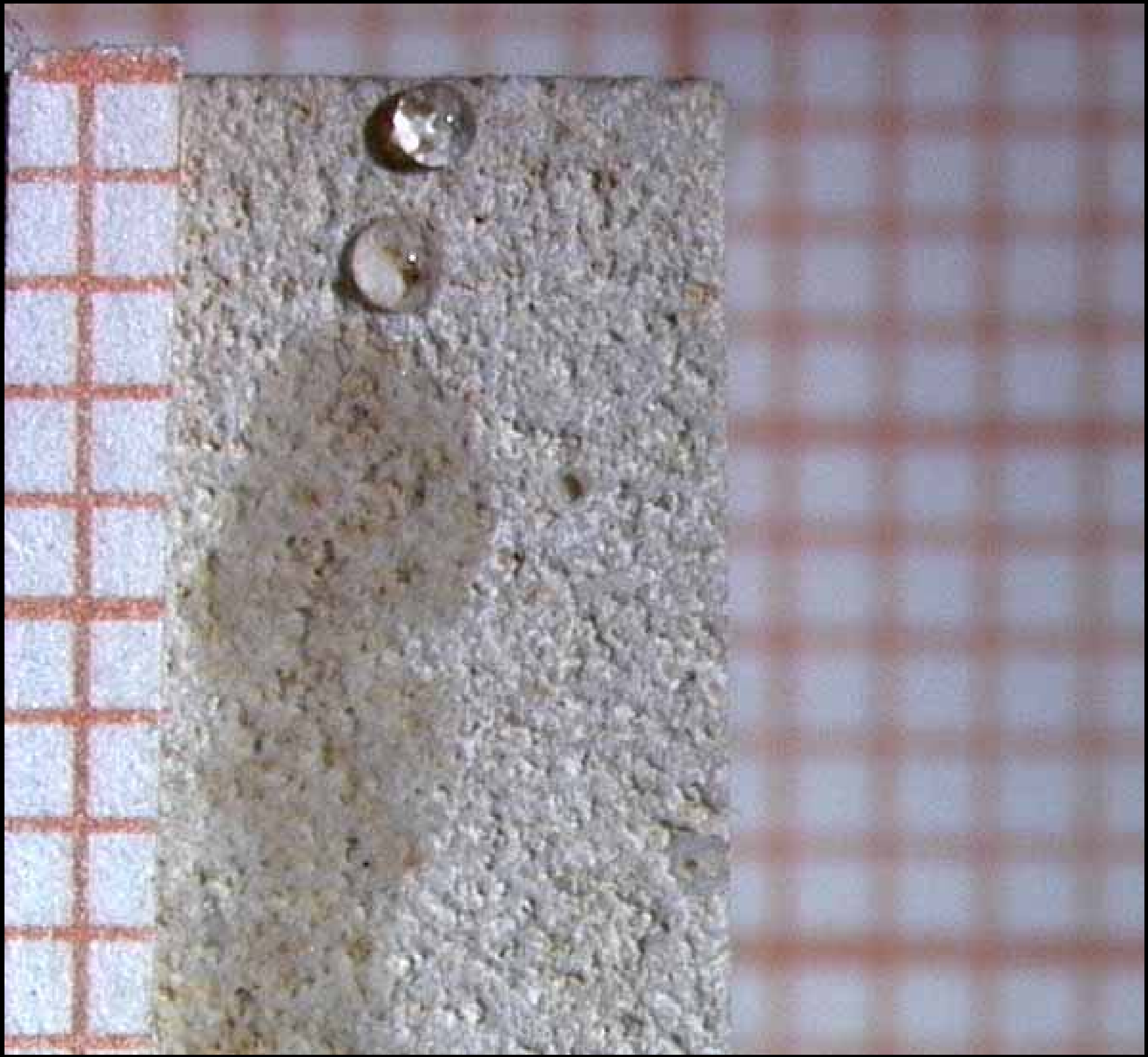
100%
64.1%
0
1
2.5
10.1%
0%
10
15
20
PARALOID B72
100%
66.4%
0
2.5
14.4%
4.5
10
15
20
TFEMA/MA
100%
0
53.6%
5
21.8%
10
15
24.8%
20
WACKER 290

Paraloid B72treatment on Noto Stone, 200 µm underneath surface

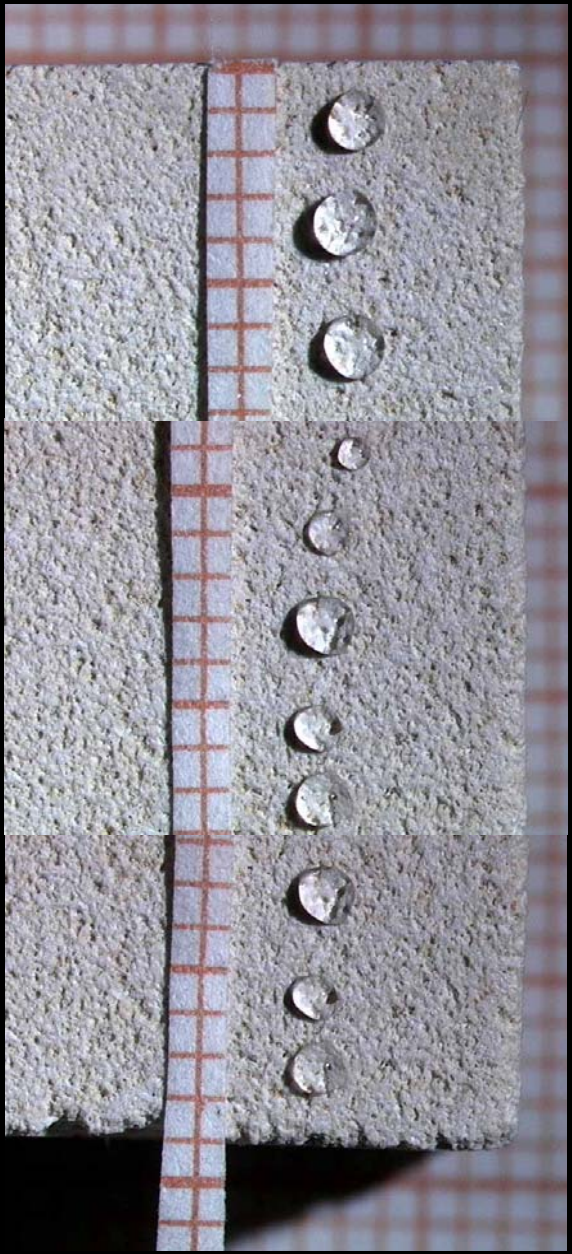


Wacker 290 treatment on Noto Stone, 200 µm underneath surface

Paraloid B72treatment on Noto Stone

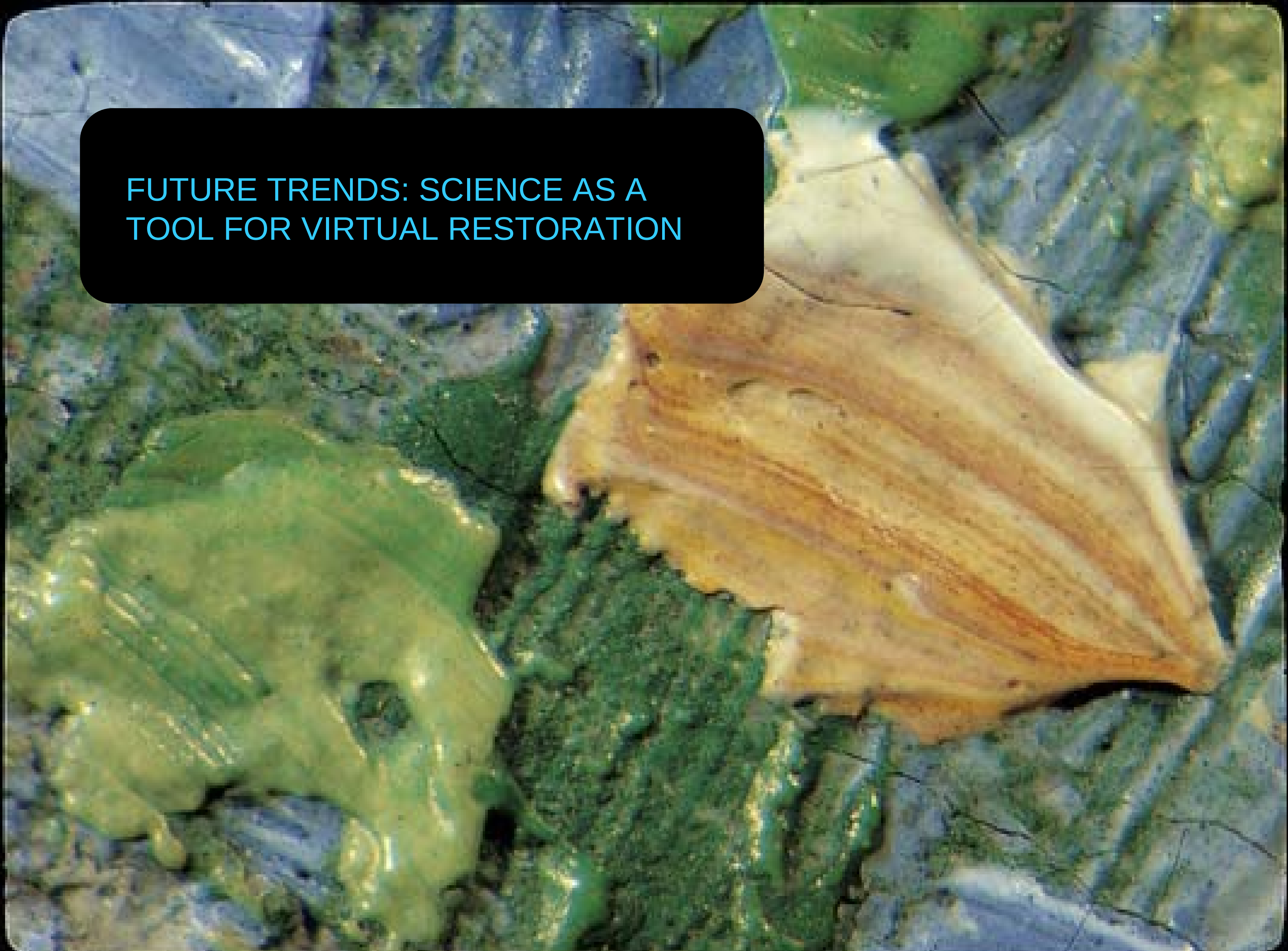


TFEMA/MA treatment on Noto Stone



Wacker 290 treatment on Noto Stone

FUTURE TRENDS: SCIENCE AS A TOOL FOR VIRTUAL RESTORATION



Seurat painted *La Grande Jatte* in 3 distinct stages

First Stage: May 1884 - March 1885

Second Stage: October 1885 - March 1886

Third Stage: 1888/1889

(re-stretching of canvas and addition of painted borders)

The deterioration and darkening of the zinc yellow

“Because of the colors which Seurat used [in *La Grande Jatte*] toward the end of 1885 and in 1886, this painting of historical importance has lost its luminous charm: while the reds and blues are preserved, the Veronese greens are now olive-greenish, and the orange tones which represented light now represent nothing but holes.”

Felix Feneon, April 1892 (*review of Seurat’s memorial exhibition*)

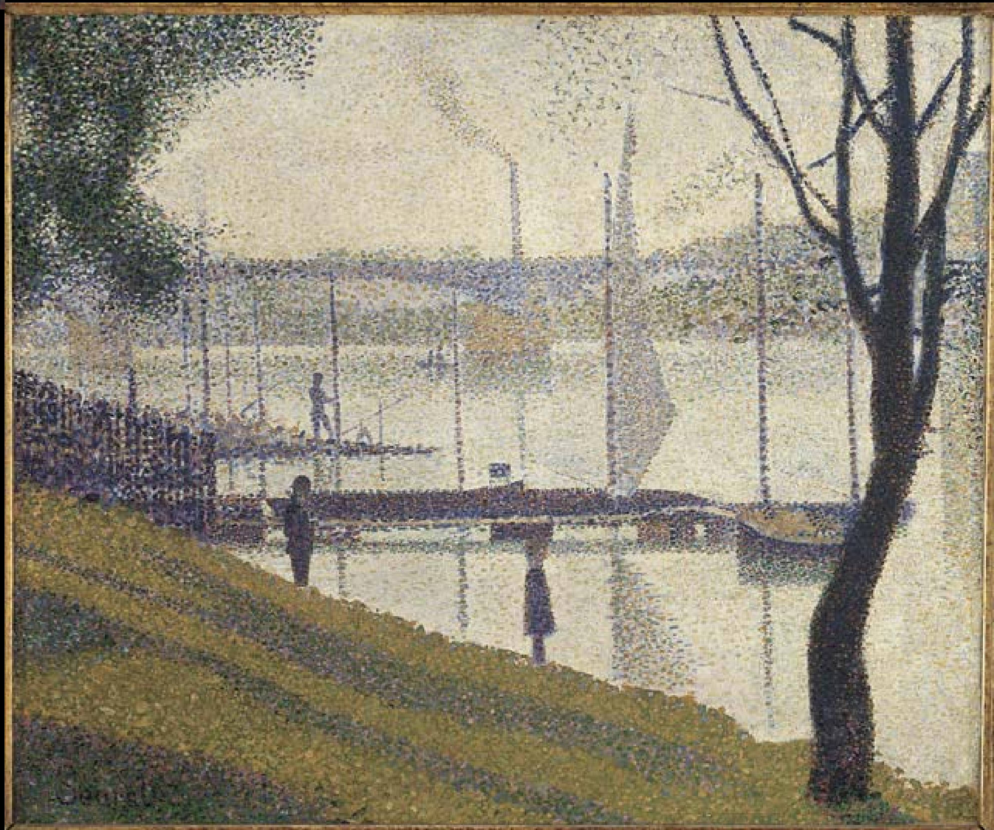
ZINC YELLOW

- Zn yellow: (K_2O*$4ZnCrO_4$*$3H_2O$)
- First commercially available in 1847
- Not hugely popular. Still listed by J.G. Vibert in “Science of Painting” among pigments that could be used with “perfect certainty” (1892)
- Not especially lightfast and apt to turn gray-green owing to the formation of chromic oxide
- Currently mainly used as corrosion resistant primer

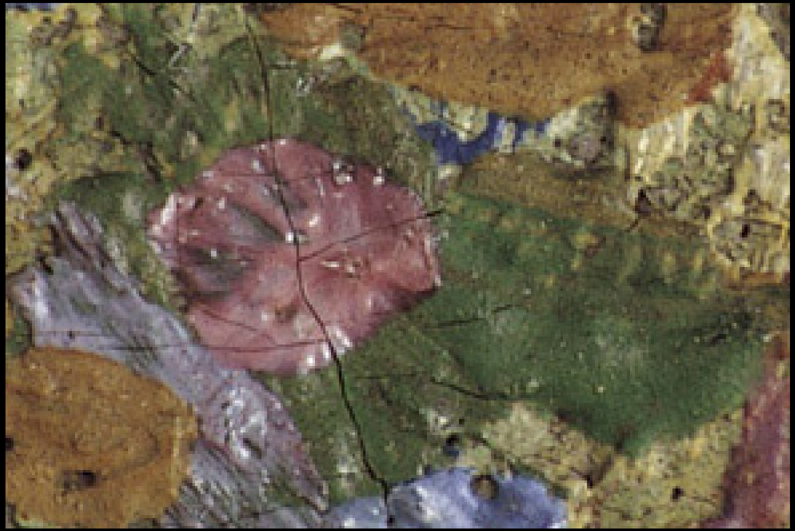
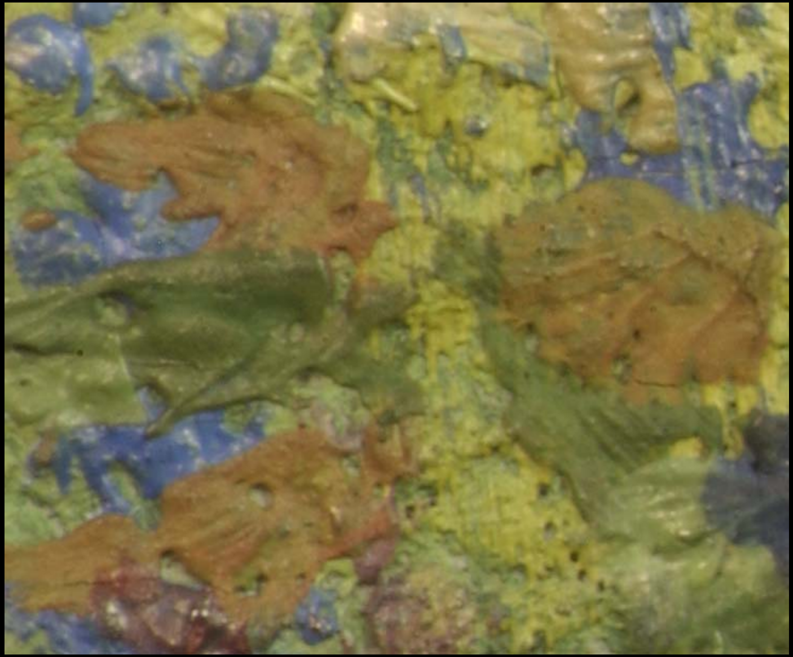
Zinc yellow also….

Bathers at Asnières 1884
(National Gallery, London)

The Bridge at Courbevoie, 1886,
(Courtauld Institute, London)





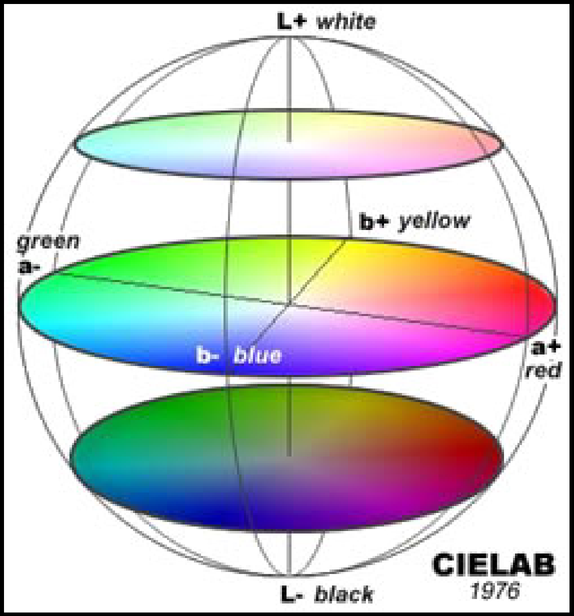



COLOR RECONSTRUCTION OF LA GRANDE JATTE USING COLOR SCIENCE AND DIGITAL IMAGING

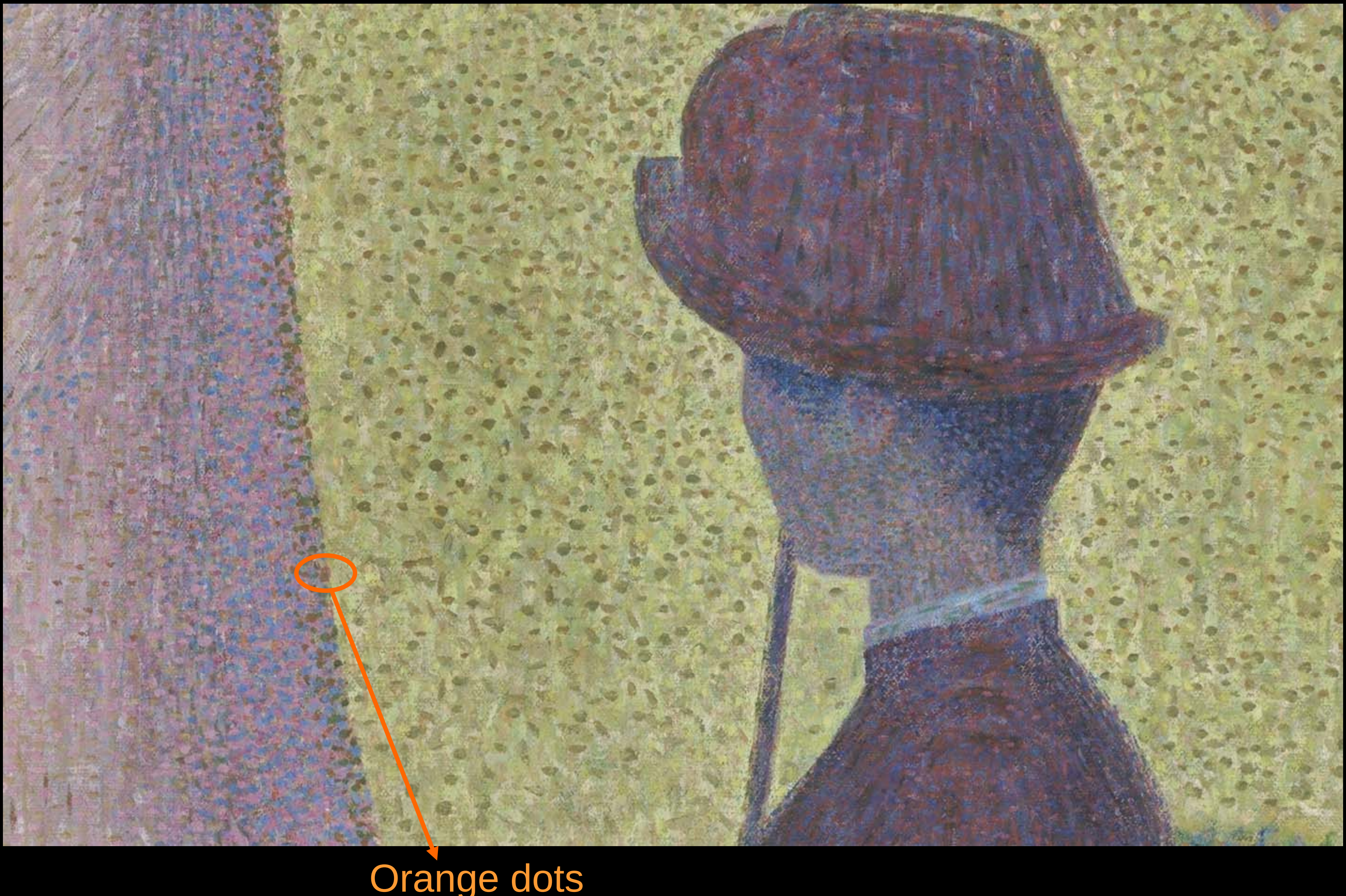
STEP 1.

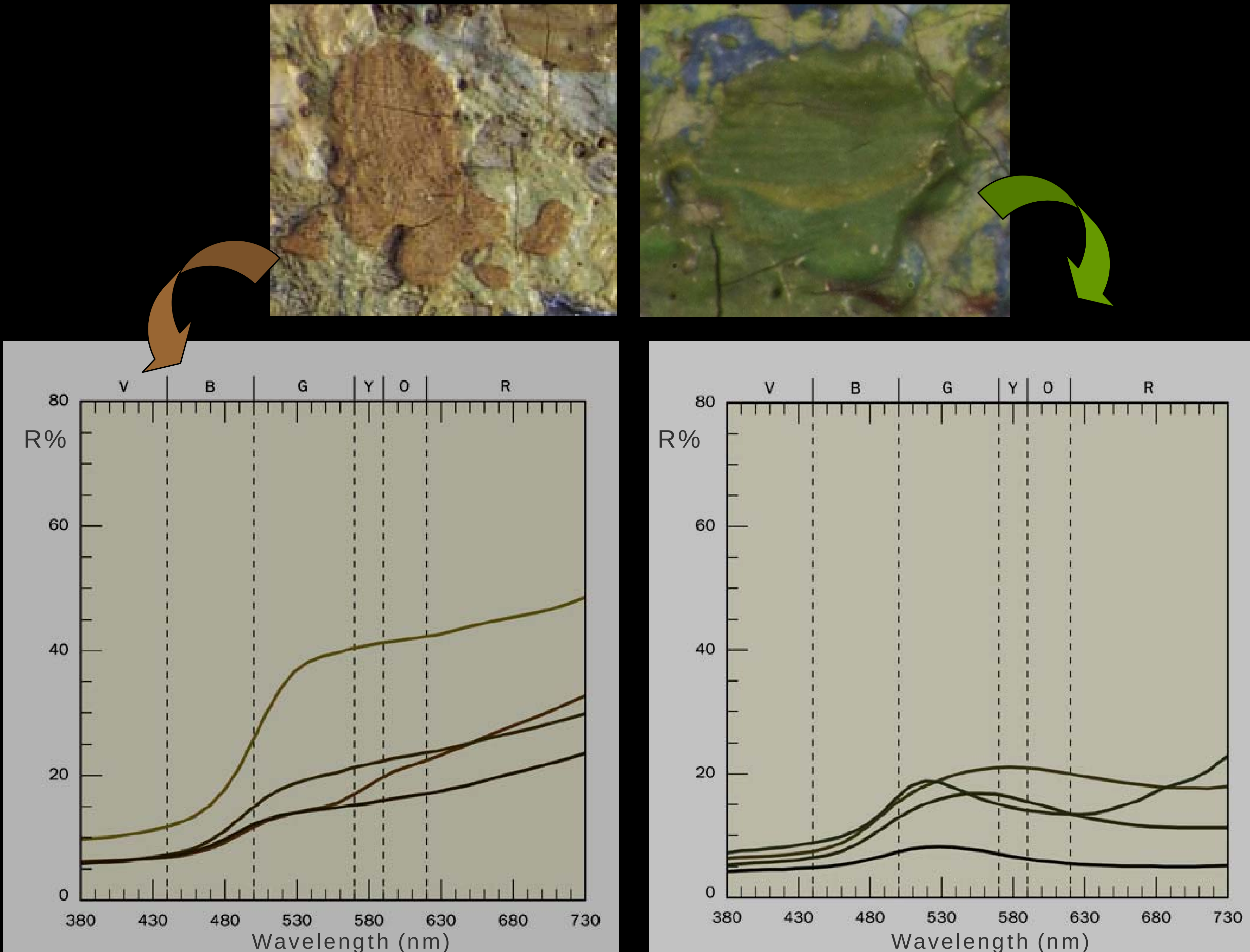
•*Non-destructive measurements on La Grande Jatte with a portable Visible-spectrophotometer .*

•*Spectral reflectance of a number of dots, and CIELAB coordinates for each color*




Zn Yellow dots
Zn Yellow and Emerald green dots


Orange dots



V
B
G
Y
O
R
80
60
40
20
0
R%
380
430
480
530
580
630
680
730
Wavelength (nm)
V
B
G
Y
O
R
80
60
40
20
0
R%
380
430
480
530
580
630
680
730
Wavelength (nm)

STEP 2.

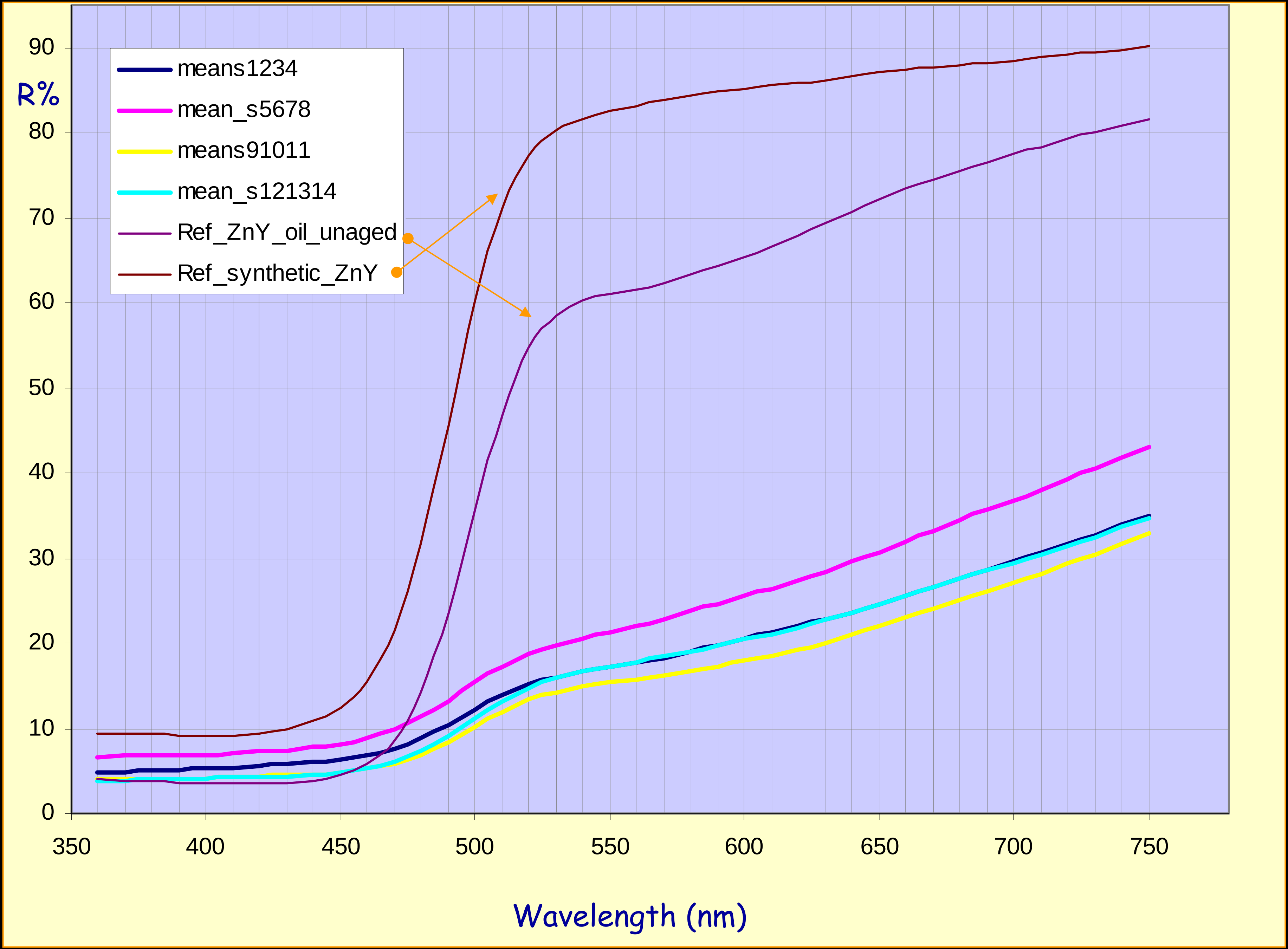
Spectrophotometric and Colorimetric data collected on fresh paintouts of

- *lead white,*
- *zinc yellow + red (vermillion) and green pigments (Emerald green)*

in linseed oil

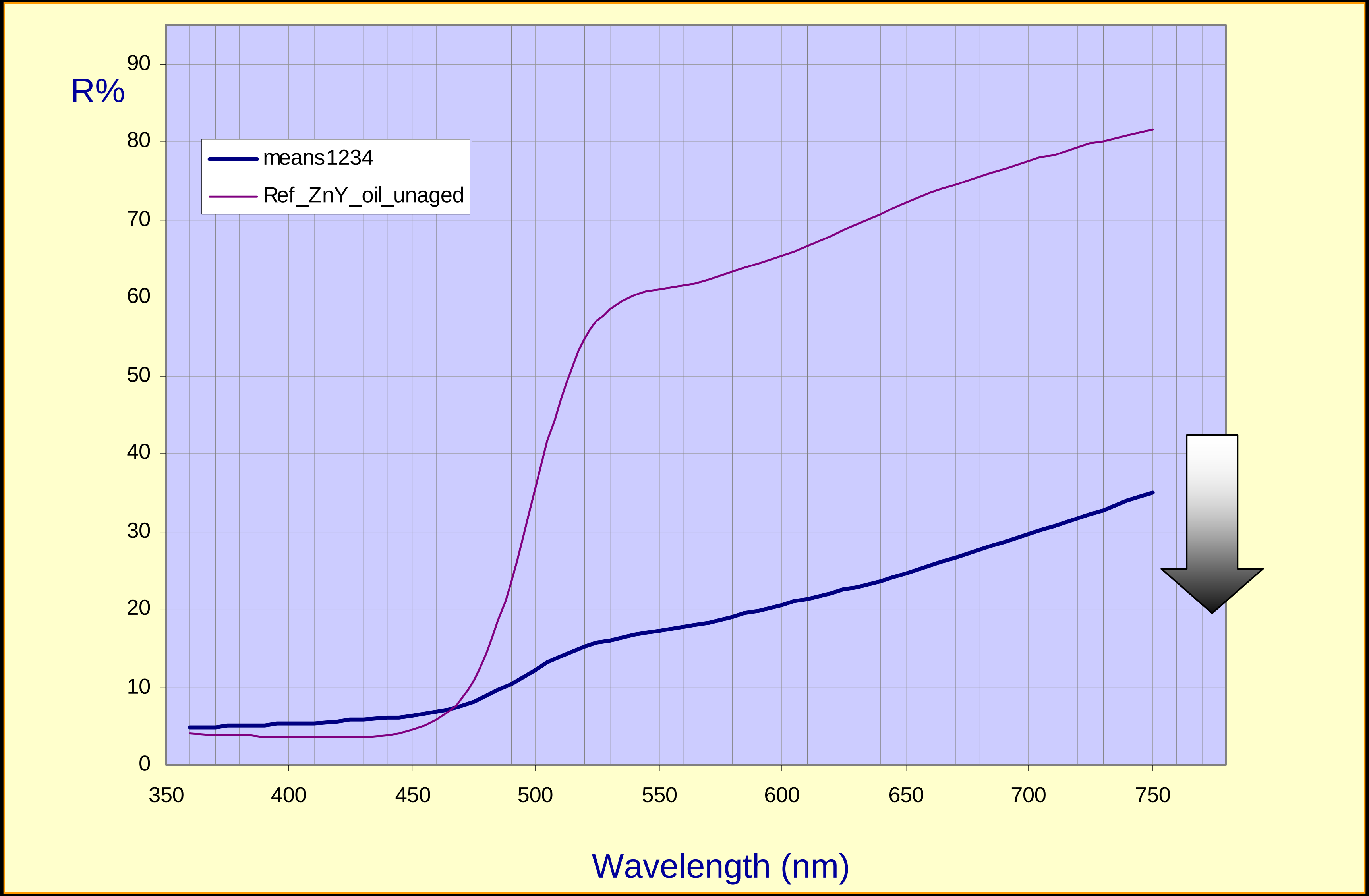

Zn Yellow in oil
Emerald Green in oil
Windsor & Newton Chrome Yellow
Windsor & Newton Vermilion
ZnY mixed w HgS
ZnY mixed w Emg
Windsor & Newton Silver White
Windsor & Newton Zn Yellow
Bocour Bellini Zn Yellow
Lead White
Zn Yellow
Emerald green
in synthetic medium

YELLOW



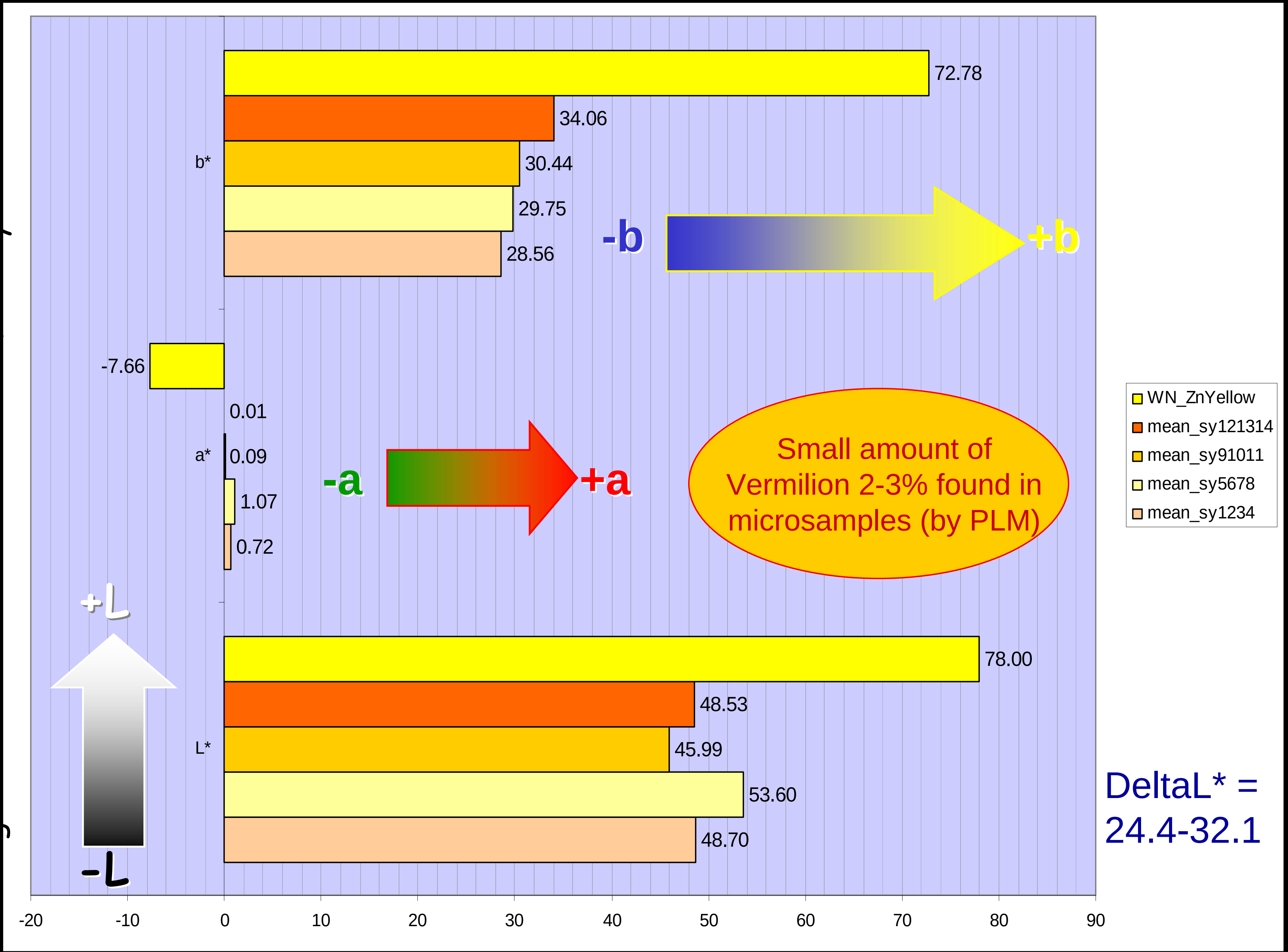
R%
90
80
70
60
50
40
30
20
10
0
350
400
450
500
550
600
650
700
750
Wavelength (nm)
means1234
mean_s5678
means91011
mean_s121314
Ref_ZnY_oil_unaged
Ref_synthetic_ZnY

YELLOW



R%
90
80
70
60
50
40
30
20
10
0
350
400
450
500
550
600
650
700
750
means1234
Ref_ZnY_oil_unaged
Wavelength (nm)

YELLOW



b*
72.78
34.06
30.44
29.75
28.56
-b
+b
a*
-7.66
0.01
0.09
1.07
0.72
-a
+a
Small amount of Vermilion 2-3% found in microsamples (by PLM)
+L
-L
L*
78.00
48.53
45.99
53.60
48.70
WN_ZnYellow
mean_sy121314
mean_sy91011
mean_sy5678
mean_sy1234
DeltaL* = 24.4-32.1
-20
-10
0
10
20
30
40
50
60
70
80
90

COLOR RECONSTRUCTION OF LA GRANDE JATTE USING COLOR SCIENCE AND DIGITAL IMAGING

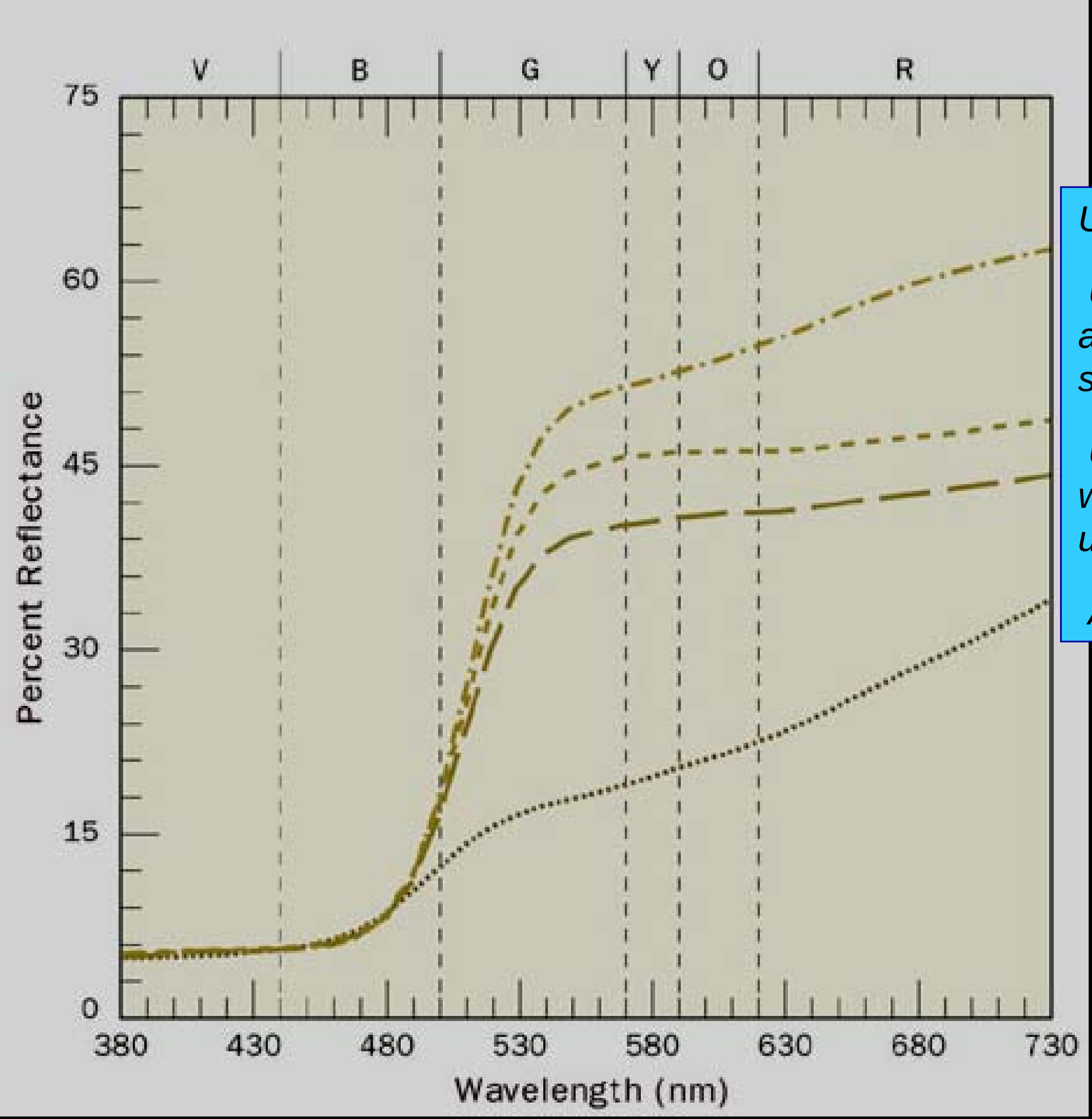
STEP 3.

$$(K/S)_{\lambda,\text{un-darkened}\atop\text{yellow}} = c_{\text{yellow}} (K/S)_{\lambda,\text{fresh}\atop{\text{yellow}\atop\beta=0.75}} + (K/S)_{\lambda,\text{ageing}\atop\text{spectrum}}$$

$$\text{Minimize}\left[\sum_{\lambda=380-470}\left\{(K/S)_{\lambda,\text{average}\atop{\text{in-situ}\atop\text{yellow}}} - (K/S)_{\lambda,\text{undarkened}\atop\text{yellow}}\right\}^2\right]$$

To calculate the rejuvenated colors:

- Use of a theoretical color-mixing model as an analytical tool to determine the amount of Zinc Yellow in any given mixture.
- Replace it with the proper amount of chemically unaltered zinc yellow.
- Take into account the effect of underlying paint (translucency)
- Mathematically manipulate the spectral curves to simulate a measurement of Seurat's original Zn Yellow



Undarkened average yellow dot

Undarkened and un-aged average yellow dot with 25% showthrough of underlying paint

Undarkened average yellow dot with 25% showthrough of underlying paint

Average darkened yellow dot

$$(K/S)_{\lambda,mix} = c_g (K/S)_{\substack{\lambda,fresh \\ green \\ \beta=0.75}} + c_y \left((K/S)_{\substack{\lambda,average \\ in-situ \\ yellow}} - (K/S)_{\lambda,aging\ spectrum} \right)$$

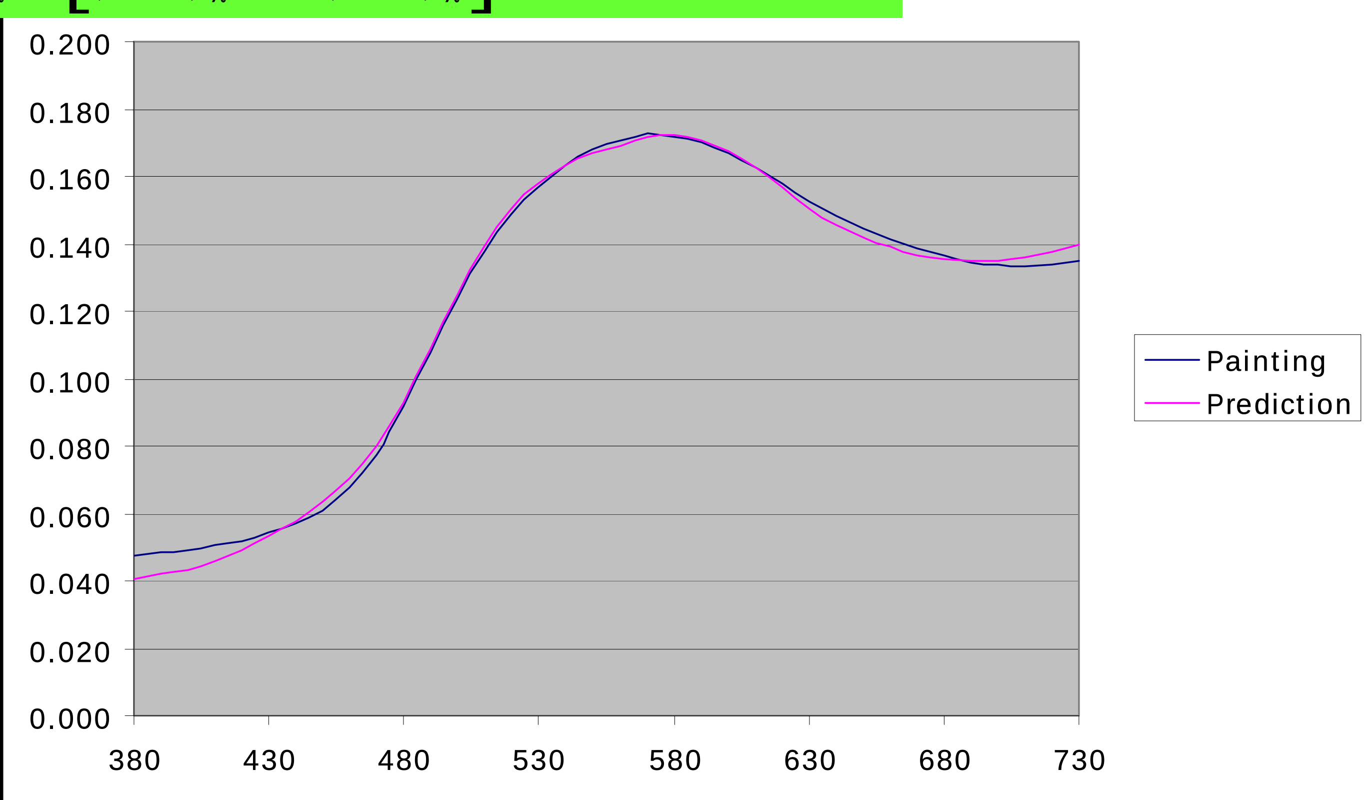
$$+ c_w (K/S)_{\substack{\lambda,fresh \\ white}} + (K/S)_{\lambda,aging\ spectrum}$$

$$\text{Minimize} \left[\sum_{\lambda} \left\{ R_{\substack{\lambda,average \\ in-situ \\ green}} - R_{\lambda,mix} \right\}^2 \right]$$

$$\text{where}\quad R_\lambda = 1 + (K/S)_\lambda - \left[(K/S)_\lambda^2 + 2(K/S)_\lambda \right]^{1/2}$$

GREEN

Zinc Yellow, Emerald green, lead white



STEP 4.

- Correct for the aging of the painting (yellowing & darkening of the binding medium)

- "aging spectrum" = measurement of fresh lead white in linseed oil - measurements on an area of pure white on LGJ

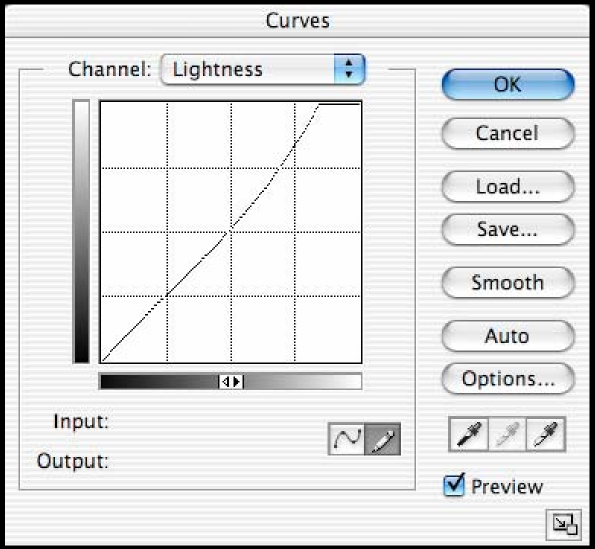
- The aging spectrum can be subtracted from all the colors of LGJ (Kubelka Munk turbid media theory)

$$(K/S)_{\lambda,\text{un-aged}} = (K/S)_{\lambda,\text{in-situ measurement}} - (K/S)_{\lambda,\text{aging spectrum}}$$

Before unaging

After unaging

•STEP 5.



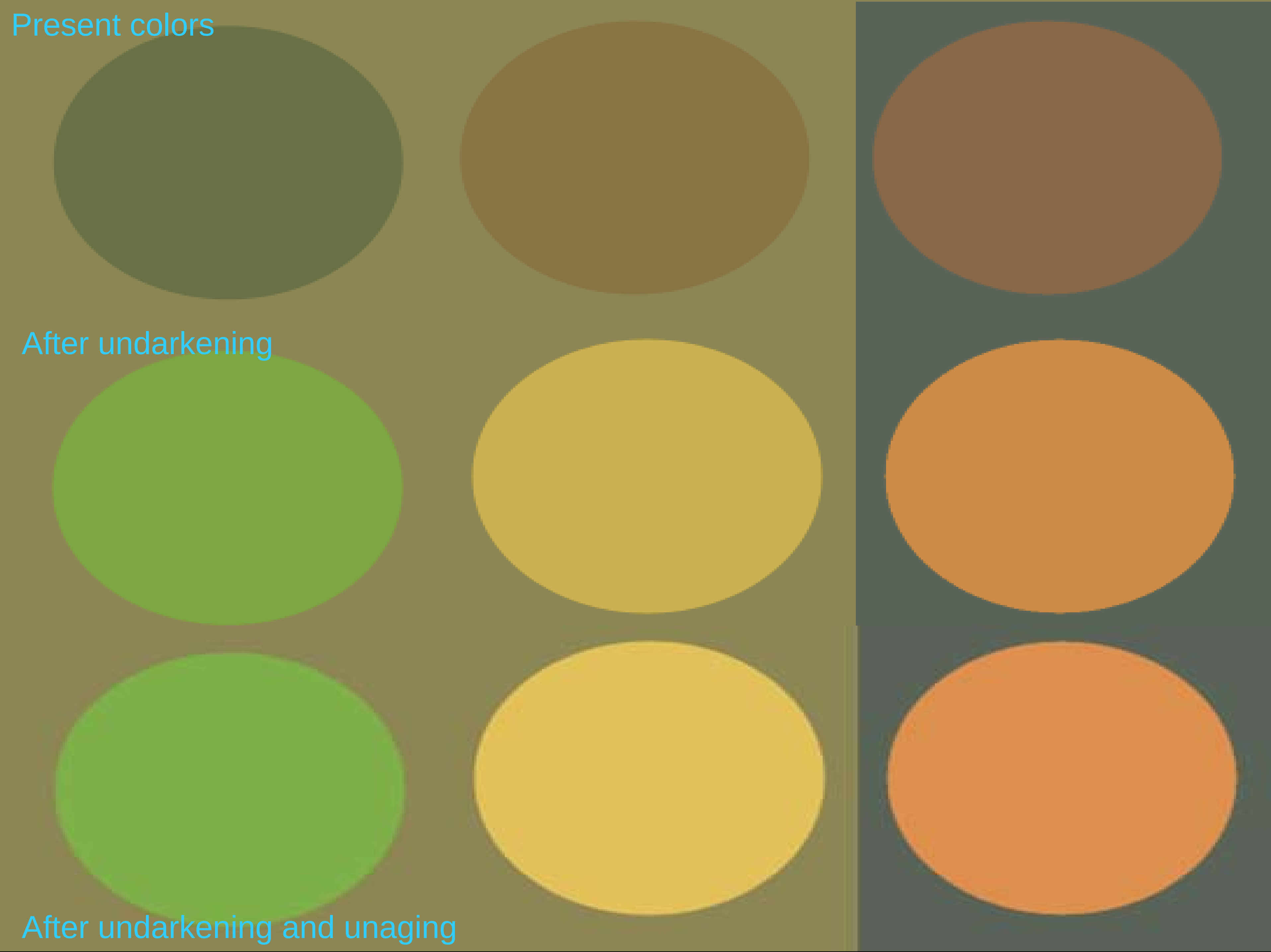
•The CIELAB coordinates of the average dots both before and after un-darkening at each opacity calculated

•Shift in color described as a translation.

•By applying the appropriate translation to each dot containing zinc yellow, the colors could be un-darkened

•Data used to create one-dimensional look-up tables that could be accessed by Photoshop as custom *Curves*

•Finally,use of such curves to rejuvenate the dots.


Present colors
After undarkening
After undarkening and unaging

STEP 6.

To perform the ultimate correction and digital rejuvenation of LGJ measurements of all of the colors in the painting needed.

- Digital imaging of whole painting with a color managed digital camera, converting RGB information to CIELAB coordinates for each point.

- Unaging correction to the whole image.

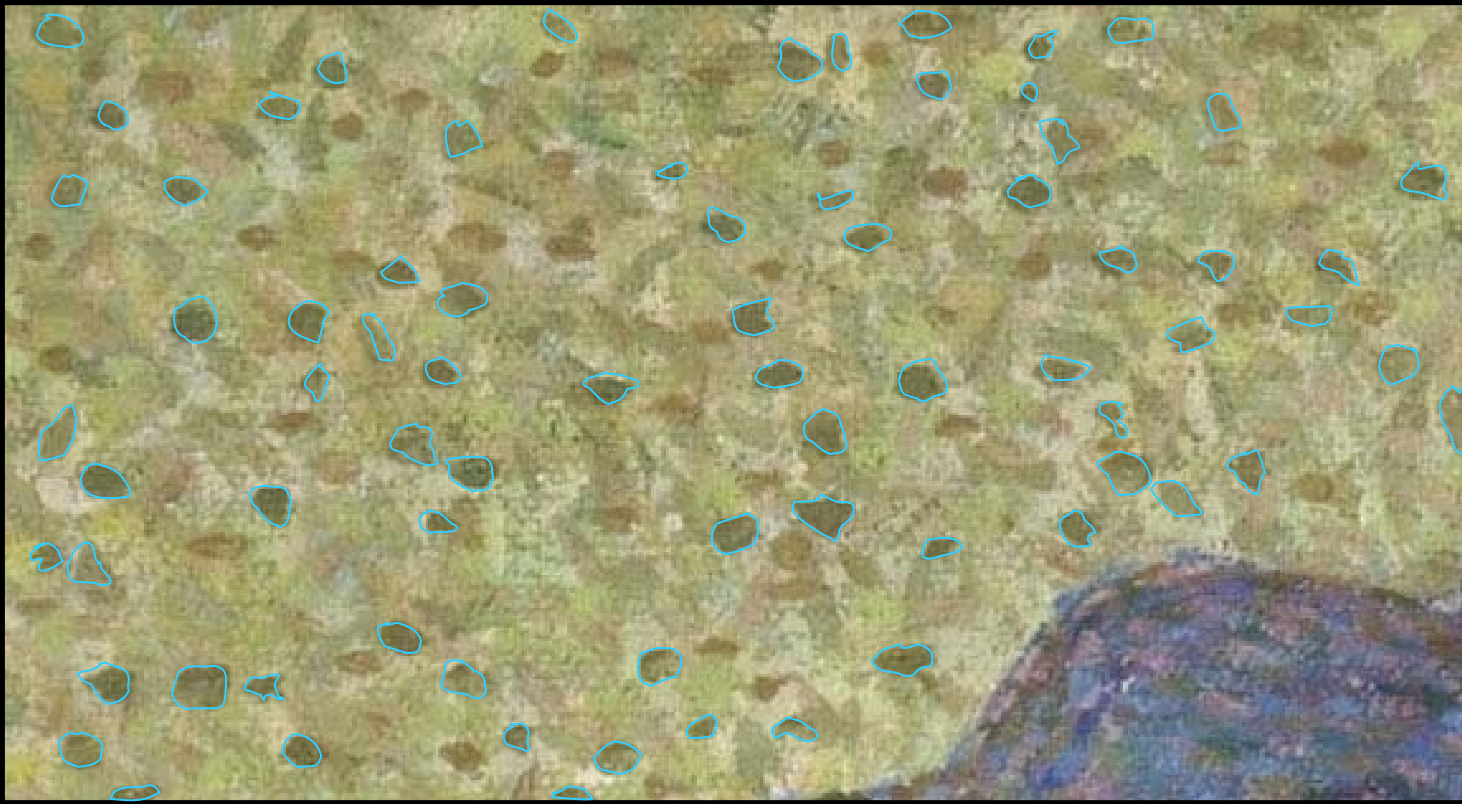
Uniform gray card

Gretagmacbeth
ColorChecker DC

Gamblin Paint target

STEP 7.

- With Photoshop tools, altered dots isolated on the image
- Use of new curves to correct for the darkening.



after

before


SYNCHROTRON RADIATION STUDIES OF ART AND ARCHAEOLOGICAL MATERIALS

Synchrotron SOLEIL, France, starting (2006) to develop a specific program on archaeometry and cultural heritage

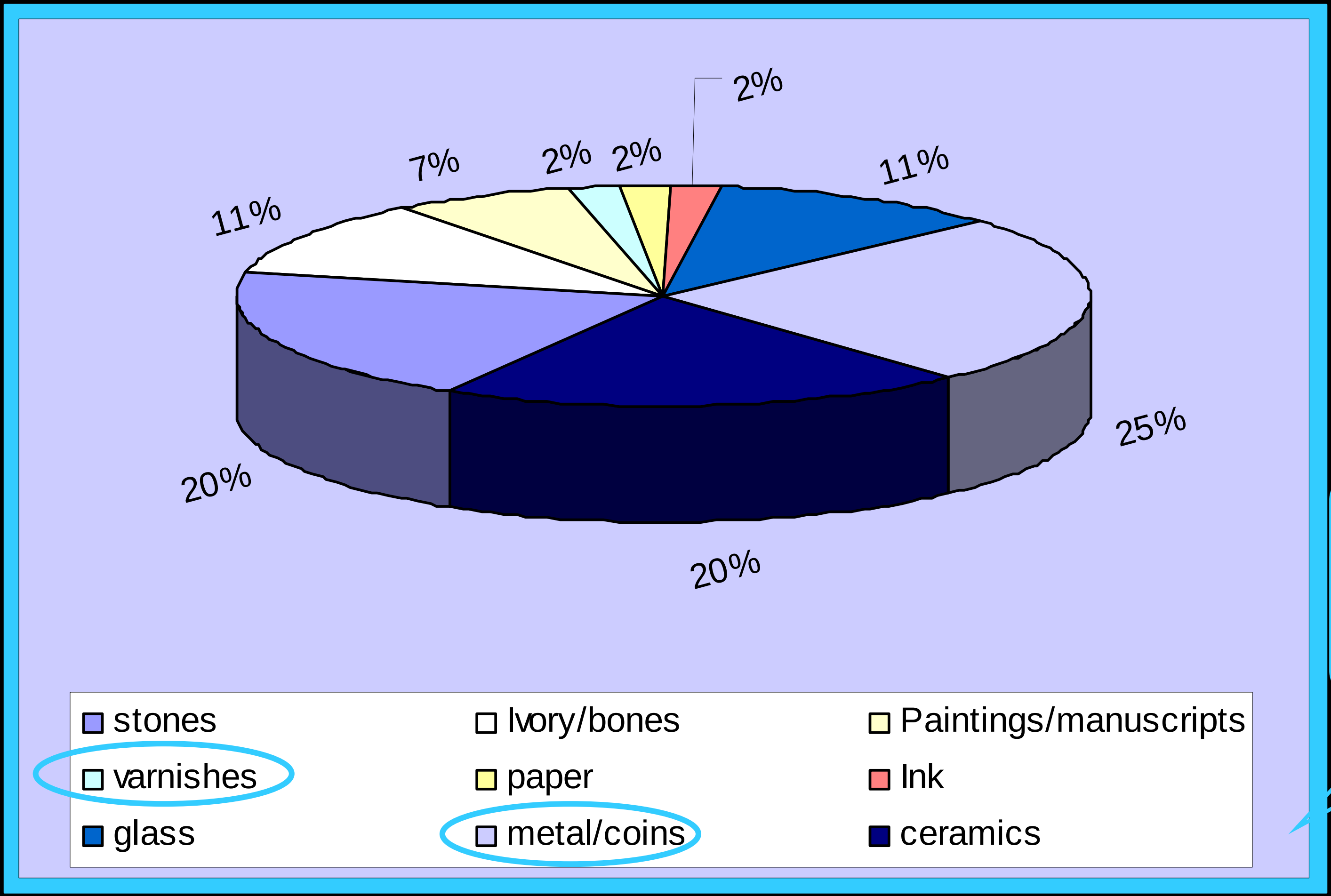
1986 G.Harbottle, B.M.Gordon and K.W.Jones
Use of Synchrotron Radiation in Archaeometry
Nucl. Instr. and Meth. B 14 (1986) 116-122

- 1991, 1992, 1994 : 1 citation
- 1995: 3 citations
- 1996, 1998: 5 citations
- 1997: 6 citations
- 1999: 9 citations
- 2000: 17 citations
- 2001: 13 citations
- 2002: 20 citations
- 2003: 23 citations
- 2004: 21 citations

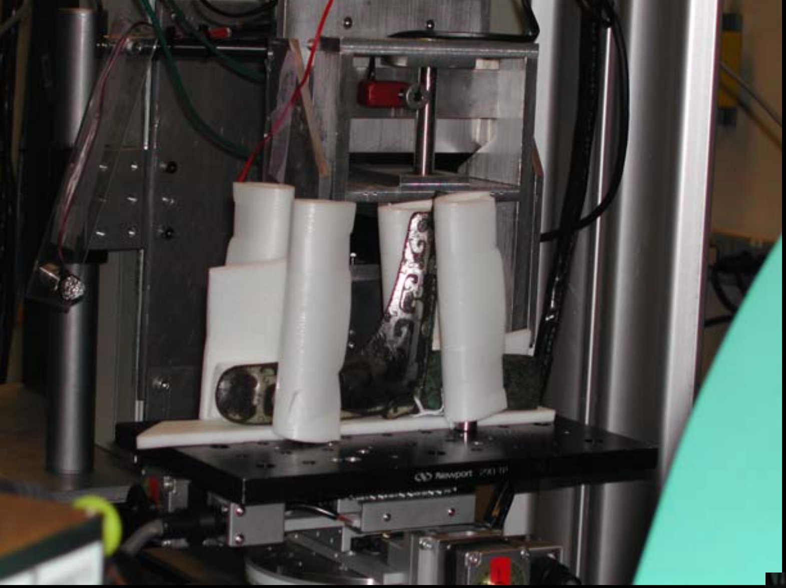
http://srs.dl.ac.uk/arch/other-communications.html

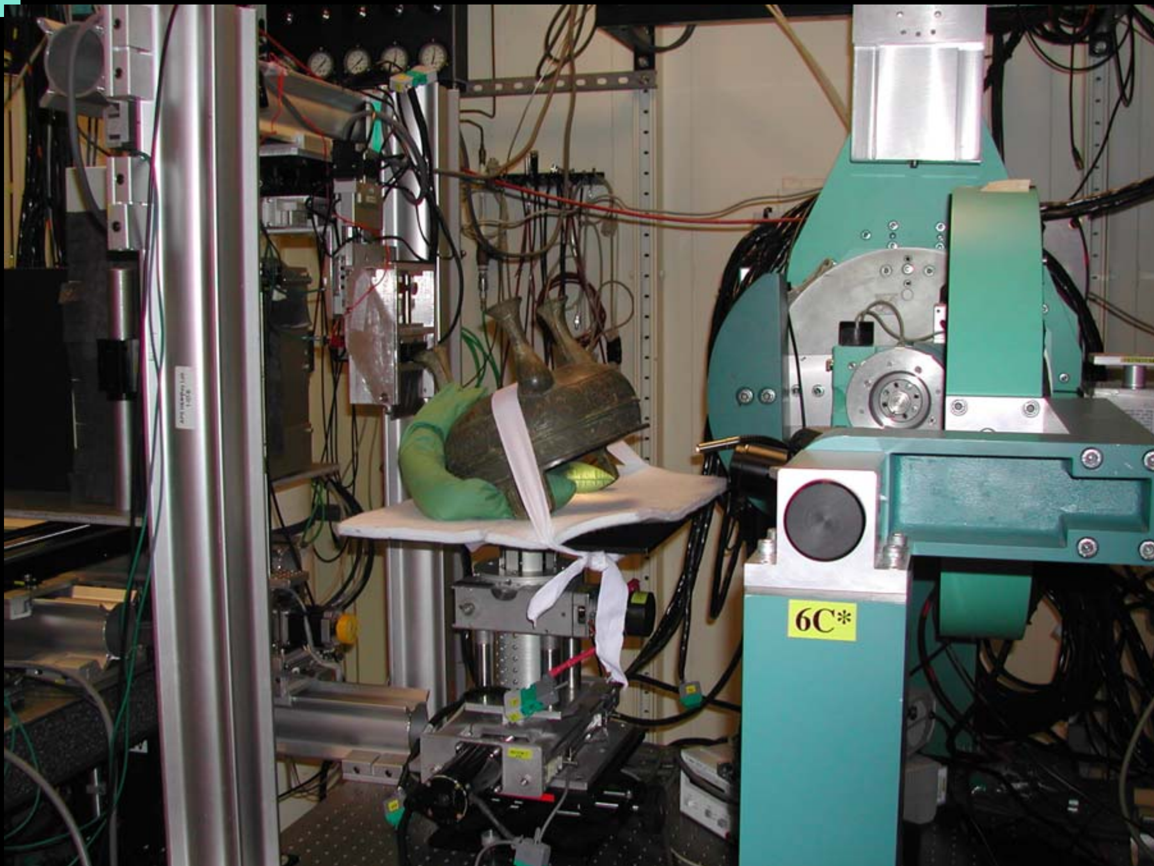
E. Pantos, Daresbury Laboratory, UK

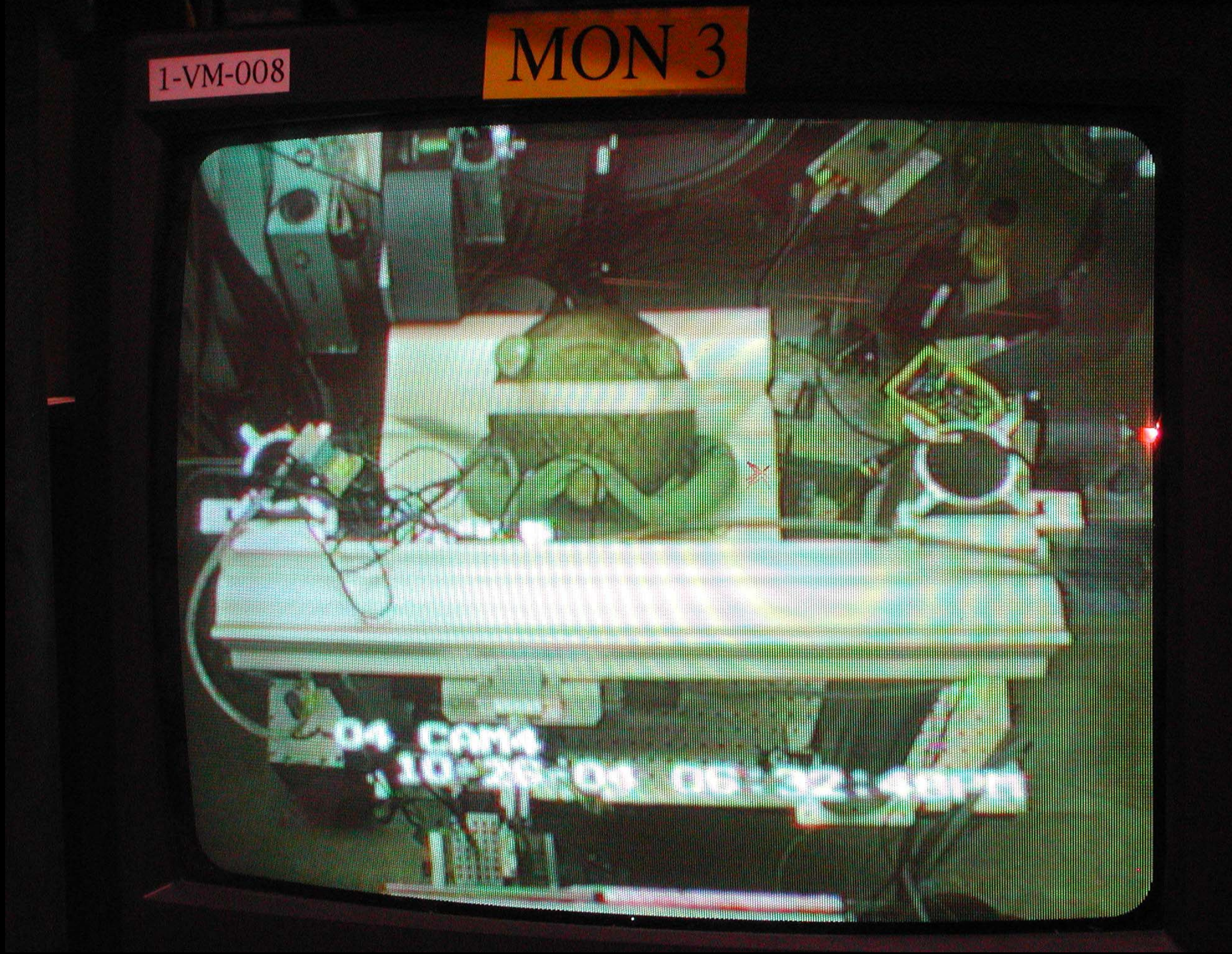
Relative importance (1995-1998) of different X-Ray application fields in archaelogy and art history



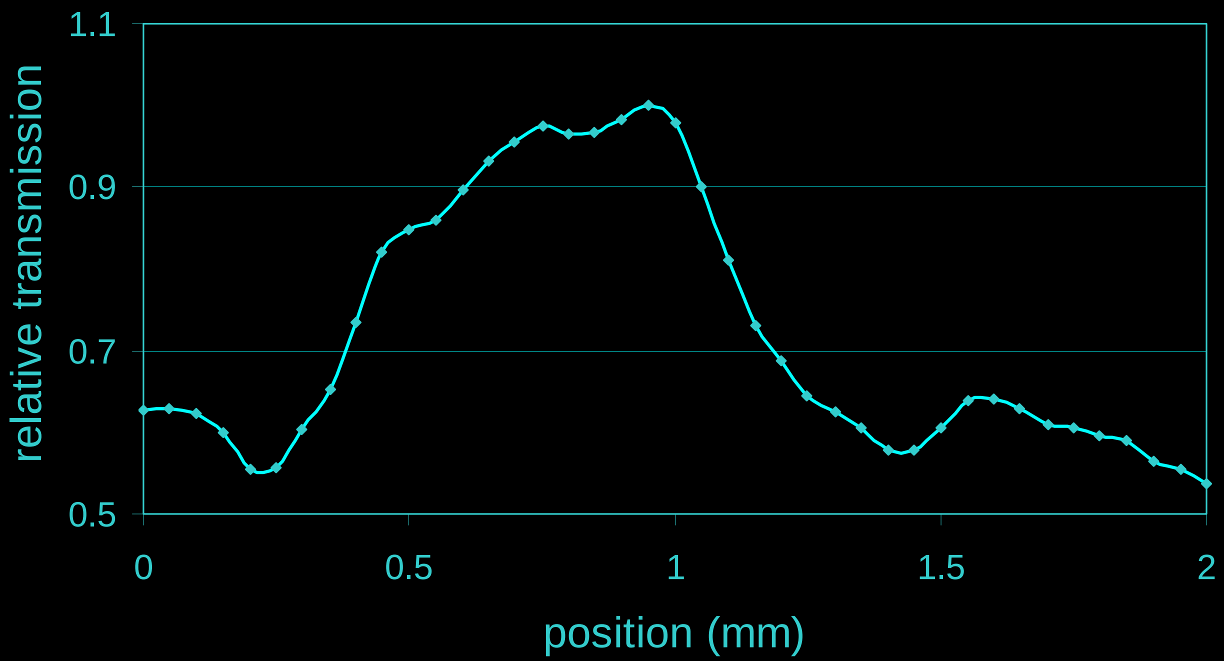
New application: photographs

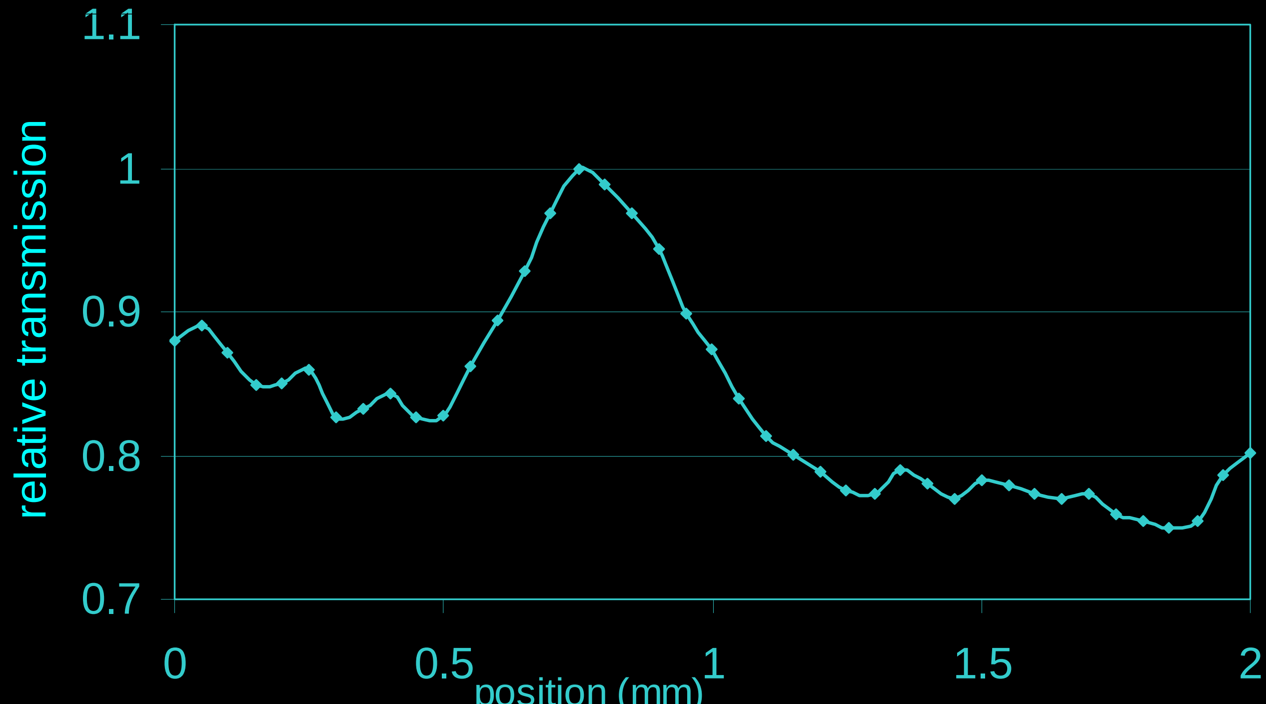



6C*


1-VM-008
MON 3
04 CAM4


Sector 1


1.1
0.9
0.7
0.5
relative transmission
0
0.5
1
1.5
2
position (mm)


1.1
1
0.9
0.8
0.7
relative transmission
0
0.5
1
1.5
2
position (mm)

SYNCHROTRON RADIATION STUDIES OF ART AND ARCHAEOLOGICAL MATERIALS

- Depth – profiling
- Spatial resolution
- Non-destructivity

Thanks to :

•the A.W. Mellon Foundation;

•my colleagues at the Art Institute of Chicago;

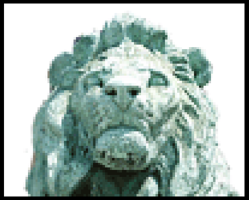
•Marco Leona (The Metropolitan Museum of Art);

•Giacomo Chiari (The Getty Conservation Institute);

•Lucia Toniolo (CNR-ICVBC, Milano)

•Colleagues at Northwestern University

•Dean Haeffner and his group at APS



The most beautiful thing we can experience is the mysterious.

It is the source of all true art and science.

- Albert Einstein