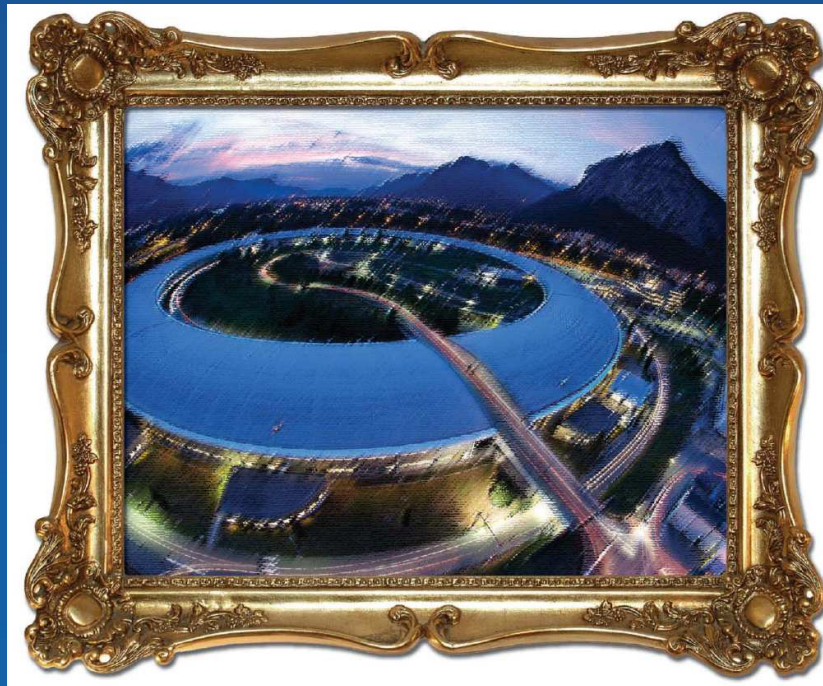


Synchrotron-based FTIR microscopy for the analysis of ancient artistic materials

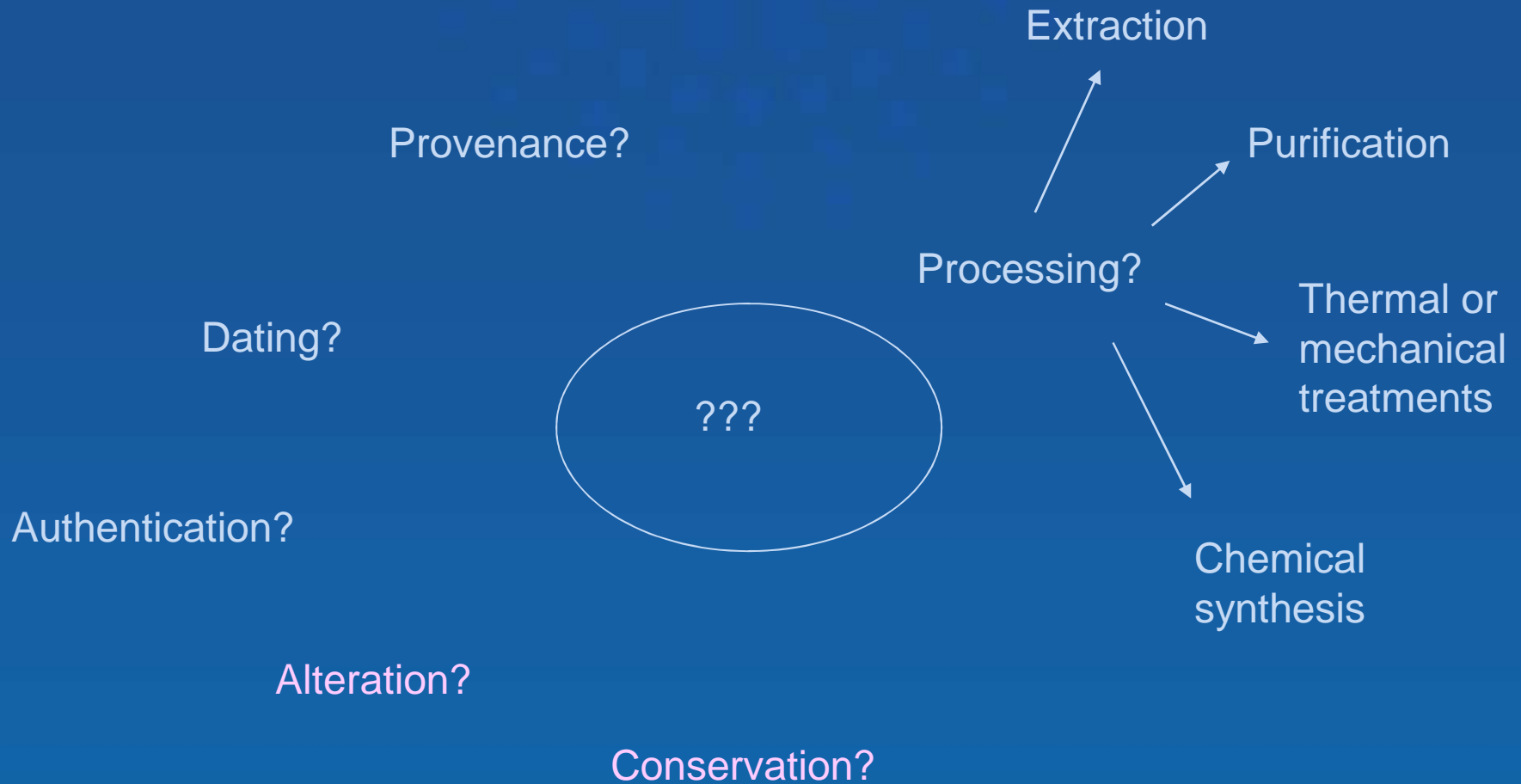


M. Cotte^{1,2}

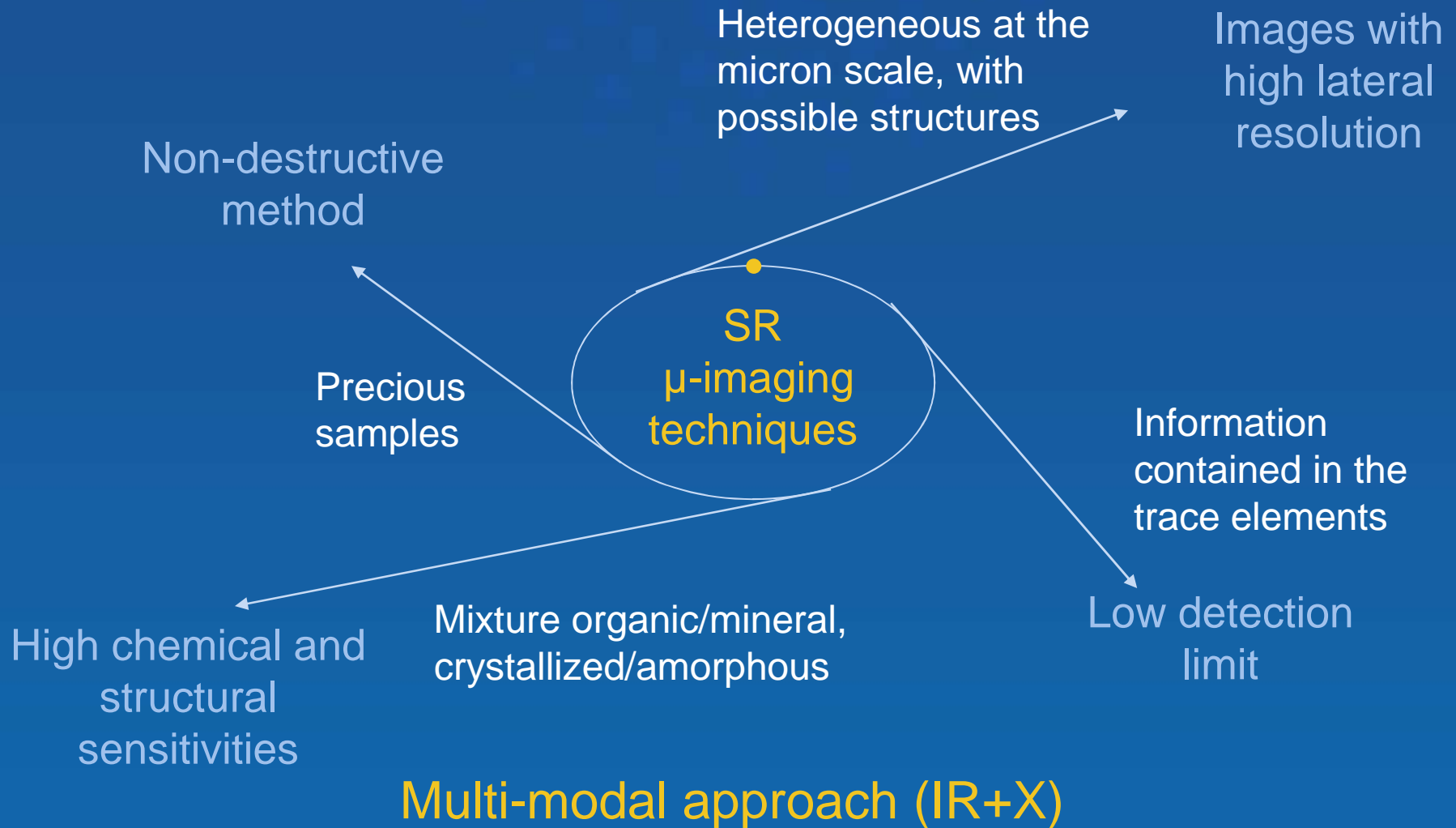
- 1- European Synchrotron Radiation Facility (Grenoble)
- 2- Centre of Research and Restoration of the French Museums (Paris)

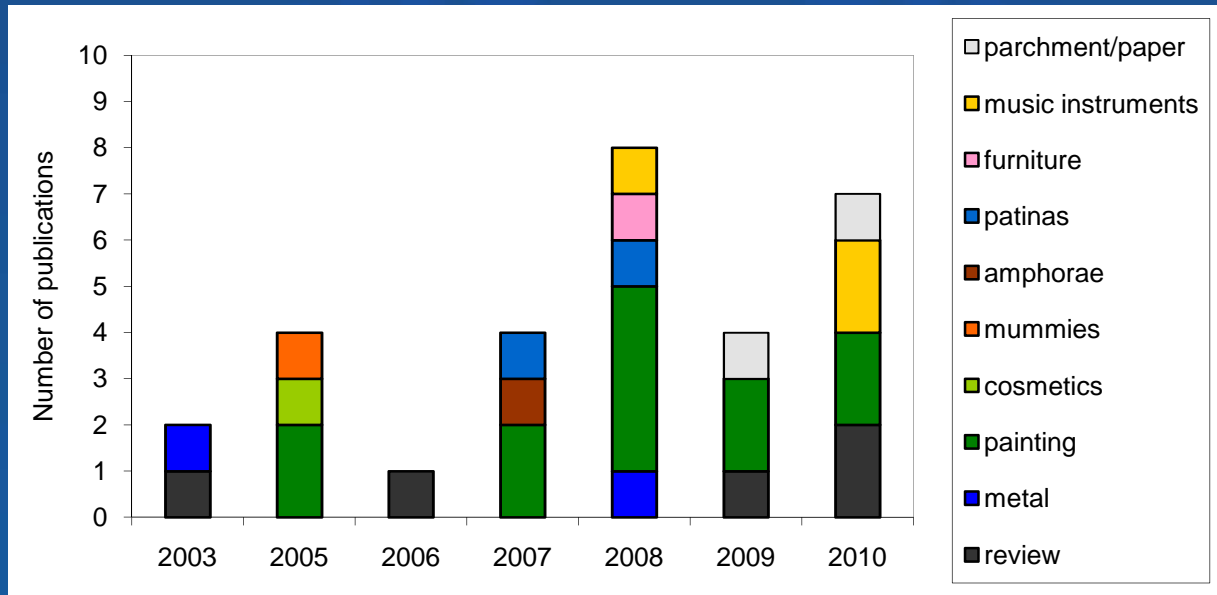
Different objectives of analyses on CH items

The archaeologists, conservators and restorators' point of view



The chemists and physicists' point of view





An increasing interest...

... that may be slow down due to difficult sample preparation

... and to high competition with lab instruments

“Recent applications and current trends in Cultural Heritage Science using Synchrotron-based Fourier transform infrared micro-spectroscopy”

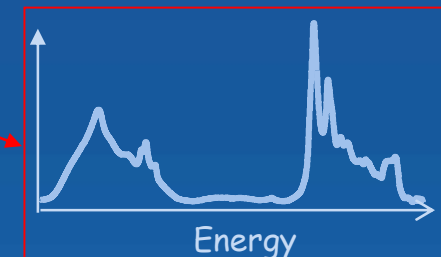
Cotte, M., Dumas, P., Taniguchi, Y., Checroun, E., Walter, P. and Susini, J., Comptes Rendus Physique, Académie des Sciences, (2009), 10, 590.

Combination of FTIR with X-ray techniques

μ FTIR
spectroscopy

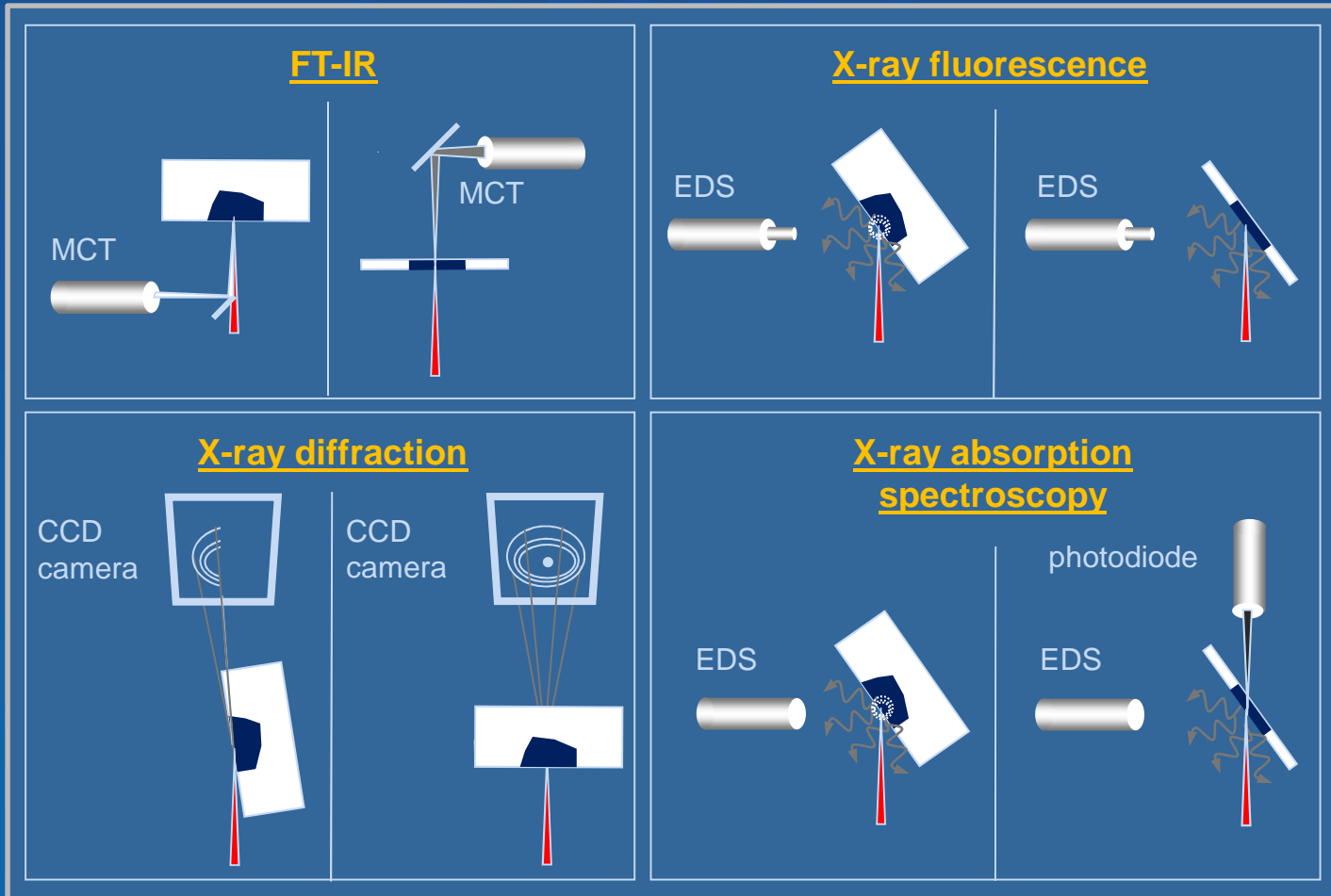
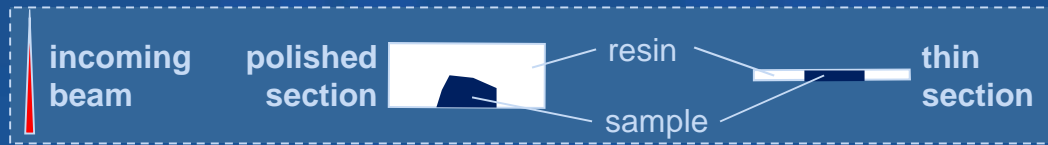


μ X-ray analysis
fluorescence
diffraction
absorption spectroscopy



A similar approach but different technical constraints

Experimental configuration: "reflection" vs. "transmission"



Polished cross-section: importance of surface quality (ion milling, ultra-microtome...):



- ☺ classical preparation for Cultural Heritage
- ☹ no signal in transmission, interference of embedding resin

Measurement in ATR or reflection

Thin cross-section: requires a microtome to get to appropriate thickness (2-5 μ m)

- ☺ Measurement in transmission: better quality of spectra
- ☹ sample preparation can be arduous, possible interference of resin



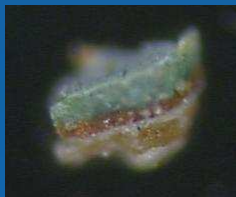
Embedding in KBr and single face or double-face polished

- ☺ No interference from embedding resin
- ☹ sample preparation can be arduous, possible complete loss of the sample for double-face polishing

Pressing with a micro-compression diamond cell:

requires a good positioning of the fragment before pressure

- ☺ better quality of spectra in transmission, no interference from embedding media
- ☹ structure is somewhat distorted, sample removing can be difficult



Cosmetics in Ancient times



Reed from Egypt, 13th BC
Louvre Museum

In collaboration with

Ph. Walter

Centre of Research and Restoration of French Museums,
Paris, France

P. Dumas

LURE/SOLEIL, Orsay, France

B. Fayard, J. Susini

European Synchrotron Radiation Facility, Grenoble, France

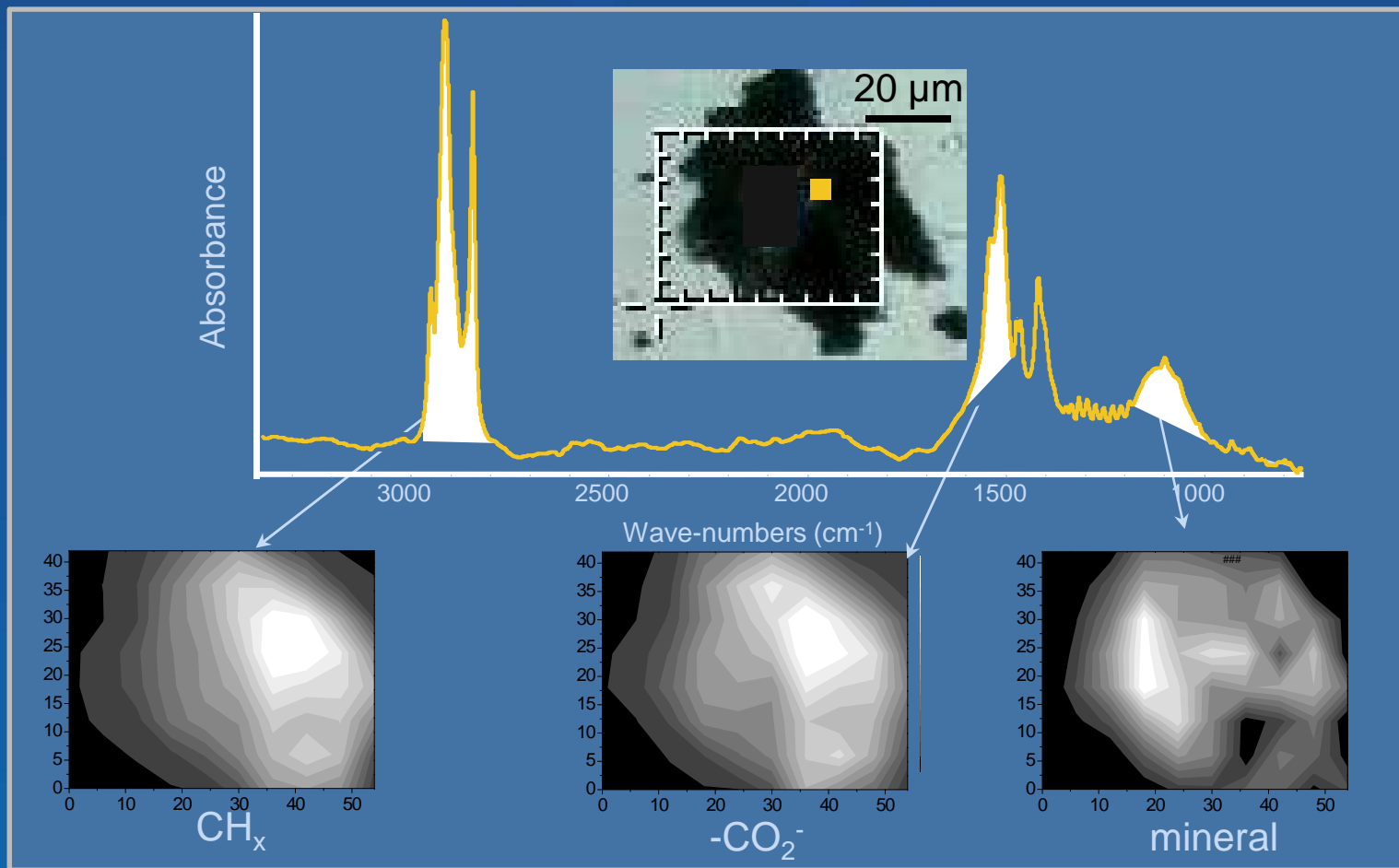
M. Cotte et al, *Journal of Controlled Release* (2004) **97**, 269

M. Cotte et al., *Analytica Chimica Acta* (2005), **553**, 105

M. Cotte et al, *Talanta* (2006), **70**, 1136

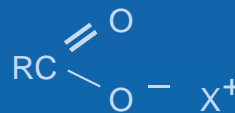
Chemical analysis of ancient cosmetics

Identification of the ingredients by μ -FTIR:

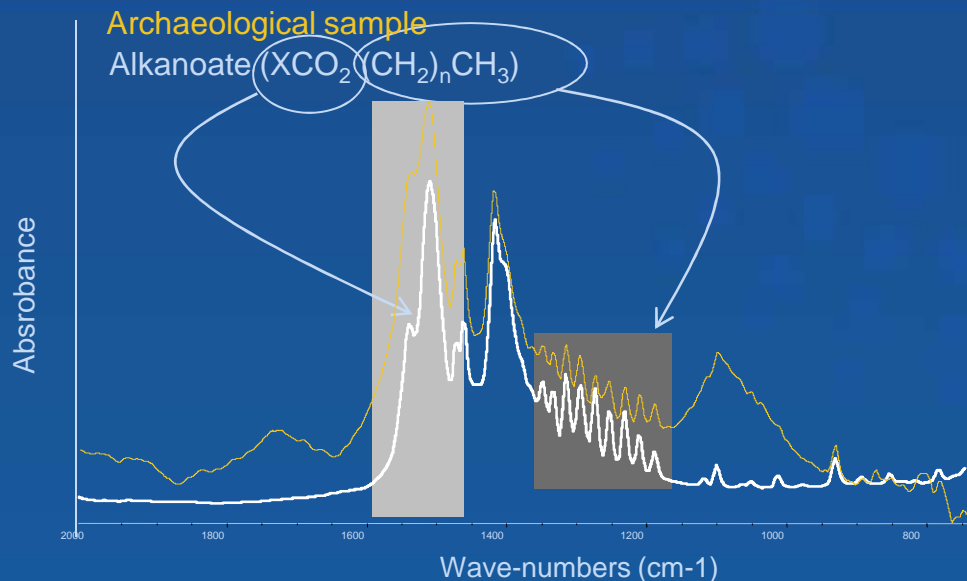


Band identification easier thanks to chemical images

fatty soap

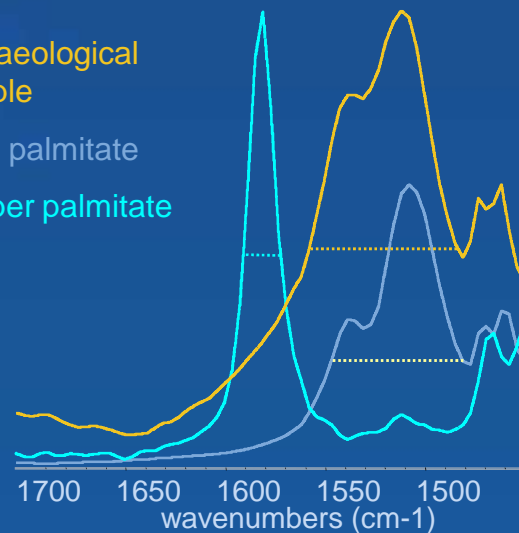


Chemical analysis of ancient cosmetics



Alkyl chain identification

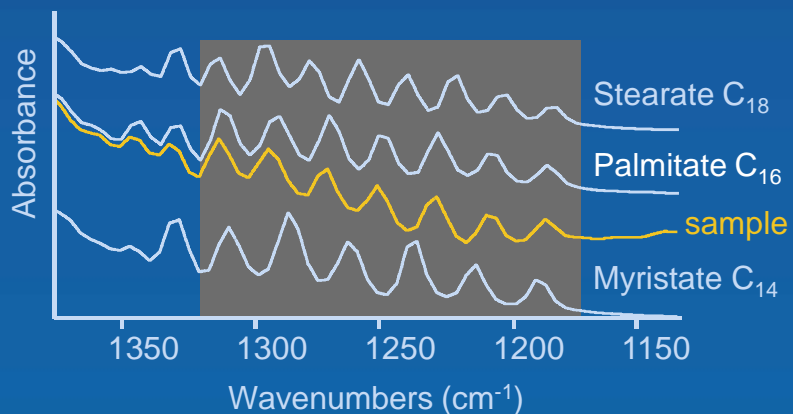
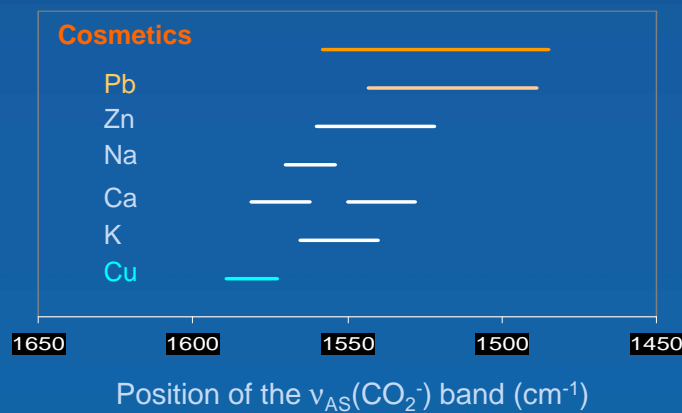
Archaeological sample
Lead palmitate
Copper palmitate



Cation identification

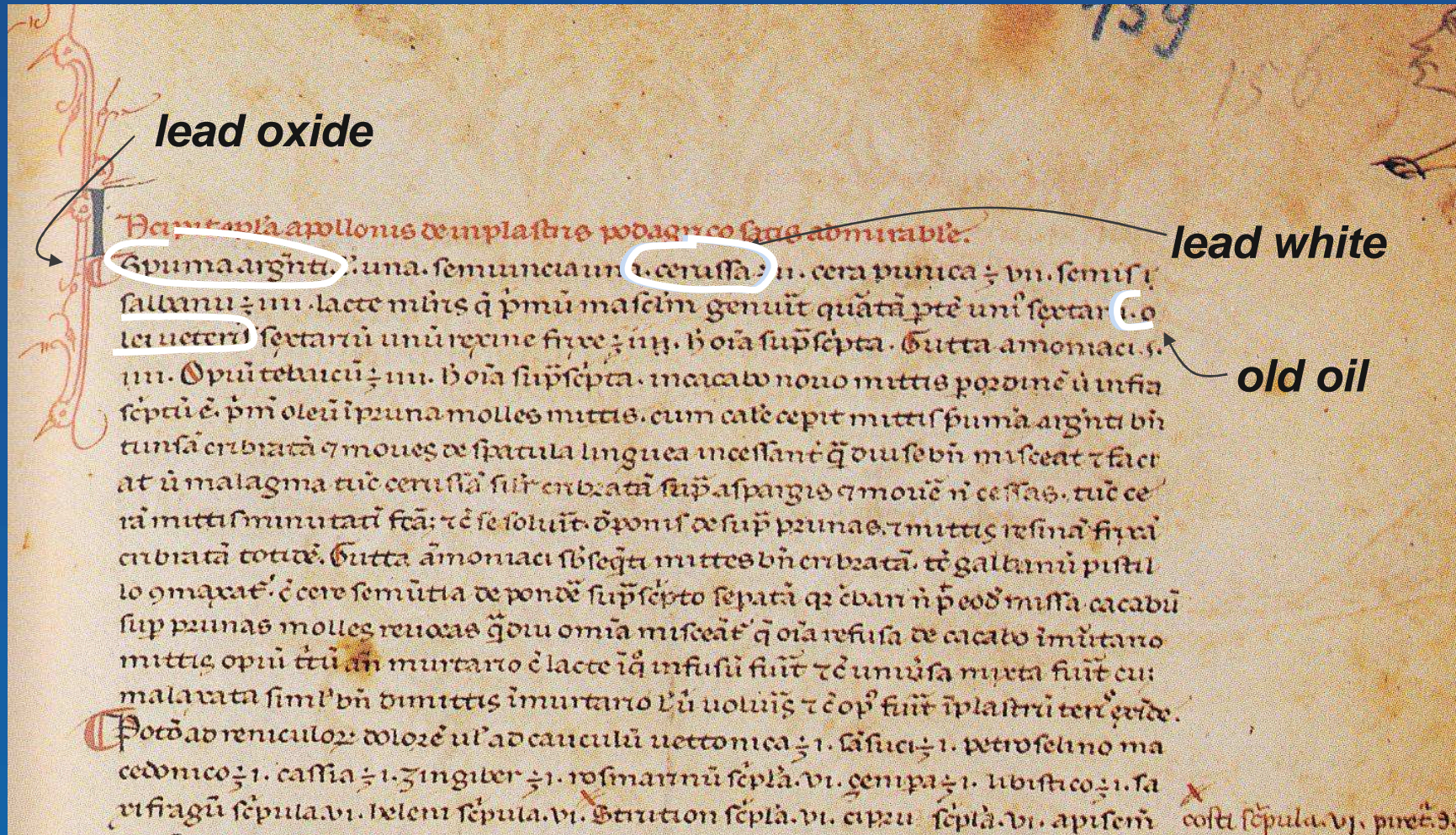
Cosmetics

- Pb
- Zn
- Na
- Ca
- K
- Cu



On purpose synthesis or result of a long term interaction fat/lead salts?

Reconstitution of ancient recipes



T(°C)

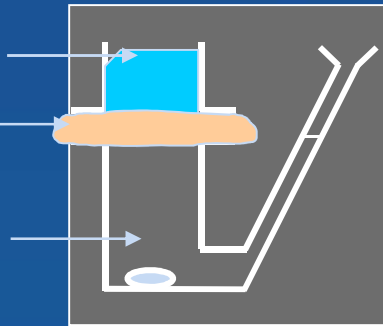
Oil (2) + PbO (1) + water (2) (+ extra ingredients) → lead plaster

saponification of fat by PbO

Study of lead transdermal penetration

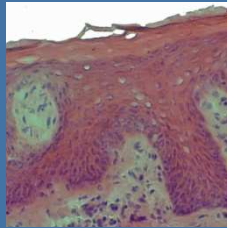
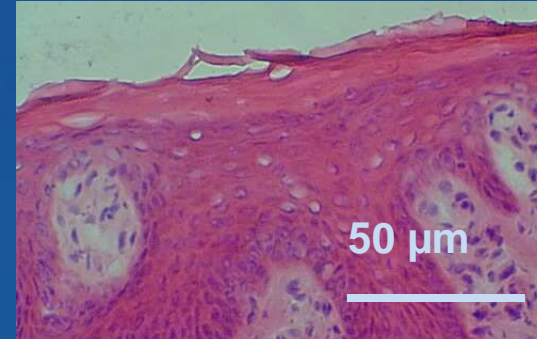
Principle of the diffusion experiment

solution with or without lead
 skin
 buffer solution
 pH=7.4



24h at 37°C

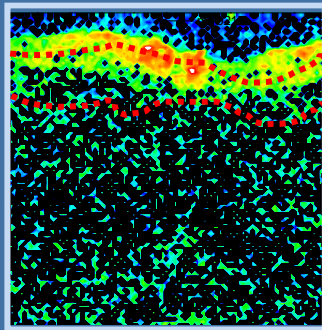
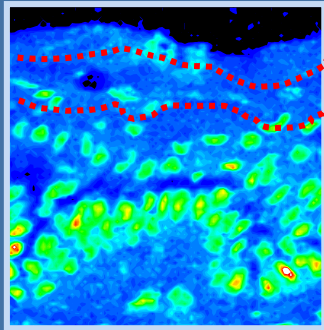
Microtomy



μXRF @ ID21,
 ESRF, Grenoble

P

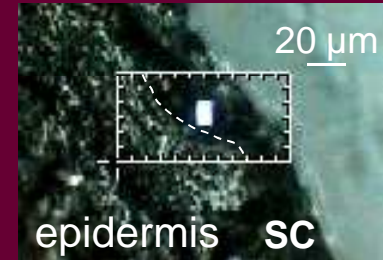
Pb



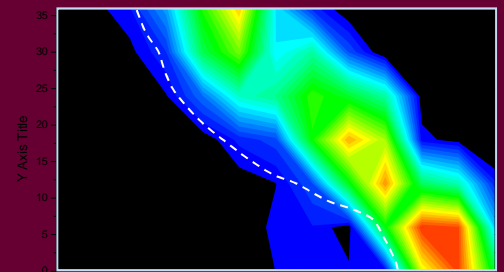
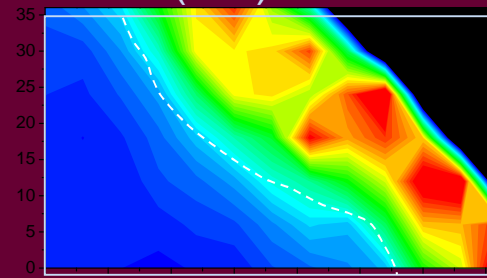
Map: 100×100 μm², pixel: 1×1 μm²



μFTIR @ LURE,
 Paris



Palmitic acid (C16) (deuterated)
 ν(CH)/amide I ν(CD)



Map: 72×36 μm², pixel: 6×6 μm²

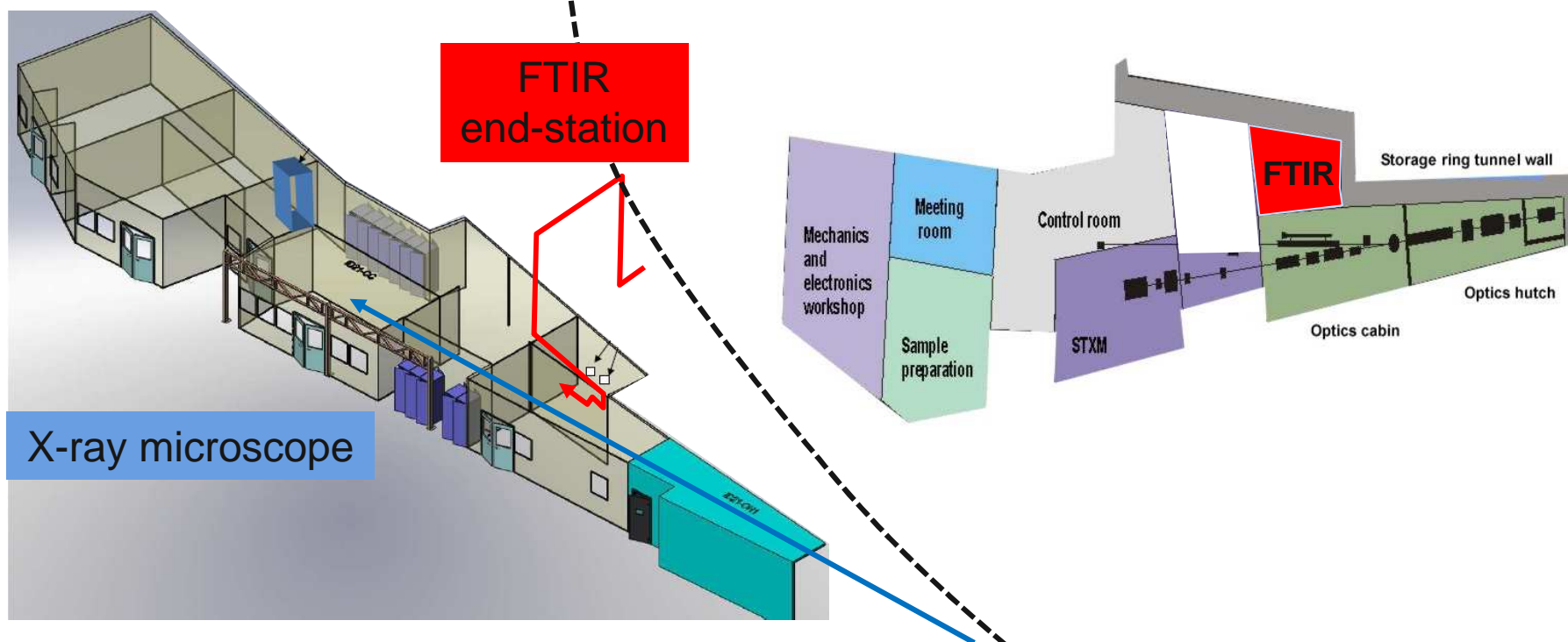
Combination of FTIR with X-ray techniques



The ID21 beamline, ESRF

FTIR end-station

X-ray microscope



Ritual patina of African statuettes

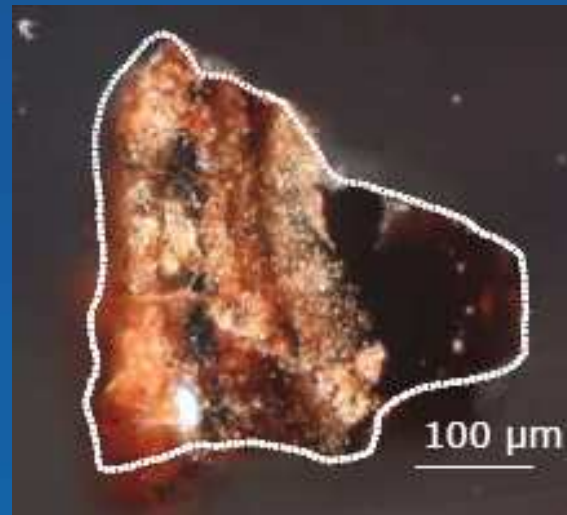


Dogon statuette, beginning 20th,
Quai Branly Museum, Paris

In collaboration with

V. Mazel, P. Richardin, Ph. Walter

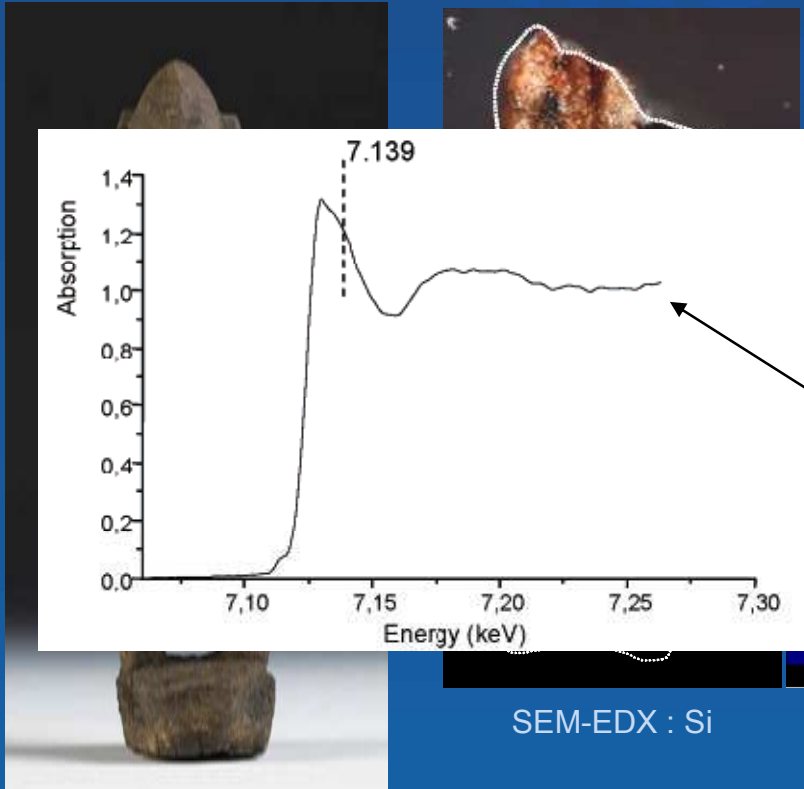
Centre of Research and Restoration of French Museums,
Paris, France



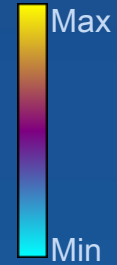
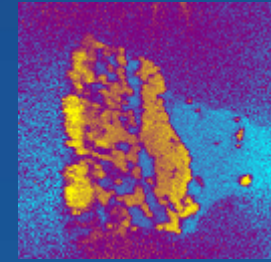
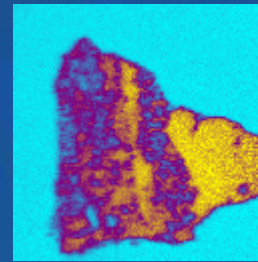
V. Mazel et al., *Analytical Chemistry*, (2007) **79**, 9253

V. Mazel et al., *Studies in Conservation*, (2008) **9**, 347

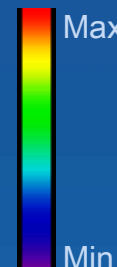
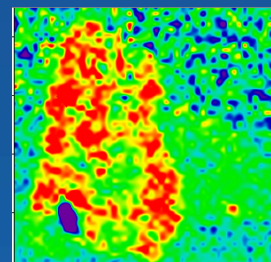
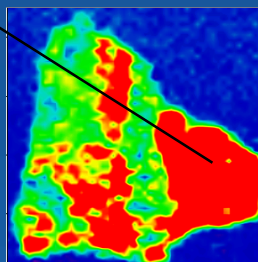
Analysis of polished cross-sections of African patina Combination of μ FTIR, μ XRF and μ XANES



Dogon statuette, beginning 20th,
Quai Branly Museum, Paris



ToF-SIMS



SR-FTIR

+ Fe XANES =
blood

+ SEM = starch grains
(mil)

Heterogeneous patina, four layers of ritual materials
⇒ Compatibility with successive libations

V. Mazel et al., *Analytical Chemistry*, (2007) **79**, 9253
V. Mazel et al., *Studies in Conservation*, (2008) **9**, 347

Protrusions in oil paintings



In collaboration with

E. Checroun

Institut National du Patrimoine, Paris

M. Cotte et al, *Talanta* (2006), **70**, 1136

M. Cotte et al, *Applied Physics A*, (2007) 89 (4), 841-848

Analysis of thin cross-sections of original and model protrusions Combination of μ FTIR, μ XRF and μ XANES

Anonymous portrait, 1610, Châtillon-sur-Seine



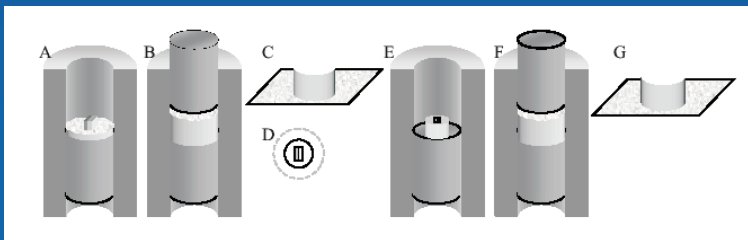
Main degradation signs: protrusions



Modern fac-simile, 1 month old



Thin sections obtained by polishing KBr pellet:



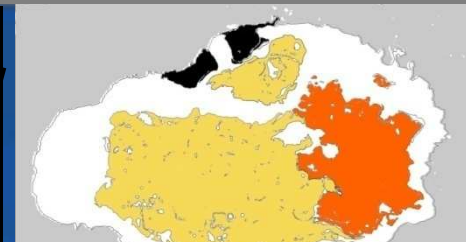
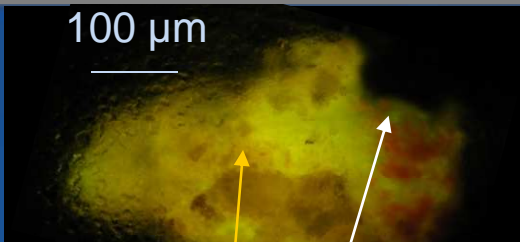
<http://www.amolf.nl/publications/theses/weerd/>

Fragment covered with an Al foil and cut with a microtome



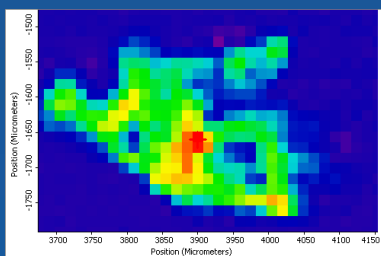
Analysis of thin cross-sections of original protrusions

Combination of μ FTIR and μ XRF

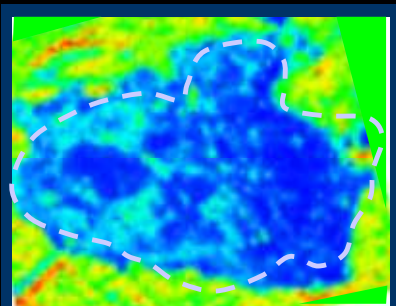


Thin sections were prepared by double-face polishing of KBr pellet embedding a painting fragment

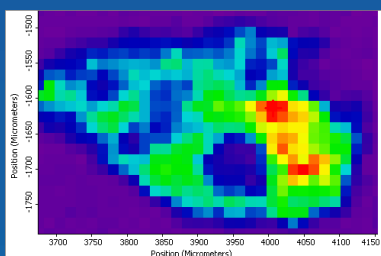
K: kaolinite



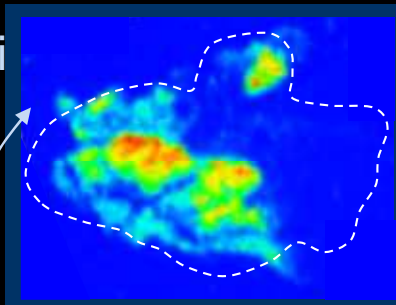
Br



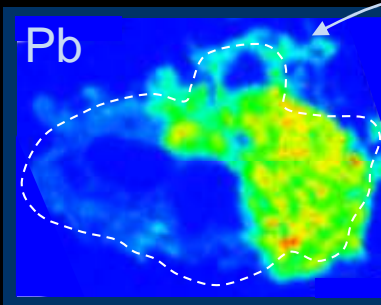
F: fatty chains



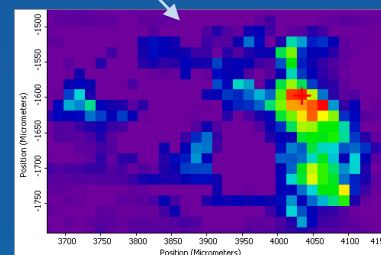
Si



Pb



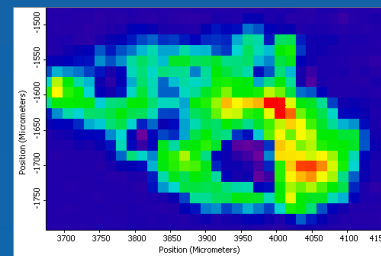
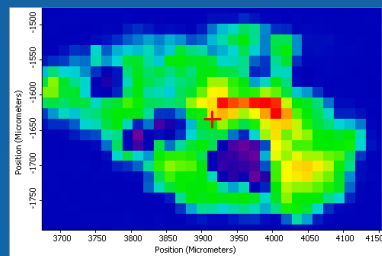
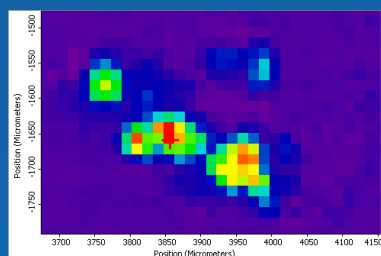
C: carboxylates



quartz

E: ester

A: acid



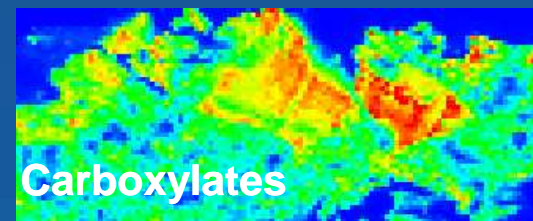
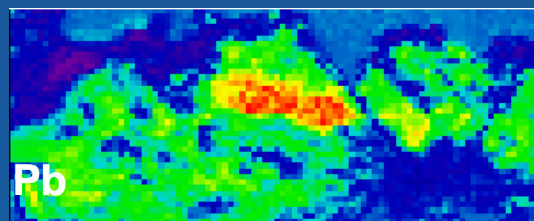
Analysis of thin cross-sections of model protrusions

Combination of μ FTIR, μ XRF and μ XANES

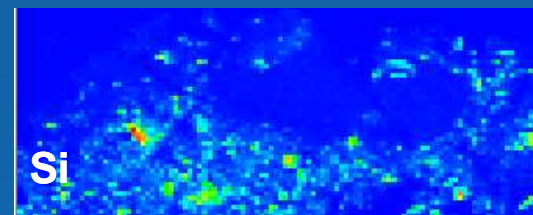
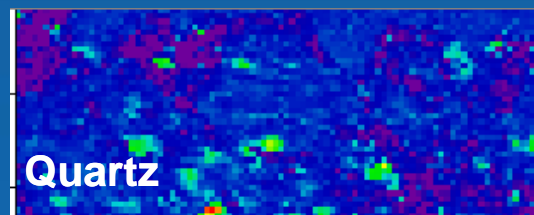
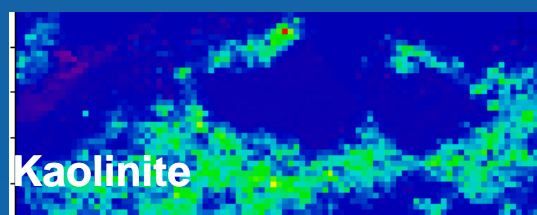
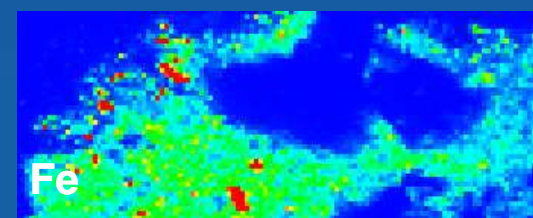
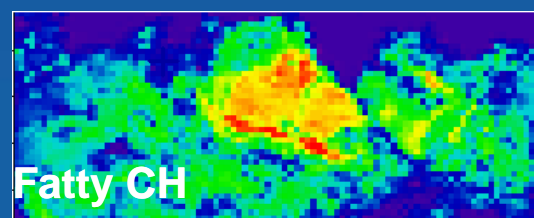
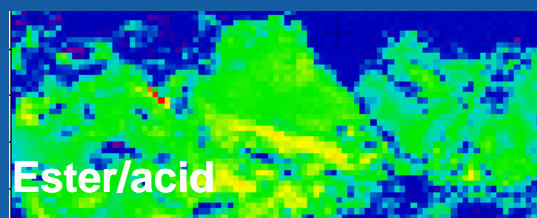


Thin sections were obtained with a microtome: sample was previously covered with an Al foil

max



min

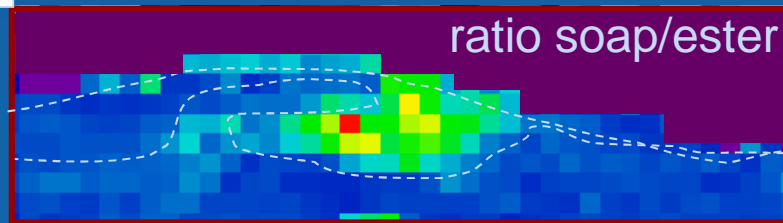
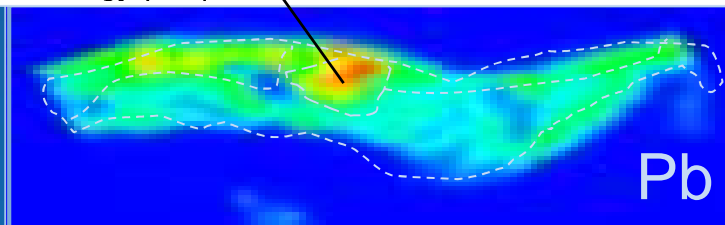
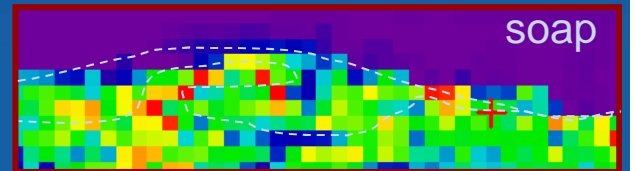
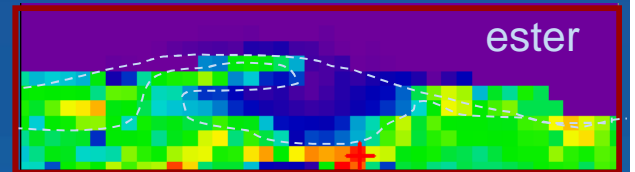
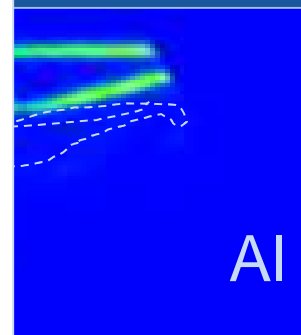
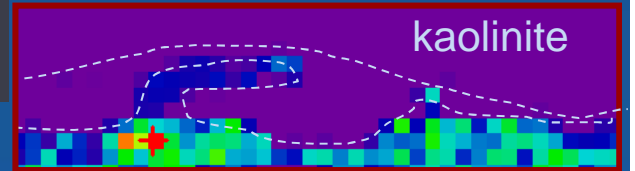
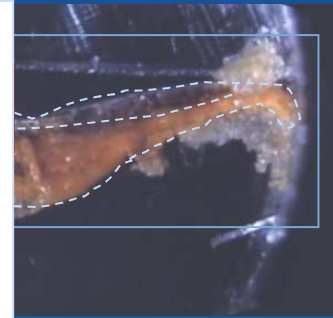
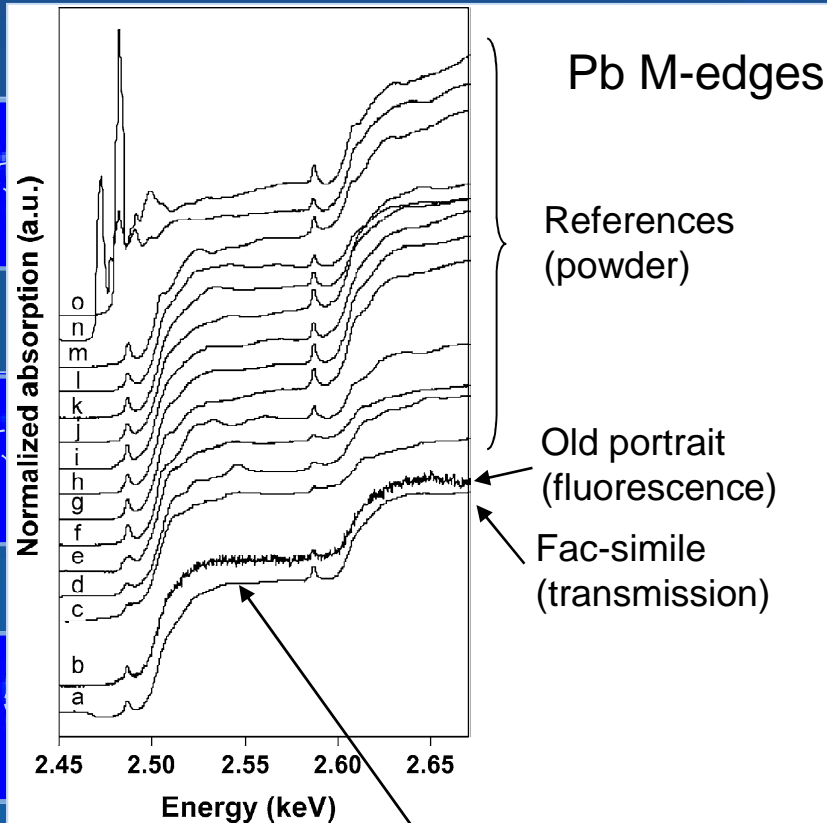


Very good similarity after only 1 month

μ X-ray fluorescence

5 μ m sections obtained with a microtome

μ -FTIR



Adequate preparation to carry out XANES at lead M-edges

Metal carboxylates in paintings

Meilunas	Studies in Conservation	1990	Pb
Plater	Polyhedron	2002	Pb
Boon	ICOM proceeding	2002	Pb
Noble	Art Matters	2002	Pb
Van der Weerd	Zeitschrift for Kunsttechnologie und Konservierung	2002	Pb
Higgit	The National Gallery Technical Bulletin	2003	Pb
Van der Weerd	Zeitschrift for Kunsttechnologie und Konservierung	2004	Zn
Keun	Analytical chemistry	2004	Pb
Boon	Microscopy and microanalysis	2005	Pb
Cotte	Applied physics A	2007	Pb
Mazzeo	Analytical and Bioanalytical Chemistry	2008	Cu, Pb, Mn, Zn, Cd
Salvado	Talanta	2009	Ca, Cu, Pb

Not an exhaustive list

Metal carboxylates in paintings

Meilunas	Studies in Conservation	1990	Pb	degradation
Plater	Polyhedron	2002	Pb	degradation
Boon	ICOM proceeding	2002	Pb	degradation
Noble	Art Matters	2002	Pb	degradation
Van der Weerd	Zeitschrift for Kunsttechnologie und Konservierung	2002	Pb	degradation
Higgit	The National Gallery Technical Bulletin	2003	Pb	degradation
Van der Weerd	Zeitschrift for Kunsttechnologie und Konservierung	2004	Zn	degradation
Keun	Analytical chemistry	2004	Pb	reaction over centuries
Boon	Microscopy and microanalysis	2005	Pb	degradation
Cotte	Applied physics A	2007	Pb	synthesis
Mazzeo	Analytical and Bioanalytical Chemistry	2008	Cu, Pb, Mn, Zn, Cd	degradation
Salvado	Talanta	2009	Ca, Cu, Pb	Reaction compounds

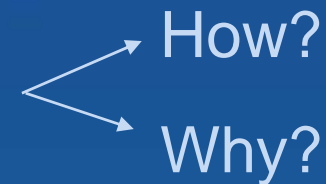
When does the controlled synthesis stop and the degradation start?

Question 1:

Are they willingly synthesized ?

or

Are they due to long term interactions ?



Question 2:

Can we determine their age?

Looking for information in ancient recipes



© NPG 6538

Sir Theodore Turquet de Mayerne
(1573-1655)

J'ay pris quatre onces d'huile de noix fort bonnes non puantes et ay jetté dedans une once de Litharge d'or bien lavée, puis les ay nourri ensemble dans un poelson sur un petit feu que la litharge s'est entièrement dissoulte et incorporée avec l'huile. Alors j'y ai jetté quatre ou cinq ceiullerées d'eau laquelle estant froide fait un fort grand bruit et y doibt estre mise chaude. Alors le feu a été augmenté et la matière a bouilli remuant tousjours jusques à tant que par la consommation de l'eau le tout se soit expaissi en Ebullition en consistance de beurre en Esté, un peu plus espais que du miel, comme un unguent liquide. Ceste mixtion n'est pas puante. Et peult servir de vernix au fer pour empescher la rouille. Au bois sur des couleurs obscures comme sur noir ou terre d'ombre et est bonne pour du cuir, taftas, toile, et choses semblables.

Pour imprimer tableaux. Broyés de l'ocre jaulne avec cet unguent ou huyle. L'ocre ayant esté au préalable broyée avec eau, et bien séchée, et couchés cette mixtion sur vostre toile bien tendue sur le châssis sans aucune colle ou autre chose, qui puisse faire rompre ou escailer la toile. Laissés seicher puis polissés avec une pierre ponce, et donnés une seconde couche avec vostre huile et ocre l'estendant avec le cousteau selon l'art et ainsi vostre toile estant seichée sera imprimée suffisamment. »

4 walnut oil + 1 PbO

Little fire
+ water
↗ heating

“huile de litharge”

ochre

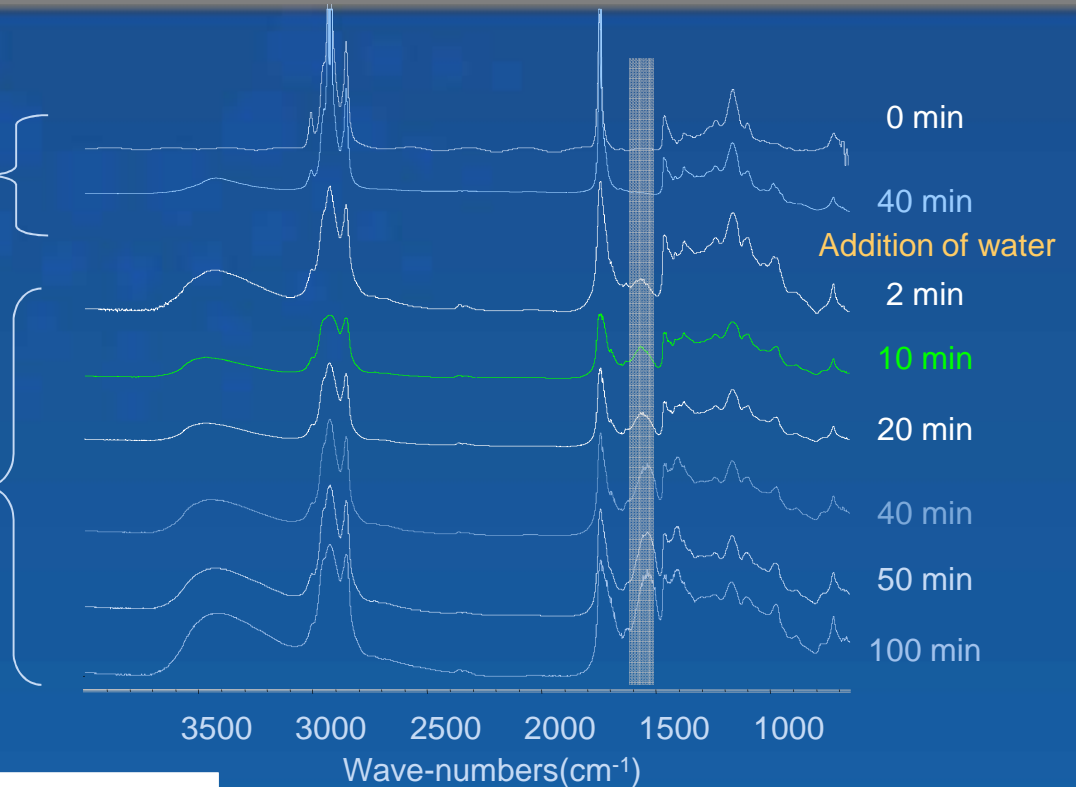
Oil for canvas ground layer

Reconstruction of painting lead medium

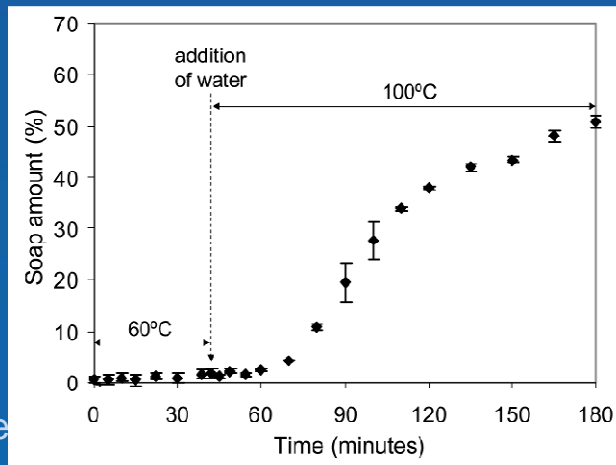
4 walnut oil
+
1 PbO
↓
“huile de litharge”

1/ Little fire 60°C
(0h40)

2/ + water
↗ heating 100°C
(1h30)



Sir Theodore Turquet de Mayerne (1573-1655)



The product is a pasty mixture of lead soaps (solid) and unsaponified oil (liquid).

⇒ Good mechanical properties for application on canvas

Answer 1a:

Lead soaps can be synthesized in only ~2 hours by mixing oil, water and lead oxide.

Answer 1b:

The synthesis of lead soaps provides a better **control of the consistency** of the product (paste).

The addition of water enables the control of curing temperature, hence the colour of the product.

Answer 2:

It is **difficult to determine the age** of lead soaps as we cannot determine precisely the conditions of preparation (reacting compounds? Water? Temperature?).

“Chemical reactions” does not systematically means alteration

naturenews

Published online 22 April 2008 | Nature | doi:10.1038/news2008770
News

Ancient

Were painters c

Philip Hall

Artists in Afghanis
practice in Europ

Yoko Taniguchi of
of Buddhist painti
say that the paint



Los Angeles Times | Business

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Oil painting appeared centur earlier -- in Asia

The real discovery is that
oil is present as metallic soaps



Earliest oil paintings discovered in Afghanistan

Posted Wed Apr 23, 2008 8:23am AEST
Updated 5 hours 54 minutes ago

Scientists say they have proved the world's first ever oil paintings were in caves near two destroyed giant statues of Buddha in Afghanistan.

Samples from paintings, dating from the 7th century AD, were taken from caves in Bamiyan.

The European Synchrotron Radiation Facility (ESRF) in



The Taliban destroyed two 6th century giant Buddhas in 2001 (file photo). (Reuters: Goran Tomasevic)

stan (CNN) -- Scientists have found what they described this week as the earliest oil covered.



FILE FOR CULTURAL PROPERTY TOKYO, JAPAN
v oil painting was going on for centuries Europe.

medium of drying oil, such as linseed oil.

In many European history and art books, oil painting is said to have started in the 15th century in Europe. But the team that used

Murals found on cave walls in Afghanistan prove that painting with oil had been going on in Asia for centuries before artists used the technique in Europe, scientists said this week.

Until now, art historians believed that oil painting started in Europe in the 15th century.

Scientists found the murals in a network of caves where monks lived and prayed in the Afghan region of Bamiyan, according to a statement on the Web site of the European Synchrotron Radiation Facility, where the ancient paintings were analyzed.

Until 2001, two colossal 6th-century statues of Buddhas stood at the mouth of the caves. Then the Taliban, which then ruled Afghanistan, blew up the statues on the grounds that they were un-



Examples of oil paintings in the Afghanistan caves

Bamiyan Buddhist mural paintings

In collaboration with

Y. Taniguchi

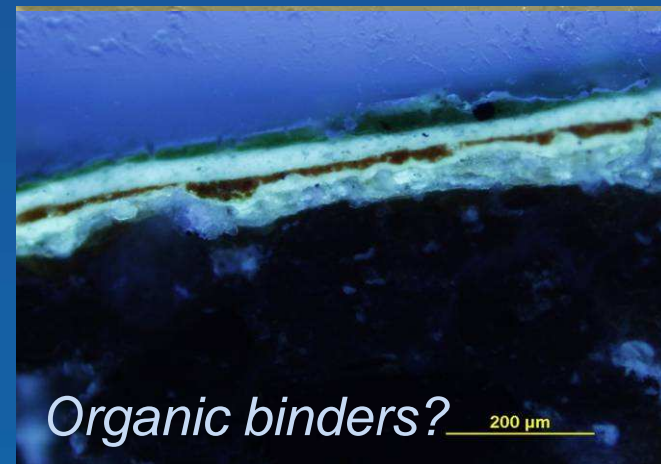
National Research Institute for Cultural Properties
Tokyo-Japan

E. Checroun

Institut National du Patrimoine, Paris



Buddhist paintings
Bamiyan
Afghanistan
5th-9th Century



- Historical knowledge/techniques?
- Degradation phenomena?

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

The context: Bamiyan Buddhist mural paintings



Samples were taken under the Ministry of Information and Culture of Afghanistan in a framework of Conservation Project of the Bamiyan Site. Credit/ (National Research Institute for Cultural Properties, Tokyo-Japan/UNESCO. Special thanks to Yoko Taniguchi and Emilie Checroun.

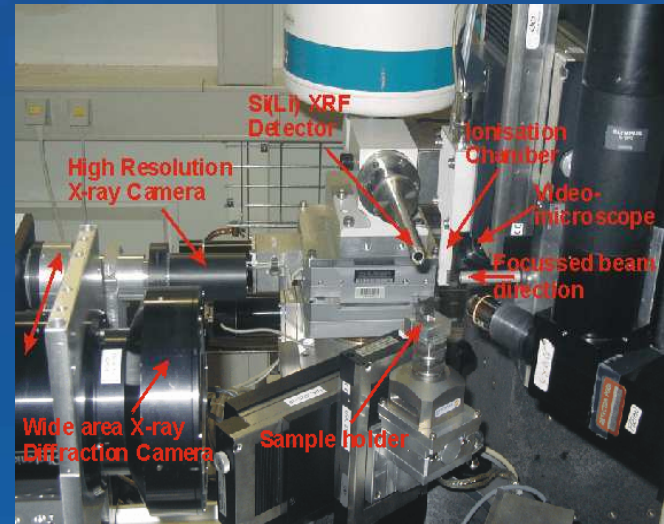
2 different set-ups for FTIR and X-rays

μ -FTIR ID21



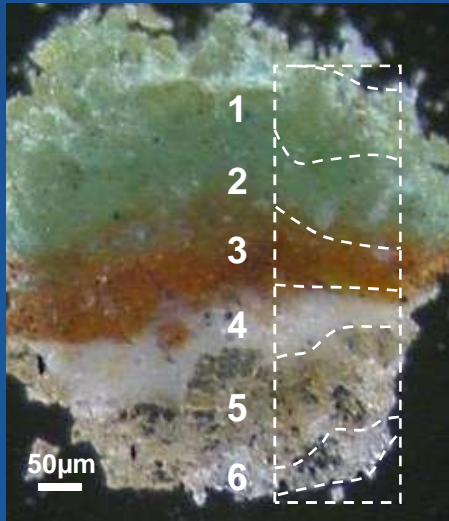
- Thin sections (~5 μ m)
- Pressed fragments

μ -XRF / μ -XRD ID18F



- Thin sections (~30 μ m)

SR-based micro-FTIR analysis

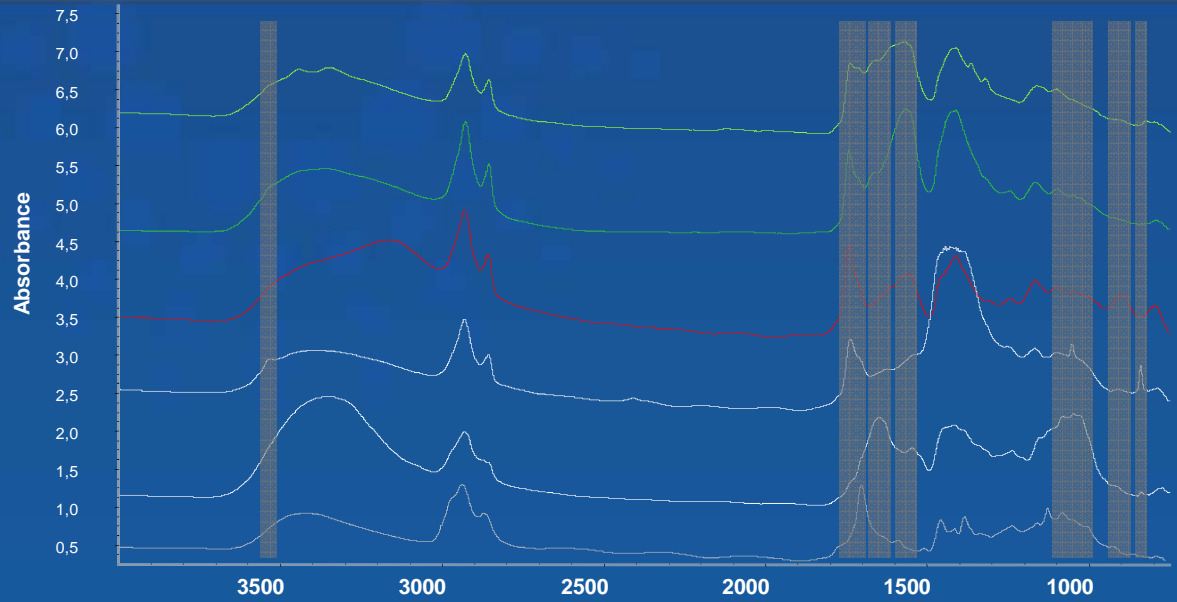


Step / beam size: 12×12 μm²

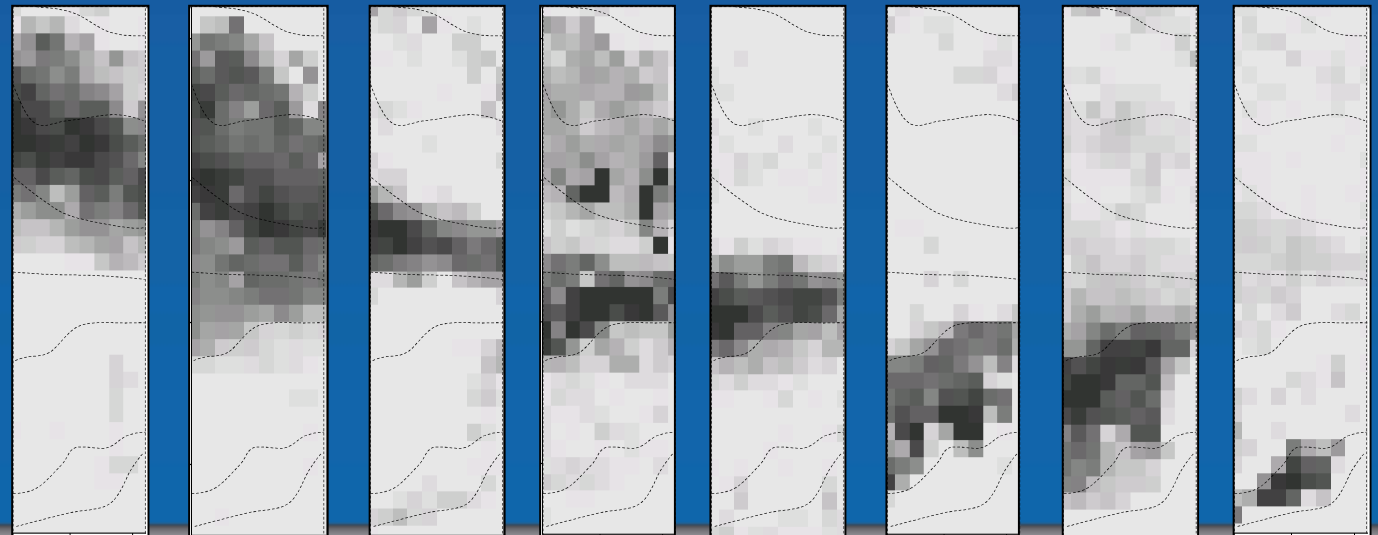
Map size: 144×384 μm²

Pb and Cu
carboxylates

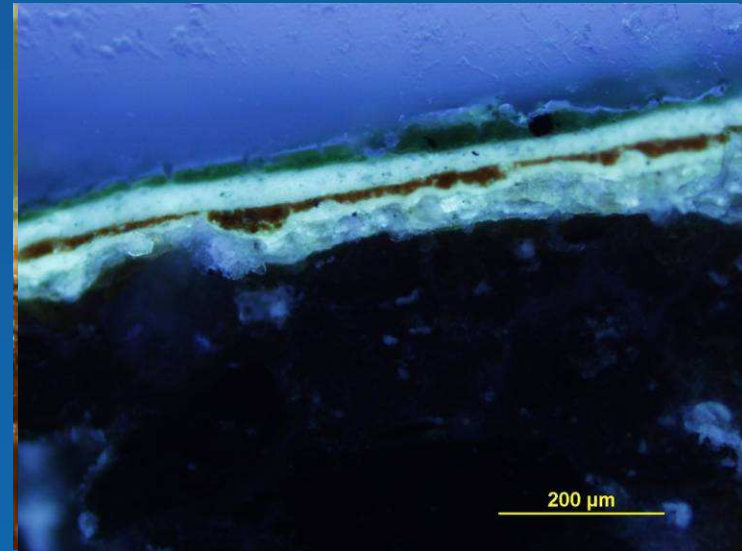
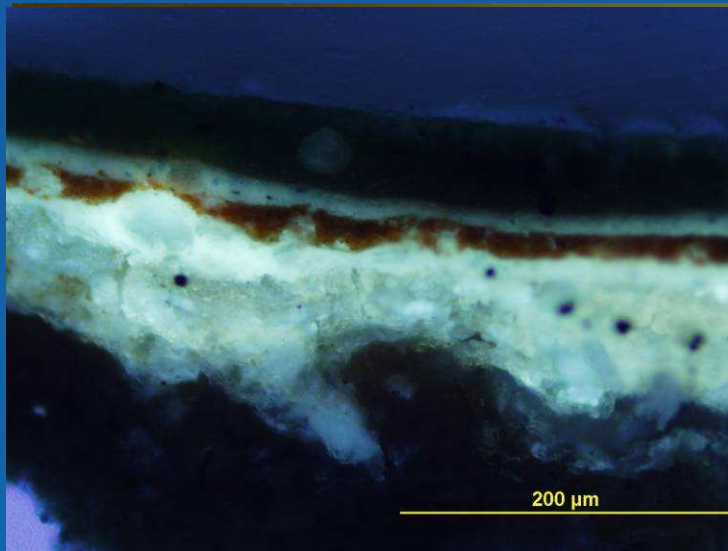
ID21



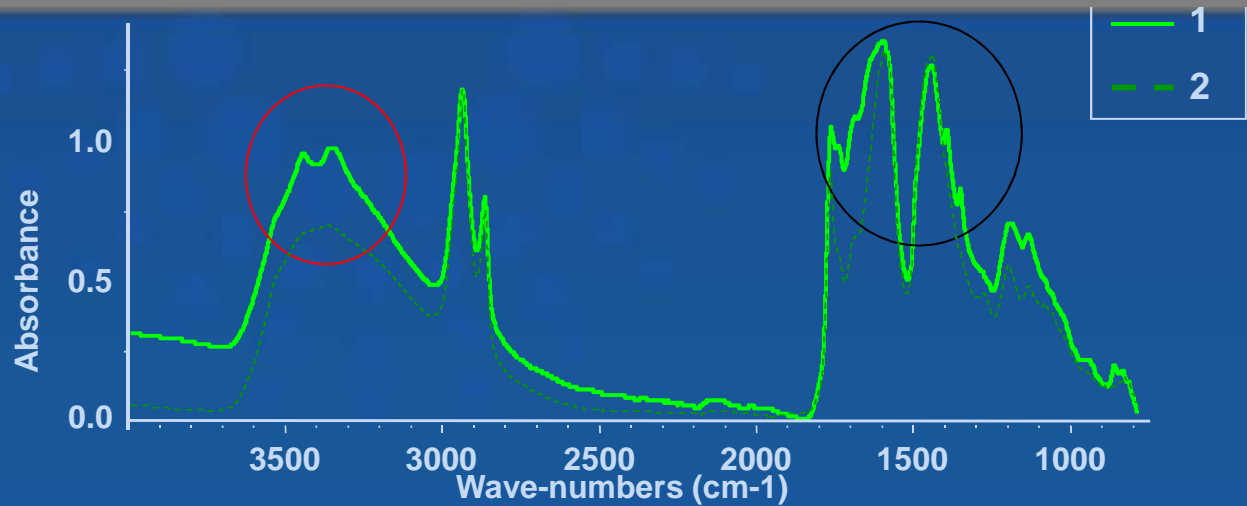
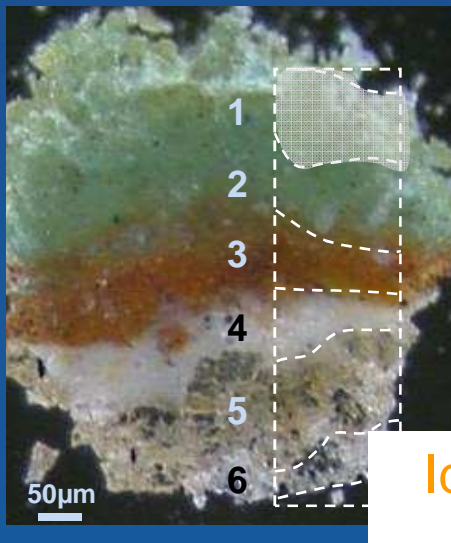
esters goethite hydro-cerussite cerussite amides poly-saccharides acids



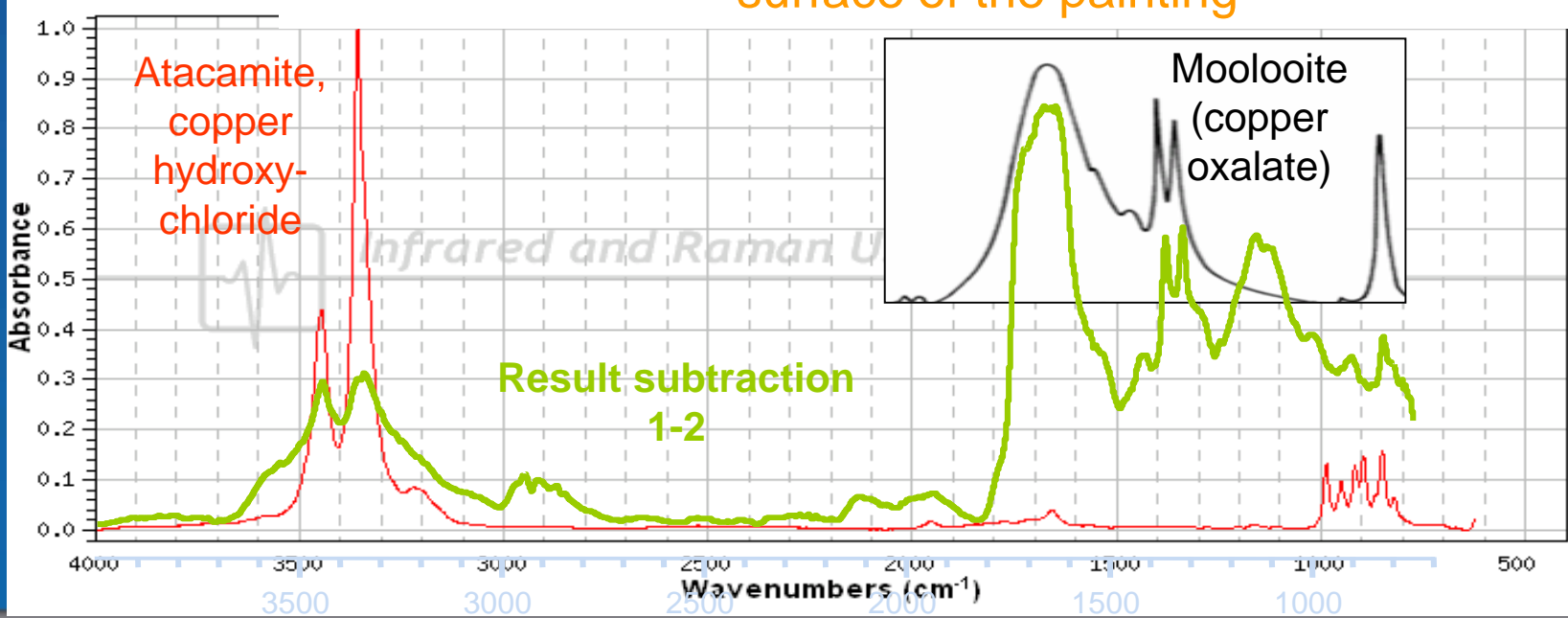
This sample is indeed altered, on the surface



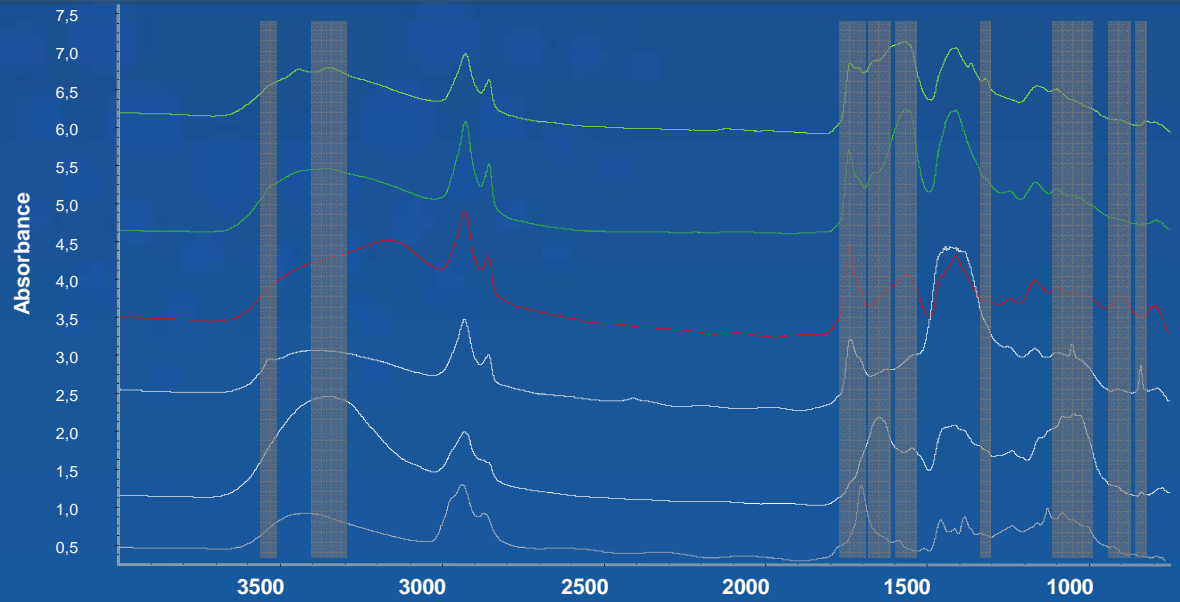
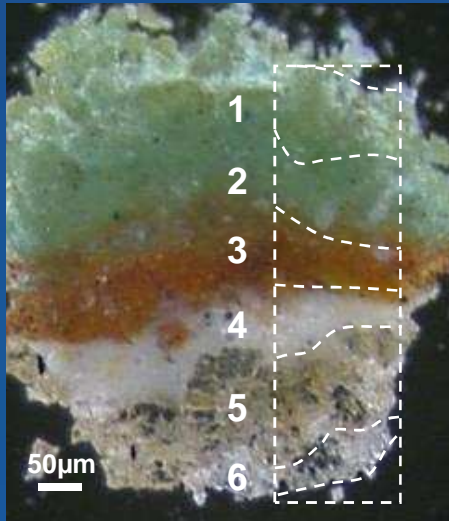
Light green superficial layer (1)



Identification of some copper alteration compounds on the surface of the painting



SR-based micro-FTIR analysis



Cu oxalates

Cu hydroxides

Pb and Cu carboxylates

esters

goethite

hydro-cerussite

Wave-numbers (cm⁻¹)

cerussite

amides

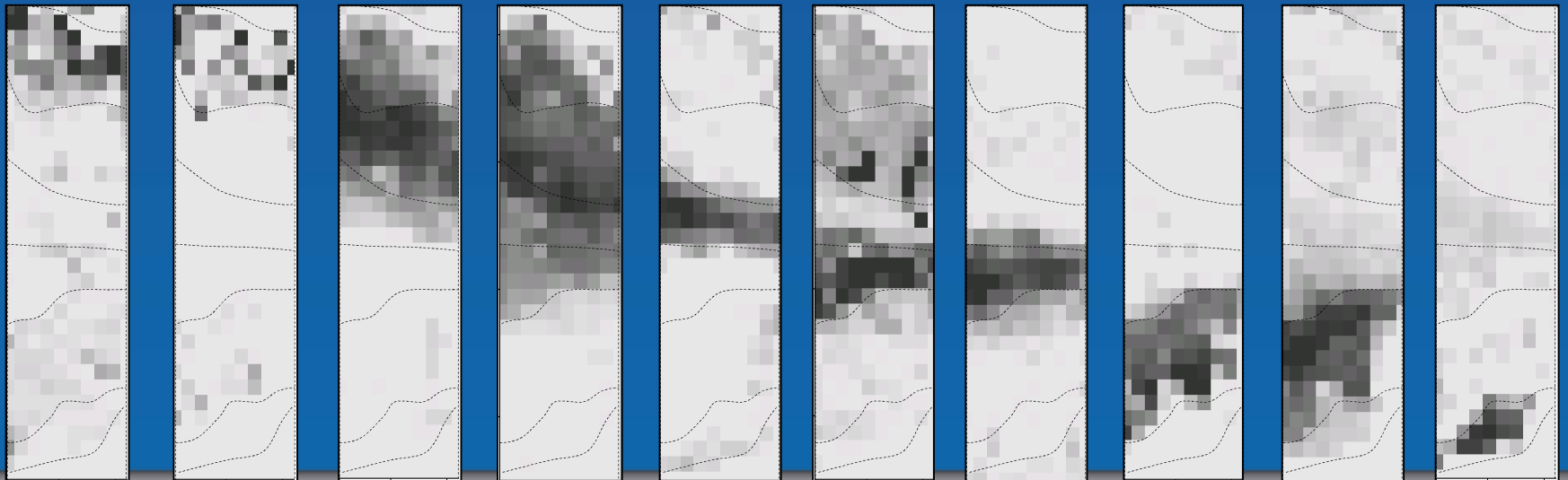
poly-saccharides

acids

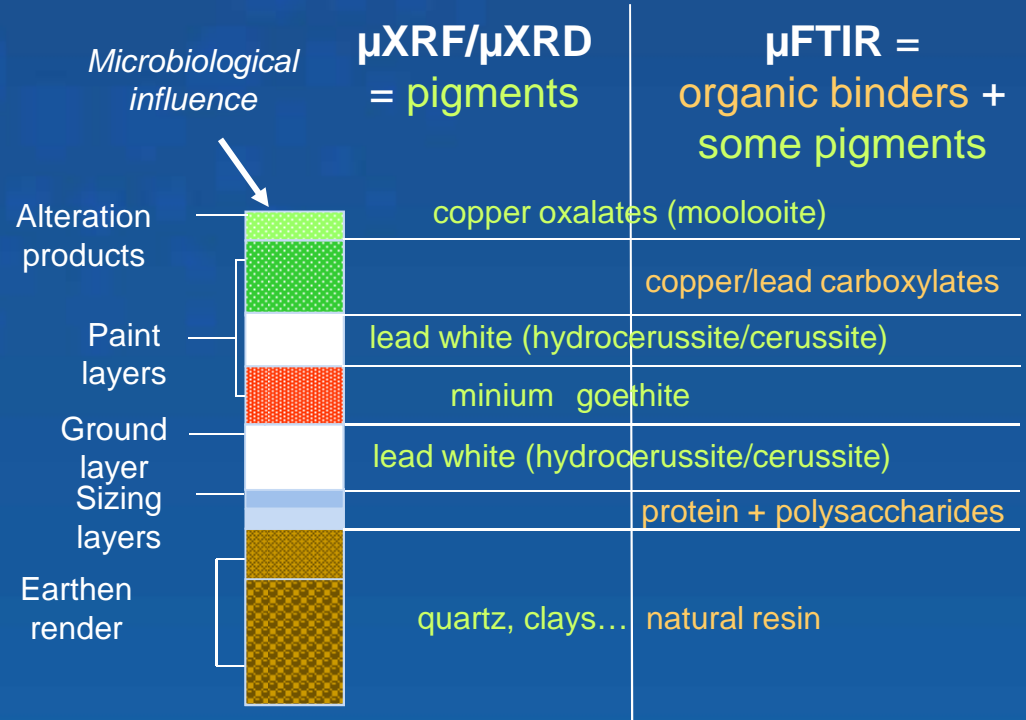
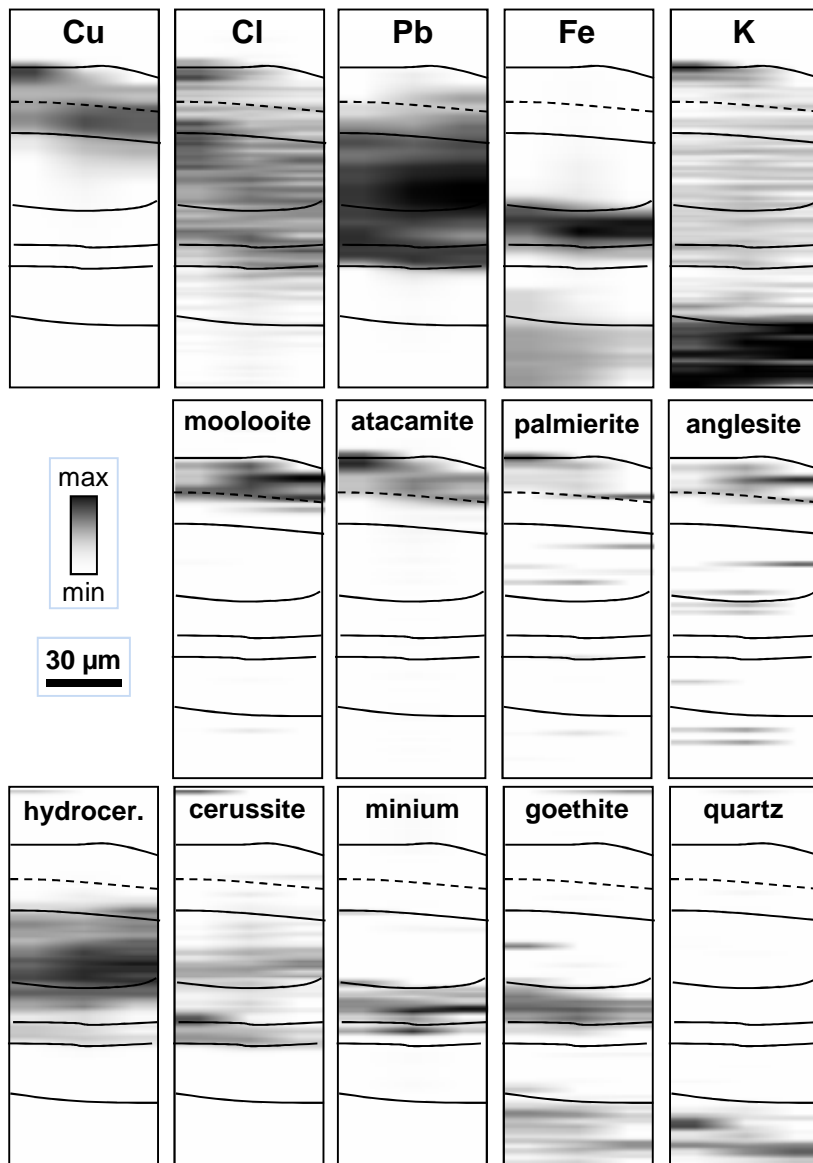
max



min



Combination of μ XRF/ μ XRD with μ FTIR mapping



✓ Interest of mapping towards punctual analysis: better identification in addition to localization

✓ Interest of combining different micro-analytical techniques: complementary information

Map: 150×60 μ m² Step: 1×30 μ m² Beam: 1×15 μ m²

FTIR:

- Transmission is suitable
- Embedding resin can be a problem
- Appropriate thickness is $\sim 2\text{-}5\mu\text{m}$

XRD:

- Transmission is suitable
- Embedding resin is not a problem
- Appropriate thickness is $\sim 30\mu\text{m}$

XRF/XANES:

- Thin sections are useful when contribution from in-depth materials must be avoided
- Transmission is better, when element of interest is sufficiently concentrated
- Embedding resin is not a problem

Polished sections are easier to prepare and to handle

Transmission on thin sections offers higher spectral quality

Diamond windows used to press samples are compatible for X-ray analysis performed in “reflection mode”

Micro-FTIR is a highly potential method to identify and to localize both organic and mineral compounds.

Combination with other analytical techniques is essential

- Micro X-ray fluorescence: elemental identification (up to traces)
- Micro X-ray spectroscopy: focus on a specific element, even in a complex mixture, even in an amorphous state
- Micro X-ray diffraction: better identification of mineral phases

Experimental configurations

Unique or adapted sample preparation



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C. R. Physique 10 (2009) 590–600



COMPTES RENDUS

PHYSIQUE

A Light for Science

Physics and heritage / Physique et patrimoine

Recent applications and current trends in Cultural Heritage Science using synchrotron-based Fourier transform infrared micro-spectroscopy

Marine Cotte ^{a,b,*}, Paul Dumas ^c, Yoko Taniguchi ^d, Emilie Checroun
Philippe Walter ^a, Jean Susini ^b

Trends in Analytical Chemistry, Vol. 29, No. 6, 2010

Trends

Recent applications and current trends in analytical chemistry using synchrotron-based Fourier-transform infrared microspectroscopy

Michael C. Martin, Ulrich Schade, Philippe Lerch, Paul Dumas

Radiation Physics and Chemistry 78 (2009) 367–374



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Review

Recent and future developments in the use of radiation for the study of objects of cultural heritage significance

Dudley Creagh ^{*}, Alana Lee ¹, Vincent Otieno-Alego ², Maria Kubik ³

Cultural Heritage Research Centre, Division of Health, Design and Science, University of Canberra, Canberra ACT 2601, Australia

Thank you for your attention

cotte@esrf.fr

To apply for a proposal
on X-ray AND/OR on FTIR microscopes!

dead lines 1st of March, 1st of September,
<http://www.esrf.fr>