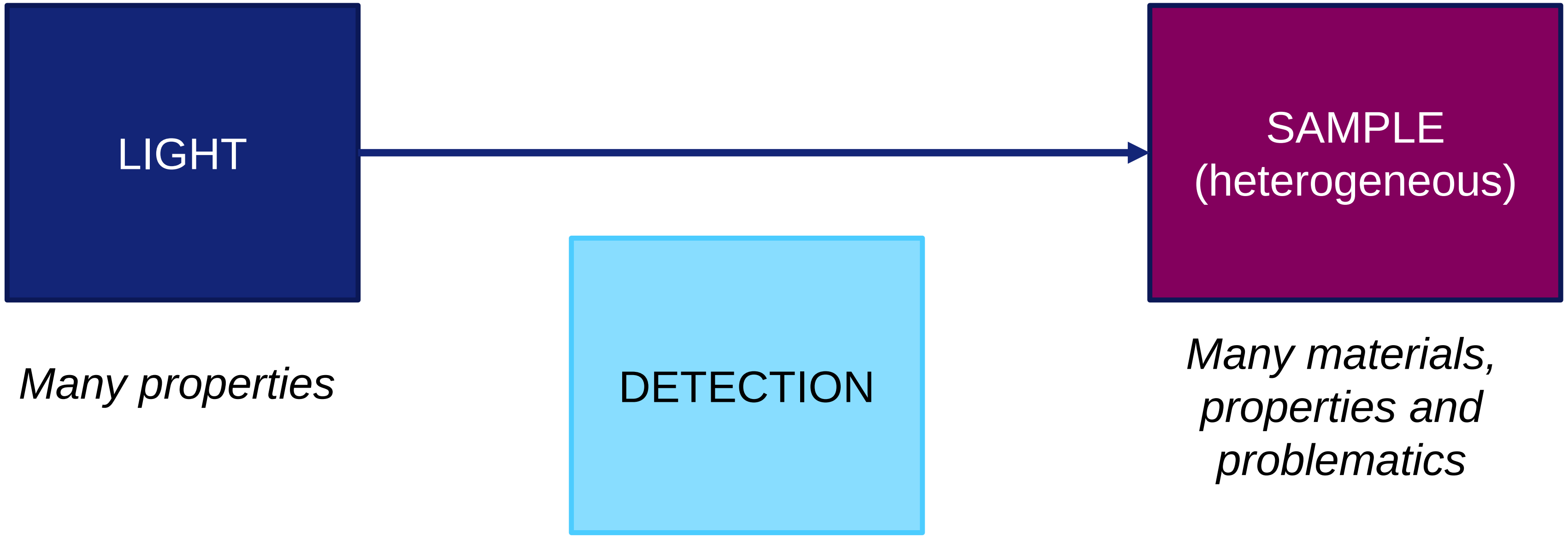
Scanning microscopies at the ESRF:
a synergy between imaging and chemistry

Marine Cotte, scientist in charge of ID21

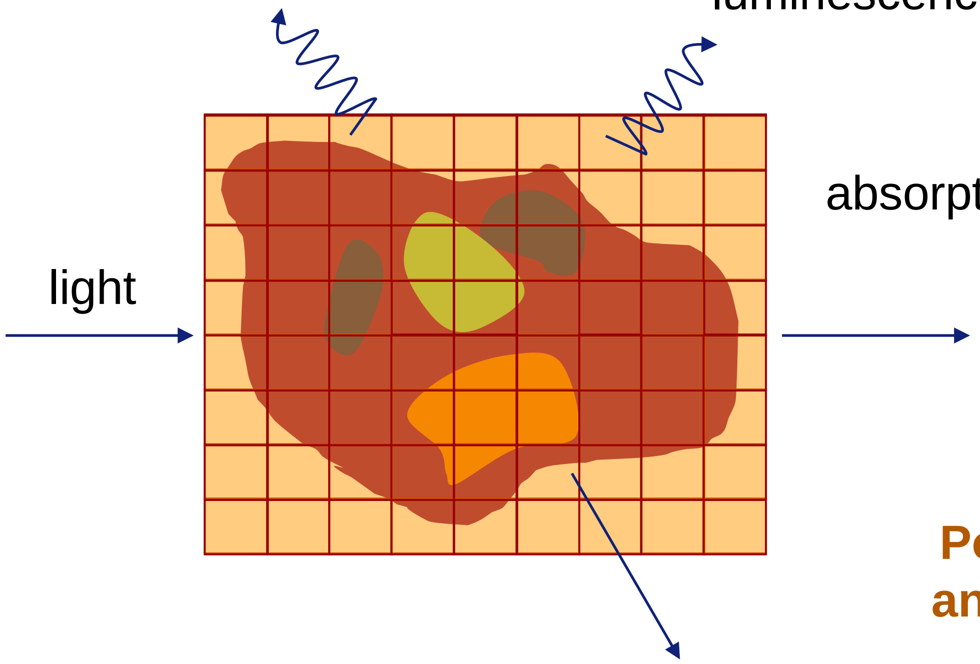
A FUNDAMENTAL TRIPTYCH



Many properties

Many materials, properties and problematics

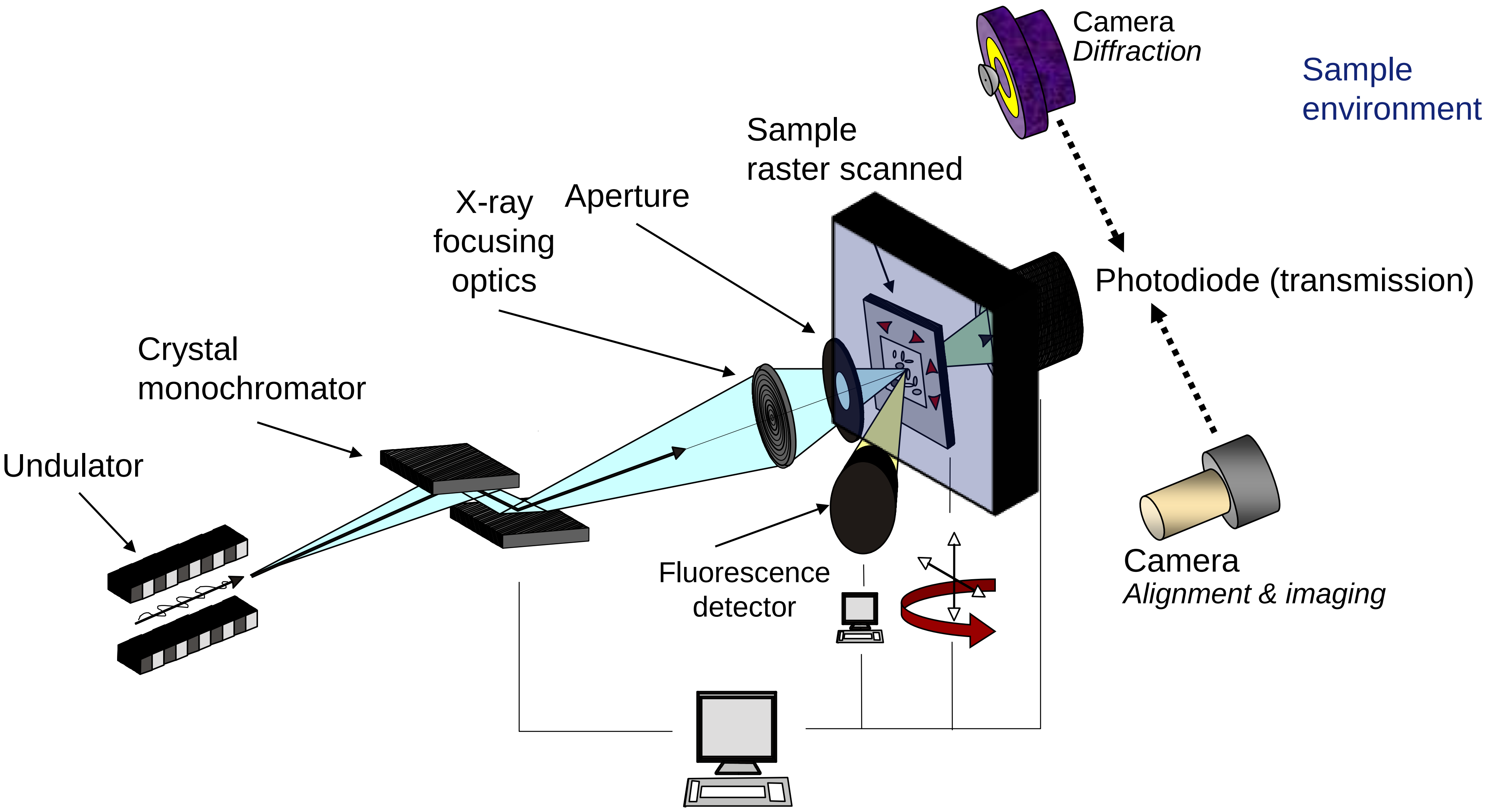
Many detection schemes
(here focus on scanning microscopies)



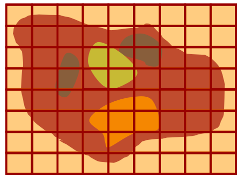
Possibility to obtain 2D, and even 3D information

Possibility to combine (simultaneously) different chemical / physical analyses

SYNCHROTRON BASED X-RAY MICROSCOPY



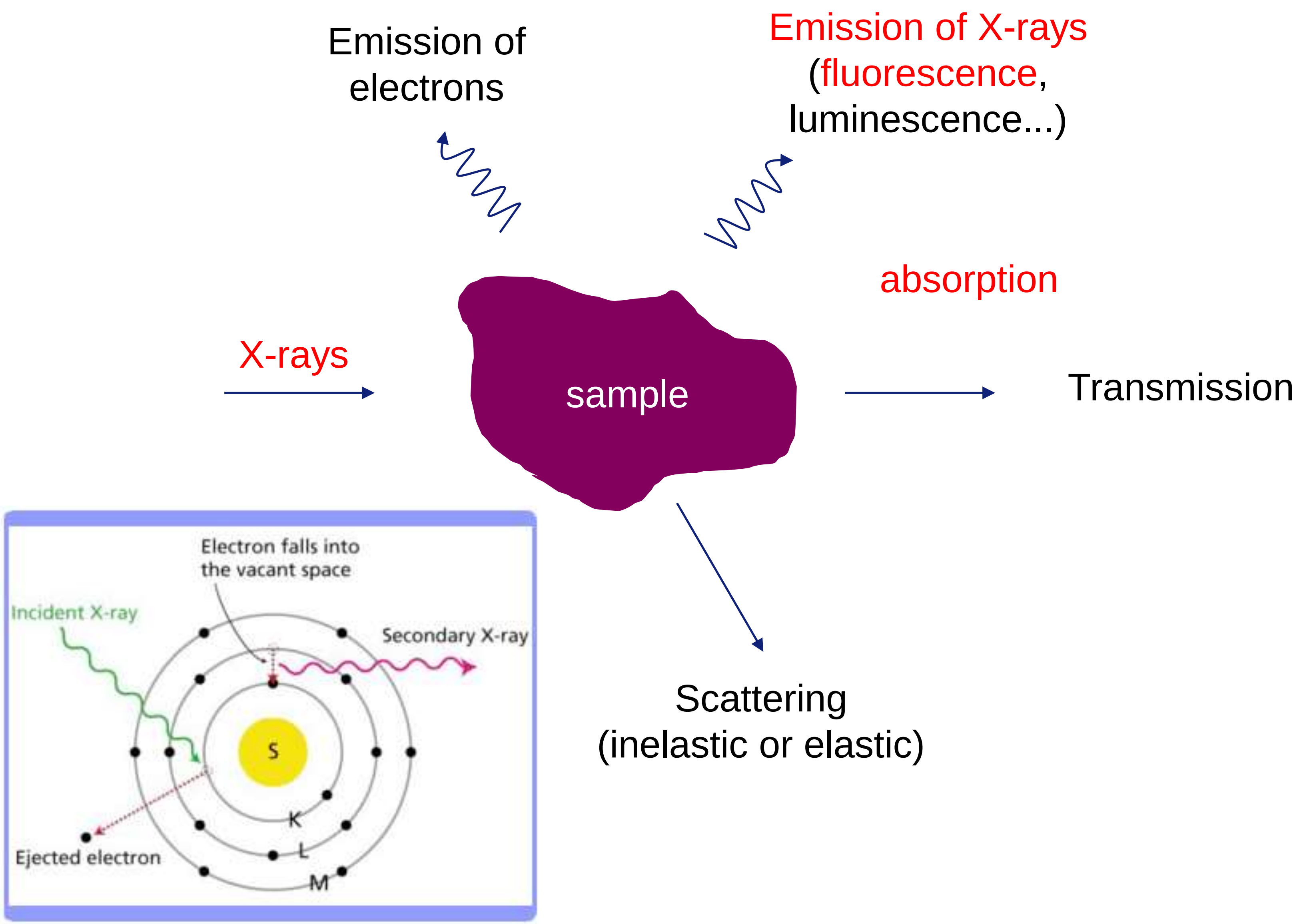
OUTLINE



Which information? Which technique?

Elemental composition? X-ray fluorescence (XRF)

X-RAY FLUORESCENCE: ELEMENTAL IDENTIFICATION



DEGRADATION OF CINNABAR PIGMENT

“Villa Sora”, in Torre del Greco near by Pompeii (1st C. AD)

Blackening of Pompeian Cinnabar Paintings: X-ray Microspectroscopy Analysis. *Analytical Chemistry, (2006) 78:7484 - 7492.*

Marine Cotte,*,† Jean Susini,† Nicole Metrich,‡ Alessandra Moscato,§ Corrado Gratziu,§ Antonella Bertagnini,| and Mario Pagano^
† European Synchrotron Radiation Facility.
‡ Laboratoire Pierre Suë, CEA-CNRS.
§ Università di Pisa.
| Istituto Nazionale di Geofisica e Vulcanologia.
^ Soprintendenza per i Beni Archeologici del Molise.

“The Adoration of the Magi’’, P. P. Rubens (1617–1618)

The use of microscopic X-ray diffraction for the study of HgS and its degradation products corderoite (α-$Hg_3S_2Cl_2$), kenhsuite (γ-$Hg_3S_2Cl_2$)and calomel (Hg_2Cl_2) in historical paintings.
JAAS, (2011) 26:959-968.

Marie Radepont,*[ab] Wout de Nolf,[a] Koen Janssens,[a] Geert Van der Snickt,[a] Yvan Coquinot,[b] Lizet Klaassen[d] and Marine Cotte[bc]
a Department of Chemistry, University of Antwerp, Belgium
b Centre de Recherche et de Restauration des Musees de France—UMR171, CNRS, Paris, France
c European Synchrotron Radiation Facility,
d Royal Museum of Fine Arts (KMSKA), Antwerp, Belgium

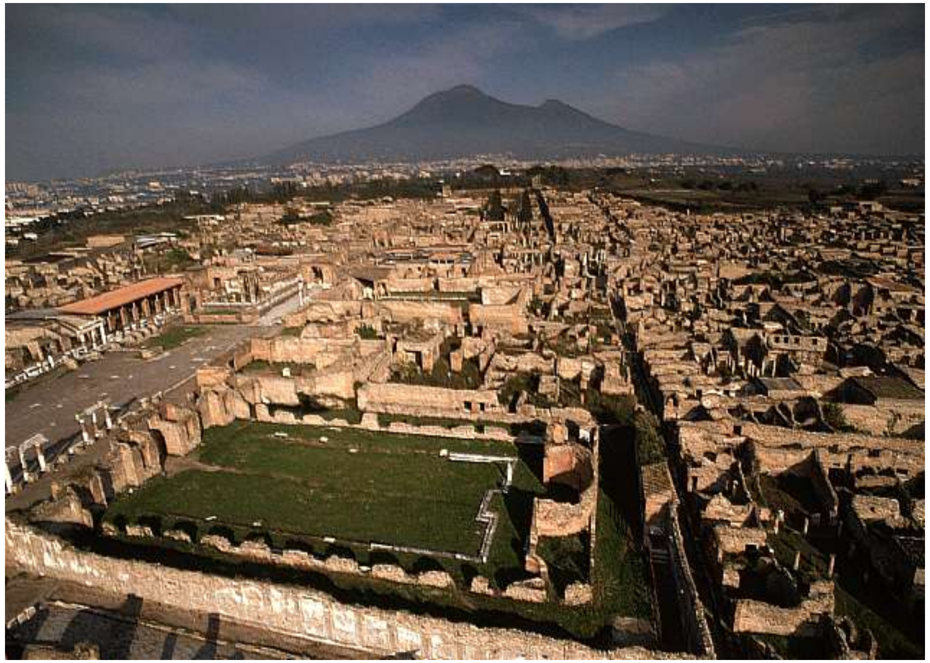
“Madonna with Child, St. Sebastian, St. John the Baptist and two donors”, Boltraffio, 1500

Watching Ancient Paintings through Synchrotron-Based X-Ray Microscopes. *Interfaces, MRS, (2009) 34:403-405.*

Marine Cotte,[ab] Jean Susini,[b]
a Centre of Research and Restoration of the French Museums - UMR171, CNRS, Paris, 75001, France.
b European Synchrotron Radiation Facility

Synchrotron | ESRF

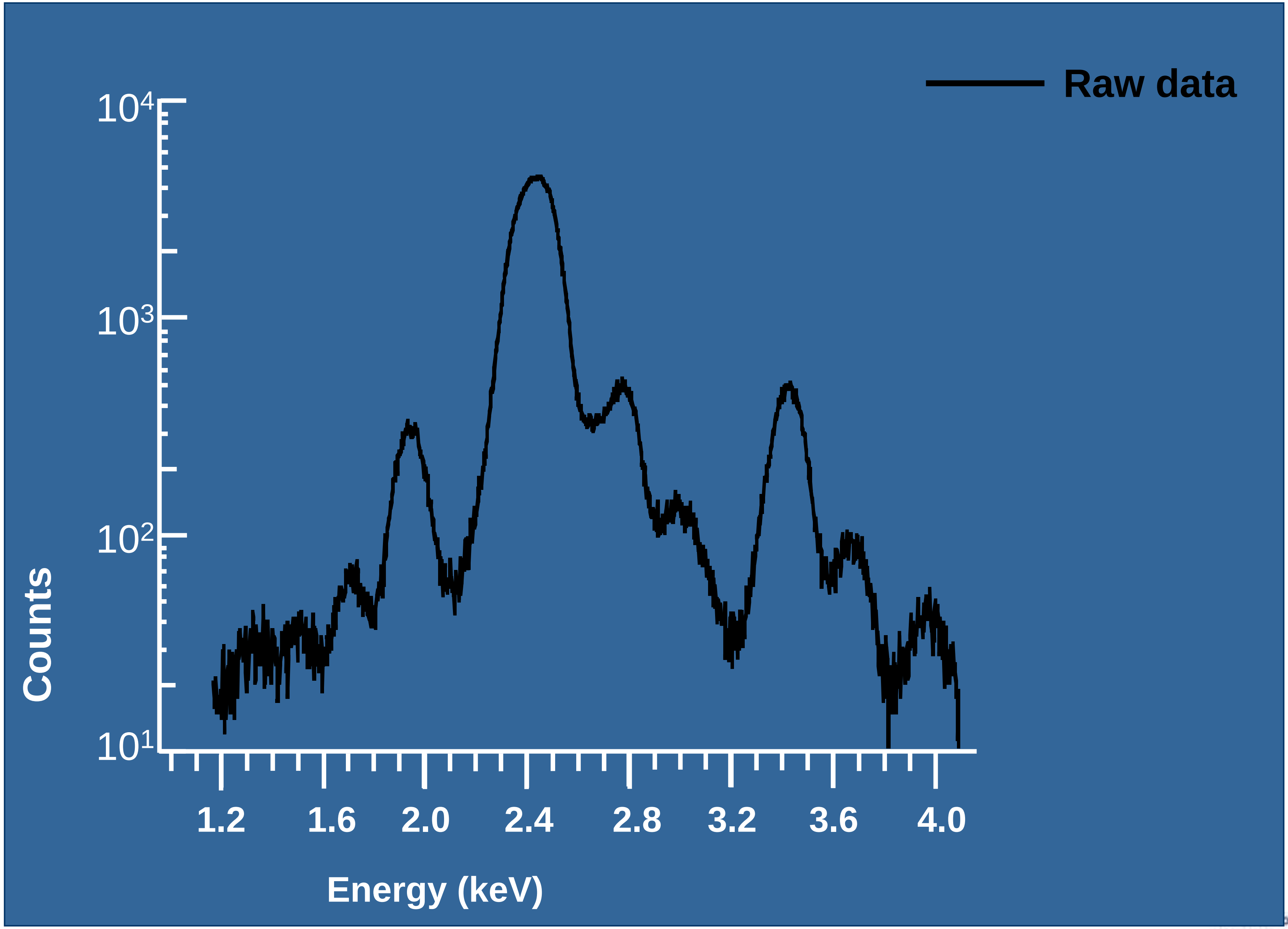
POMPEIAN WALL PAINTINGS



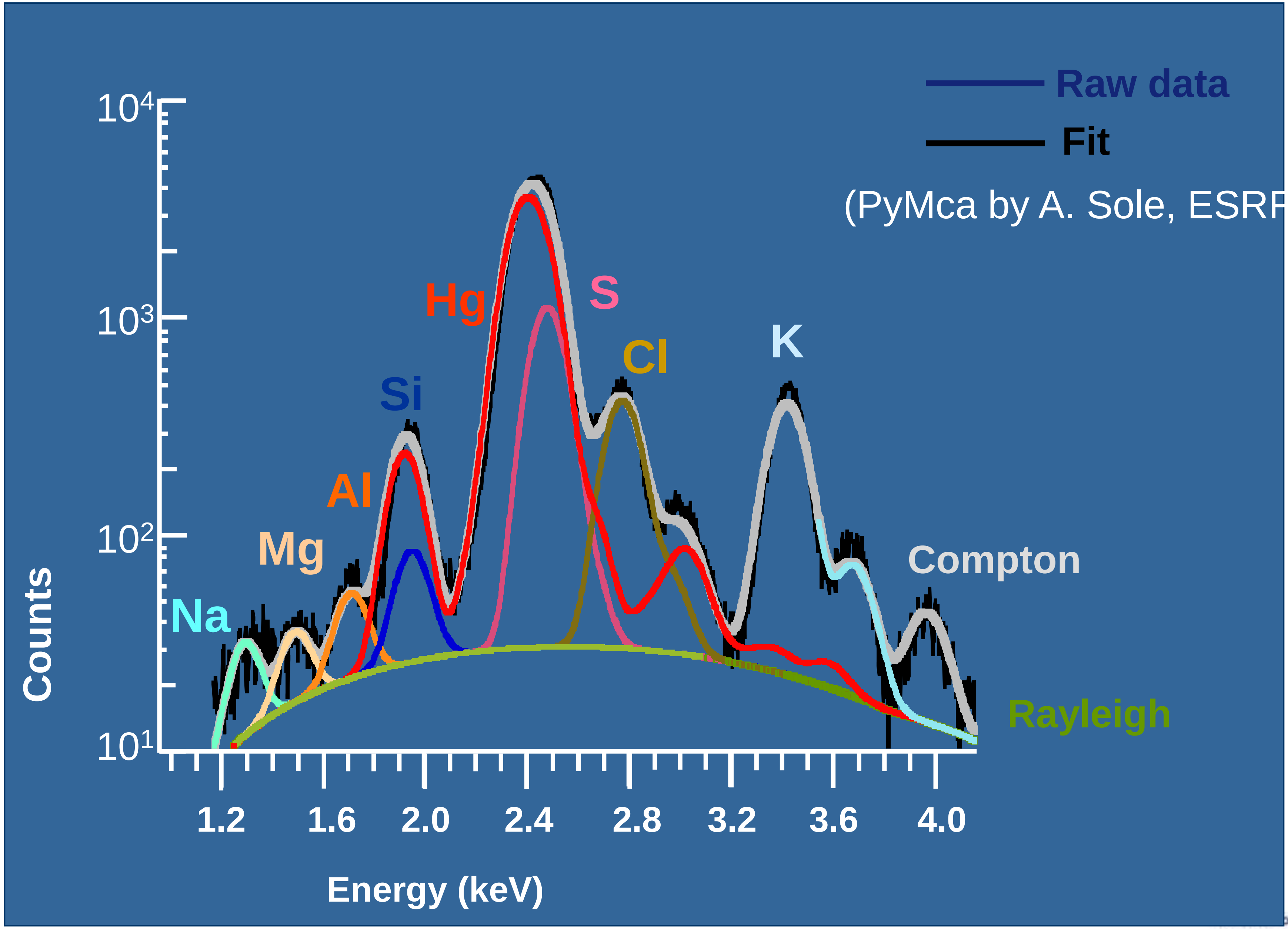
- Excavation started in 1988 and was completed in 1992
- Rapid blackening since 1990

Collaboration:
C. Gratziu[1], A. Moscato[1], A. Bertagnini[2]
1 Dipartimento Scienze della terra
2 Istituto Nazionale di Geofisica e Vulcanologia, Pisa, Italy

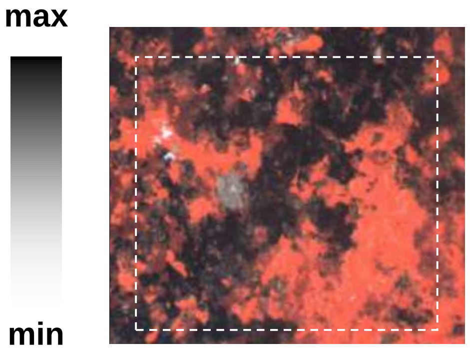
POMPEIAN WALL PAINTINGS: ELEMENTAL XRF MAPPINGS

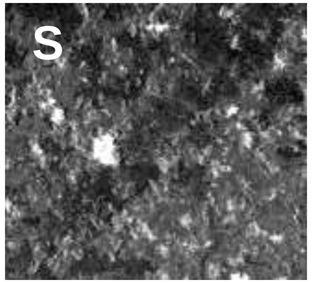


POMPEIAN WALL PAINTINGS: ELEMENTAL XRF MAPPINGS



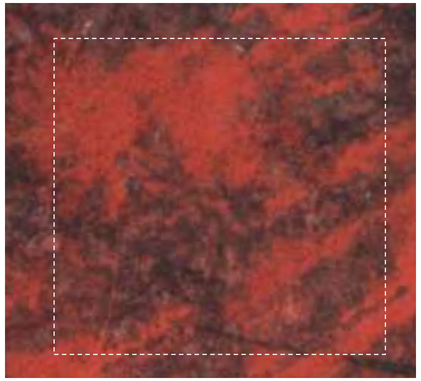
POMPEIAN WALL PAINTINGS: ELEMENTAL XRF MAPPINGS

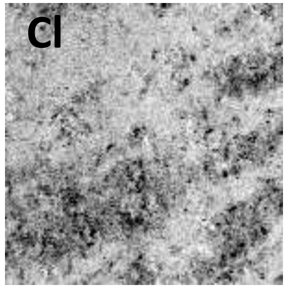




Correlation :
[sulphur] – black color

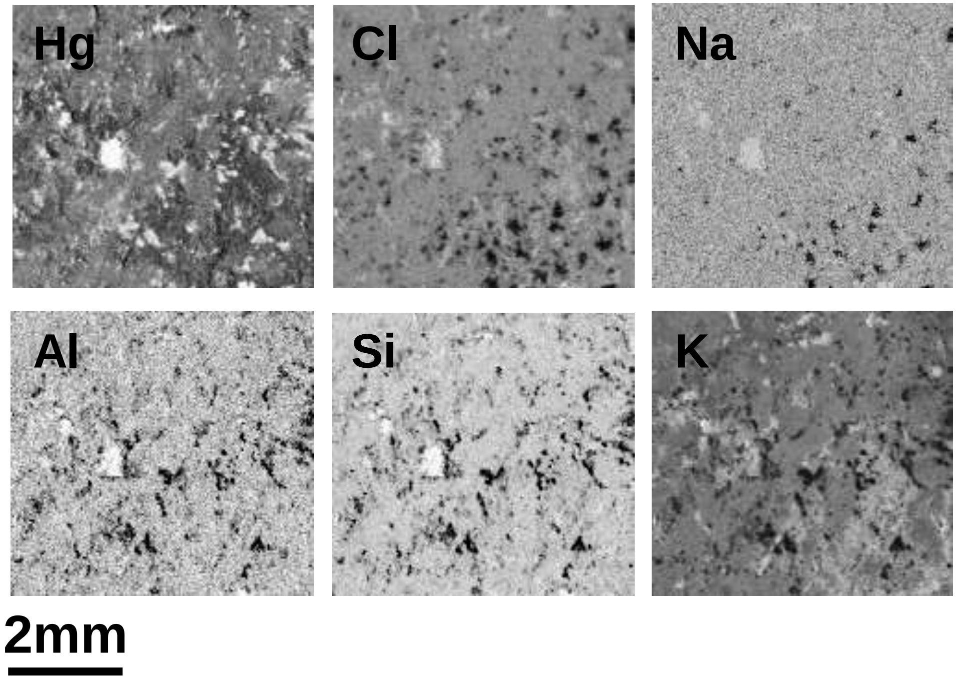
Are the sulphur compounds the same in the two regions?

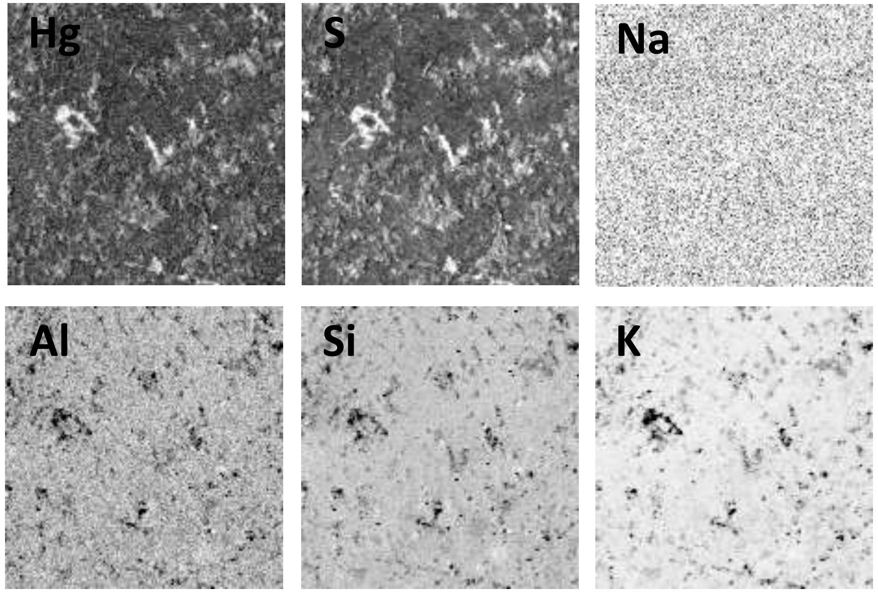




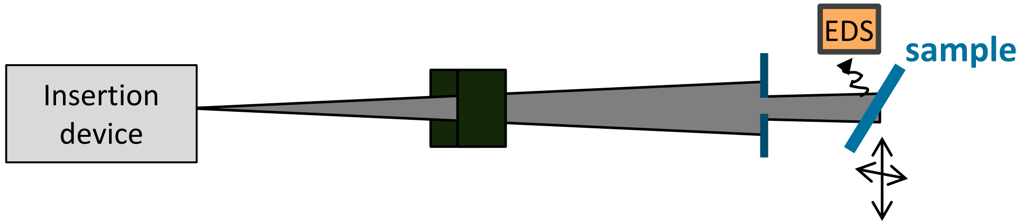
Correlation:
[chlorine] – grey color

Several mechanisms can occur

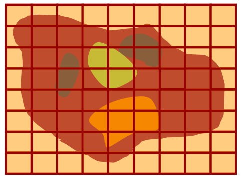




Beam size : 100µm Ø

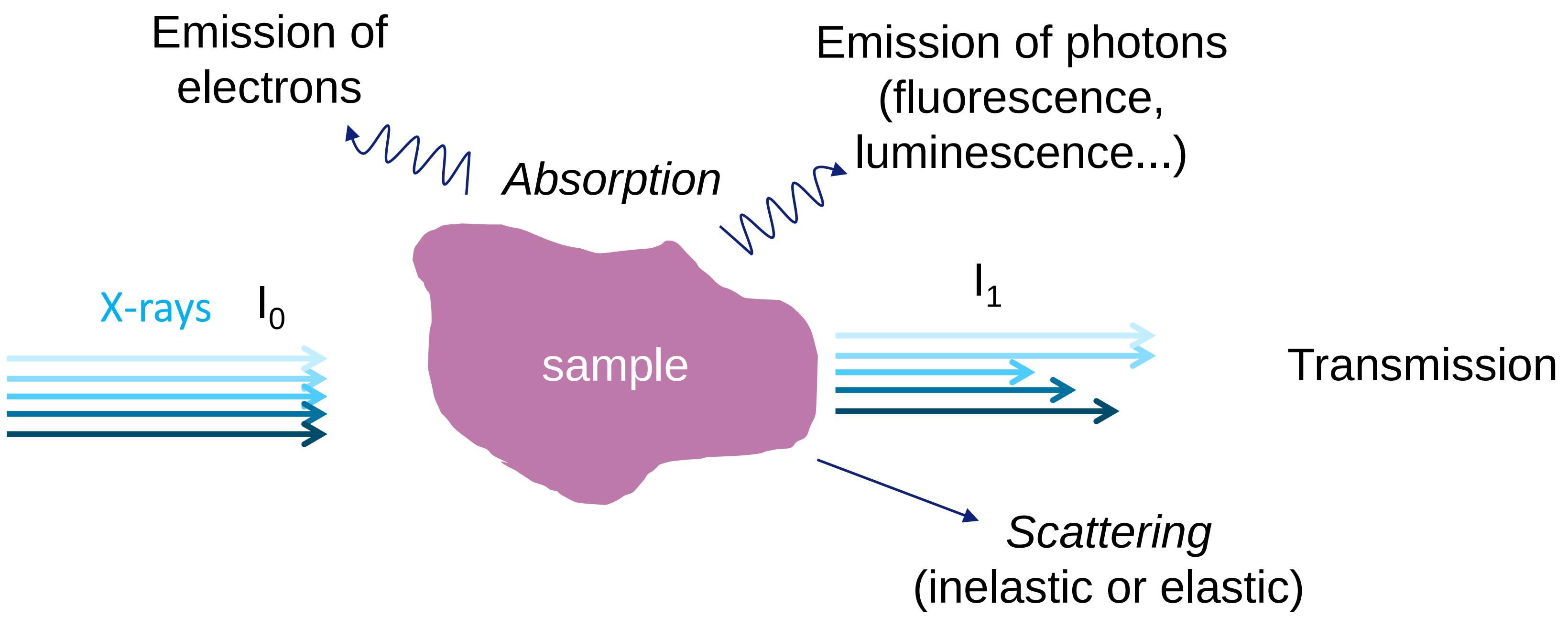


OUTLINE

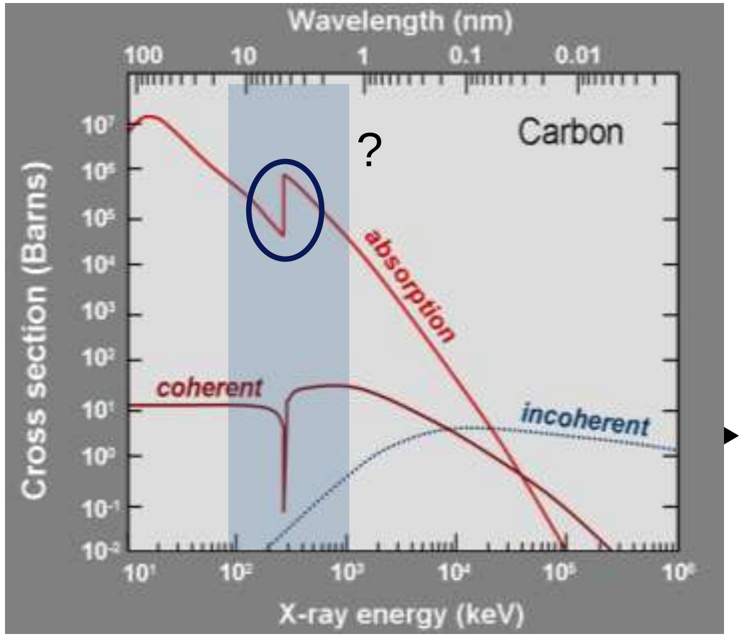


Which information?	Which technique?
Elemental composition?	X-ray fluorescence (XRF)
Surrounding atoms?	X-ray absorption spectroscopy (XAS)

PRINCIPLES OF X-RAY ABSORPTION SPECTROSCOPY



attenuation
≈
absorption

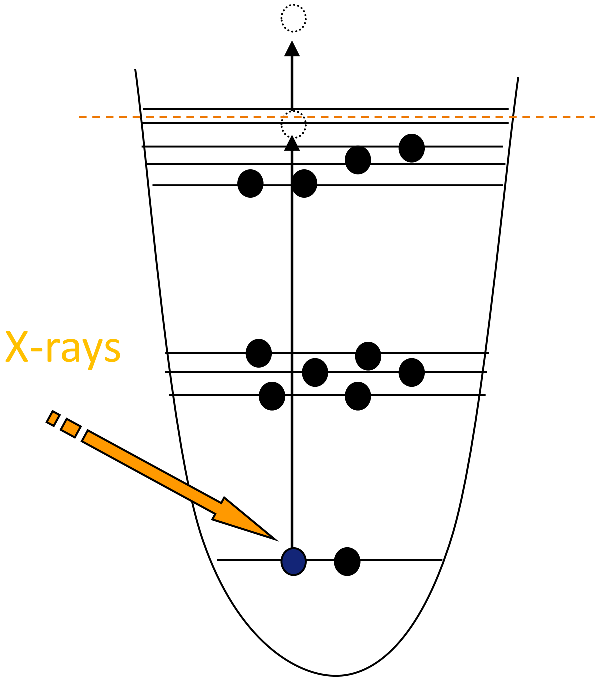


X-ray energy

Absorbance A

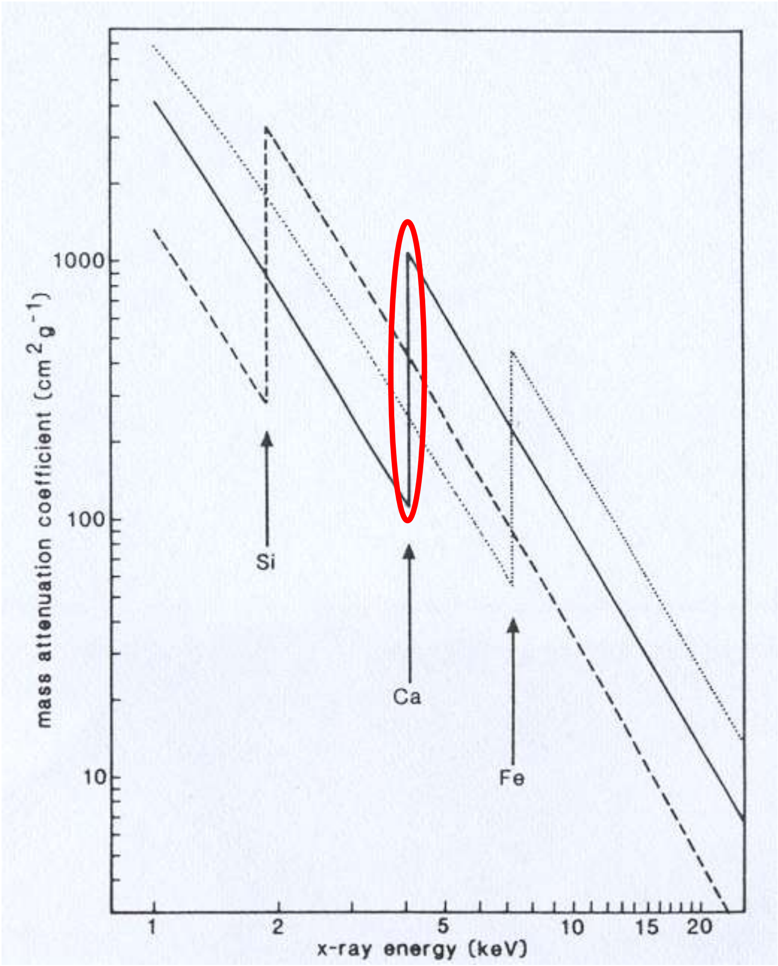
$$A = -\ln(I_1 / I_0)$$

What is absorption?



Photon absorbed = energy consumed by the excitation of an electron.

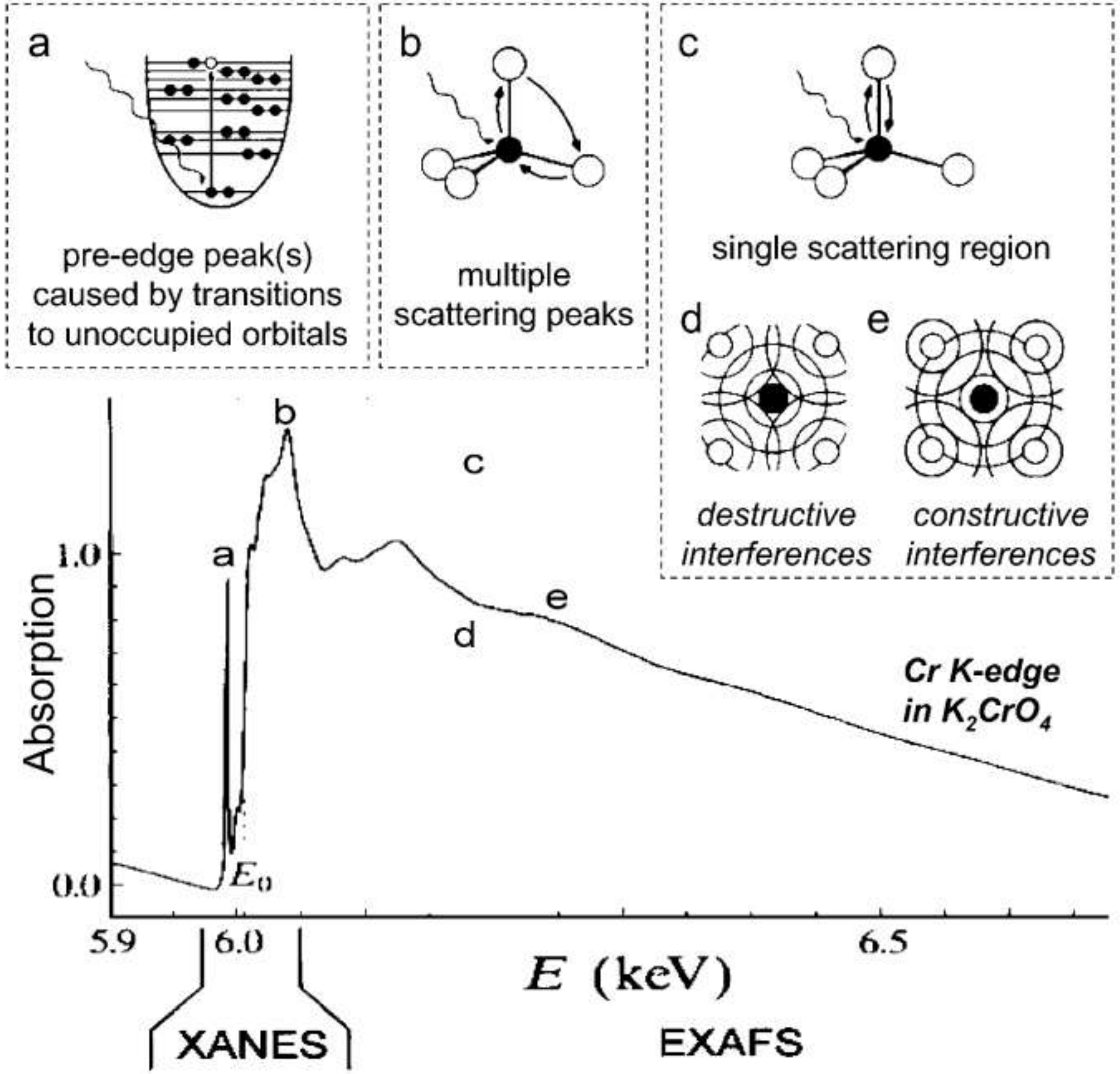
The photon energy must be greater than the binding energy of the electron.



The edge depends on the element

= specific excitation

PRINCIPLES OF X-RAY ABSORPTION SPECTROSCOPY



transitions of the photoelectron to unoccupied bound states

photoelectron promoted to a free or continuum state

XAS = X-ray Absorption Spectroscopy

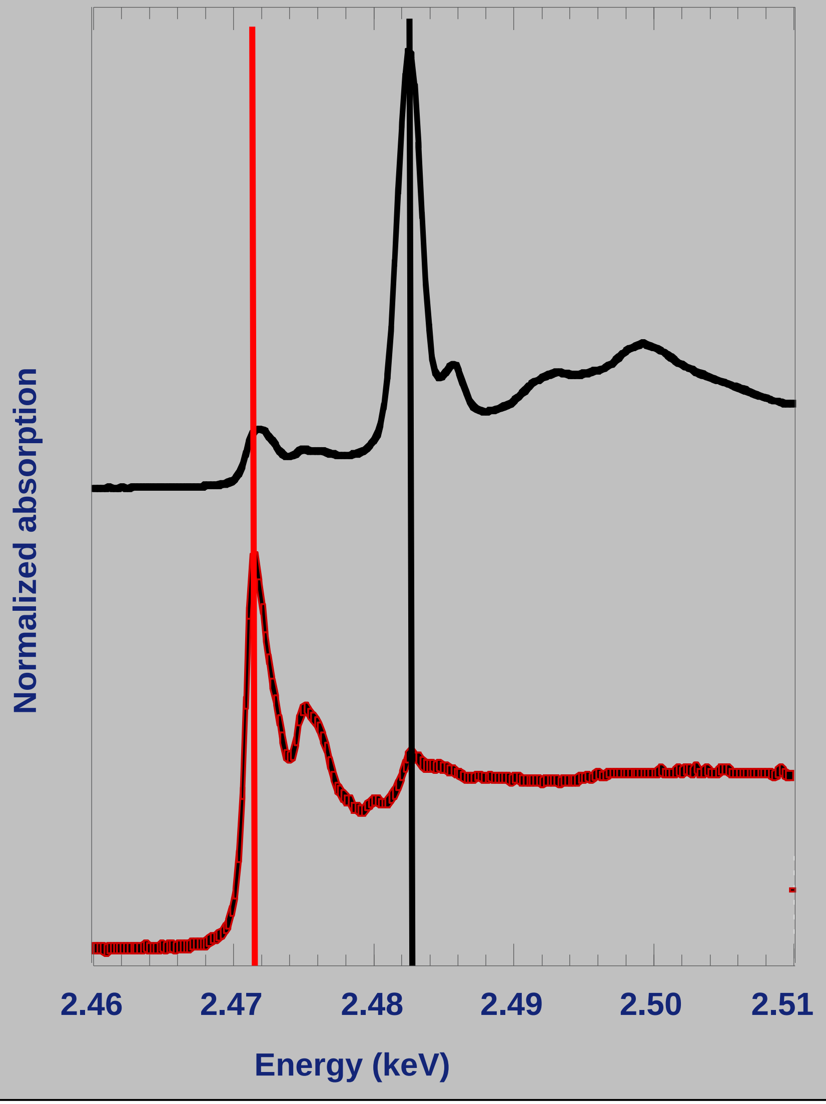
XANES = X-ray Absorption Near-Edge Structure

=> Chemical bonding :Oxidation state; geometry

EXAFS = Extended X-ray Absorption Fine Structure

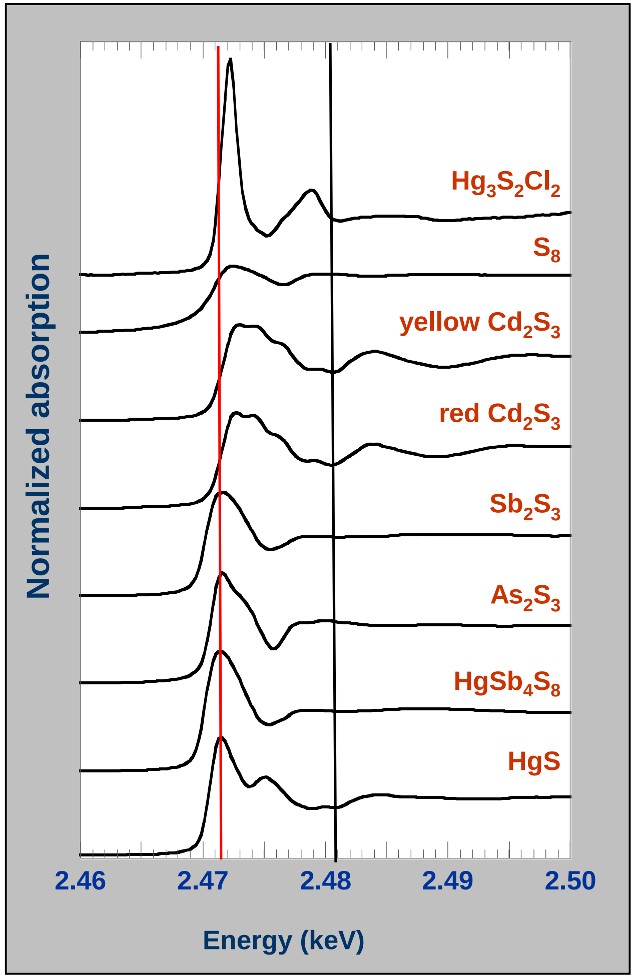
=> depends on the atomic arrangement around the absorber. Contains information about the coordination number, interatomic distances and structural and thermal disorder around a particular atomic specie

POMPEIAN WALL PAINTINGS: XANES AT SULFUR K-EDGE

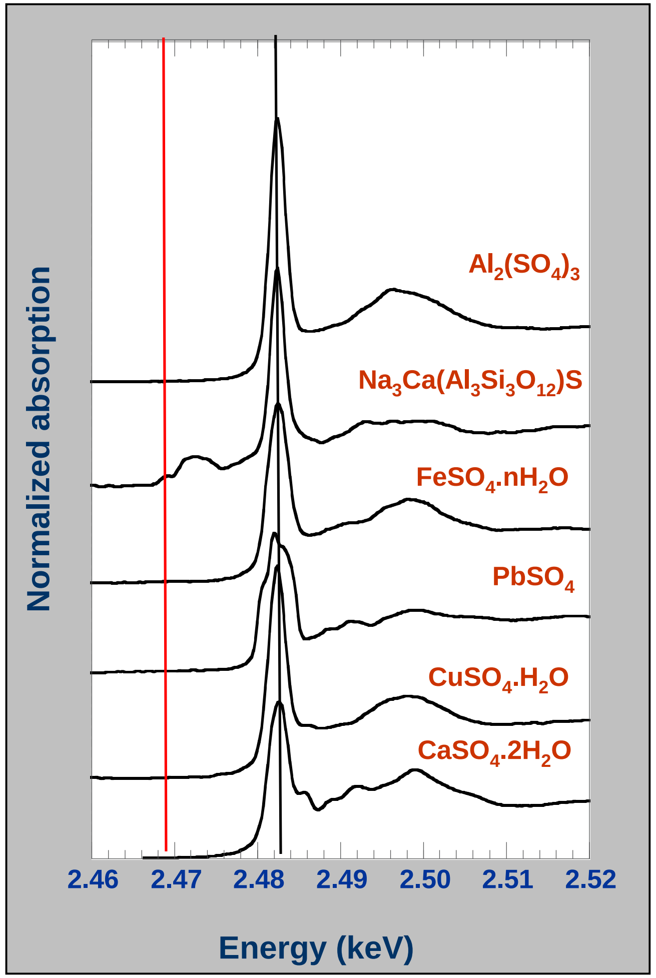


Black alteration

Sulfides (S^{-II}, reduced)

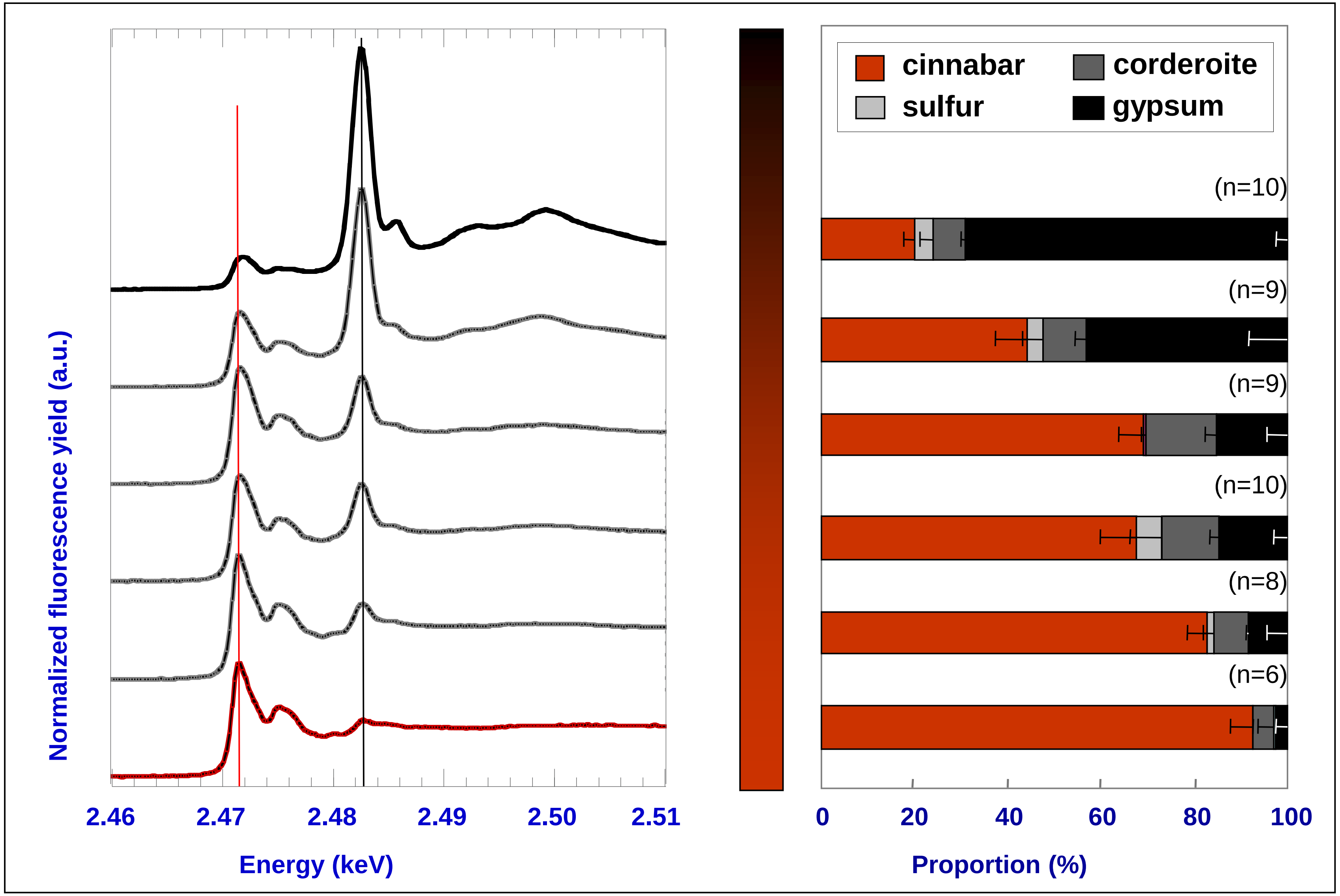


Sulfates (S^{+VI}, oxidized)



Direct identification of the oxidation state

POMPEIAN WALL PAINTINGS: XANES AT SULFUR K-EDGE ON DIFFERENT POINTS



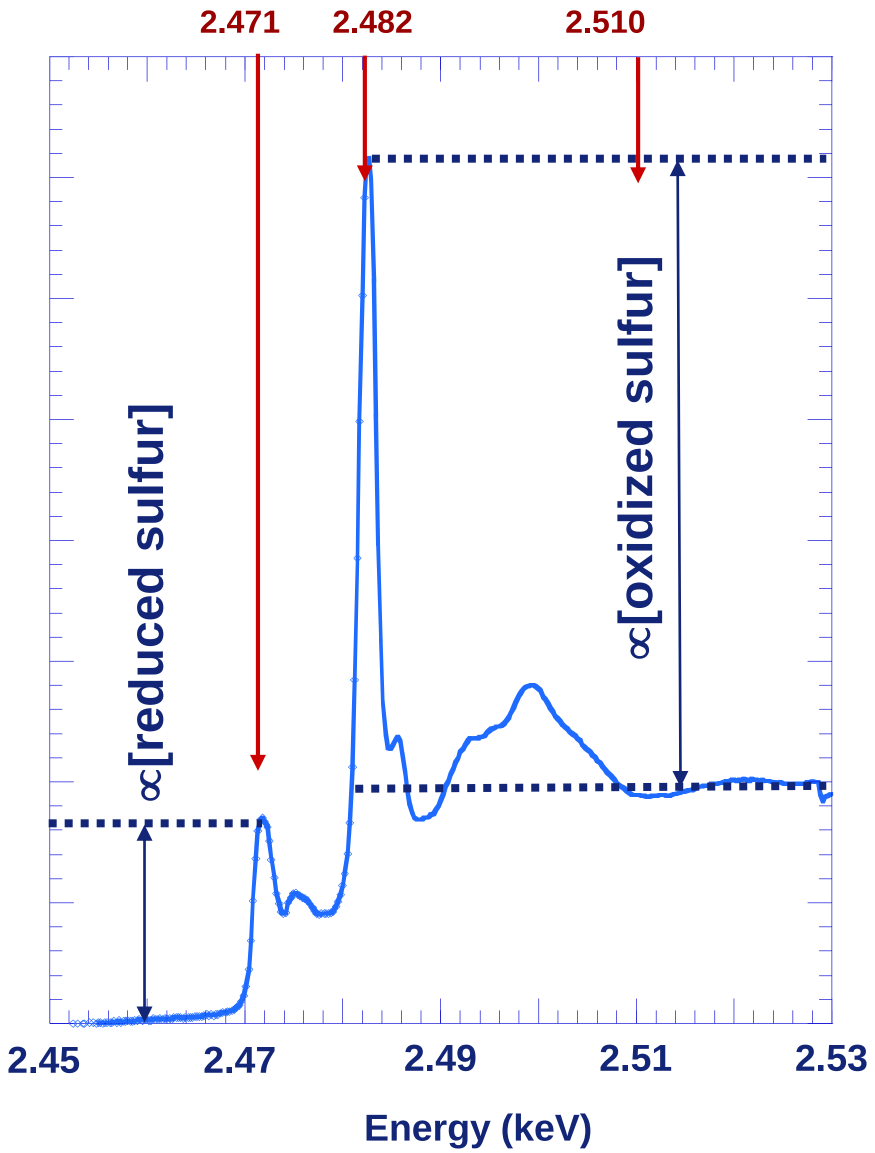
Reduced sulphur

Oxidized sulphur

TOWARDS QUALITATIVE CHEMICAL MAPPING

$$[\text{Sulfides}] \propto \frac{I(2.471)}{I(2.510)}$$

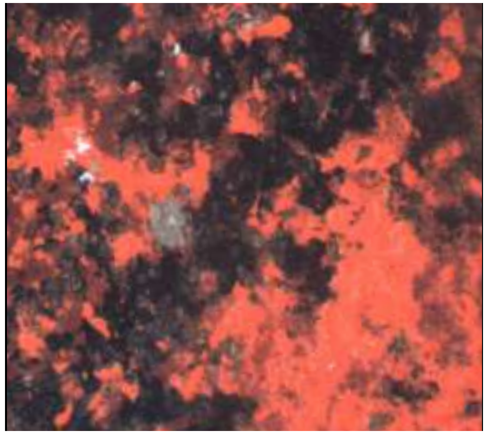
$$[\text{Sulfates}] \propto \frac{I(2.482) - I(2.510)}{I(2.510)}$$



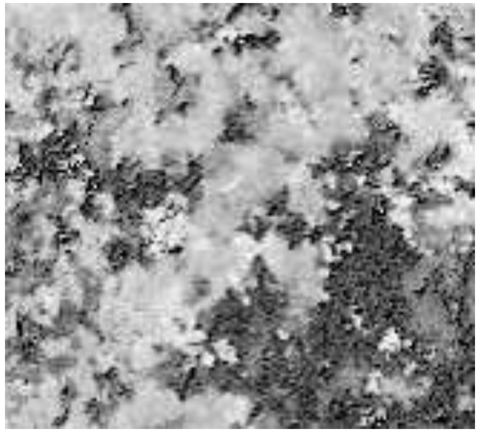
POMPEIAN WALL PAINTINGS: QUALITATIVE SPECIATION MAPS OF SULPHIDES AND SULPHATES

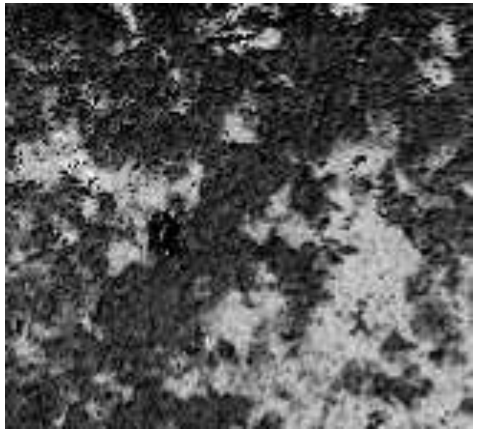
Light microscopy | **Sulphides** | **Sulphates**

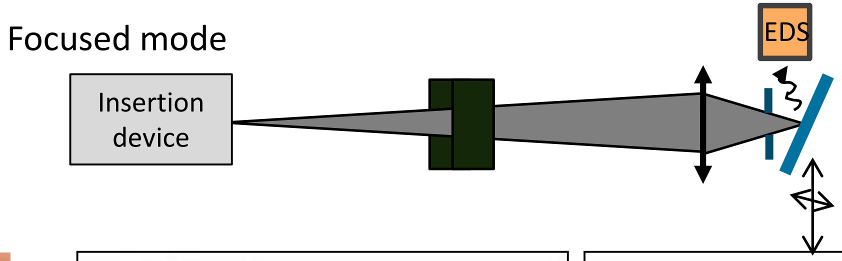
In-plane analysis

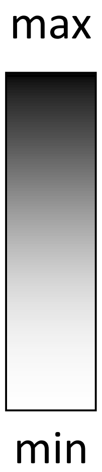


map size, 2×2mm² beam size 100µmØ

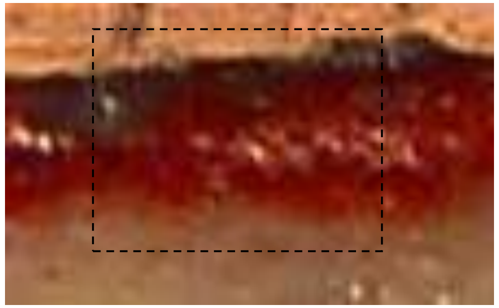




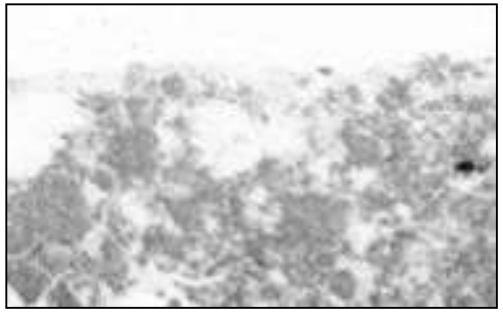


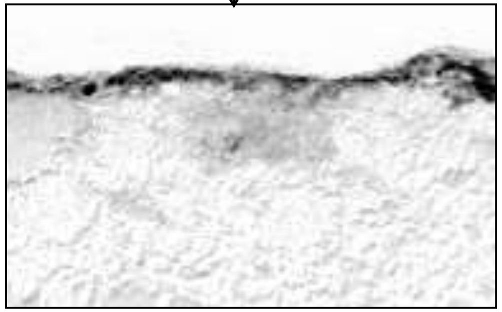


In-depth analysis



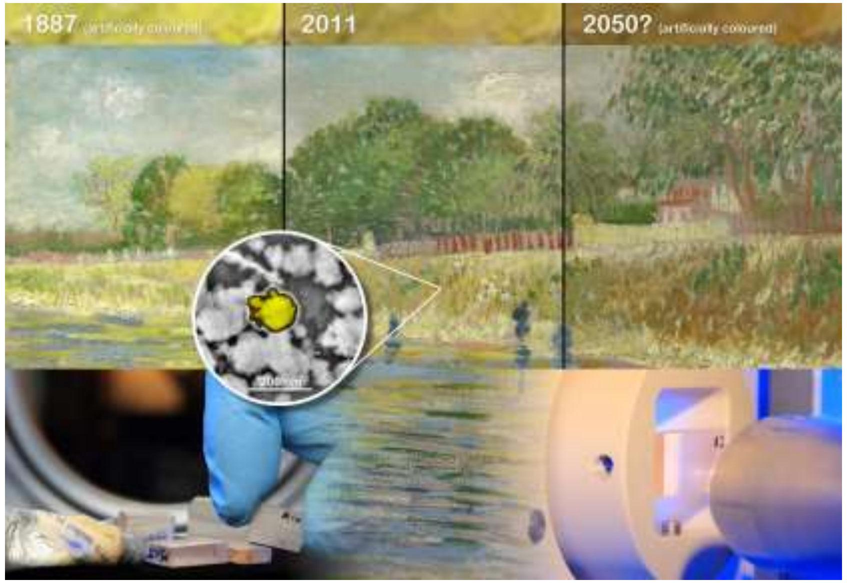
map size, 60×95 μm^2 beam size 0.3×0.7µm²





Very superficial alteration (~5µm)

Degradation Process of Lead Chromate pigments in Van Gogh’s paintings



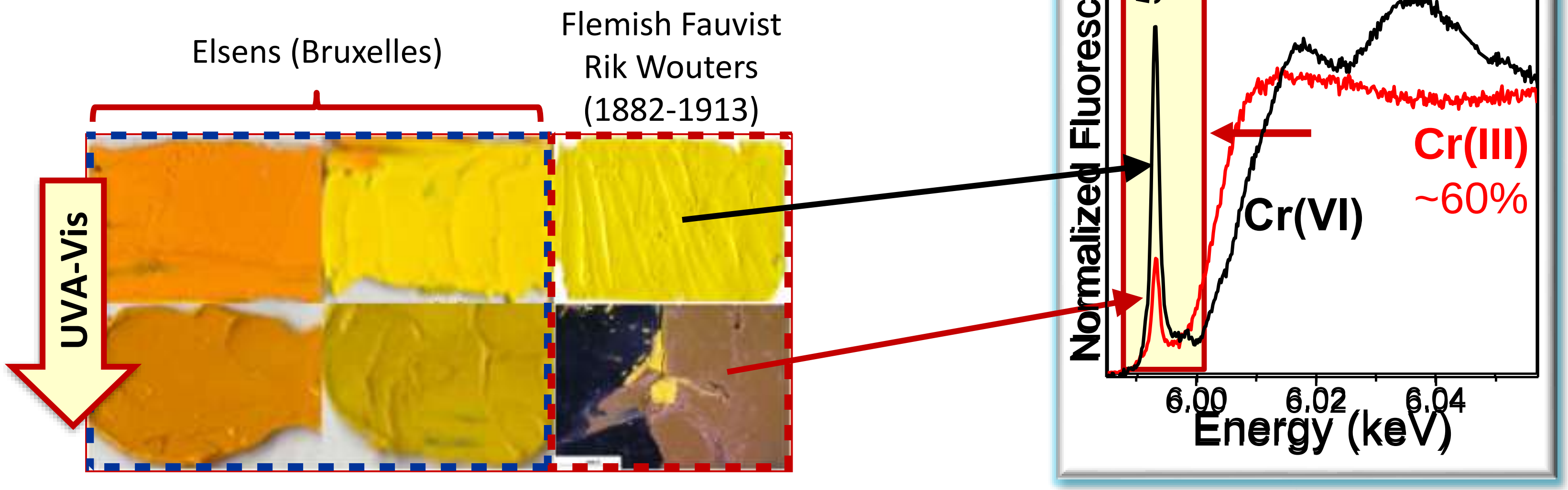
Identifying lead chromate pigments in Van Gogh paintings in particular with portable instruments

Characterizing the photo-sensitivity of model lead chromate pigments and proposing a risk assessment of color modification in paintings

Letizia Monico,
Koen Janssens, Brunetto Brunetti, Costanza Miliani
† Centre SMAArt and Dipartimento di Chimica, Università degli Studi di Perugia, Perugia, Italy.
§ Department of Chemistry, University of Antwerp, Belgium

Universiteit Antwerpen
Consiglio Nazionale delle Ricerche
The European Synchrotron | ESRF

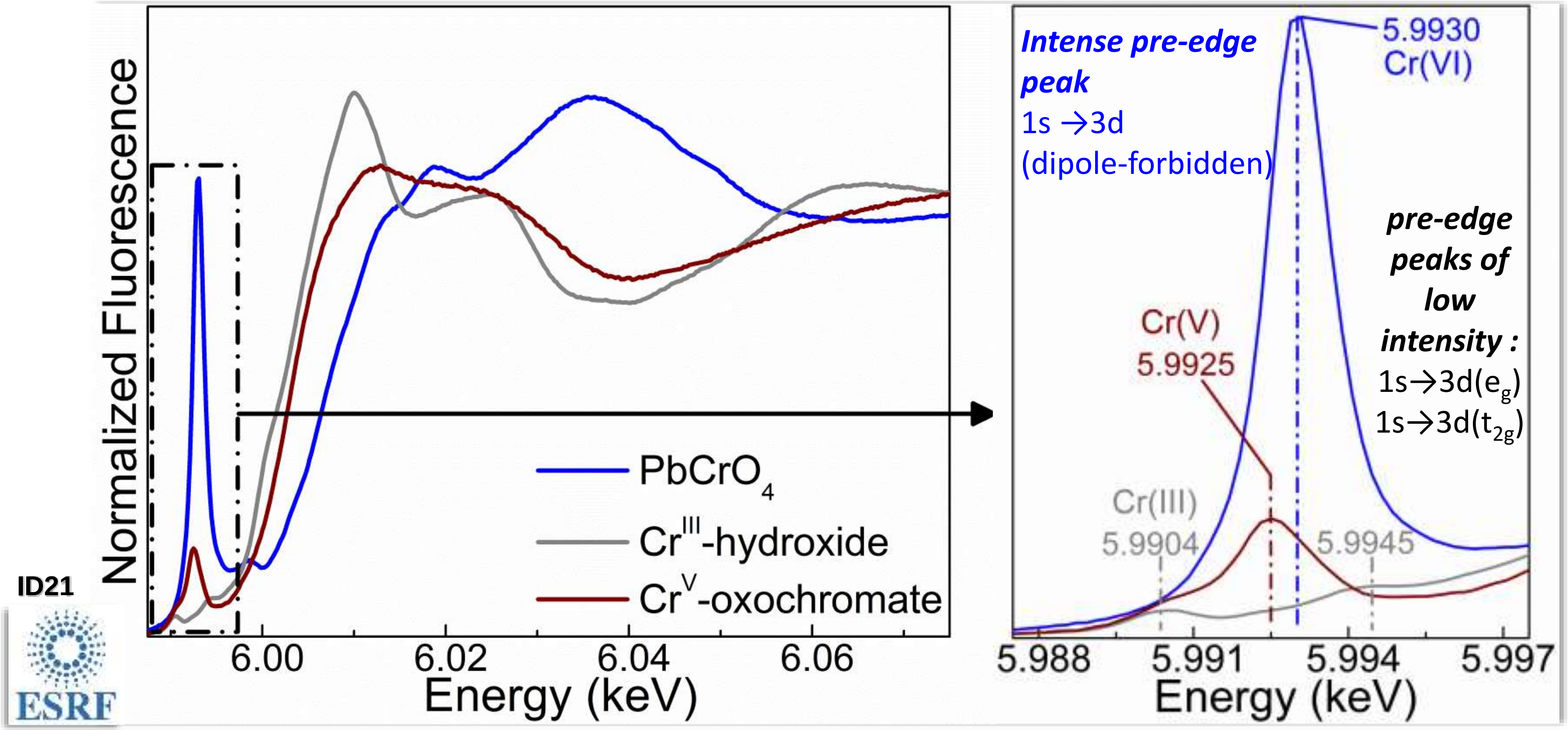
FIRST STUDIES: OBSERVATION OF PHOTOCHEMICAL AGING OF LATE-19TH CENTURY OIL PAINT TUBES



L. Monico, et al., "Degradation Process of Lead Chromate in Paintings by Vincent van Gogh Studied by Means of Synchrotron X-ray Spectromicroscopy and Related Methods. 1. Artificially Aged Model Samples", *Analytical Chemistry, (2011),* ***83, 1214-1223.***

Courtesy L. Monico

Cr REFERENCE COMPOUNDS: Cr K-EDGE XANES SPECTRA



- **Cr(VI) compounds:** non-centrosymmetric tetrahedral coordination.
- **Cr(III) compounds:** centrosymmetric octahedral geometry.

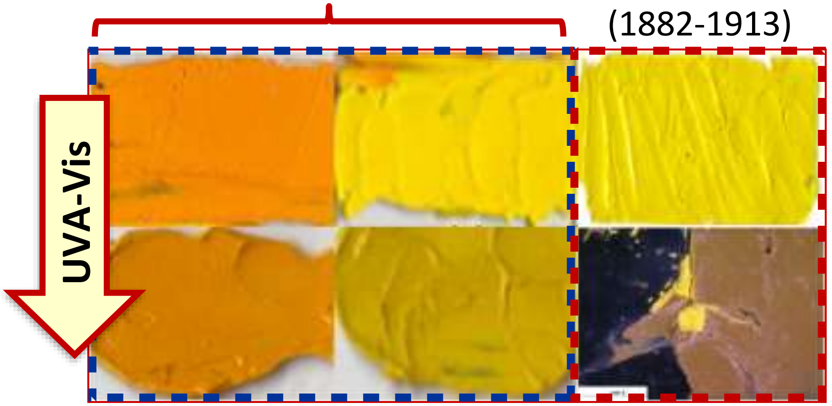
- Pre-edge peak area proportional to the amount of Cr(VI).
- Shift of the absorption edge position towards higher energies: ***increase of the valency*** of the absorbing atom and/or of the ***electronegativity*** of the nearest neighbour atoms.
- Identification of specific reduced Cr-compounds challenging, when different Cr-species are co-present.

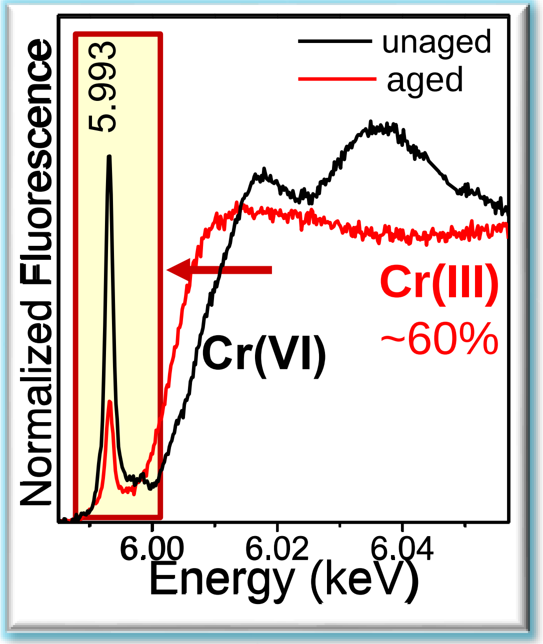
Courtesy L. Monico

FIRST STUDIES: OBSERVATION OF PHOTOCHEMICAL AGING OF LATE-19TH CENTURY OIL PAINT TUBES

Elsens (Bruxelles)

Flemish Fauvist
Rik Wouters
(1882-1913)

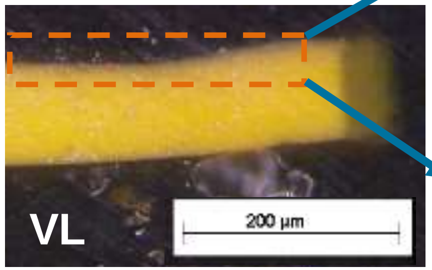




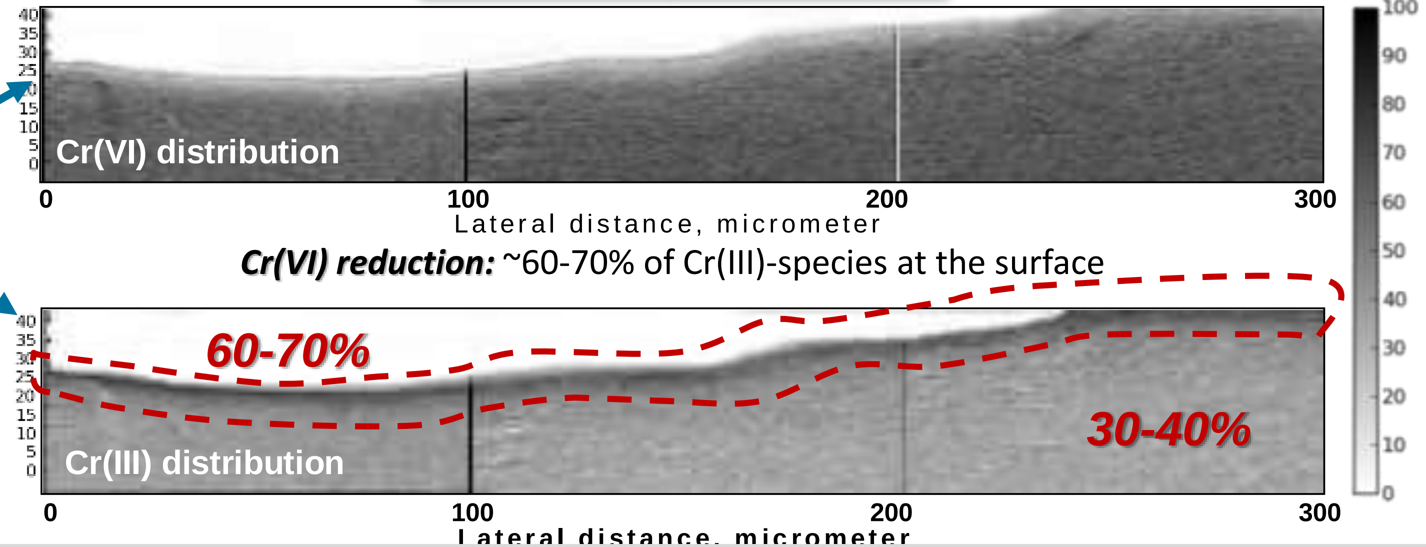
$$c_{Cr(VI)}(x,y)\ (\%) = \frac{I^{Cr}_{E_0=5.993\,keV}(x,y)/I^{Cr,\,PbCrO_4}_{E_0=5.993\,keV}}{I^{Cr}_{E_0=6.086\,keV}(x,y)/I^{Cr,\,PbCrO_4}_{E_0=6.086\,keV}} \times 100\%$$

$$c_{Cr(III)}\ (\%) = 100\% - c_{Cr(VI)}\ (\%)$$

Cross-sectioned sample



Pixel size: 0.25×1 µm²

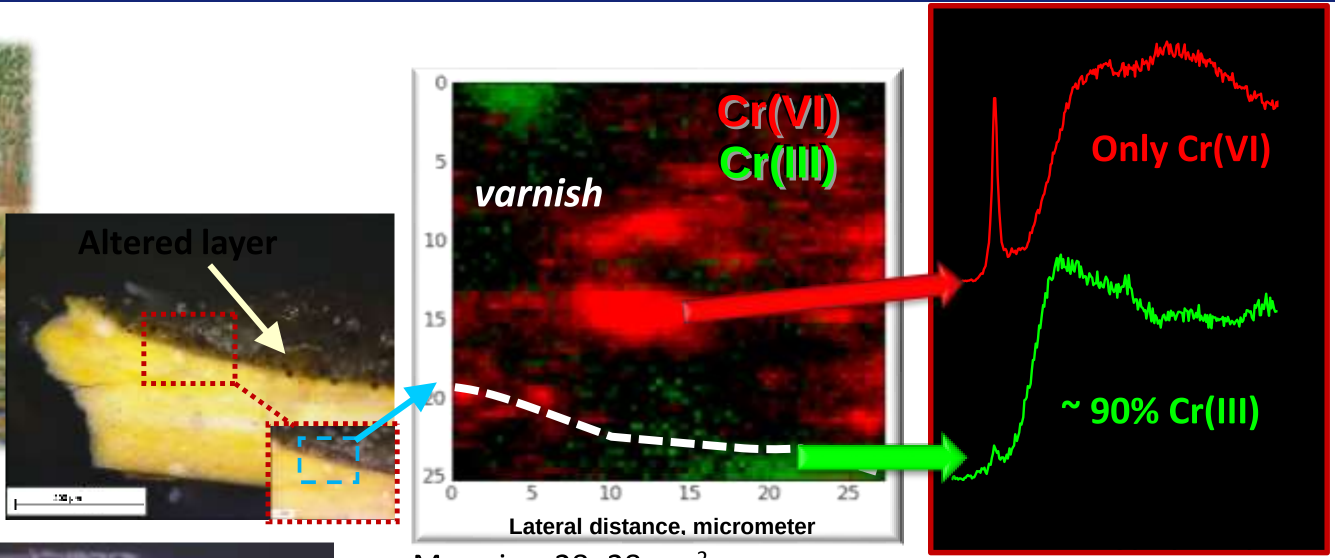


Cr(VI) reduction: ~60-70% of Cr(III)-species at the surface

Courtesy L. Monico

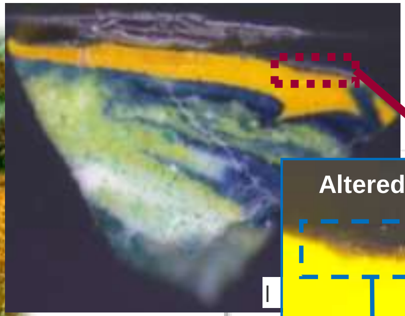
L. Monico, et al., "Degradation Process of Lead Chromate in Paintings by Vincent van Gogh Studied by Means of Synchrotron X-ray Spectromicroscopy and Related Methods. 1. Artificially Aged Model Samples", *Analytical Chemistry, (2011),* ***83, 1214-1223.***

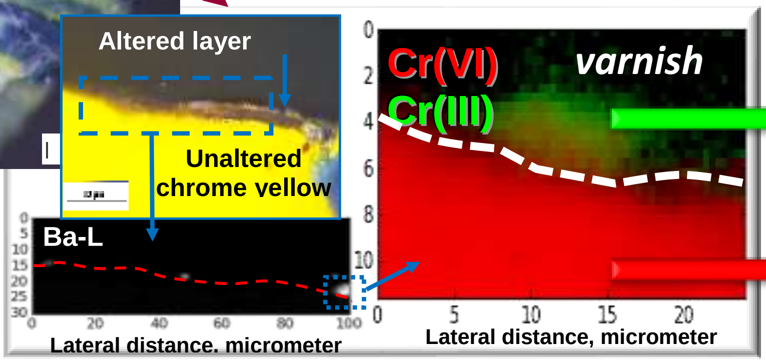
Bank of the Seine (1887, V. van Gogh; Van Gogh Museum, Amsterdam, NL)

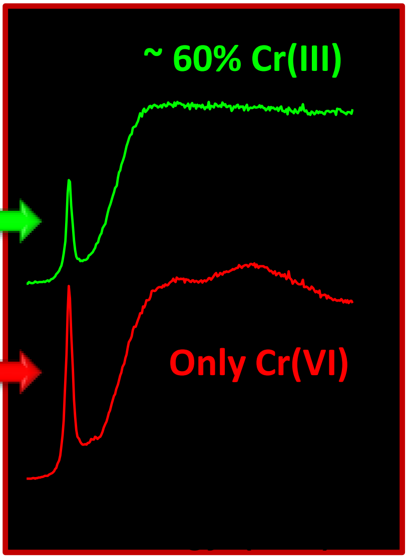


Map size: 28×28 µm^2
pixel size: 0.4 ×0.4 µm^2
dwell time: 300 ms/pixel.

Field with flowers near Arles (1888, V. van Gogh; Van Gogh Museum, Amsterdam, NL)







Map size: 11.6×24 µm^2; pixel size: 0.4 ×0.4 µm^2; dwell time: 300 ms/pixel.

Local presence of Cr(III)-secondary products: Cr(III) oxide/hydroxide, organo-Cr(III) compounds

Courtesy L. Monico

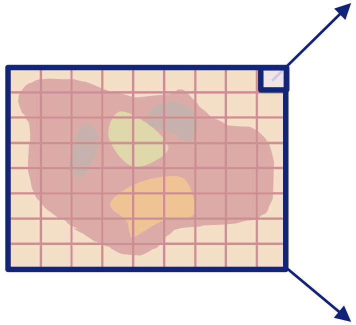
L. Monico, et al., "Degradation Process of Lead Chromate in Paintings by Vincent van Gogh Studied by Means of Synchrotron X-ray Spectromicroscopy and Related Methods. 2. Original Paint Layer Samples", *Analytical Chemistry, (2011),* ***83, 1224-1231.***

HOW TO GET FULL 2D FULL SPECTRAL INFO?

Standard XANES dwell time in XRF mode : >1 minute (>0.1s/energy)

⇒ Decrease dwell time:

- Improvement of double crystal monochromators
- Improvement of XRF detector



1 XANES spectrum over e energy steps, repeated over p pixels

1 XRF map over p pixels, repeated over e energy steps

JAAS

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online

View Journal

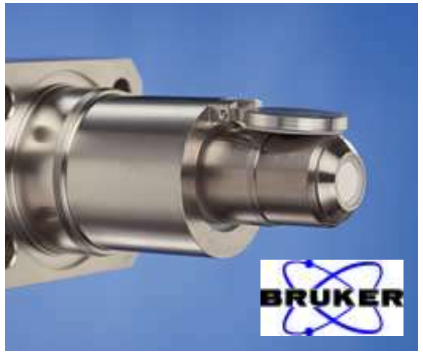
CrossMark

Cite this: DOI: 10.1039/c4ja00419a

Full spectral XANES imaging using the Maia detector array as a new tool for the study of the alteration process of chrome yellow pigments in paintings by Vincent van Gogh†

The Bedroom (V. van Gogh, October 1888, Van Gogh Museum, Amsterdam).

COMPARISON SDD AND SI DIODE ARRAY (MAIA)

	ID21 (ESRF)	P06 (DESY) /XFM (AS)
	Xflash 5100	**Maia**
		
	Si drift diode (SDD)	384-element *Si diode array*
Active area/solid angle	80 mm^2 few 10^{-1} sr	~1.3 sr
Geometry	Incident angle: 62° Detection angle: 69°	~ 180°-backscattering
Energy resolution (eV)	140 at 6 keV	290 (P06)/ 375 (XFM) at ~ 6keV
Typical dwell time	0.1-2 sec/pixel	0.5-50 msec/pixel

BROOKHAVEN NATIONAL LABORATORY
CSIRO

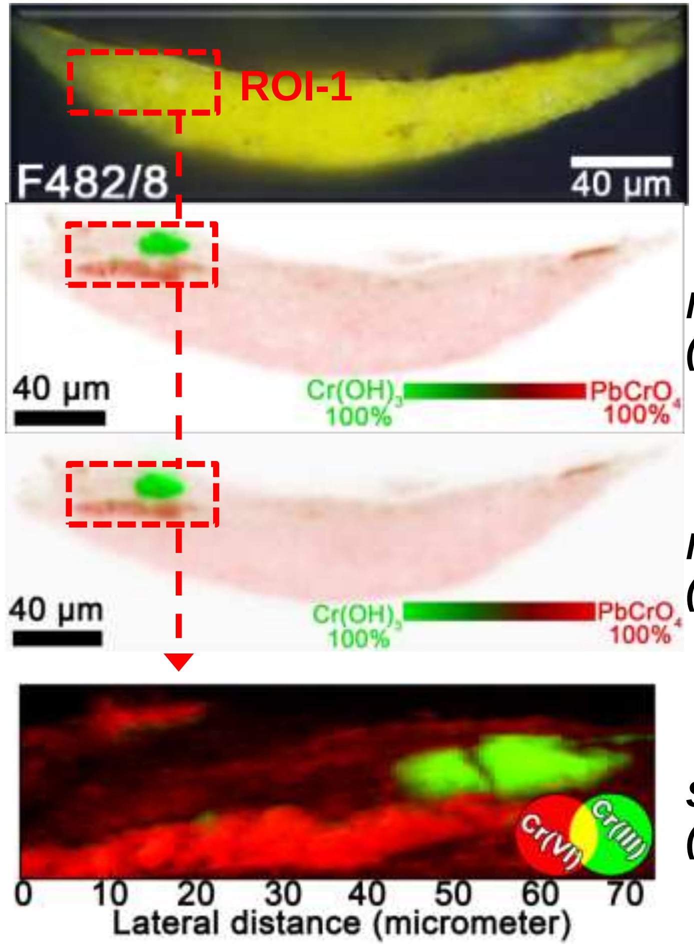
fast detector:
capabilities of process high count rates resulting from an XRF signal collected in an extended solid angle

- full spectral XANES imaging experiments
- less probability of X-ray beam induced damage

achieve the best compromises between exposure times, spatial/energy resolution and detection limits

Courtesy L. Monico

MAIA AND SSD-DETECTOR BASED MICROPROBE SYSTEMS: THE BEDROOM



Maia-XFM* *(126 maps)

Maia-P06* *(126 maps)

SDD-ID21* *(2 maps)

Beamline (SR facility)	Focusing optics	Beam size ($h \times v$) (μm^2)	Change of beam position during a scan ($h \times v$) (μm^2)	Detector	Active area/ solid angle	Geometry	Energy resolution at 6 keV (eV)	Dwell time (ms per pixel)	Attenuated photon flux[g] ($ph\ s^{-1}$)
XFM (AS)	KB mirrors	2 × 2	~3 × 3[b]	Maia 384A	384 mm^2/ ~1.3 sr	180°-backscattering	375	0.5–2	~1–3 × 10^8
P06 (DESY)[a]	KB mirrors	0.7 × 0.6	~4 × 3[c]	Maia 384B	384 mm^2/ ~1.3 sr	180°-backscattering	290	0.5–3[e]	~4 × 10^6; ~9 × 10^8
ID21 (ESRF)[a]	Fresnel zone plates	Down to 0.6 × 0.2	~0.3 × 0.5[d]	Silicon drift diode (Xflash 5100, Bruker)	80 mm^2/ few 10^{-2} sr	Incident angle: 62°, detection angle: 69°	150–170	100–300[f]	~2–9 × 10^8

↑ Faster acquisition time (factor of 10^2 -10^3 shorter per energy scan)
↑ More representative (analysis of larger areas- large n. of XANES spectra)
↑ Lower doses (2-3 order of magnitude; no/ limited beam damage)

↓ Lower spatial resolution (~0.7-2 µm)
↓ Lower spectral energy resolution
↓ stage platform less stable (Y drift correction /re-alignment)
↓ Lower doses (lower signal to noise ratio)

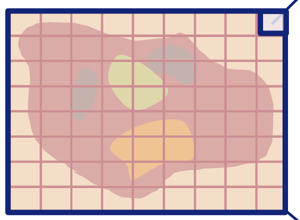
Courtesy L. Monico

HOW TO GET FULL 2D FULL SPECTRAL INFO?

Standard XANES dwell time in XRF mode : >1 minute (>0.1s/energy)

⇒ Decrease dwell time:

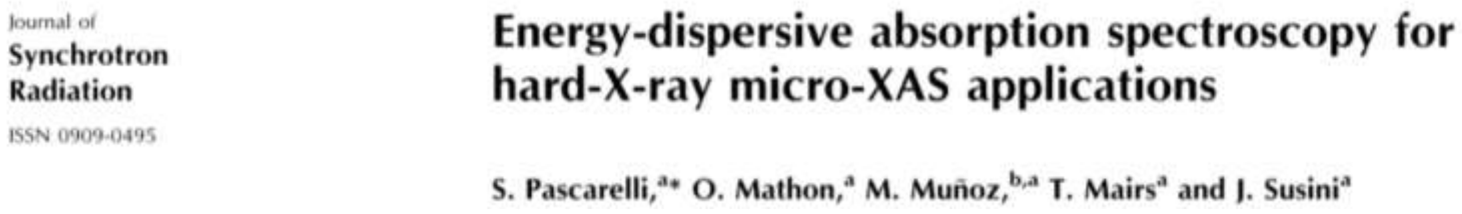
- Improvement of double crystal monochromators
- Improvement of XRF detector



1 XANES spectrum
over e energy steps,
repeated over p pixels

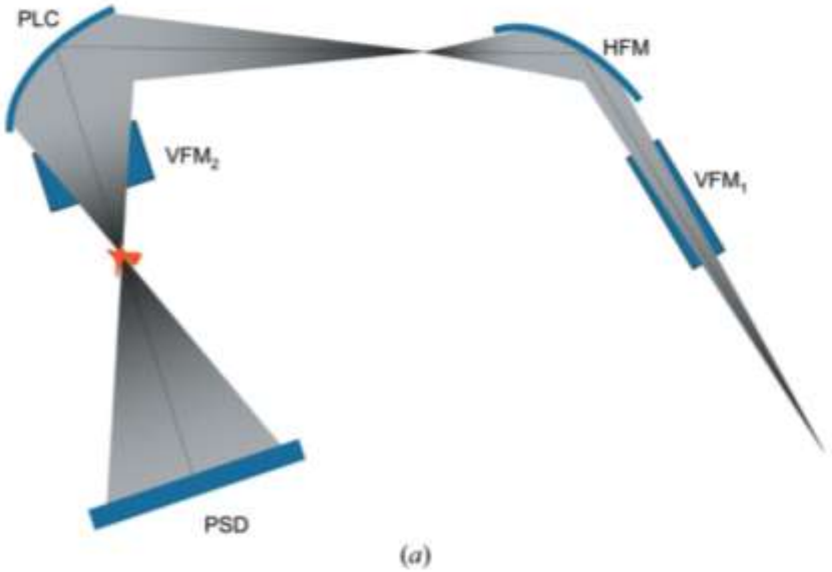
1 XRF map
over p pixels,
repeated over e energy steps

- Dispersive set-up (e.g. ID24)

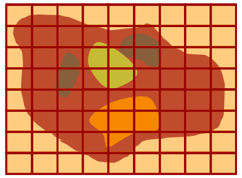

Journal of
Synchrotron
Radiation
ISSN 0909-0495

Energy-dispersive absorption spectroscopy for hard-X-ray micro-XAS applications

S. Pascarelli,[a*] O. Mathon,[a] M. Muñoz,[b,a] T. Mairs[a] and J. Susini[a]

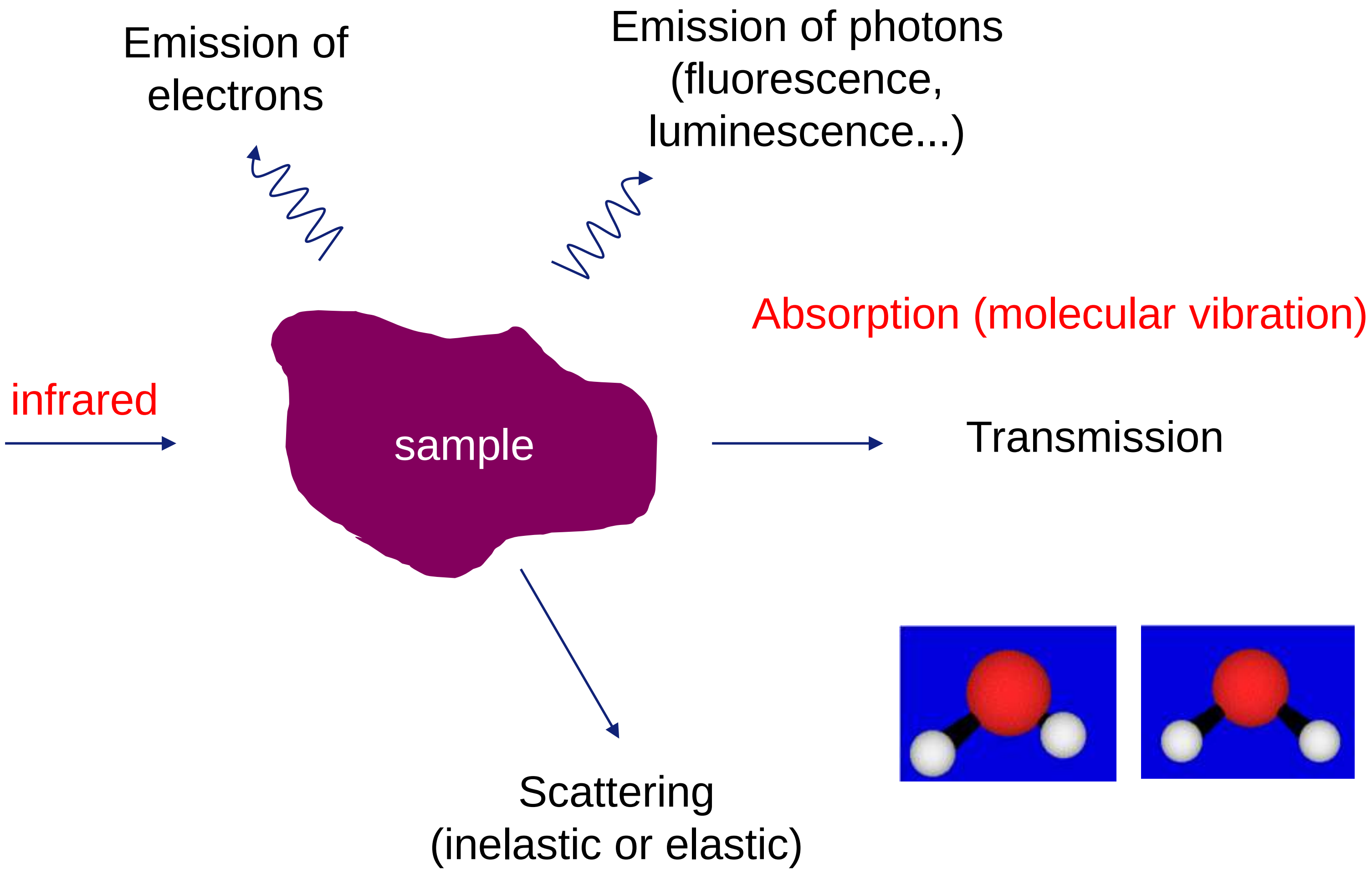


OUTLINE



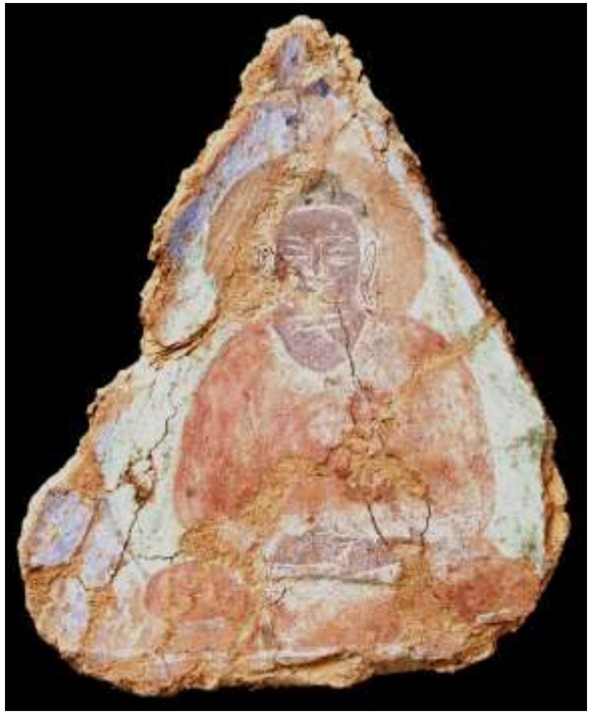
Which information?	Which technique?
Elemental composition?	X-ray fluorescence
Surrounding atoms?	X-ray absorption spectroscopy
	Infrared absorption spectroscopy (FTIR)

INFRARED SPECTROSCOPY: MOLECULAR IDENTIFICATION



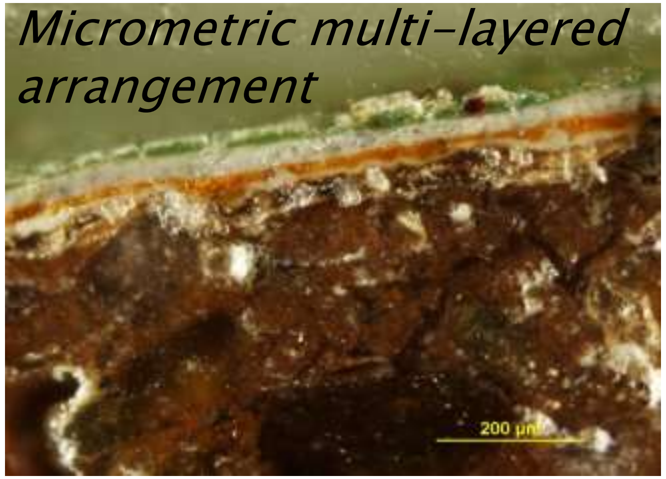
Buddhist mural paintings: creation and degradation

2D Micro FTIR spectroscopy, micro X-ray fluorescence and micro X-ray Diffraction



Buddhist paintings Bamiyan, Afghanistan
5th-9th Century

Yoko Taniguchi
Japan Centre for International Cooperation in Conservation- National, Tokyo



Determining the painting composition:
- pigments?
- organic binders?
- degradation compounds?

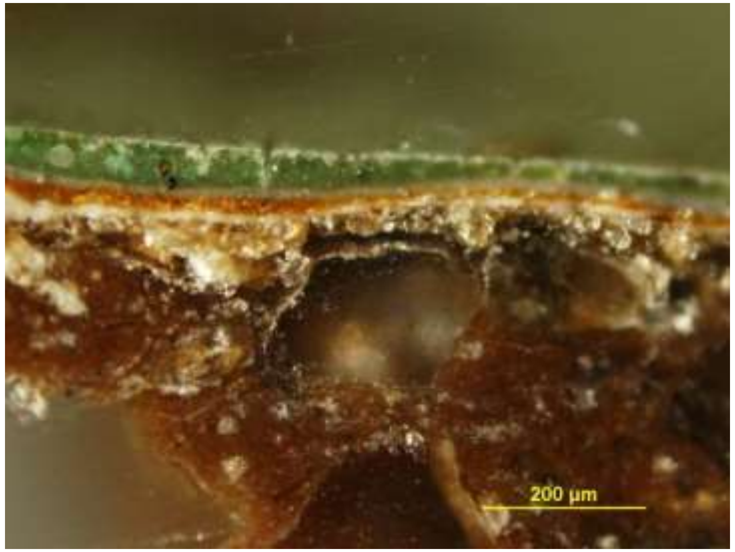
文化遺産国際協力センター
Japan Center for International Cooperation in Conservation

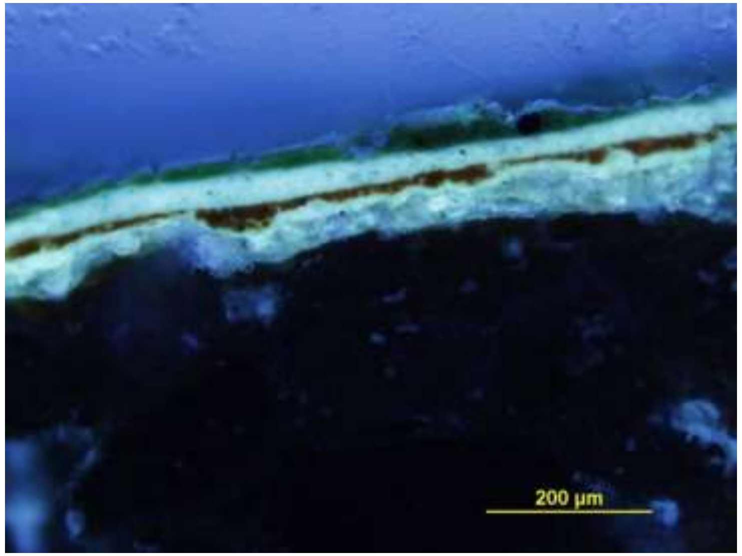
Cotte et al., JAAS, 23 (2008)

THE CONTEXT: BAMIYAN BUDDHIST MURAL PAINTINGS

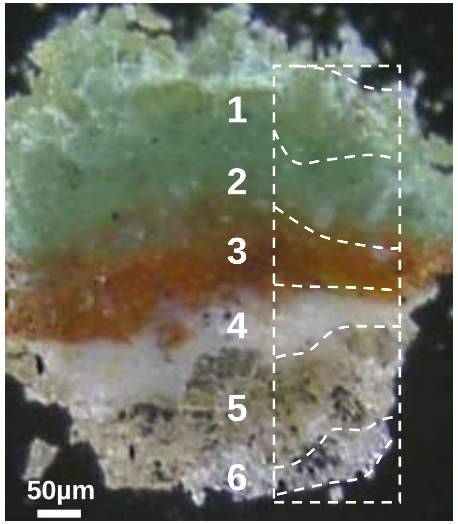
Samples were taken under the Ministry of Information and Culture of Afghanistan in a framework of Conservation Project of the Bamiyan Site. Credit/ (National Research Institute for Cultural Properties, Tokyo-Japan/UNESCO. Special thanks to Yoko Taniguchi and Emilile Checroun.

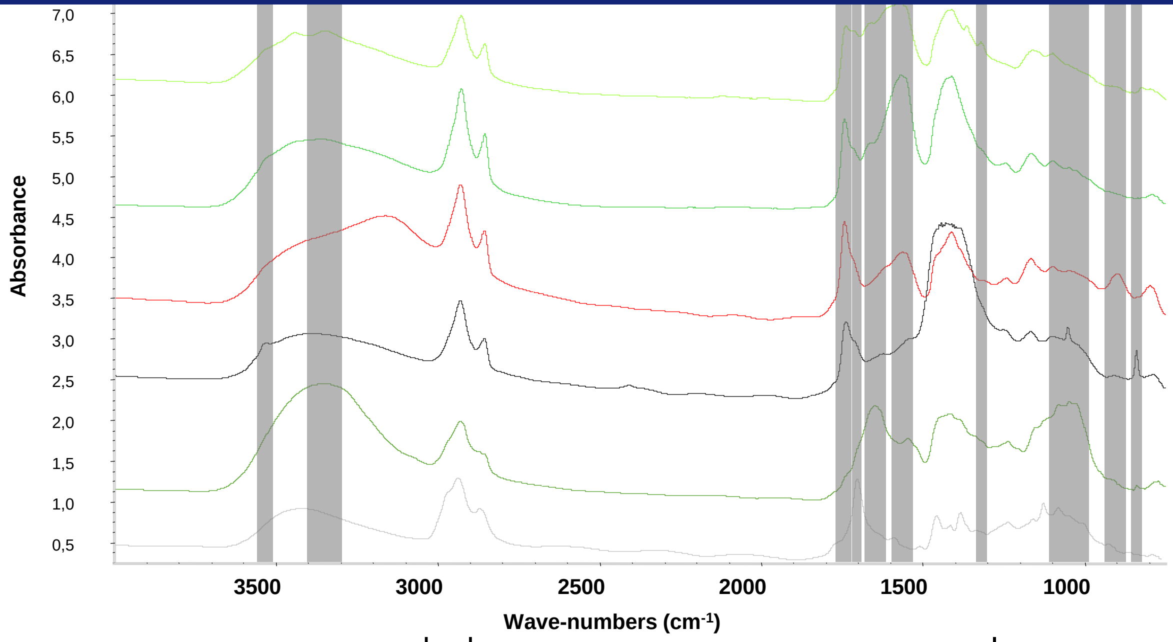
FOCUS ON A "GREEN" SAMPLE, ALTERED ON ITS SURFACE

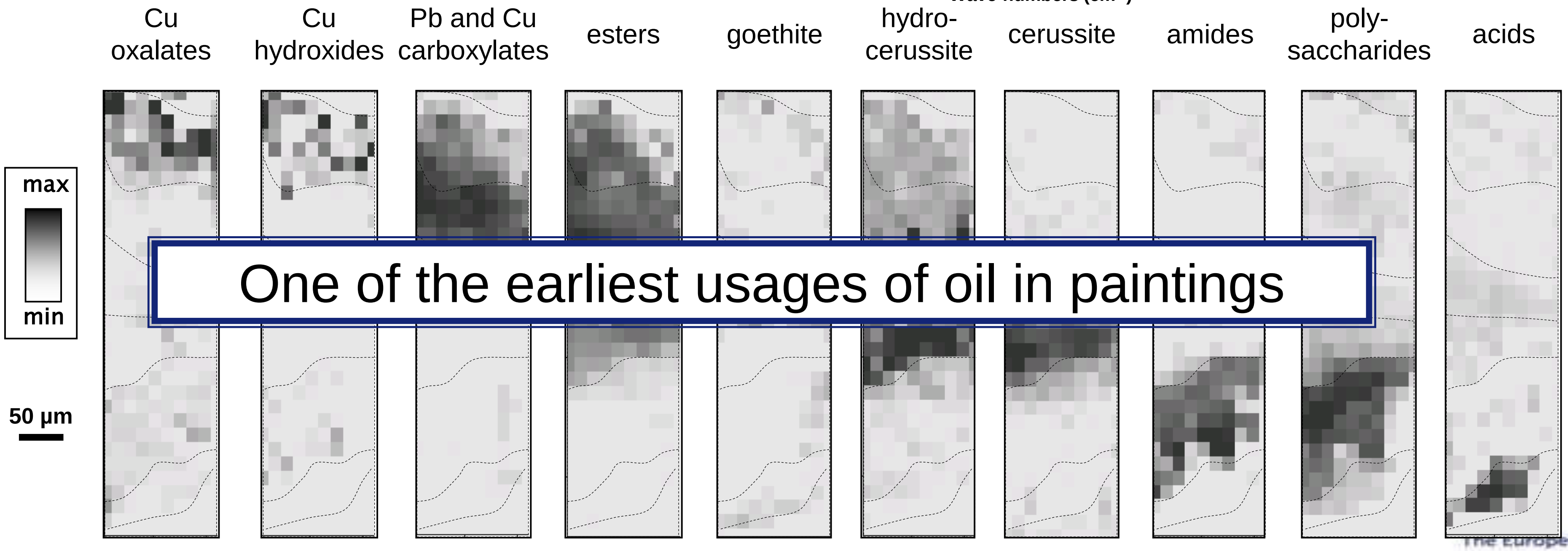




2D MICRO-FTIR ANALYSIS



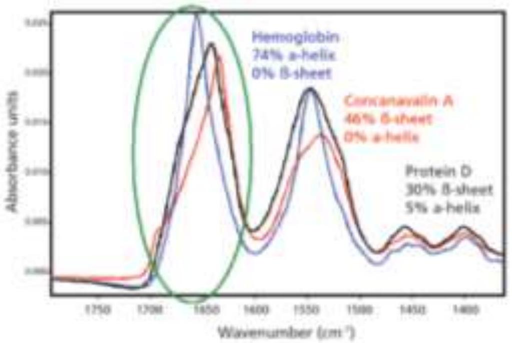




One of the earliest usages of oil in paintings

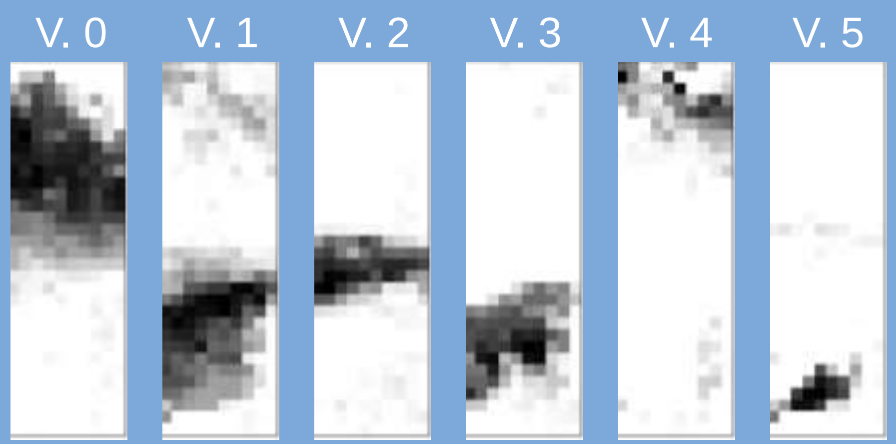
The European Synchrotron | ESRF

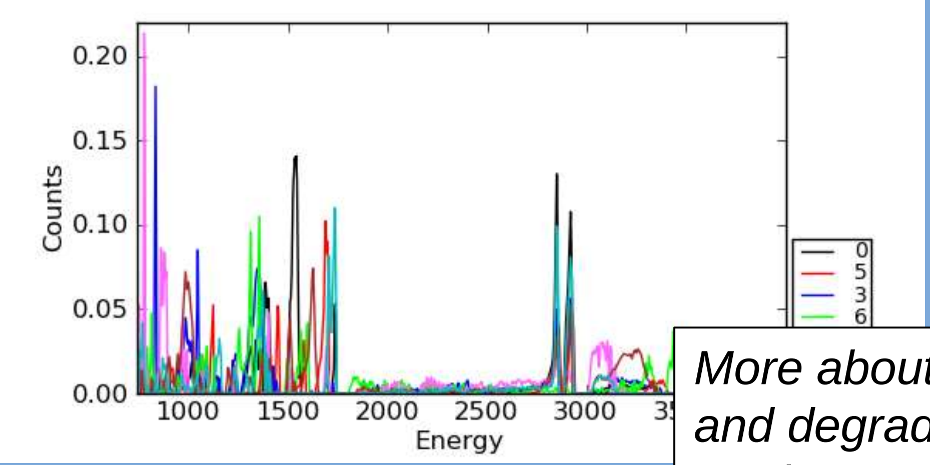
FTIR ANALYSIS: GOING BEYOND REGION OF INTEREST (ROI)



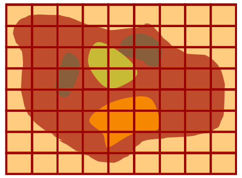
- ROI is the simplest way to analyze data.
- However, useful information in peak shape.
- Statistic methods such as Principal Component Analysis (PCA) are a classical way to analyse FTIR data
- Baseline contribution can be a problem. Hence, analysis is usually done on 1st or 2nd derivative.

Same data, analyzed by Non-Negative Matrix Approximation (NNMA) with PyMca



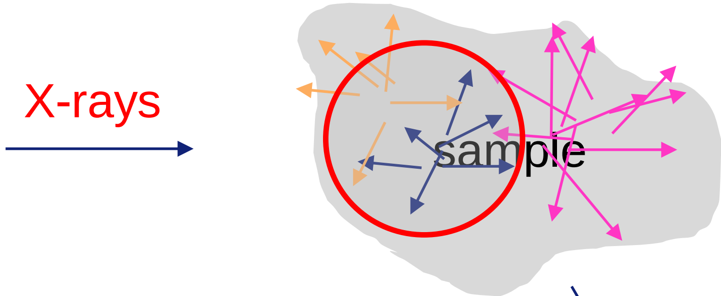


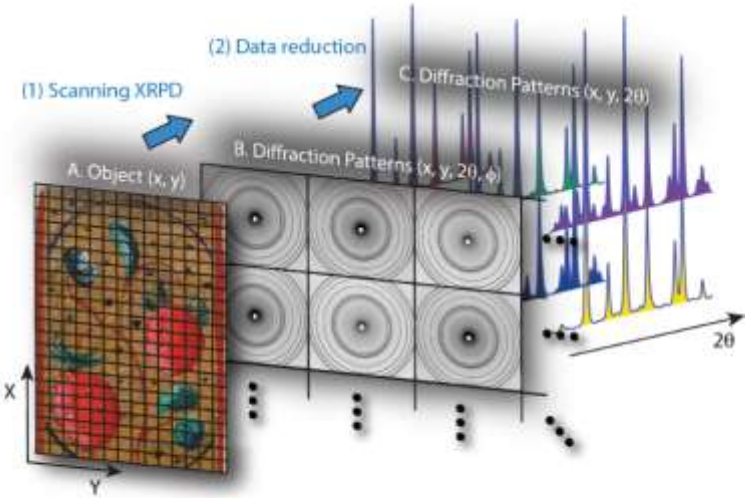
More about pigments and degradation products?



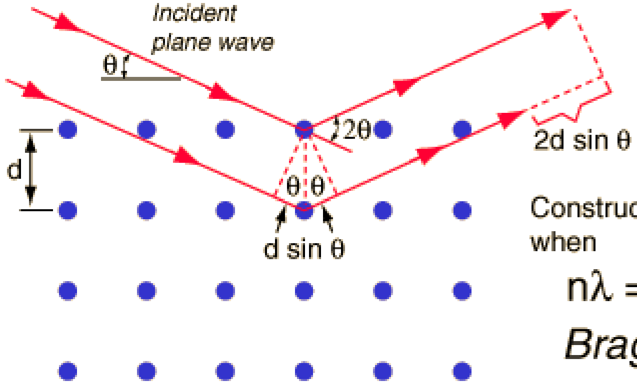
Which information?	Which technique?
Elemental composition?	X-ray fluorescence (XRF)
Surrounding atoms?	X-ray absorption spectroscopy (XAS)
	Infrared absorption spectroscopy (FTIR)
Crystalline phases?	X-ray diffraction (XRD)

Locally, many small crystals, under variation orientations: “powder-like”





Scattering
(inelastic or elastic)

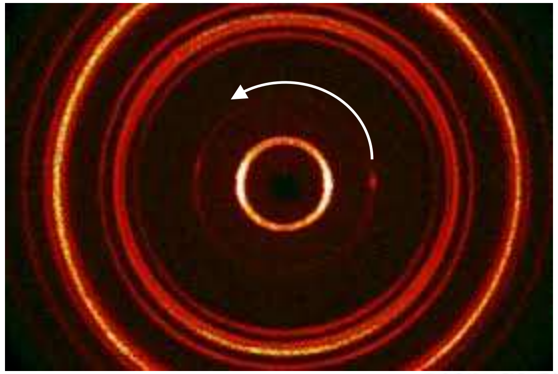


Constructive interference when

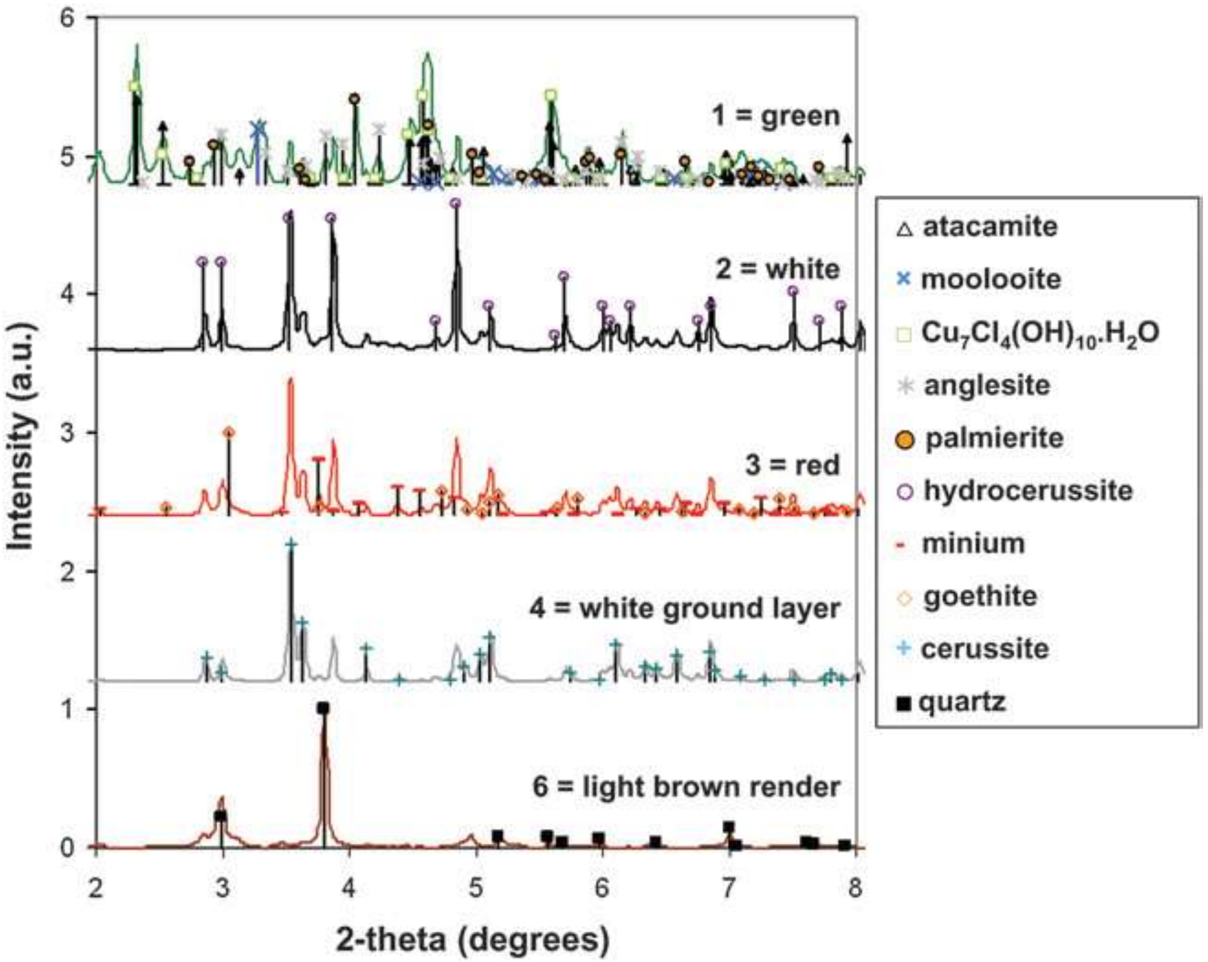
$$n\lambda = 2d \sin \theta$$

Bragg’s Law

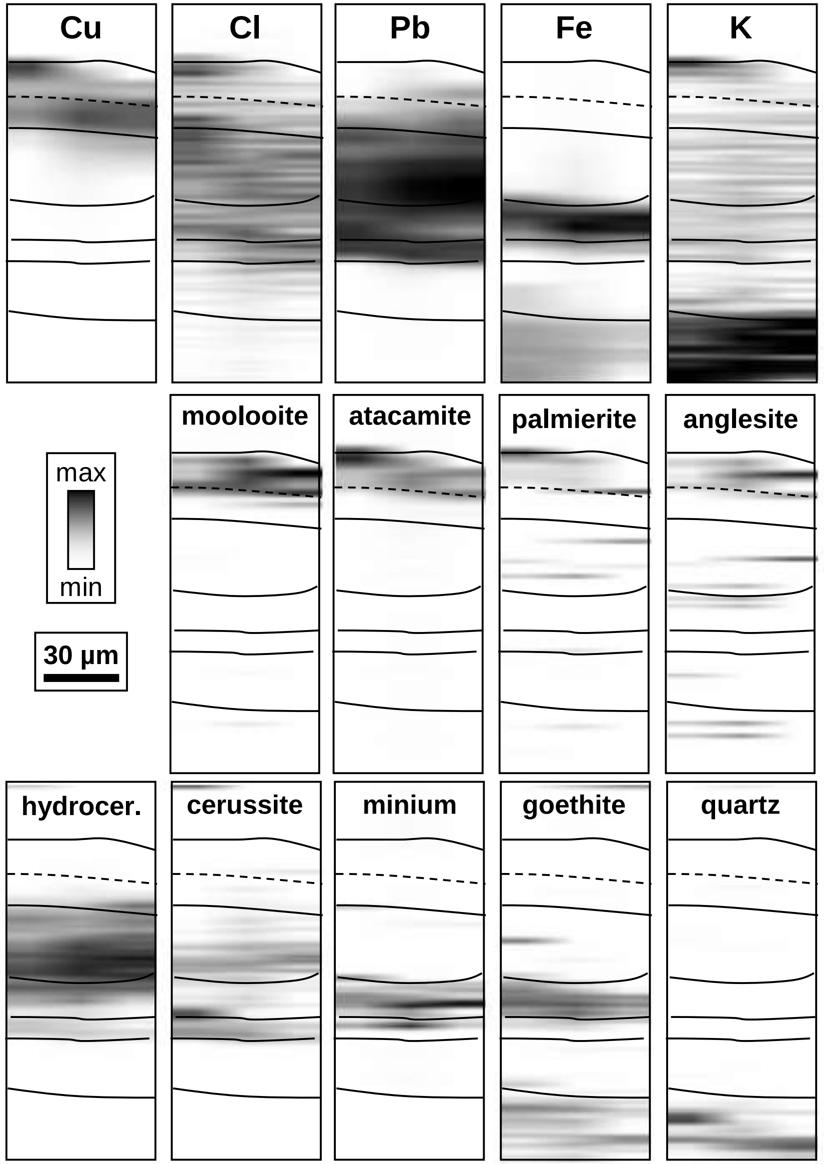
Azimuthal integration



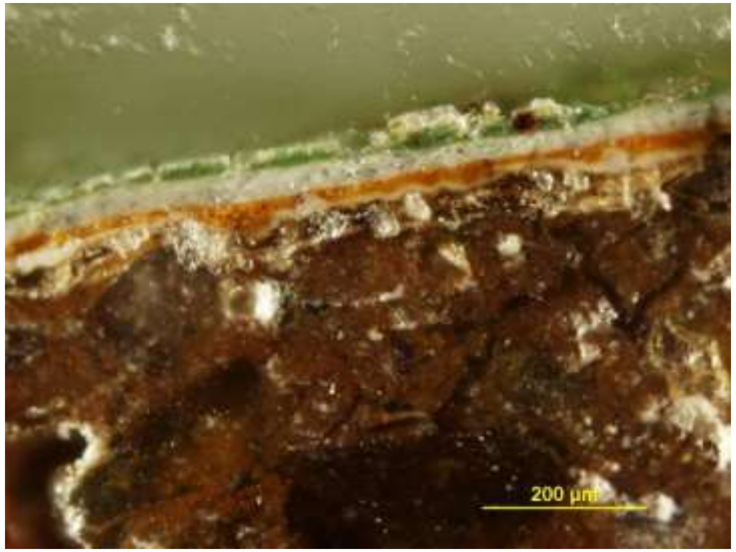
PHASE IDENTIFICATION WITH MICRO-X-RAY DIFFRACTION



μXRF/μXRD 2D MAPPING



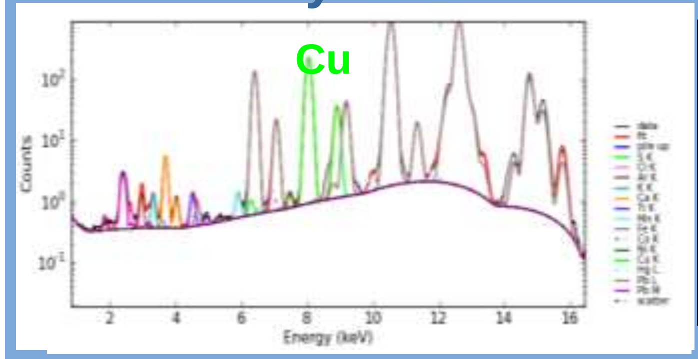
Map: 150×60µm² Step: 1×30µm² Beam: 1×15µm²

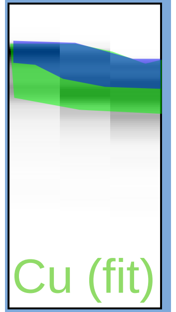


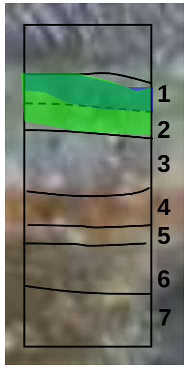
✓ Identification of pigments (in particular different composition for the same color)

✓ Identification of degradation products

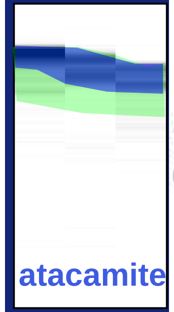
Micro X-ray fluorescence

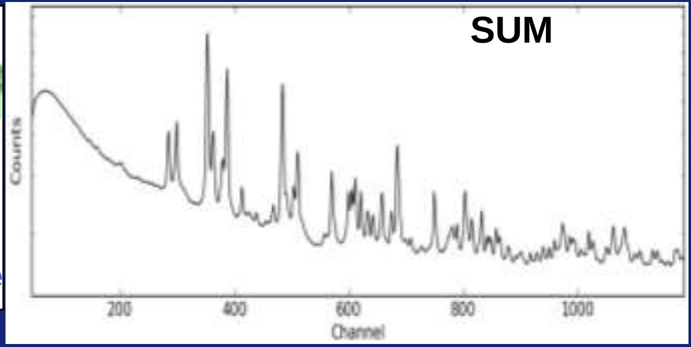


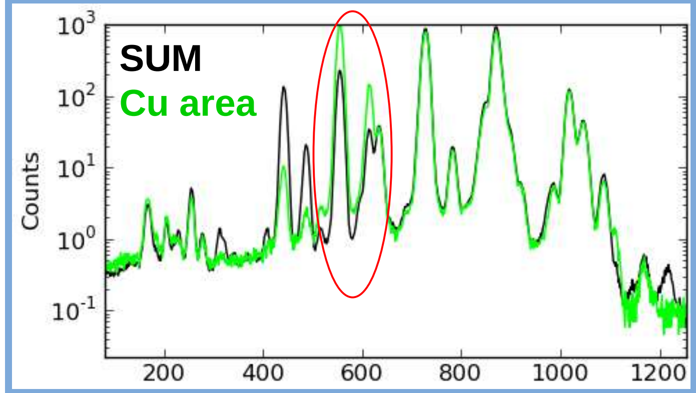


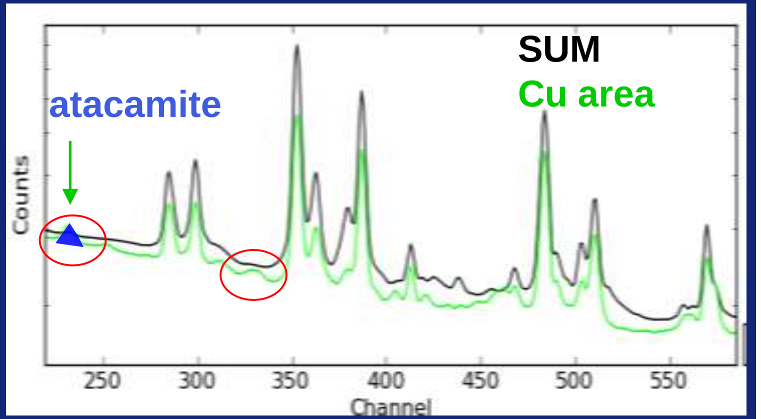


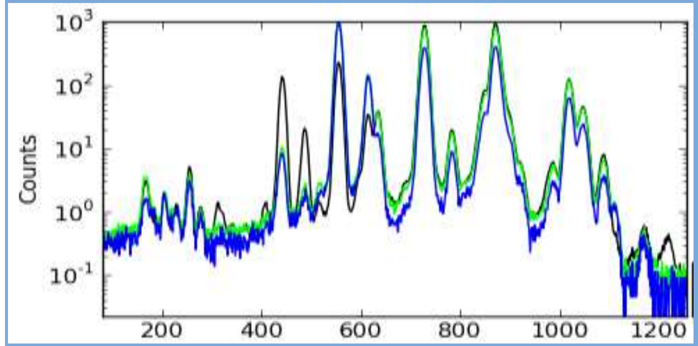
Micro-X-ray diffraction



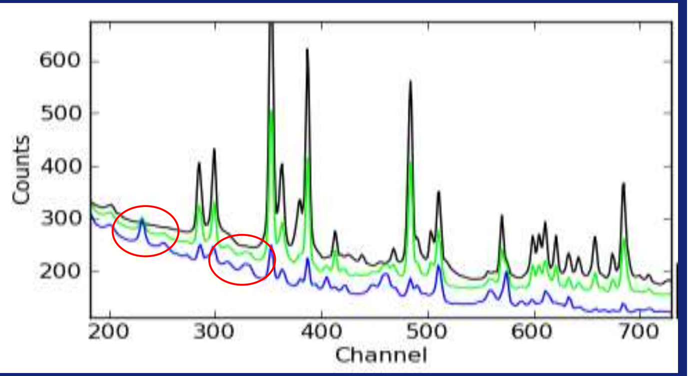




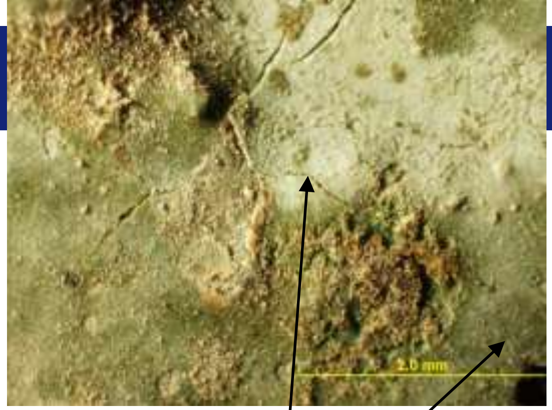


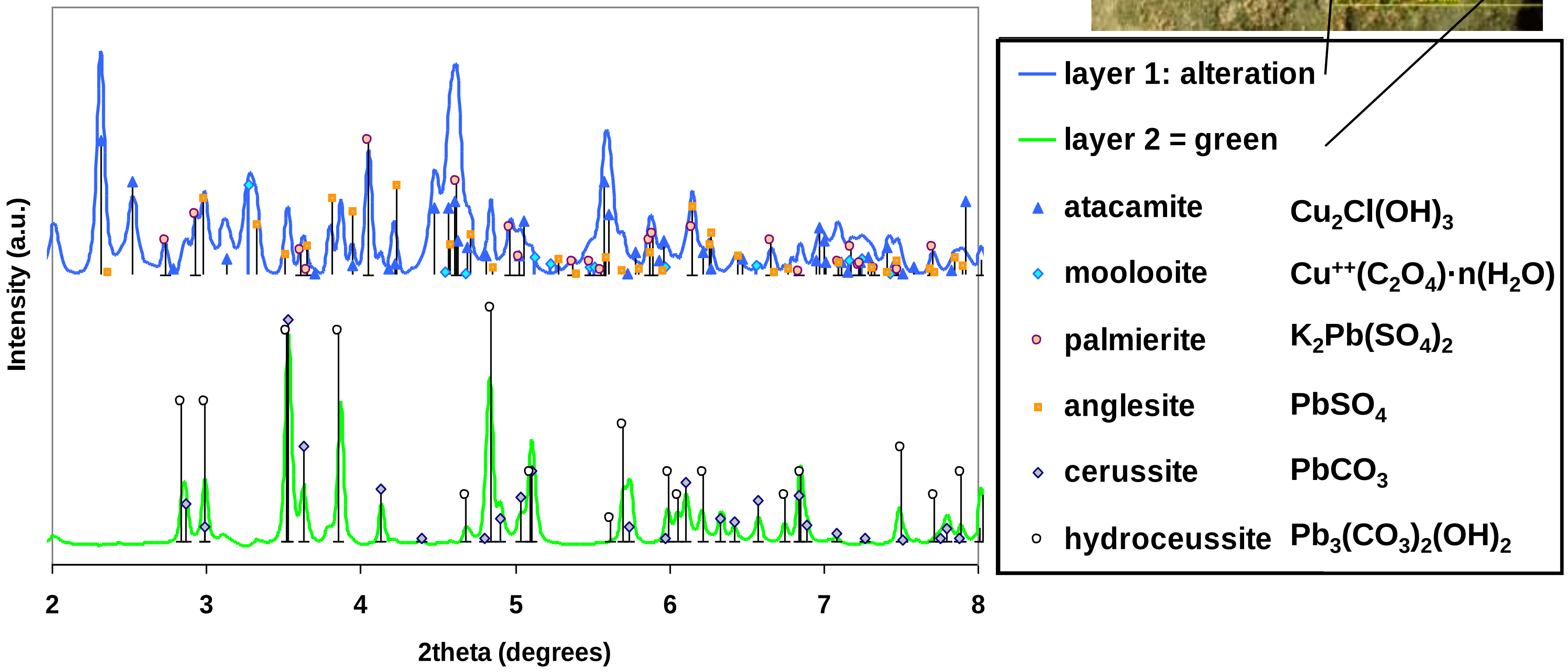


SUM
Cu area
atacamite area



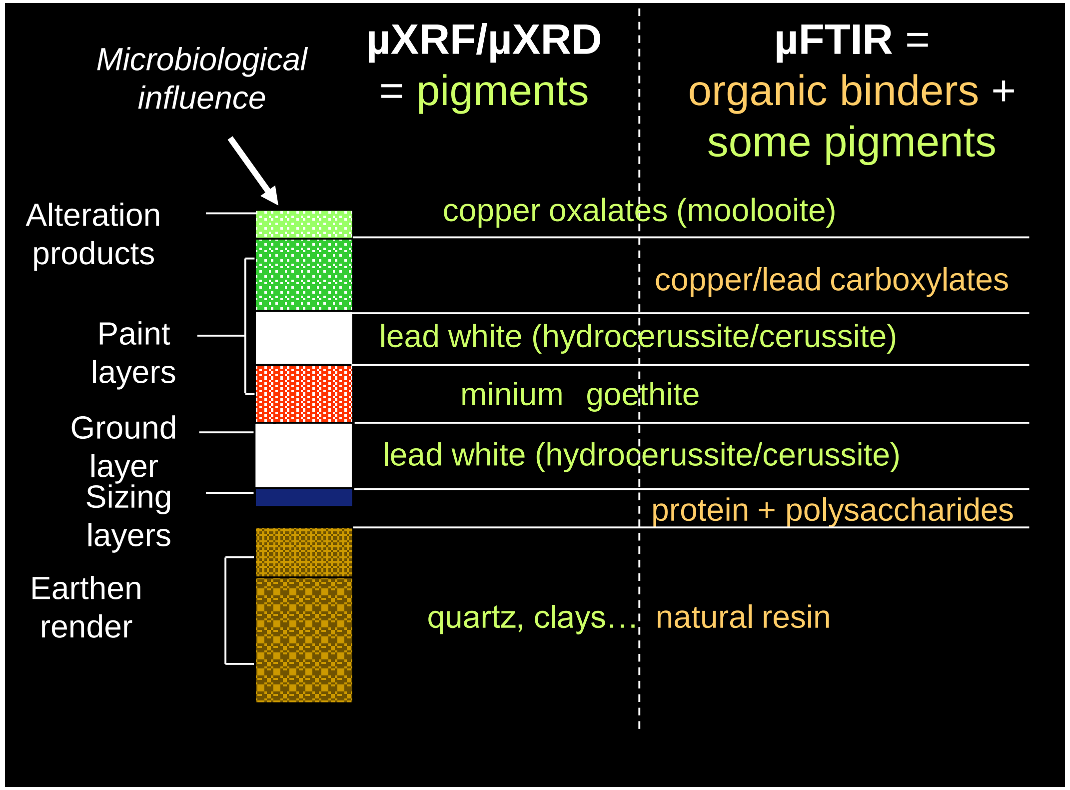
EXPLOITING THE COMBINATION XRF/ XRD





Identification of different alteration products, which were not detectable in the global sum XRD pattern

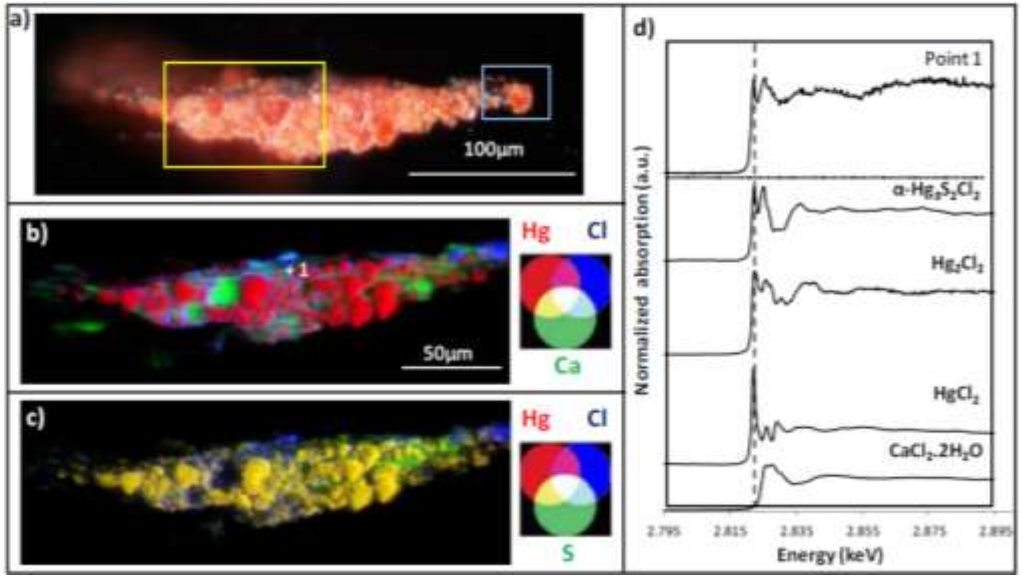
COMBINATION µXRF/µXRD 2D MAPPING WITH µFTIR



✓ Identification of ingredients
(pigments and binders) and interaction products (soaps)

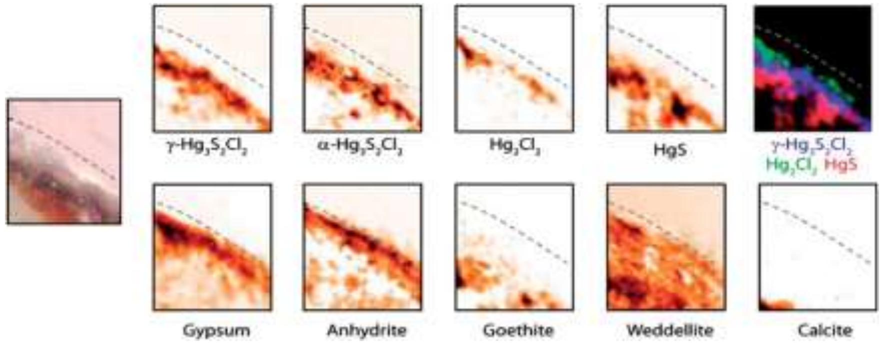
✓ Identification of degradation products

THE GREY POMPEIAN SAMPLE STUDIED BY µXRD

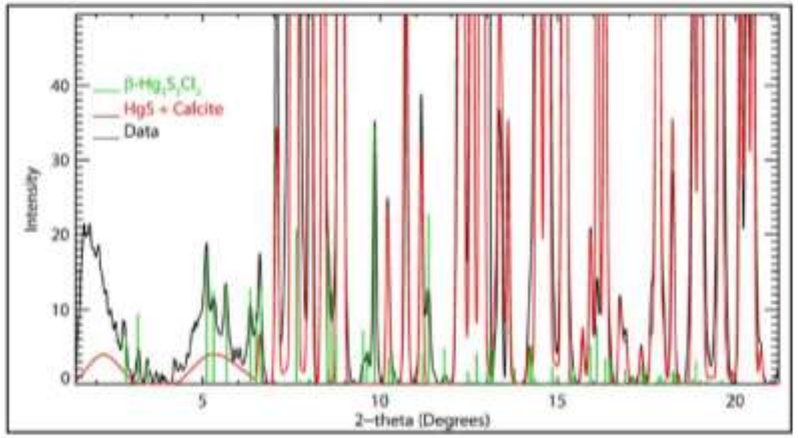


XANES @ Cl K-edge characteristic of "Cl-Hg" compounds

Different phases (α, γ) of this compound have been identified on historical and model samples (here sample from Pedralbes' monastery)



α-HgS → γ-$Hg_3S_2Cl_2$ → α-$Hg_3S_2Cl_2$ → Hg_2Cl_2



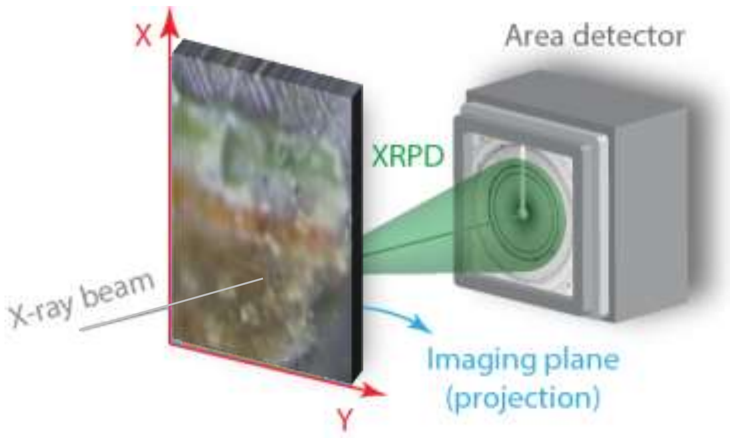
XRD allows identifying β-$Hg_3S_2Cl_2$

↳Combination **of µXRF, µXANES & µXRD** for the identification and localization of different degradation products. Visualization of the progressive substitution of S by Cl.

Radepont et al, 2011, *JAAS*

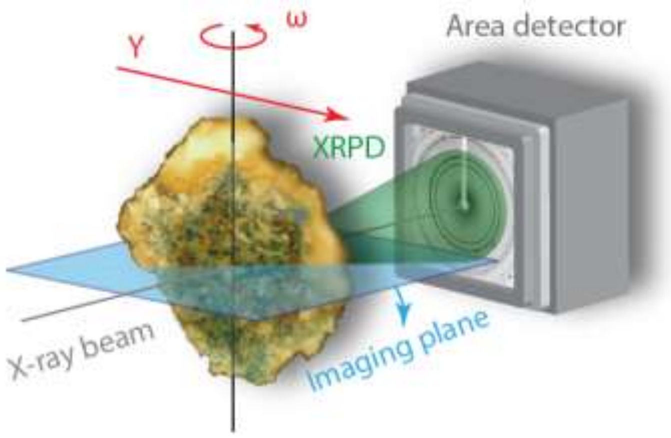
FROM 2D TO 3D µXRD

2D scanning



=> Physical cross section

Tomography



=> Virtual cross section

Pigment Discoloration

DOI: 10.1002/ange.201411691

Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting**

*Frederik Vanmeert, Geert Van der Snickt, and Koen Janssens**

Figure 1. a) Photograph of *Wheat Stack Under a Cloudy Sky* by Van Gogh (October 1889, oil on canvas, Kröller-Müller Museum, NL). The sample area is indicated by the white circle. b) Detail of the severed pustular mass on the painting surface. c) Detail of the paint sample.

P06, PETRA III at DESY

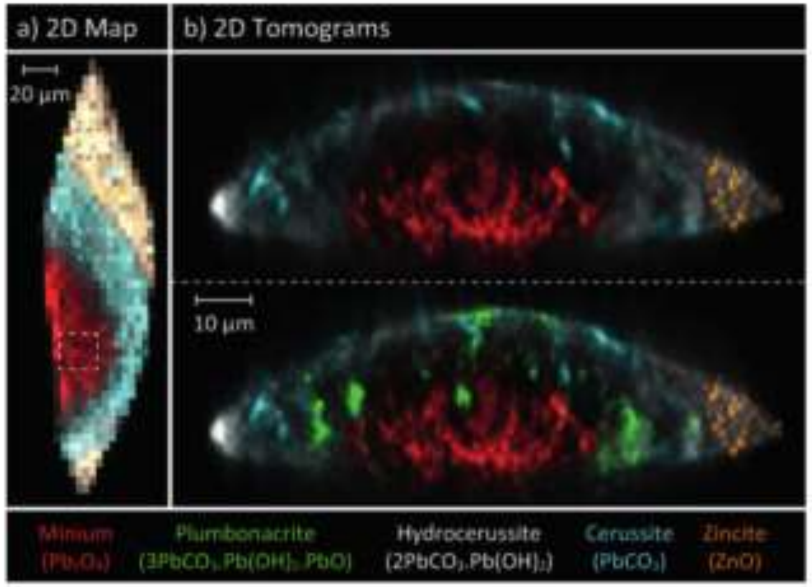
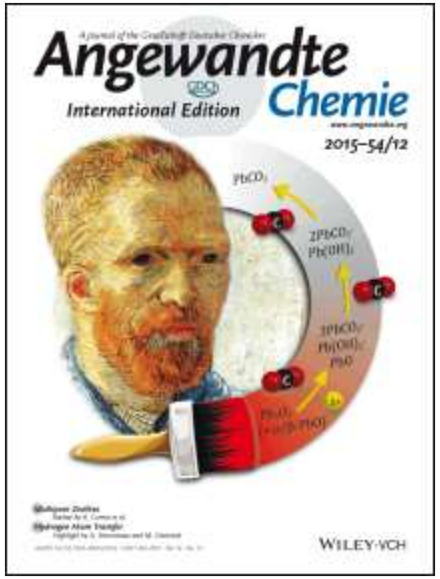
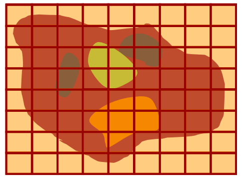


Figure 3. Color reconstructions of a) the projected and b) the internal crystalline distribution of the paint sample. Pixel size: a) $4\times5\ \mu m^2$, b) $1\times1\ \mu m^2$. The dashed boxes show the regions from which averaged diffractograms were extracted (see Figure S1–3, Supporting Information).

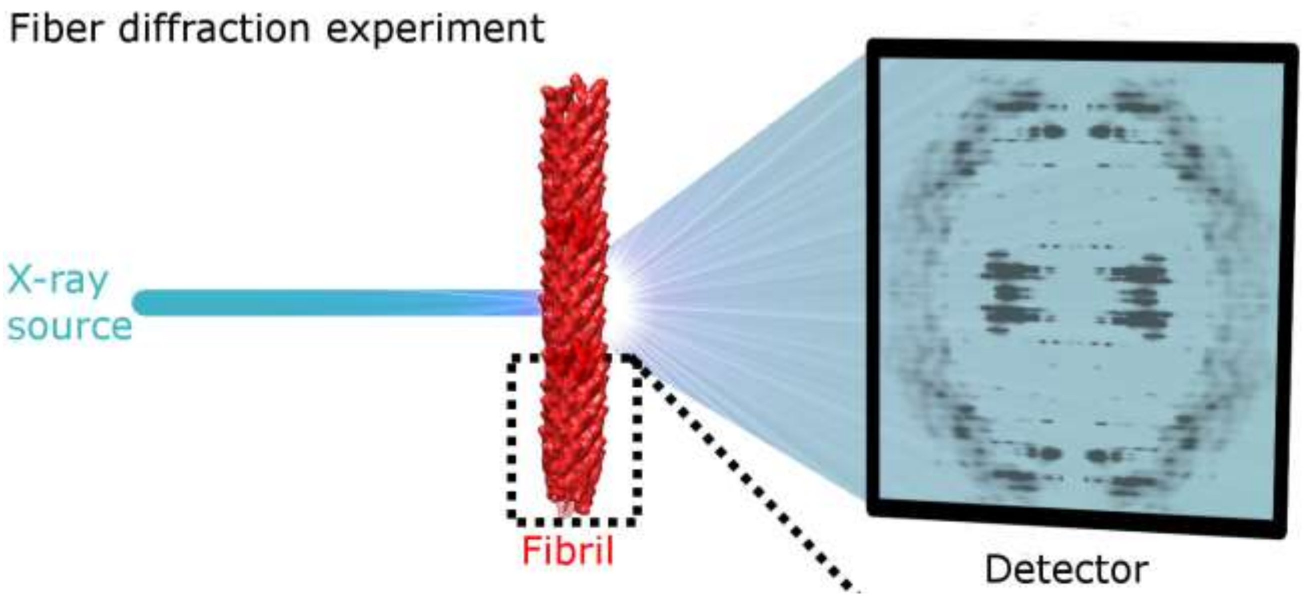


OUTLINE

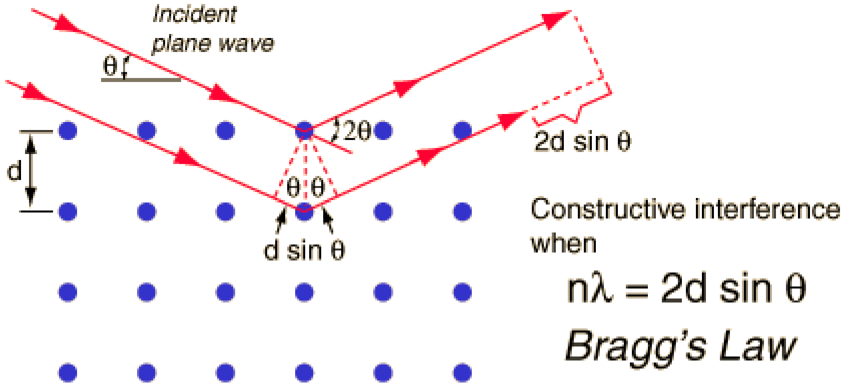


Which information?	Which technique?
Elemental composition?	X-ray fluorescence (XRF)
Surrounding atoms?	X-ray absorption spectroscopy (XAS)
	Infrared absorption spectroscopy (FTIR)
Crystalline phases?	X-ray diffraction (XRD)
Orientation?	Small angle and wide angle scattering (SAXS and WAXS)

X-RAY DIFFRACTION-2: FIBER DIFFRACTION EXPERIMENT

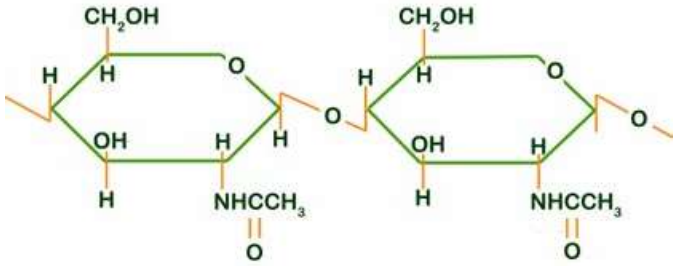


One preferential orientation



Scattering
(inelastic or elastic)

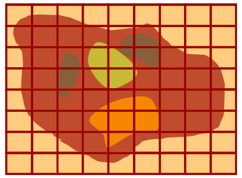
Dragonfly
(Aeshna spec.)



α-chitin based exoskeleton

Courtesy M. Burghammer, ID13

OUTLINE



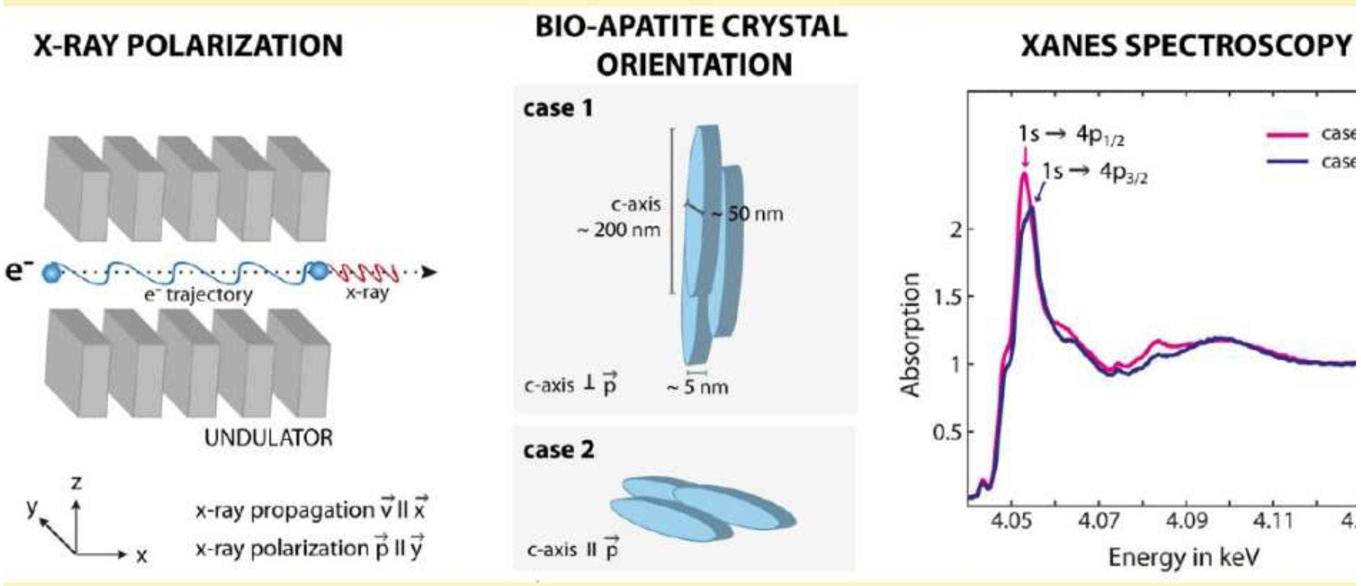
Which information?	Which technique?
Elemental composition?	X-ray fluorescence (XRF)
Surrounding atoms?	X-ray absorption spectroscopy (XAS)
	Infrared absorption spectroscopy (FTIR)
Crystalline phases?	X-ray diffraction (XRD)
Orientation?	Small angle and wide angle scattering (SAXS and WAXS)
	X-ray and infrared absorption spectroscopy

MAPPING CRYSTAL ORIENTATION BY USING POLARIZED XANES MAPS

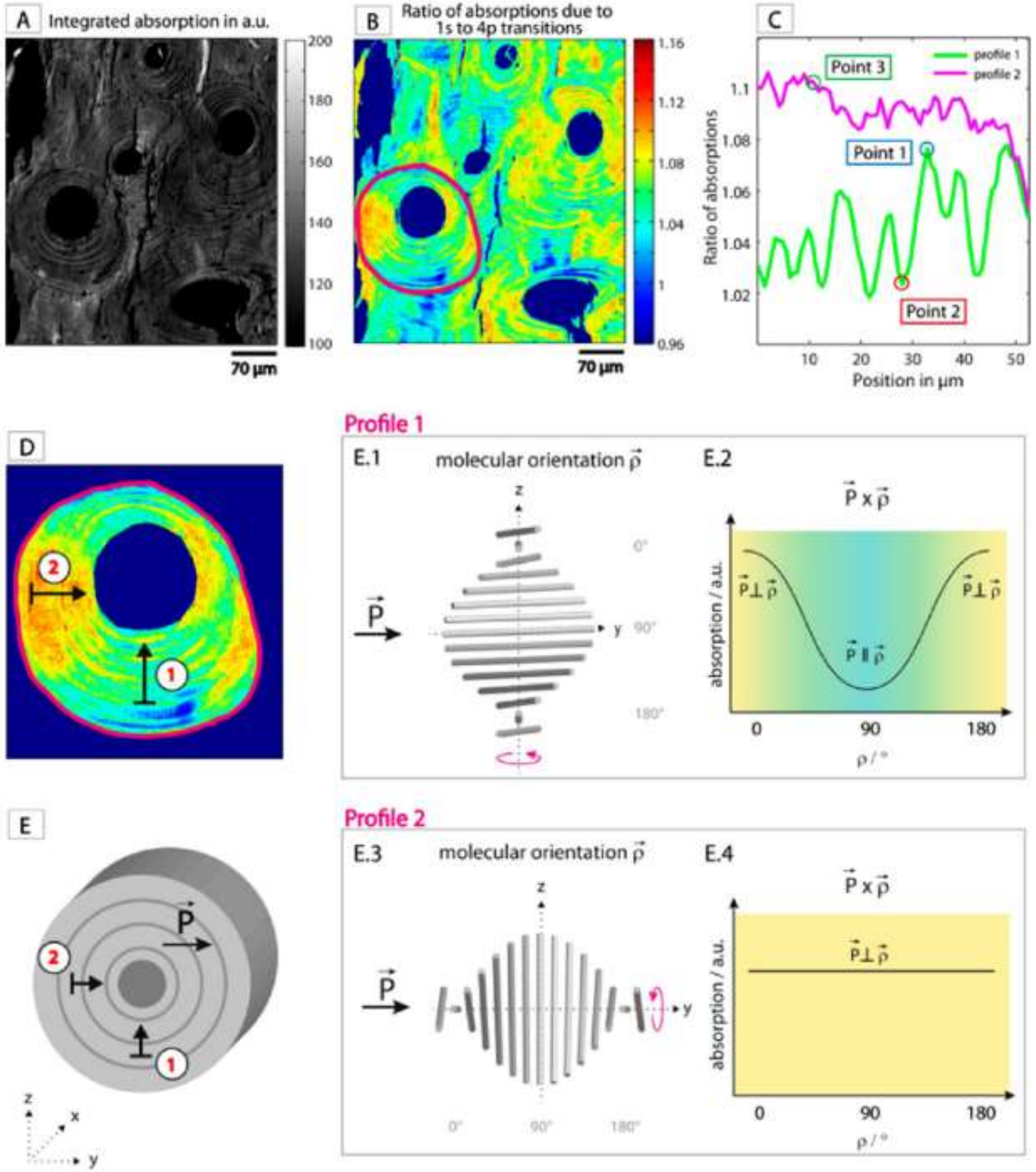
analytical chemistry
Article
pubs.acs.org/

Full-Field Calcium K-Edge X-ray Absorption Near-Edge Structure Spectroscopy on Cortical Bone at the Micron-Scale: Polarization Effects Reveal Mineral Orientation

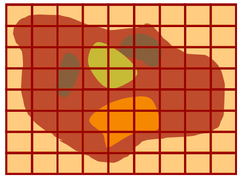
Bernhard Hesse,*[†] Murielle Salome,[†] Hiram Castillo-Michel,[†] Marine Cotte,[†,‡] Barbara Fayard,[†,○] Christoph J. Sahle,[†] Wout De Nolf,[†] Jana Hradilova,[§,∥] Admir Masic,[⊥] Birgit Kanngießer,[#] Marc Bohner,
Peter Varga,[▽] Kay Raum,[§] and Susanne Schrof[§]



Bone osteons



OUTLINE

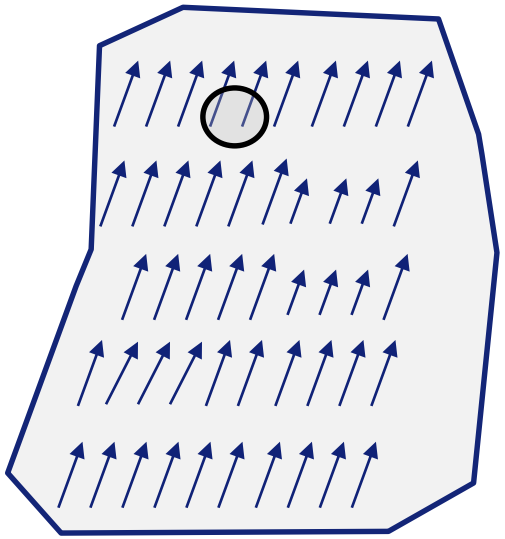


Which information?	Which technique?
Elemental composition?	X-ray fluorescence (XRF)
Surrounding atoms?	X-ray absorption spectroscopy (XAS)
	Infrared absorption spectroscopy (FTIR)
Crystalline phases?	X-ray diffraction (XRD)
Orientation?	Small angle and wide angle scattering (SAXS and WAXS)
	X-ray and infrared absorption spectroscopy
Strain and tilt?	K-mapping

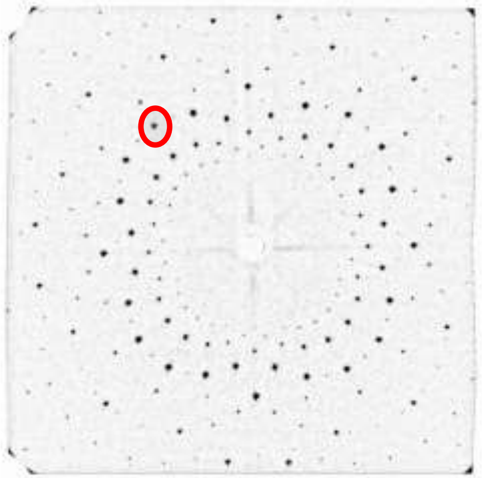
X-RAY DIFFRACTION-3: K-MAPPING

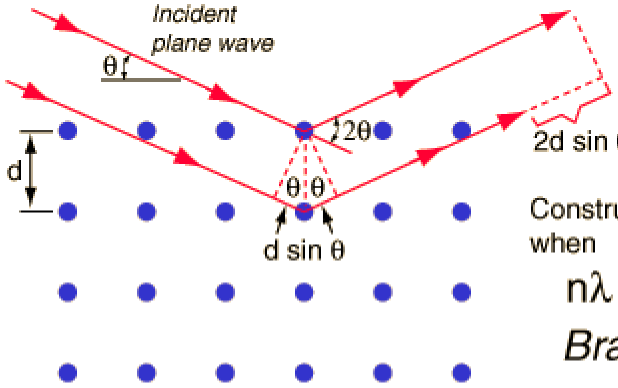
Locally, pure phase
Local modification of interatomic distance or tilt

X-rays



Scattering
(inelastic or elastic)





Constructive interference when

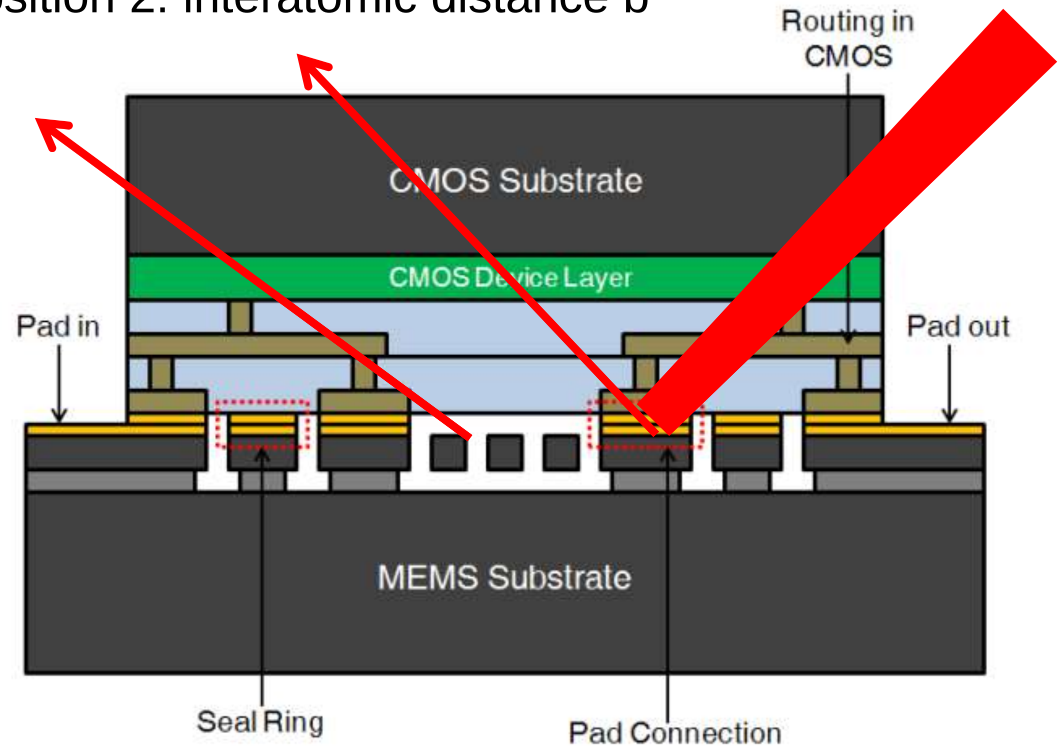
$$n\lambda = 2d \sin \theta$$

Bragg's Law

K-MAPPING: A TYPICAL EXAMPLE

Position 1: interatomic distance a

Position 2: interatomic distance b



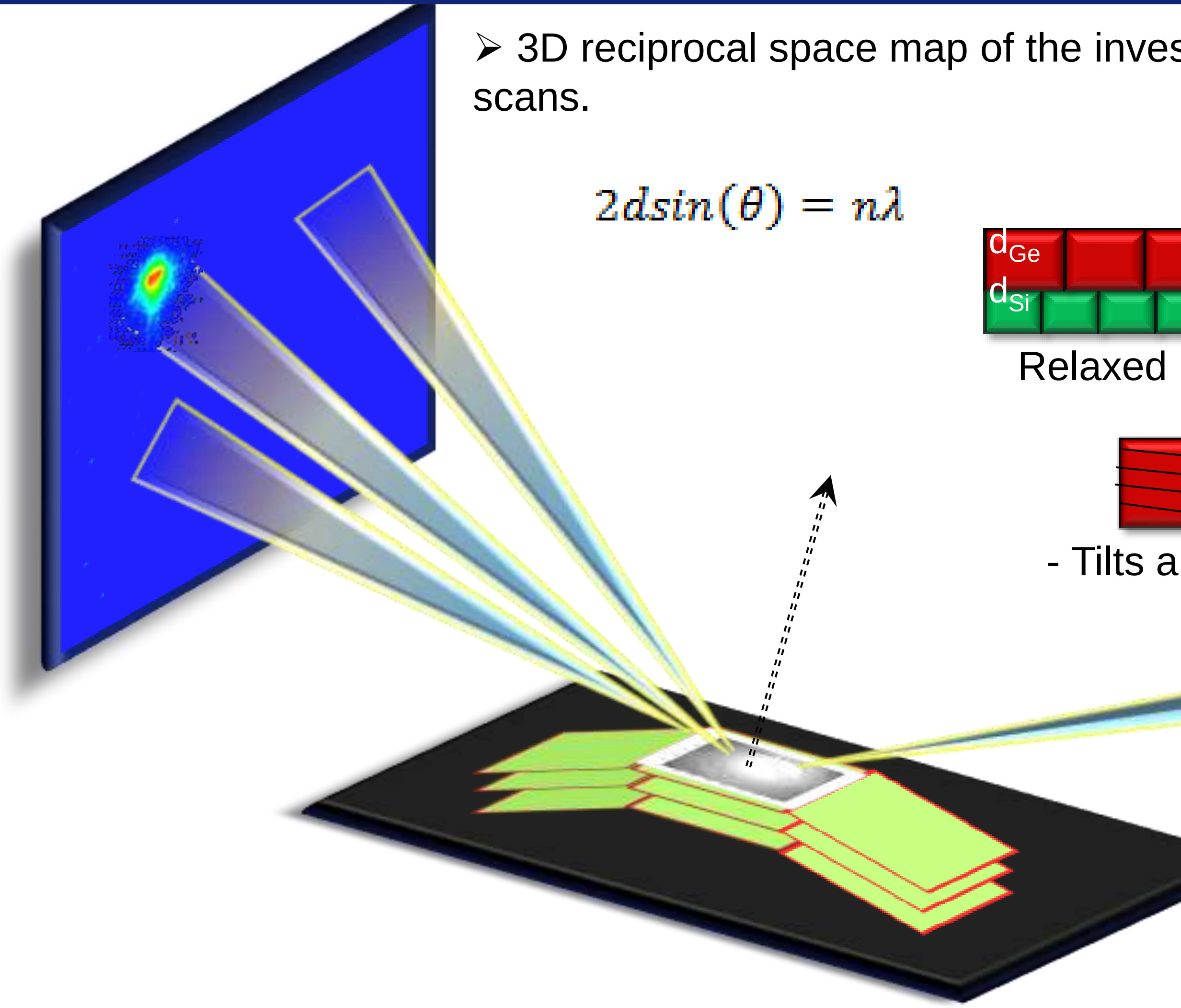
Measurements not necessarily on the surface of the object: analysis of working devices, *in-situ*, without sample preparation

Limits: requires spatially homogeneous samples

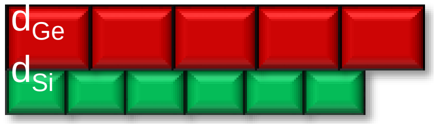
Courtesy T. Schulli, ID01

3D RECIPROCAL SPACE MAP

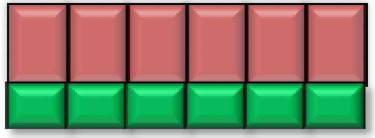
- 3D reciprocal space map of the investigated structure by making θ -2θ scans.



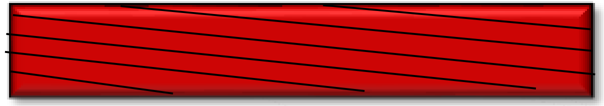
$$2d\sin(\theta) = n\lambda$$



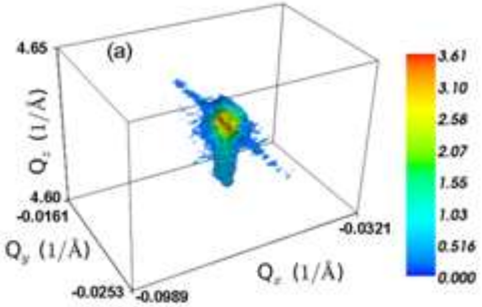
Relaxed Film



Strained Film

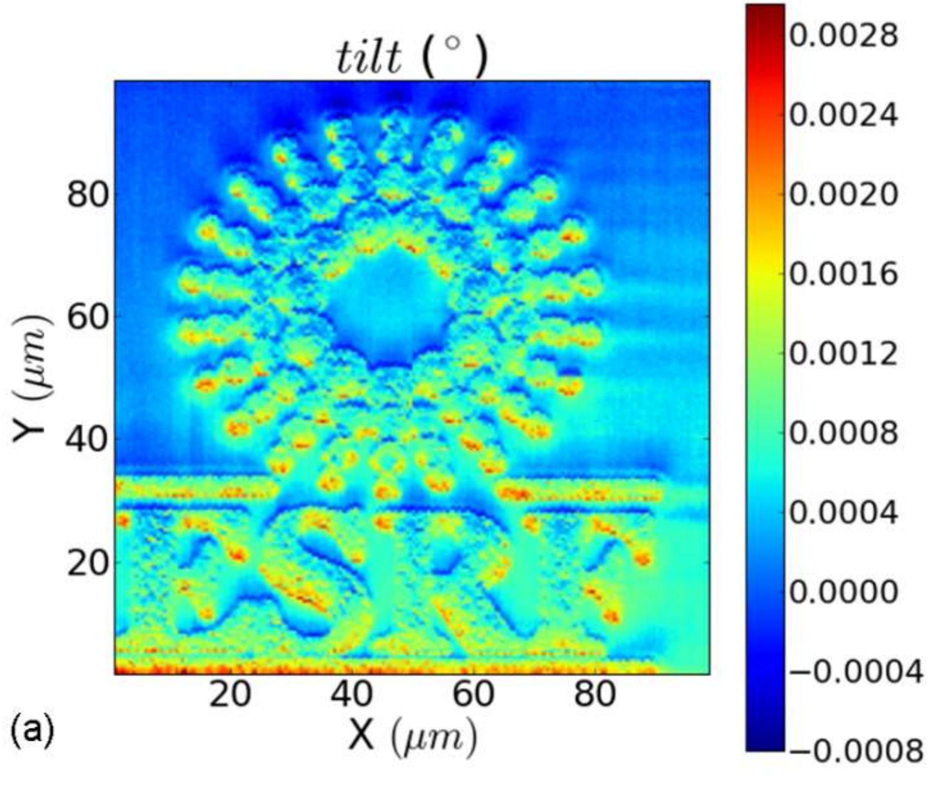


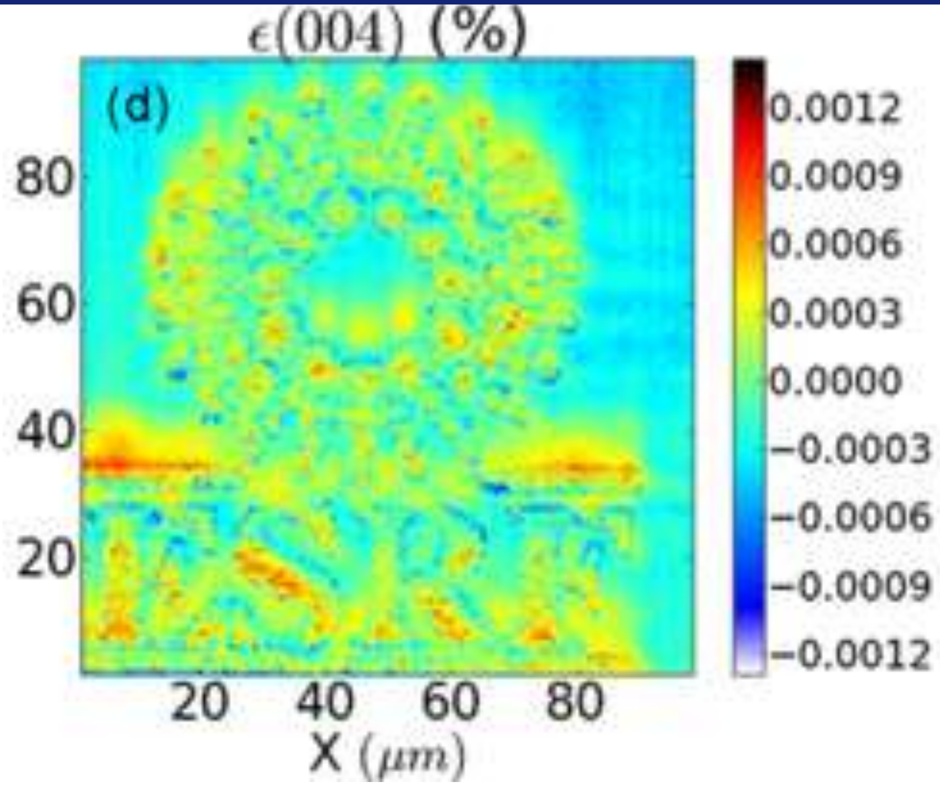
- Tilts appears as perpendicular shifts.



- Several scans, for several θ angles, are necessary to record the 3D reciprocal (~30 θ values)

Courtesy T. Schulli, ID01





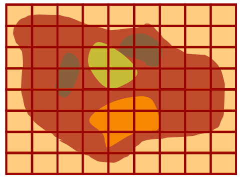
***Tilt* < 10^{-3} °**

***Δd/d* < 10^{-5}**

Relative strain levels of Δd/d 10^{-6} can trace a landscape
= we can "see" a ΔT of a few K potentially in buried systems (working devices)
Spatial resolution:100 nm (today)

Courtesy T. Schulli, ID01

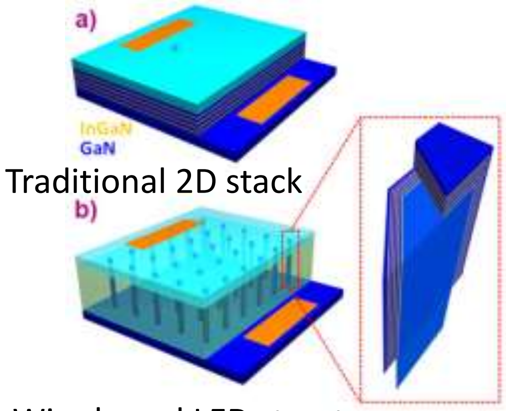
G. A. Chahine, M.-I. Richard, R. A. Homs-Regojo et al., *J. Appl. Cryst.* (2014)



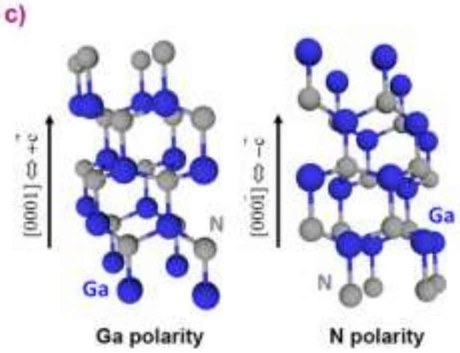
Which information?	Which technique?
Elemental composition?	X-ray fluorescence (XRF)
Surrounding atoms?	X-ray absorption spectroscopy (XAS)
	Infrared absorption spectroscopy (FTIR)
Crystalline phases?	X-ray diffraction (XRD)
Orientation?	Small angle and wide angle scattering (SAXS and WAXS)
	X-ray and infrared absorption spectroscopy
Strain and tilt?	K-mapping
Luminescence?	X-ray excited optical luminescence (XEOL)

X-RAY EXCITED OPTICAL LUMINESCENCE ON GaN NANOWIRES

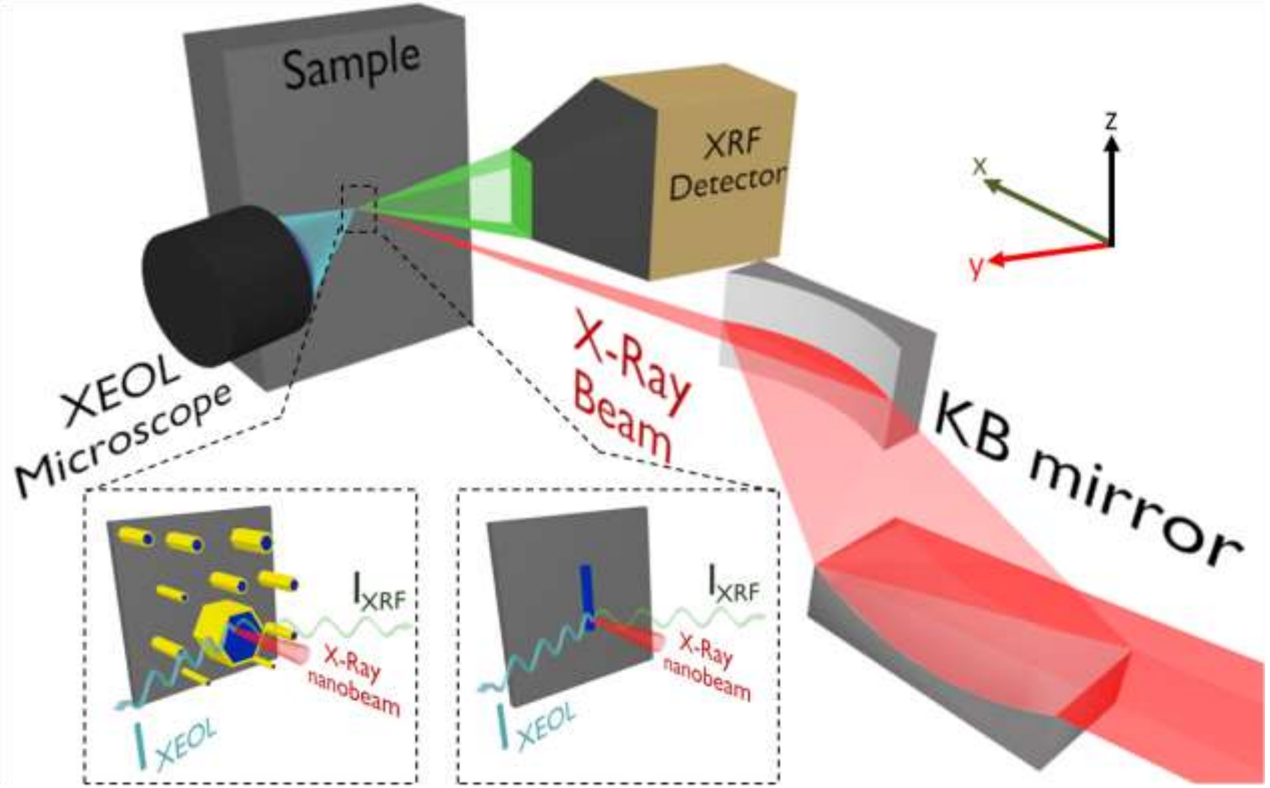
GaN nanowires have potential to improve the performance of light emitting diodes. The optical properties of a device based on nanowires are highly dependent on the growth conditions of the nanowires. X-ray excited optical luminescence microscopy has been used to map single GaN wires and reveal the influence of silane injection during growth on the material quality.



Wire based LED structures



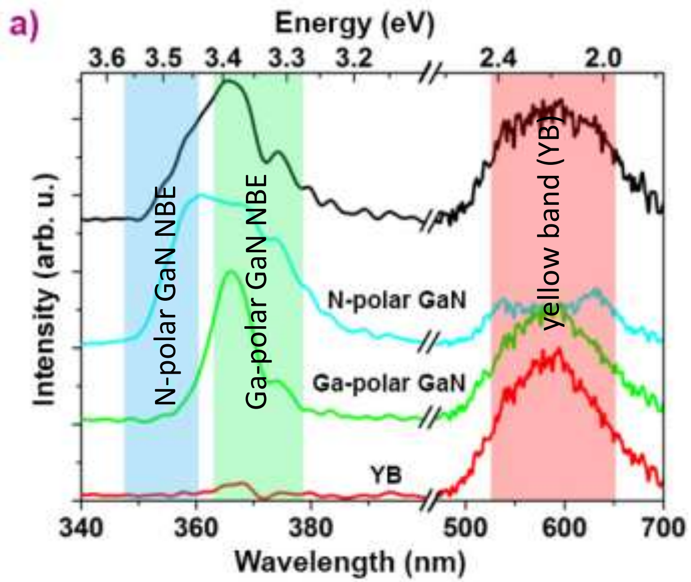
In standard conditions, GaN crystallises in the wurtzite structure (not centro-symmetric): growths along the +c (Ga-polarity) and –c (N-polarity) axis not equivalent:
=> dopant incorporation and chemical reactivity are different for these two polarities.
Ga- and N-polar GaN incorporates Si differently: different luminescence



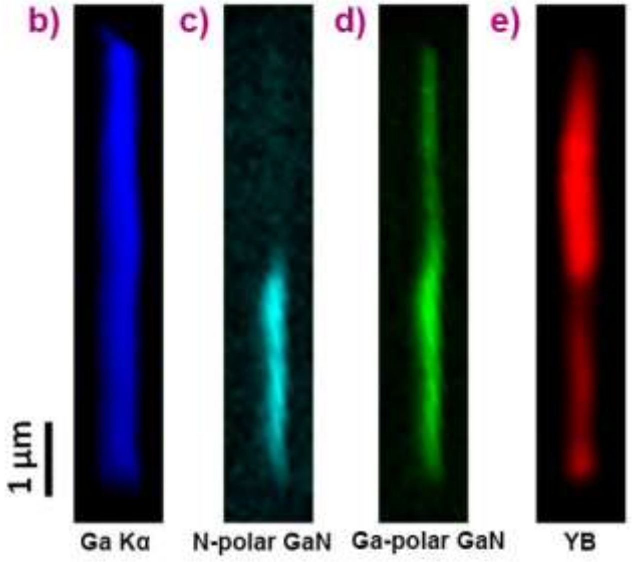
Simultaneous collection of XRF and XEOL signals

Courtesy D. Salomon, ID16B

XEOL total spectrum



XRF and XEOL maps



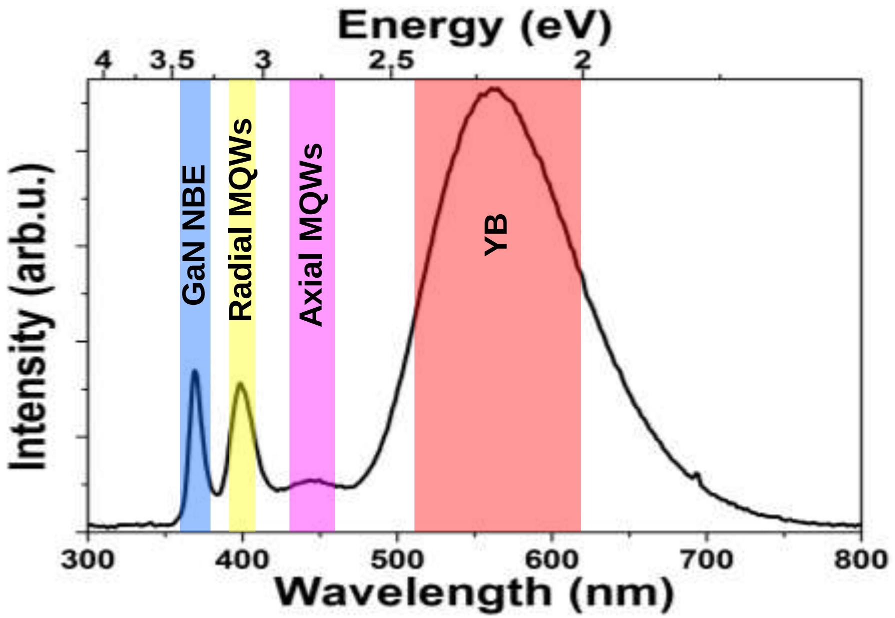
Upper part of the wire, grown without silane injection: increase of the defect band intensity and a decrease of the other contributions => reduction of the material quality

N-polar GaN emission mainly present in the bottom part of the wire grown under high silane flow.

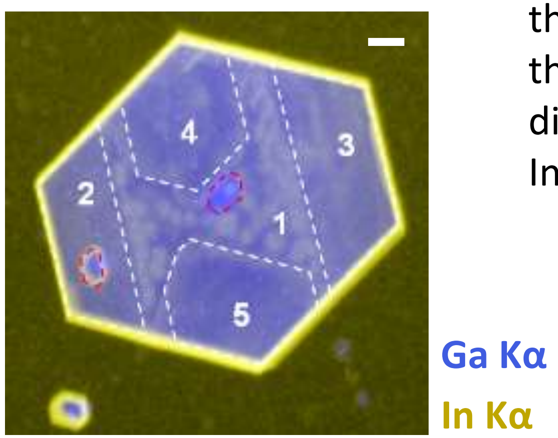
Courtesy D. Salomon, ID16B

XRF/XEOL ON A GaN/InGaN CORE SHELL WIRE (LARGE DEFECTIVE WIRE)

XEOL total spectrum

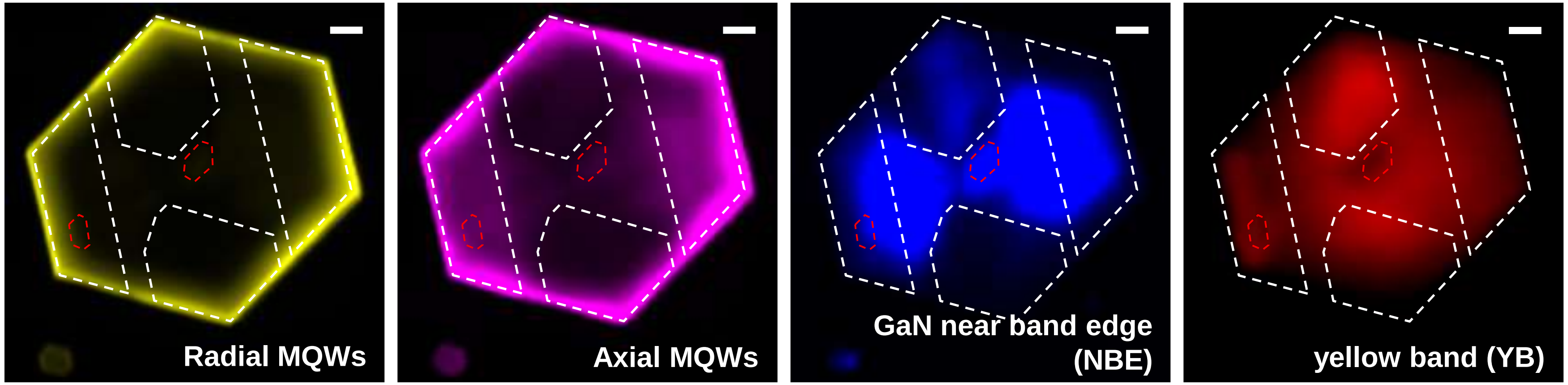


Fluorescence map



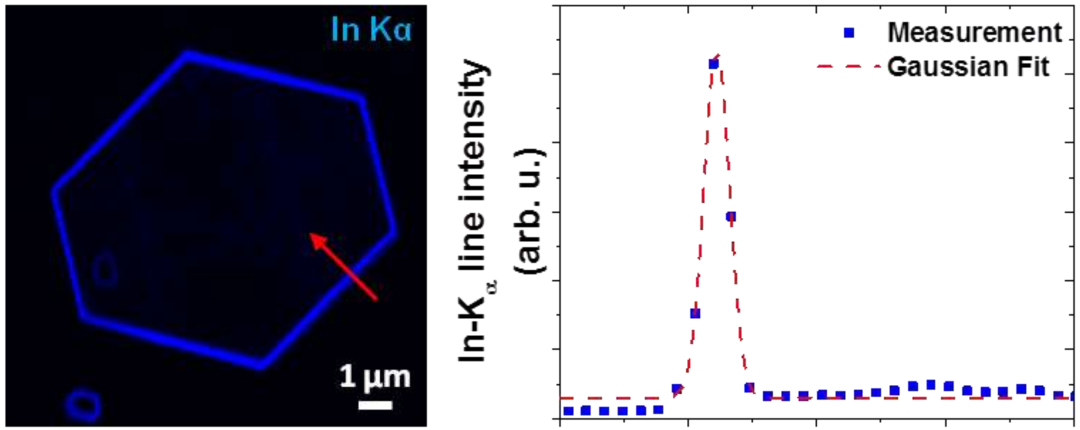
Core/shell InGaN/GaN wires studied from the top facets to gain information about the influence of polarity on the **In** distribution and on the emission of InGaN/GaN multi quantum wells (MQWs).

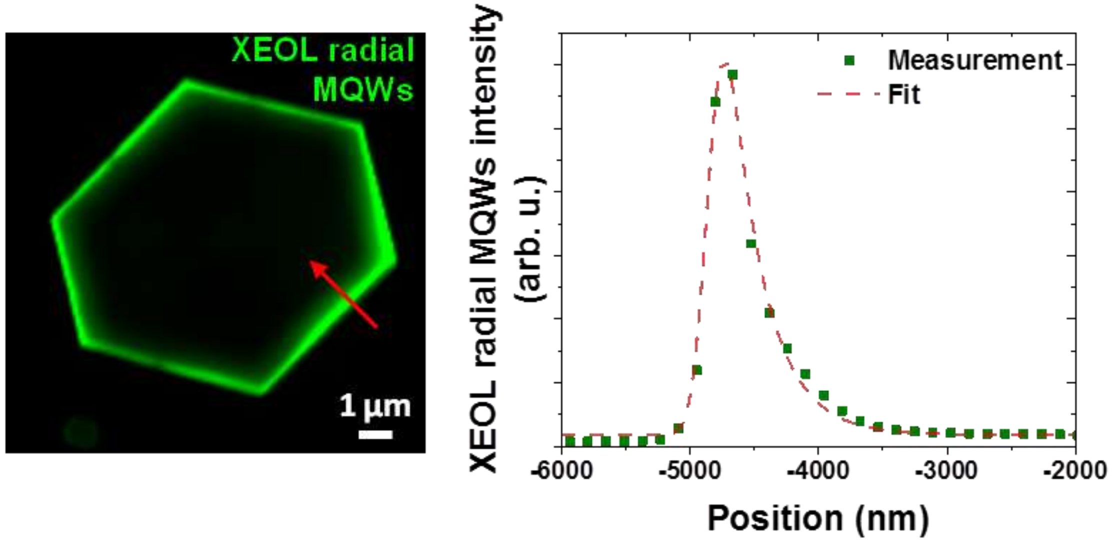
XEOL maps



Courtesy D. Salomon, ID16B

CARRIERS DIFFUSION LENGTH IN SEMICONDUCTORS





In Kα intensity => X-ray beam (50nm) ∗ In content
=> Probe size

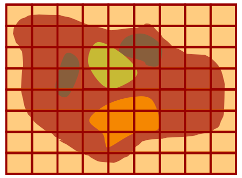
InGaN QW XEOL intensity
=> Probe ∗ Carriers diffusion
=> Gaussian ∗ Exponential decay

Diffusion length = 370 nm

Courtesy D. Salomon, ID16B

SCANNING END-STATIONS AT THE ESRF

Beam-line	Technique contrast	Information	2D/3D	Energy range	Spokesperson
ID01	nano-XRD	strain and orientation map	2D	6-11keV 19-24 keV	Tobias Schulli
ID11	µXRD-CT	grain orientations + phase map	2D/3D	20-65keV	Jon Wright
ID13	µXRF	element map	2D	12.7-15 keV	Manfred Burghammer
ID13	µXRD	phase and orientation map	2D	12.7-15 keV	Manfred Burghammer
ID15A	µXRF	element map	2D/3D	20 - 90 keV	Marco Di Michiel
ID15A	µXRD-CT	phase map	2D/3D	20 - 90 keV	Marco Di Michiel
ID16A	nano-XRF	element map	2D/3D	17 & 33.6 keV	Peter Cloetens
ID16B	nano-XRF	element map	2D/3D	3-30 keV	Rémi Tucoulou
ID16B	nano-XRD	phase map	2D/3D	30 keV	Rémi Tucoulou
ID16B	nano-XANES	speciation	2D	3-30 keV	Rémi Tucoulou
ID16B	nano-XEOL	XEOL map	2D	17-30 keV	Rémi Tucoulou
ID21	µXRF	element map	2D	2.0-9.1keV	Marine Cotte
ID21	µXANES	speciation	2D	2.0-9.1keV	Marine Cotte
ID21	µFTIR	molecular groups	2D	700-4000cm^{-1}	Marine Cotte
ID21	µXRD	phase map	2D	8.5keV	Marine Cotte
ID24	µXANES	speciation	2D/3D	5-12keV (13-27keV)	Sakura Pascarelli
BM23	µXANES	speciation	2D	5-40 keV	Sakura Pascarelli
ID31	µXRD-CT	phase map	2D/3D	20-100keV	Veijo Honkimaki

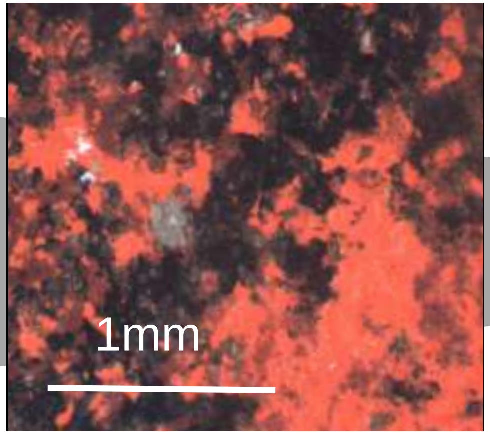


Which information?	Which technique?	Which resolution/ field of view?
Elemental composition?	X-ray fluorescence (XRF)	
Surrounding atoms?	X-ray absorption spectroscopy (XAS)	
	Infrared absorption spectroscopy (FTIR)	
Crystalline phases?	X-ray diffraction (XRD)	
Orientation?	Small angle and wide angle scattering (SAXS and WAXS)	
	X-ray and infrared absorption spectroscopy	
Strain and tilt?	K-mapping	

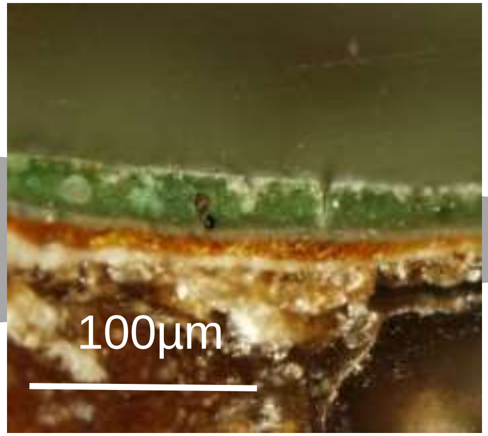
CHOOSING THE RIGHT BEAM SIZE

>8m²

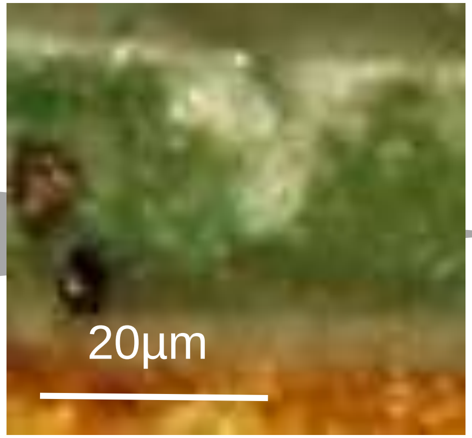
Beam ~0,7mm



Beam ~0,1mm



Beam <1µm

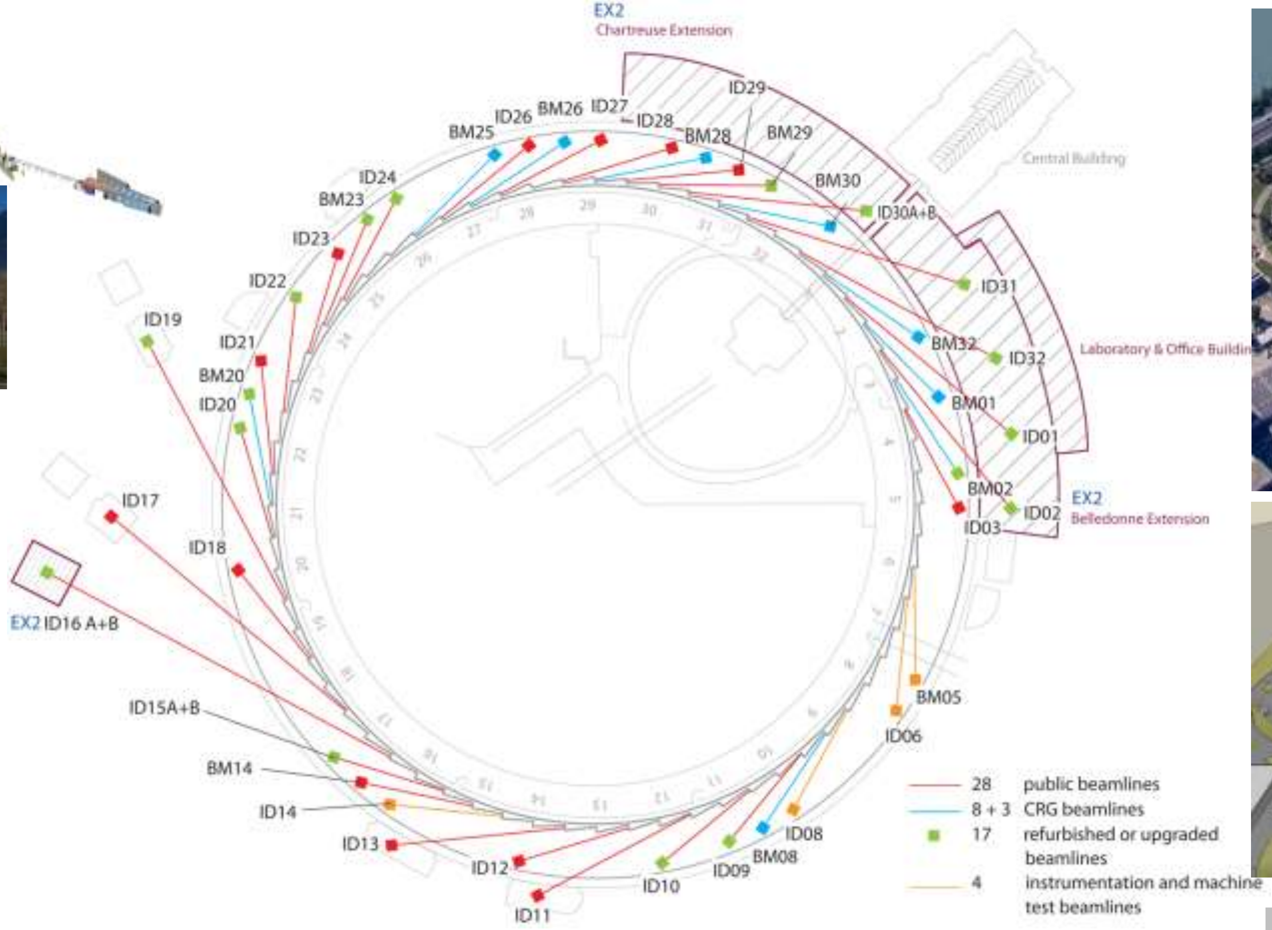


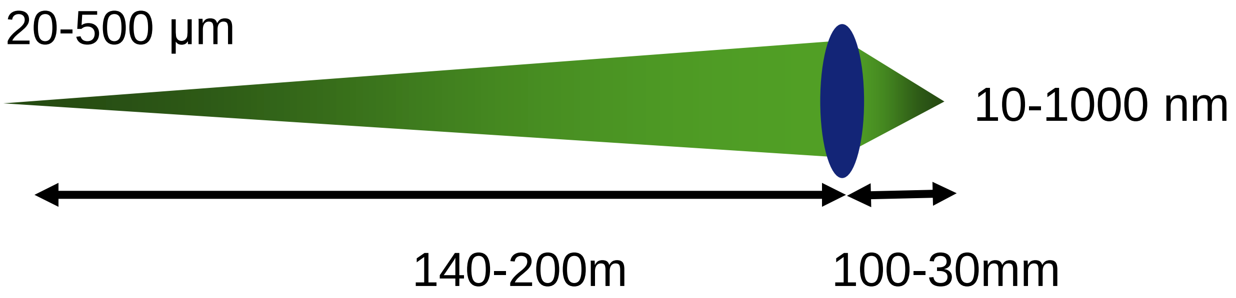
Beam <0.1 µm

SCANNING END-STATIONS AT THE ESRF

Beam-line	Technique contrast	Information	2D/3D	Energy range	Typical beam size	Spokesperson
ID01	**nano-XRD**	**strain and orientation map**	2D	6-11keV 19-24 keV	0.1x0.2 µm²	Tobias Schulli
ID11	**µXRD-CT**	**grain orientations + phase map**	2D/3D	20-65keV	0.2x0.2 µm²	Jon Wright
ID13	**µXRF**	**element map**	2D	12.7-15 keV	100-200 nm	Manfred Burghammer
ID13	**µXRD**	**phase and orientation map**	2D	12.7-15 keV	100-200nm or 2µm	Manfred Burghammer
ID15A	**µXRF**	**element map**	2D/3D	20 - 90 keV	1x1µm² - 20x20µm²	Marco Di Michiel
ID15A	**µXRD-CT**	**phase map**	2D/3D	20 - 90 keV	1x1µm² - 20x20µm²	Marco Di Michiel
ID16A	**nano-XRF**	**element map**	2D/3D	17 & 33.6 keV	14-37 nm	Peter Cloetens
ID16B	**nano-XRF**	**element map**	2D/3D	3-30 keV	50x50 nm²	Rémi Tucoulou
ID16B	**nano-XRD**	**phase map**	2D/3D	30 keV	50x50 nm²	Rémi Tucoulou
ID16B	**nano-XANES**	**speciation**	2D	3-30 keV	50x50 nm²- 100x100 nm²	Rémi Tucoulou
ID16B	**nano-XEOL**	**XEOL map**	2D	17-30 keV	50x50 nm²	Rémi Tucoulou
ID21	**µXRF**	**element map**	2D	2.0-9.1keV	0.3x0.7µm²	Marine Cotte
ID21	**µXANES**	**speciation**	2D	2.0-9.1keV	0.3x0.7µm²	Marine Cotte
ID21	**µFTIR**	**molecular groups**	2D	700-4000cm^{-1}	~5-10µm	Marine Cotte
ID21	**µXRD**	**phase map**	2D	8.5keV	1x1µm²	Marine Cotte
ID24	**µXANES**	**speciation**	2D/3D	5-12keV (13-27keV)	5x5µm² (50x50µm²)	Sakura Pascarelli
BM23	**µXANES**	**speciation**	2D	5-40 keV	5x5µm²	Sakura Pascarelli
ID31	**µXRD-CT**	**phase map**	2D/3D	20-100keV	0.2-50µm	Veijo Honkimaki

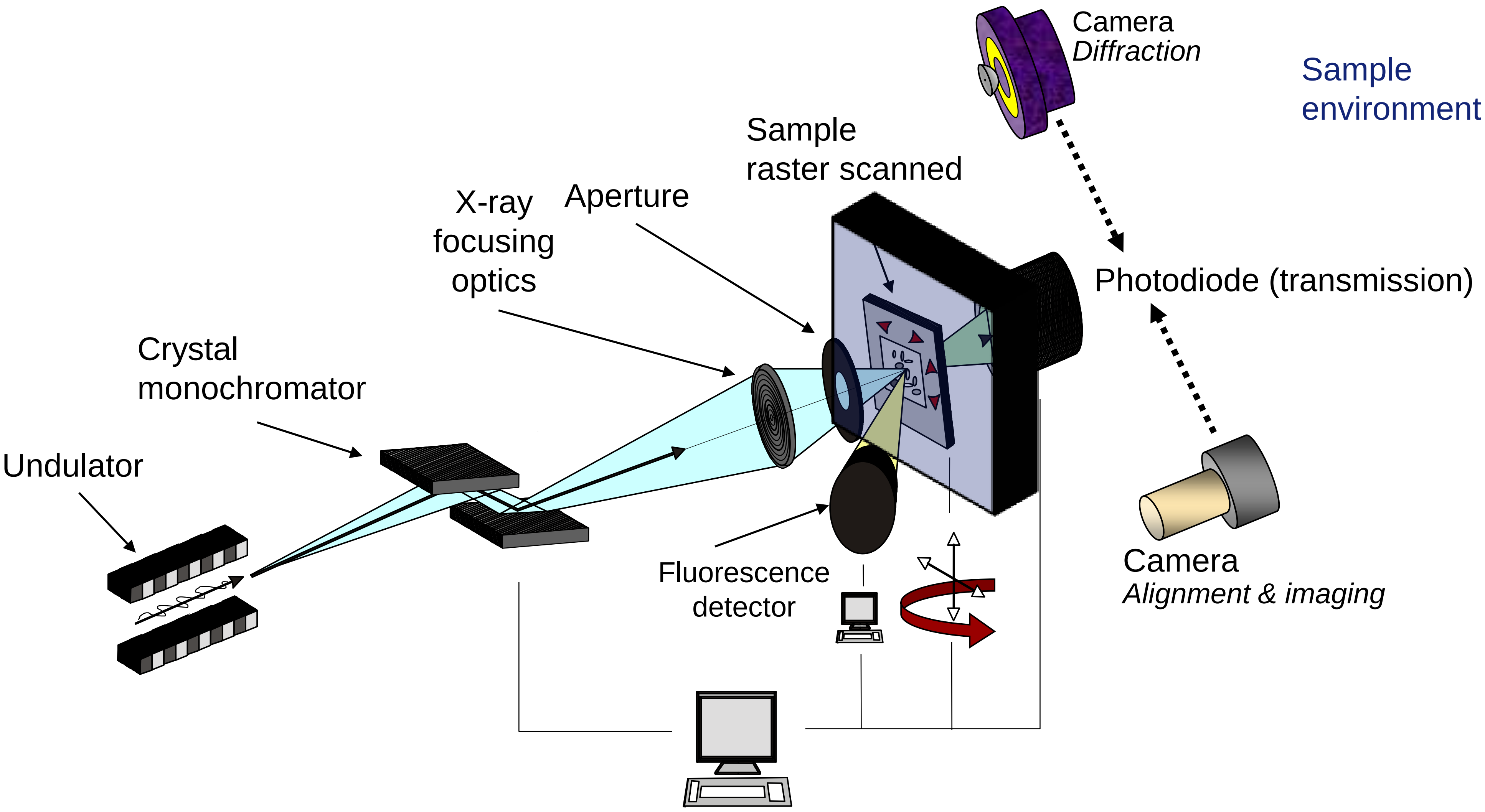
THE ESRF UPGRADE PROGRAMME: MORE AND LONGER BEAMLINES





Long beamlines =
smaller beams
+ more space for sample environments

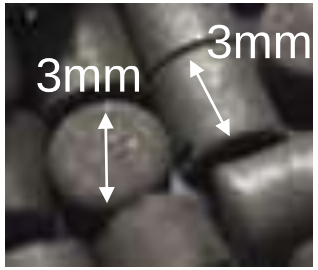
SAMPLE ENVIRONMENT



Sample environment

Catalyst design optimization

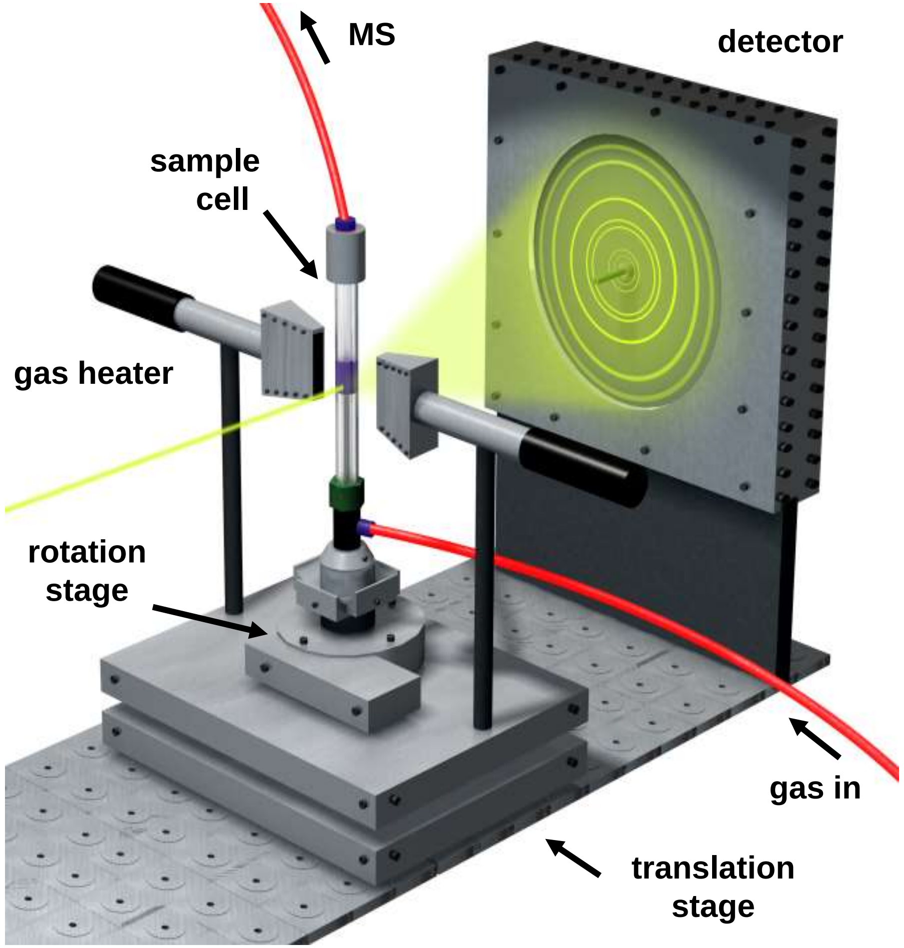
- metals and metal oxides anchored to porous support (widely used as heterogeneous catalysts)
- efficiency of a catalytic reactor depends on the behavior and efficiency of catalyst body
- understand which factors influence the distribution and nature of the active phase during preparation
- **desirable**
  - **to mimic the real conditions as closely as possible → *in-operando* condition**
  - **to understand the chemistry in different parts of the sample**

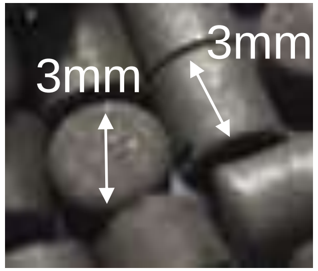


⇒ map chemistry during calcination in time and space using 3D µXRD

Courtesy M. Di Michiel, ID15A

DIFFRACTION TOMOGRAPHY STUDY OF CATALYST BODIES OF Ni SUPPORTED ON γ-Al_2O_3





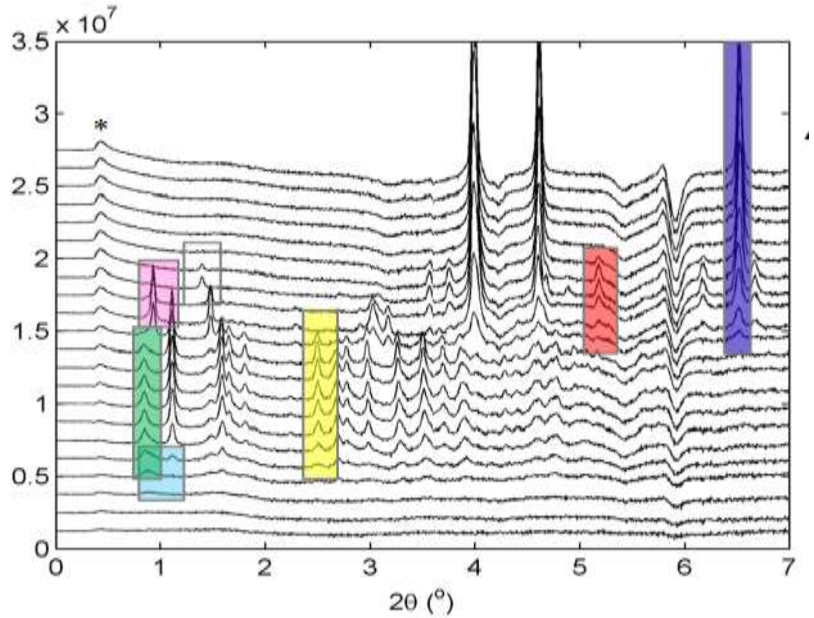
ID15A
86.8keV
100µm beam
in situ calcination (ambient to 500◦C at 2.5 ◦ C/min with dwell of 2 h) of a cylindrical catalyst body (γ-Al_2O_3, diameter=3 mm; length=3 mm) impregnated with a Ni catalyst precursor material ($[NiCl_2(en)(H_2O)_4]$ where en=ethylenediamine).
The calcination was performed under flowing He

Courtesy M. Di Michiel, ID15A

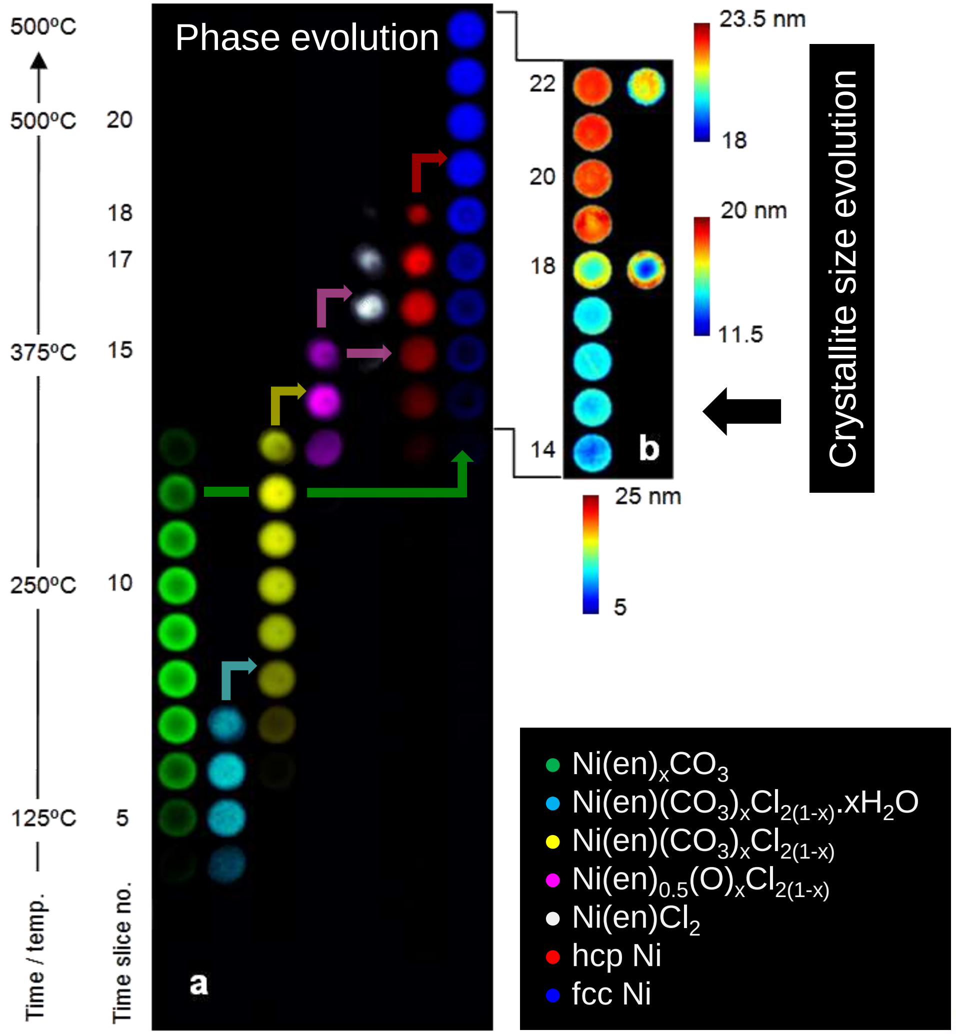
DIFFRACTION TOMOGRAPHY STUDY OF CATALYST BODIES OF Ni SUPPORTED ON γ-Al_2O_3

Jacques et al., *Angew. Chem. Int. Ed*. **50** (2011)

"TRADITIONAL" *IN-SITU* RESULT



3D µXRD *IN-SITU* RESULT

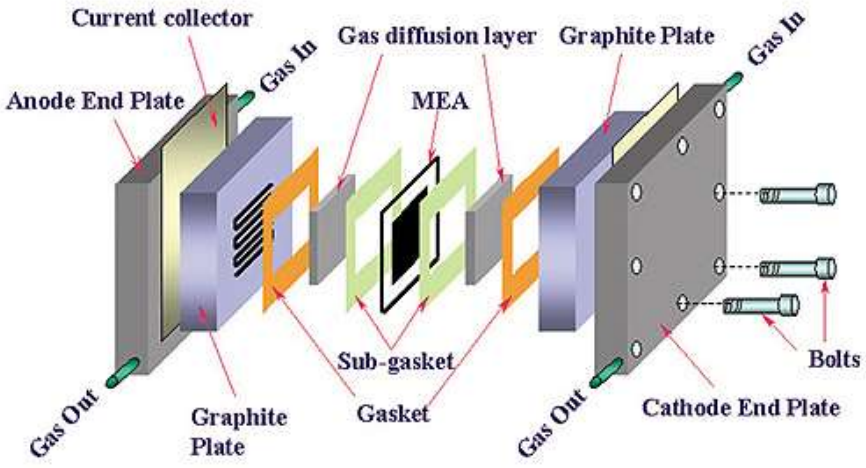


- Two routes to the formation of metallic fcc Ni active phase from the precursor $NiCl_2(en)(H_2O)_4$ (en=ethylenediamine)
- Two different spatial distributions: egg-shell and egg white
- Different nano particle size
- Important implications for the activity/selectivity in a catalytic reaction

Courtesy M. Di Michiel, ID15A

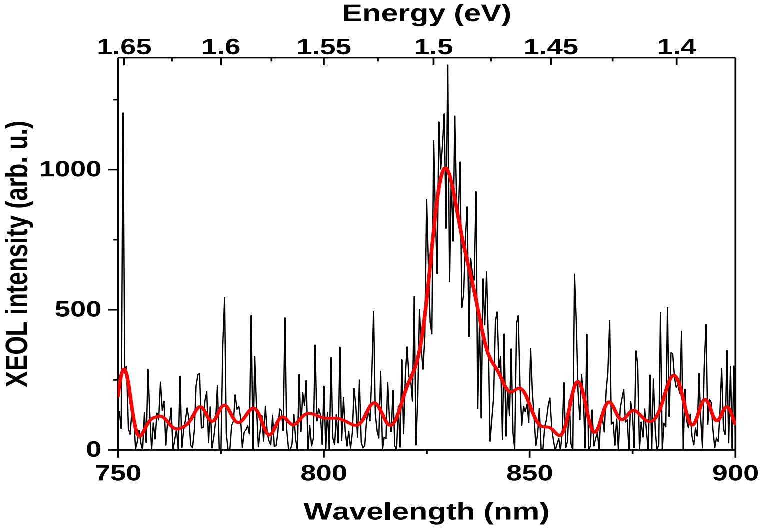
Industrial fuel cell test bench with gas control and potentiostat

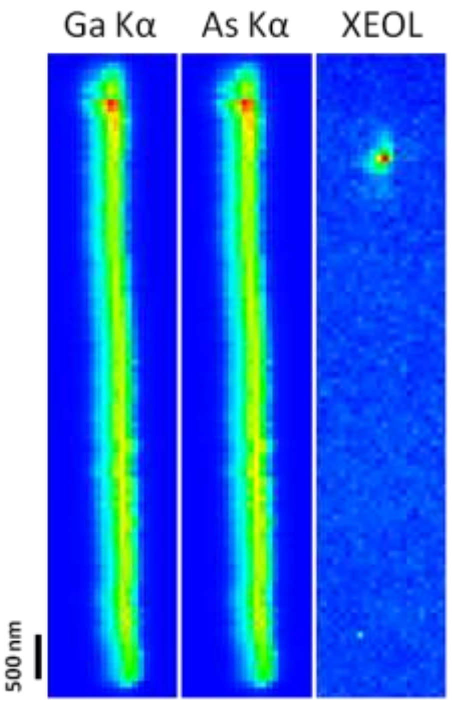
Fuel cells



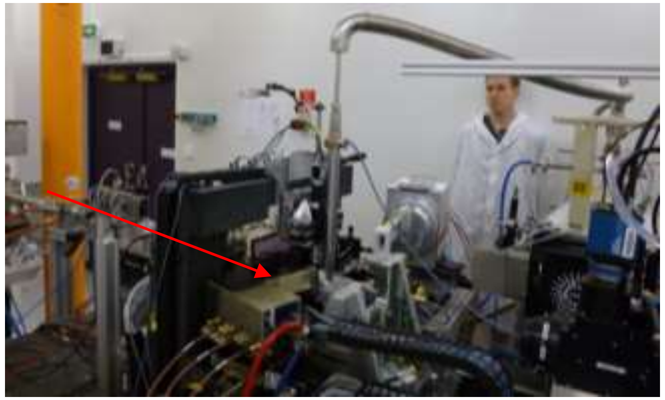
XEOL MEASUREMENTS AT 5K

A liquid He cryostat (5K) can be used to measure XEOL signal from semiconductor:
For GaAs based sample, low temperature is necessary for light emission.





Maps acquired simultaneously at 5 K with a resolution of 70 nm per pixel



Only one point of the nanowire emits light. One reason could be that the protective coating layer (AlGaAs) grown around the nanowire was good enough only in that specific region.
This kind of measurement can be used to analyze defects in nanostructures and their effect on optical properties.

Courtesy D. Salomon, ID16B

To reduce radiation damage on biological samples:
Cryogenic sample preparation and cooling during experiment

Cryogenic sample preparation

Cryo loading chamber and transfer system

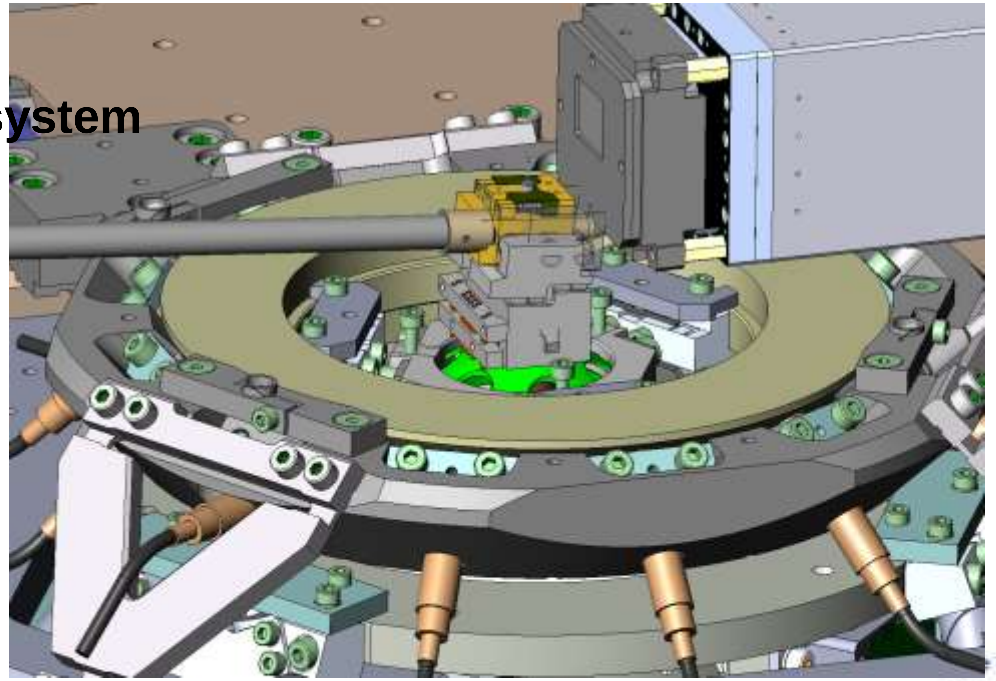
Cryogenic cooling of the sample stage

Courtesy P. Cloetens, ID16A

P. van der Linden, S. Bohic, F. Villar, L. Andre

CRYOGENIC WORKFLOW FOR BIOLOGY

Leica EM-VCT
Cryo-transfer system



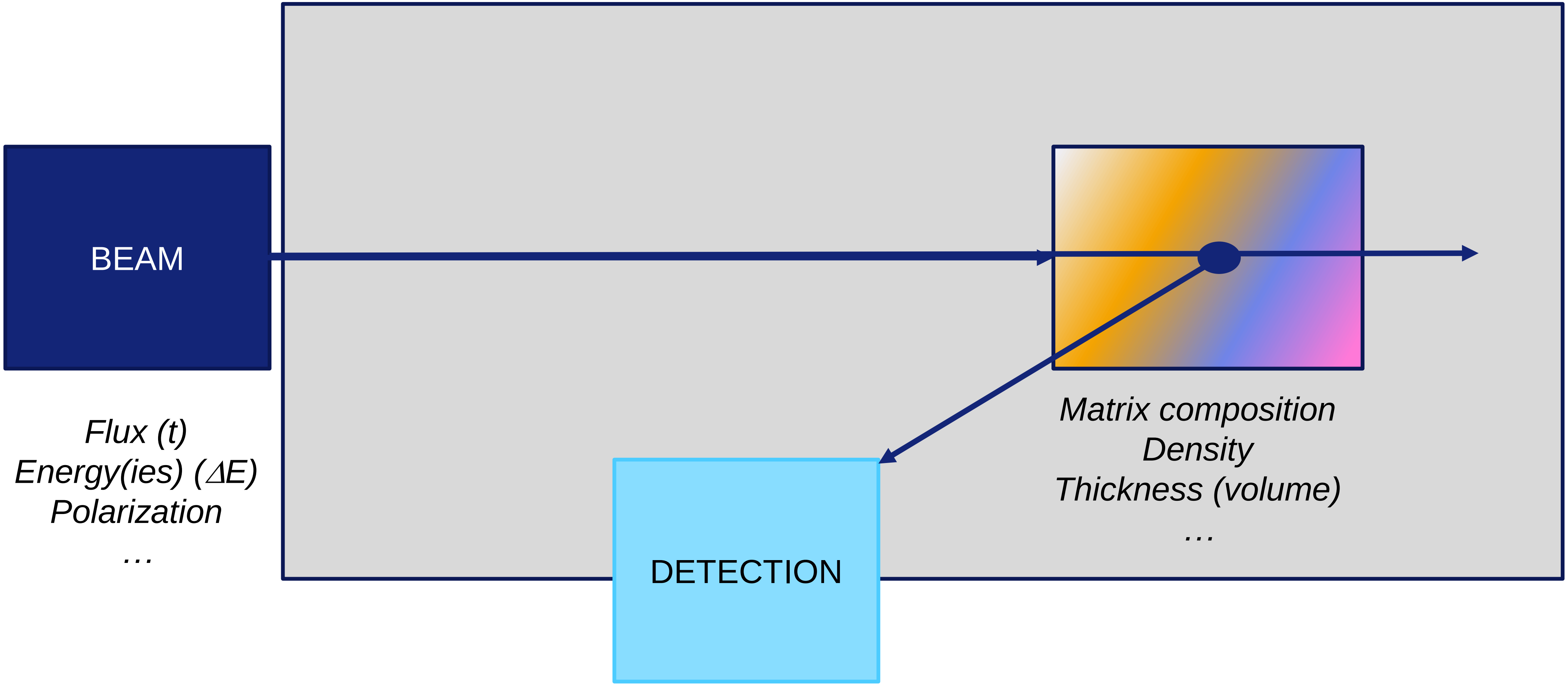
Integrated to the "Hexapiezo" end-station

Courtesy P. Cloetens, ID16A

SCANNING END-STATIONS AT THE ESRF

Beam-line	Technique contrast	Information	2D/3D	Energy range	Typical beam size	Sample environment	Spokesperson
ID01	**nano-XRD**	**strain and orientation map**	2D	6-11keV 19-24 keV	0.1x0.2 μm^2	furnace (300-1200 K) and catalysis chamber; cryo, primary vacuum, air	Tobias Schulli
ID11	**µXRD-CT**	**grain orientations + phase map**	2D/3D	20-65keV	0.2x0.2 μm^2	Usually no sample environment (air)	Jon Wright
ID13	**µXRF**	**element map**	2D	12.7-15 keV	100-200 nm	none, in combination with XRD	Manfred Burghammer
ID13	**µXRD**	**phase and orientation map**	2D	12.7-15 keV	100-200nm or 2µm	humidity, micro-fluidics, cryostream, heating, nanocalorimetry, mechanical testing, electrical testing, static magnetic fields	Manfred Burghammer
ID15A	**µXRF**	**element map**	2D/3D	20 - 90 keV	1x1μm^2 - 20x20μm^2	air, furnace, capillary, cryostream, high pressure gas or liquid	Marco Di Michiel
ID15A	**µXRD-CT**	**phase map**	2D/3D	20 - 90 keV	1x1μm^2 - 20x20μm^2	air, furnace, capillary, cryostream, high pressure gas or liquid	Marco Di Michiel
ID16A	**nano-XRF**	**element map**	2D/3D	17 & 33.6 keV	14-37 nm	Vacuum, cryo (LN_2)	Peter Cloetens
ID16B	**nano-XRF**	**element map**	2D/3D	3-30 keV	50x50 nm^2	in air, cryo (He)	Rémi Tucoulou
ID16B	**nano-XRD**	**phase map**	2D/3D	30 keV	50x50 nm^2	in air	Rémi Tucoulou
ID16B	**nano-XANES**	**speciation**	2D	3-30 keV	50x50 nm^2- 100x100 nm^2	in air, cryo (He)	Rémi Tucoulou
ID16B	**nano-XEOL**	**XEOL map**	2D	17-30 keV	50x50 nm^2	in air, cryo (He)	Rémi Tucoulou
ID21	**µXRF**	**element map**	2D	2.0-9.1keV	0.3x0.7μm^2	vacuum, cryo (LN_2)	Marine Cotte
ID21	**µXANES**	**speciation**	2D	2.0-9.1keV	0.3x0.7μm^2	vacuum, cryo (LN_2)	Marine Cotte
ID21	**µFTIR**	**molecular groups**	2D	700-4000cm^{-1}	~5-10µm	in air (possibility to install Linkam stage)	Marine Cotte
ID21	**µXRD**	**phase map**	2D	8.5keV	1x1μm^2	in air	Marine Cotte
ID24	**µXANES**	**speciation**	2D/3D	5-12keV (13-27keV)	5x5μm^2 (50x50μm^2)	in air	Sakura Pascarelli
BM23	**µXANES**	**speciation**	2D	5-40 keV	5x5μm^2	in air	Sakura Pascarelli
ID31	**µXRD-CT**	**phase map**	2D/3D	20-100keV	0.2-50µm	gas flow, HP, HT, H_2/O_2	Veijo Honkimaki

GOING TO QUANTITATIVE ANALYSES



Flux (t)
Energy(ies) (ΔE)
Polarization
…

Intrinsic characteristics
Geometry

ELSEVIER

TrAC Trends in Analytical Chemistry

Volume 29, Issue 6, June 2010, Pages 464–478

Recent trends in quantitative aspects of microscopic X-ray fluorescence analysis

Koen Janssens, Wout De Nolf, Geert Van Der Snickt
Department of Chemistry, University of Antwerp, Belgium

Laszlo Vincze, Bart Vekemans
Department of Analytical Chemistry, University of Ghent, Belgium

Roberto Terzano
Dipartimento di Biologia e Chimica Agroforestale e Ambientale, University of Bari, Italy

Frank E. Brenker
Geoscience Institute, Goethe University Frankfurt, Germany

Available online 19 March 2010

ELSEVIER

TrAC Trends in Analytical Chemistry

Volume 91, June 2017, Pages 104–111

Analytical requirements for quantitative X-ray fluorescence nano-imaging of metal traces in solid samples

Laurence Lemelle[a], Alexandre Simionovici[b], Tom Schoonjans[c], Rémi Tucoulou[d], Emanuele Enrico[e], Murielle Salomé[d], Axel Hofmann[f], Barbara Cavalazzi[f, g]

Show more

SCANNING TECHNIQUES DURING THIS SCHOOL

HSC19 Final Programme, 14-19 May 2017

	Sunday 14 May	Monday 15 May	Tuesday 16 May	Wednesday 17 May	Thursday 18 May	Friday 19 May	
	Room	ESRF Auditorium		Beamlines & MD-1-21		ESRF MD-1-21	
		Introductory lectures on imaging techniques		Hands-on training		Specialized lectures	
08:30							08:30
08:45		Welcome					08:45
09:00		Intro: X&n imaging *B. Kanngießer*	CDI & Ptychography *M. Guizar-Sicairos*	Practicals id1, bm05, id6, id16a, id17, id21	Tutorials ESRF + ILL (in parallel)	3D metrology in geomaterials *A. Tengattini*	**09:00**
09:15							09:15
09:30							09:30
09:45						Medical Imaging *E. Brun*	09:45
10:00		Radiography & Tomography *F. Marone*					**10:00**
10:15							10:15
10:30			Coffee break			Coffee break	10:30
10:45							10:45
11:00		Coffee break	Scanning Microscopy *M. Cotte*			PyMCA: quick overview & recent developments *V. A. Solé*	**11:00**
11:15							11:15
11:30		Phase Imaging *P. Cloetens*					11:30
11:45				Lunch	Lunch W. De Nolf, XRD	Image correlation/4D analysis *E. Andò*	11:45
12:00							**12:00**
12:15							12:15
12:30			Lunch			Lunch	12:30
12:45							12:45
13:00		Lunch			Tutorials ESRF + ILL (in parallel)		**13:00**
13:15							13:15
13:30							13:30
13:45				Practicals id1, bm05, id6, id16a, id17, id21		Industrial Imaging *S. Zabler (Fraunhofer)* *B. Fayard (Novitom)* *F. Curnier (Digisens)*	13:45
14:00			Neutron Imaging *E. Lehmann*				**14:00**
14:15		Optics & Soft Imaging *M. Osterhoff*					14:15
14:30							14:30
14:45							14:45
15:00						Time resolved X-Ray Holography *S. Eisebitt*	**15:00**
15:15							15:15
15:30			Coffee break		Tutorials ESRF + ILL (in parallel)		15:30
15:45		Coffee break				Coffee break	15:45
16:00			Visual Perception of Complex data *G.-P. Bonneau*				**16:00**
16:15		Bragg Imaging *A. King*				Fast & Ultrafast Imaging *R. Mokso*	16:15
16:30							16:30
16:45							16:45
17:00						Round table	**17:00**
17:15							17:15
17:30			TBA *B. Kanngießer*				17:30
17:45		DECTRIS				Conclusion	17:45
18:00	*Welcome Barbecue*	*Poster session Wine & Cheese*		X-ray Imaging & Paleontology *P. Tafforeau* *ESRF MD-1-21*			**18:00**
18:15			Discussion, questions,..				18:15
18:30							18:30
18:45							18:45
19:00							**19:00**
19:15					*School Dinner*		19:15
19:30							19:30
19:45							19:45
20:00							**20:00**

“PIERO CALDIROLA” INTERNATIONAL CENTER FOR THE PROMOTION OF SCIENCE
and International School of Plasma Physics

INTERNATIONAL WORKSHOP ON

IMAGING

Villa Monastero, Varenna, Italy
September 4 – 8, 2017

Purpose

Imaging techniques are used across many applications and research fields. The public at large is familiar with biomedical imaging where main techniques are CT, SPECT/PET, MRI and Optical Microscopy. Other applications are found in engineering, cultural heritage research, security etc. where neutron and X-ray radiography and tomography play an increasing role.

The workshop will try to identify common approaches across different fields of research, techniques and scale lengths. Topics addressed will include

Overview of the different imaging techniques
Multi-parametric molecular imaging
Imaging for the Heritage Science
Imaging for Homeland security
Image formation and processing
Algorithms for reconstruction and correction
Hybrid technologies
Imaging at the nanoscale

The Conference strongly encourages participation by young scientists.

The programme will include tutorial lectures, invited oral presentations and posters.

Applications

Application/hotel reservation form can be downloaded from our web site www.ispp.it or obtained from Donatella Pifferetti imaging@ispp.it

Deadline for registration is **June 16th, 2017.**

The conference hall capacity is limited to 90 participants.