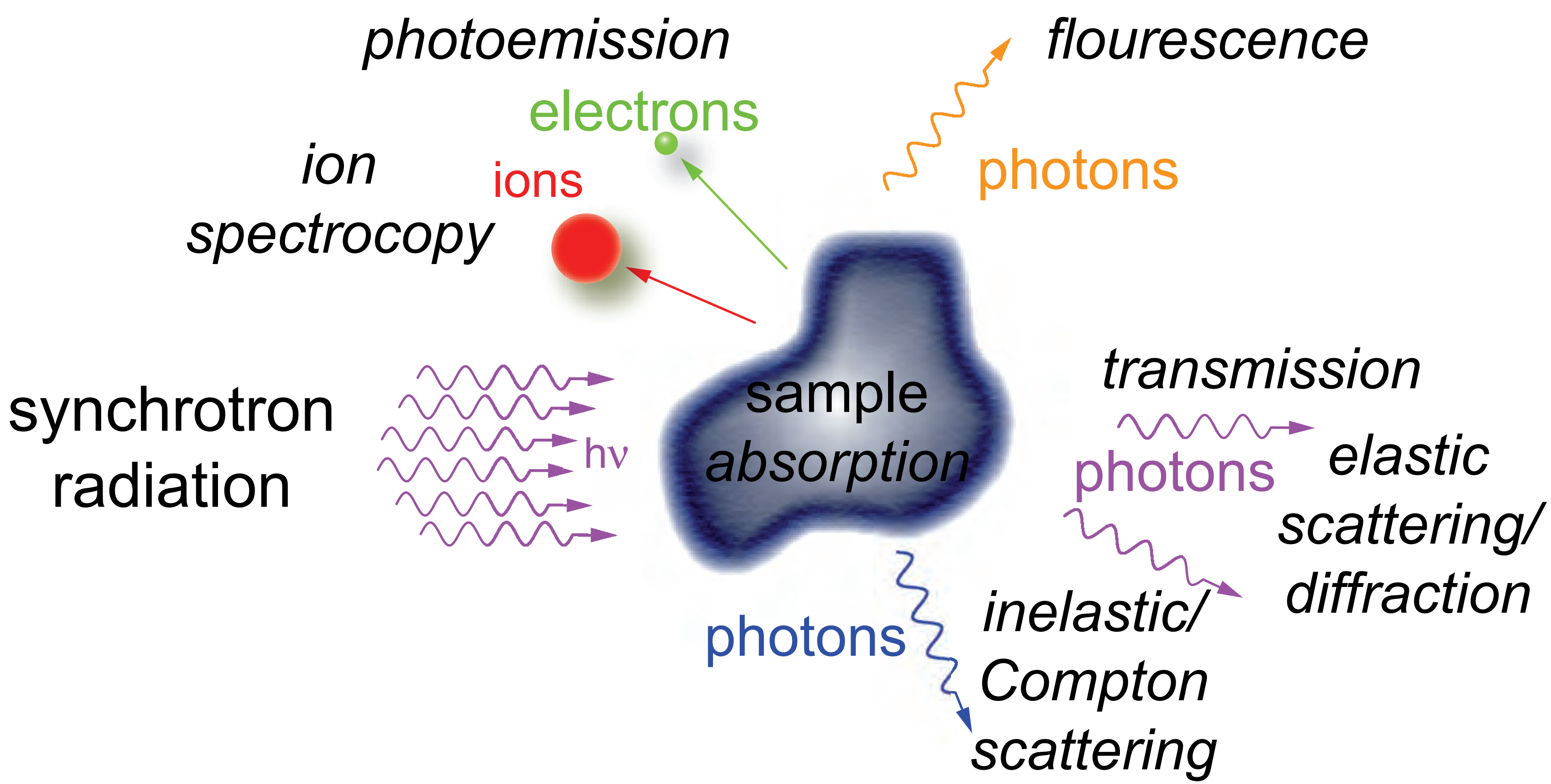
Research with Synchrotron Radiation.

Part II - Experimental Techniques

Jens Viefhaus
HASYLAB at DESY
DESY Summer Student Common Lectures.
July 30, 2009

Interaction of Synchrotron Radiation with Matter

- Synchrotron Radiation enables the use of various experimental techniques



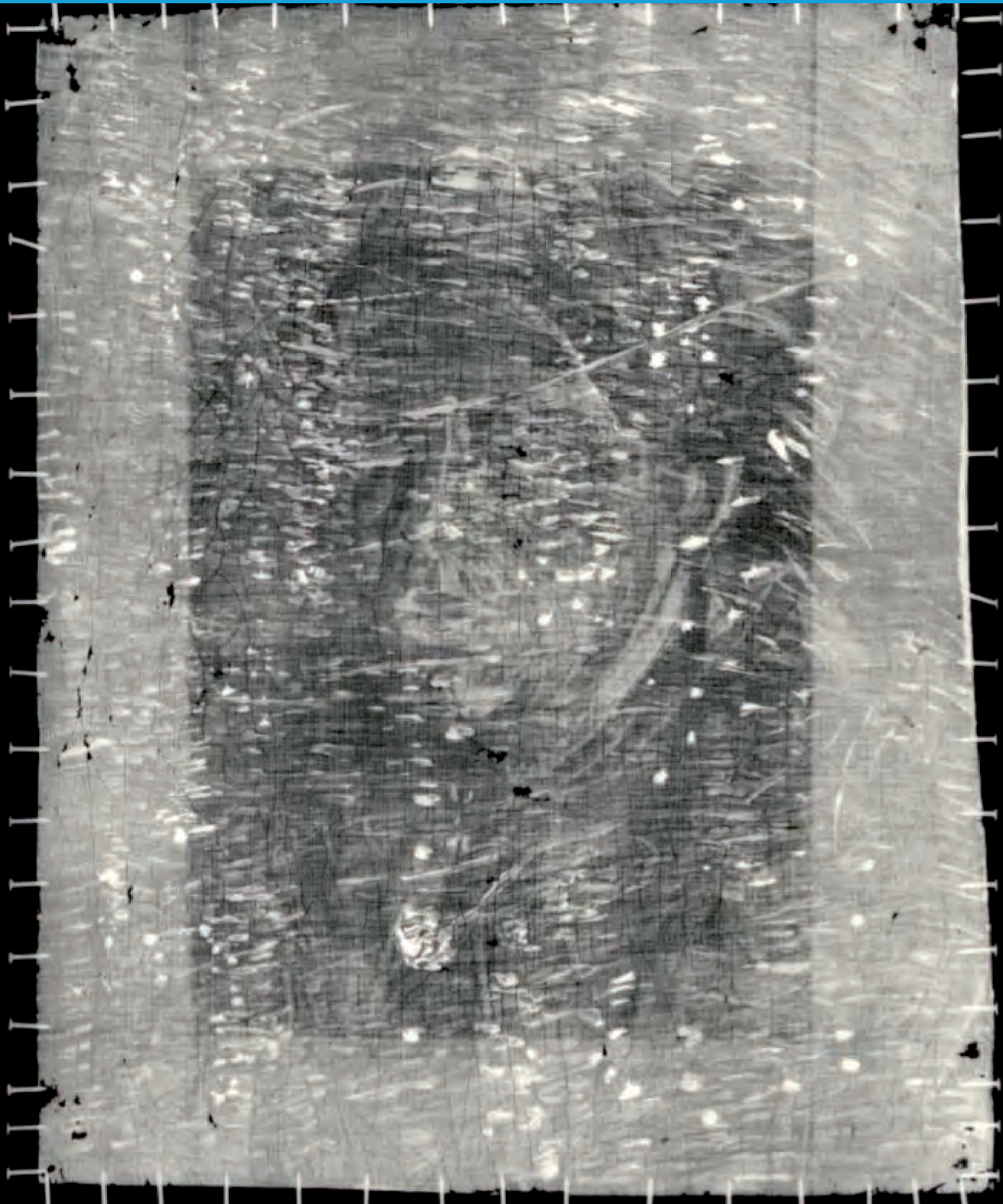
- *Imaging* analyzes the scattered particles (e,γ) in real space
- *Diffraction* analyzes the scattered particles (e,γ) in reciprocal space
- *Spectroscopy* analyzes the energy of the emitted/transmitted particles (e,i,γ)

Imaging - Van Gogh

Vincent van Gogh
Patch of Grass
Paris, 1887

Kröller-Müller Museum
Otterlo, the Netherlands

Imaging - Van Gogh



Vincent van Gogh
Patch of Grass
Paris, 1887

Kröller-Müller Museum
Otterlo, the Netherlands

X-ray radiography

Portrait of a Woman?
Nuenen, 1884/1885?

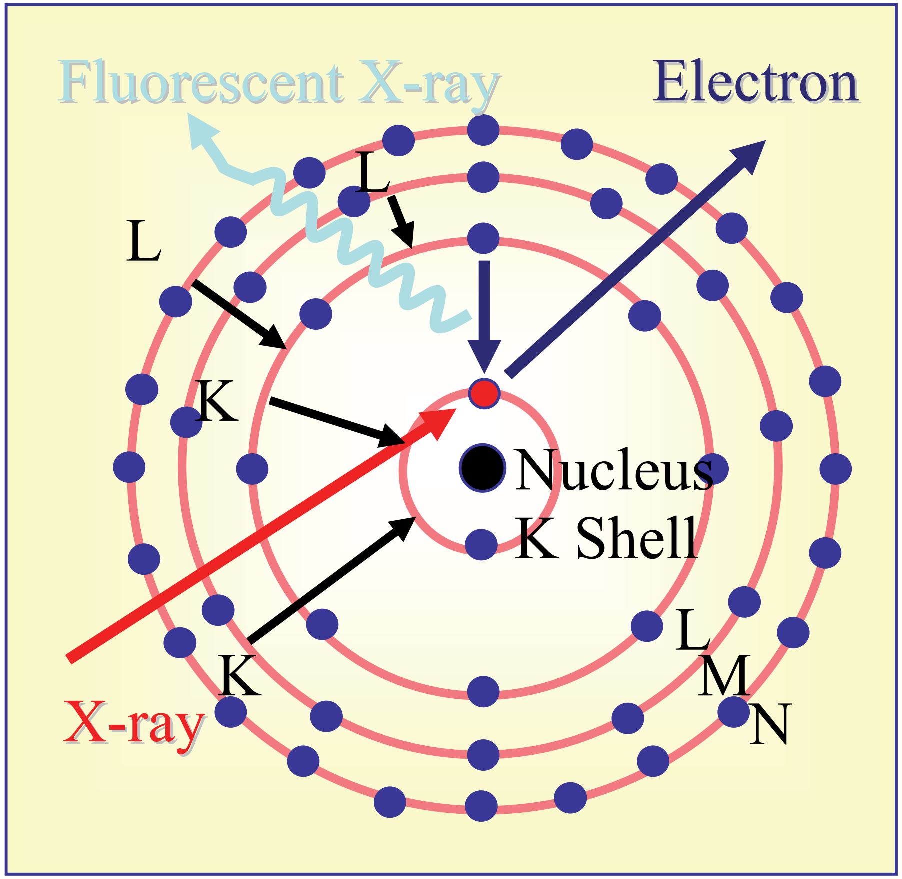
> X-ray radiograph

- reveals hidden face
- difficult to identify

Imaging with X-ray Fluorescence

> X-ray Fluorescence Spectrometry (XRF):

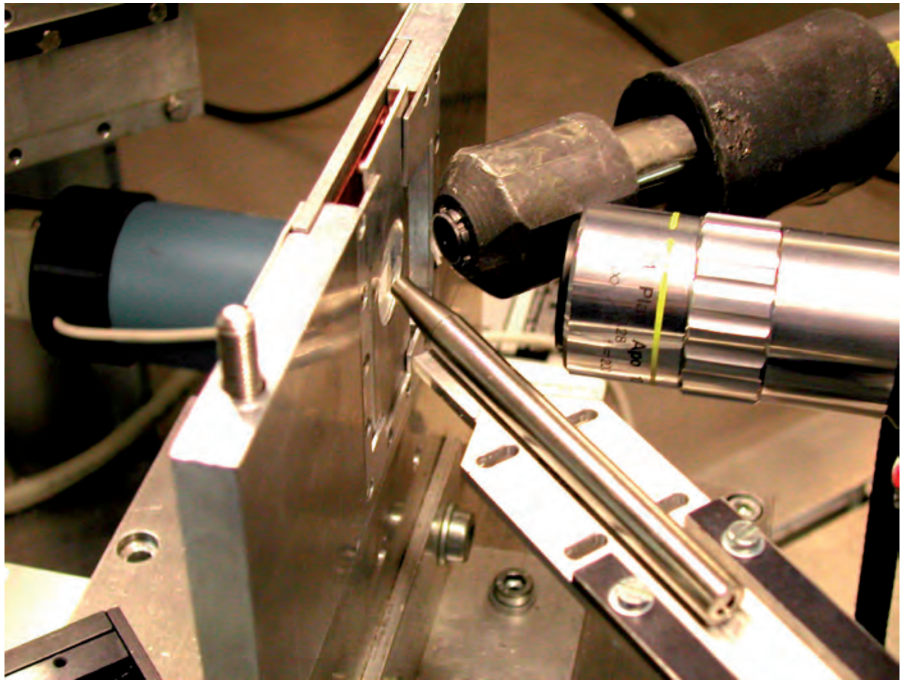
- X-ray emission excited by X-rays is called “fluorescence”
- Characteristic energy of fluorescence for each element
- Intensity of fluorescence is proportional to the number of excited atoms
- suitable for quantitative analysis

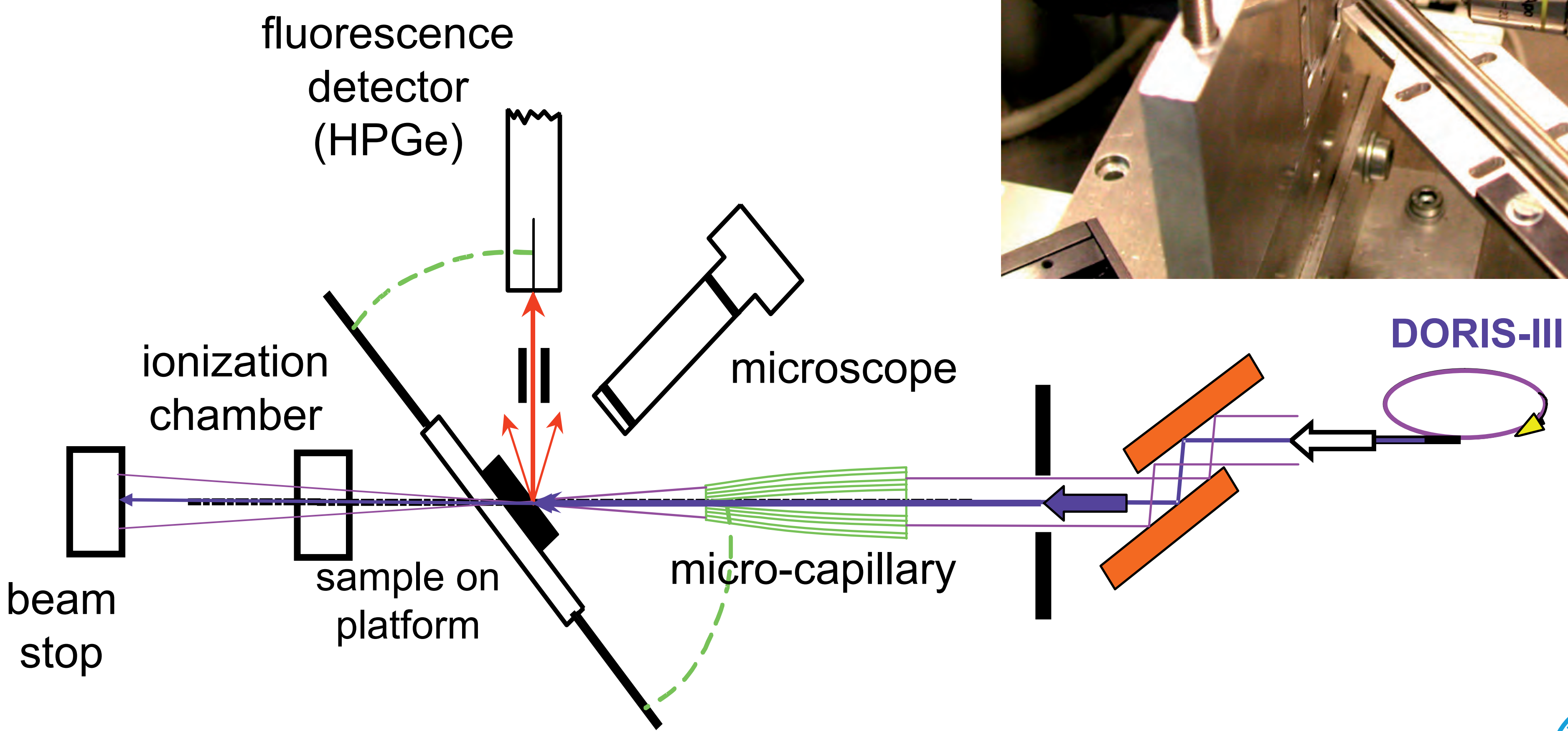


www.spring8.or.jp/ENGLISH/general_info/ overview/pri_fl_x.jp

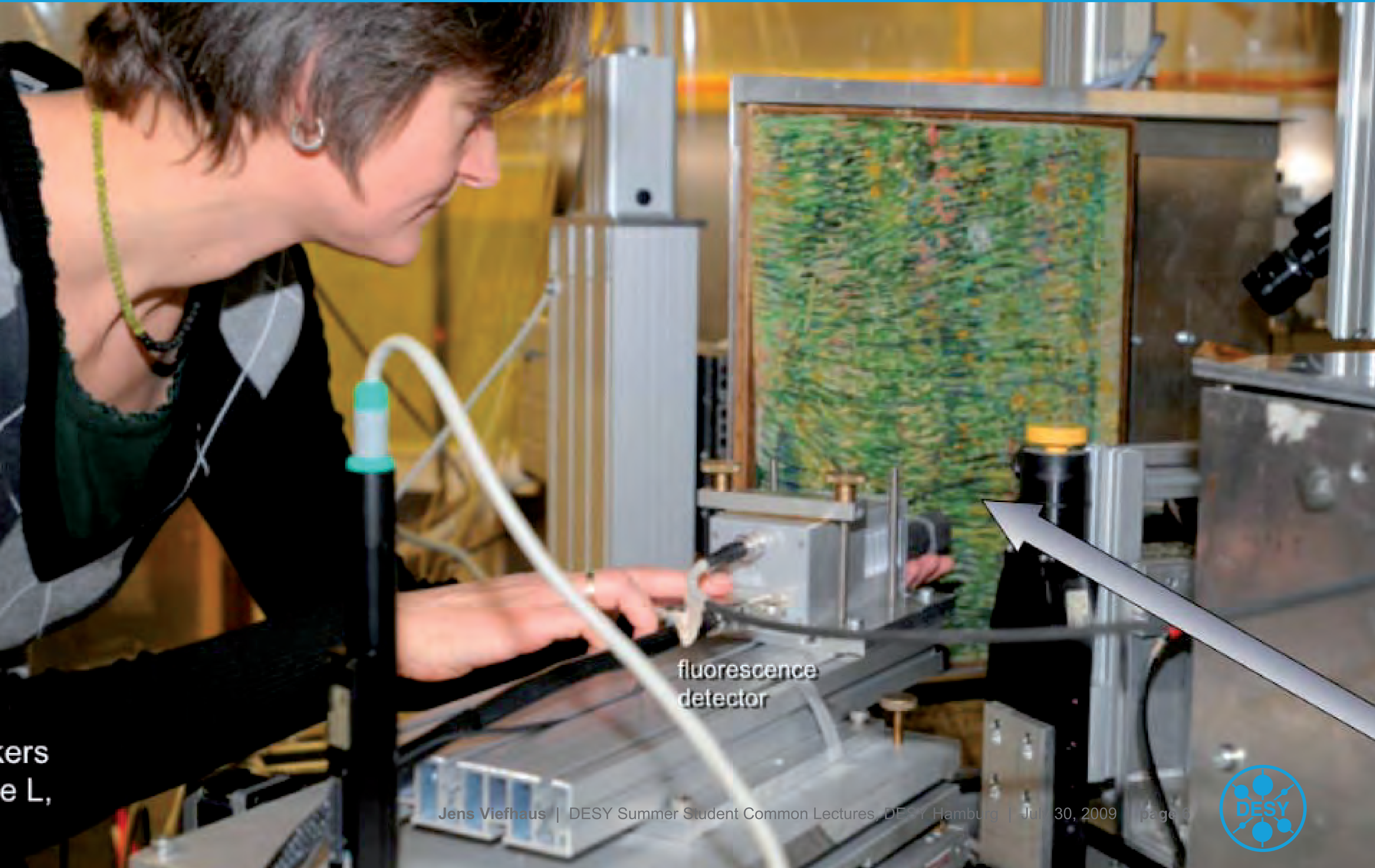
Imaging - The X-ray Fluorescence Setup

- The experiment at DORIS:
  - scanning the picture with a micro beam
  - detection of the emitted fluorescence photons





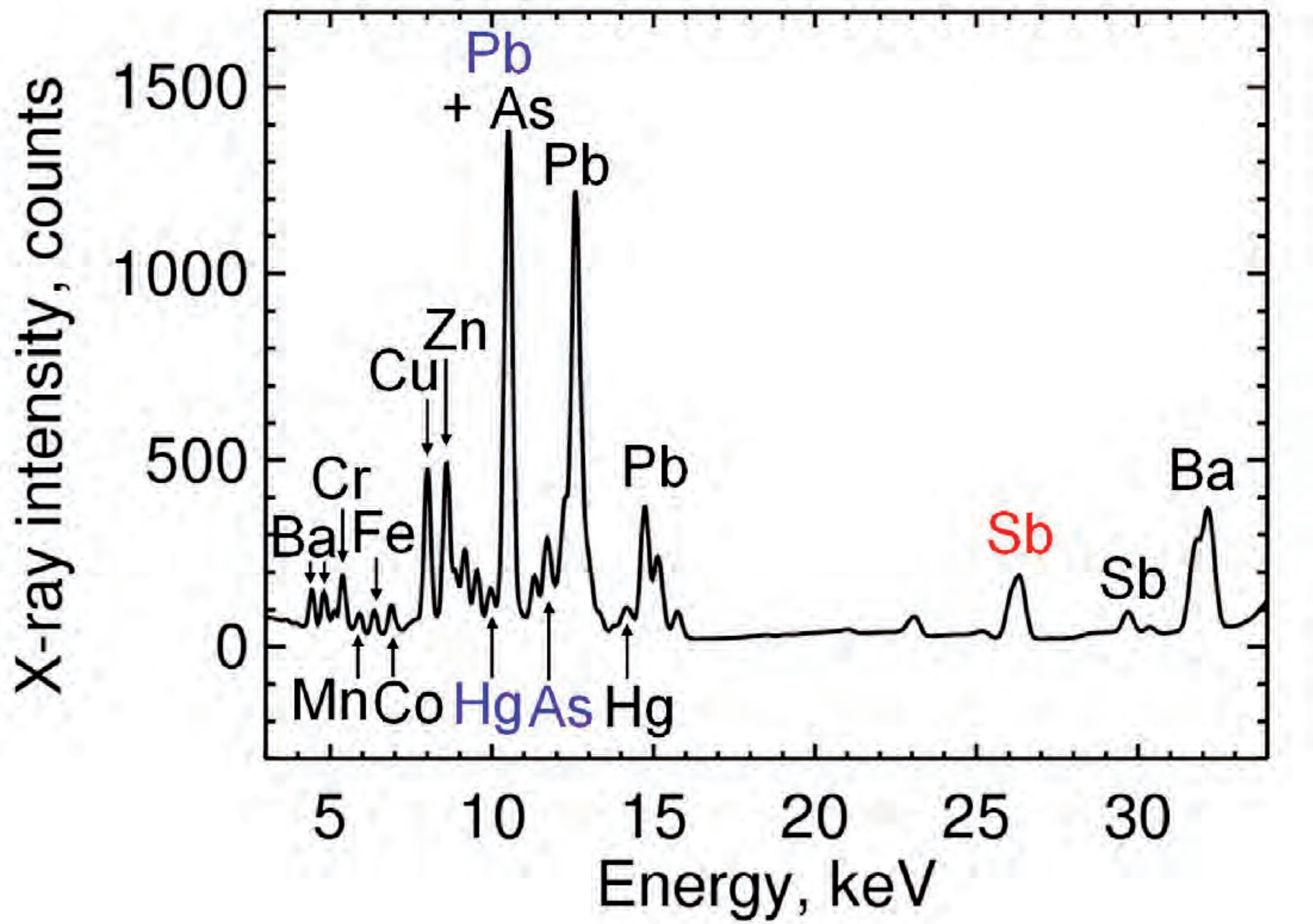
Imaging - Van Gogh at Beamline L of DORIS



Imaging - Van Gogh at Beamline L of DORIS

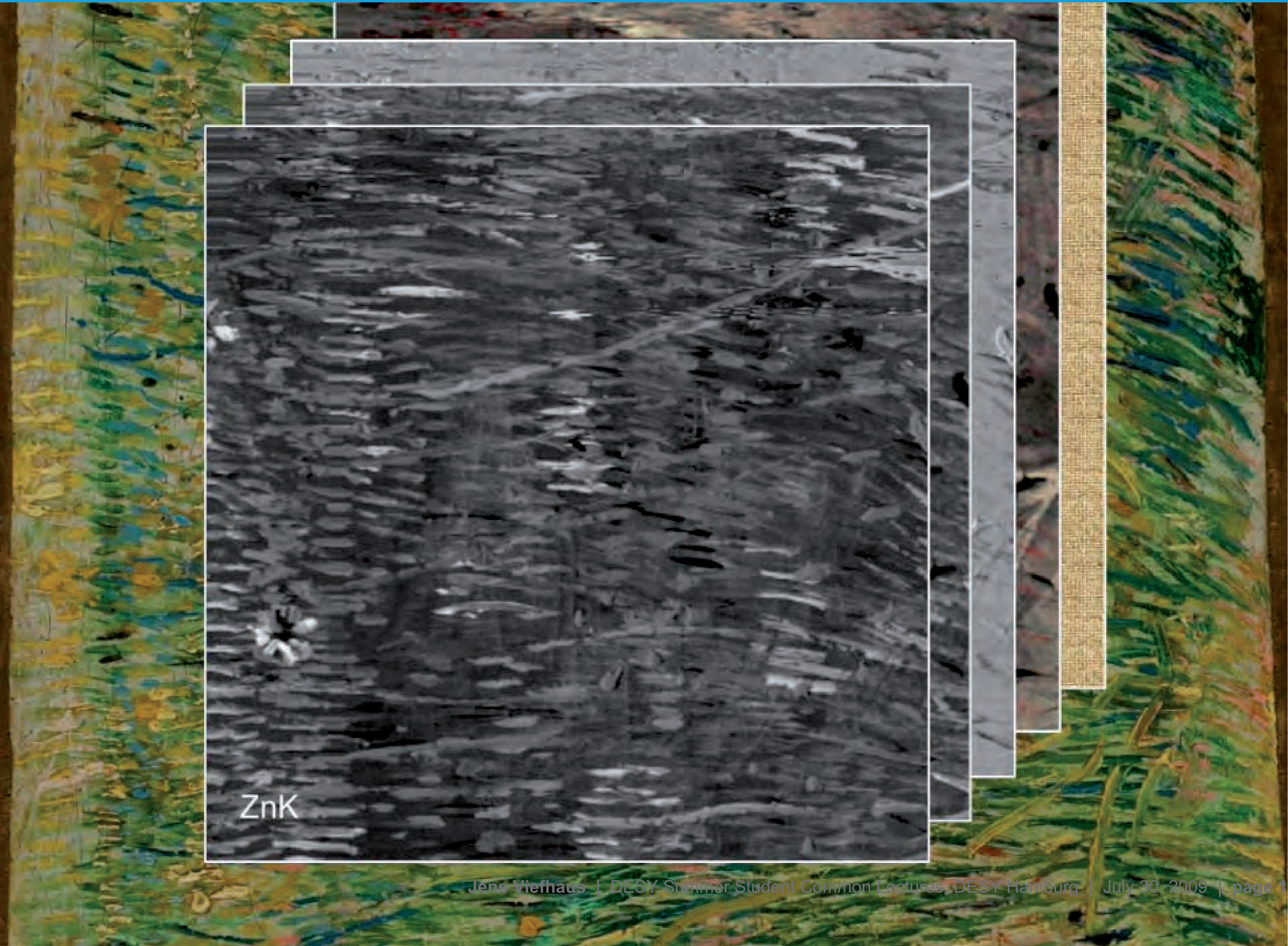
Imaging - Van Gogh Pixel by Pixel

- Painting is scanned with 0.5 mm resolution
  - For each of the 90,000 pixels a full spectrum is recorded:

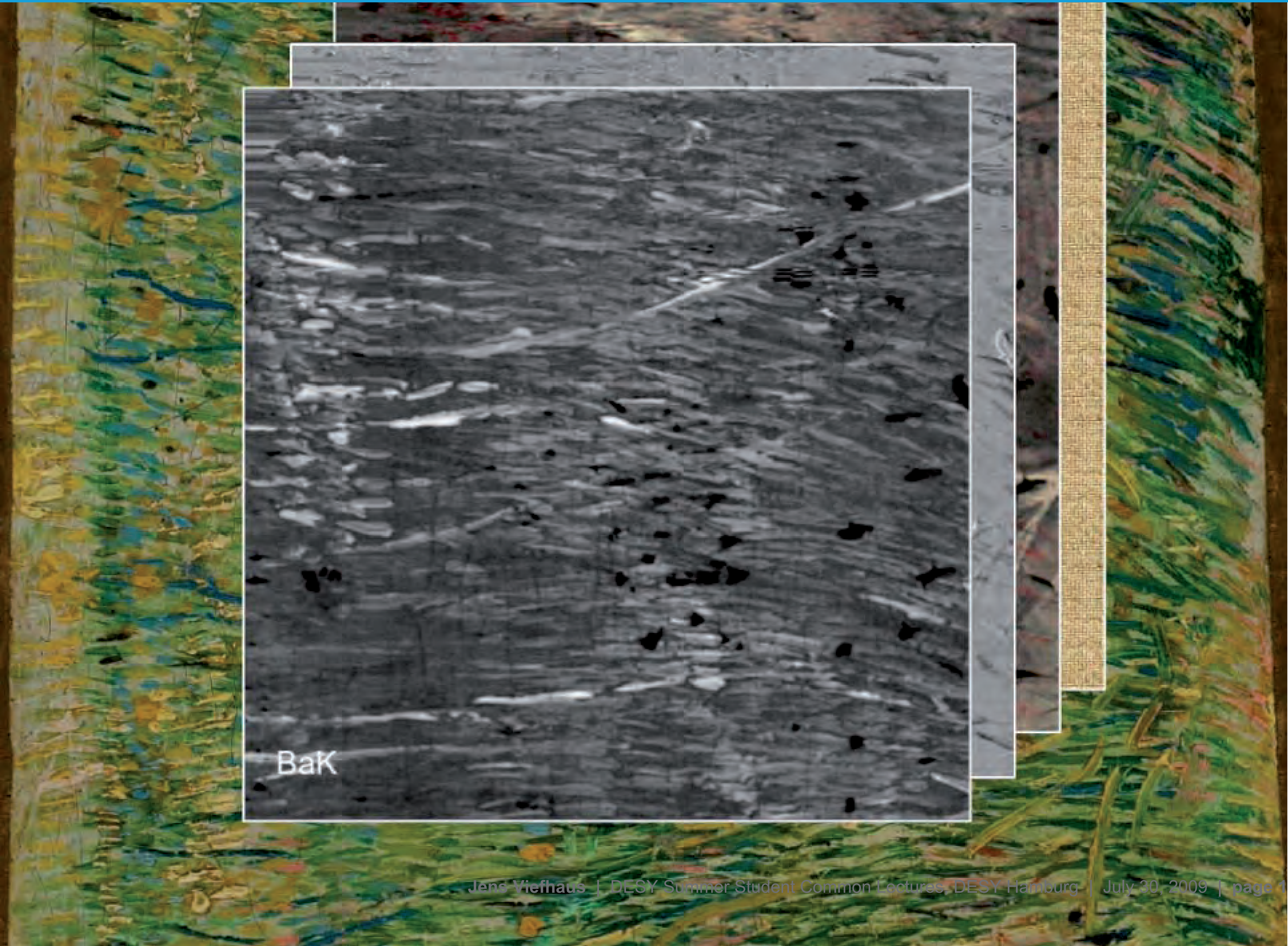


Imaging - Van Gogh

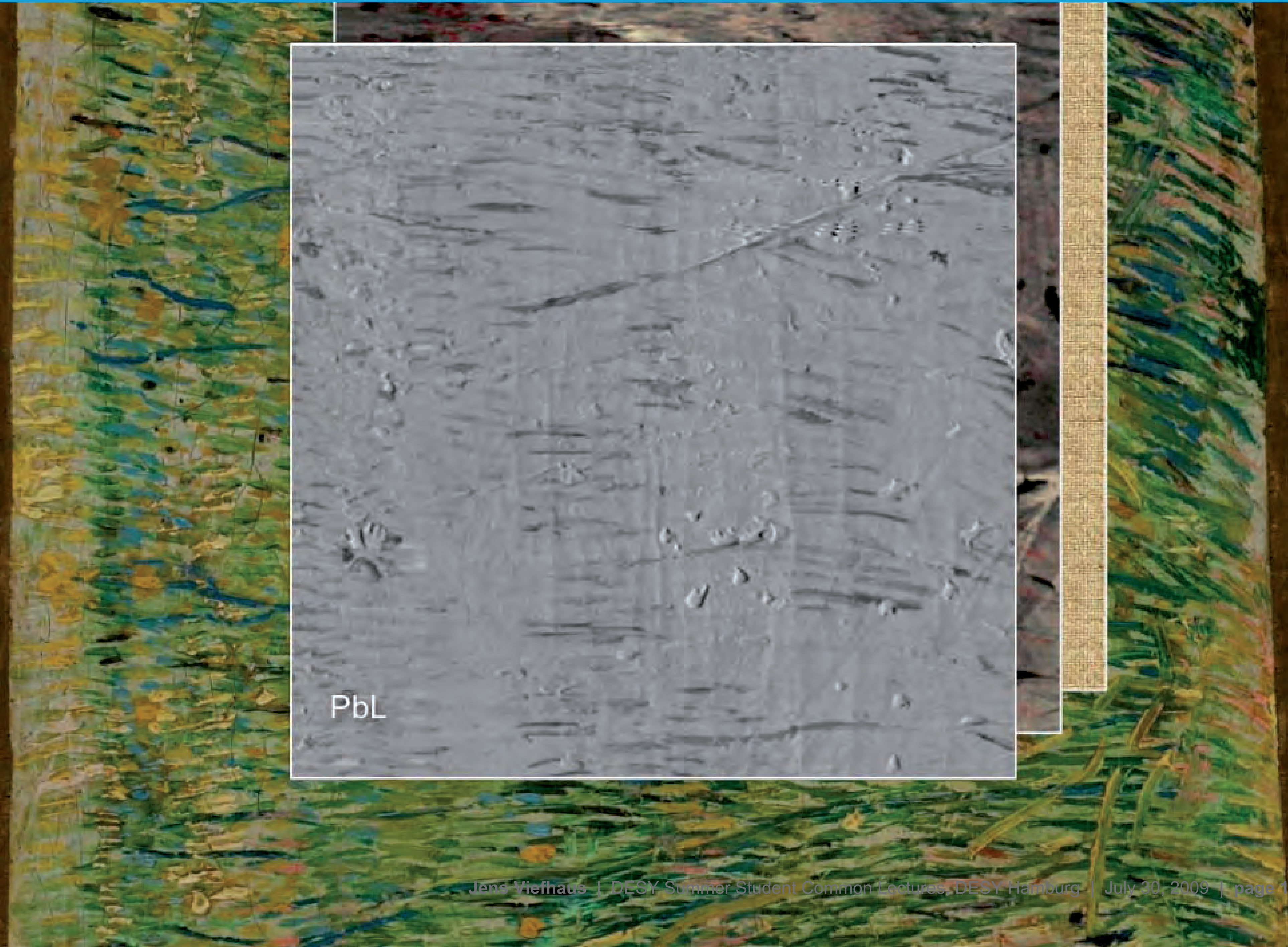
Imaging - Van Gogh (Zn K-shell Fluorescence)



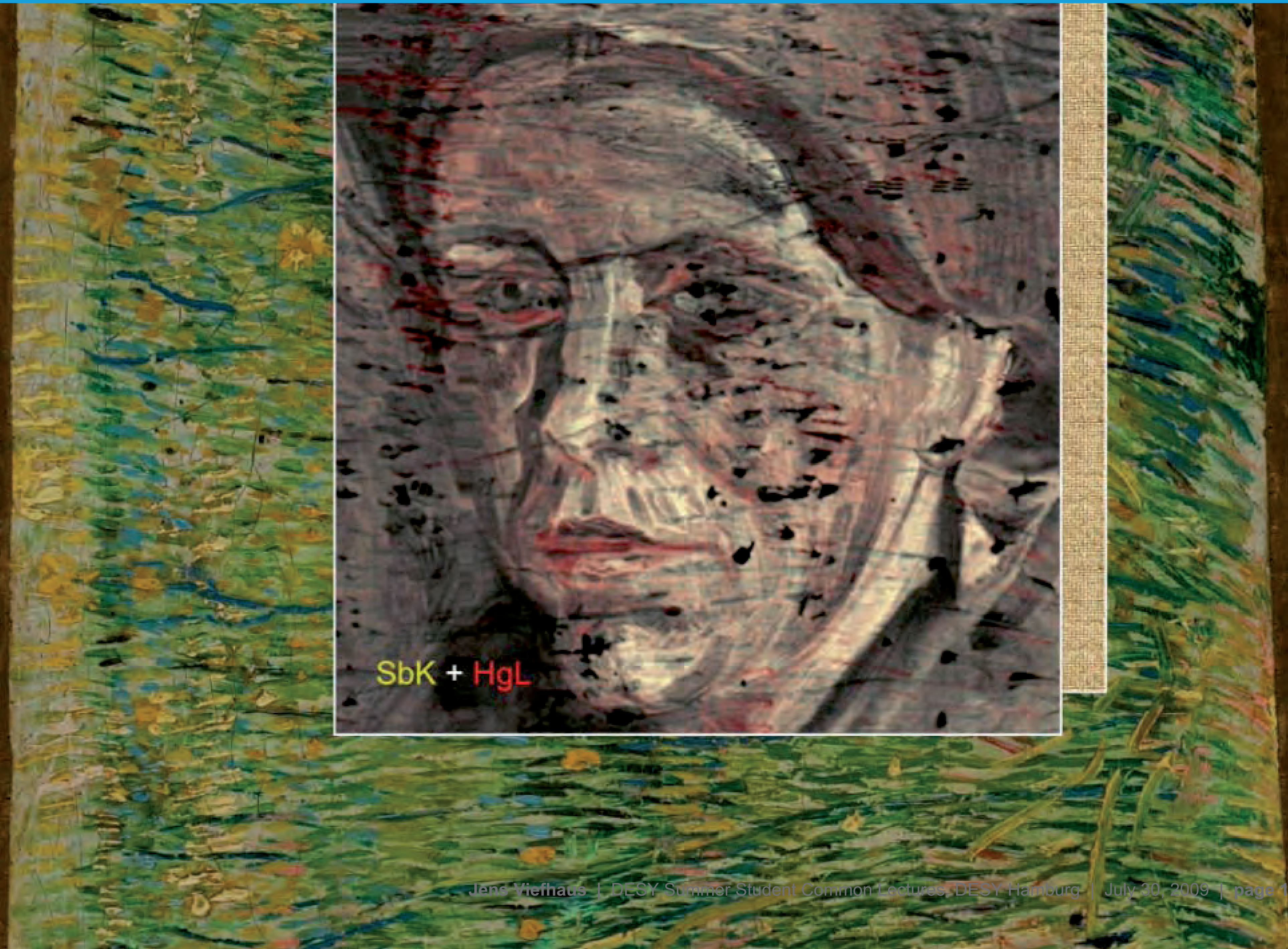
Imaging - Van Gogh (Ba K-shell Fluorescence)



Imaging - Van Gogh (Pb L-shell Fluorescence)

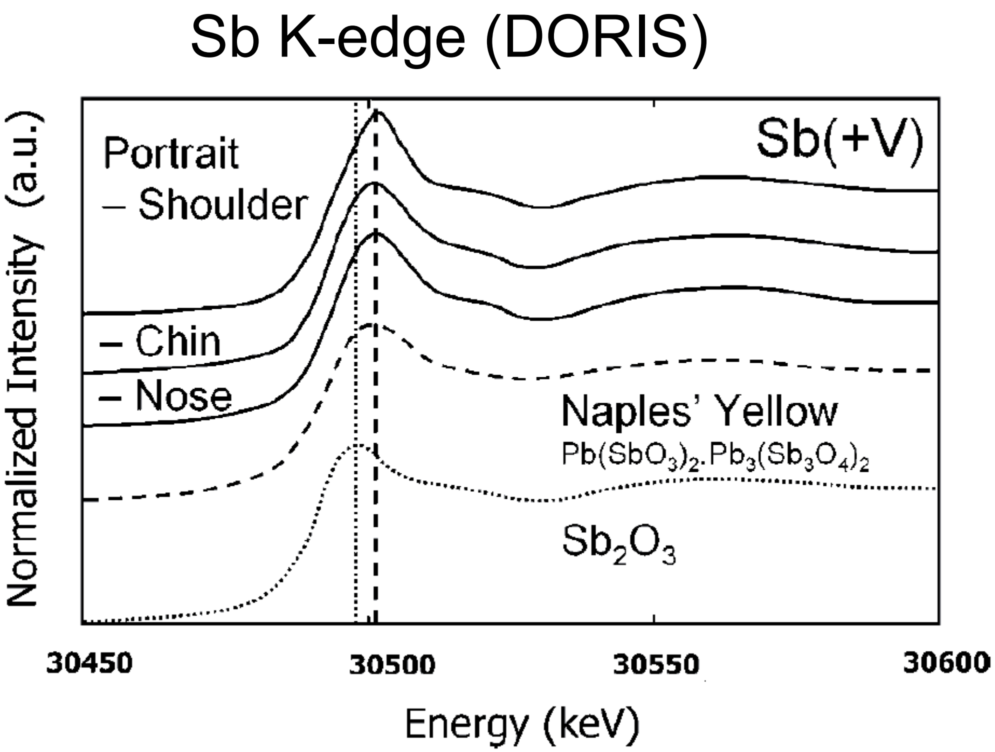


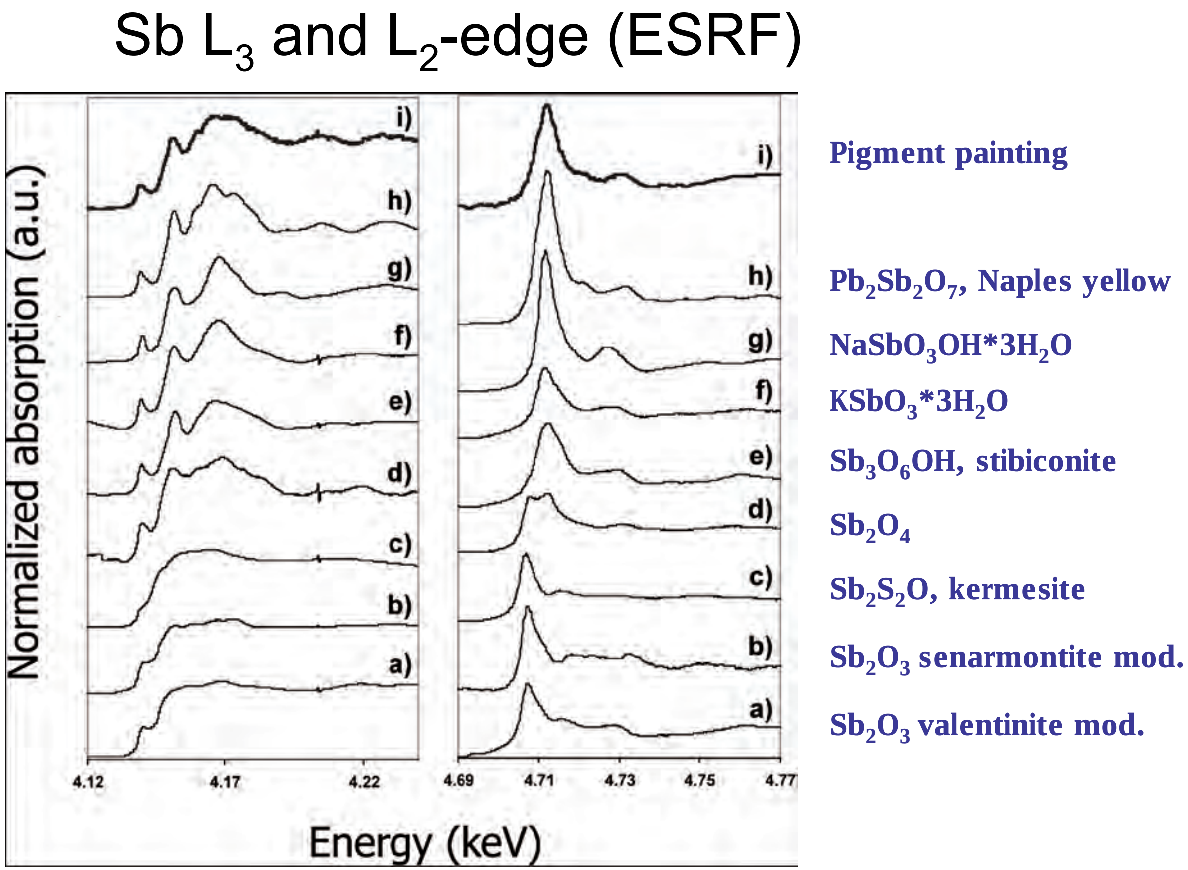
Imaging - Van Gogh (Sb K-shell and Hg L-shell Fluorescence)



X-ray Absorption Near Edge Structure - Paint Fingerprint

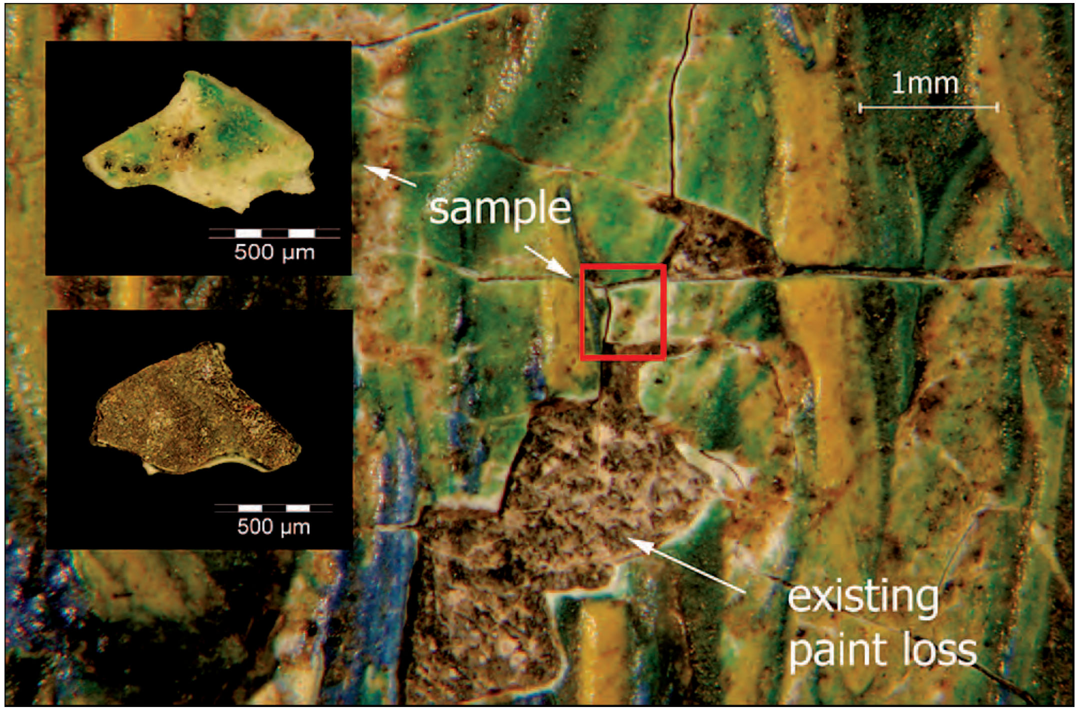
- In order to identify the actual colour used by Vincent van Gogh, additional XANES scans were taken:

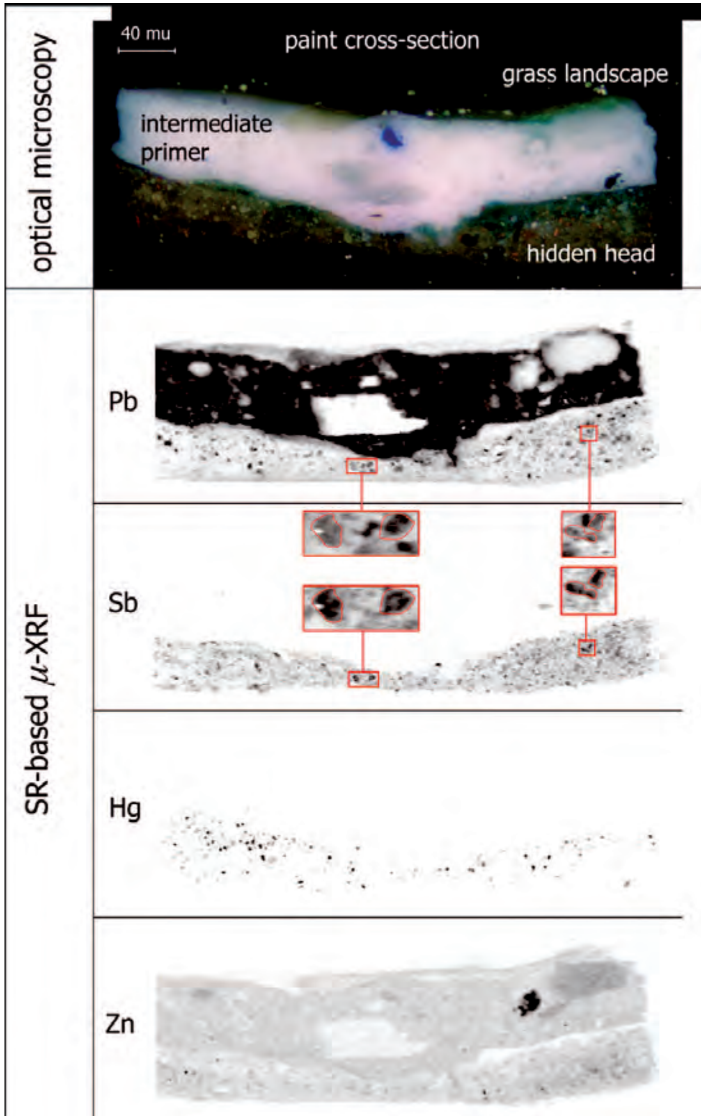




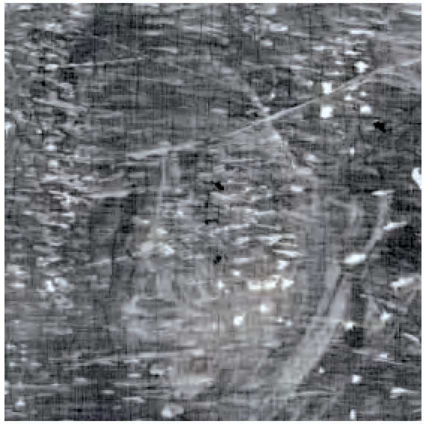
Van Gogh - Micro X-ray Fluorescence

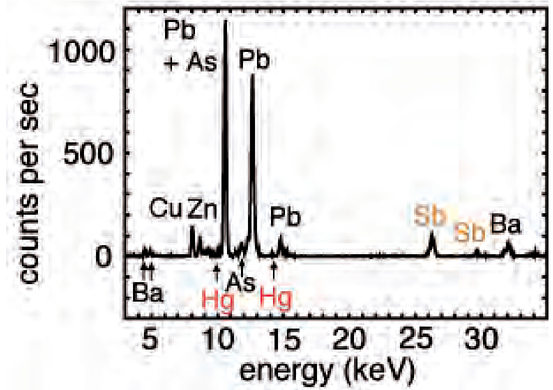
> To verify the fact that Sb and Hg are predominantly at the 2nd layer additonal µ-XRF scans were performed:

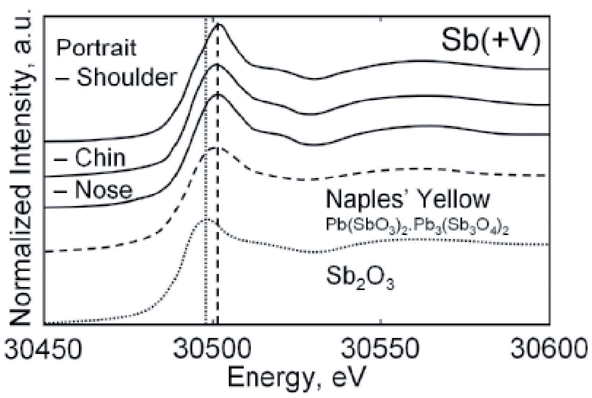




Visualizing a Lost Painting by *Vincent van Gogh*







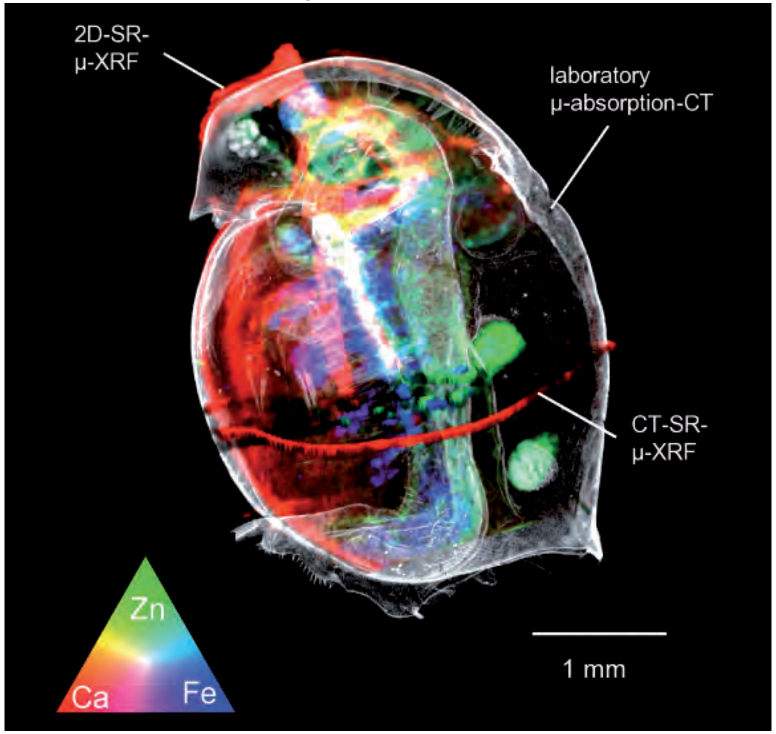
> In conclusion, the analytical techniques above nicely complement each other.

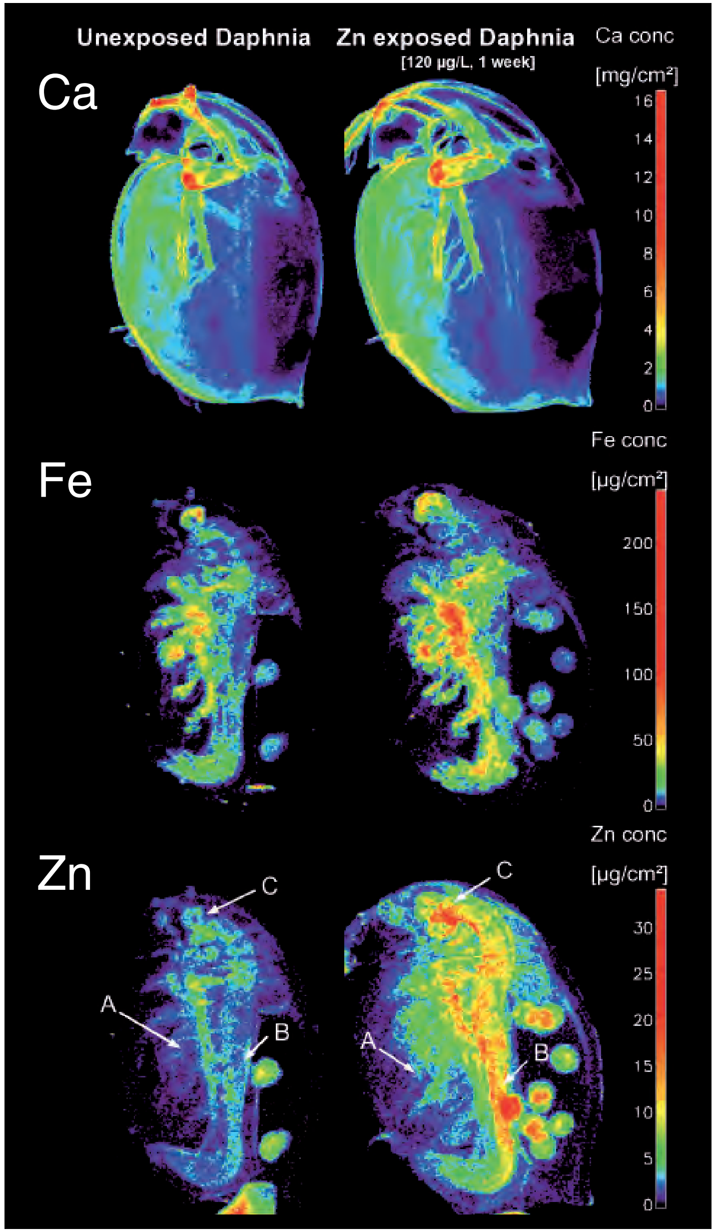
- Anal. Chem., 80, 16, 6436 - 6442, 2008

Metal Contaminations in Small Water Fleas

> µ-XRF can determine the concentration of trace-level distributions within a water flea Daphnia magna

- combining 2D/3D fluorescence with micro-probe and X-ray absorption tomography allows to create a detailed map of metal concentrations.
- This enables scientifically based environmental regulations



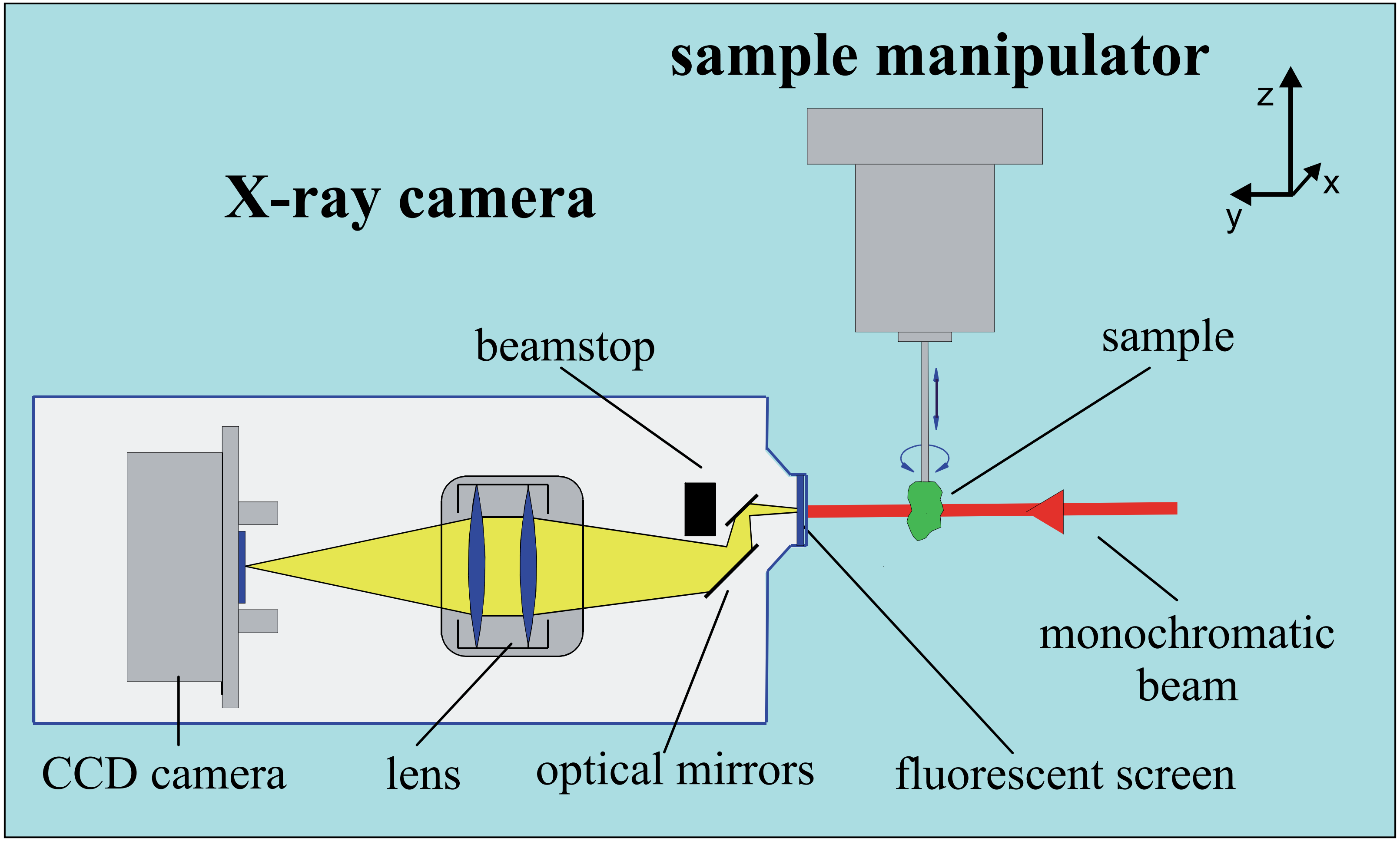


- J. Anal. At. Spectrom, 23, 829-839 (2008) , Anal Bioanal Chem, 390, 267-271 (2008)

Micro-Tomography at DORIS III

> Principle: Measurement of many different projections

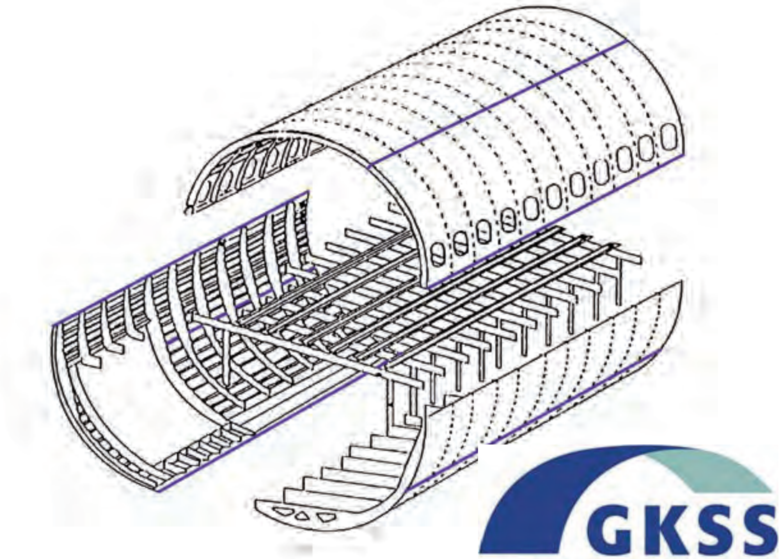
- Numerical reconstruction of a 3-dimensional data set "absorption per voxel"



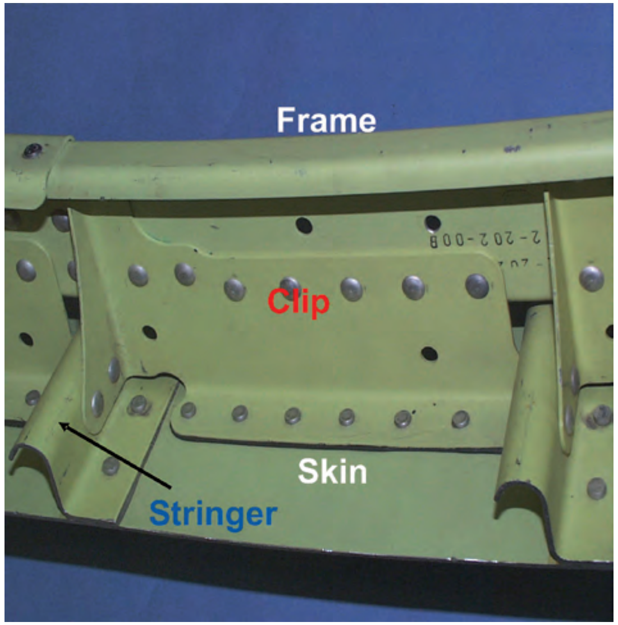
Micro-Tomography of Complex Samples

> Characterization of Al-alloy T-joints

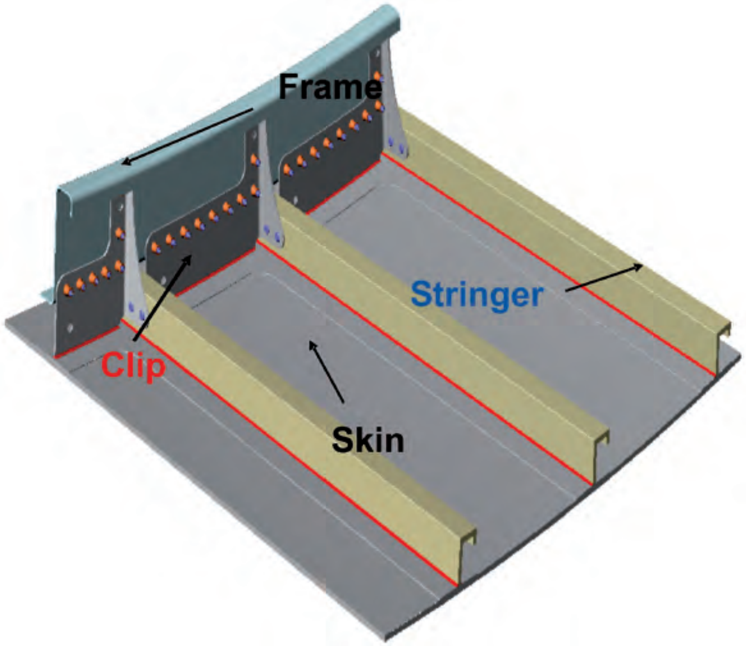
- In aircraft construction so-called stingers are currently used as pore-free laser-welding is still too expensive
- Welded clips could instead reduce the weight provided that the technology is being further developed



Conventional riveted airframe structure



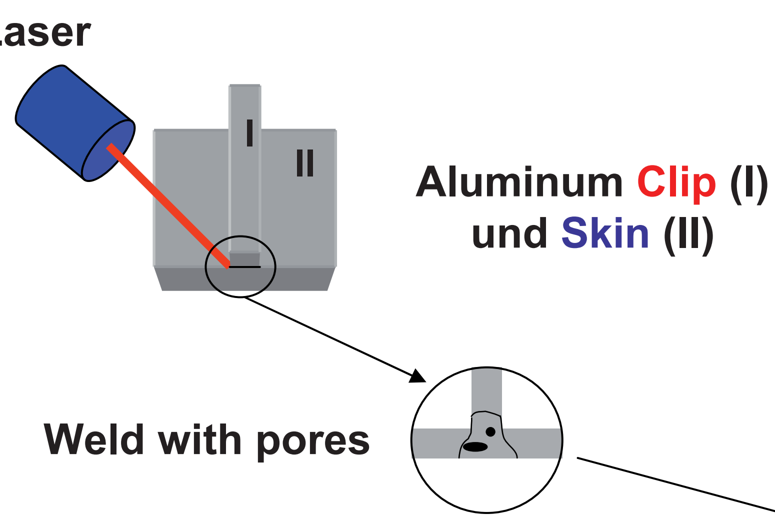
Welded metallic airframe

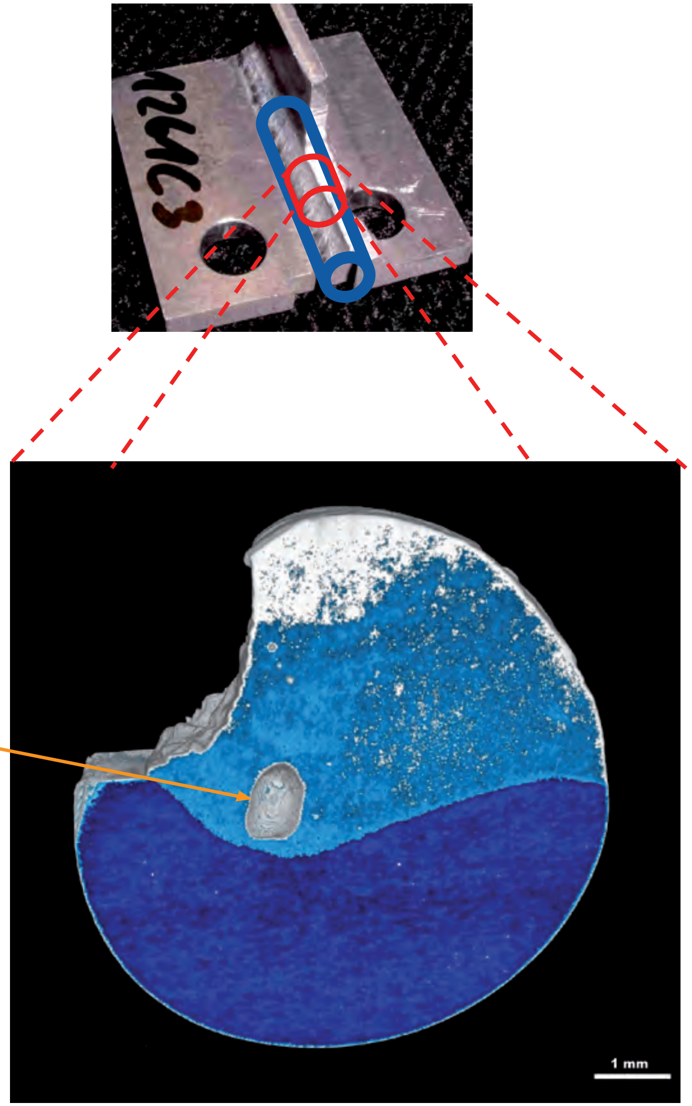


GKSS FORSCHUNGSZENTRUM

Courtesy: J. Herzen, F. Beckmann (GKSS)

Micro-Tomography of Complex Samples





> Characterization of Al-alloy T-joints, first results:

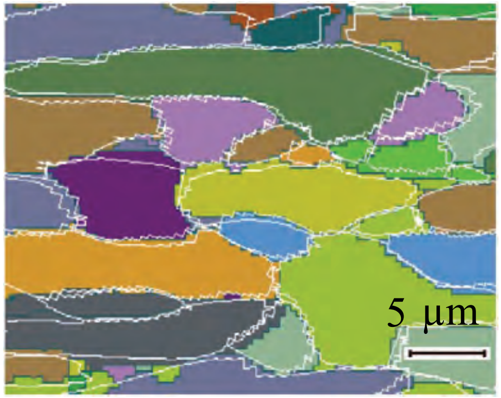
- Visualisation of different sorts of pores
- Clear separation of the weld and raw materials
- High density resolution using absorption contrast

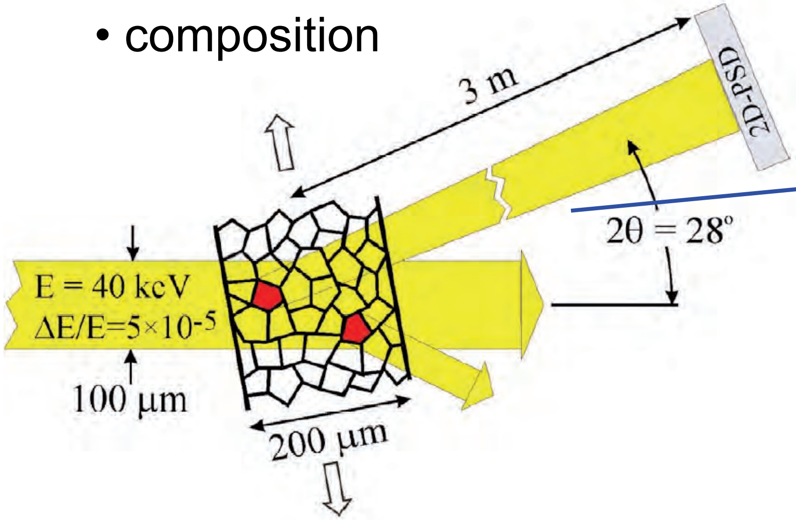
Micro-Tomography at 40 keV

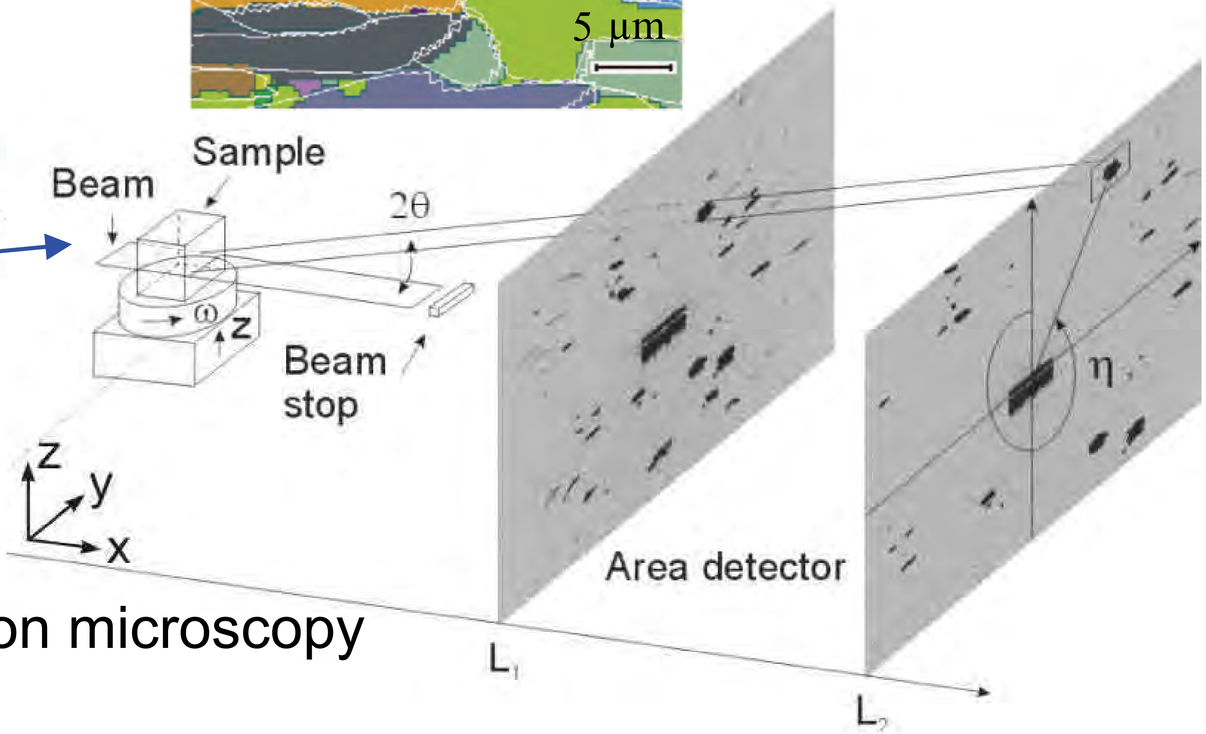
Courtesy: J. Herzen, F. Beckmann (GKSS)

Grain mapping of metals and alloys

- Change of microstructure of a material upon mechanical load and deformations?
- Grain properties to be determined:
  - position
  - morphology
  - orientation
  - deformation (plastic/elastic)
  - composition



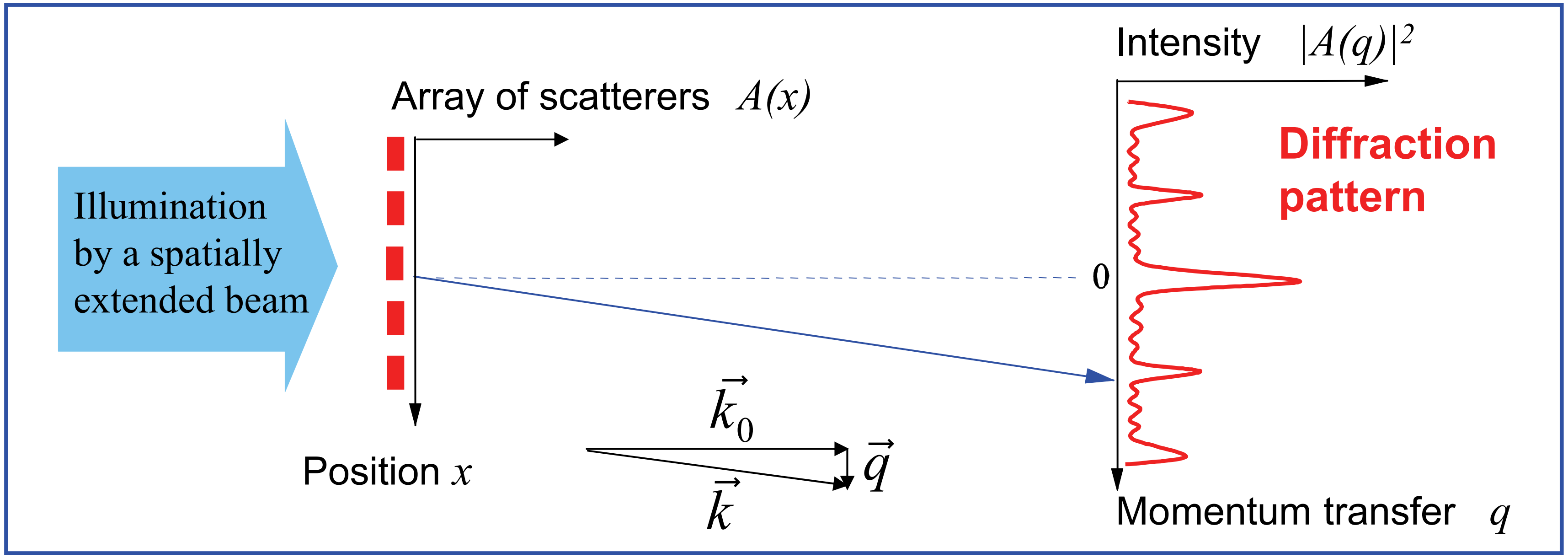




3D X-ray diffraction microscopy

H. F. Poulsen et al., J. Appl. Cryst. 34, 751 (2001)

Principles of Structure Determination



$\vec{q} = \vec{k} \quad \vec{k}_0$ momentum transfer

Relation between $A(x)$ and $A(q)$:

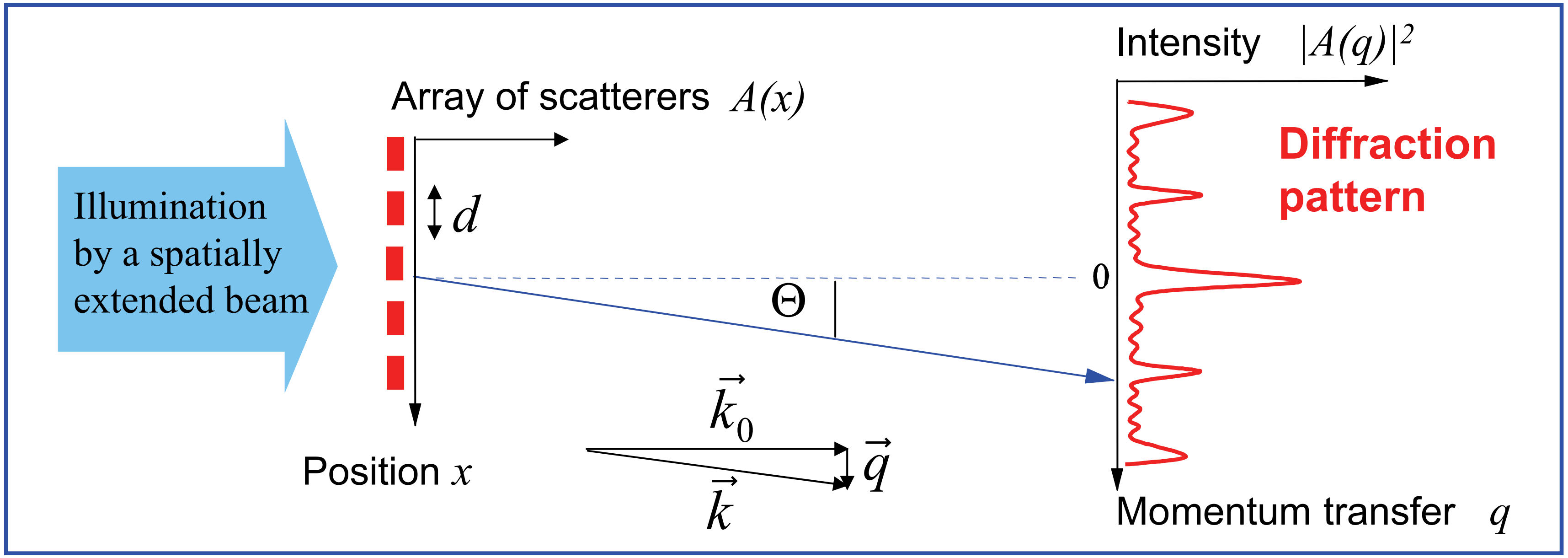
$$\boxed{A(q) = \int A(x)\, e^{iqx}\, dx} \quad (1)$$

Task: Determine $A(x)$ from measured $|A(q)|^2$

Problem: Eq. (1) cannot be simply inverted, because the phase is lost

(Phase problem of crystallography)

Principles of Structure Determination



Position of diffraction peaks given by Bragg's equation:

$$\frac{n}{\sin\Theta} = 2d_{h,k,l}$$

X-ray Diffraction - The Phase Problem

> Nobel prize in chemistry 1985:

- For the developement of direct methods for the structur determination of cristals

Jerome Karle Herbert A. Hauptman

amplitude and phase correct

Fourier-transformed, using the correct amplitude but changing the phase

Finding Solutions for the Phase Problem in X-ray Diffraction

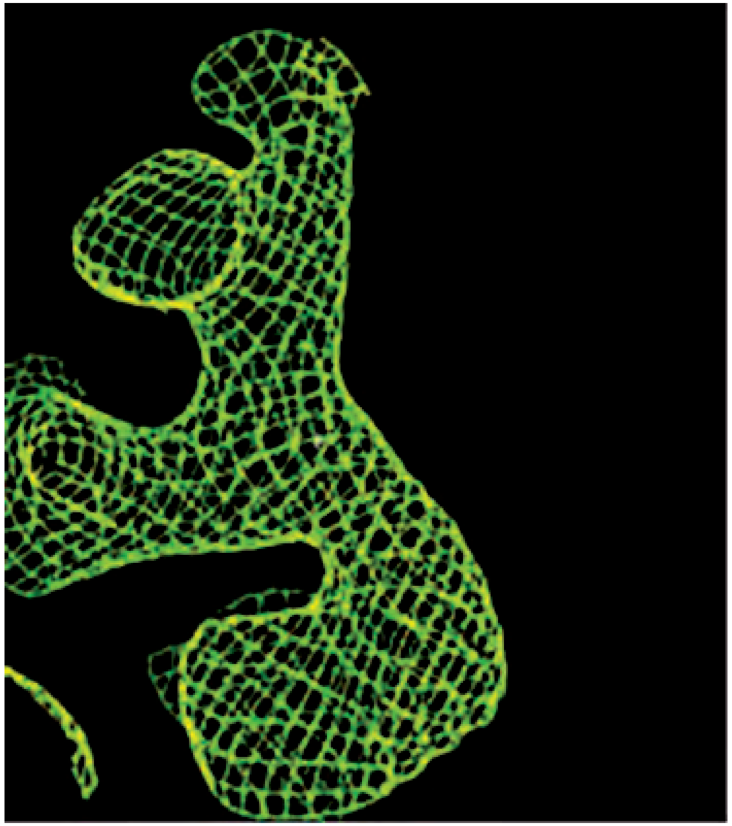
> A priori information on the structure
  - ("educated guess" and then compare with model)

> MIR - Multiple Isomorphous Replacement
  - Besides the structure determination of the original crystal, at least two more crystals doped with heavy atoms have to be measured

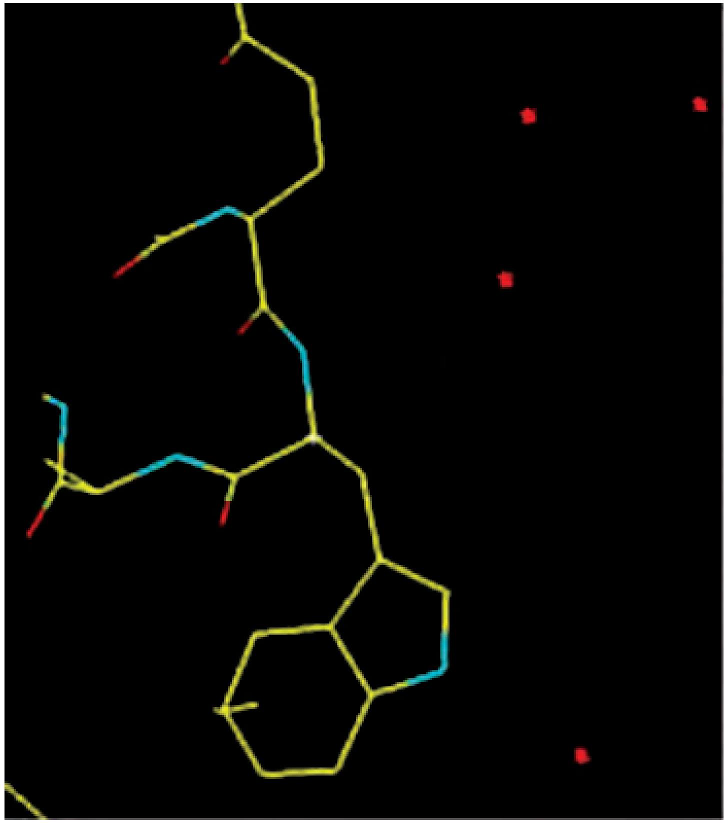
> S/MIRAS - Single/Multiple Isomorphous Replacement with Anomalous Signal
  - In addition to the original crystal at least one more crystals has to be measured and its doped heavy atoms have to be excited to anomalous diffraction

> MAD - Multiple Anomalous Dispersion
  - The crystal has to be doped with an anomalously diffracting atom, which must be measured at several different wavelength

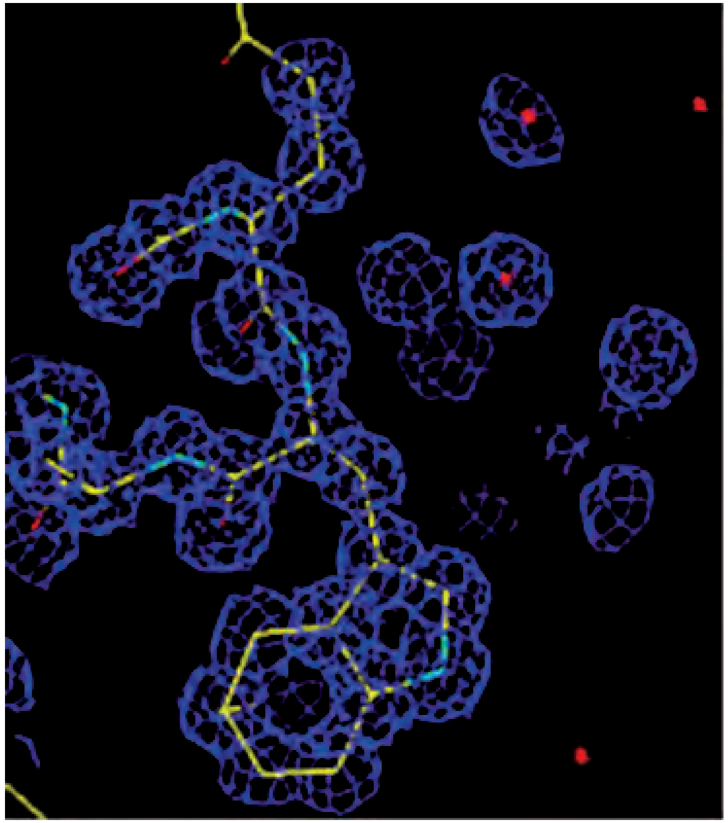
X-ray diffraction - "Guessing" the structure



Measured electron density-distribution

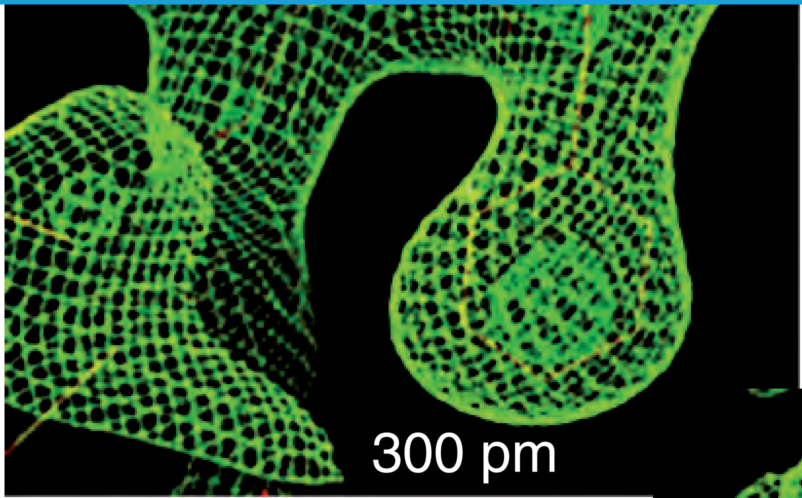


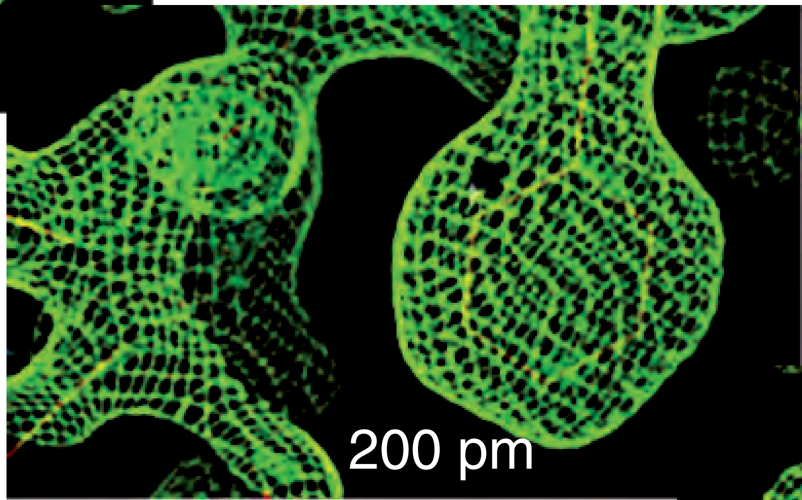
Structure of the a priori information

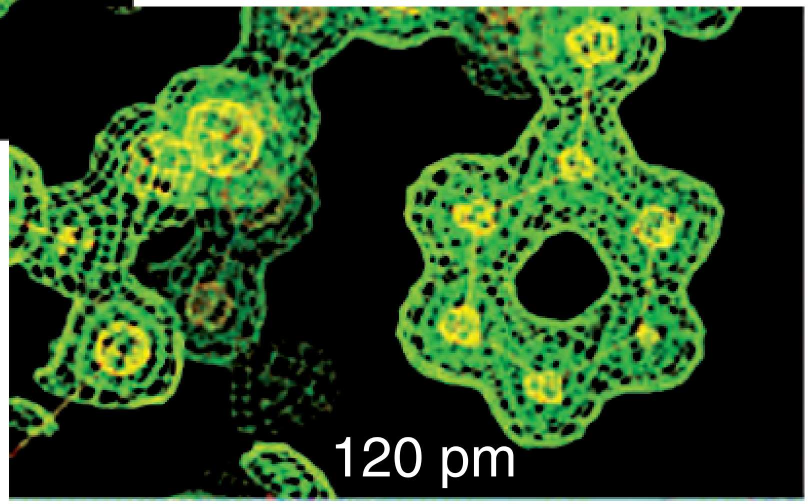


Result

X-ray diffraction - resolution



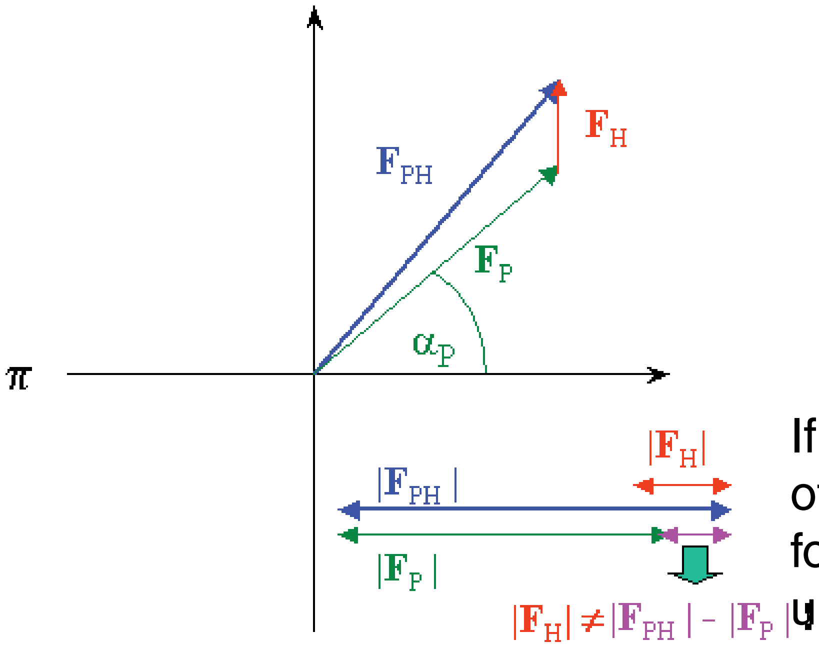




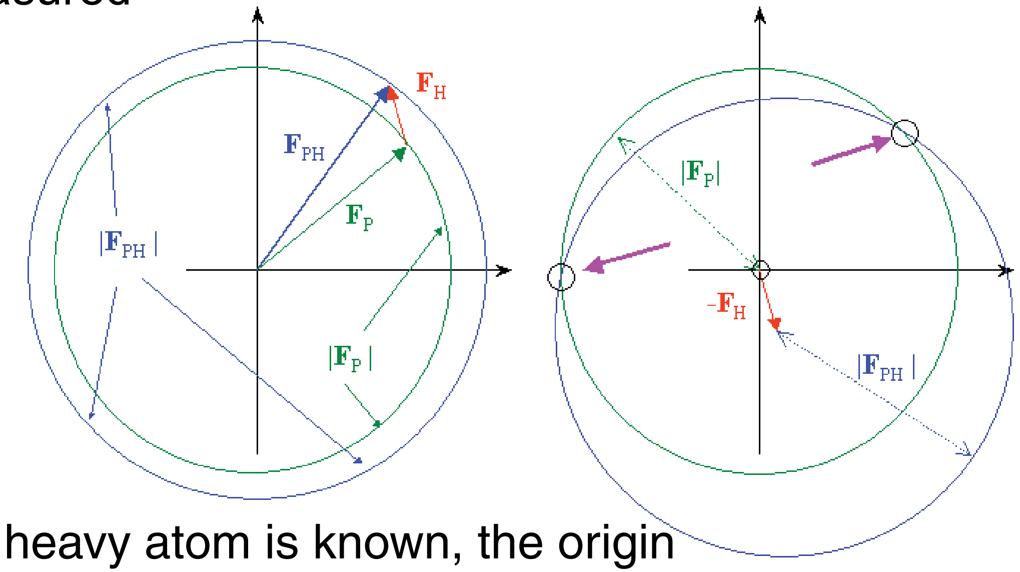
> Naturally the quality of the resulting structure model depends strongly on the required resolution. Resolutions in the order of 120 pm are state-of-the-art.

Phase Problem - Multiple Isomorphous Replacement

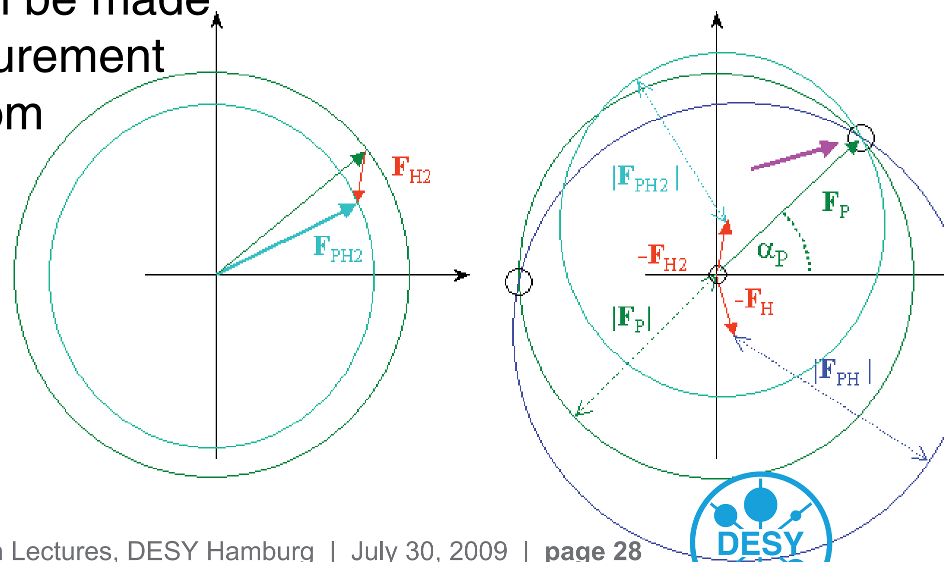
- Besides the structure determination of the original crystal, at least two more crystals doped with heavy atoms have to be measured



The phase α_P is unknown (circle):



If the location of the heavy atom is known, the origin of F_H is determined. This rersults in two solutions for the phase, which can be made unique via a third measurement using another heavy atom and its corresponding scattering factor F_{PH2}



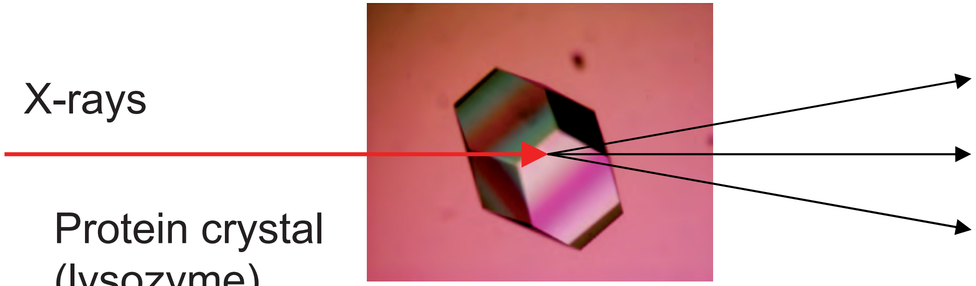
Measured quantities are the absolute values of the scattering factors F_P (original) and F_{PH} (doped).

Single Crystal Diffractometer

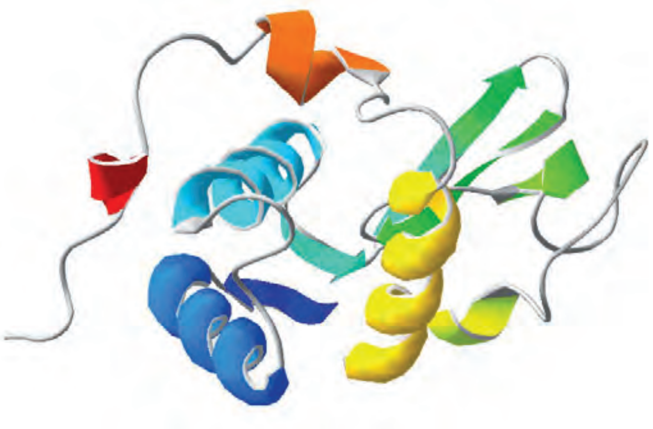

> Single crystal diffractomter in κ-geometry with CCD and scintillation counter. Crystal mounted on a glass fiber. the diffractometer has 3 rotations for the crystal
□ and one for the detector

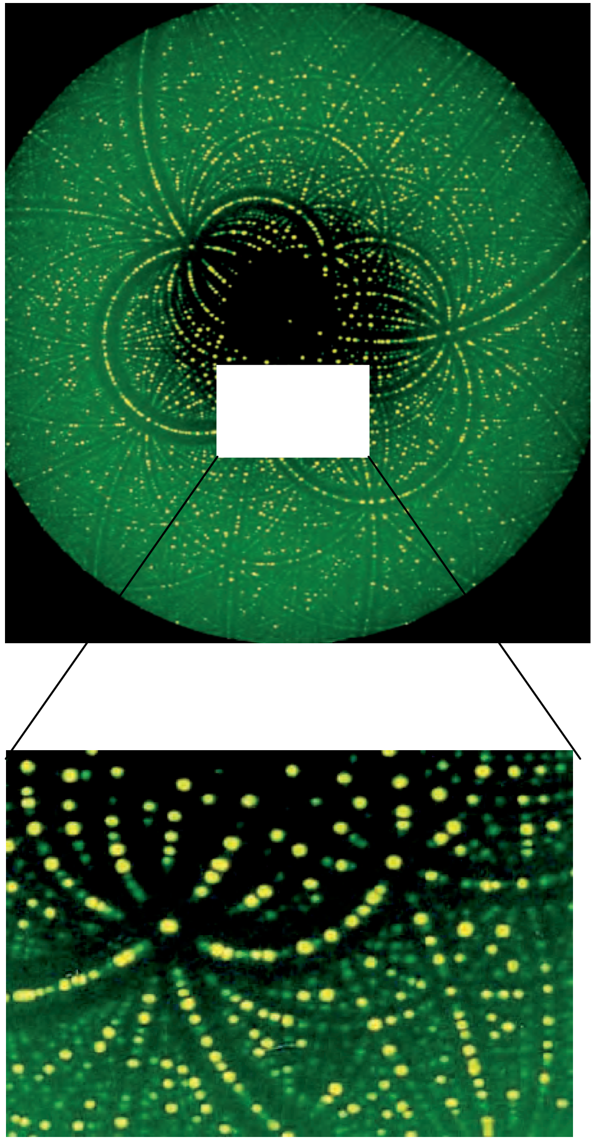
X-ray diffraction of Bio-Molecules

X-rays

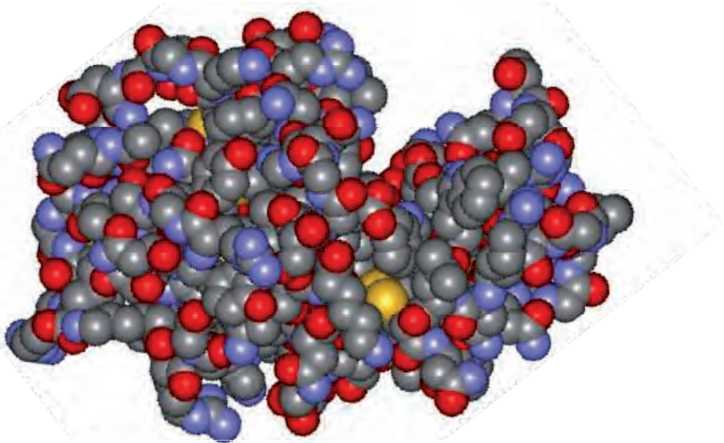


Protein crystal
(lysozyme)

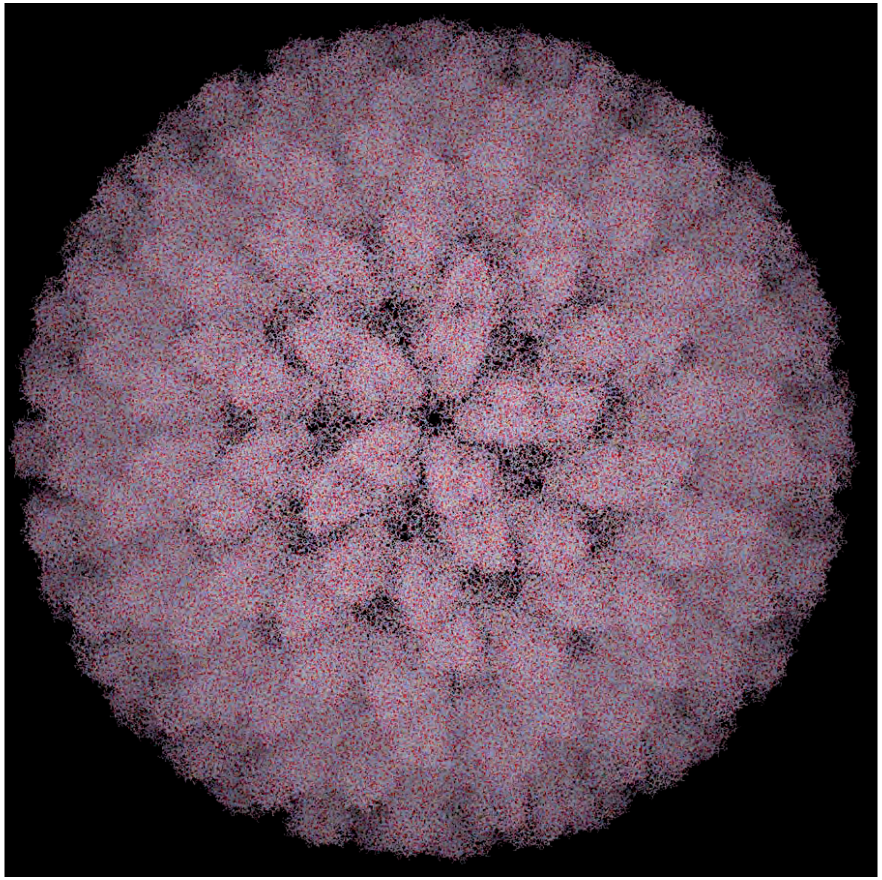




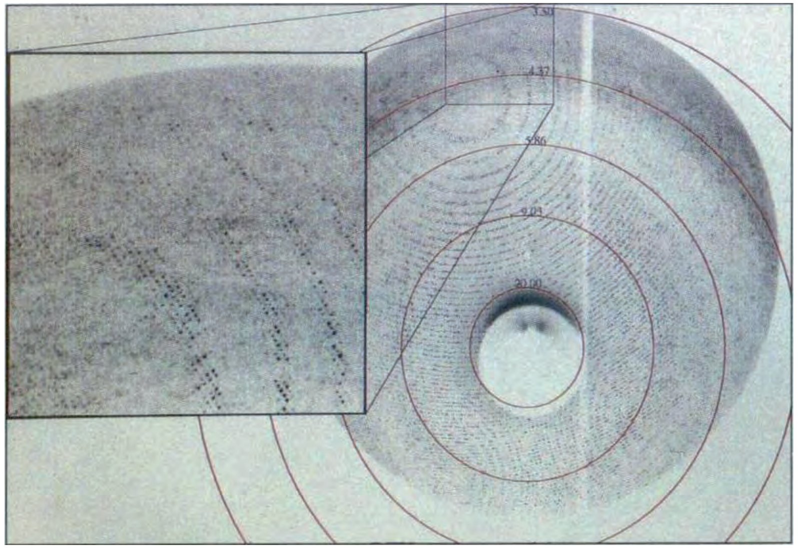
Carbon: Grey
Nitrogen: Blue
Oxygen: Red
Sulphur: Yellow



X-ray diffraction of extremely large complexes



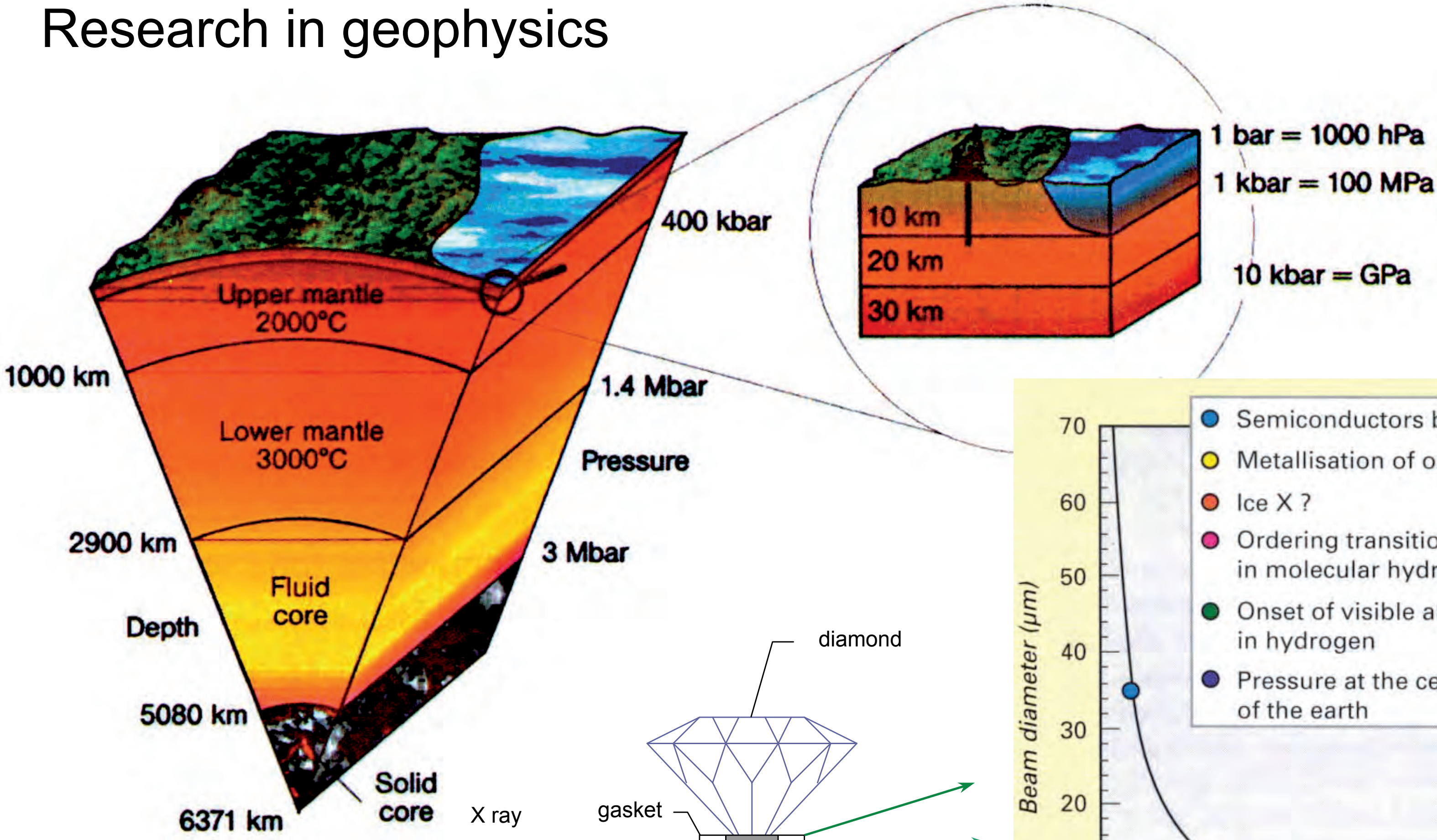
Example: Blue Tongue Virus

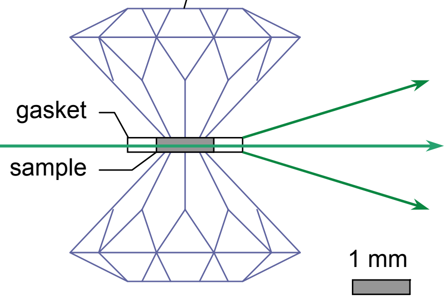


J .M. Grimes et al., Nature 395, 470-478 (1998)

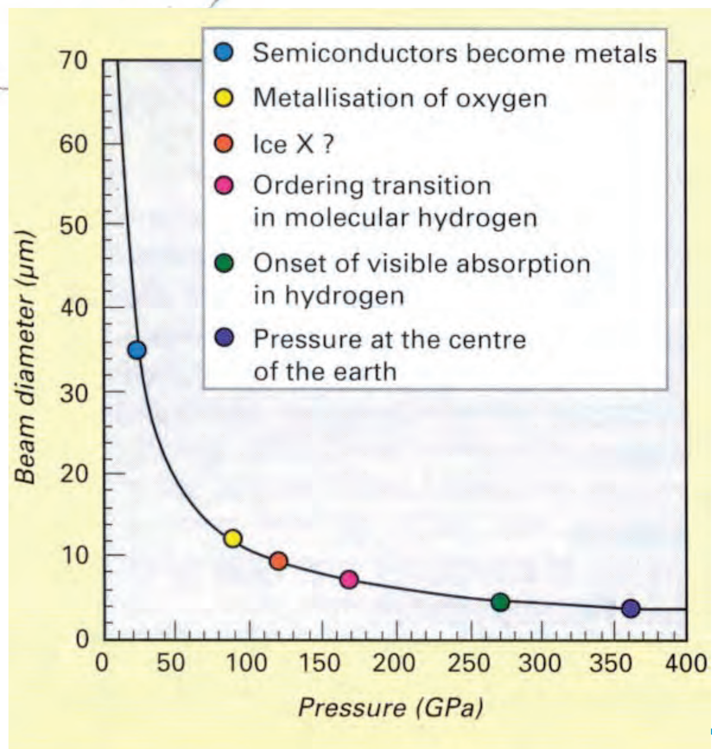
X-ray Scattering from Samples Under High Pressure

Research in geophysics





Diamond anvil cell



X-ray Scattering Under High Pressure

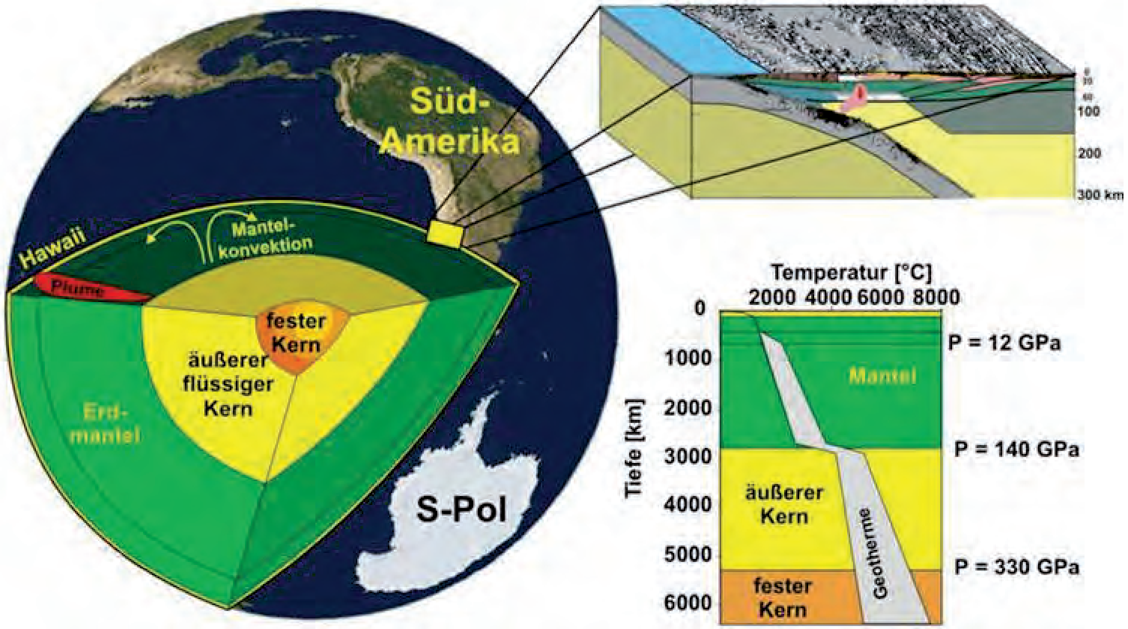
GFZ (GeoForschungs Zentrum Potsdam) @ DESY

1750 t press for in situ studies of large sample volumes

Maximum pressure ~ 25GPa

Temperature: > 2000K

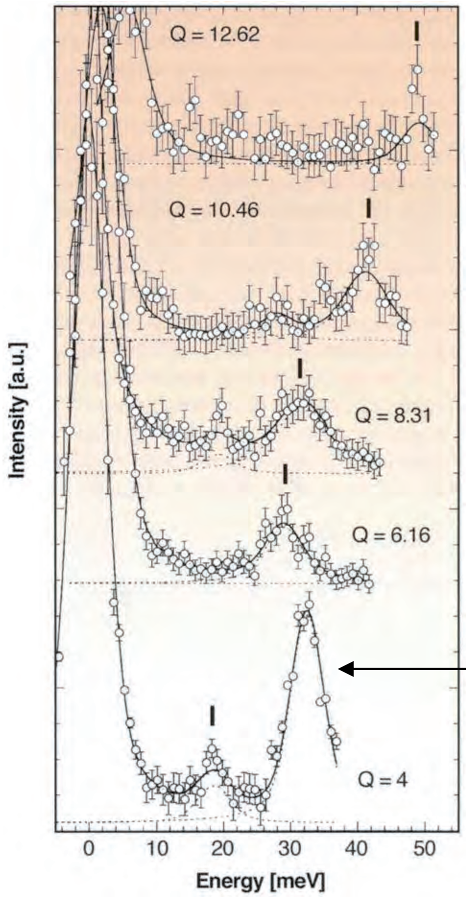
Study of material under the conditions of the earths lower mantle



Inelastic X-ray Scattering under High Pressure

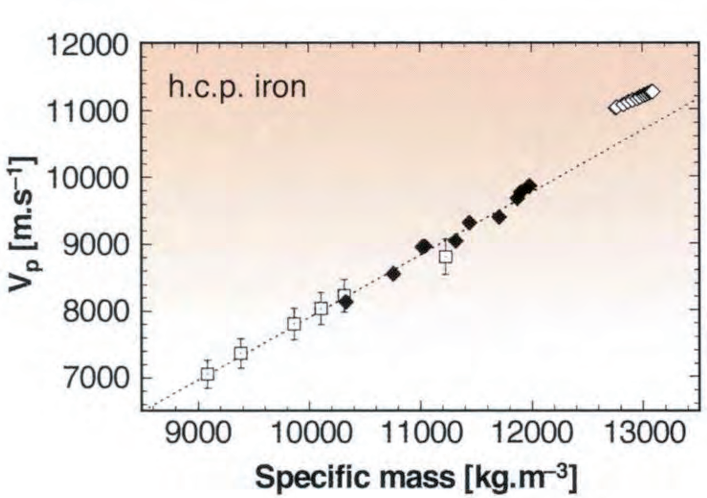
X-rays change energy due to interaction with phonons

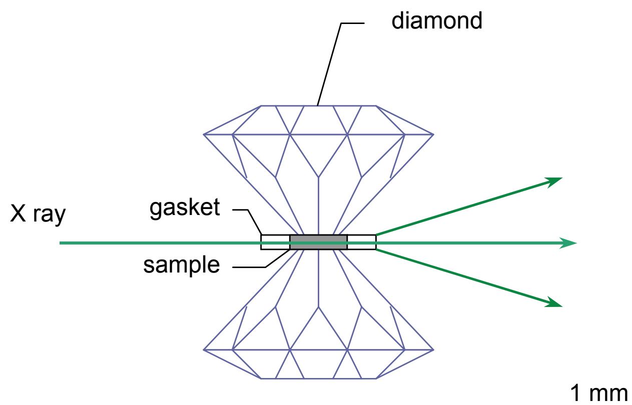
Example: Determine the speed of sound in Fe under pressure



P = 28 GPa

Peaks are due to phonons

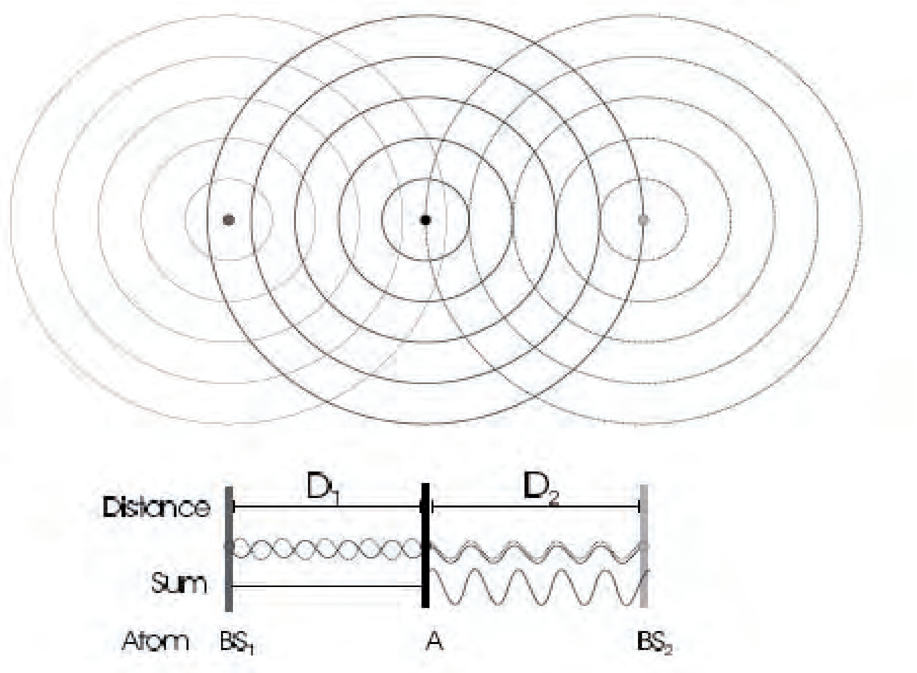




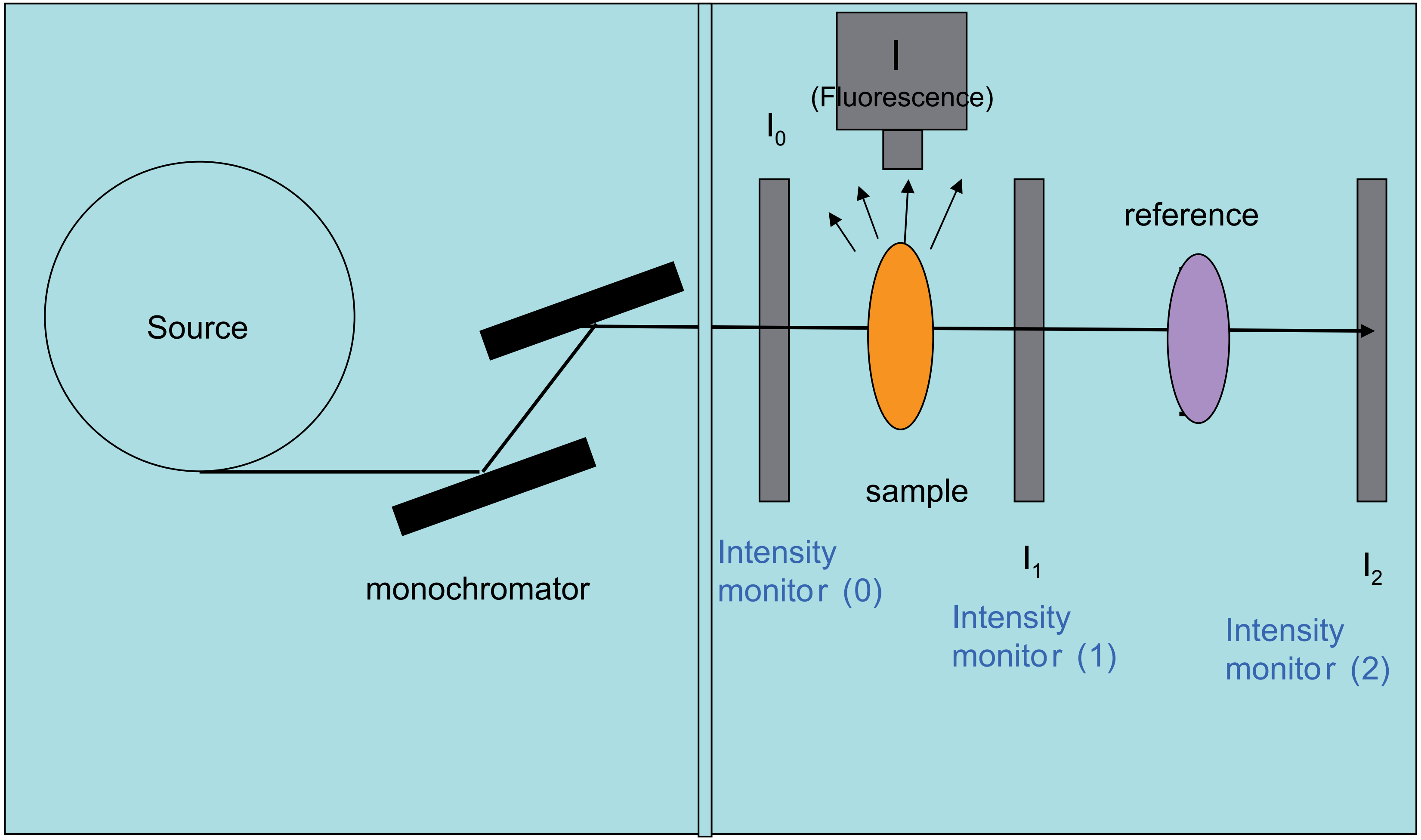
G. Fiquet et al., Science (2000)

X-ray Absorption Spectroscopy

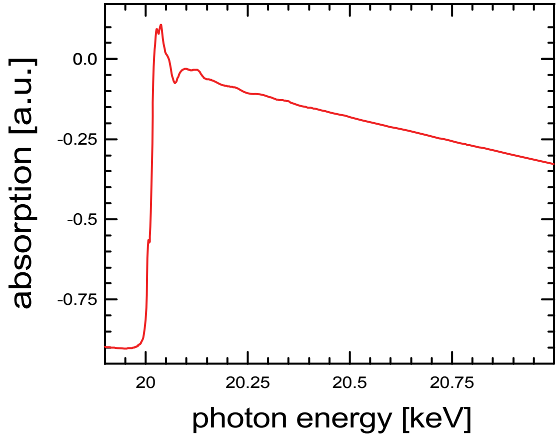
- Photons are resonantly absorbed near an absorption edge
- The outgoing electron is scattered by the surrounding atoms
- Interference of the outgoing electron wave with the backscattered electron waves:
  - Modulation of the cross section as a function of energy provides access to information on the distance of neighbour atoms:



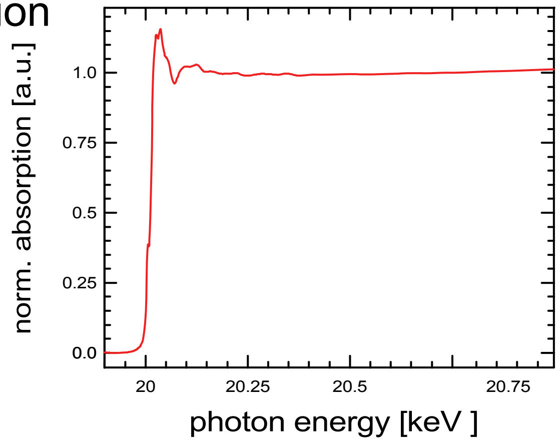
X-ray Absorption Spectroscopy: Experimental setup



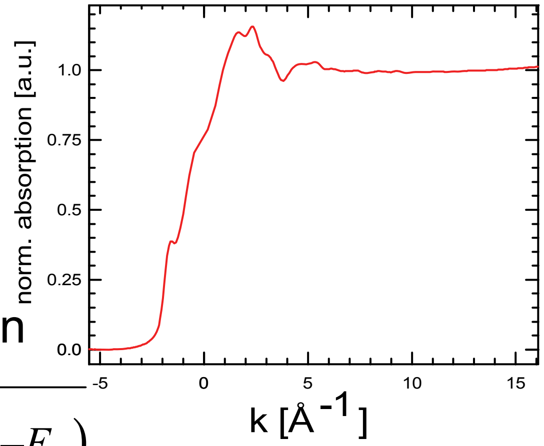
X-ray absorption spectroscopy



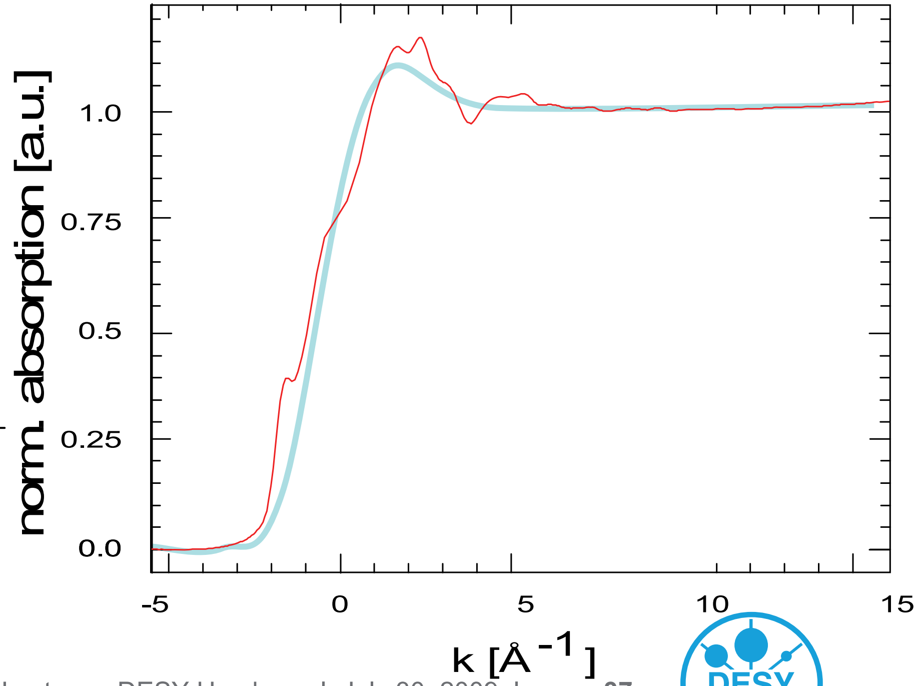
energy calibration,
background substraction,
normalization



conversion



$$k = \sqrt{\frac{2m}{\hbar}(E - E_0)}$$

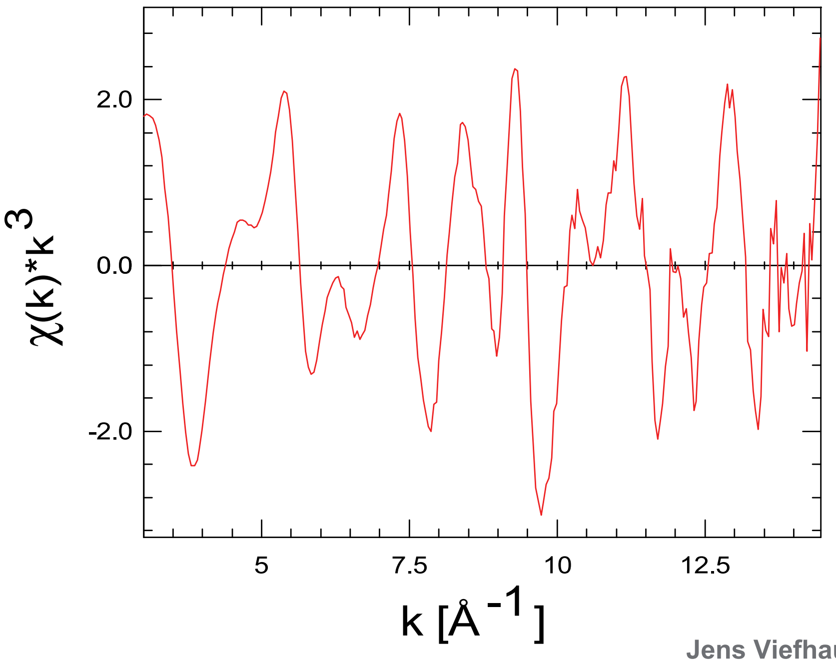


Substraction

of μ_0

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$$

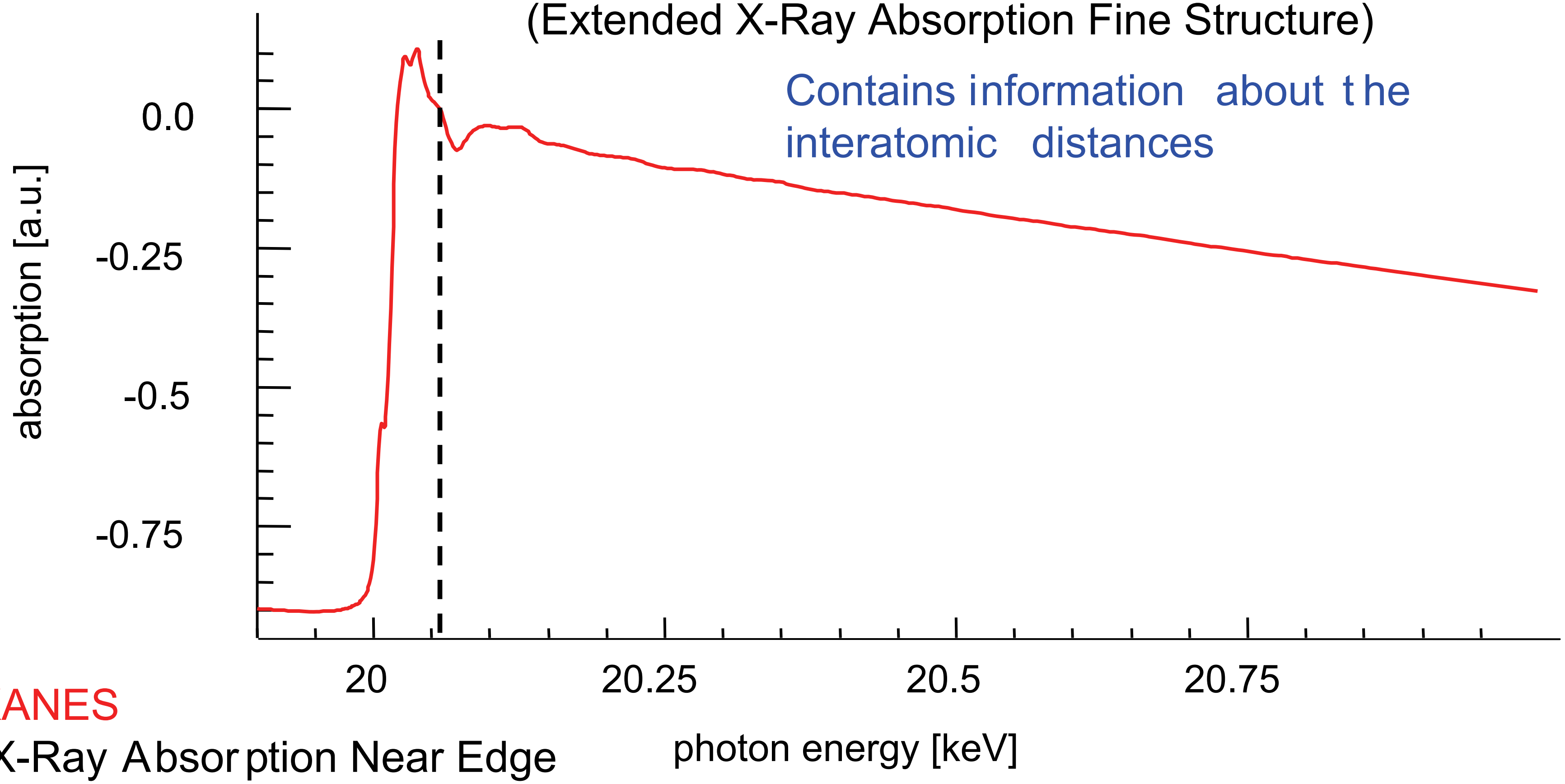
χ(k)



Regions in the X-ray Absorption Spectrum

EXAFS
(Extended X-Ray Absorption Fine Structure)

Contains information about the interatomic distances



XANES
(X-Ray Absorption Near Edge Structure)
NEXAFS
(Near Edge X-Ray Absorption Fine Structure)

Contains information about the chemical binding state of the absorbing atoms

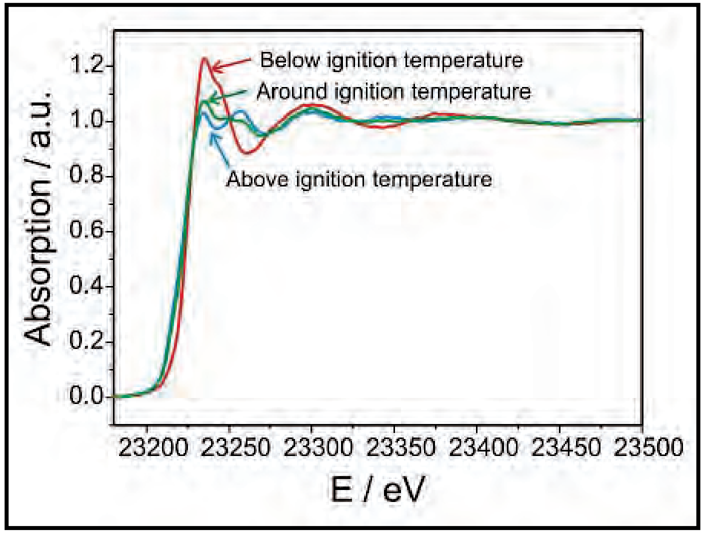
2D-Mapping of the Structure of a Heterogeneous Catalyst

In-situ 2D-mapping of the catalyst inside a catalytic micro-reactor

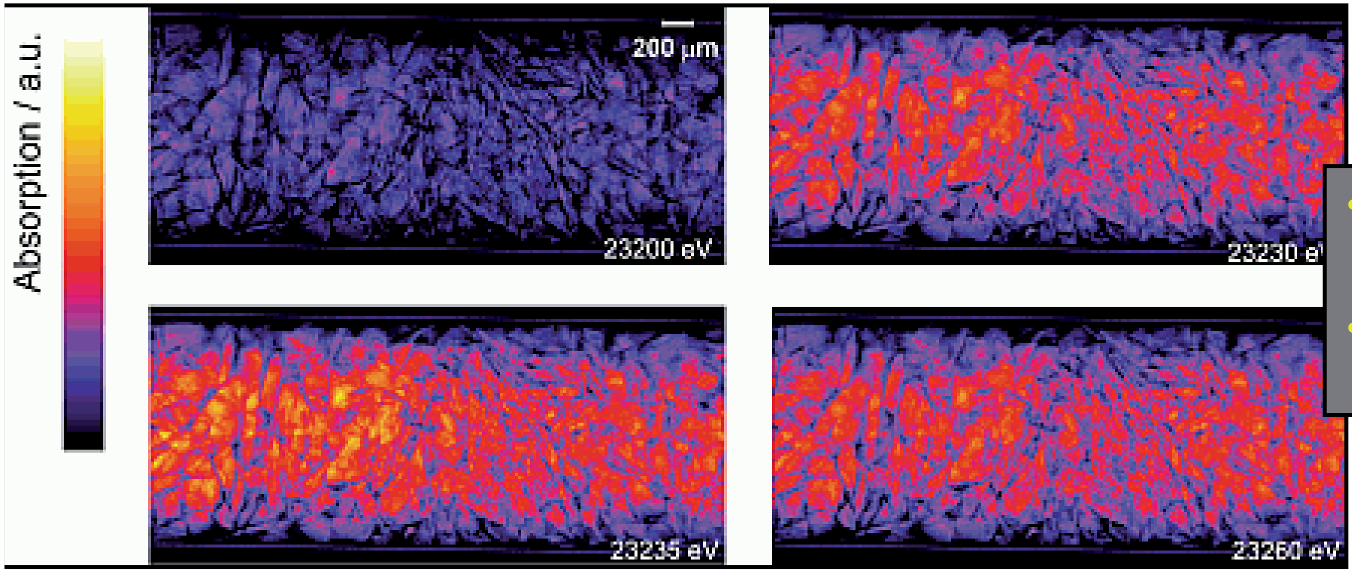
Catalyst structure at the atomic level under industrial reaction conditions (dynamic, in situ, in operando)

Example: partial oxidation of methane over Rh/Al_2O_3 promising reaction for the production of hydrogen from natural gas

$$CH_4 + ½\, O_2 \rightarrow CO + 2\, H_2$$



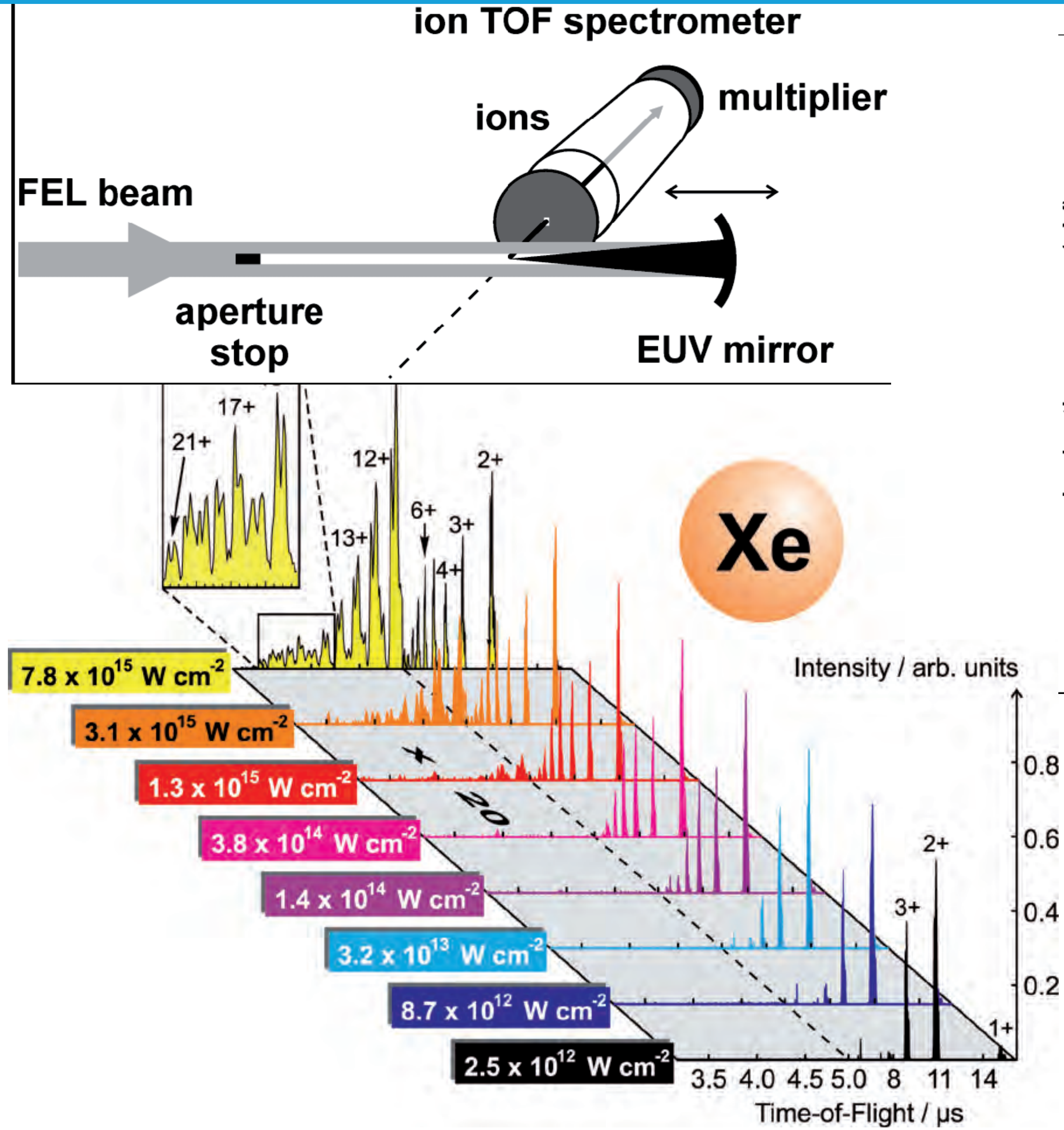
Rh K-edge absorption spectra

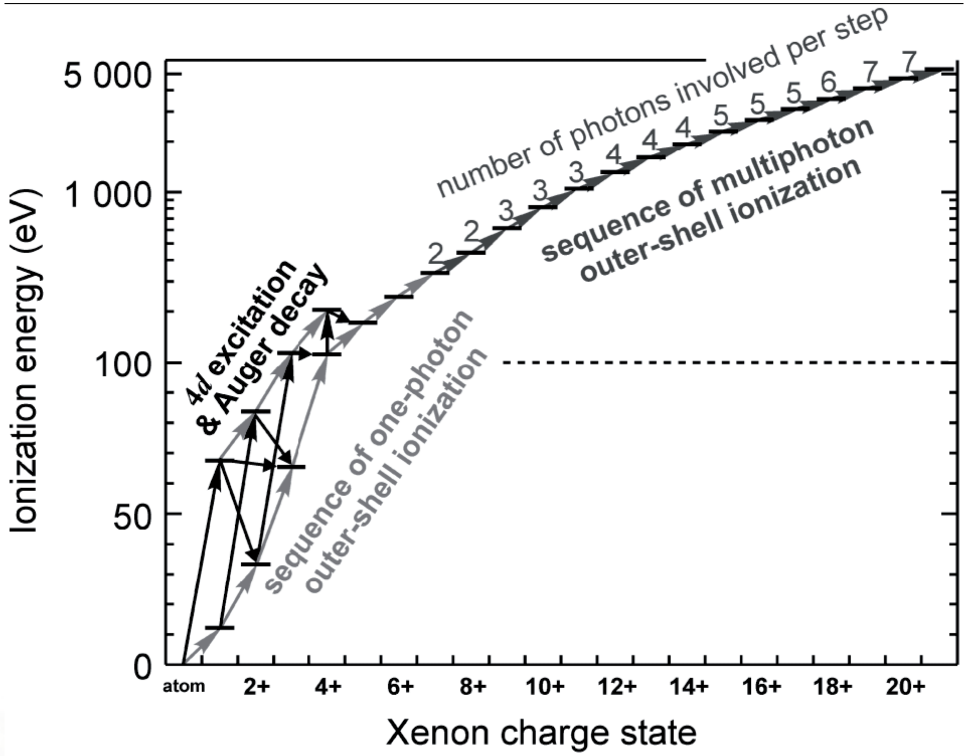


- *spatial distribution of Rh oxidations states*
- *strong gradients within < 100 m*

J.-D. Grunwaldt et al., **J. Phys. Chem. B 110**, 8674 (2006)

Photoelectric Effect at Ultrahigh Intensities of FLASH (13.5 nm)





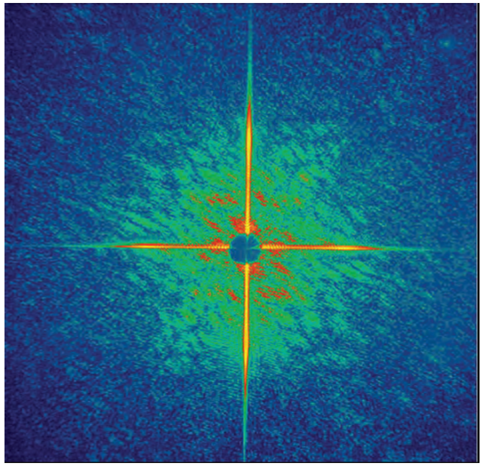
- Dramatic changes in the ion charge state at high power densities
- One atoms has to absorb >50 photons

Phys. Rev. Lett. 99, 213002 (2007)

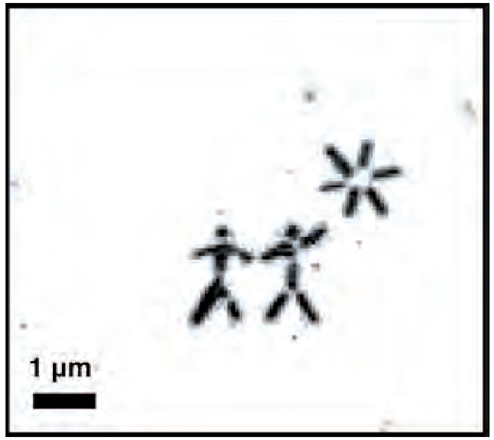
Ultrafast Coherent Diffractive Imaging at FLASH

> Single shot diffractive imaging
  - resolution 50 nm
  - next shot reveals that target is destroyed

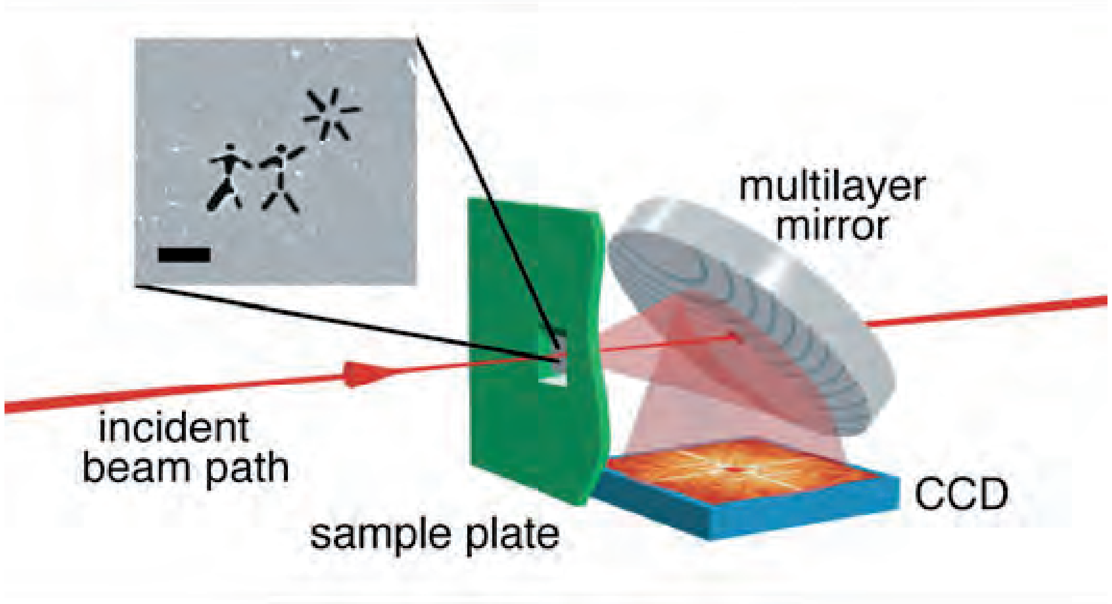
Nature Physics 2, 839 (2006)

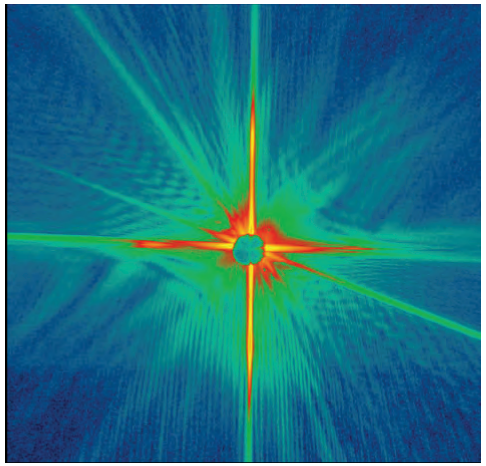


Diffraction image (1st shot)



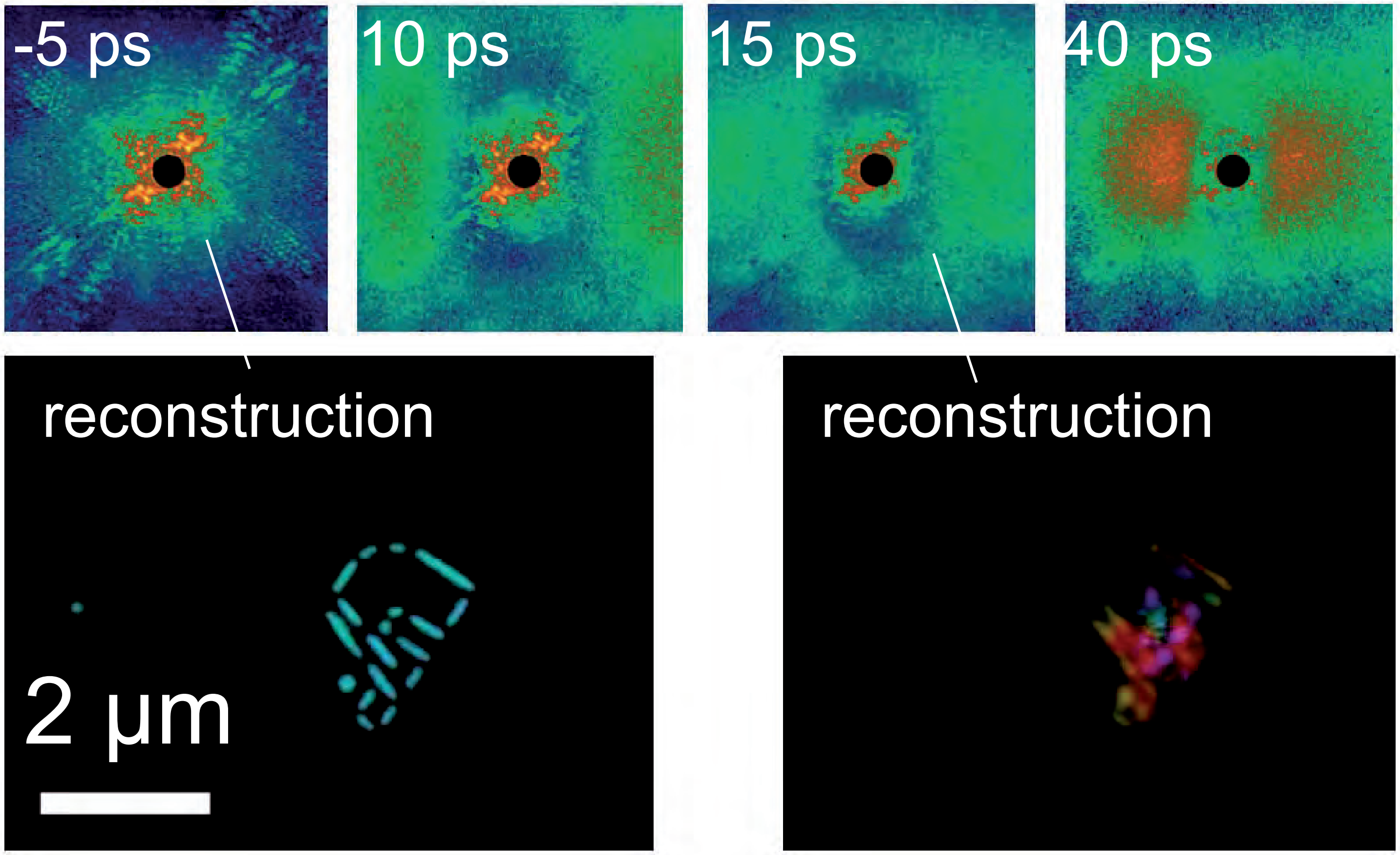
reconstruction (1st shot)





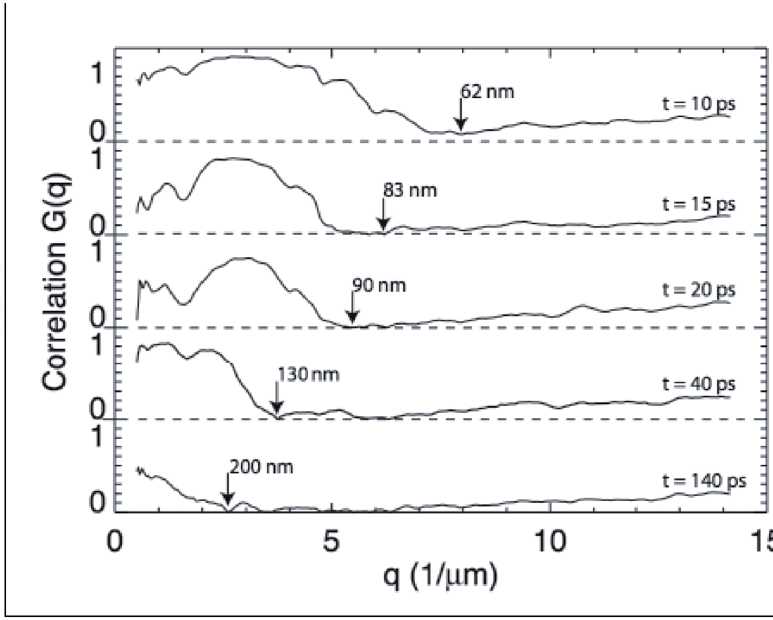
Diffraction image (2nd shot)

Ultrafast Movies of Nanoscale Dynamics



after Nd:YAG pulse

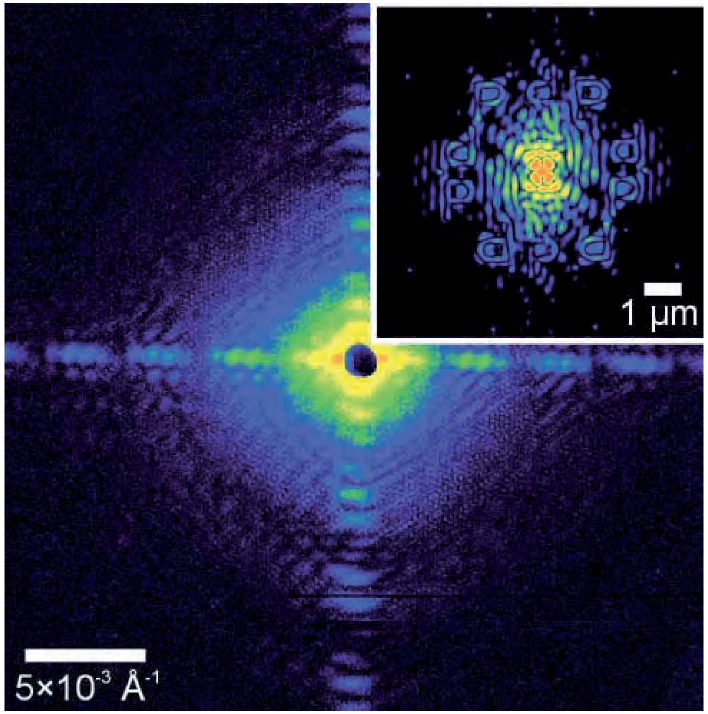
> "scale of destruction":



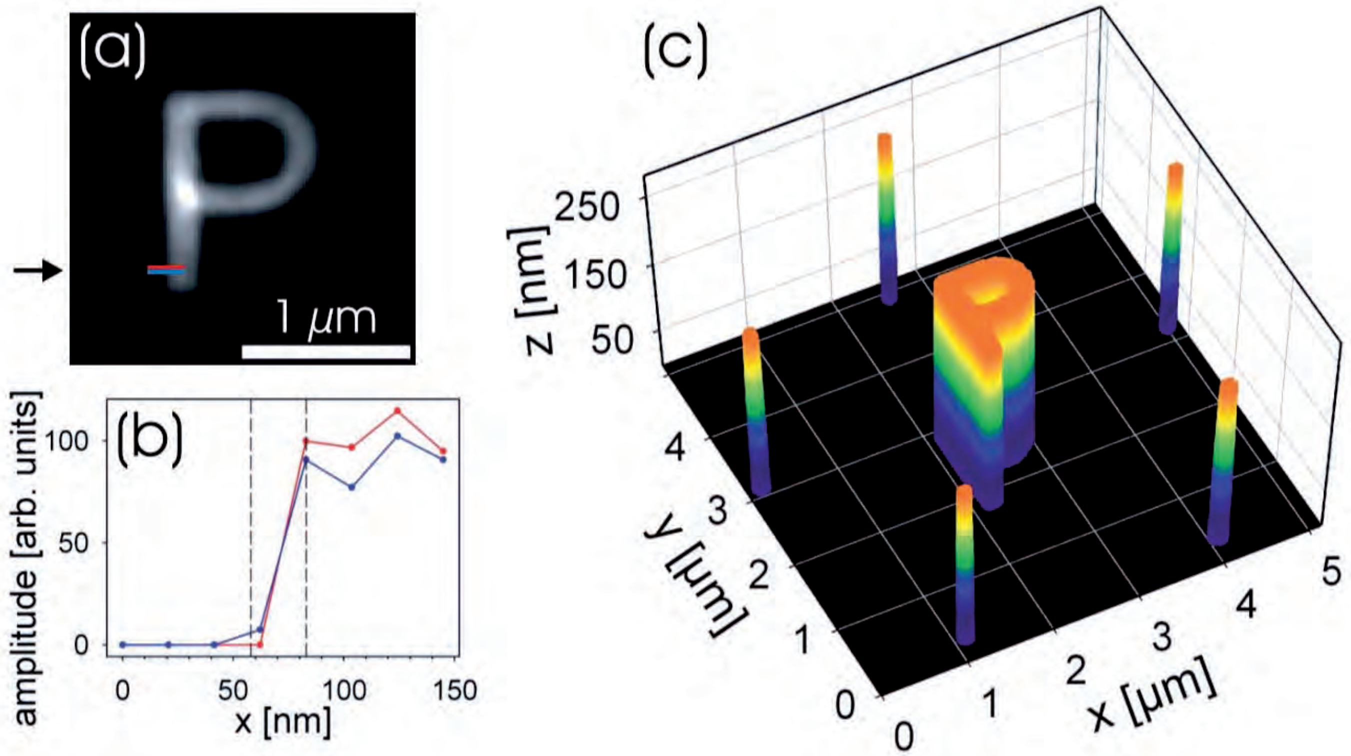
> Pump-probe investigation of damage evolution

Nature Photonics 2, 415–419 (2008)

Hard X-ray Holographic Diffraction Imaging



Diffraction image
(and Fourier transform)



Reconstruction (a), resolution test (b) and original structure (c)

- Testbed for single shot imaging at SR ring
  - only 100 spectra with 10^8 photons each
  - resolution 25 nm

Phys. Rev. Lett. 100, 245503 (2008)