

# Micro-X-ray absorption spectroscopy (XANES, EXAFS)

F. d'Acapito

*CNR-INFM - OGG c/o European Synchrotron Radiation  
Facility - GILDA CRG, B.P.220, F-38043 Grenoble (France)*

*dacapito@esrf.fr*

# Layout

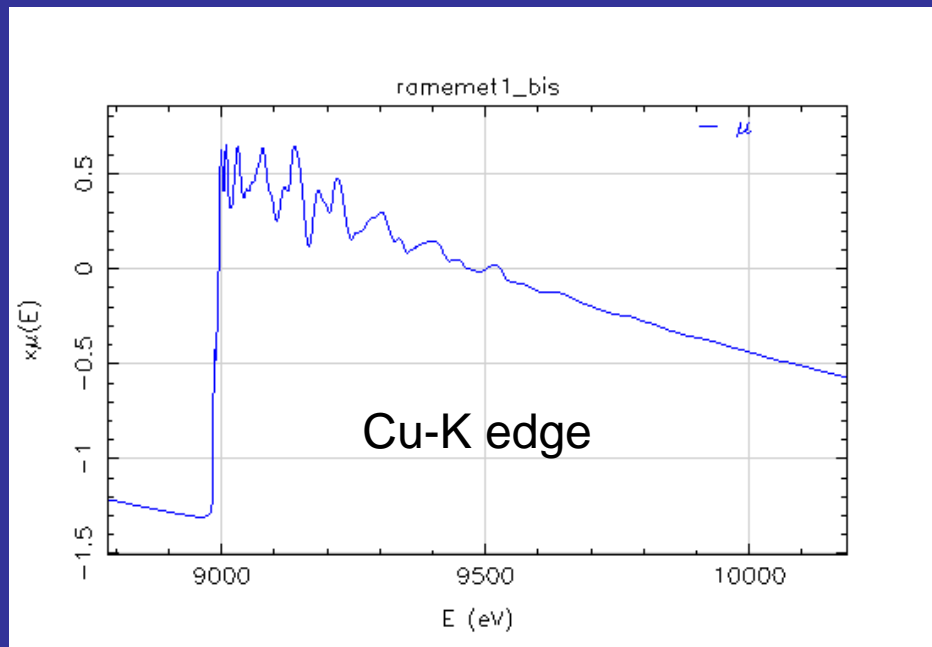
- Introduction to XAS
- Instrumental issues
- Practical examples
- A look in the future

# Introduction to XAS

- Theory
- EXAFS data analysis
- XANES data analysis

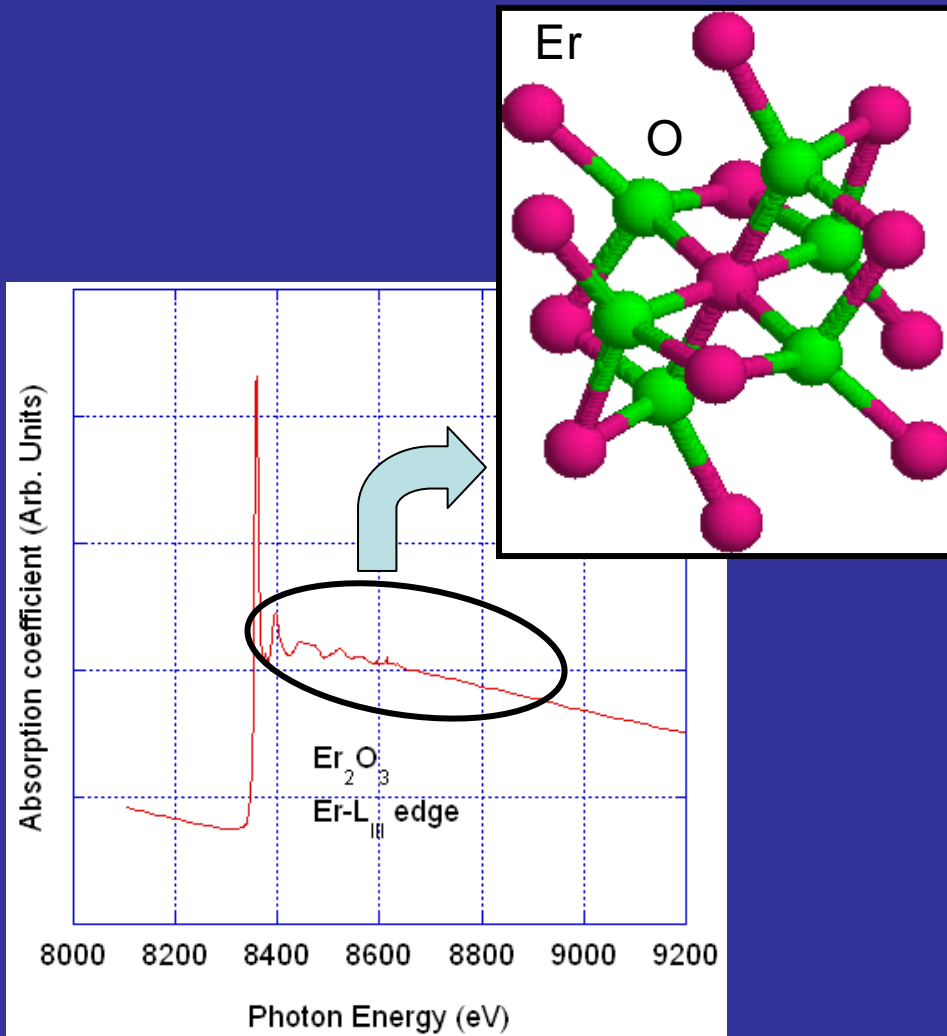
# X-ray Absorption Spectroscopy

- XAS  $\Rightarrow$  information on the electronic and atomic structure around a given element.
- Analysis of structures above an absorption edge.



Raw absorption spectrum

# EXAFS

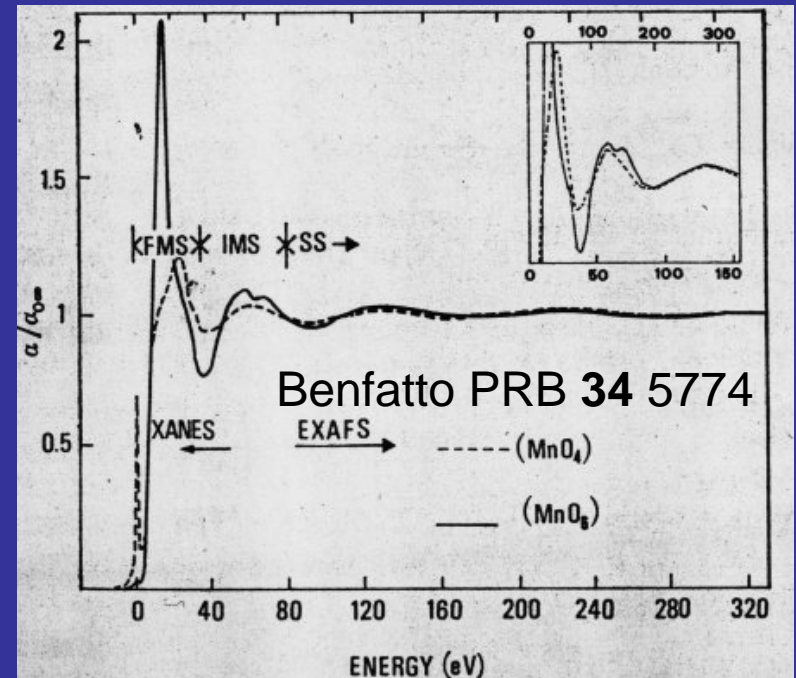


## Extended X-ray Absorption Fine Structure

- Local structural parameters
  - N (number of neighbors),
  - R (distance),
  - $\sigma^2$  Debye-Waller factor (disorder)
- No need for long range order
- Typical accuracy 1% R, 10% N, 20%  $\sigma^2$

# XANES

- Low PhotoElectron (PE) energy ( $< 50$  eV)
- PE wavelength comparable with interatomic distances
- PE mean free path very long



# XAS Theory

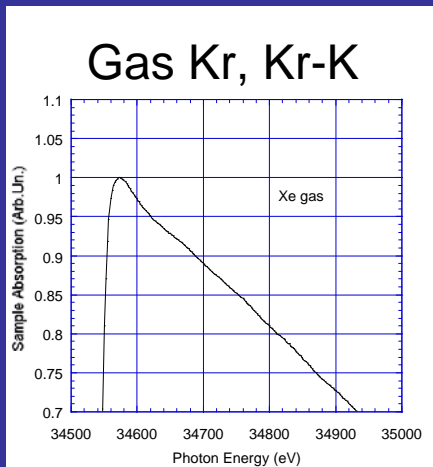
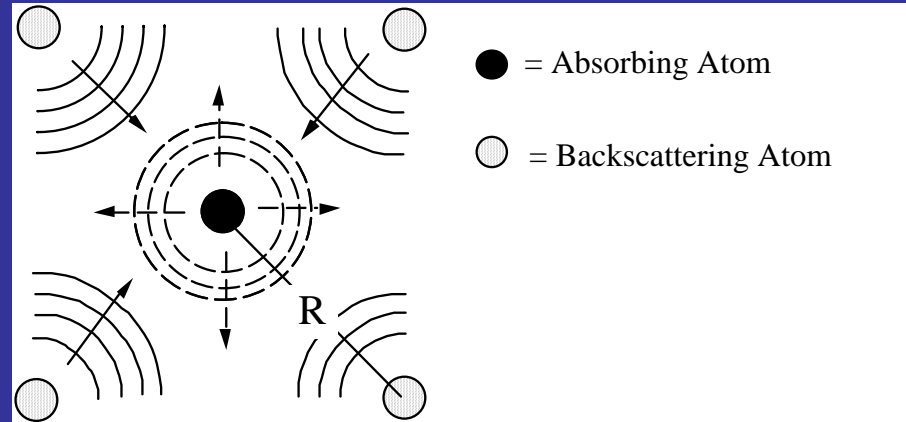
- General formula for the interaction cross section  $\sigma$  X-rays-matter:

$$\sigma = 4\pi^2 E \alpha \sum_f \left| \langle i | \vec{p} \cdot \vec{D} | f \rangle \right|^2 \delta(E - E_f + E_0)$$

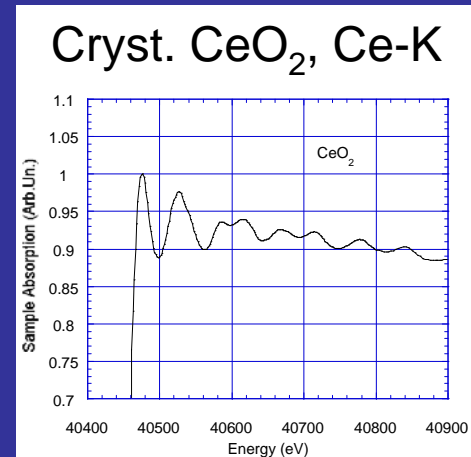
- $\langle i |$  initial state ,  $\langle f |$  final state
- $p$  PE momentum  $D$  dipole operator
- $E$  photon energy,  $E_f$  edge energy

# XAS Theory

$\langle i | =$  core state S, P



$\langle f | =$  outgoing spherical wave



$\langle f | =$  perturbed wave

# XAS Theory

- Some definitions ( $R = \text{\AA}$ ,  $k = \text{\AA}^{-1}$ ,  $E = \text{eV}$ ):

$$k = \sqrt{2m(E - E_0)/\hbar} = 0.51\sqrt{E - E_0}$$

PE wavevector  $k$

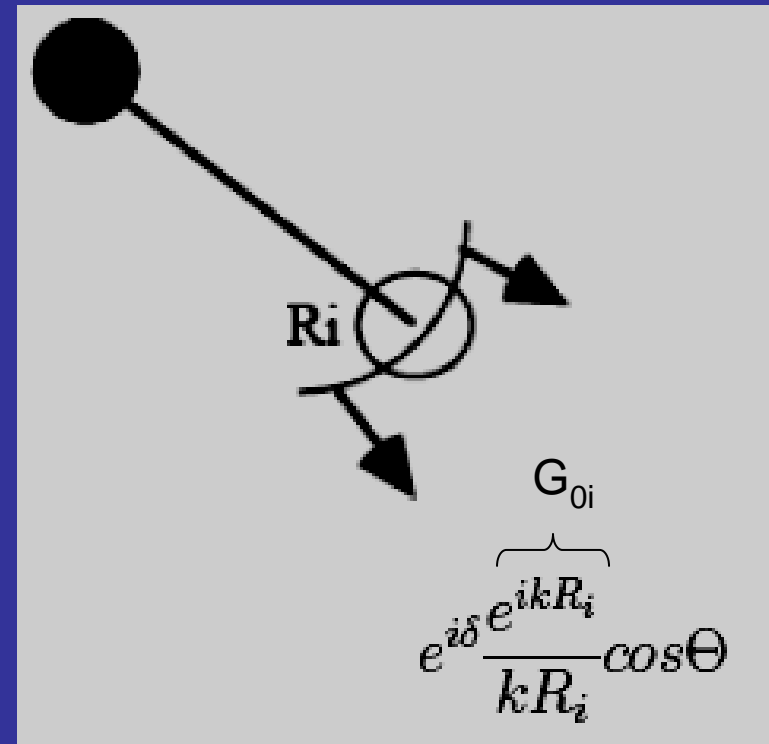
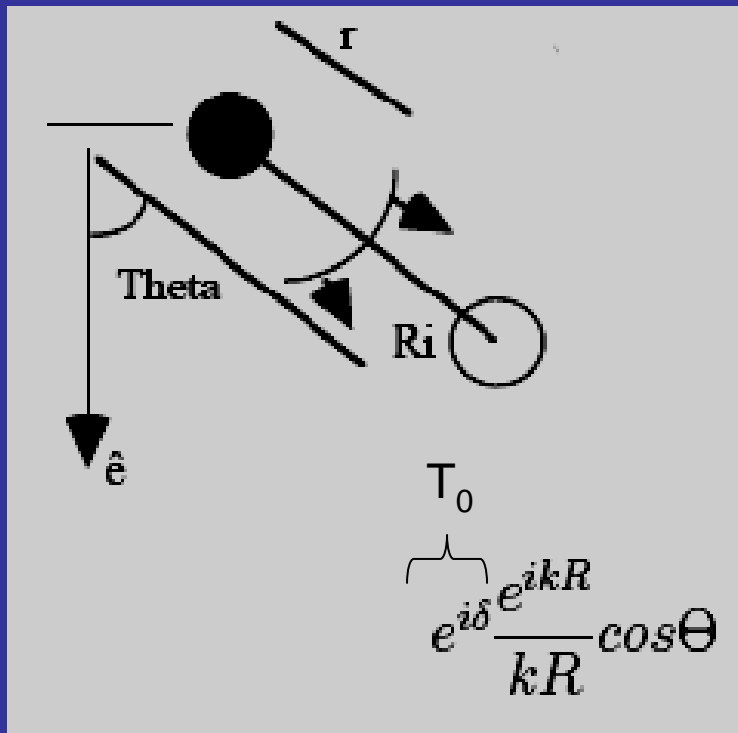
$$\chi \equiv \frac{\sigma - \sigma_0}{\sigma_0}$$

$\chi$  function

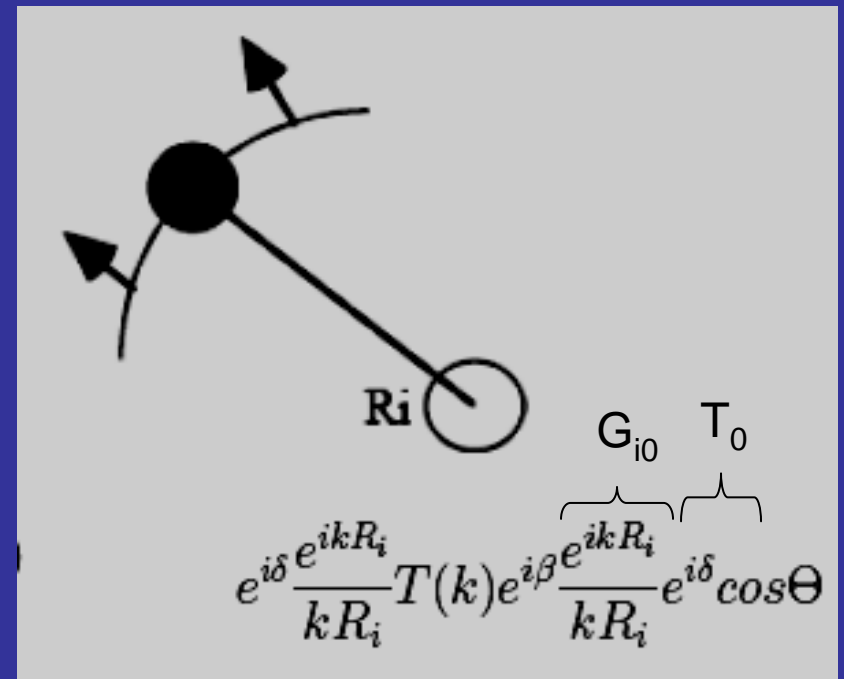
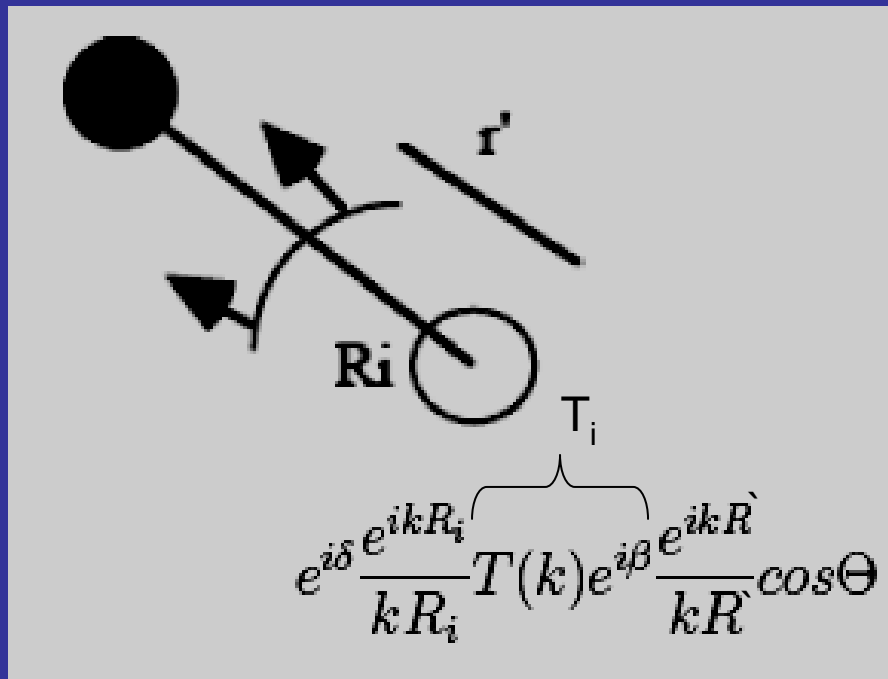
$$\chi(k) = S_0^2 \frac{NA(k)}{kR^2} e^{-\frac{2R}{\lambda}} \sin(2kR + \phi(k) + \phi_c) e^{-2k^2\sigma^2}$$

EXAFS formula for a single coordination shell

# Simple derivation



# Simple derivation

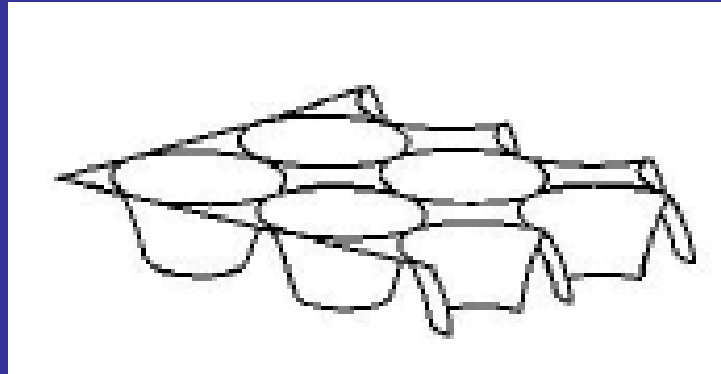


# Scattering potential

T depends on the potential that scatters the photoelectron i.e. on the electron density.

Muffin-tin approximation:

- radial potential around the atomic position ('cause spherical harmonics are solutions)
- uniform potential in the interstitial region
- '*just touching*' spheres



# EXAFS data analysis

$$\chi(k) = S_0^2 \frac{NA(k)}{kR^2} e^{\frac{-2R}{\lambda}} \sin(2kR + \phi(k) + \phi_c) e^{-2k^2\sigma^2}$$

EXAFS formula for a single coordination shell

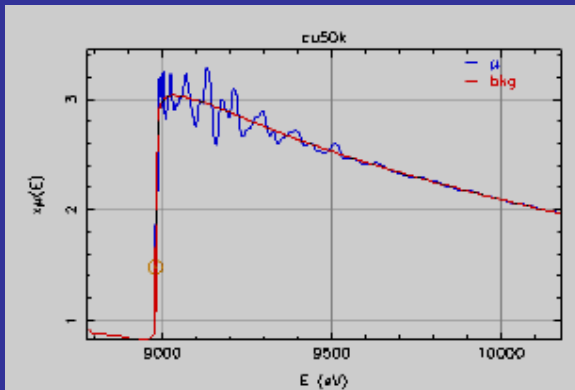
- $S_0^2, A(k), \phi(k), \phi_c(k), \lambda$

Parameters depending on the electron scattering. Can be calculated *ab initio*

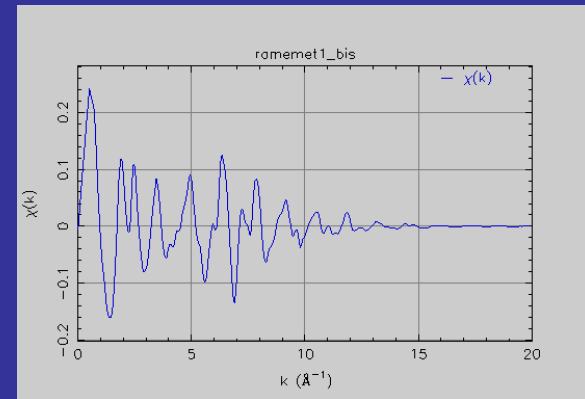
- $N, R, \sigma^2$

Structural parameters, can be derived from a multiparameter fit

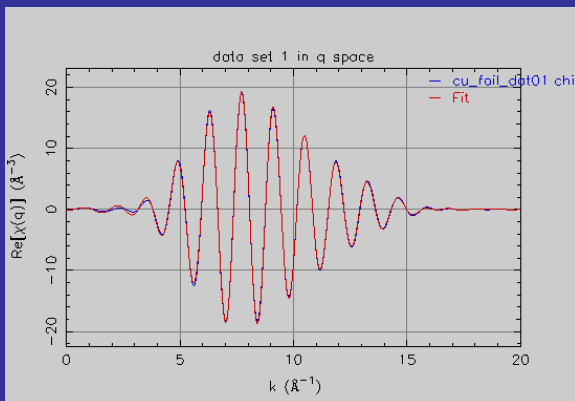
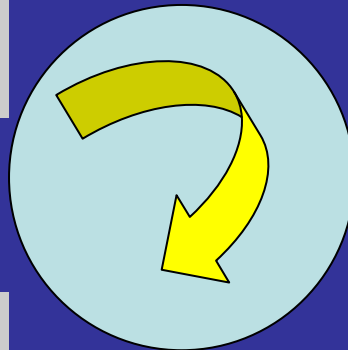
# EXAFS data analysis



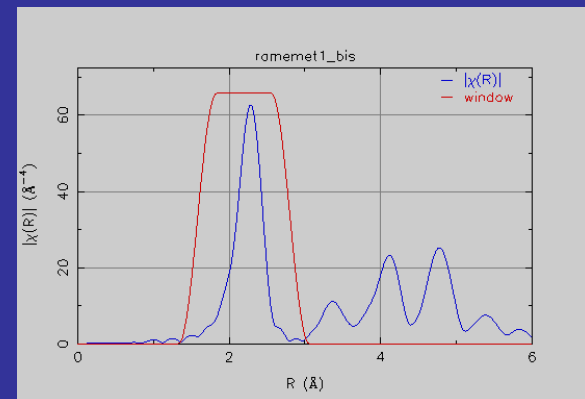
Background subtraction



Oscillatory  $\chi$  function



Back-transform and  
Multiparameter fit



Fourier Transform

F. d'Acapito CNR-INFM-OGG

# Quantitative XANES data analysis

Natoli, C. R. & Benfatto, M. (1986). *J. Phys. Paris Colloq.* **47**, 11-23.

- Fit of the experimental data to the total cross section formula:

$$\sigma = \sigma_0 \left[ \frac{1}{(2L_0 + 1) \sin^2 \delta_l^0} \sum_m \Im \left[ (I - TG)^{-1} T \right]_{lm,lm}^{0,0} \right]$$

T = Matrix containing scattering details

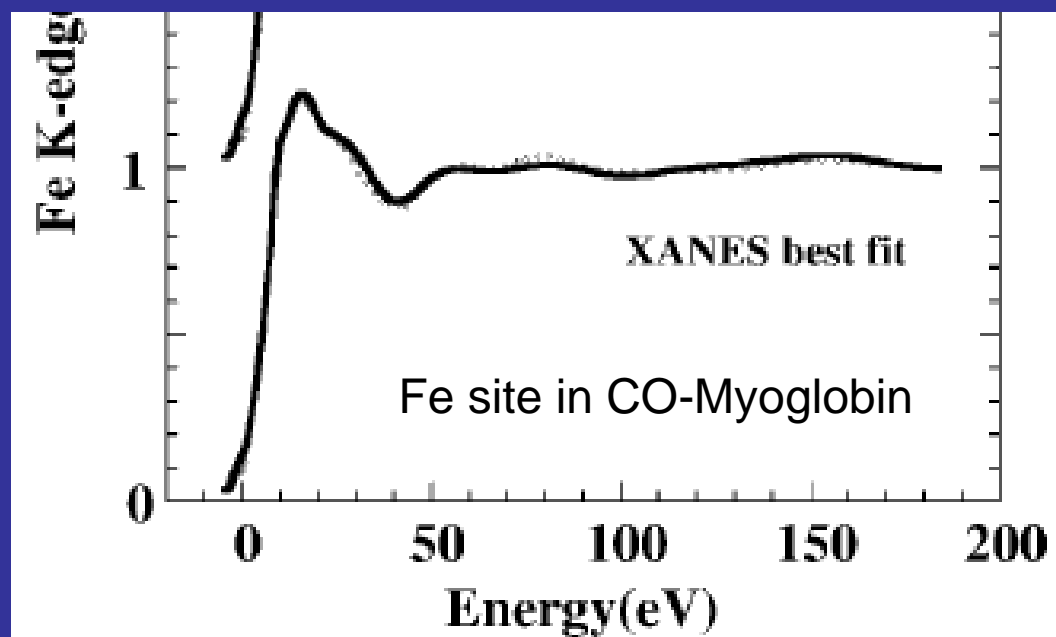
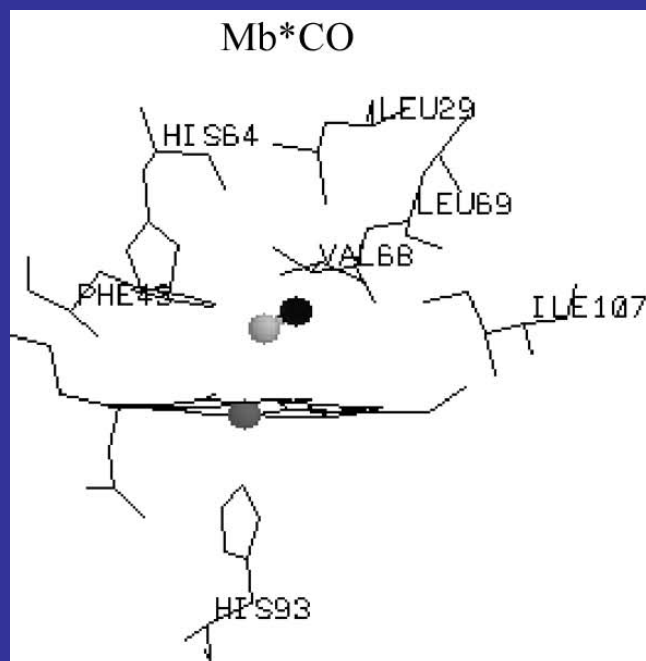
G = Matrix containing geometrical details

The method is extremely demanding in computing resources.

# Quantitative XANES data analysis

M. Benfatto,<sup>a\*</sup> S. Della Longa<sup>b</sup> and C. R. Natoli<sup>a</sup>

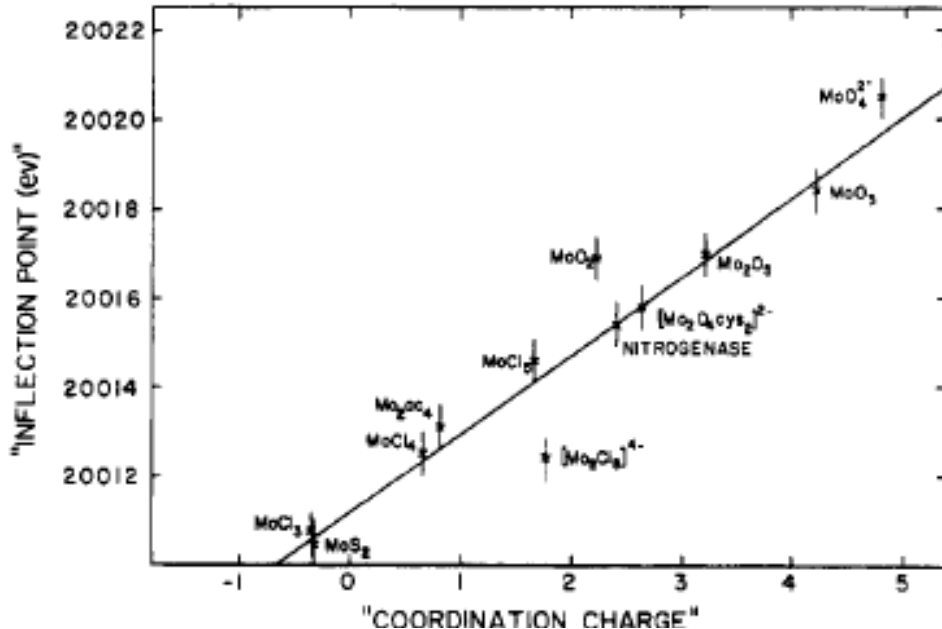
*J. Synchrotron Rad.* (2003), **10**, 51–57



Experiment	Fe–Np	Fe – Nhis	Fe – C	$\alpha$	$\beta$	C–O
XANES	2.03 (2)	2.05 (2)	3.08 (7)	37 (7)	31 (5)	1.24

# Qualitative XANES data analysis

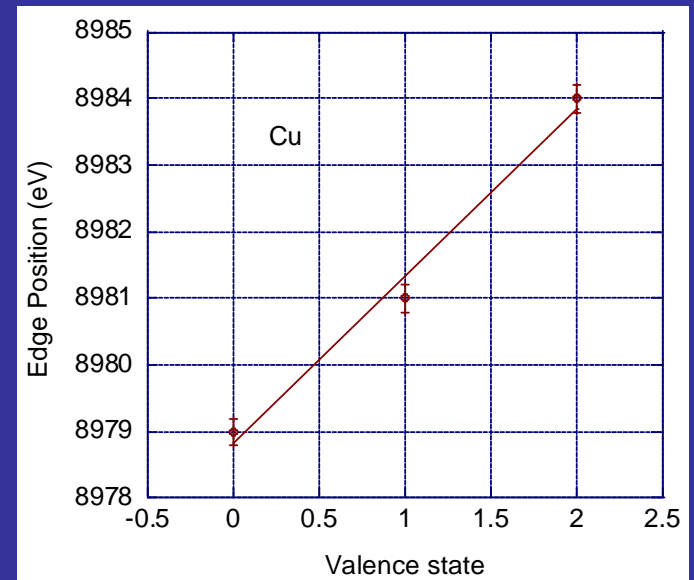
The valence state of a chemical specie can be derived from the position of the first inflection point of  $\mu(E)$ .



S. P. Cramer, T. K. Eccles, F. W. Kutzler, Keith O. Hodgson

L. E. Mortenson

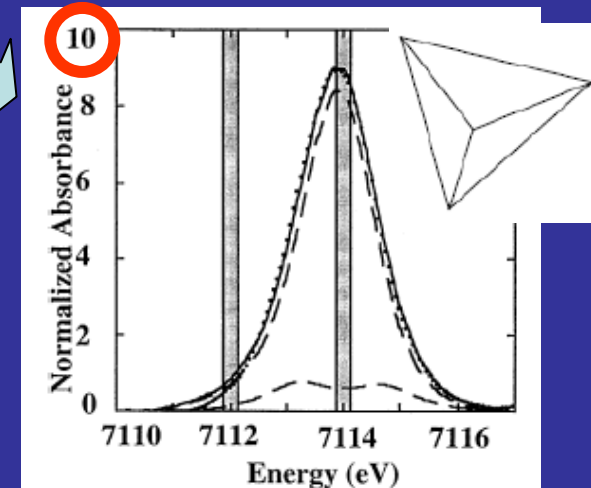
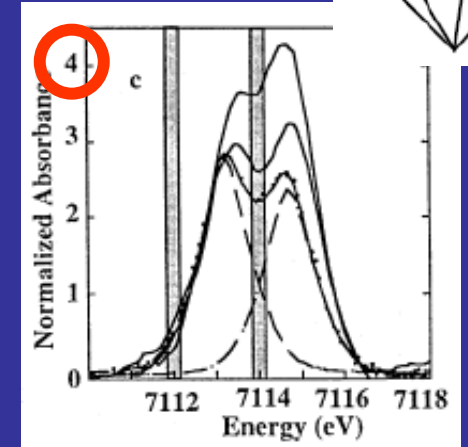
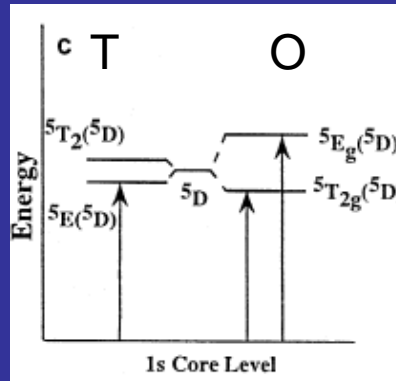
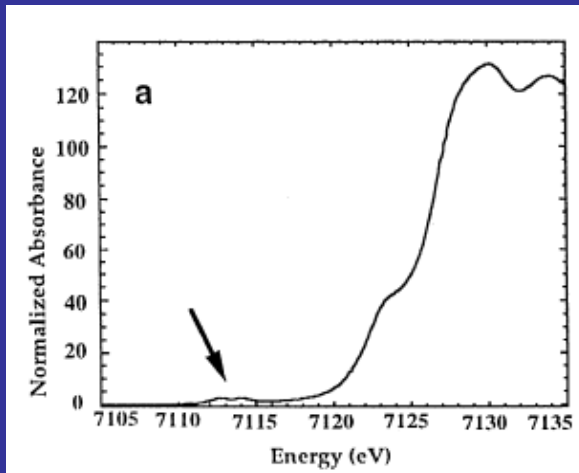
*Journal of the American Chemical Society* / 98:5 / March 3, 1976



# Qualitative XANES data analysis

L. Galoisy \*, G. Calas, M.A. Arrio *Chemical Geology* 174 (2001) 307–319

- Octahedral vs Tetrahedral site

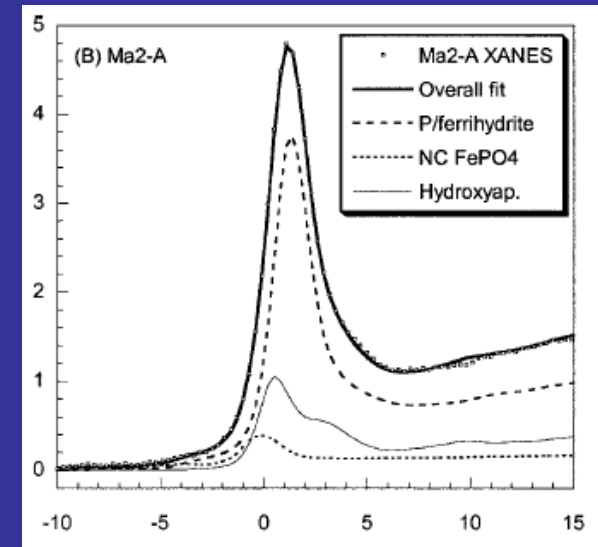
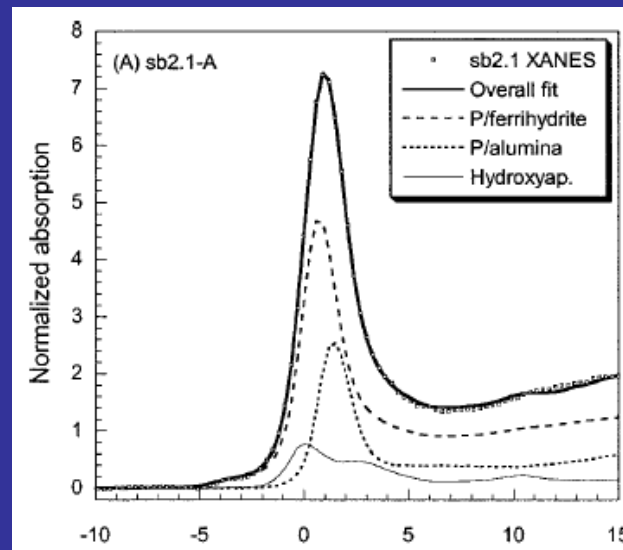


Analysis of the small features before the edge (1s-3d in  $Fe^{3+}$  comp.)

# Qualitative XANES data analysis

Suzanne Beauchemin,\* Dean Hesterberg, Jeff Chou, Mario Beauchemin, Régis R. Simard, and Dale E. Sayers  
 J. Environ. Qual. 32:1809-1819 (2003).

- Phosphorous environment in soils
- Linear combination of model spectra.



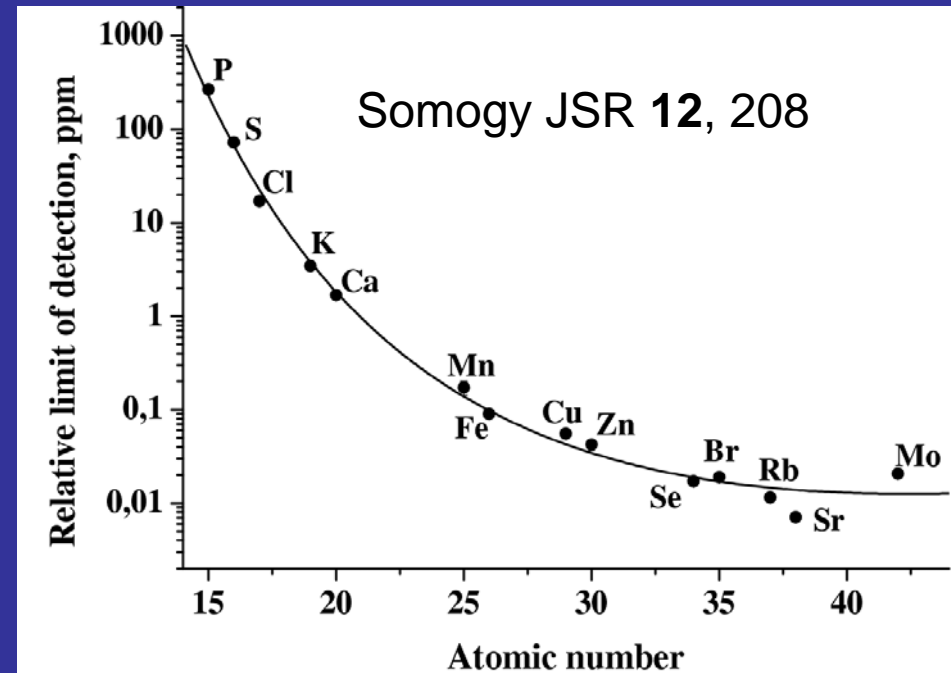
Sample	Goodness of fit ( $\chi^2$ )	Sum of fractions before normalization	PO <sub>4</sub> on ferrhydrite	PO <sub>4</sub> on goethite	PO <sub>4</sub> on Al hydroxide	PO <sub>4</sub> on alumina	Noncrystalline FePO <sub>4</sub>	Hydroxyapatite
sb2.1-A	0.15	1.32	54 ± 2			34 ± 3		12 ± 1
Ma2-A	0.06	0.95	60 ± 1				22 ± 2	18 ± 1

# Instrumental issues

- Data collection modes
- The source
- Focusing devices

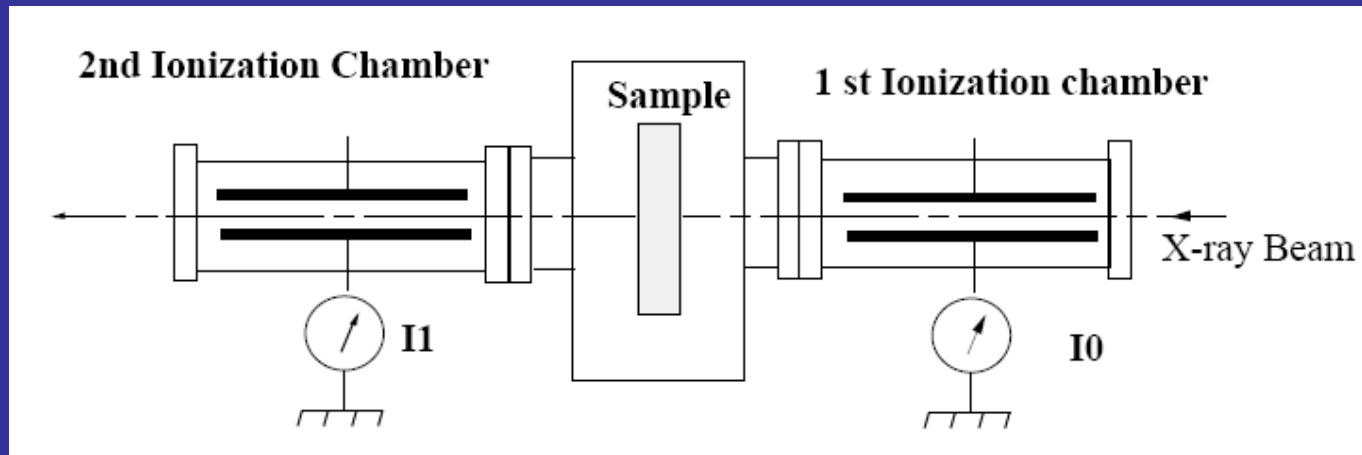
# Peculiarities of $\mu$ -XAS

- Element sensitive
- Chemical sensitive
- Penetrating ( $\mu\text{m}$ )
- Non destructive
  
- Moderately small beam ( $\mu\text{m}$ , UP TO NOW)



# Data collection modes

The simplest one: transmission mode



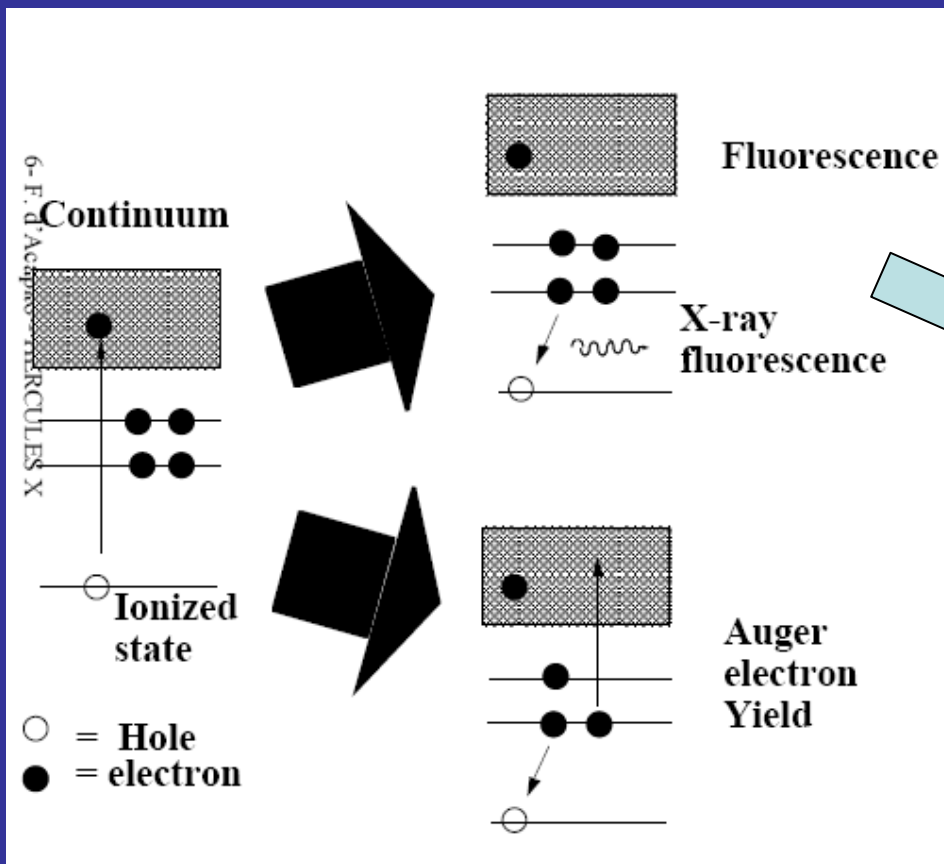
$$\mu = -\ln (I1/I0)$$

Applicable only if:

- the absorber contributes significantly to the total  $\mu$
- Sample has a suitable thickness

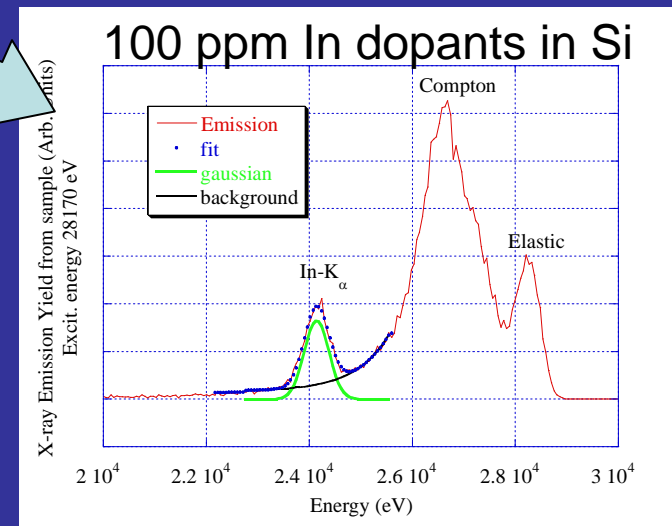
# Data collection modes

- Fluorescence mode



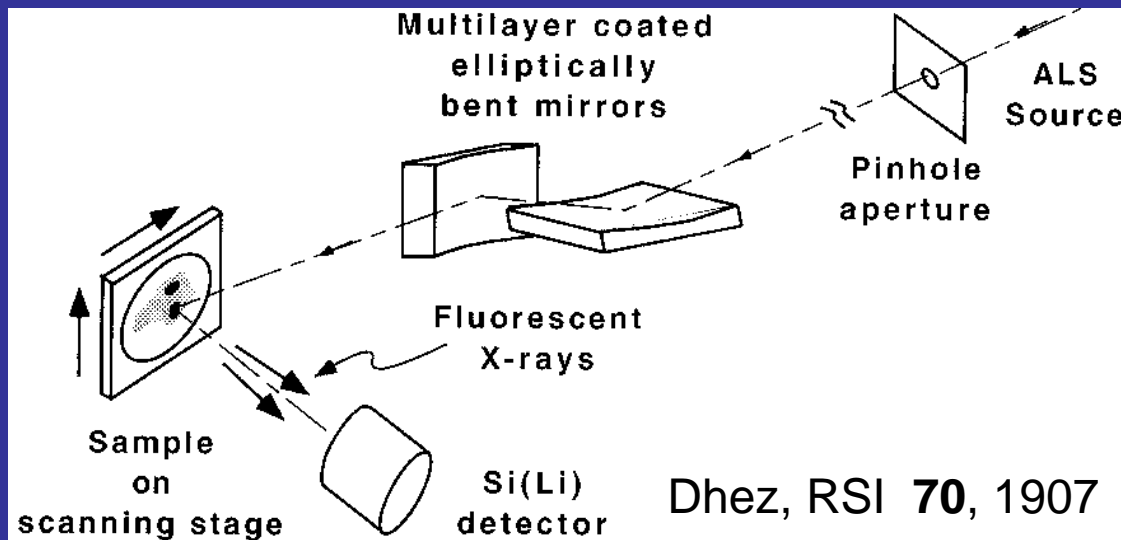
Suitable for

- Diluted samples
- Thick samples



# Micro analyses

- Micrometric sized beam (current  $5\mu\text{m} - 90\text{ nm}$ )
- Scan of the sample
- Fluorescence analysis with a ED detector



## Key issues

- Source brilliance
- Efficient focusing devices

# 3<sup>rd</sup> generation sources

- Optimized for the emission of synchrotron radiation:
  - High energy  $\Rightarrow$  vertical emittance  $\cong 1/\gamma$
  - Optimized for minimum e-beam size/dvg
  - Use of insertion devices, notably **UNDULATORS**

$$\gamma = \text{electron energy}/m_e c^2$$

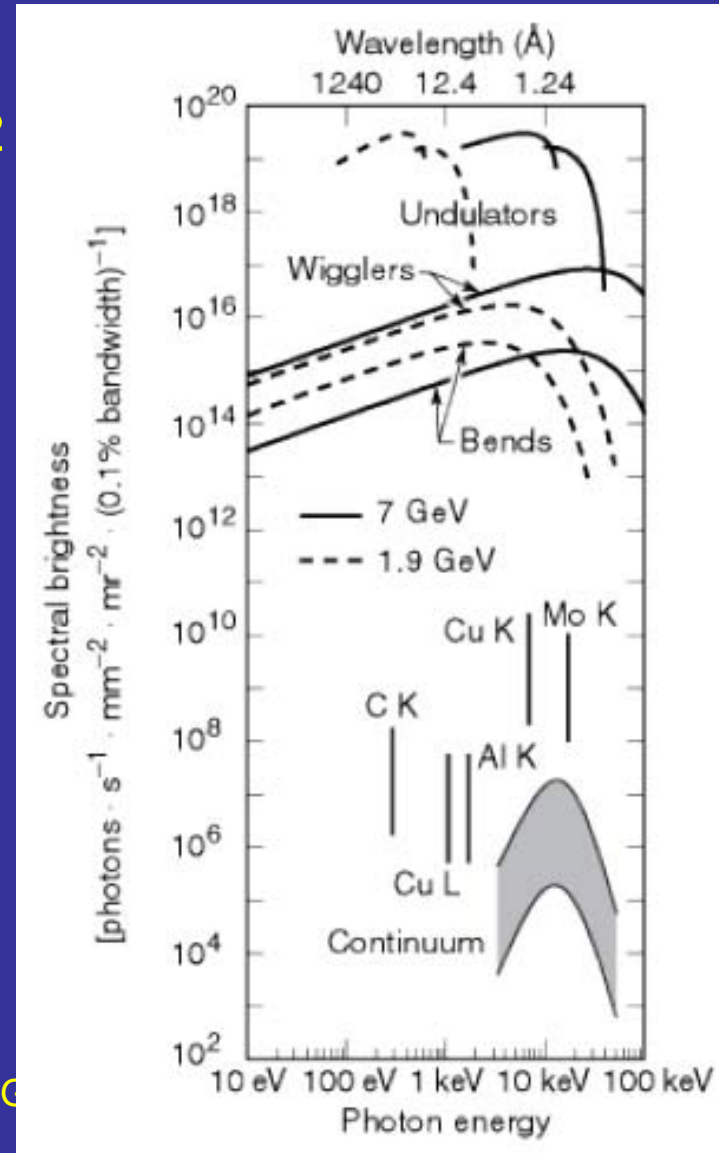
# The Brilliance of the source

Ph/s/ 0.1% BW /mm<sup>2</sup> /mrad<sup>2</sup>

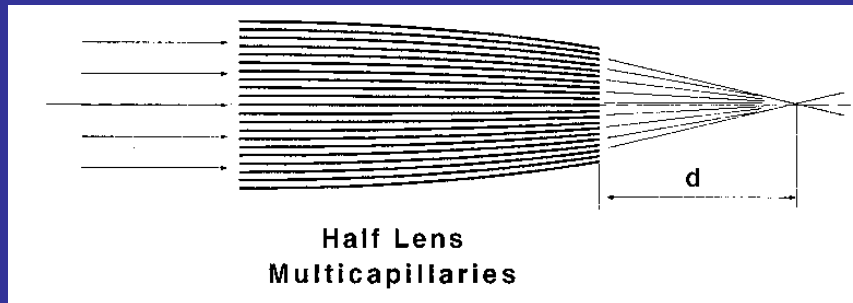
Photon flux in a useful BandWidth (usually 0.1 – 0.001 %)

Source size: the smaller it is, the easier is to de-magnify it in a small image

Source divergence  $h \cdot v$ .  
The smaller it is the smaller will be the beam on the focusing devices.

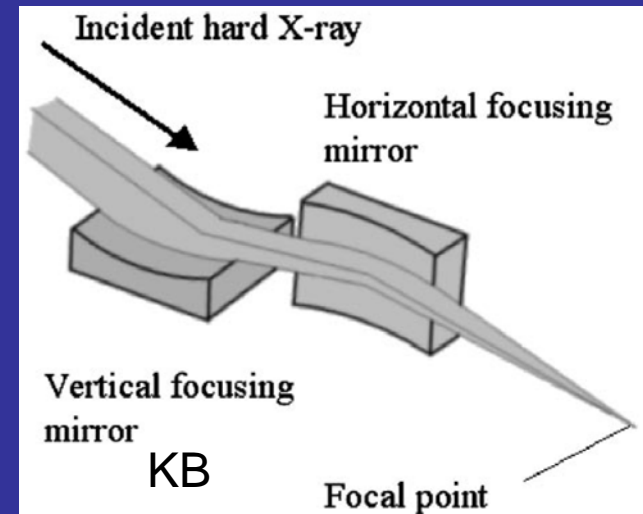
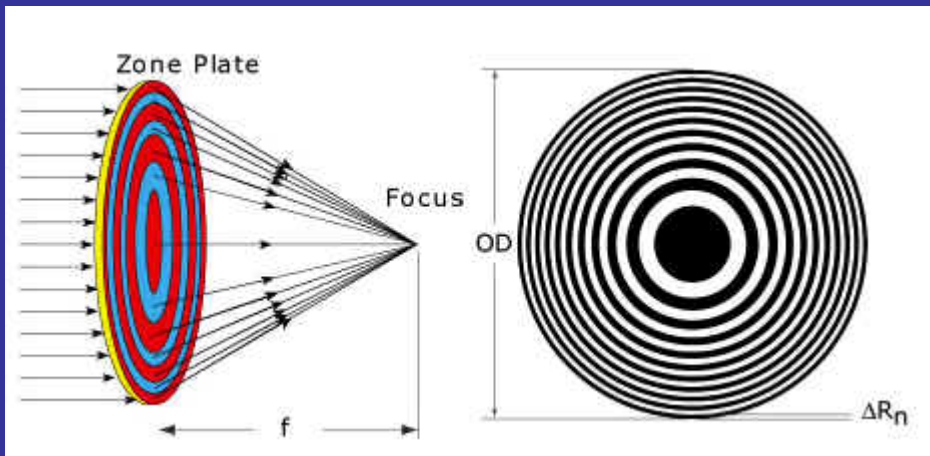


# Focusing devices



## Ideal requests

- High demagnification
- Achromaticity
- Sufficient focal length



# A noticeable example

REVIEW OF SCIENTIFIC INSTRUMENTS 76, 063709 (2005)

## Efficient sub 100 nm focusing of hard x rays

O. Hignette, P. Cloetens, G. Rostaing, P. Bernard, and C. Morawe  
*European Synchrotron Radiation Facility (ESRF), BP220 38240, Grenoble, France*

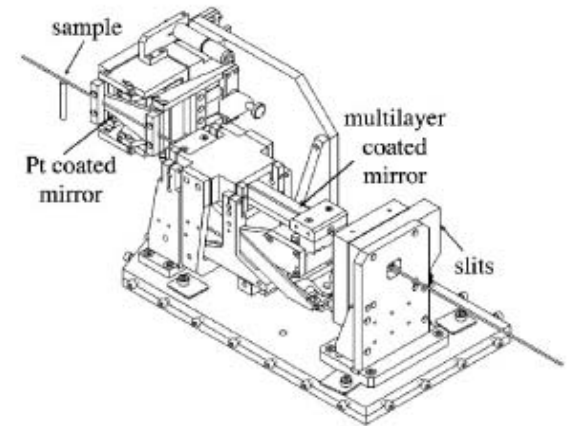
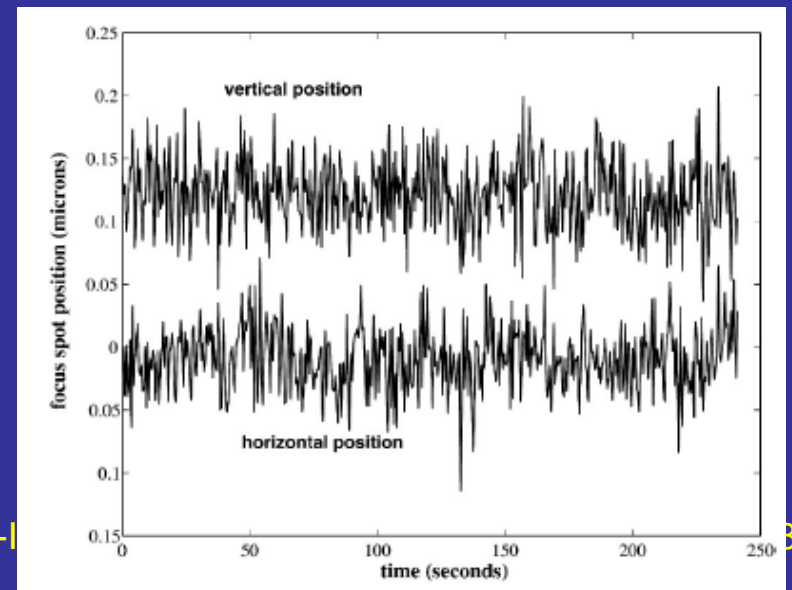
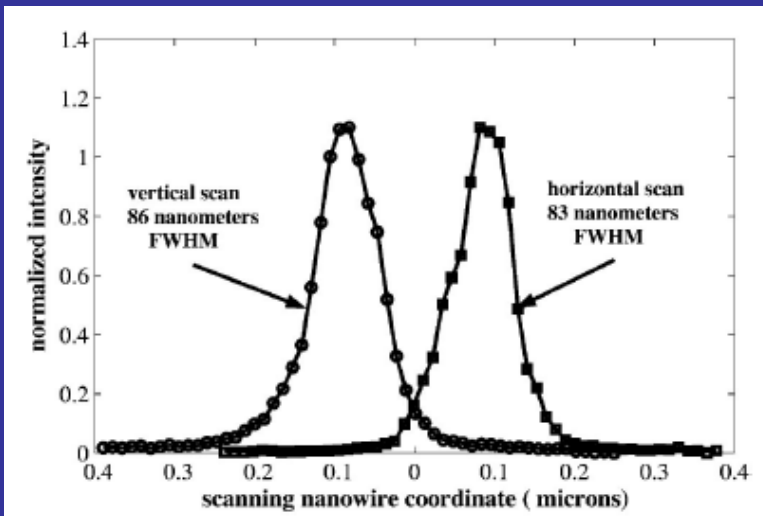
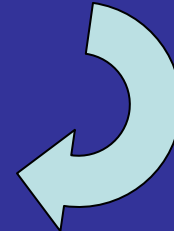


FIG. 1. Kirkpatrick-Baez nanofocusing device design.



# Practical examples

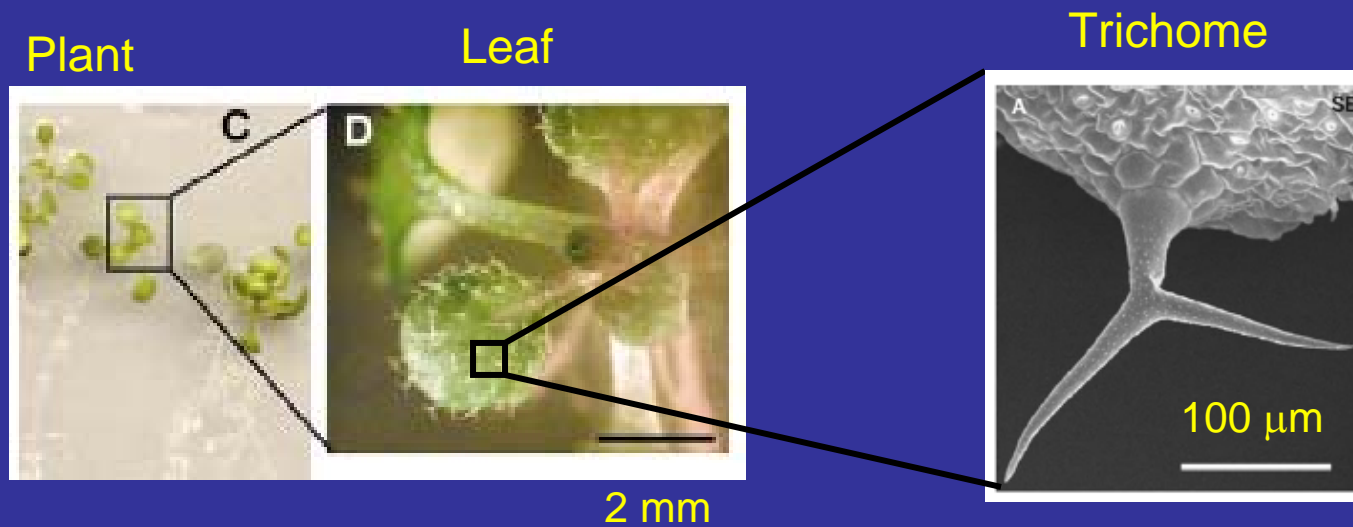
- Cd in plants
- Cr in bacteria
- Pigment blackening

Localization and chemical forms of cadmium in plant samples by combining analytical electron microscopy and X-ray spectromicroscopy

Marie-Pierre Isaure <sup>a,b,\*</sup>, Barbara Fayard <sup>c,d</sup>, Géraldine Sarret <sup>b</sup>,  
Sébastien Pairis <sup>e</sup>, Jacques Bourguignon <sup>f</sup>

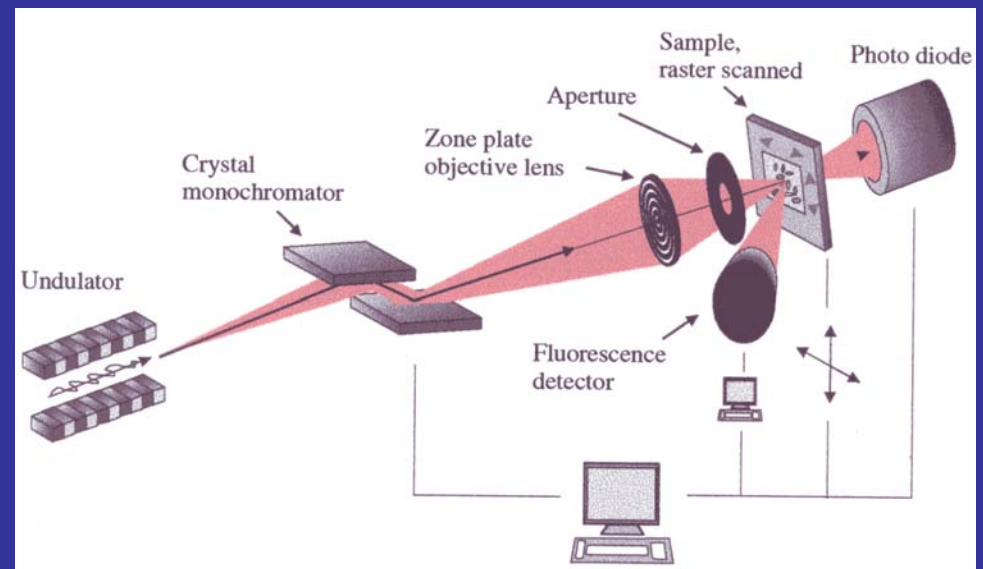
Spectrochimica Acta Part B 61 (2006) 1242–1252

Problem: locate and speciate Cd in *Arabidopsis thaliana* plant samples

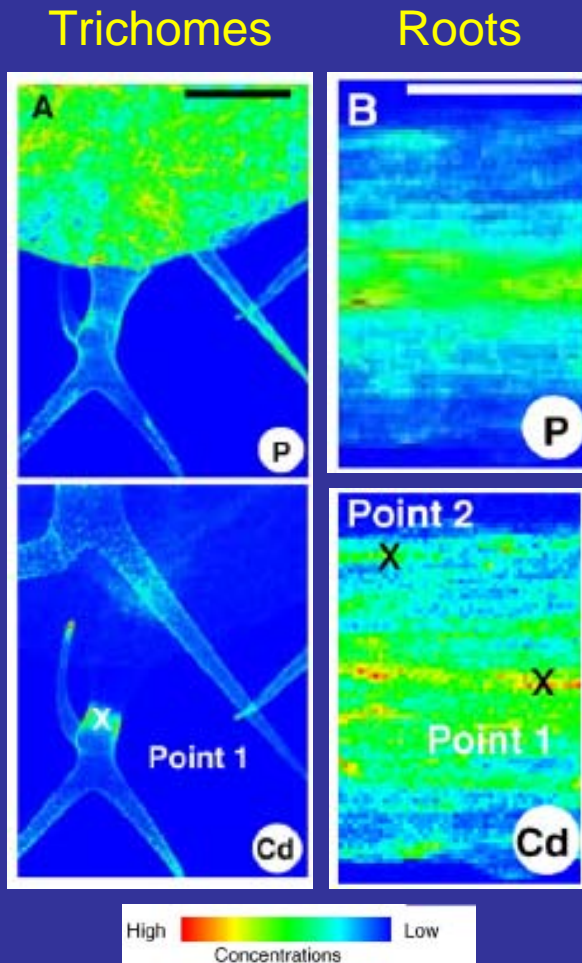


# Experimental

- ID21, ESRF
- Cd-L<sub>III</sub> edge
- Beam size: 0.9\*0.3  $\mu\text{m}$
- Analyses on leaf trichomes and roots



# $\mu$ -XRF



$\mu$ -XRF collected at the Cd-L $\alpha$  line

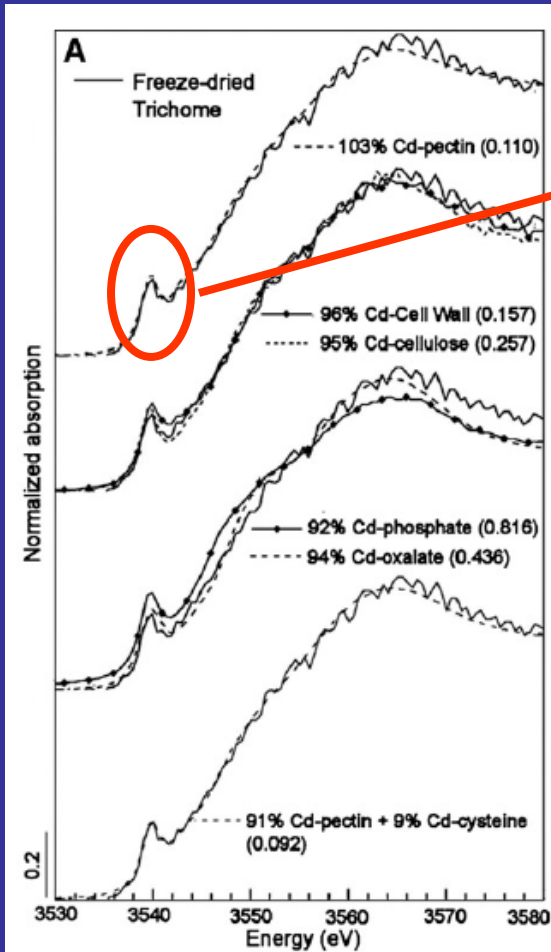
Pixel size = 1  $\mu$ m

Dwell time = 100-500 ms/ point

Cd is concentrated on Trichomes and in the inner part of the roots

# $\mu$ -XAS

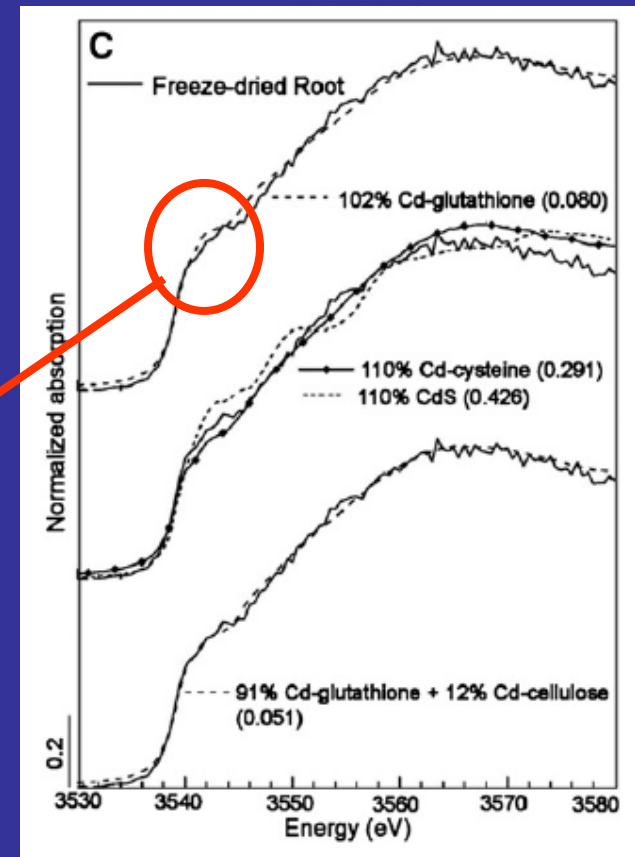
## Trichomes



Peak in the edge:  
Typical of O- or N- coordinated Cd

Shoulder in the edge:  
Typical of S- coordinated Cd

## Roots



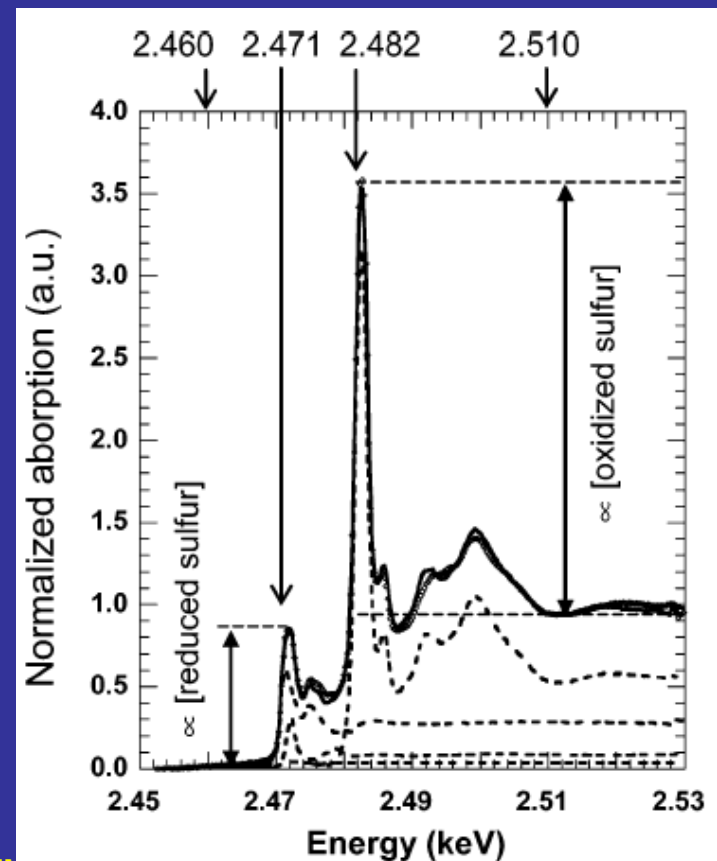
# Conclusion

- X-ray spectro-microscopy used to characterize Cd uptake by *Arabidopsis thaliana* plant specimens
- Cd concentrated in roots and trichomes
- Different coordination for Cd in the two cases (S or O/N coordinated).

# Blackening of Pompeian Cinnabar Paintings: X-ray Microspectroscopy Analysis

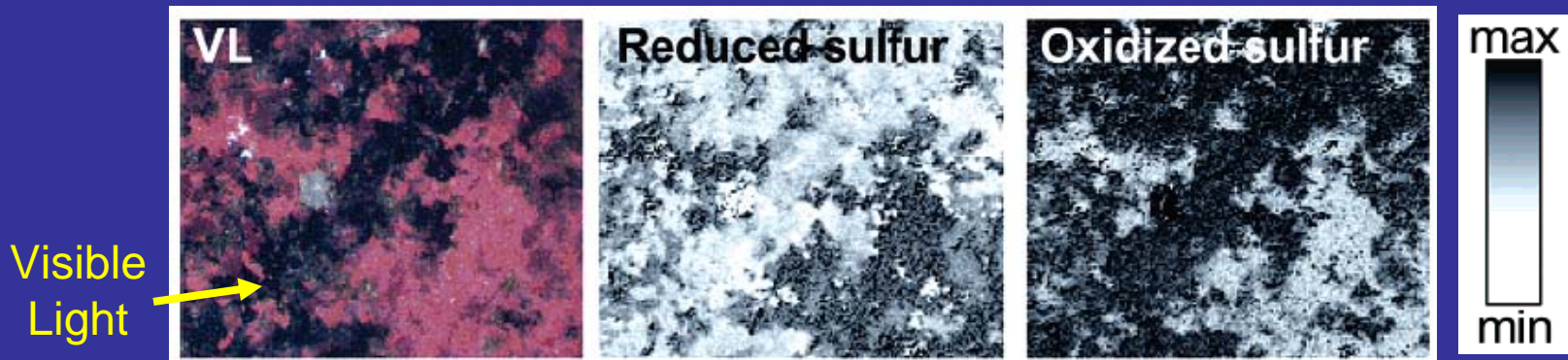
Marine Cotte,<sup>\*,†</sup> Jean Susini,<sup>†</sup> Nicole Metrich,<sup>‡</sup> Alessandra Moscato,<sup>§</sup> Corrado Gratziu,<sup>§</sup> Antonella Bertagnini,<sup>||</sup> and Mario Pagano<sup>⊥</sup>

- Blackening of HgS-based pigments of roman production (Pompeii)
- ESRF, ID 21 beamline
- Sulphur-K edge
- Zone plate focusing
- Micrometric beam



# Blackening of roman pigments

- Valence-state imaging



- Blackening not due to the hex-cub transformation of HgS
  - Related to a S oxidation
- Proposed mechanism Calcite sulfation (formation of  $\text{CaSO}_4$ )

# Elemental and Redox Analysis of Single Bacterial Cells by X-ray Microbeam Analysis

Kenneth M. Kemner,<sup>1\*</sup> Shelly D. Kelly,<sup>1</sup> Barry Lai,<sup>1</sup> Joerg Maser,<sup>1</sup> Edward J. O'Loughlin,<sup>1</sup> Deirdre Sholto-Douglas,<sup>1</sup> Zhonghou Cai,<sup>1</sup> Mark A. Schneegurt,<sup>2</sup> Charles F. Kulpa Jr.,<sup>3</sup> Kenneth H. Nealson<sup>4</sup>

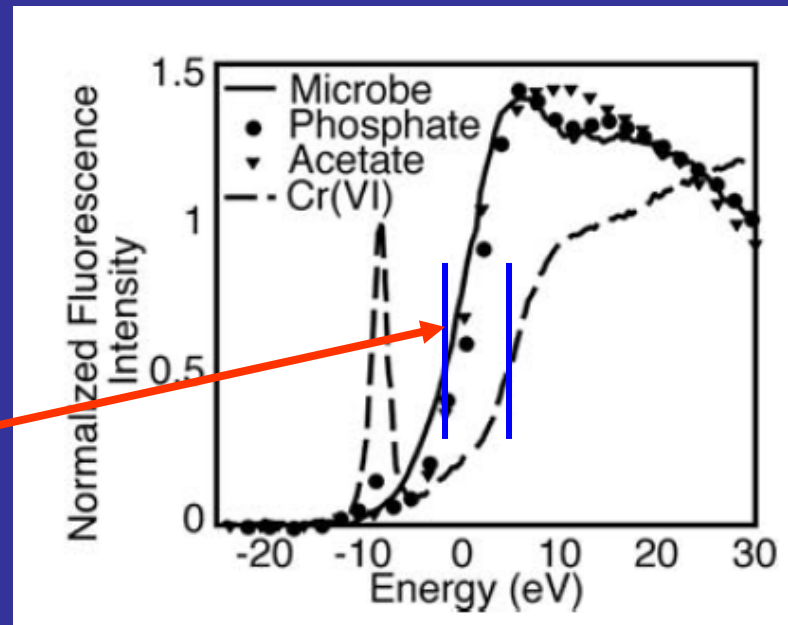
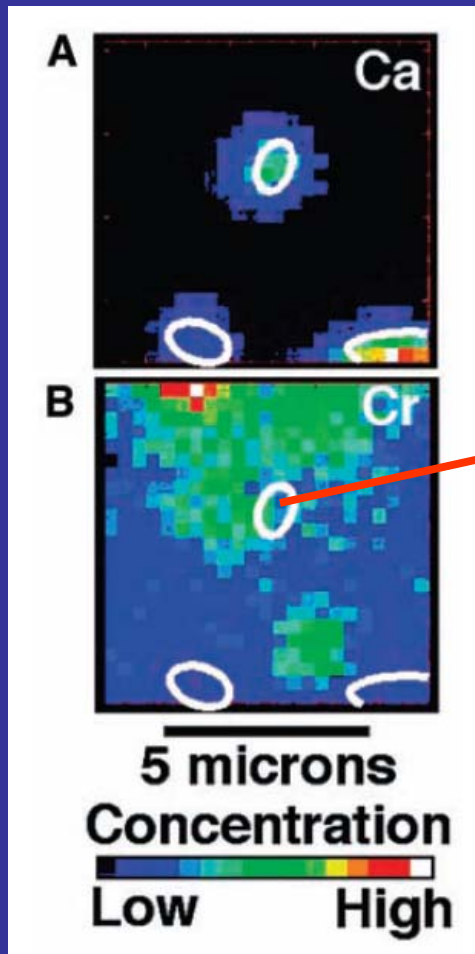
686

22 OCTOBER 2004 VOL 306 SCIENCE

Problem: locate and speciate Cr in *Pseudomonas Fluorescens* bacteria

- Cells deposited on a substrate
- exposed to a solution containing 1000 ppm of Cr<sup>6+</sup>
- Measurement carried out at APS
- Beam Size 150 nm
- Zone plates as focusing device

# $\mu$ -XAS and XRF

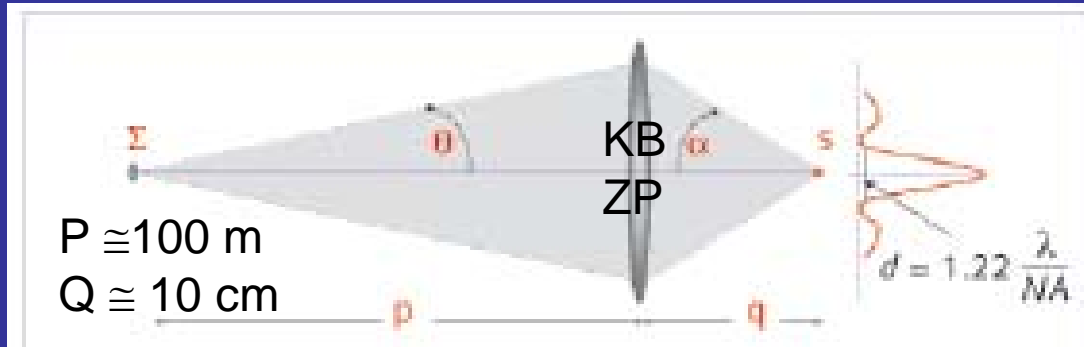


Ca map used to locate bacteria  
Cr found in some bacteria  
Cr present as  $\text{Cr}^{4+}$  in a phosphoryl group

# A look in the future

- Sources
- Foc. Devices
- Exp. Techniques

# Upgrade ESRF



Budget 238 M€ in 10 Y

Main objectives:

- Routinely available 50 nm range focusing

- Develop technology for nano-manipulation & measurement

- Simple optics

- Long beamlines

- Drift and vibration control



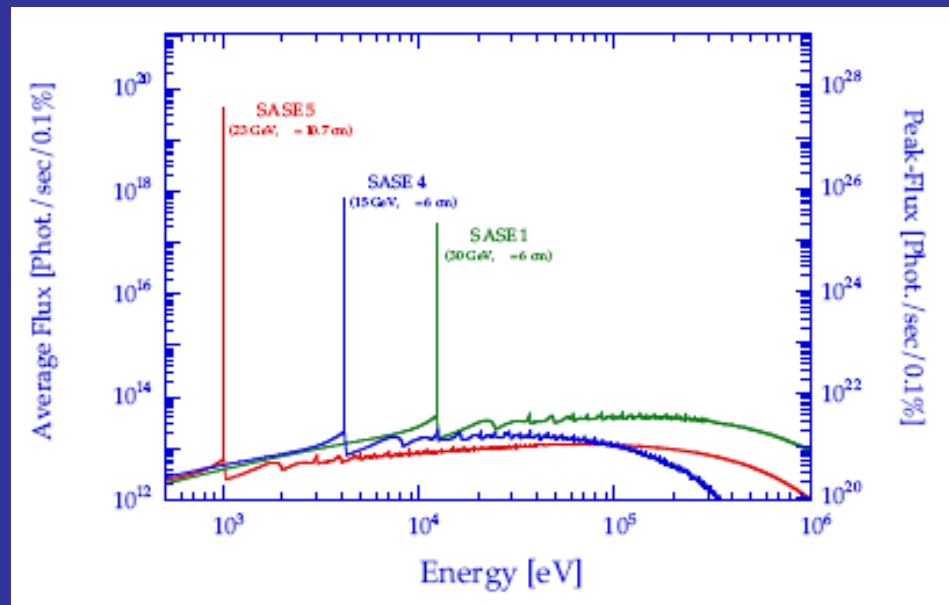
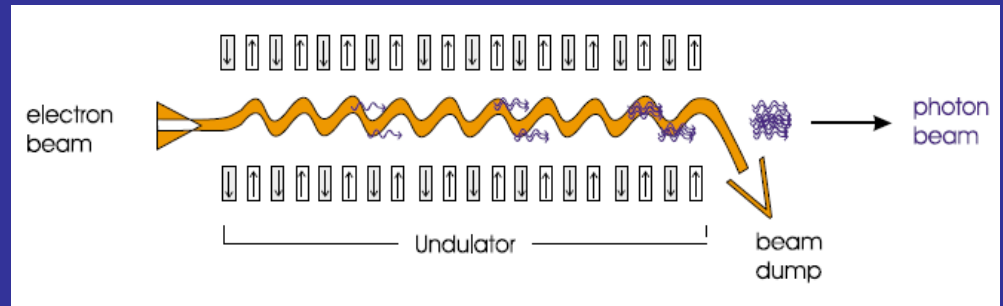
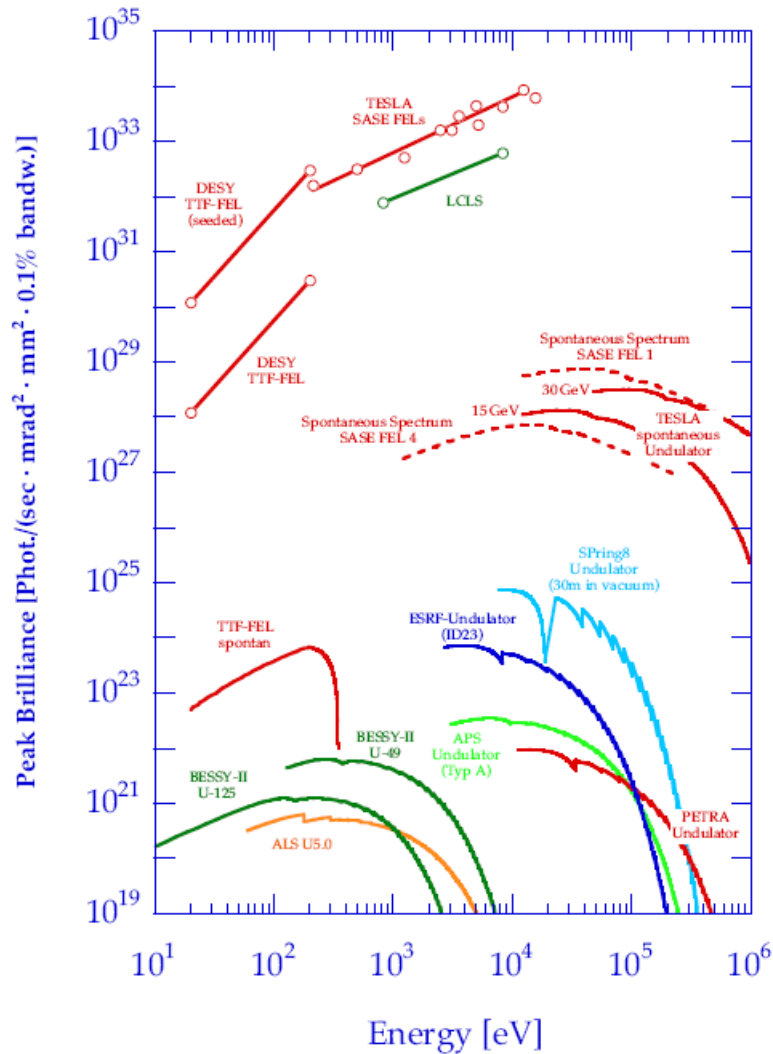
# Some proposed projects

<b>SFINX</b>	<b>Scanning Fluorescence and Imaging at the Nanoscale using X-rays:</b> An intense state-of-the-art nanoprobe providing unique very high resolution capabilities for 3D imaging and fluorescence microanalysis.	page 119
<b>SMILE and XMAN</b>	<b>Spectro-Microscopy and Imaging at Low Energies and X-ray Spectroscopy Multi-Imaging Analysis:</b> A multimodal analysis platform based on the use of infrared and X-ray microspectroscopies, microdiffraction and X-ray imaging techniques.	page 121
<b>EDXAS-S</b>	<b>Energy Dispersive Absorption Spectroscopy (small spot):</b> Microprobe applications such as fluorescence mapping and absorption spectroscopy under high pressure, exploiting the small focal spot and ultimate stability of the energy dispersive XAS method.	page 87

Source *ESRF Purple Book* available at [www.esrf.eu](http://www.esrf.eu)

# SASE-FEL

TESLA Technical Design Report March 2001



# Future of focusing

F. Adams<sup>a,\*</sup>, L. Van Vaeck<sup>a</sup>, R. Barrett<sup>b</sup> *Spectrochimica Acta Part B* 60 (2005) 13–26

Table 4

Technological roadmap showing current state-of-the-art for the most common microfocussing optics based on the achievable focal spot size

	Focal spot size						
	1 $\mu$ m	500 nm	250 nm	100 nm	50 nm	25 nm	10 nm
Fresnel Zone Plates						[1]	
Compound Refractive Lenses				[2]			
Waveguides					[3]		
Kirkpatrick-Baez Mirrors					[4]		
Capillary optics		[5]					
	Solutions exist		Solutions being pursued		No known solutions		

[1] Fresnel Zone Plates are currently operating with ultimate resolutions of 30–40 nm. A major challenge is to improve efficiencies for higher energies (>2 keV).

[2] Current technologies based on mechanically formed paraboloidal Be lenses are approaching 100 nm focussing. Emergent technologies based on lithographic fabrication techniques are proving promising for 1D (line) focussing; their extension to 2D (spot) focussing is now becoming feasible.

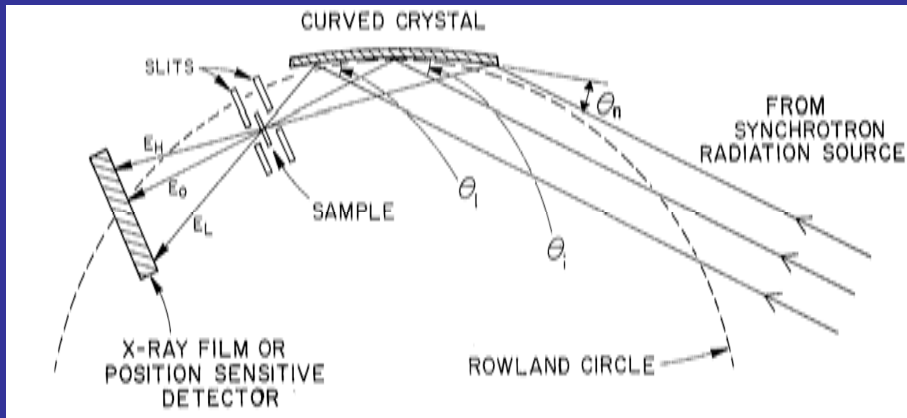
[3] Waveguides have demonstrated beam sizes ~70 nm x 30 nm (H x V). Currently beam acceptance apertures (and hence photon fluxes) are rather small and the requirement to work in the near-field regime may exclude certain applications.

[4] Systems based on bent mirrors allow spot sizes of ~90 nm with achromatic focussing at energies as high as 20 keV. Further improvements may require fundamental changes in the mirror figuring technology.

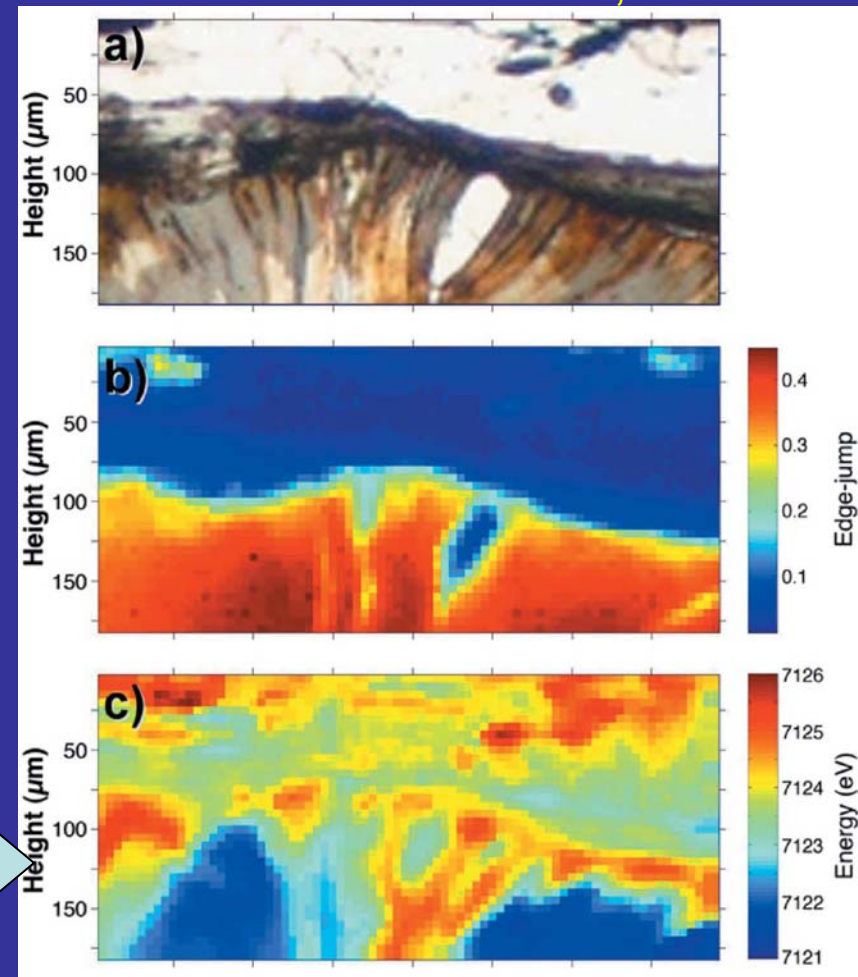
[5] One hundred-nanometer spot sizes have been demonstrated but flux is limited. Practically useful systems would probably require pre-focussing onto entrance aperture (e.g., using K–B mirrors). Beam ‘leakage’ through capillary walls may lead to high background intensities at higher energies. Short working distances (~50  $\mu$ m) are also a probable handicap to widespread use for submicron focussing.

# Energy Dispersive XAS

Pascarelli et al. JSR 13, 351.



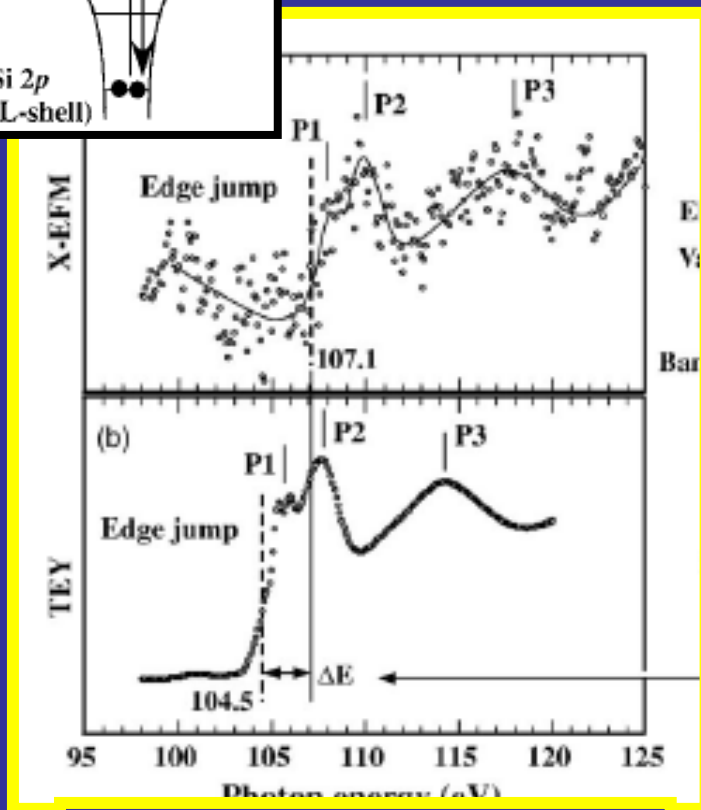
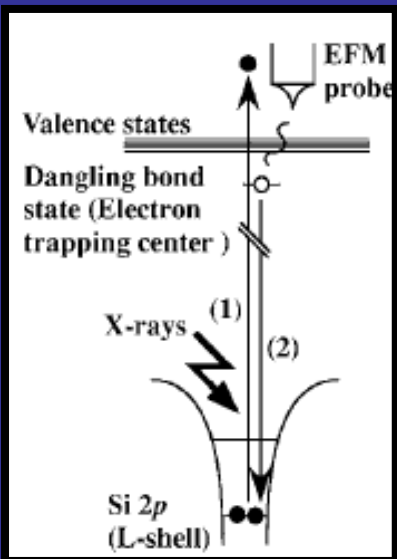
Matsushita & Phyzackerley JJAP 20, 223



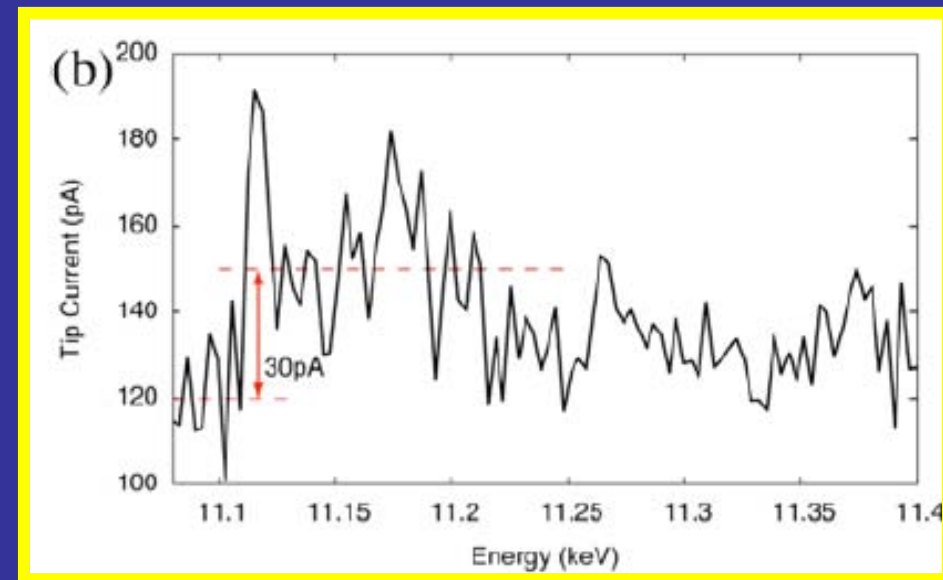
Fe speciation in rocks by XANES  
Fluo mode, 1.5 s/point  
5\*5 μm / px, 2800 px  
Possibility of 10ms/point

# Scanning microscopes

- Spatial resolution determined by the tip and not by the beam size.
- Possibility of investigating a single chosen nano-object.
- Modest results up to now.



Ishii et al. APL **90**, 063101  
Si oxide, EFM mode



Dhez et al. SRI IX Conf. Proc.  
Ge dot, TEY mode

# Conclusion

- X-ray spectro-microscopy permits the analysis down to the  $10^1$ - $10^2$  nm.
- Elemental maps and speciation
- New experimental opportunities in the near future

Thank you