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international centre for theoretical physics

ICTP 40th Anniversary

SCHOOL ON SYNCHROTRON RADIATION AND APPLICATIONS
In memory of J.C. Fuggle & L. Fonda

19 April - 21 May 2004

Miramare - Trieste, Italy

1561/41

Scanning photoemission microscopy: photoelectron and fluorescence spectromicroscopy

M. Kiskinova

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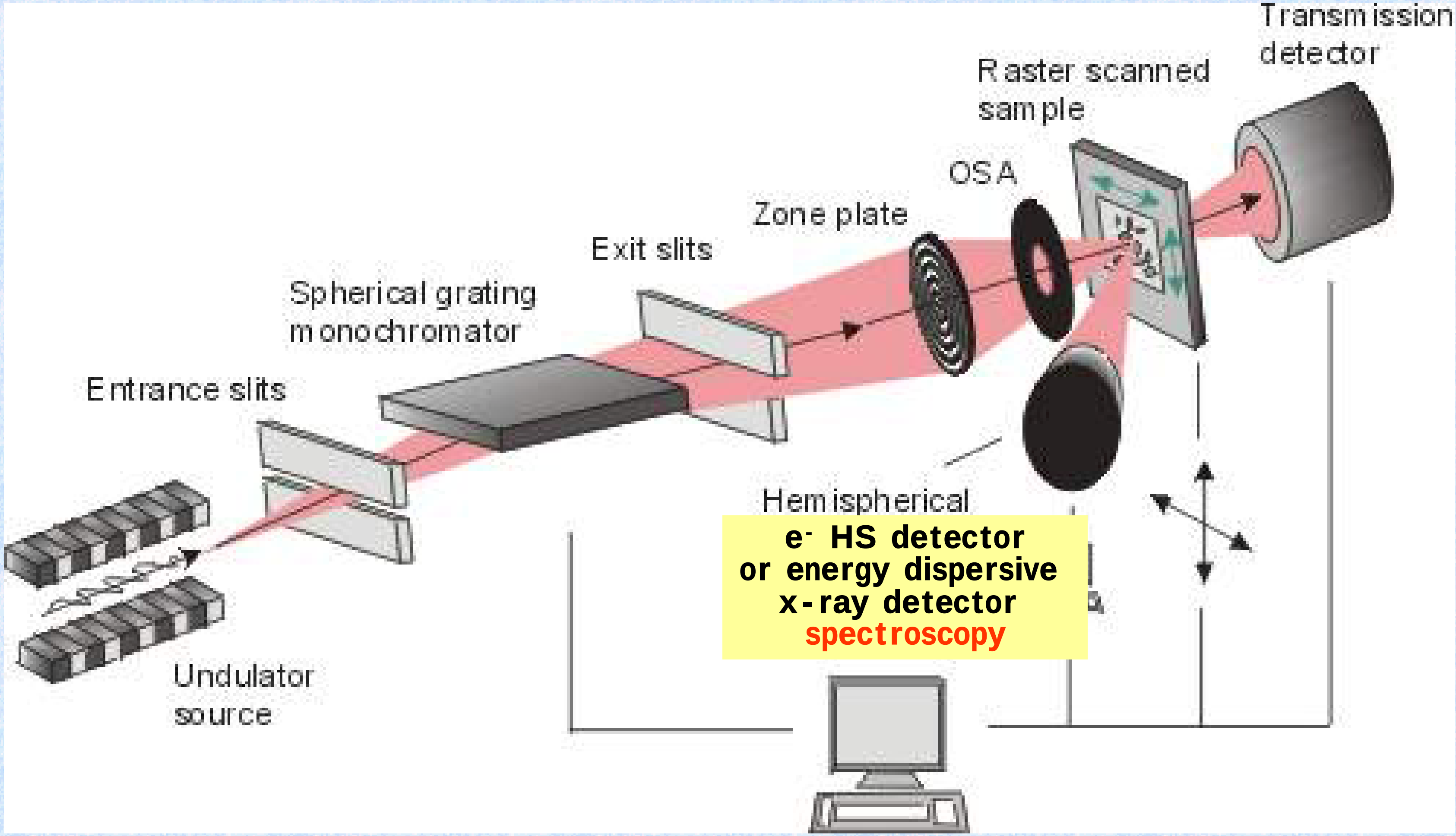
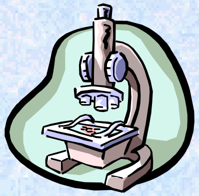
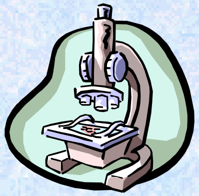
Scanning photoemission microscopy: photoelectron and fluorescence spectromicroscopy

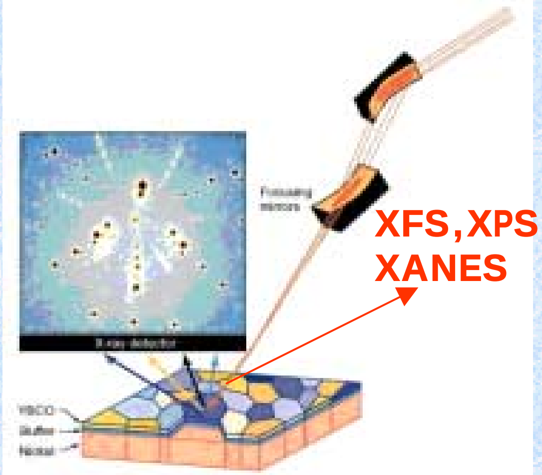




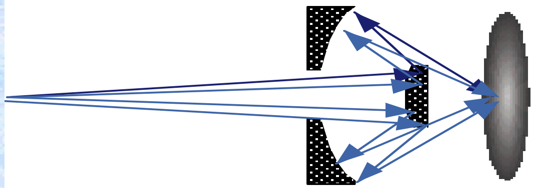
Focusing optics: zone plates, mirrors, capillaries



Zone plate optics: from ~ 200 to ~ 8000 eV
Resolution: 30 nm in transmission

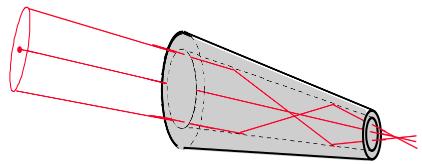


KP-B mirrors each focusing in one direction: soft & hard: ~ 1000 nm
Soft & hard x-rays!
chromatic focal point, easy energy tunability, comfortable working distance
Resolution ~ 1000 nm



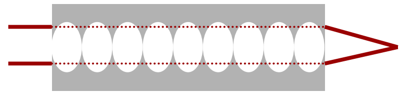
Normal incidence: spherical mirrors with multilayer interference coating (Schwarzschild objective)
not tunable, E < 100 eV
Resolution: best ~ 100 nm

Capilary: multiple reflection concentrator



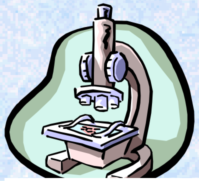
Hard x-rays ~ 8-18 keV
Resolution: > 3000 nm

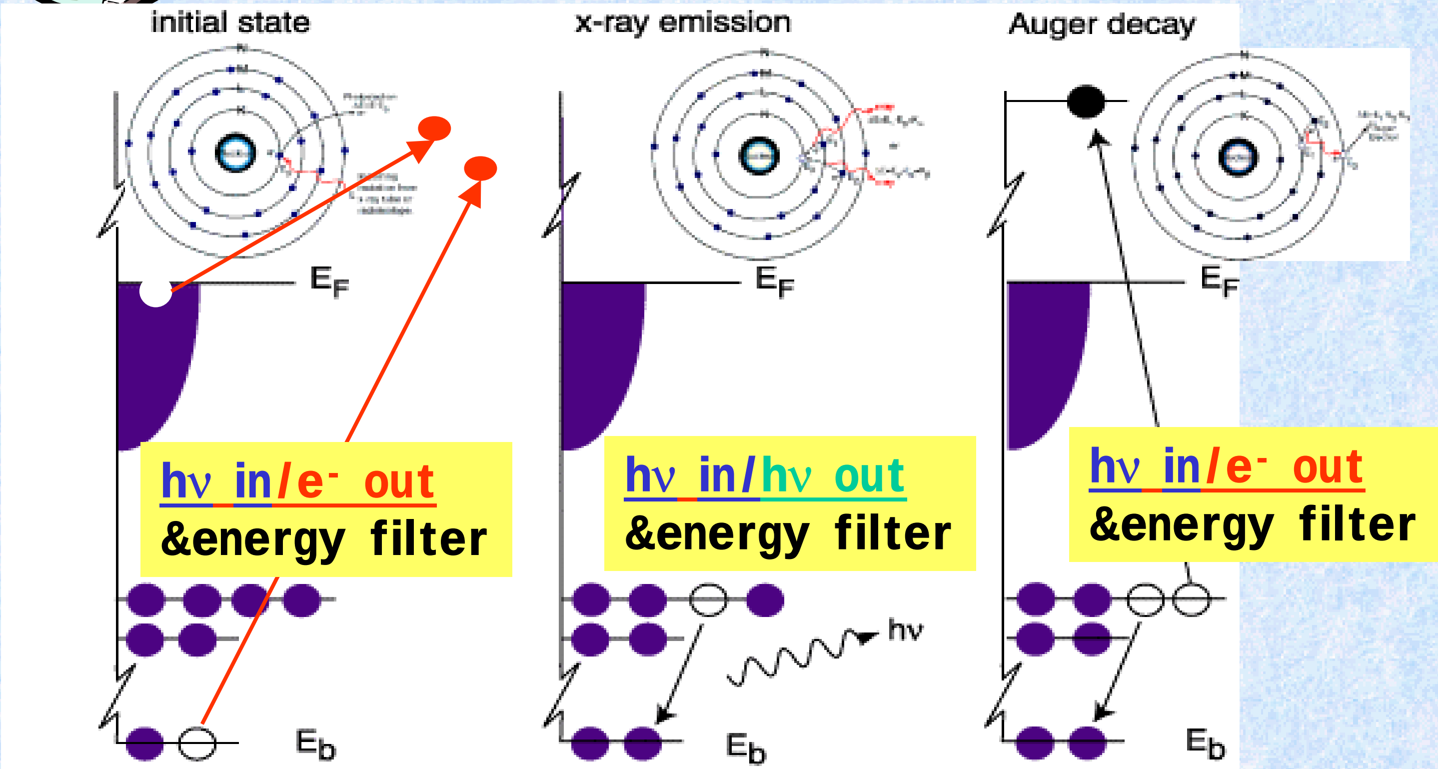
Refractive lenses



Hard x-rays ~ 4-70 keV
Resolution: > 1000 nm

Chemical specific x-ray spectroscopies are based on ‘photoelectric effect’ & de-excitation processes

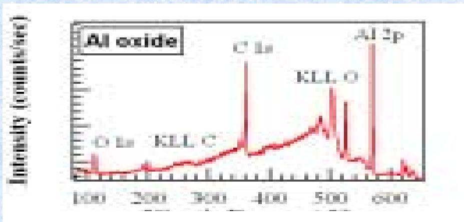




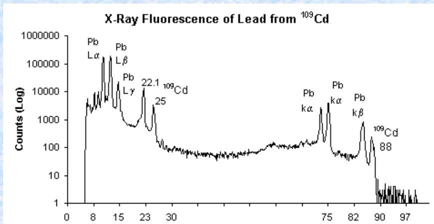
hν in/e⁻ out
&energy filter

hν in/hν out
&energy filter

hν in/e⁻ out
&energy filter



XPS/ESCA+AES



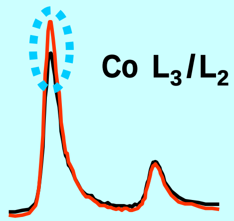
XFS

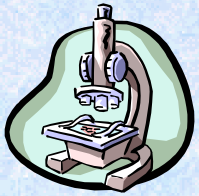
hν in/hν out
or e⁻ out
XANES

Resonant CL transitions into with unfilled states governed by established rules.

Needs scanning of $E_{h\nu}$

magnetic spin and bond orientation using SR polarization





X-ray SPECTRO-microscopy :

soft (< 1500 eV) ***hard (2-20 keV)***

SURFACES & INTERFACES:
(probing depth: max ~ 100 Å)

PE spectroscopy (XPS-AES)

ONLY CONDUCTIVE SAMPLES

Chemical surface sensitivity:

Quantitative μ-XPS (0.01 ML)

chemical & electronic (VB) structure

BULK SAMPLES
(ZP) Larger focal length (f > 10 mm) and depth of focus (>100µm); More space around the sample

X-ray Fluorescence spectroscopy (XFS)

Chemical bulk sensitivity

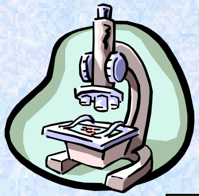
Quantitative μ-XFS

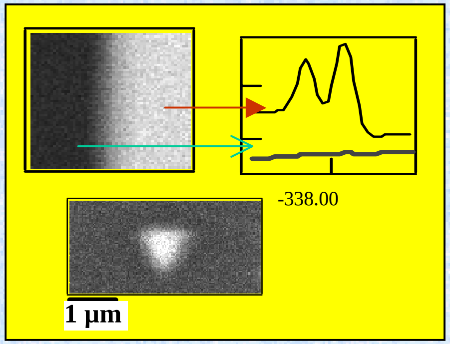
Trace element mapping
(ppm 0.01/Pb – 200/S)

Total e^- yield **Absorption spectroscopy XANES** **Total $h\nu$ yield**

Sample current

Chemical Imaging and µ-spectrscopy

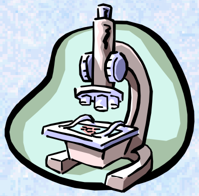




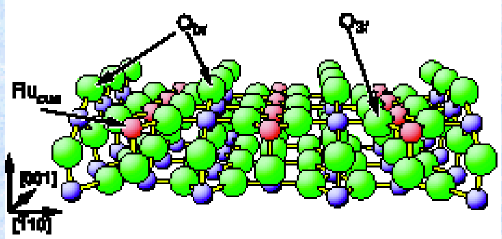
- **2D maps of energy window:** the contrast reflects element concentration (XPS&XFS), different chemical states (XPS& XANES), BB (XPS) shifts etc.

- **Detailed characterization of coexisting micro-phases:**

  XPS, XFS or XANES from selected spots: fingerprints of local composition, chemical state, electronic properties, BB, charging state, magnetic spin, MOs etc

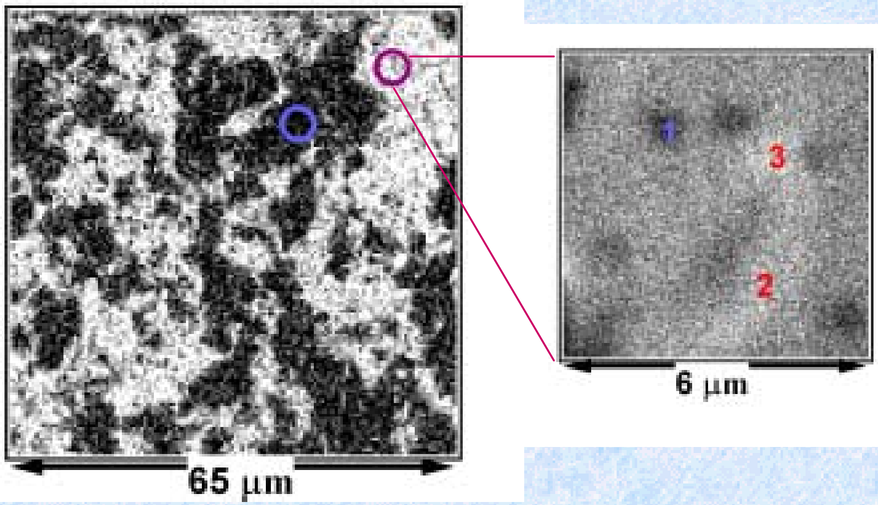


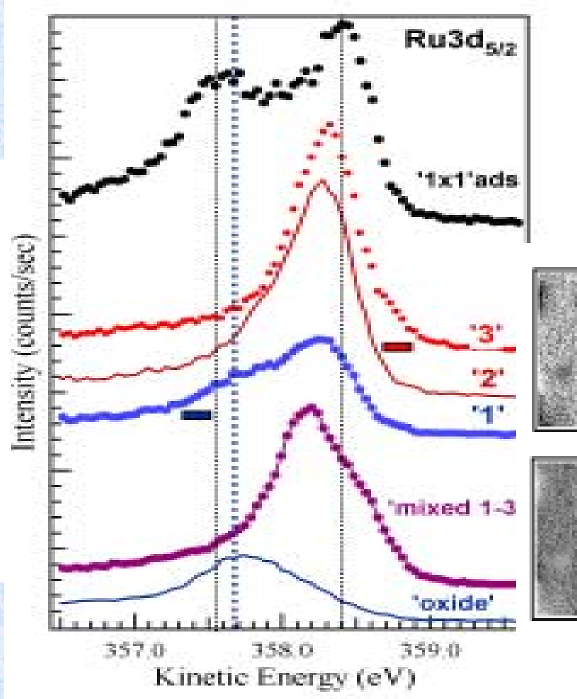
Oxide Growth on Ru(0001) Probed with SPEM

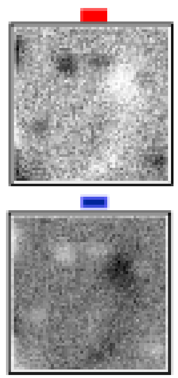


Motivation: What is the active phase of Ru catalysts used in the car exhaust gas converters?! 'Active' O-rich Ru surface consists of RuO_2(110) patches & (1x1)-O ad-phase.
Spectroscopic characterization of RuO_2 with HR-XPS, CPL 342 (2001) 476.

Oxygen exposure: $5x10^5$ L, T=775 K

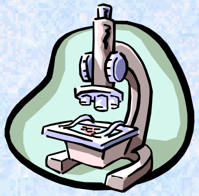






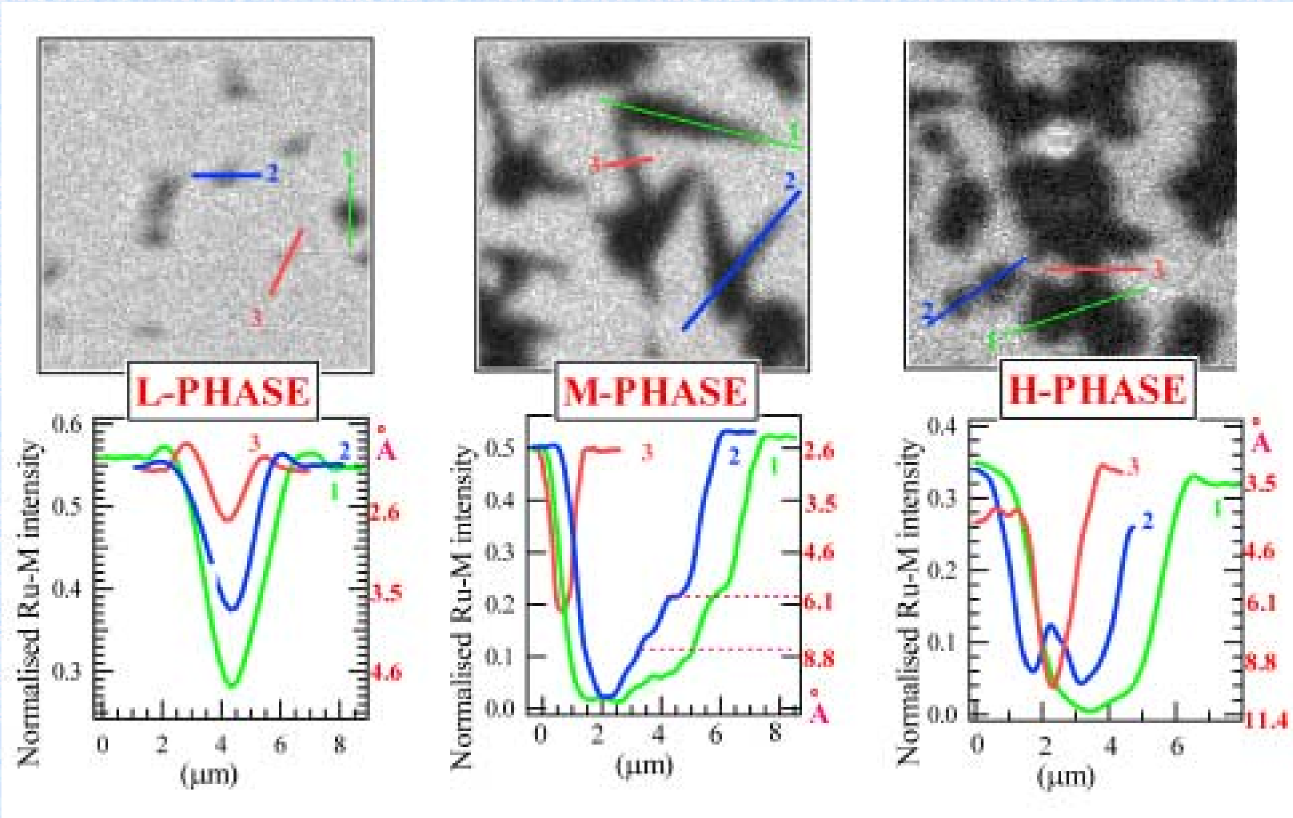
A. Bottcher, H Conrad.. FHI-Berlin/Elettra

Temperature dependence of the spatial anisotropy of the oxide growth on Ru(0001)



A. Bottcher, H Conrad et al FHI-Berlin **L. Gregoratti, M.Kiskinova et al Elettra**

Maps of the Ru 3d signal from the underlying Ru substrate and the corresponding intensity profiles illustrating the inhomogeneity in the thickness of the 'oxide' phase



Oxidation conditions: $5x10^4$ L, P=10^{-3} torr, T=625, 675, 775 K

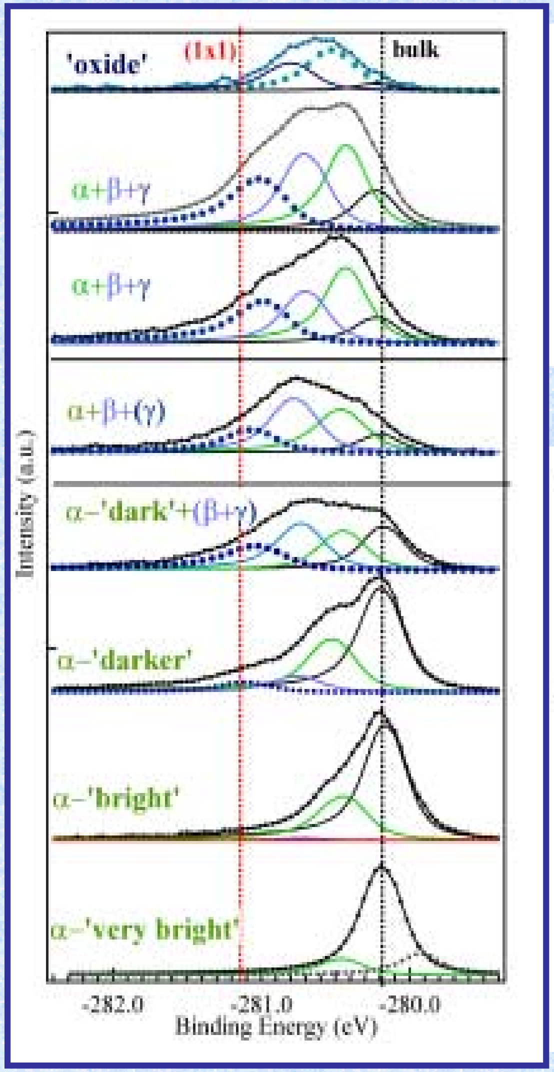
Ru intermediate oxidation stages formed in > 10^5 L range: SPEM with high spectral resolution

<u>hν = 450 eV</u>

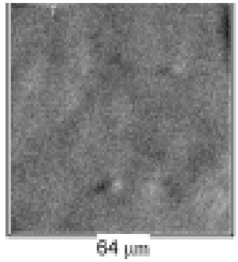
Phase– ΔE(eV)

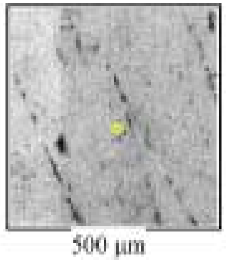
(1x1)- -0.95
α - ~-0.3
β - ~-0.6
γ - ~-0.8

Ox_b - ~-0.6
Ox_s - ~-0.3

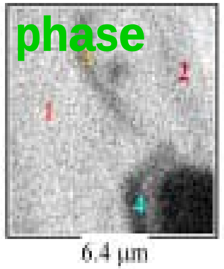


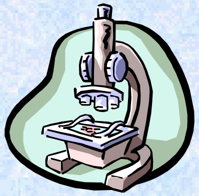
αβγ–phase



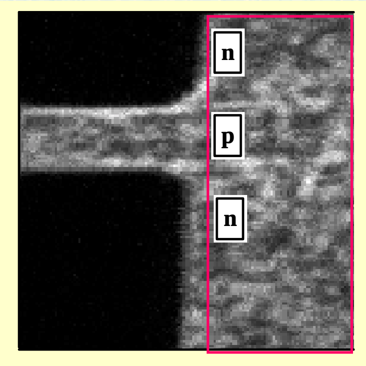


α–phase



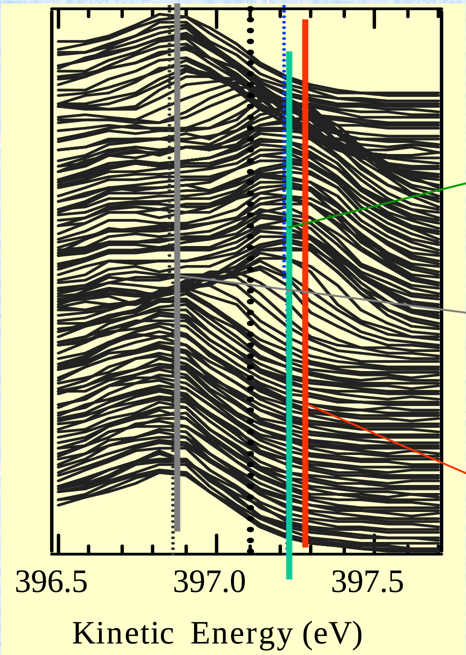


Anomalous spatial variations in the doping profile across a pn-junction Si device: enhanced dopant concentration at the p-edge

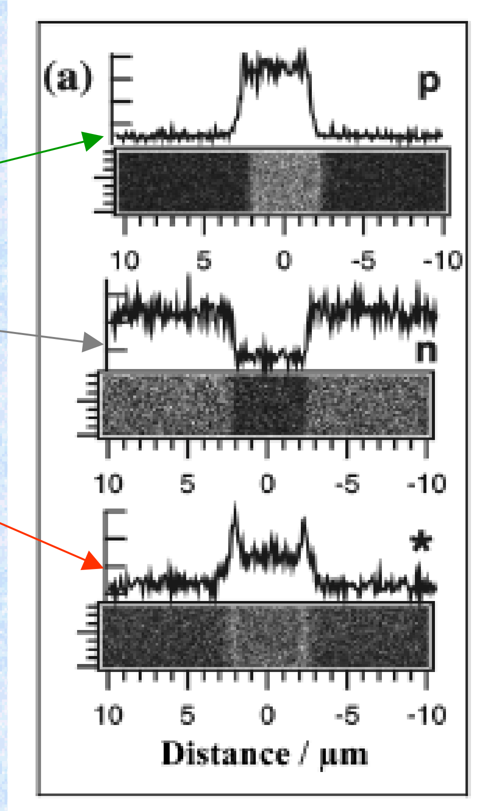


12. 8 µm

Si 2p image of Si pn device: p-stripe $N=10^{18}/cm^3$ (ion implanted B into n-doped Si(100) $N=10^{14}/cm^3$)

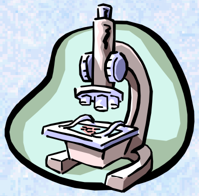


Reconstructed Si 2p spectra using single channel images.

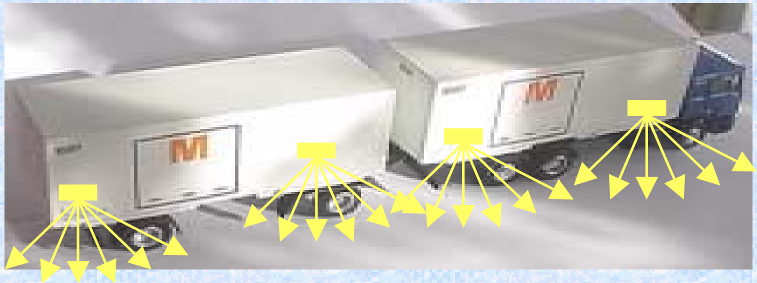


R. Phaneuf, JAP88 (2000) 863

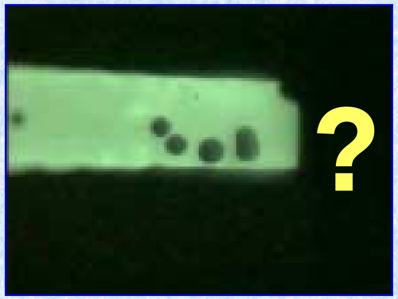
Organic light-emitting diodes (OLED): why do they degrade? What causes the break of the cathode (black spots) ?

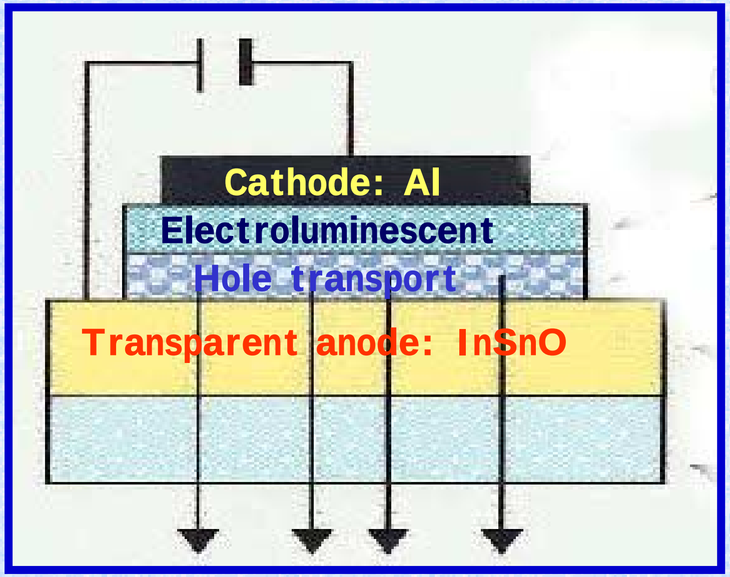


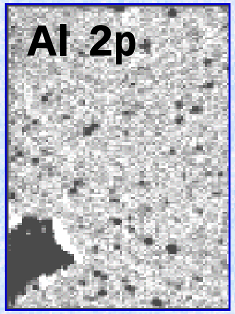
P. Melpignano*, S. Sinesi, V.Biondo*, R. Zamboni, L. Gregoratti et al



Istituto Studio Materiali Nanostrutturati Bologna CNR

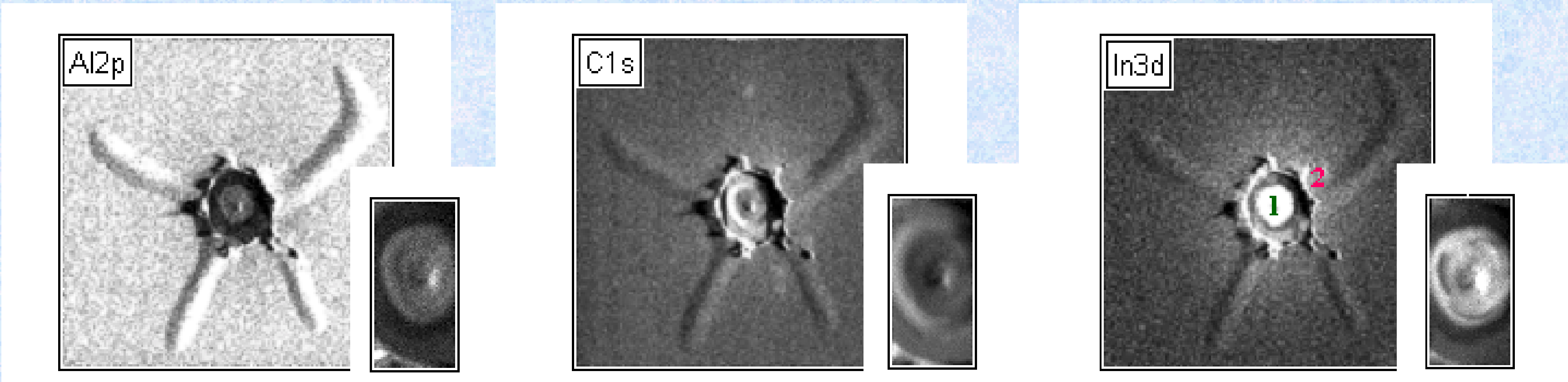


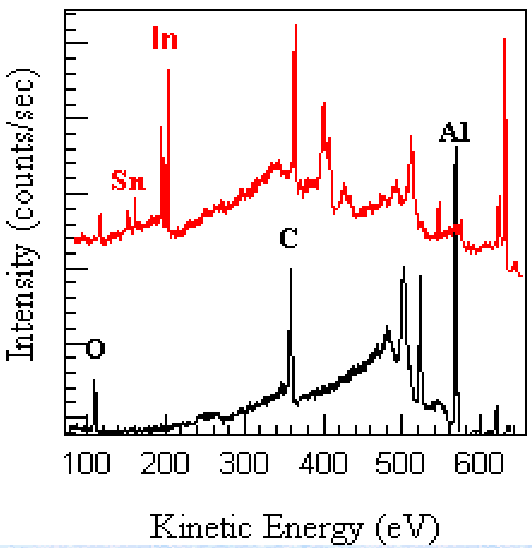




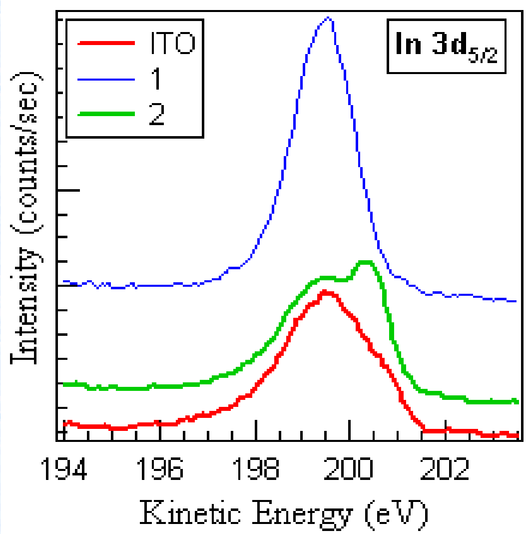
ICTP- Synchrotron Radiation School, May 2004

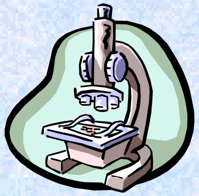
OLED degradation process followed 'in situ' in SPEM





Seems that the reason for degradation should be seek in the quality of the anode morphology: the 'explosion' leads to deposition of anode material.

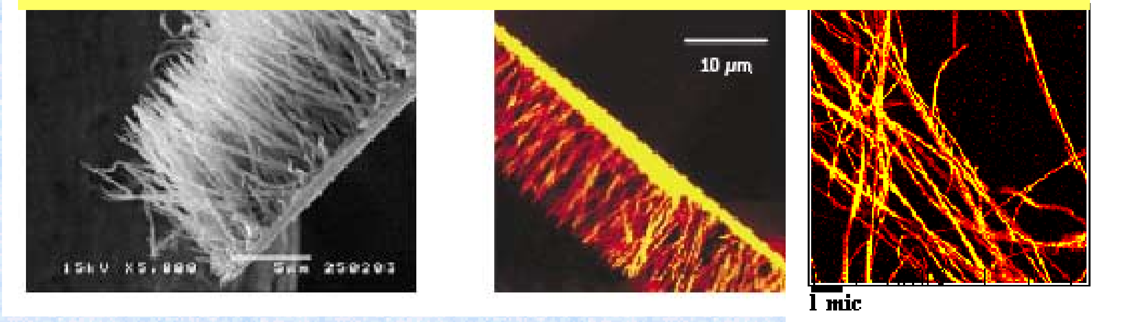


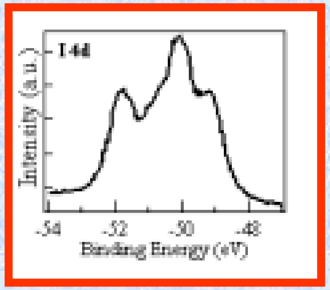


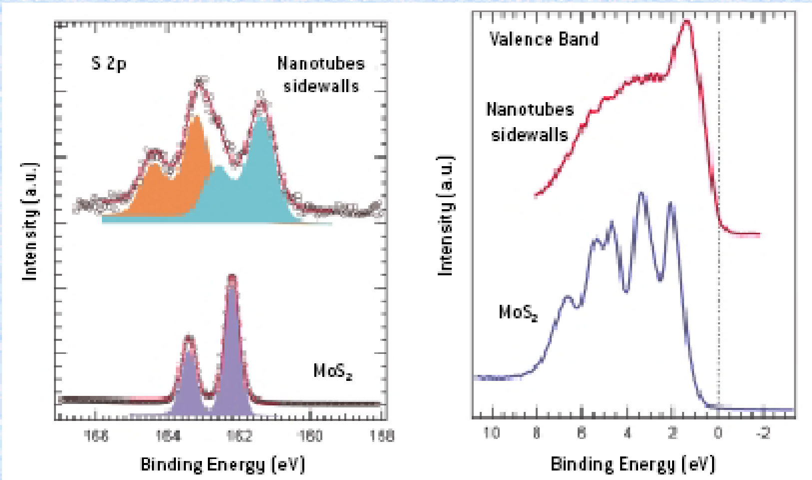
Mo-S based nanotubes: the smallest inorganic nanotubes - M. Ramaker, Science 292 (2001):

With SPEM we solved their chemical composition = $MoS_{2-x}I_y$

Twisted chiral bundles of Mo-S individual cylinders





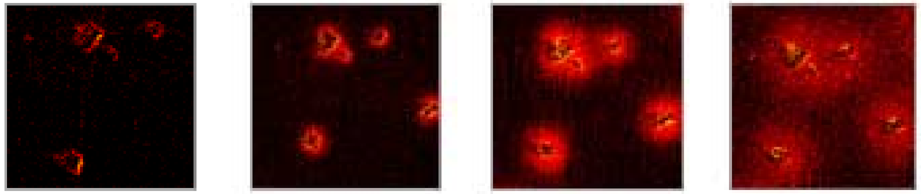


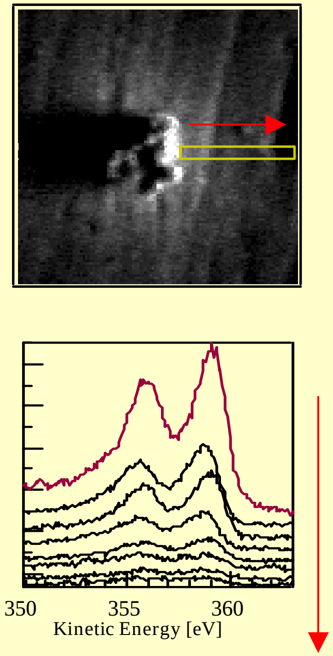
- **The Mo-S nanotubes contain also I, chemically bonded!**
- **S 2p reflect inner and outer position of of S in strongly bent S-Mo-S sheets + bonding of outer S to I at interstitial position.**
- **VB spectra show finite DOS at E_F, metallic behaviour.**

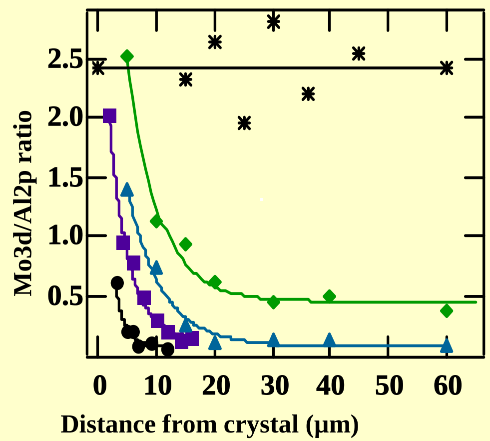
J. Kovac, A. Zalar, M. Remskar et al, Josef Stefan Inst., Luibljana,& ESCAMicroscopy

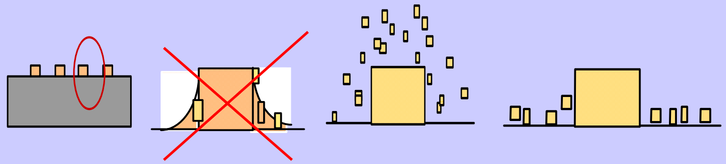
Spreading of MoO_3 on Al_2O_3 at 630 K: Mo 3d mapping and μ-XPS

• 0 min 35 min 70 min 170 min





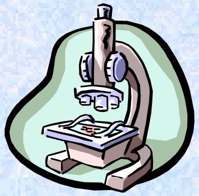


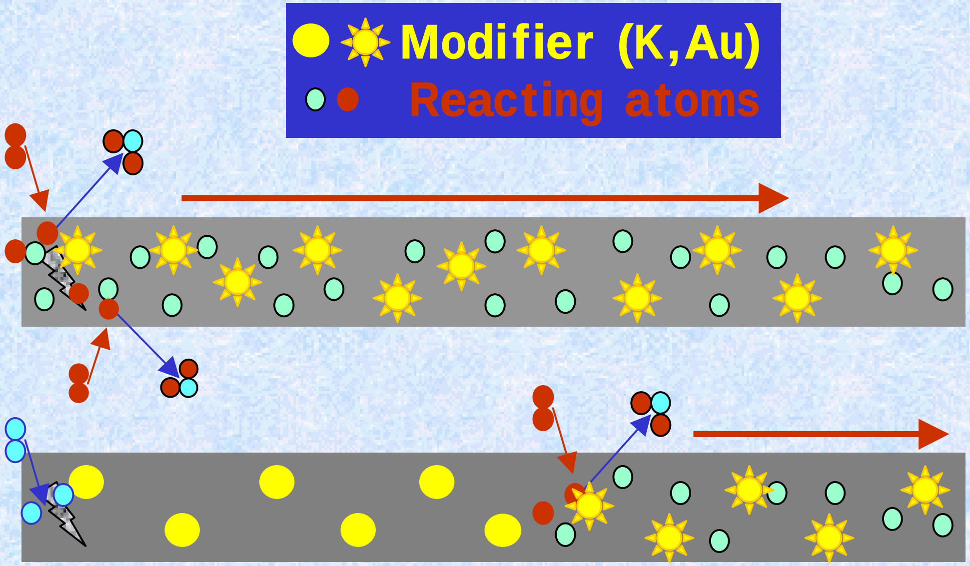


- **Ruled out the 'unrolling' carpet mechanism: coverage of the spread phase remains below 1 ML.**
- **Determined the diffusion constant at 630 K: 0.47 μm/min.**

S. Gunther, J. Chem.Phys.

What is the actual morphology of the a surface under reaction conditions?

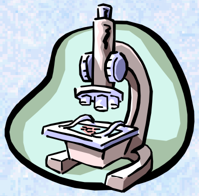




Factors that control the lateral development of the surface composition under reaction conditions:

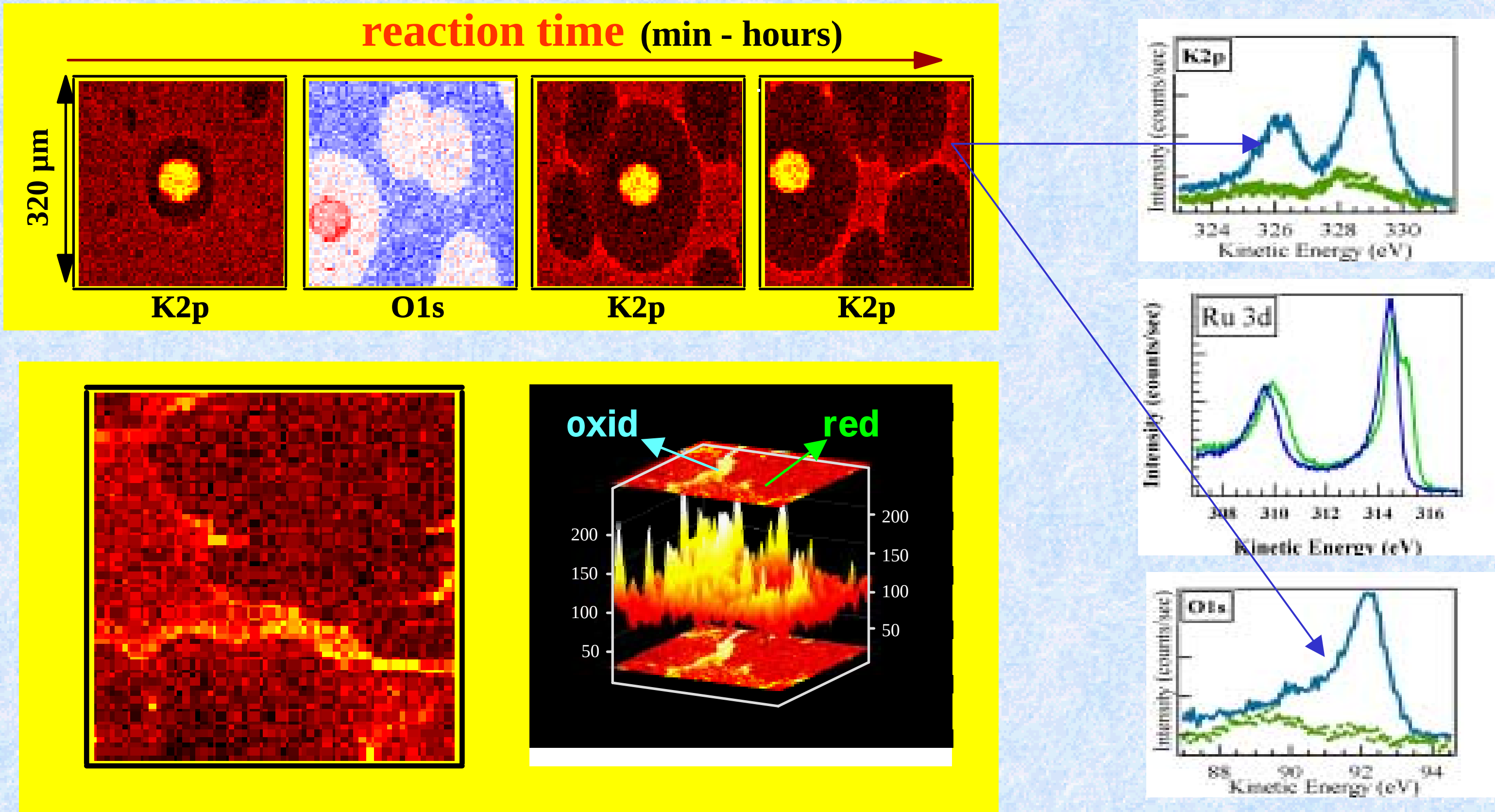
- **Binding energies of the adsorbed species;**
- **Mobility of the adsorbed species;**
- **Velocity of the propagating reaction fronts;**

Important parameters: Temperature, Pressure, Coverage, *Presence of coadsorbed species* and Substrate surface structure.

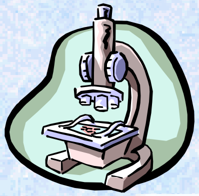


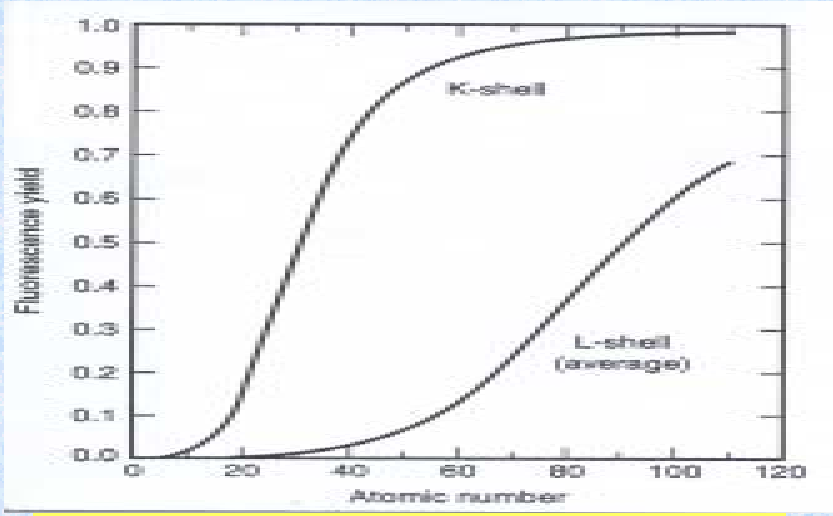
H_2+O_2 on Rh(110) modified with K: reaction driven redistribution of K and formation of condensed K+O islands

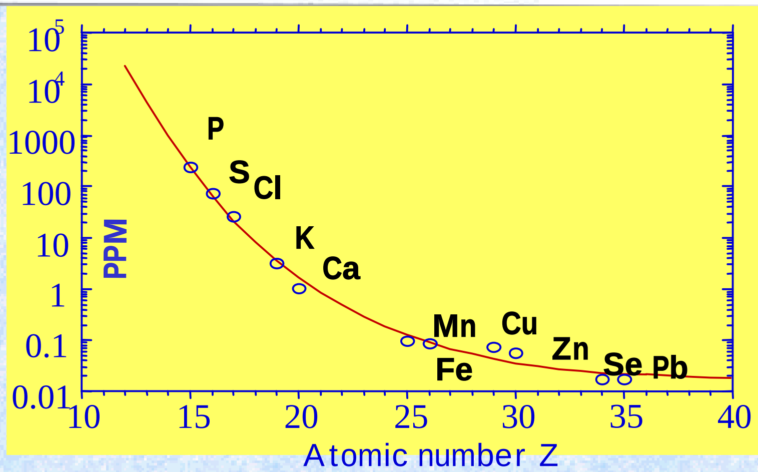
pO_2+pH_2~10^{-6} mbar; K_{init} ~ 0.08 ML + O_{init} ~ 0.8 ML; T~300 C



Hard X-ray Microscopy:
lower resolution but X-ray fluorescence





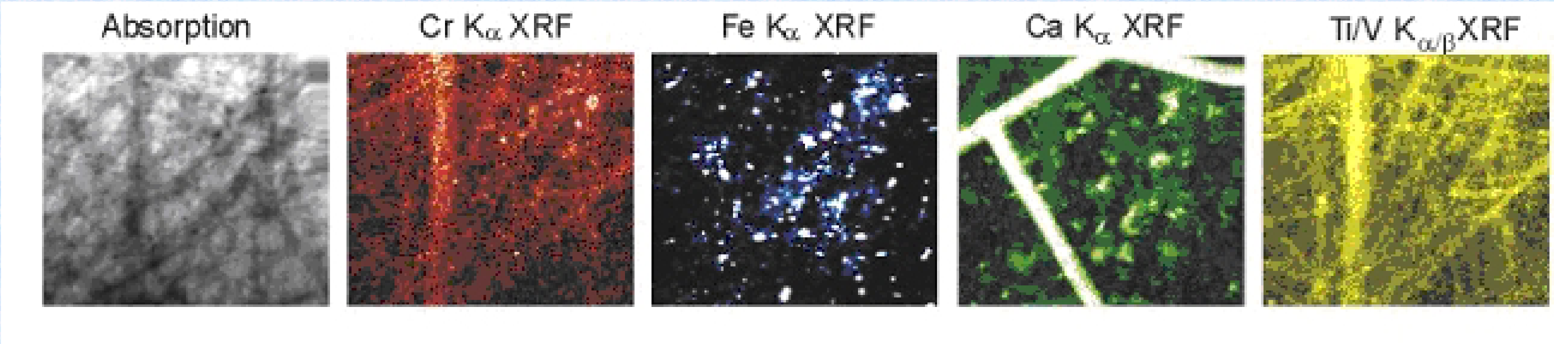


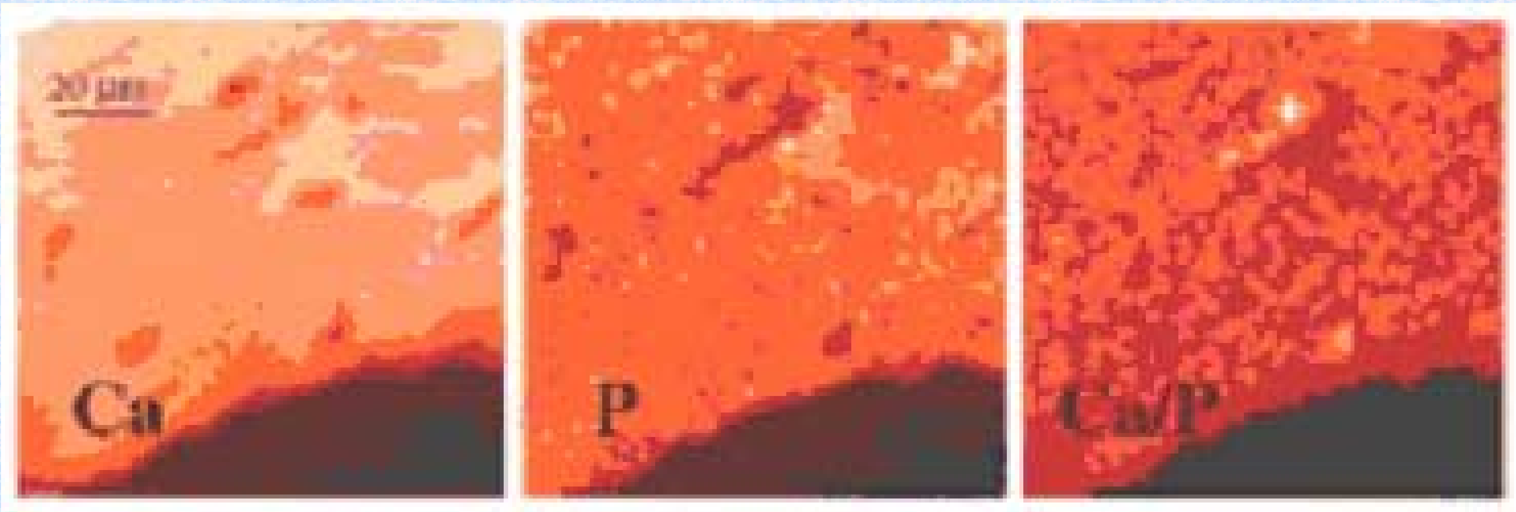
- Penetration depth: > 50µm
- Fluorescence yield.
- All type of samples
- µ-XANES (S, P, K, Ca, Fe..)

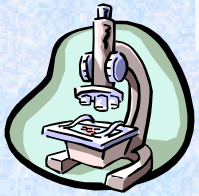
XRF (Scanning + energy/wavelength dispersive detection)

- **Element specific (no labelling)**
- **Co-localisation**
- **Low detection limit (trace element).**
- **High signal-to-background ratio (low dose)**

XF imaging of environmental samples (polluted area near metallurgic plant) and human bones (osteoporosis)







Metabolism of an As-based drug against leukaemia

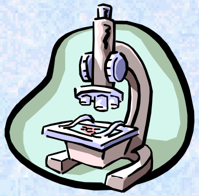
Localisation and speciation of arsenic in hair of patient treated with low pharmacological cc (<1 mmol/l) As_2O_3.

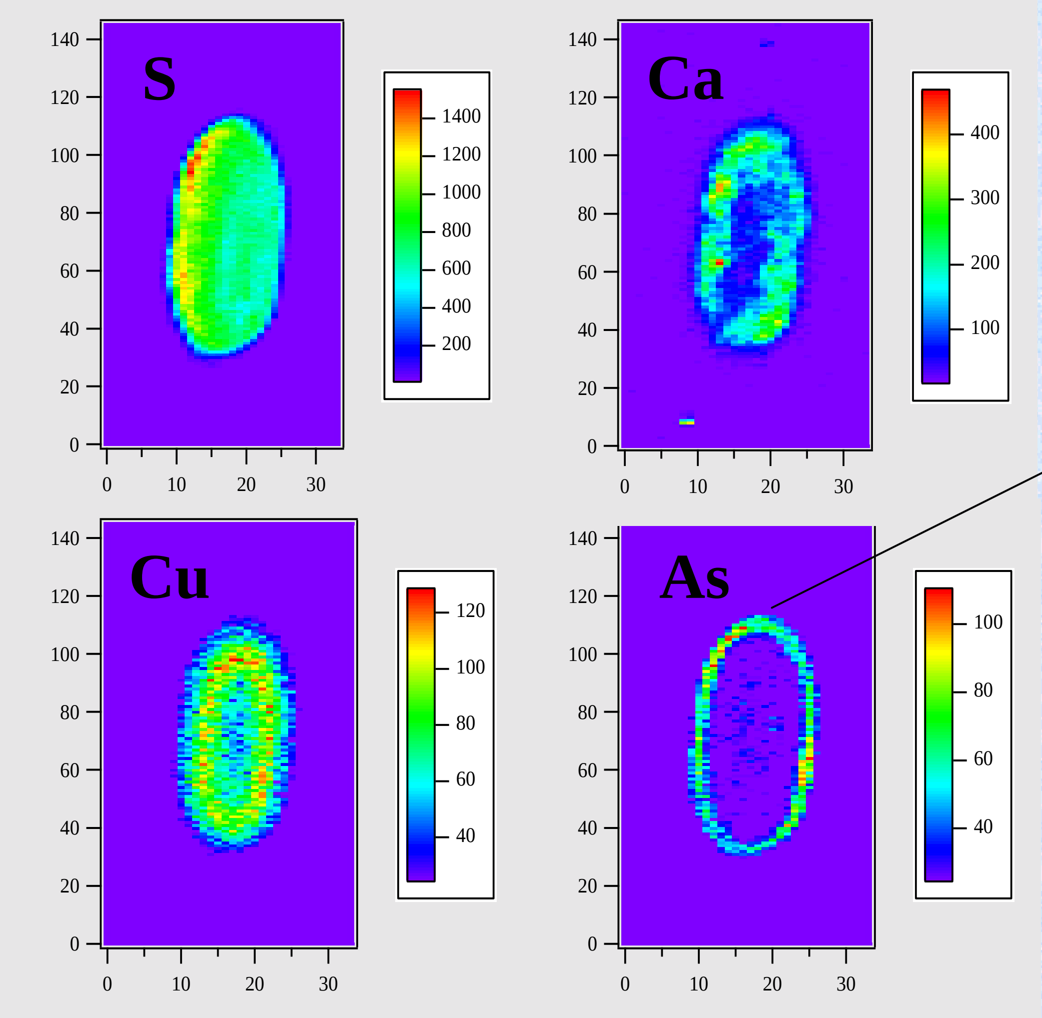
➢ **Case:**

- **Detection of therapeutical doses of As_2O_3 (< 1ppm)**
- **As principally eliminated in urine and sweat but is preferably accumulated in hairs, and nails (inorganic compounds)**

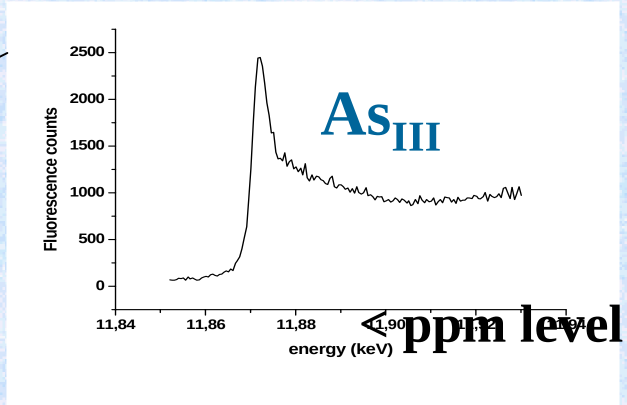
Courtesy J. Susini, ESRF

Metabolism of a new As-based drug:
μ-XF imaging and spectroscopy on patient's hair



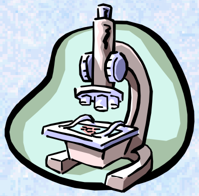


❖ Hair section from patient with acute leukemia treated with pharmacological doses of arsenic trioxide (>1 mmol/l)



I. Nicolas, Faculté de Pharmacie, Paris V
S. Benazeth, LURE

Micro-analysis of humain brain in case of neurodegenerative diseases



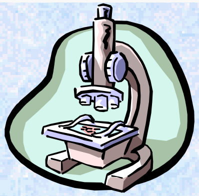
Role of metals in processes leading to degeneration and atrophy of nerve cells in Parkinson's disease (PD) & Amyotrophic Lateral Sclerosis (ALS)

- **Case:**

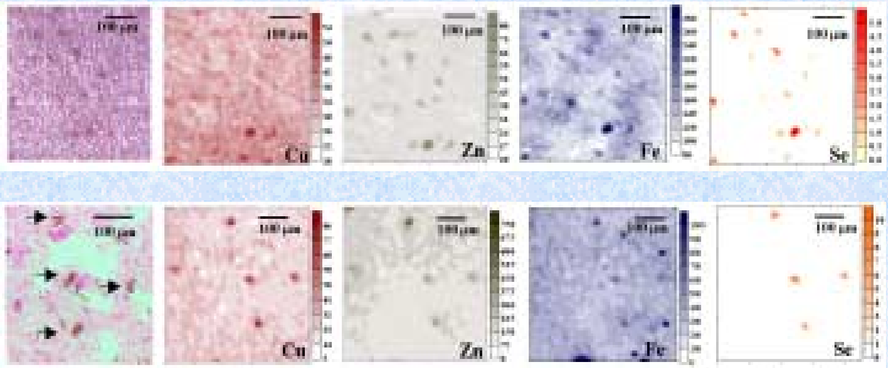
- **Unknown pathogenesis:**
  - **oxidative stress? protein aggregation? excitotoxicity?, mitochondrial dysfunctionning?**
- **Role of trace metals:**
  - **free-radical cytotoxicity?**
  - **antioxidant cellular reaction?**

Courtesy J. Susini, ESRF

Quantitative X-ray fluorescence in Parkinson's disease



Accumulation of Fe, Cu, Zn & Se



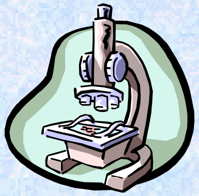
Results of quantitative analysis for substantia nigra of control group (CG), Parkinson's disease (PD) and amyotrophic lateral sclerosis

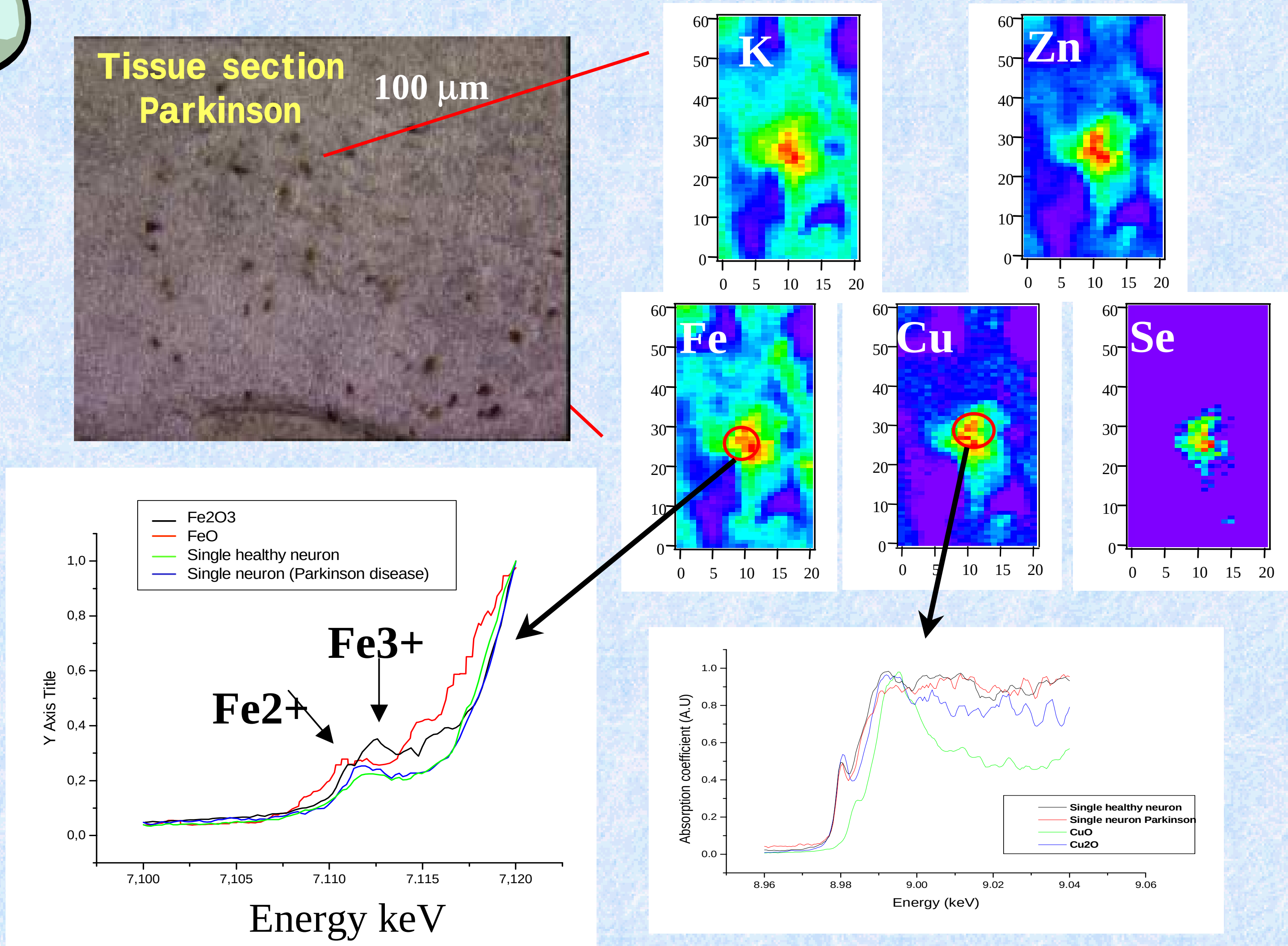
	CG		PD		ALS	
	Neurons *	*white matter***	*neurons*	*white matter*	*neurons*	*white matter*
P	13 – 17	16	19 - 25	16	7.8 - 20	13
S	5.0 - 5.6	3.3	10 - 13	3.8	2.7 - 9.9	2.8
Cl	1.0 - 3.4	2.6	4.4 - 6.6	2.9	4.6 - 10	2.1
K	8.5 -8.9	6.0	11 - 16	7.0	7.4 - 17	5.6
Ca	0.15 - 0.19	0.13	1.4 - 10.5	3.7	1.7 - 19	6.3
Fe	0.38 - 0.61	0.083	1.4 - 2.1	0.43	0.29 - 0.73	0.43
Cu	0.05 - 0.06	0.018	0.11 - 0.17	0.032	0.04 - 0.10	0.025
Zn	0.06 - 0.08	0.023	0.52 - 0.90	0.15	0.1 - 0.3	0.086
Se	0.001 - 0.004	< DL	0.006 - 0.008	< DL	0.001 - 0.009	< DL
Br	< DL - $8*10^{-04}$	< DL	0.01 - 0.02	0.0042	0.002 -0.008	0.0027
Rb	0.007 - 0.009	0.0052	0.010 - 0.014	0.0056	0.007 - 0.02	0.0043
Sr	< DL	< DL	0.006	< DL	< DL - $1.5*10^{-03}$	0.0012

* the ranges of maximal mass per unit area [$\mu g/cm^2$] of elements in neurons
** the mean value of mass per unit area of elements for areas of white matter

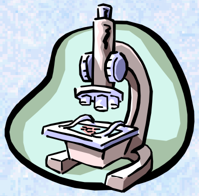
- **Cu & Zn:** **Reaction against superoxide radicals (Cu-Zn SOD)?**
- **Fe:** **Oxidative stress damages, free radical generation?**
- **Se:** **Glutathione peroxydase?**

Micro-XANES on a single neuron



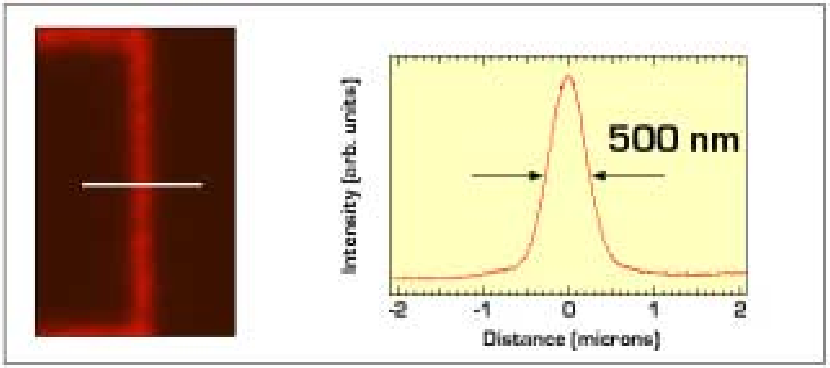


ICTP- Synchrotron Radiation School, May 2004



New perspectives for more efficient utilisation of the synchrotron facilities: direct writing of photoluminescent structures with focused beam

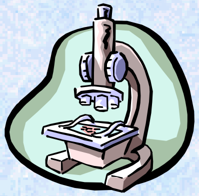
Main advantages of using x-rays for maskless writing: (i) smaller lateral spreading of the x-ray beam and (ii) weaker charging effects



Stable Color Centers with fabricated in thin LiF films using SPEM at ELETTRA

Applications: efficient point light sources in near-field optical microscopy and optical memories, novel miniaturised coherent light sources, such as active waveguides and microcavities for optoelectronics

R. Larciprete et al, Appl.Phys.Lett. 80 (2002) 3862



Multiple applications by choosing the best spectroscopic µ- approach

- Different domains of material science: (S-XPS & B-XFS, S&B XANES)

Composition, electronic and magnetic properties at micro and nano-scales complex materials, micro- and nano - structures, superconductors, polymers, astrophysics, tribology and corrosion phenomena etc.

- Mass transport due to reactions, bulk and surface electromigration: XPS & XFS.
- Environmental and Earth Sciences XFS & XANES
- Bio-science and medicine (XFS & XANES)

samples “natural” environment: liquid or air, cryo-techniques, high pressure