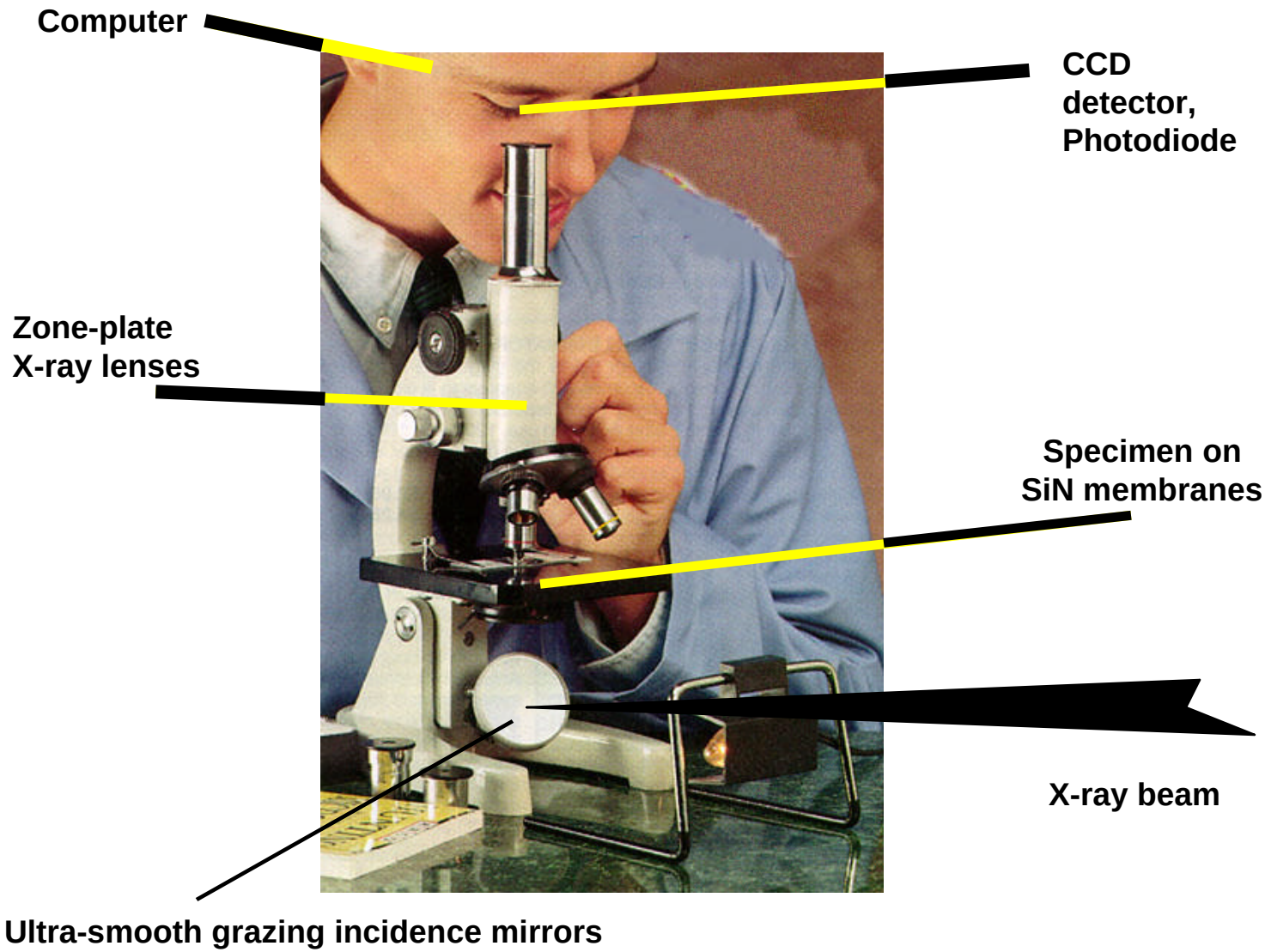
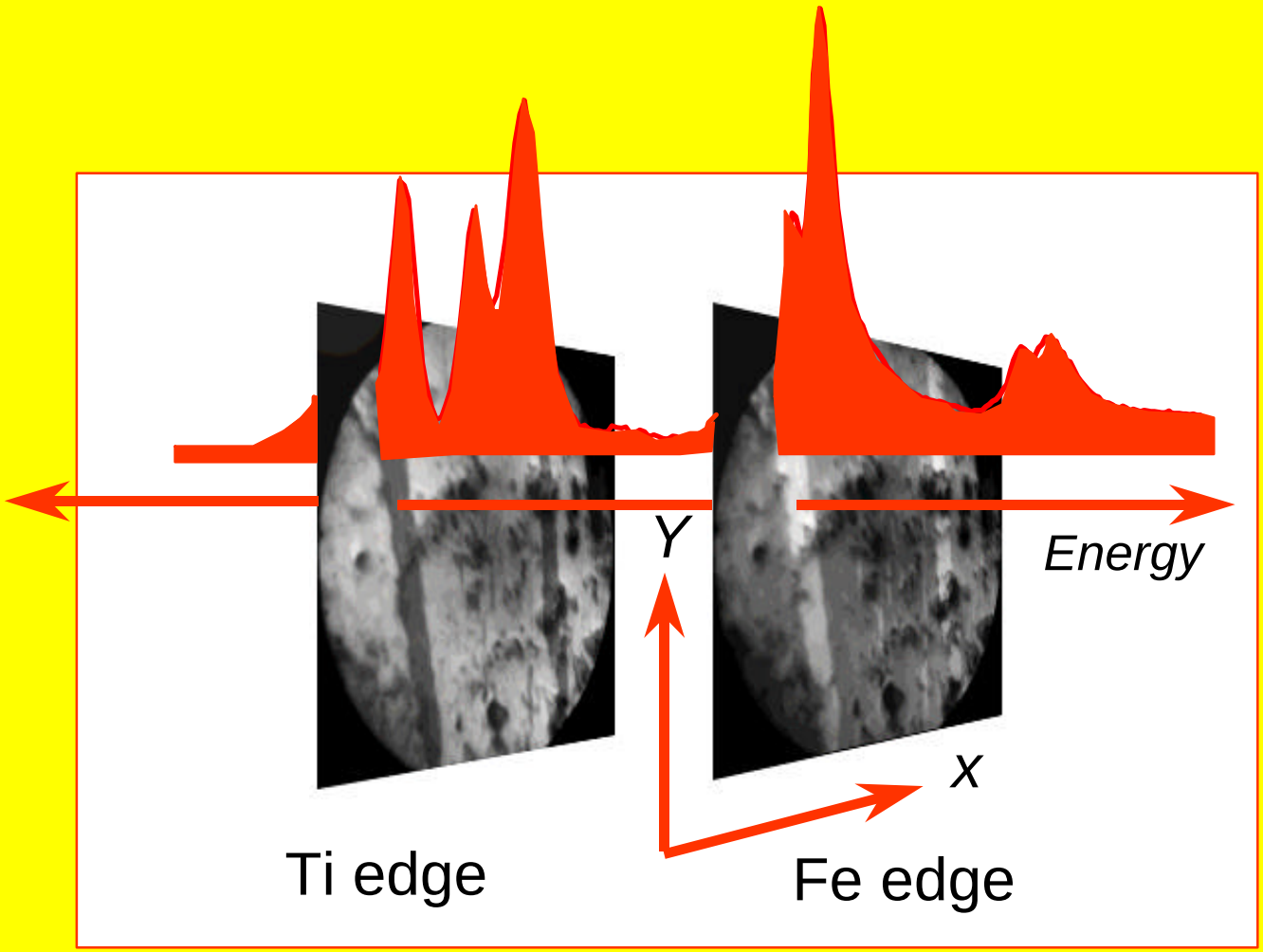
Soft X-ray Spectromicroscopy

- Concept of x-ray spectromicroscopy
- Instrumentation in spectromicroscopy
- Transmission spectromicroscopy examples
  - Polymers and polymer composites
  - Wet cell studies of bio-inorganic interfaces
- Photoemission spectromicroscopy examples
  - Transition-metal silicides
  - Microelectronics applications
  - Natural materials
- X-ray Absorption surface spectromicroscopy examples
  - Magnetic materials
- Future prospects

What is an X-ray microscope?

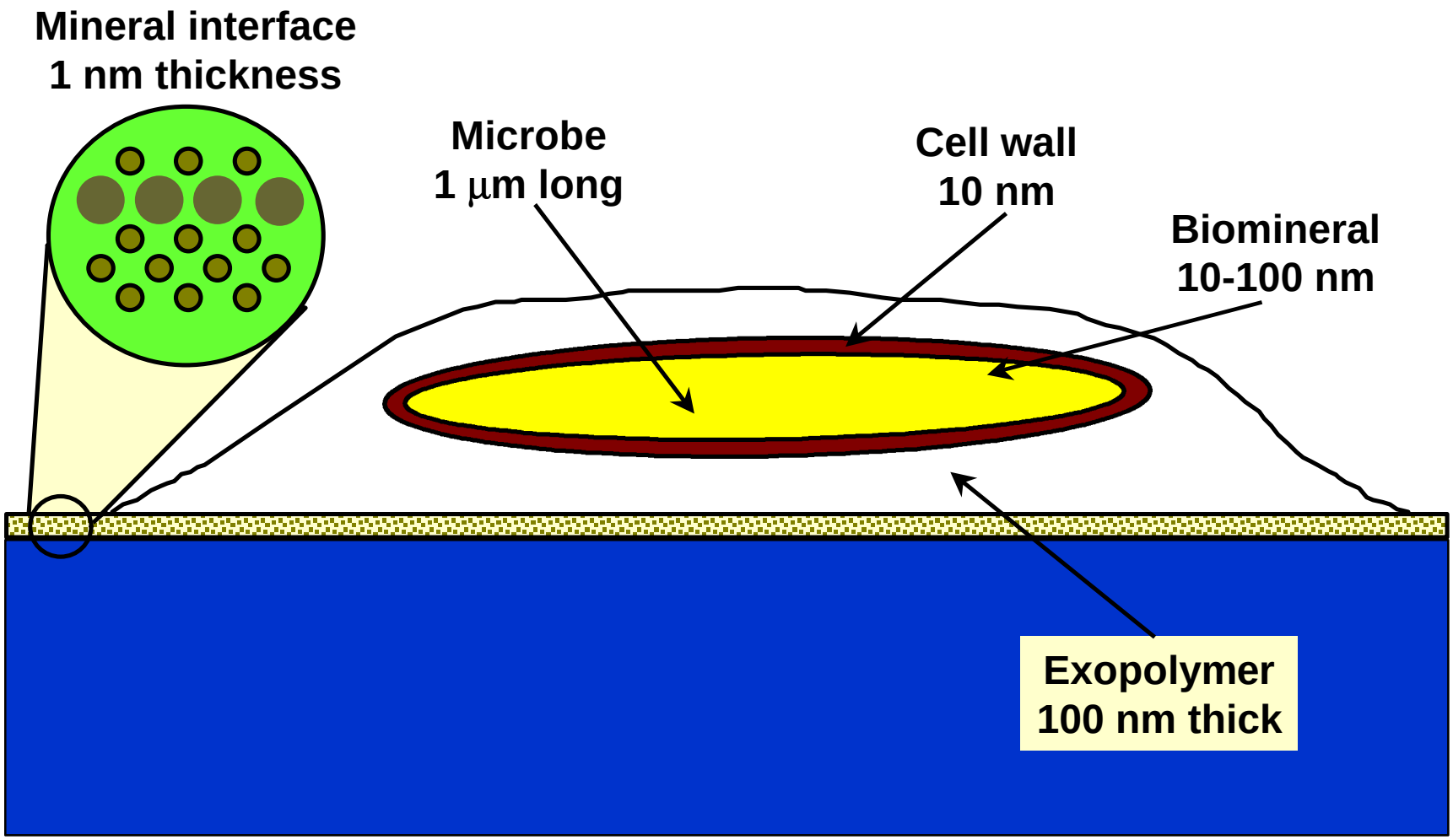


The Concept of Spectro-Microscopy



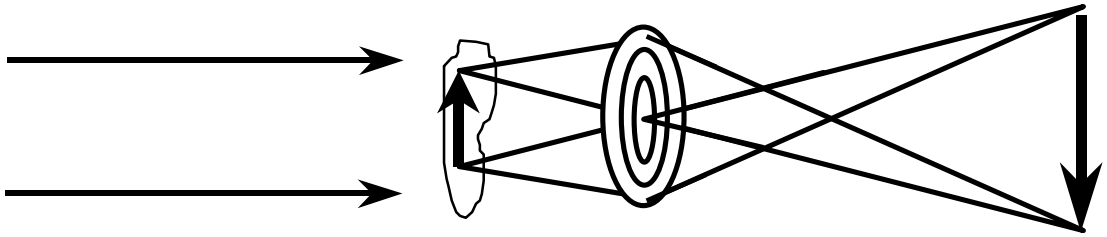
A multidimensional map: Spectral intensity as a function of energy and position.

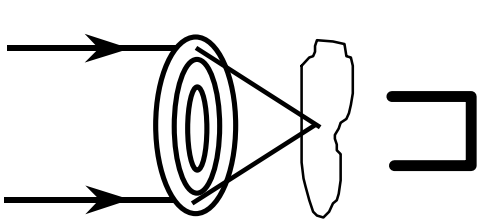
Micro-organisms at inorganic interfaces



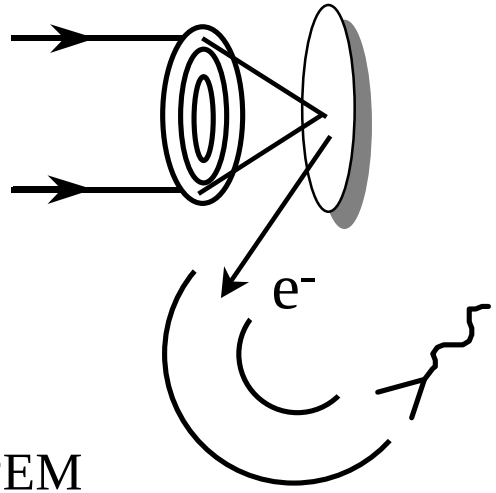
Four types of x-ray spectromicroscopy

(a) TXM (transmission x-ray microscopy)

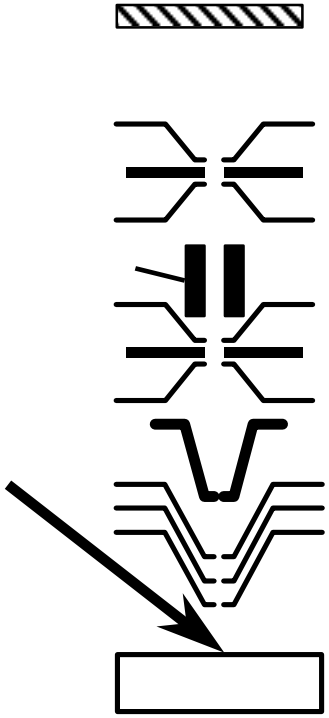




(b) STXM
(scanning TXM)

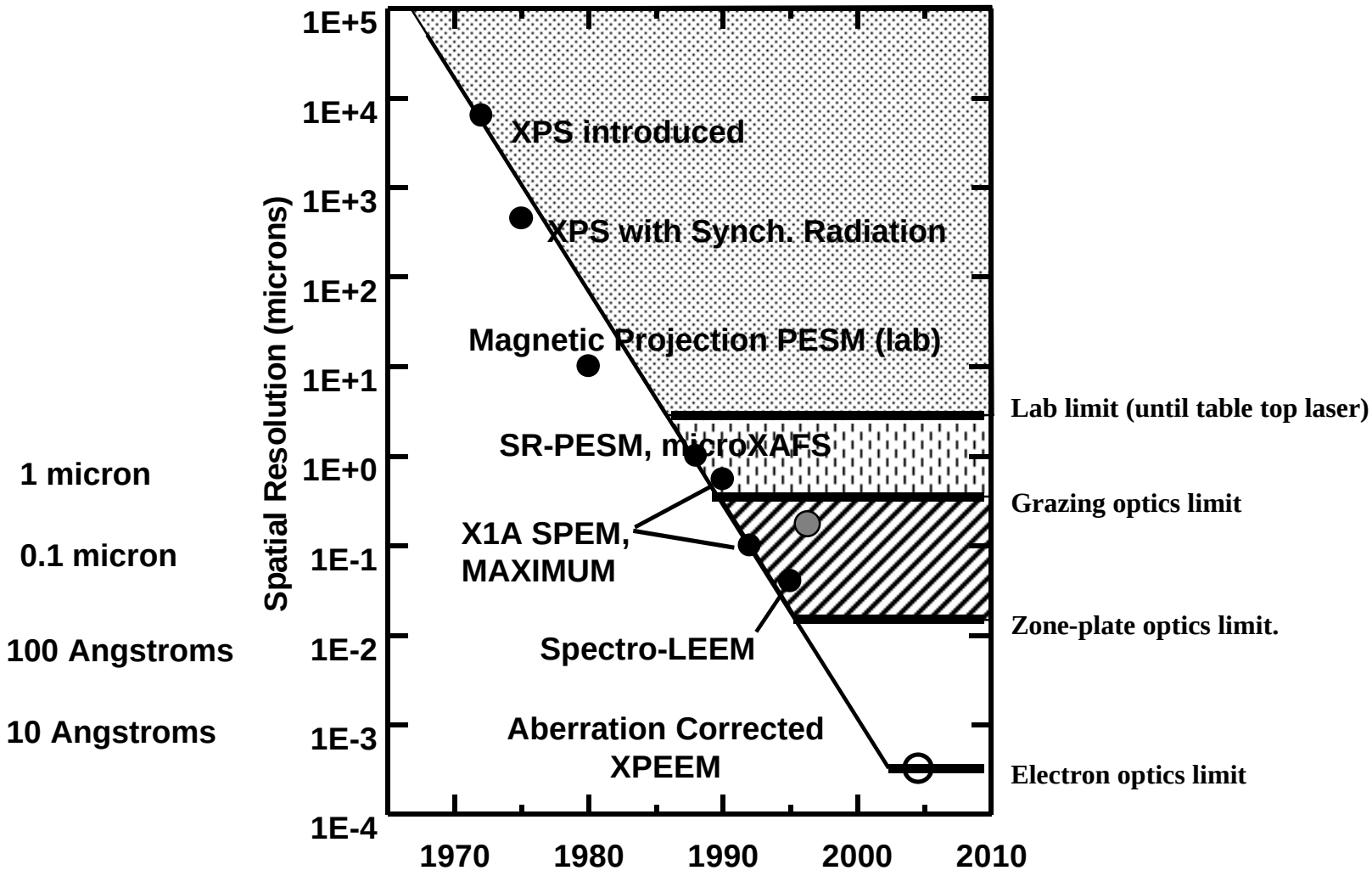


(c) SPEM
(scanning Photoemission Microscopy)

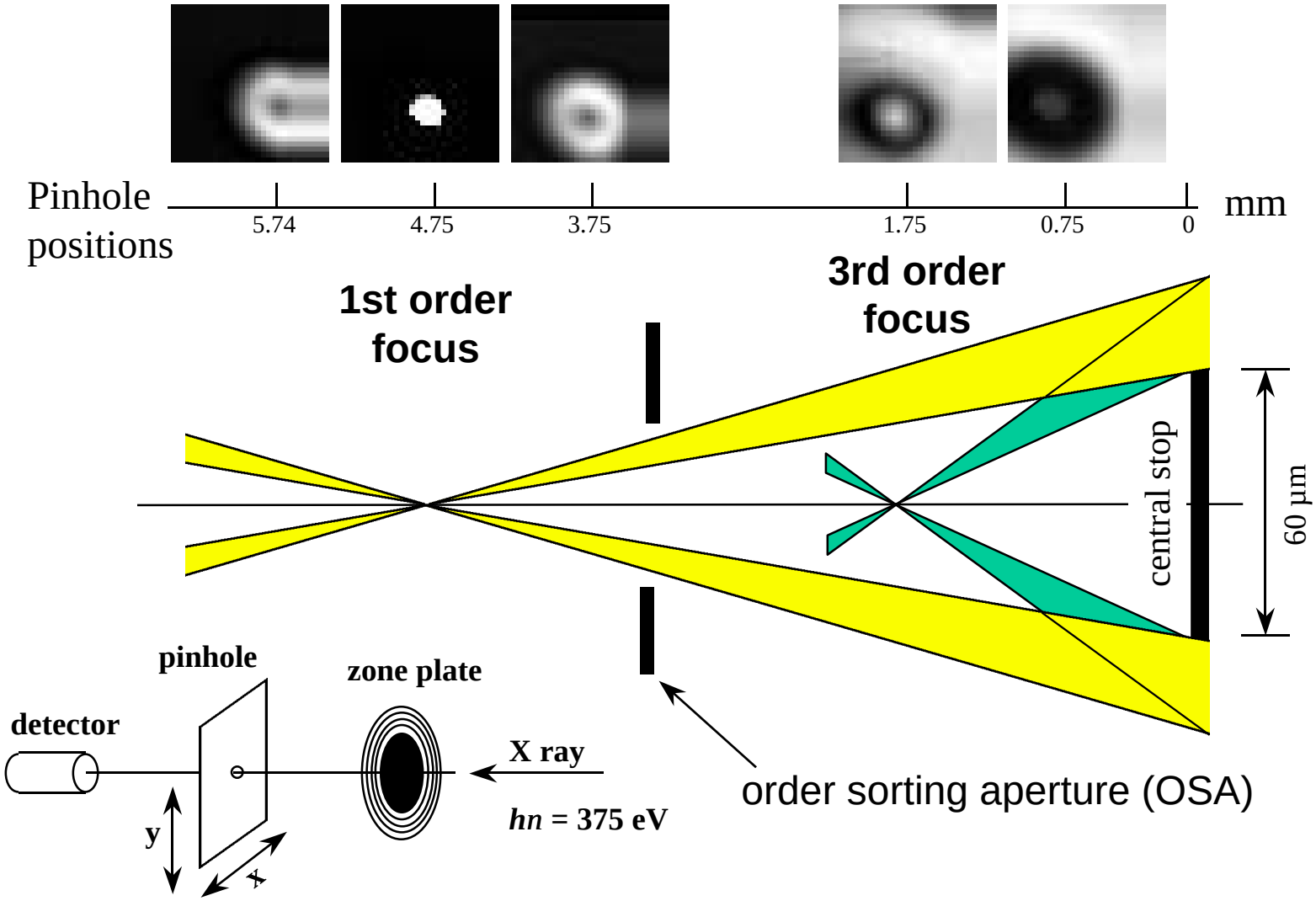


(d) XPEEM
(X-ray
Photelectron
Emission
Microscopy)

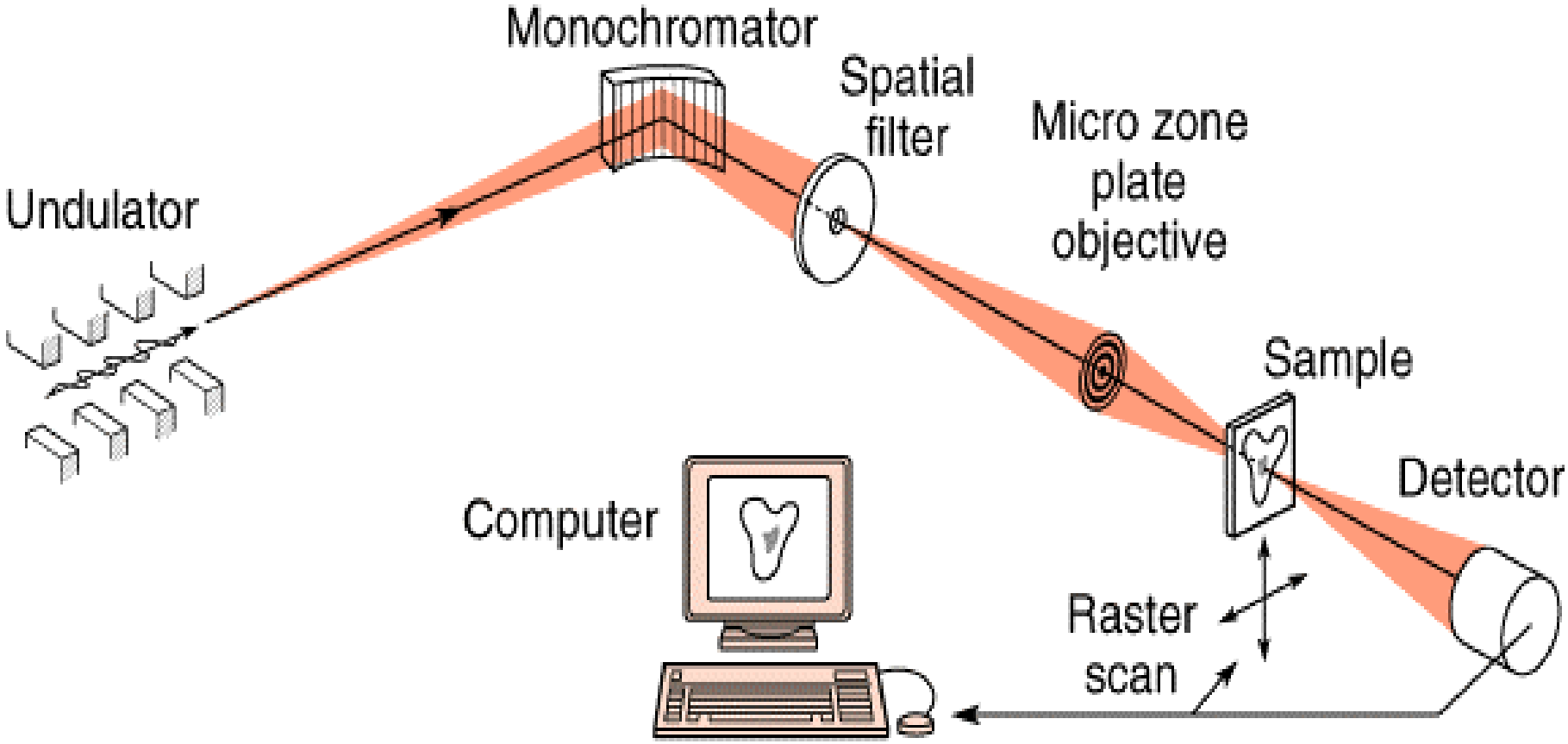
Improvement in resolution over time:
X-ray photoemission spectromicroscopy (nano-ESCA)



Micro Zone-Plate Optics



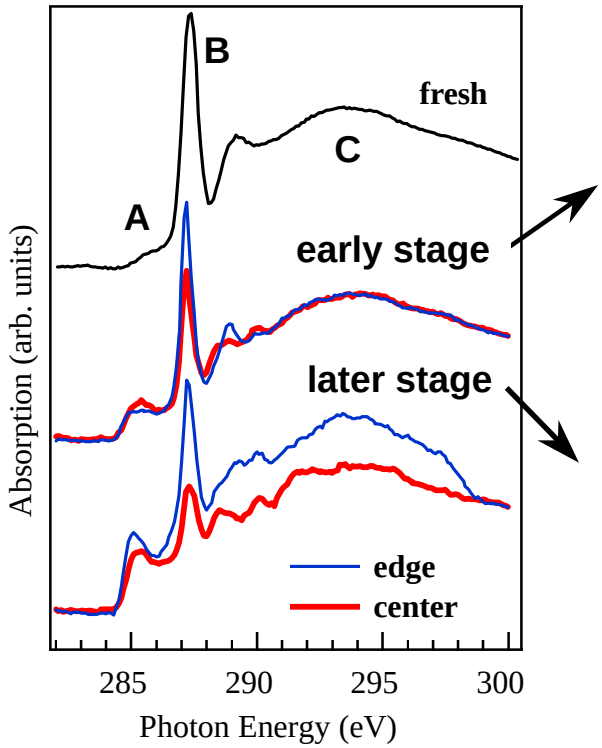
Scanning Transmission X-ray Microscope (STXM)

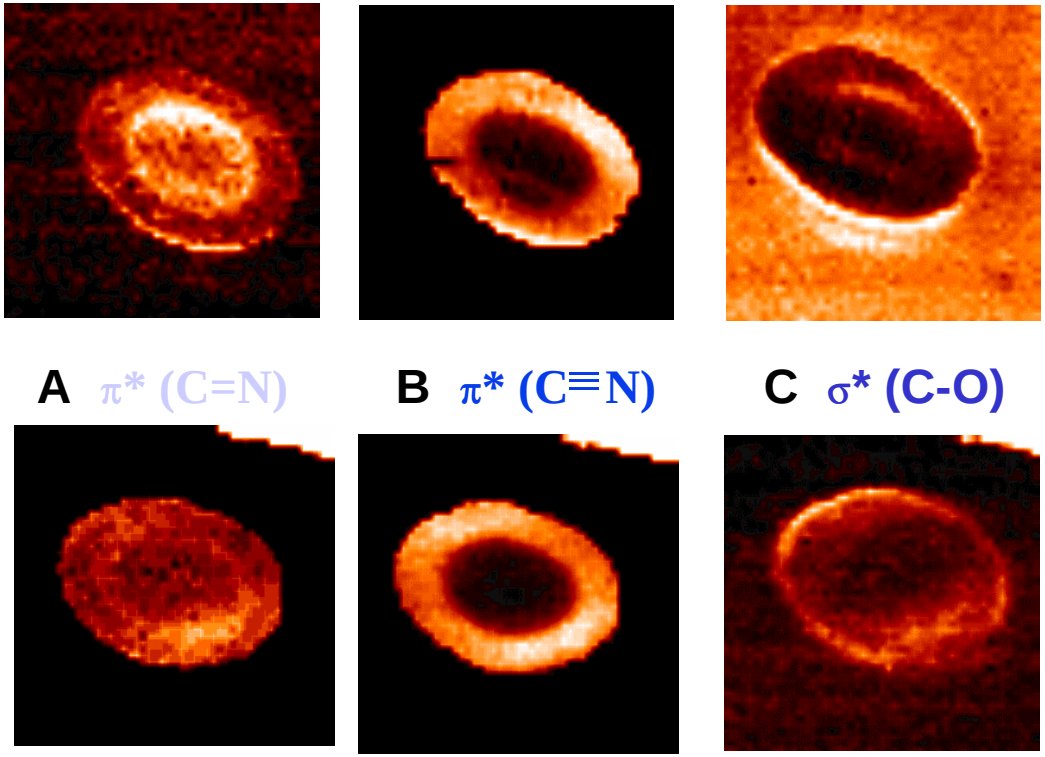


STXM

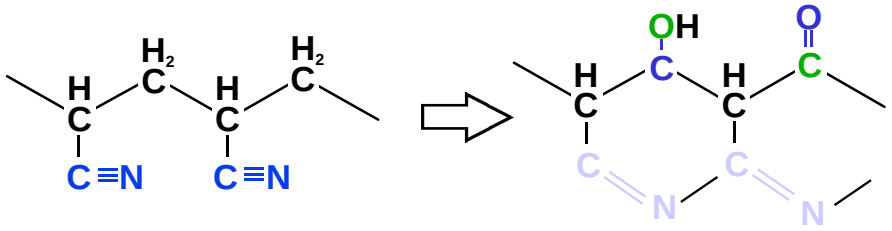
at BL 7.0.1

STXM of poly-acrylonitrile fibres (bond-type imaging)



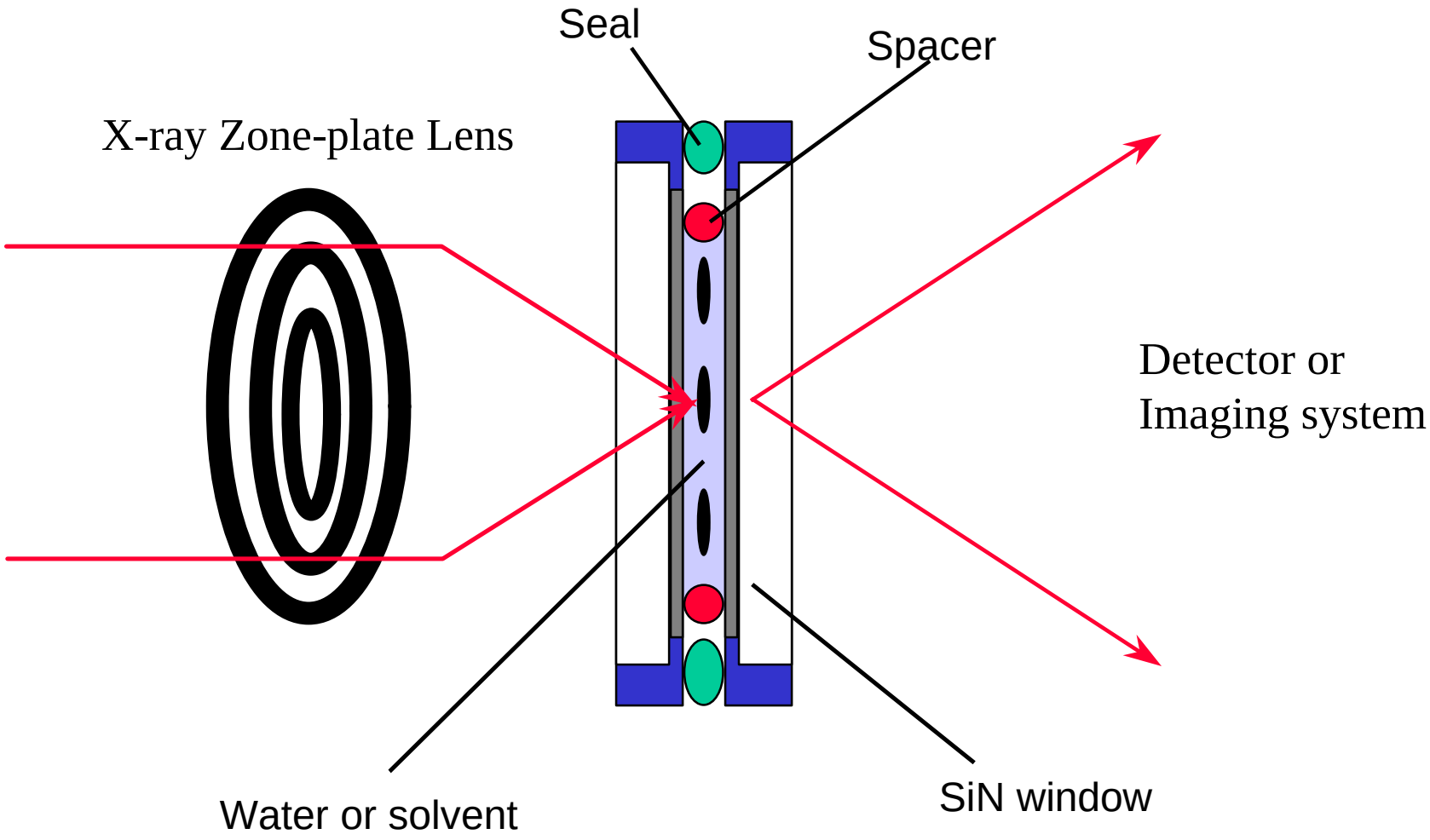


- **air furnace heating to 200-300°C —> two-phase structure**
- **Model:**
  - **Exothermic oxidation reaction at the outer edge accumulates heat in the core**
  - **Fiber center melts and loses orientation order of C≡N bonding along the fiber**



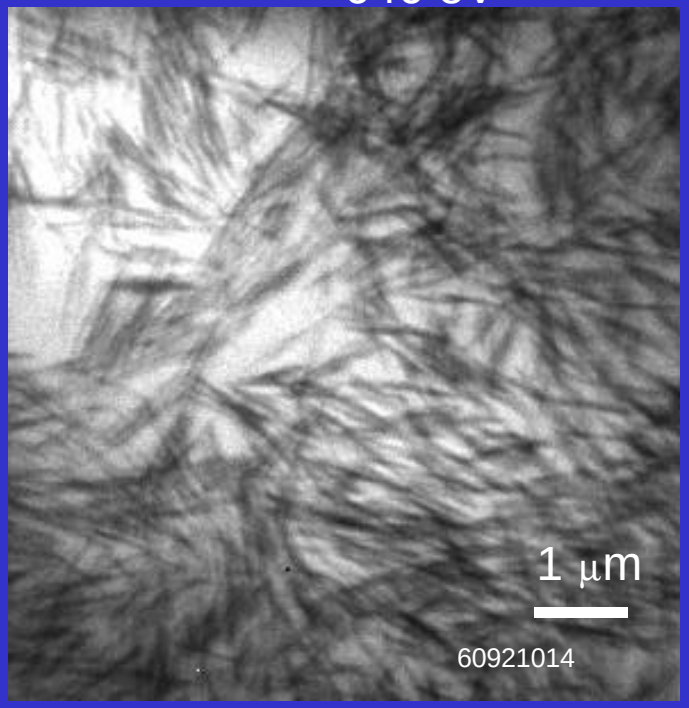
- Jun Kikuma, B. P. Tonner, H. Shin, J. Denlinger, J. Zhang, A. Warwick, 1997

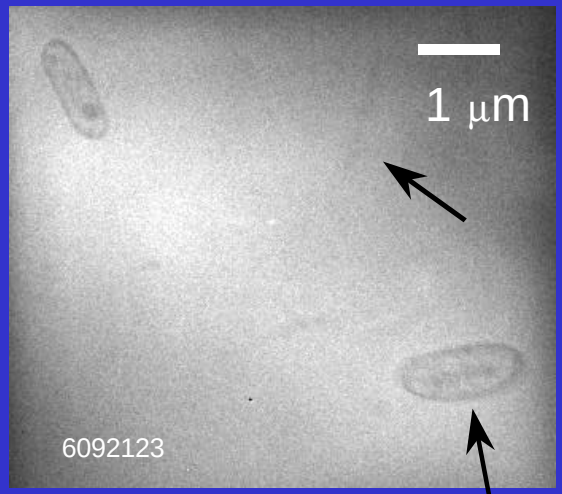
Wet-cell Soft X-ray Spectromicroscopy



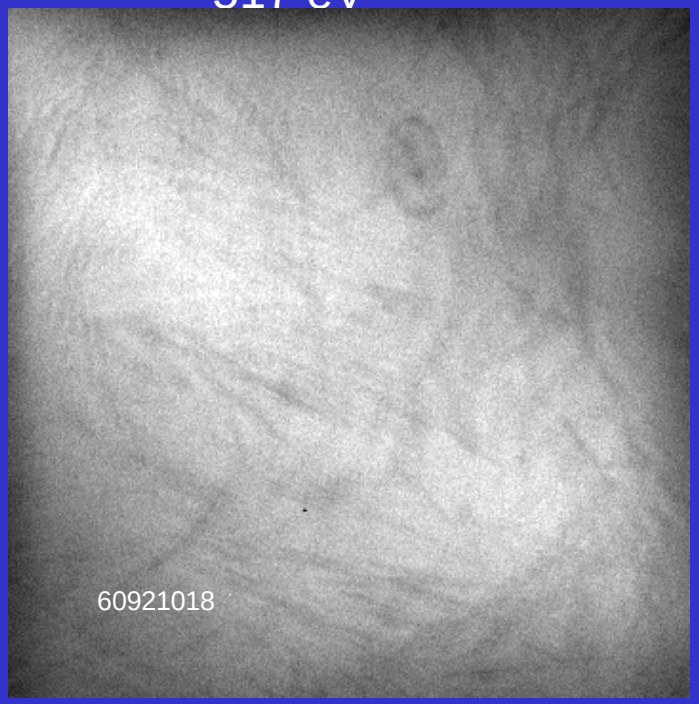
MnOOH (manganite) mineral particles and micro-organisms

646 eV

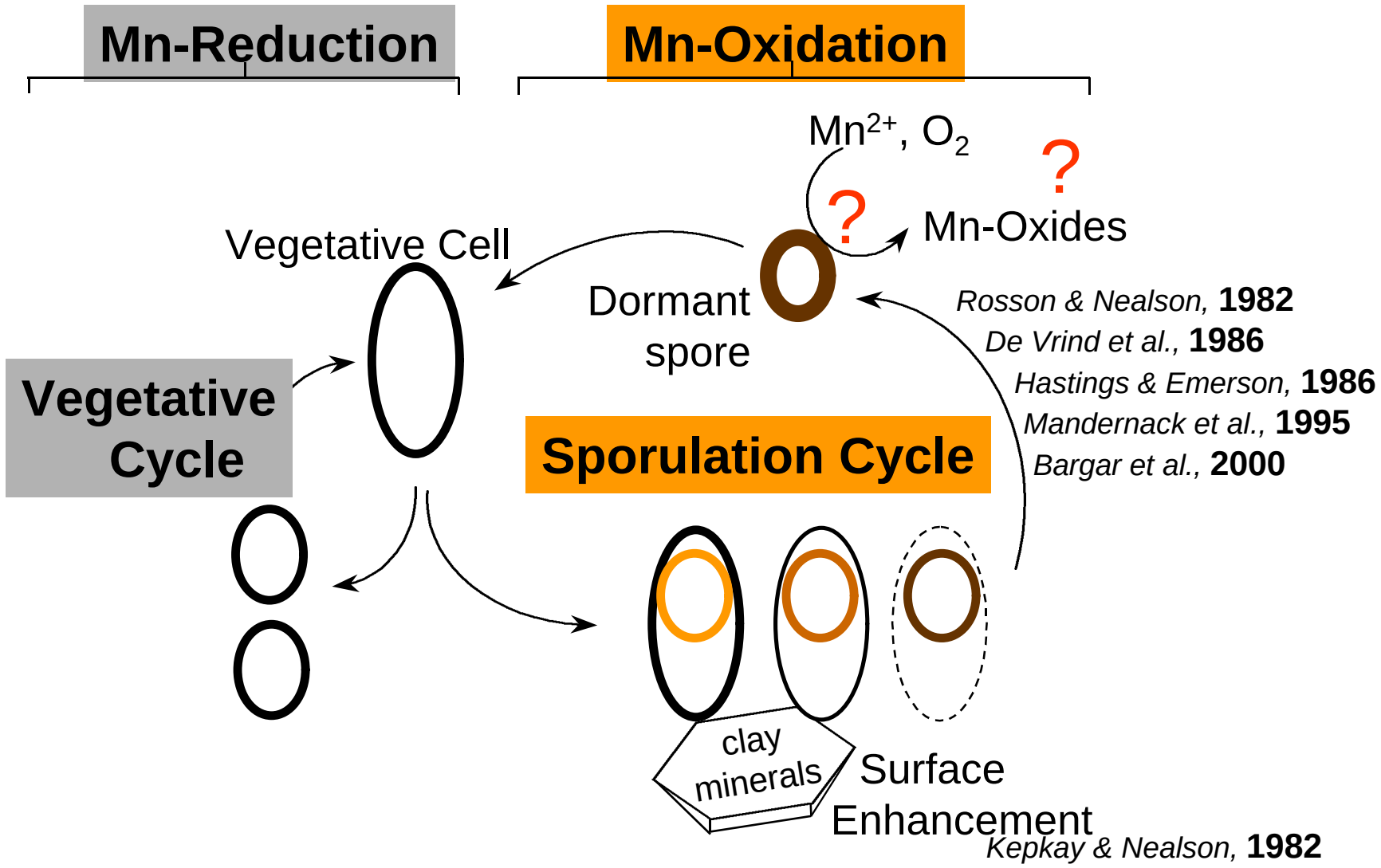




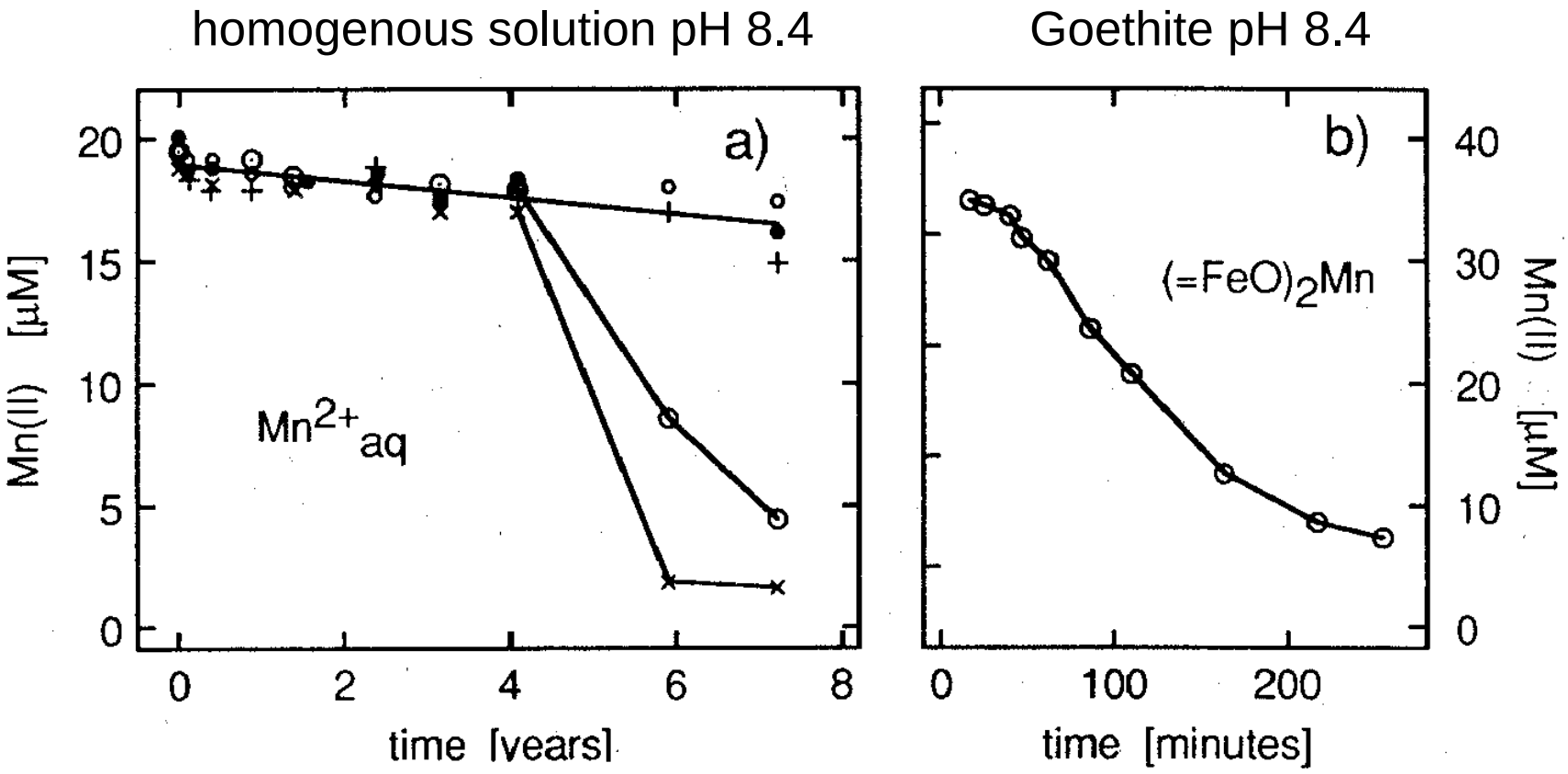
517 eV



The Marine *Bacillus*, strain SG-1



Chemical Oxidation of Mn(II) in the Presence of Water, O_2, and Catalytic Iron (Hydr)Oxide Particles



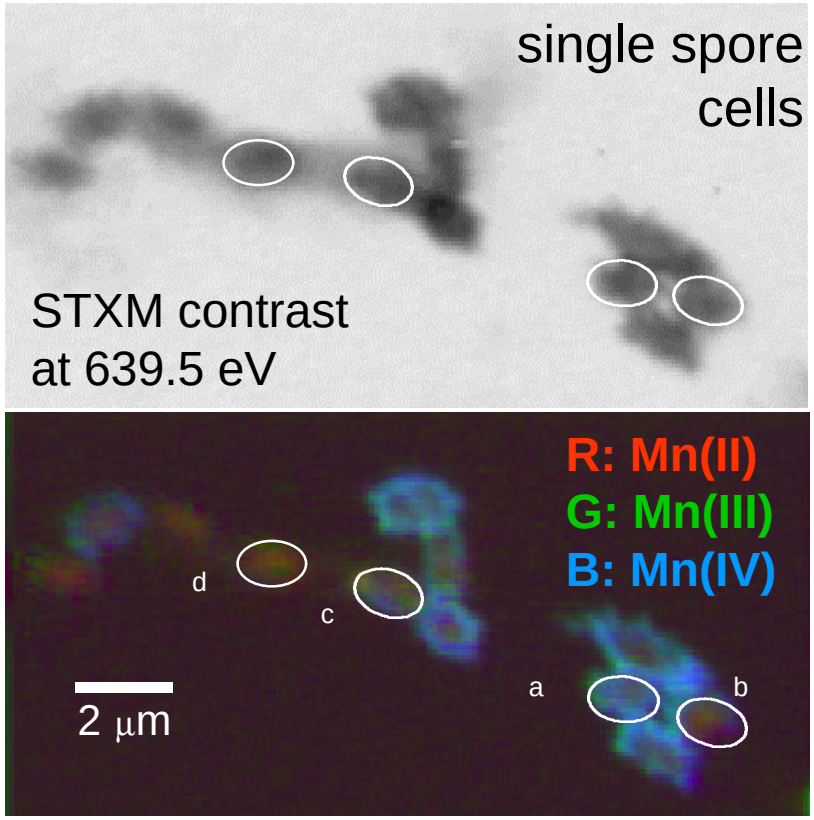
from: Wehrli, B.: *Aquatic Chemical Kinetics (Ed.:* W. Stumm), 1990, p 311ff,
data from: Diem, D., Stumm, W., Geochim. Cosmochim. Acta, 52,1984, 1571
and Davies, S. & Morgan, J., J. Colloid. Interface Sci., 129, 1989, 63

Spore Incubation: Stagnant Batch

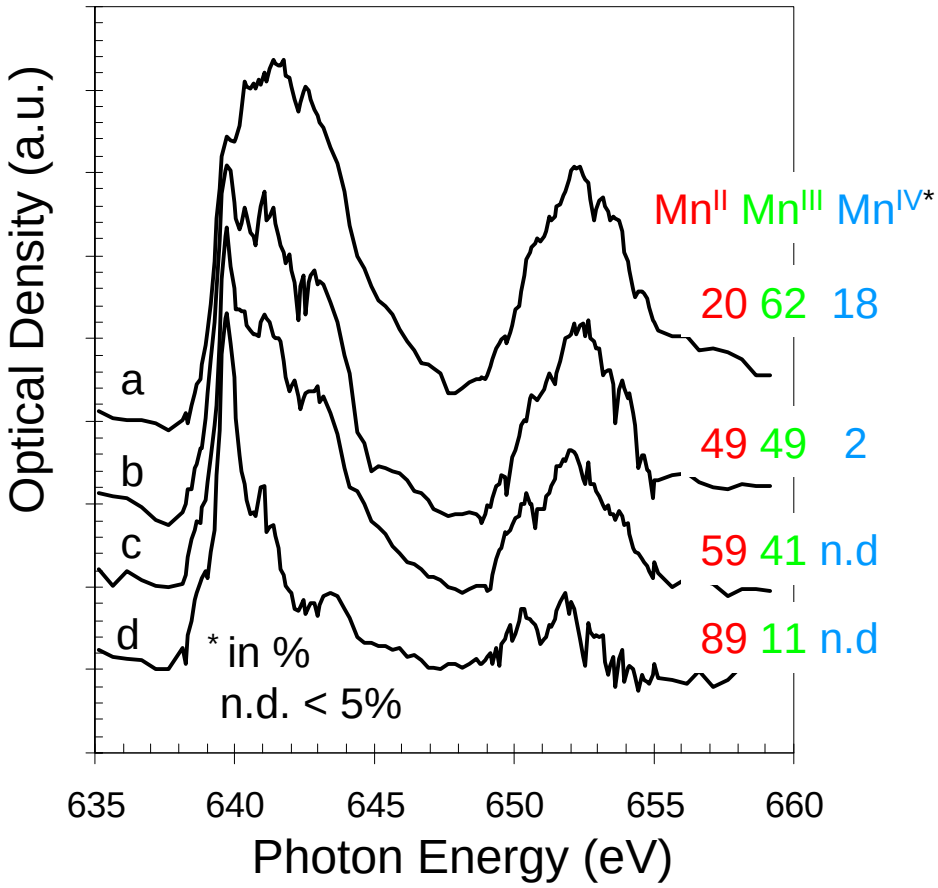
Imaging

$Mn(II)_{tot}$=10 mM
pH = 7.5

XANES

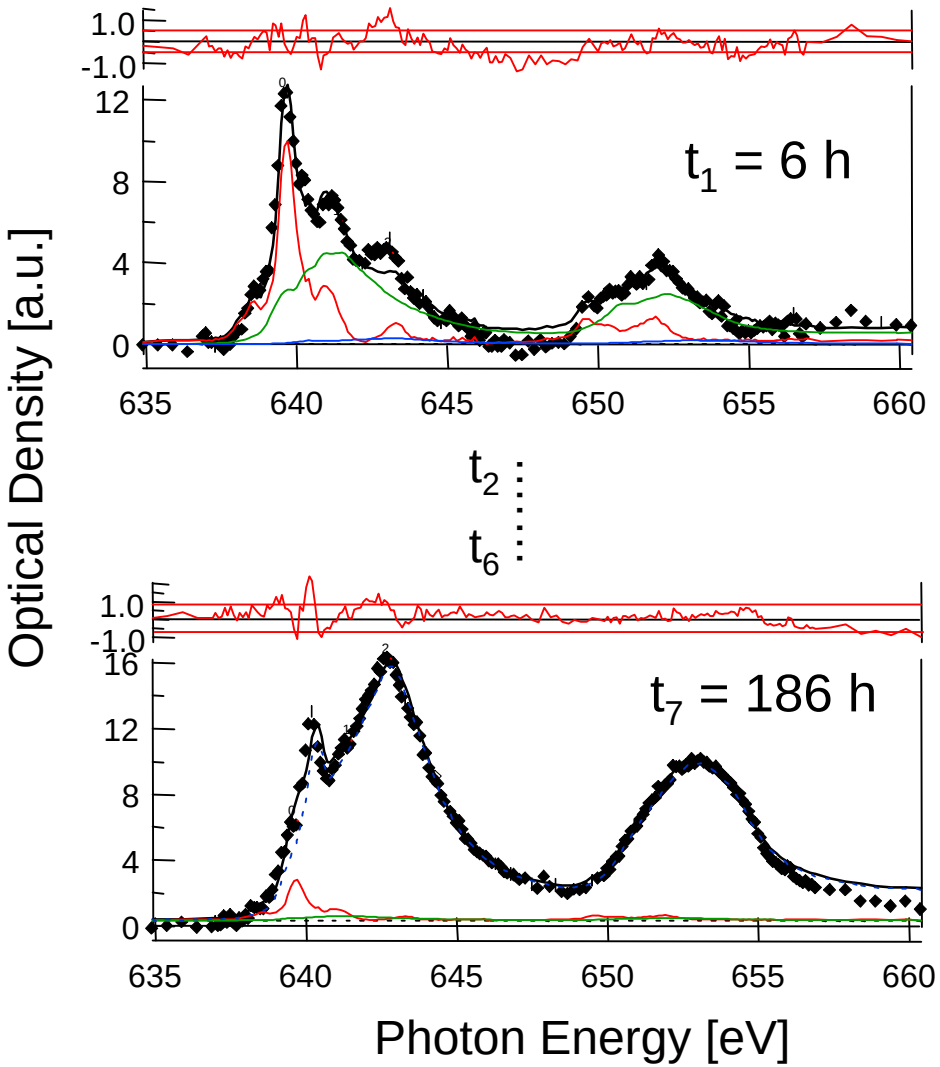


Red-Green-Blue-charge state map



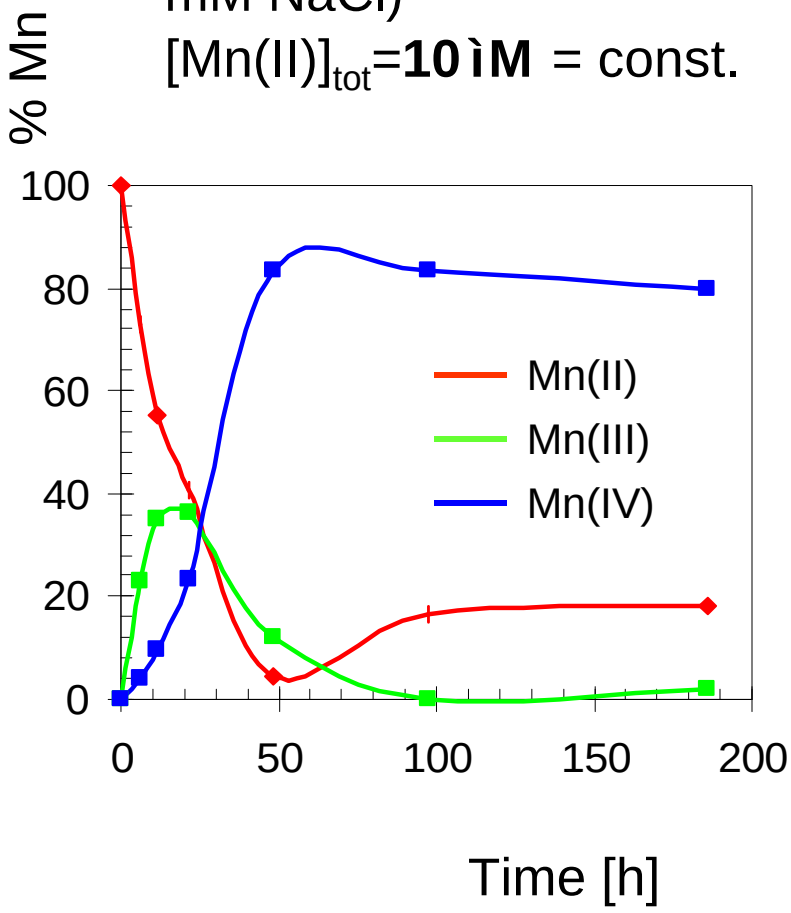
Pecher, K. et al. (2001) Quantitative charge state analysis of manganese biominerals in aqueous suspension using Scanning Transmission X-ray Microscopy (STXM) submitted to Geochimica et Cosmochimica Acta

Continuously Agitated Batch Incubation

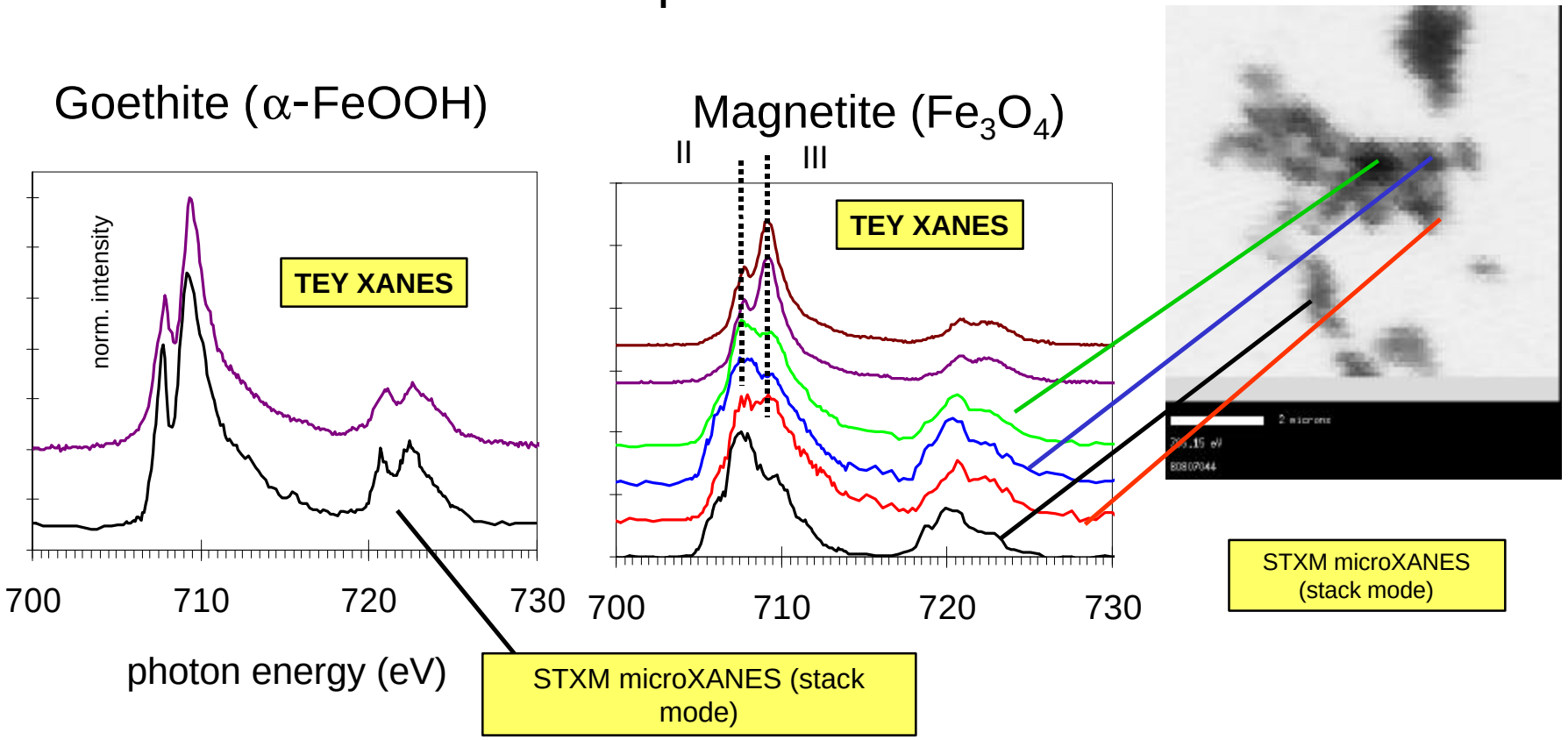


pH=7.8 (10 mM HEPES, 50 mM NaCl)

$[Mn(II)]_{tot}$=**10 ìM** = const.

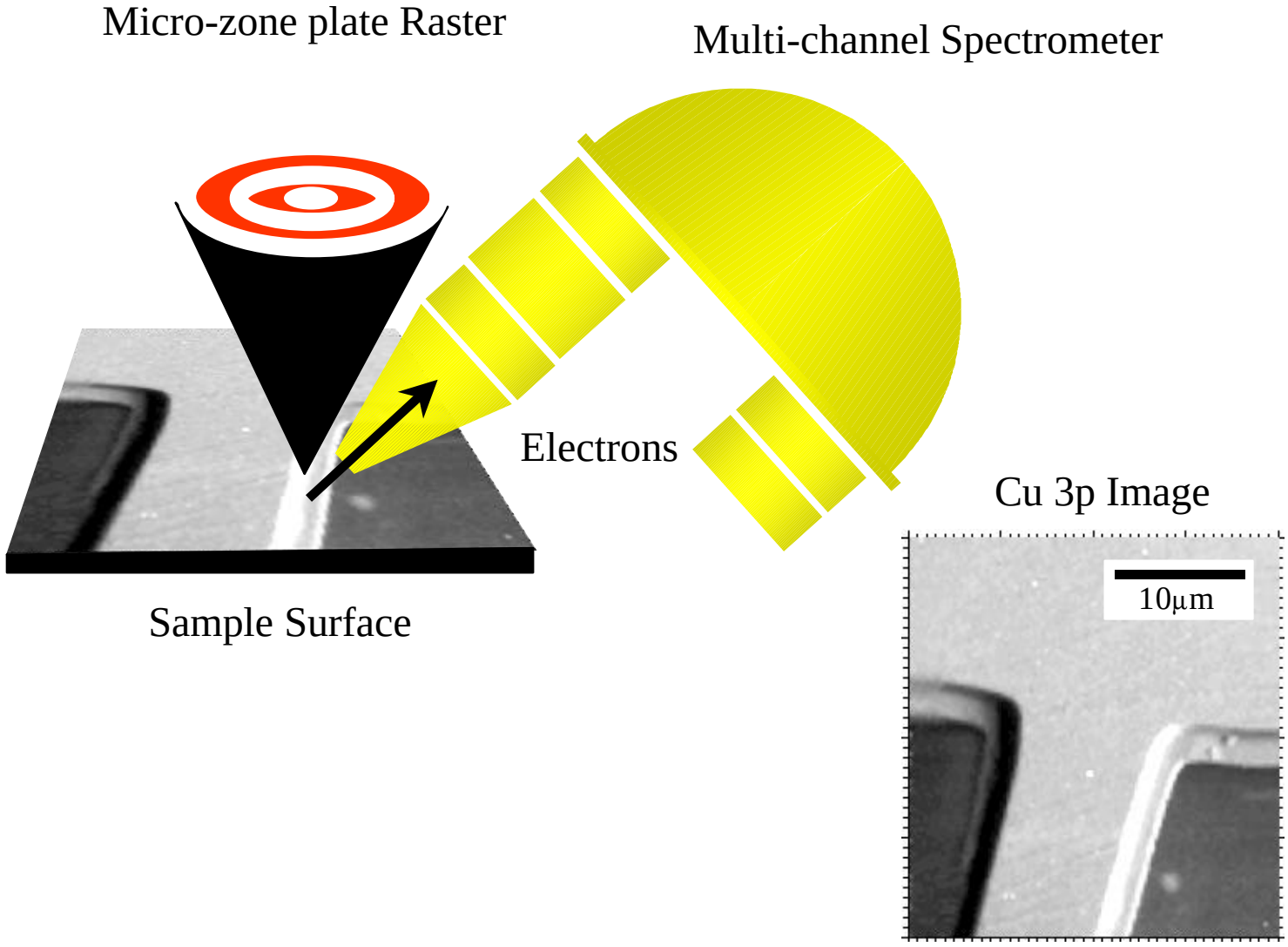


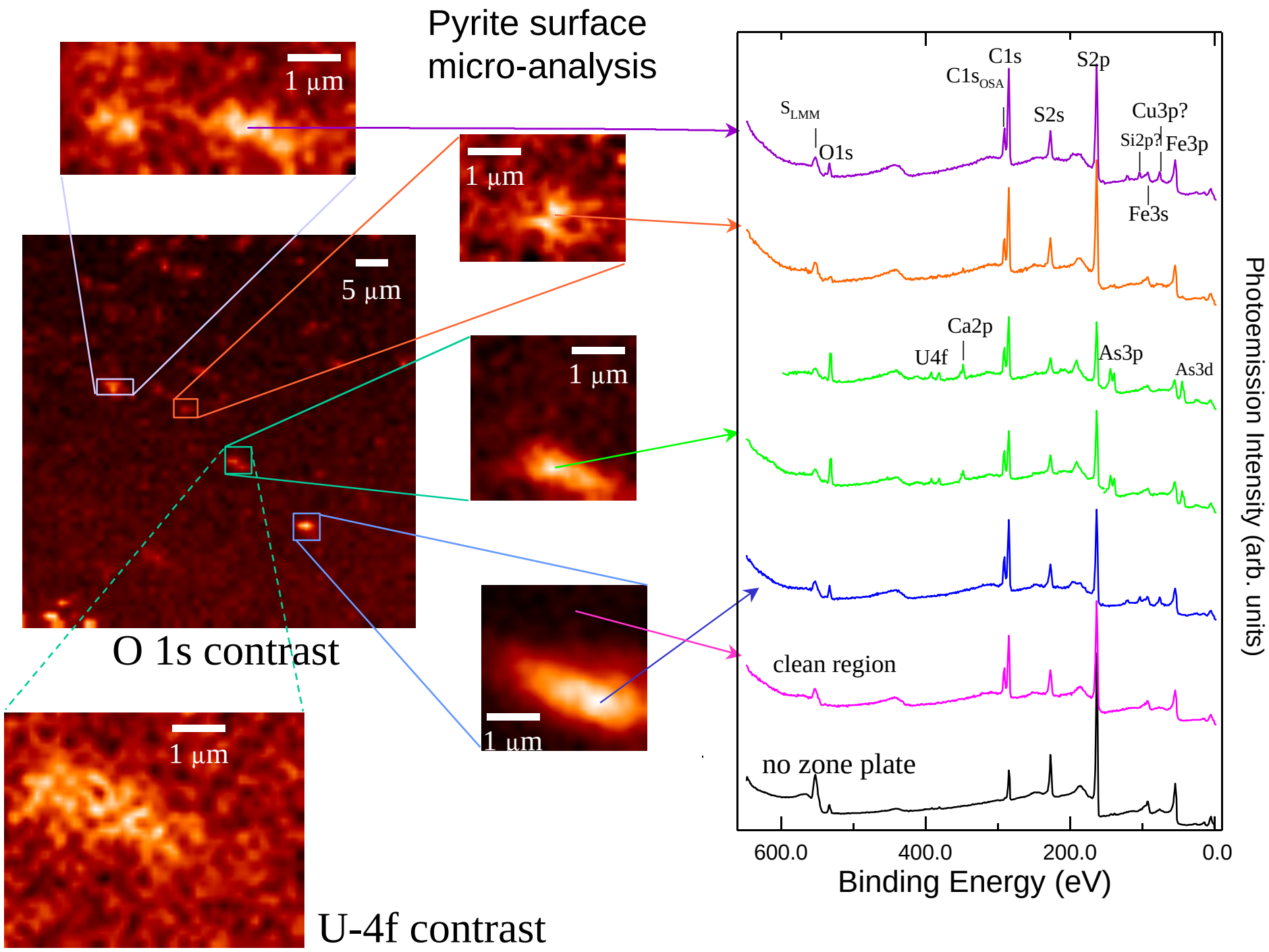
Surface and bulk composition of Fe-oxide nano-particles



Figs. A and B compare total electron yield (TEY) XANES and STXM μ-XANES of two iron oxide minerals. Magnetite which also contains structural Fe(II) seems to be oxidized within a surface near region compared to its bulk composition. In addition, the bulk Fe(II)/Fe(III) ratio varies among single particles of magnetite.

Zone-plate X-ray Photoemission Microscope: SPEM




Pyrite surface
micro-analysis
1 µm
1 µm
5 µm
1 µm
1 µm
1 µm
O 1s contrast
U-4f contrast
C1s
C1s$_{OSA}$
S2p
S$_{LMM}$
S2s
Cu3p?
Si2p?
Fe3p
O1s
Fe3s
Ca2p
U4f
As3p
As3d
clean region
no zone plate
600.0
400.0
200.0
0.0
Binding Energy (eV)
Photoemission Intensity (arb. units)

Future Prospects for X-ray Spectromicroscopy

Opportunities for PhD research

- *Improved spatial resolution by understanding the physics of imaging*
  - Zone-plates slowly improve to 10-20 nm
  - Electron imaging using aberration correction to 5 nm
  - Near-field and other scanning probe techniques to 1 nm
- *Increased use in applied science and technology*
  - Micro and nano-electronics development
  - Environmental applications
  - Biomedical research
- *Novel experiments in basic research*
  - Time and space domain; kinetics of surface reactions
  - Nonlinear optical effects
  - “Nano-spectroscopy”; quantum effects in objects of small size