Soft X-ray Spectromicroscopy in Environmental Science

Brian Tonner, UW-Milwaukee

"Scientific Directions at the Advanced Light Source: Environmental and Earth Sciences"

- **Description of research programs**
- **The role of soft x-ray spectroscopy and spectro-microscopy**
- **Needs that could be met by the ALS**

Research Programs in Environmental Bio-physics with Soft X-ray Synchrotron Radiation

NABIR Natural and Accelerated Bioremediation Research

DOE/OBER

UW-Milwaukee
JPL/Cal Tech
Stennis Space Center
CXRO, ALS/LBNL

UWM WATER Institute

Episodic Events, Great Lakes Experiment

NSF

DOE, Materials Sciences

UW-Milwaukee
ALS, CXRO/LBNL

Environmental Research with Soft X-rays

- Spectroscopy of liquids: transition metal ion speciation
- Composition of bio-minerals (surface and “bulk”)
  - Micro-nodules and macro-nodules
  - Microbially induced corrosion of stainless steels
  - Suspended sediment particles
  - “Green rust” and related “exotic” TM compounds
- High resolution imaging of mineral-microbe interactions
  - Clays, fully hydrated
  - (Mn,Fe) oxidizers and reducers
- Atomic structure of adsorbates on mineral surfaces
  - Transition metals and actinides on oxide surfaces
  - Mineral-water interfaces
- Astro-biology: spectromicroscopy of extraterrestrial minerals

Spectromicroscopy reveals unanticipated environmental chemistry.

Mn Distributions in Micronodules Produced by Bacterial Bio-mineralization

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T. Grundl, K. H. Nealson
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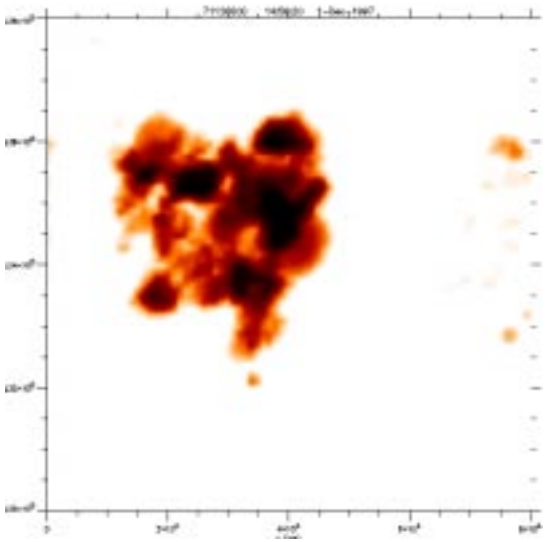
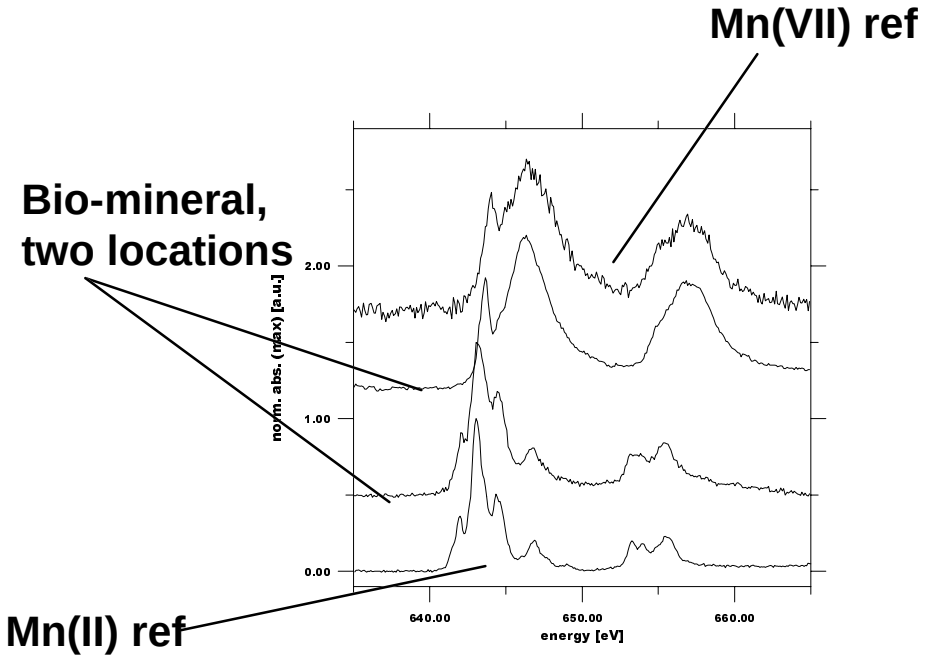
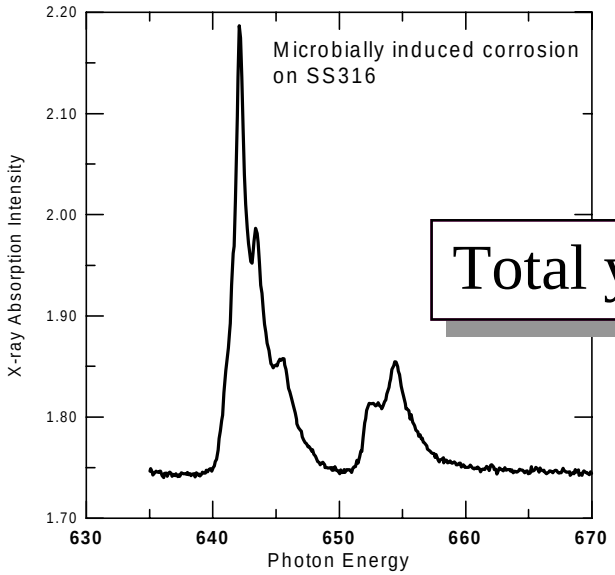


Fig. 1: Scanning X-ray micrograph (20µm×20µm) of Mn micro nodules.



- **Mn valence is inhomogeneous**
- **Predominance of Mn(II)**

Microbially Induced Corrosion: Identification of Mn(II) products on 316SS by SXAFS

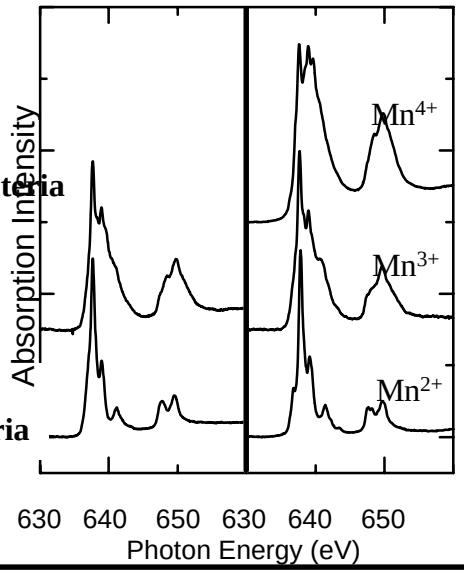


Total yield

Message: must be able to vary surface sensitivity with environmental samples.

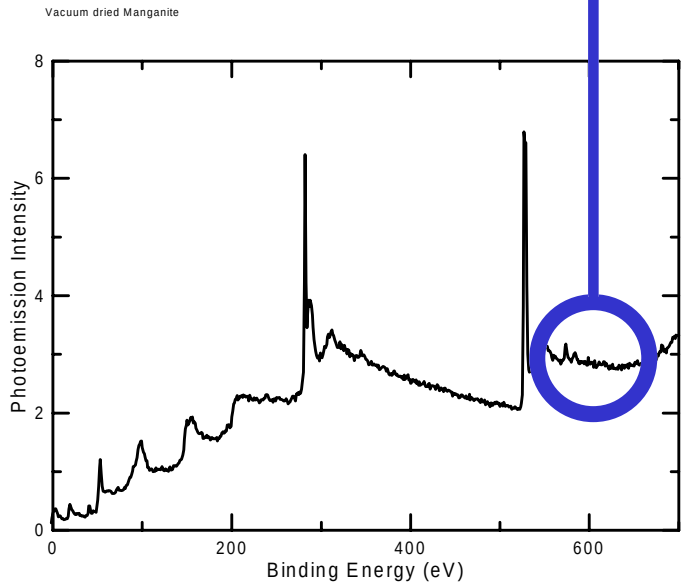
MnO_2, MR4 reducing bacteria

Mn nodule, oxidizing bacteria

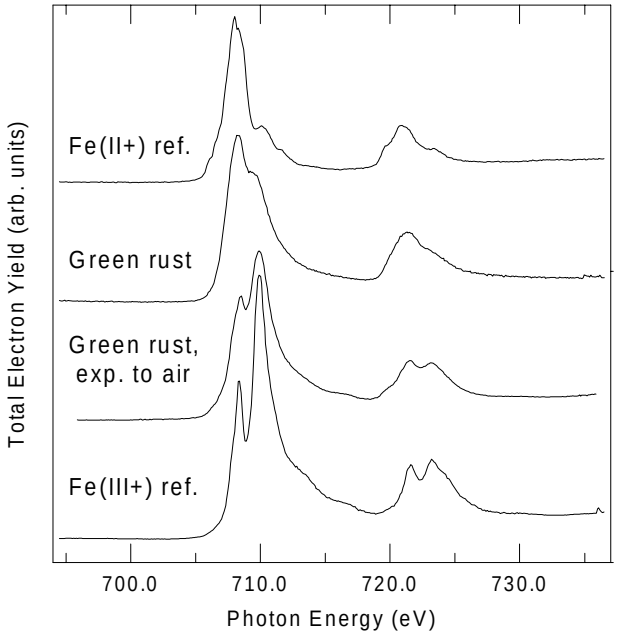


Reference SXAFS

Mn XPS



Spectroscopy of environmental compounds to identify atomic structure



The "Green Rust" problem

Mixed valence Fe(II,III) compounds have been proposed as surface species on soil particles, clays, and in some man-made precipitates. We have identified a unique soft x-ray spectroscopic signature for these compounds.

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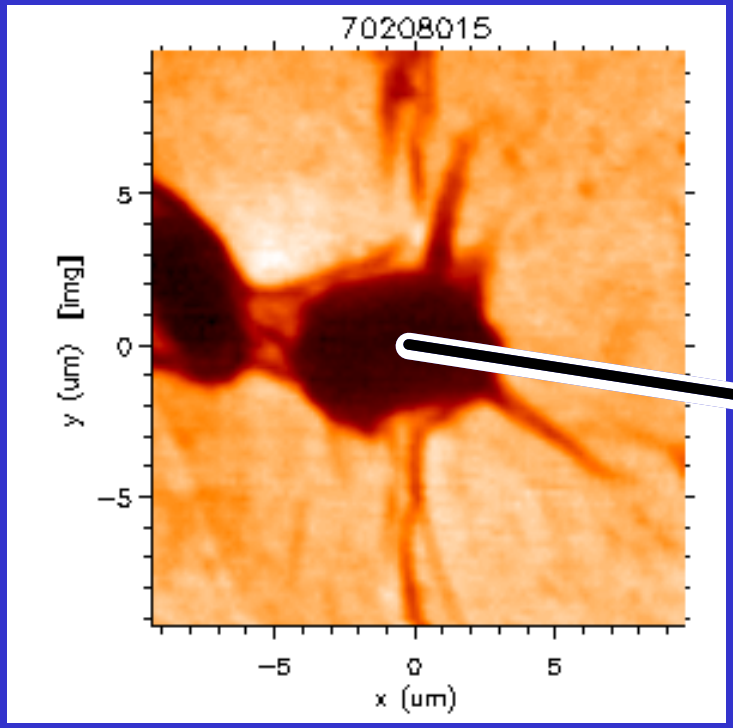
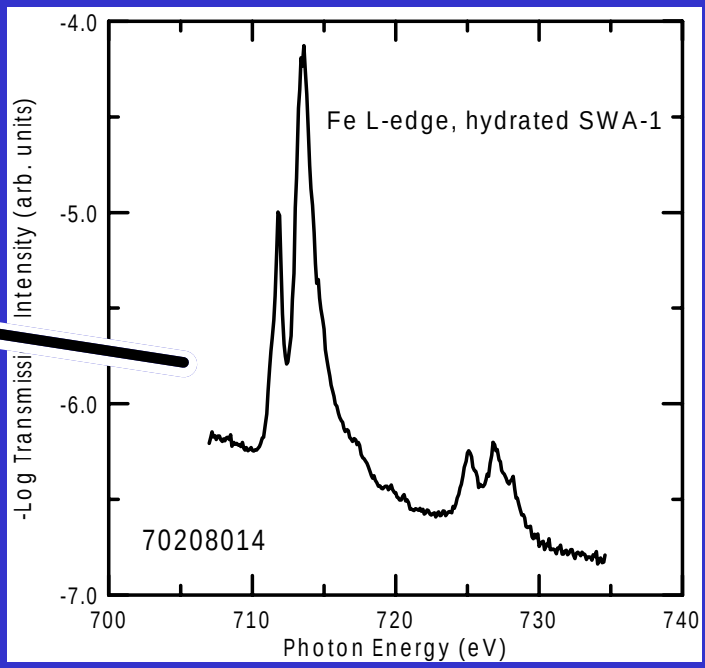
Soft x-ray techniques are well suited to the study of natural specimens.

Spectromicroscopy of Fe-doped hydrated clays

Image of hexagonal alumino-silicate clay particle doped with Fe, wet.



Spectrum from 0.2 micron area in center of crystallite.



- Can image clay micro-crystals in natural, hydrated state.
- Can determine distribution of dopant atoms, and determine the chemical species in the hydrated state.

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High resolution imaging of spatial relationships between minerals and microorganisms

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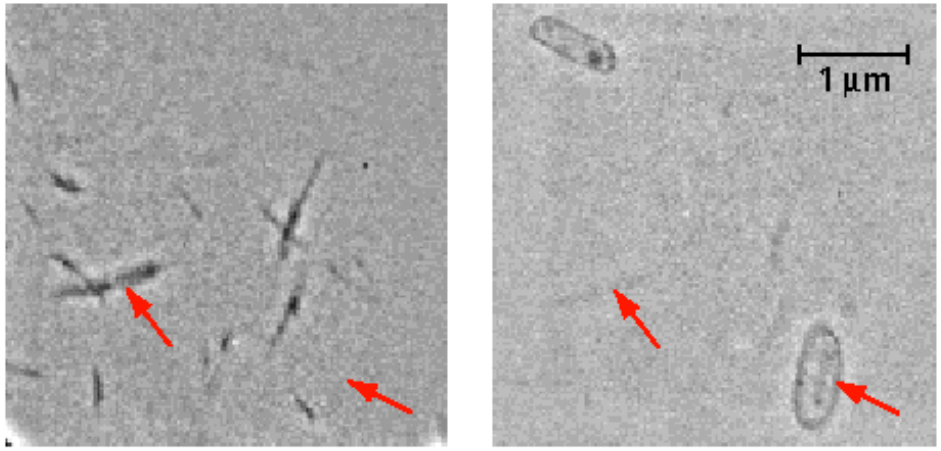
Fig 4: Images of a mixture of manganite needle particles and bacteria, taken at a wavelength that shows only the mineral (646 eV, LEFT) and at a wavelength that shows only the bacteria (517 eV, RIGHT).



646 eV 517 eV

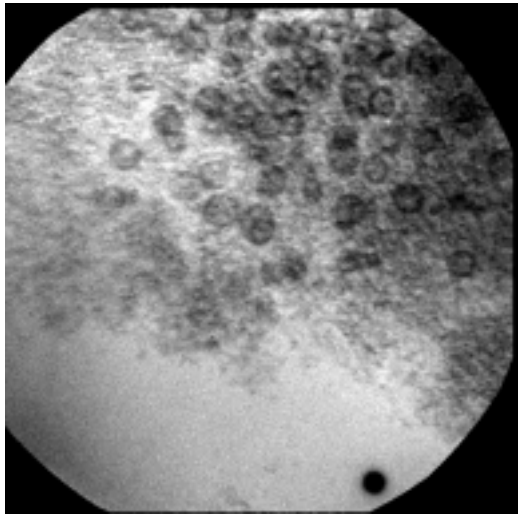


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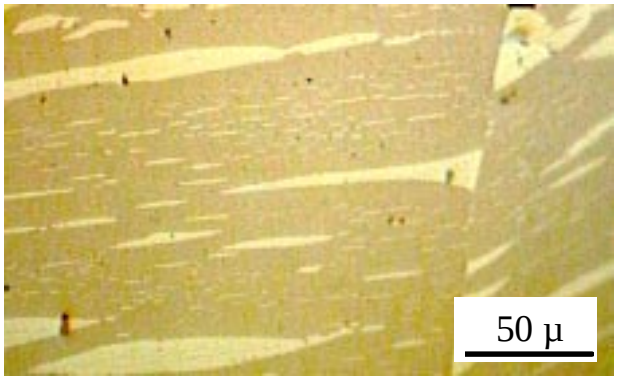
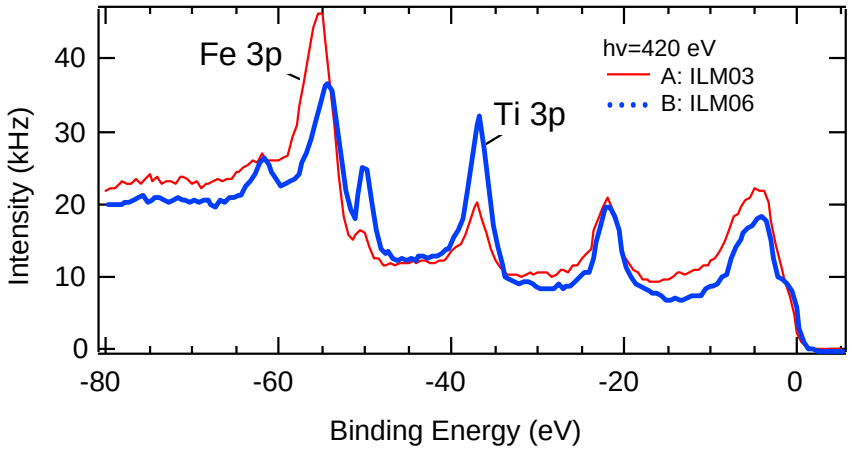
Fig. : X-ray micrograph of *S. Putrefaciens* oxidizing bacteria (dark ellipses) creating Mn-oxide precipitates (lighter material). Field-of-view 10 microns.

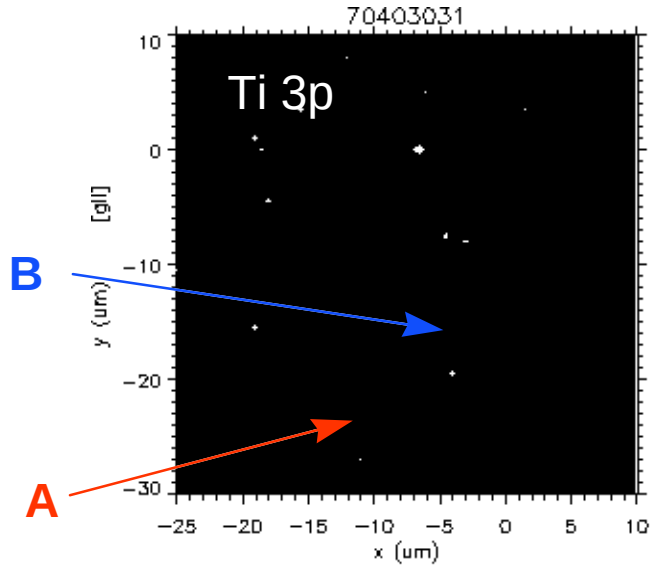
IMAGES FROM CXRO XM-1

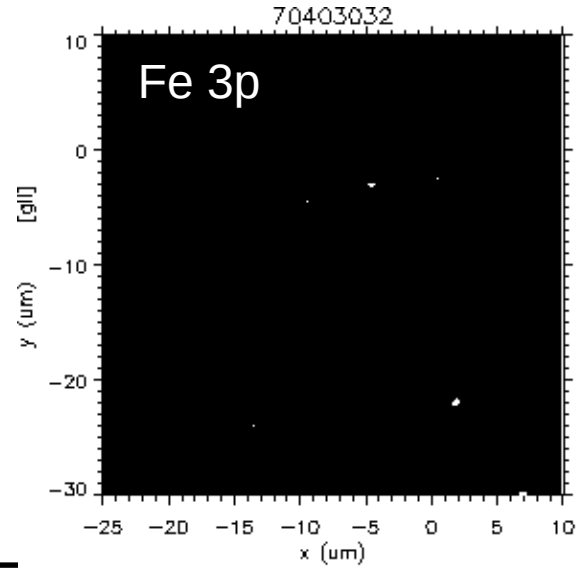
Surface Chemistry of Inhomogeneous Minerals by microESCA: Ilmenite

Optical Microscope (50X)





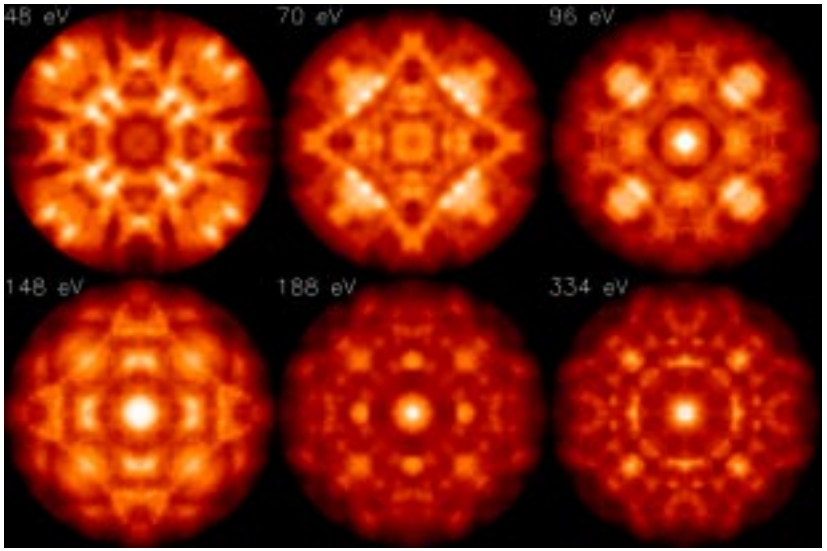




Atomic structure of adsorbates on mineral surfaces

Application of sophisticated surface science structural techniques to interfaces of environmental importance.

- **Mineral-water interfaces**
- **Actinides and transition metals on oxides**



XPD images of the S 2p core level of clean PbS(001).

Angle-Resolved Photoemission Study of Galena

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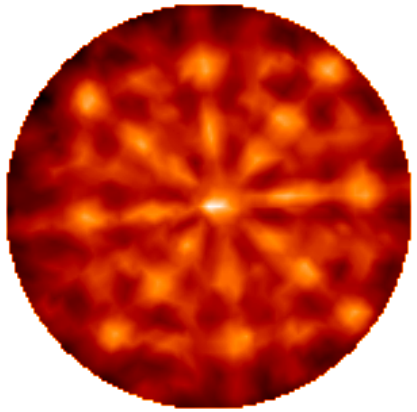


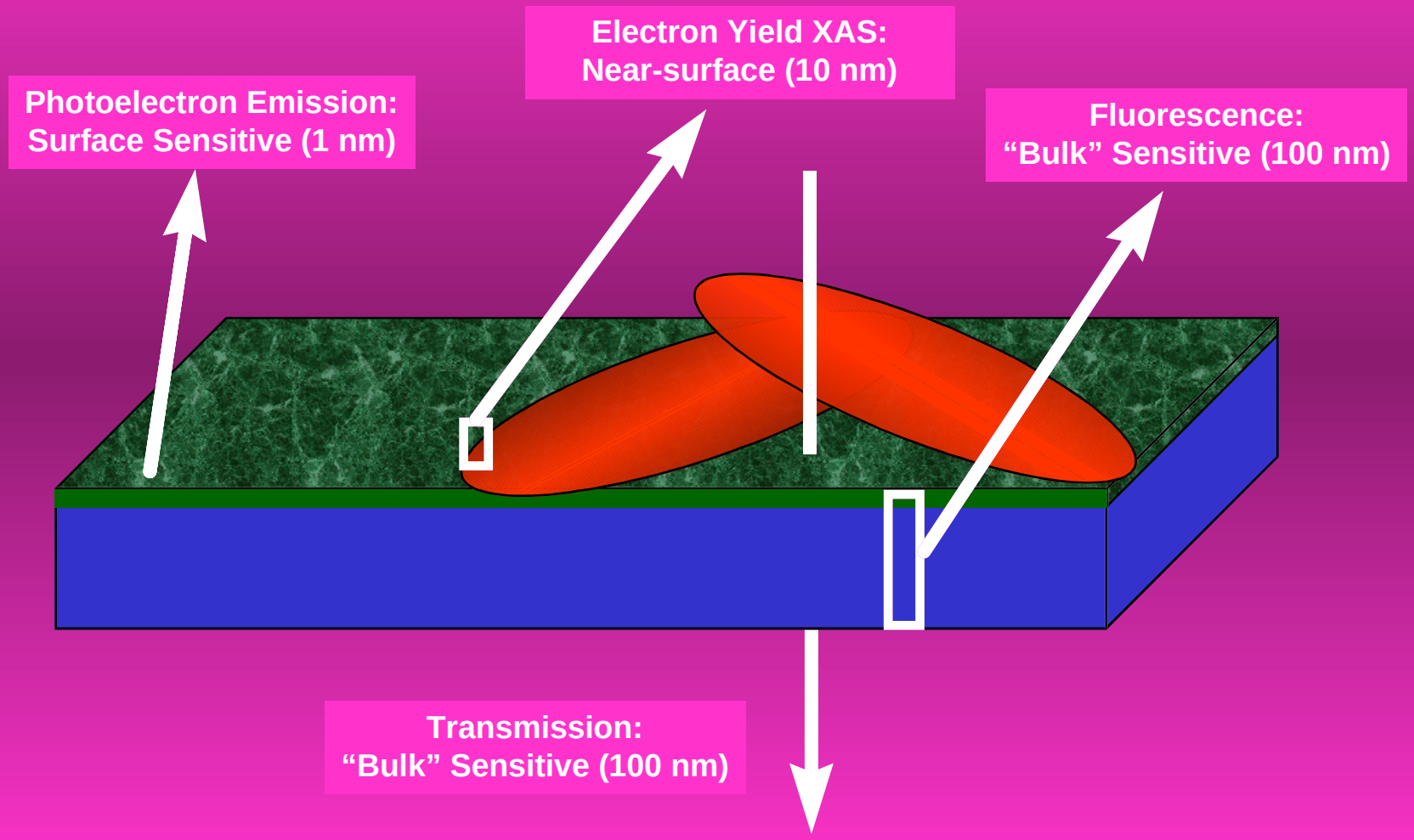
High energy XPD pattern (Al K) of the Pb 4f core-level.

X-ray Spectromicroscopy Experimental Needs in Environmental Sciences

- **Spatial resolution (a microbe is 1 micron)**
- **Spectral resolution and spectral coverage for speciation (0.1 eV)**
- **Sample environments that are relevant (high pressure, aquatic)**

10 Microns	**Tribology (friction and wear)** **Domains in alloys, small crystals** **Corrosion**
1 Micron	**Microbes (bacteria, algae)** **Soil fractions, clay particles**
0.1 Micron	**Composite interfaces, Microelectronics defects,** **Mineral-microbe interfaces, Microbial corrosion**
100 Angstroms	**Single proteins, spectroscopic/functional labels** **Artificial nanostructures** **Magnetic domain walls**

Variable surface sensitivity is needed: this means multiple analytical techniques



Sub-micron Resolution, Spectroscopic X-ray microscopes in the U.S.*†

OPERATIONAL

Location	Type	Energy Range	Scientific program	Total time/year	Outside user/year	Demand factor
NSLS X1 STXM	ZP, XAS	250-600 eV	1. Biology 2.Polymers 3. Soils 4.Exobiology	36 weeks	18 weeks/year	>2X
NSLS X1 Cryo-STXM	ZP, XAS	250-600 eV	Cell biology	9 weeks	2 weeks/year	NEW
NSLS X1 SPEM	ZP, XPS	250-600 eV	Materials/surface science	32 weeks	8 weeks/year	NEW
ALS 7.0 XAM	ZP, XAS	150-1000 eV	1. Materials science 2. Environment 3. Biology	20	10	3X
ALS 7.0 XPM	ZP, XPS	150-1000 eV	Materials/surface science	20	10	
APS 2ID-D/E SRI-CAT	ZP, XAS, XRD, XRF, PCI	2-35 keV	Materials science and biology	18	5	NEW
APS 2ID-B SRI-CAT	ZP, XAS, Holography	0.5 - 4 keV	Materials science and biology	17	4	NEW

Realistic demand: Estimates from NSLS are based on need for up to 1000 images, accumulated at the rate of about 20 per day. Estimates from ALS are based on allocating 20 8-hour shifts (about 3 weeks) to each proposal currently granted beamtime.

*DoE labs only †Contacts: NSLS-Kirz and Jacobsen; ALS-Tonner; APS-Wenbin Yun

Under Construction

Location	Type	Scientific Program
APS PNC-CAT	Capillary	
APS UNI-CAT	ZP, KB	30% time share
ALS	Schwarzschild	'MAXIMUM'
ALS	X-PEEM	Magnetic microscopy

Operating microscopes provide 57 beam-weeks per year of access.

Sub-micron X-ray Spectroscopic Microscopy: some predictions

- **A period of rapid growth in applications is now starting.**
  - –The user friendliness of instruments is improving.
  - –The word is getting out (successful applications).
- **Significant new user communities are now appearing.**
  - –Cryo-microscopy of biological samples
  - –Environmental specimens (mineral-microbe, mineral-water)
- **There is a huge, built-in user community for nano-ESCA**
  - –1000's of ESCA, 100's of 'small-spot', dozens of 'micro-ESCA' installations in the U.S.
  - –Environmental science, materials research, corrosion engineering, microelectronics.

CLAIM: One of the main 'problems' with this field in the next 5 years will be due to not having enough beam-time at all available U.S. installations to meet the needs of even the highly ranked projects. This will lead to a lack of ability to follow-through on projects of major importance in both materials science and environmental sciences.

What can ALS do that is unique?

- The ALS has the brightest soft x-ray undulators in the world
- Soft x-ray undulators make the best sources for spectromicroscopy
- Even now, there is not a dedicated beamline for soft x-ray spectromicroscopy.

Conclusion: Build it.