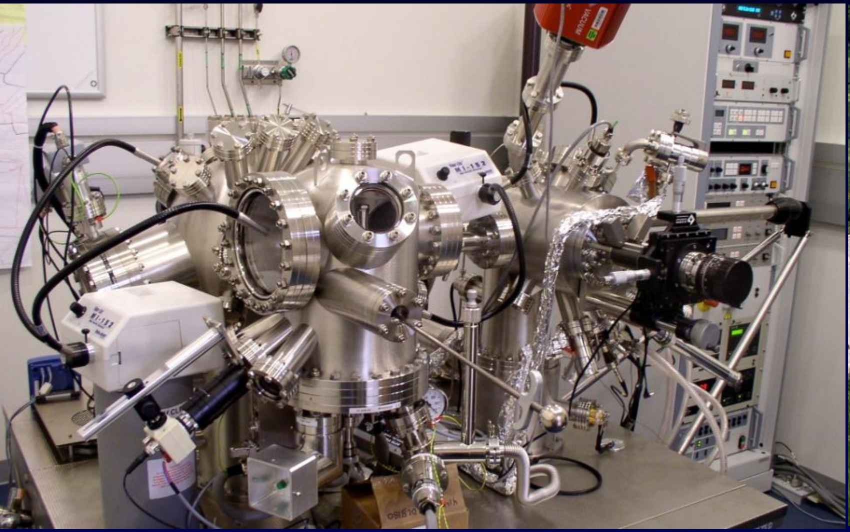
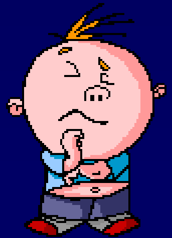
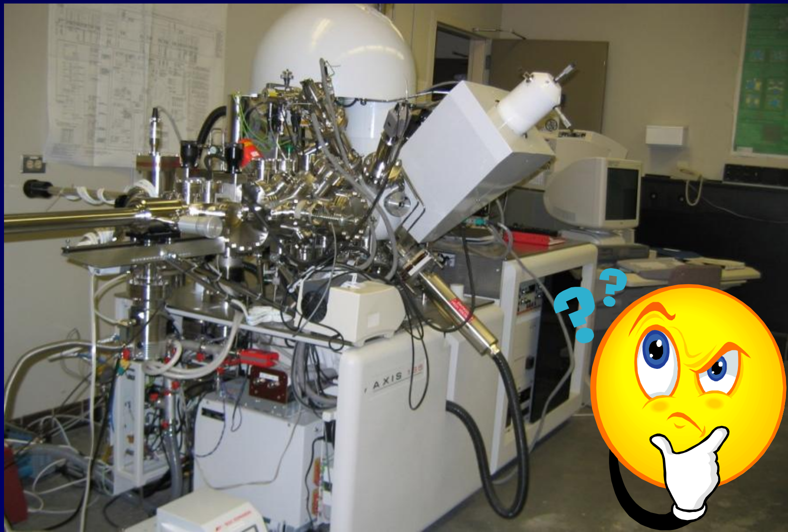
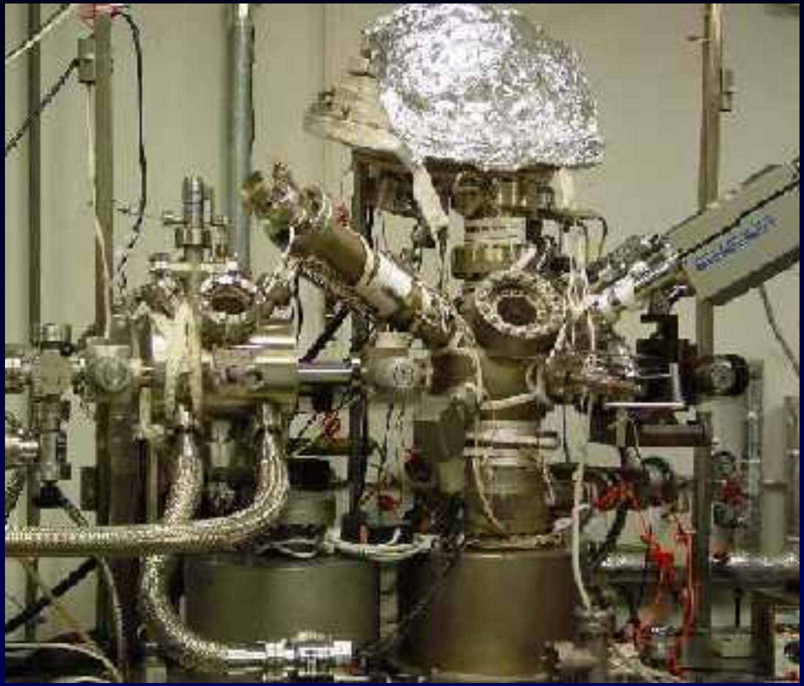
Advanced Tools in Biogeochemistry: A Fast Overview!!



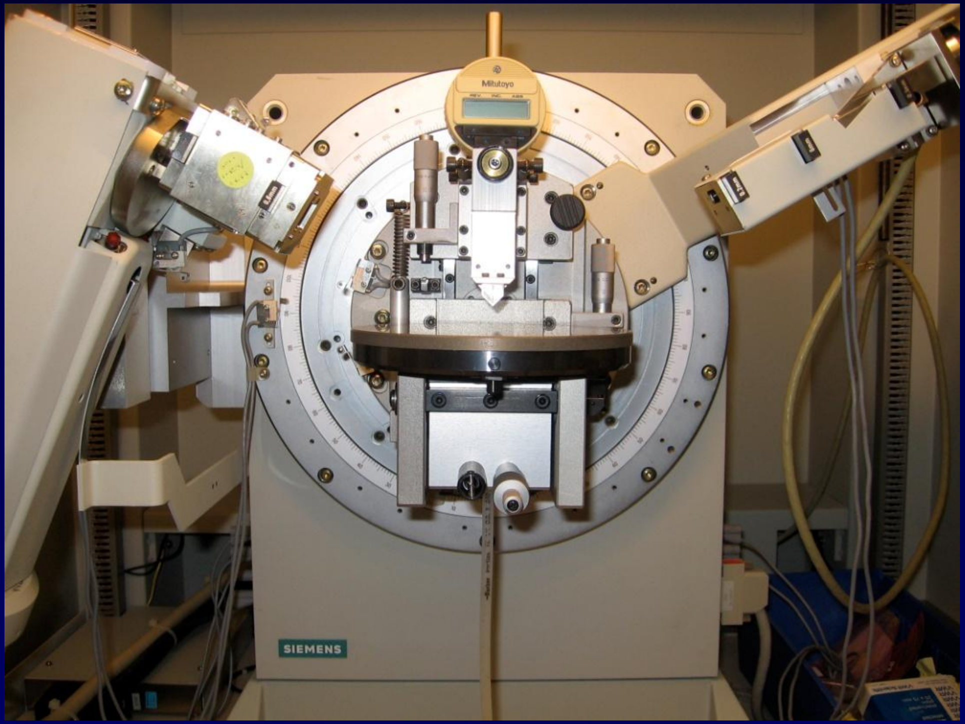




Environmental Spectroscopy and Diffractometry



X-ray Photoelectron Spectrometer(XPS)



X-ray Diffractometer (XRD)

Molecular Environmental Chemistry

- **To predict and model**

1. **Fate and transport**
2. **Toxicity**
3. **Speciation**
4. **Bioavailability**
5. **Risk assessment**

OF plant nutrients, toxic metals, radionuclides, and organic chemicals at the landscape level we MUST have fundamental information at multiple scales, and our research efforts MUST be multi- and interdisciplinary.

Molecular Environmental Chemistry

- **With state-of-the-art analytical techniques such as synchrotron radiation based techniques one can elucidate reaction mechanisms at the molecular scale.**

Synchrotron at Lawrence Berkeley National Lab

Molecular Environmental Chemistry

- **The study of the molecular scale has been one of the major advances in environmental sciences over the past decade**

DEFINITION: Molecular Environmental Science can be defined as the study of the chemical and physical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, and the atmosphere at the molecular level.

Molecular Environmental Chemistry

The application of molecular environmental science has resulted in a number of major frontiers within environmental chemistry

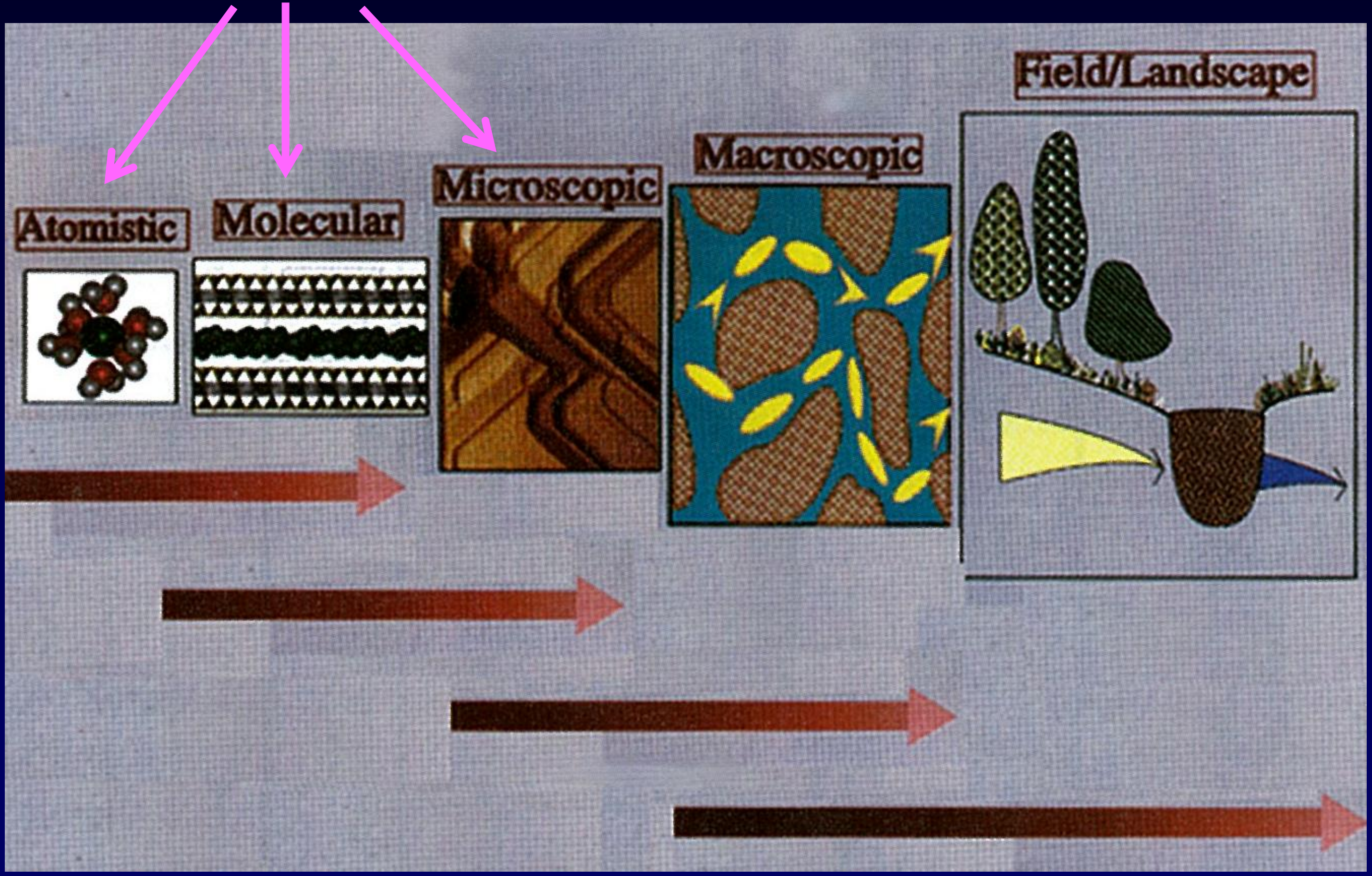
- These include:

1. Speciation of contaminants (which influence sorption)
2. Spatial resolution
3. Chemical transformations
4. Toxicity
5. Bioavailability

… and ultimate impacts on human health; mechanisms of microbial transformation, e.g. bioremediation; phytoremediation; development of predictive models; effective remediation and waste management strategies; and risk assessment.

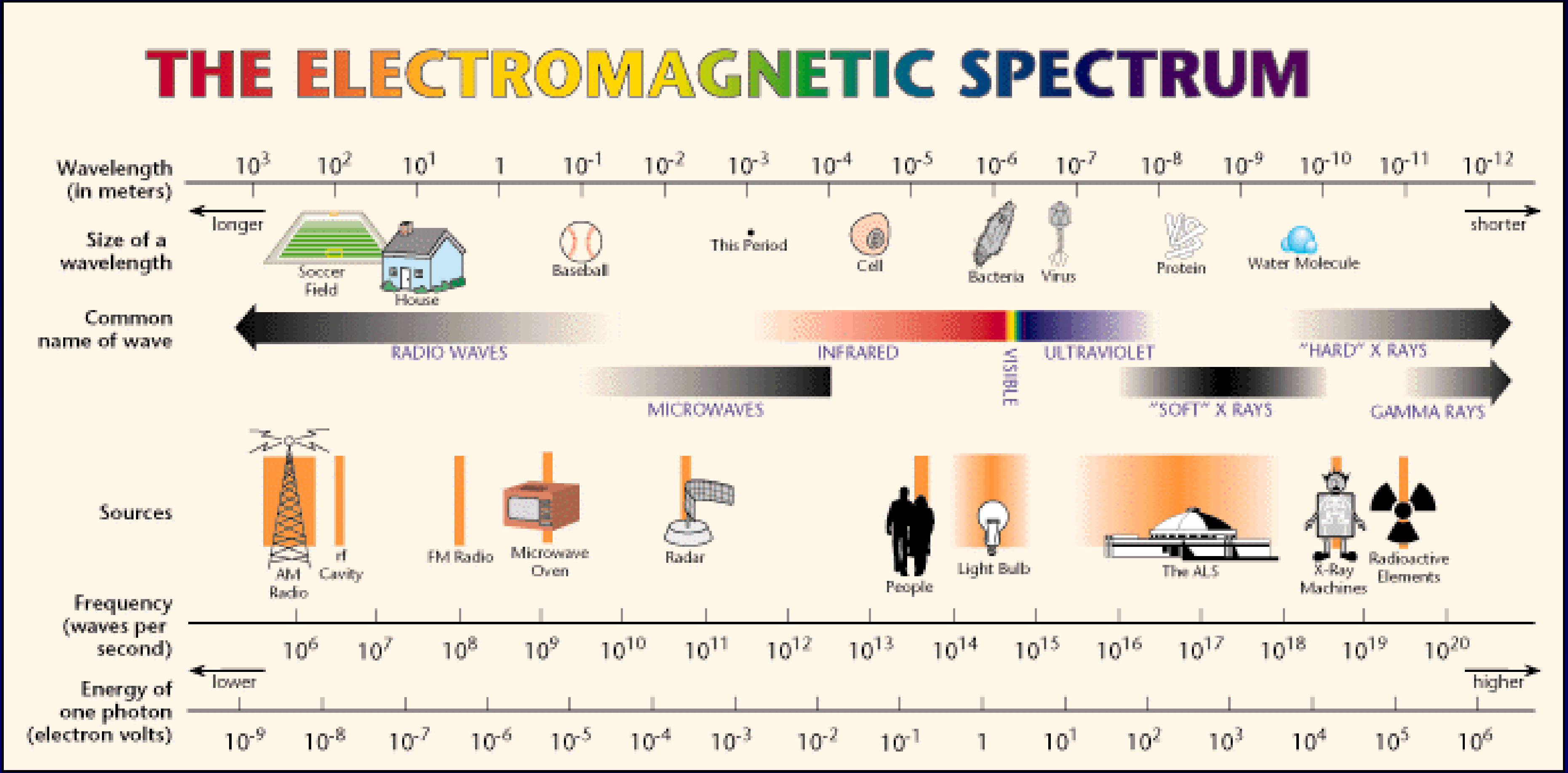
Spatial Scales of Interest for Environmental Scientists

The focus of this lecture



Electromagnetic Spectrum of Light

- Electromagnetic radiation has both particle and wave properties such that light at a particular wavelength corresponds to a particular scale of detection.
- Light employed to see an object must have a wavelength similar to the objects size.



Using Light in Chemical Analysis

Here are a few examples:

-**Infra-red spectrophotometry** - is used to determine the presence of distinct functional groups in organic molecules. IR radiation causes them to vibrate at various frequencies, allowing us to identify them.

-**Ultra-violet/Visible spectrophotometry** - is used primarily to identify how much (quantitative analysis) of a substance is present, usually in a solution. The color absorbencies are used with the Beer-Lambert Law.

- **X-ray spectroscopy** - is used in surface science or environmental science to analyze the top few atomic layers of a substance and determine chemically what elements are present and occasionally what the structure is.

Molecular Scale Techniques

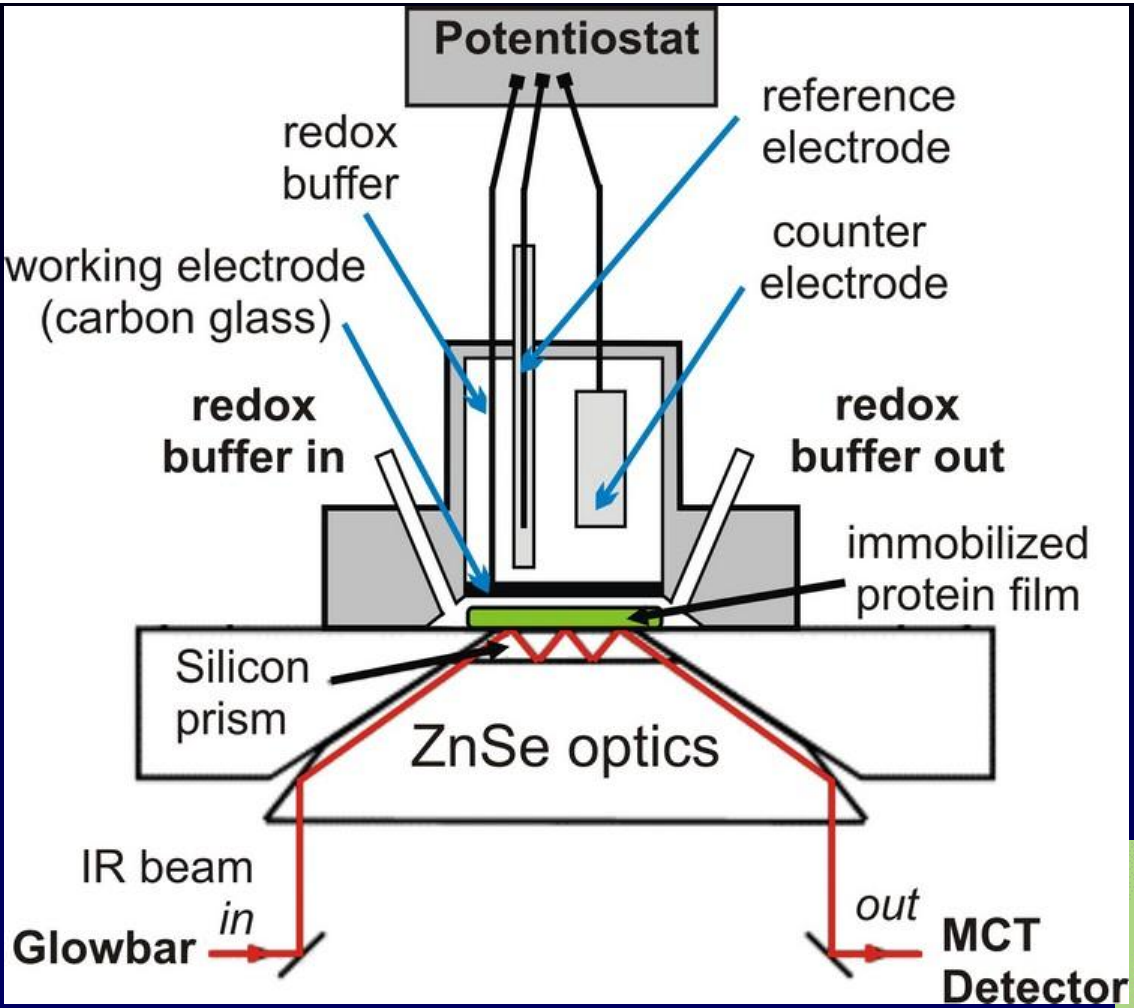
Analytical Method	Source	Signal	Chemical Information	Notes
IR and FTIR	Infrared radiation	Transmitted IR radiation	Molecular and lattice vibrations; local bonding (first neighbor)	Nonvacuum; bulk liquids, crystalline and amorphous solids
Synchrotron XAS (XANES and EXAFS)	Synchrotron X-rays	Transmitted or fluorescent X-rays; electron yield	Quantitative local structural information; oxidation state and atomic bonding geometry	Nonvacuum; element specific; liquid, crystalline, and amorphous materials
Synchrotron microanalysis (XRF, XANES)	Synchrotron X-rays	Fluorescent X-rays	Elemental analysis (XRF); oxidation state and atomic bonding (XANES)	Vacuum or nonvacuum; spatial resolution, element specific, crystalline and amorphous materials

FTIR

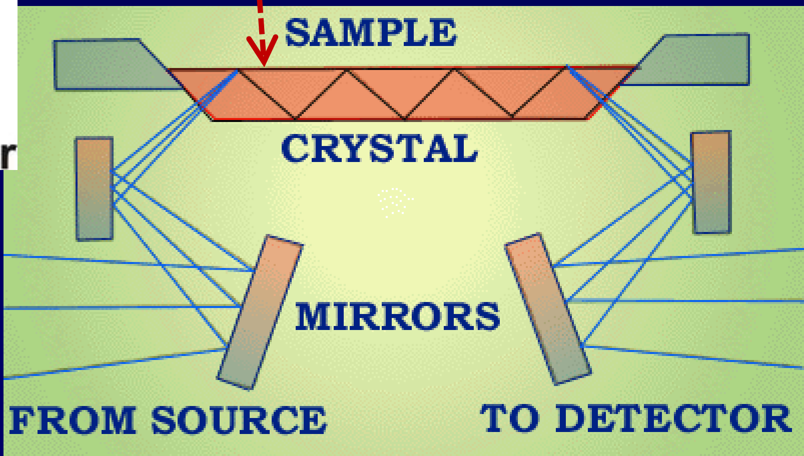
Infrared (IR) spectroscopy

- **Has been used for soil chemical processes (e.g. sorption) and reactions (kinetics). Provides information of the nature of the functional groups and nature of chemical bonds.**

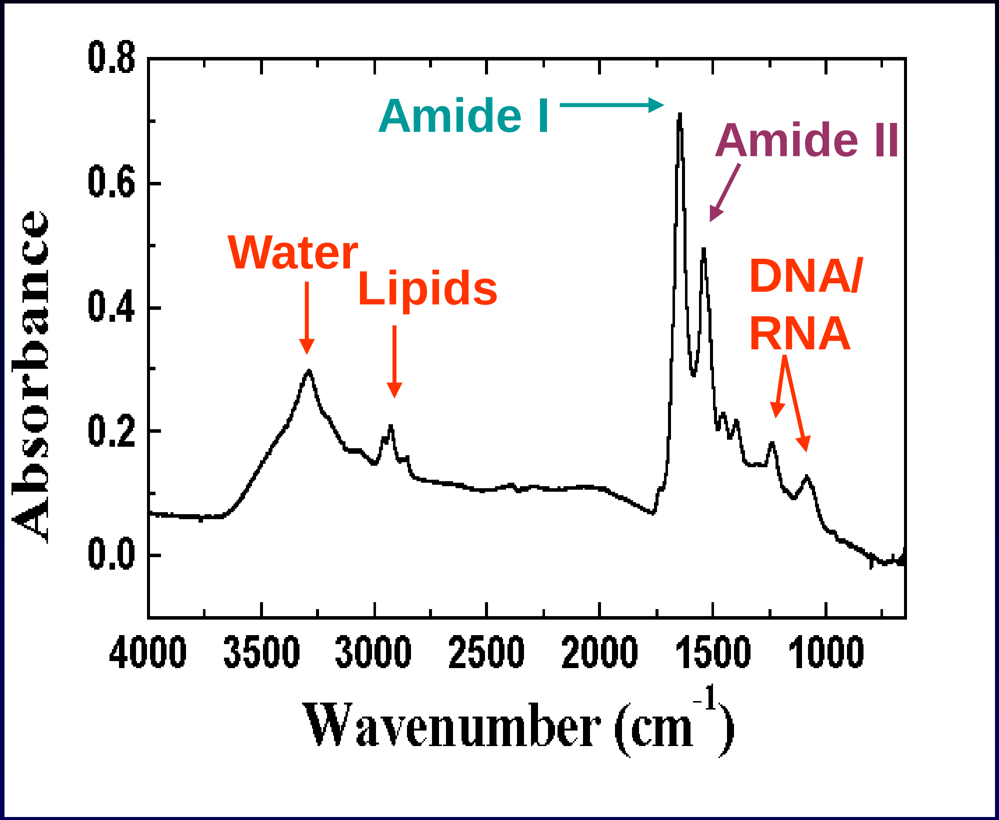
ATR-FTIR with Redox Batch Setup

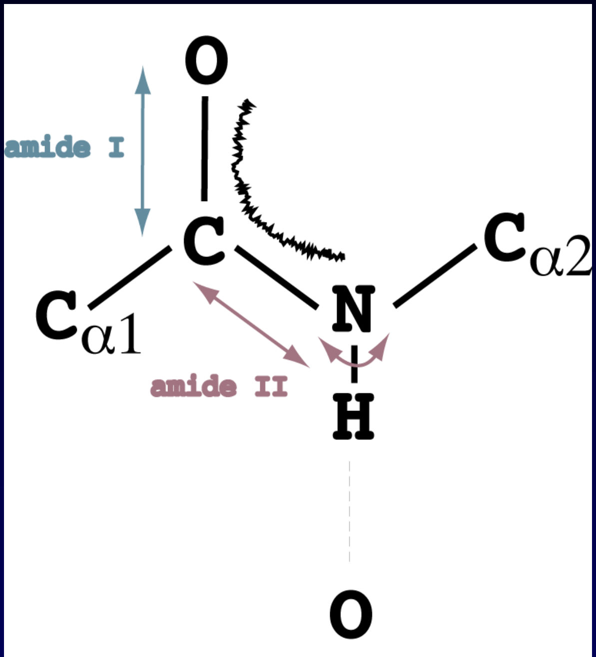


ZnSe crystal



Infrared Spectrum of a Biological System





Typical IR absorbance positions:

Protein Amide I:	1690-1600
Protein Amide II:	1575-1480
Lipid $=CH_2$:	3100-3000
Lipid $-CH_2$, $-CH_3$:	3000-2850
Nucleic Acid $-PO_2^-$:	1225, 1084

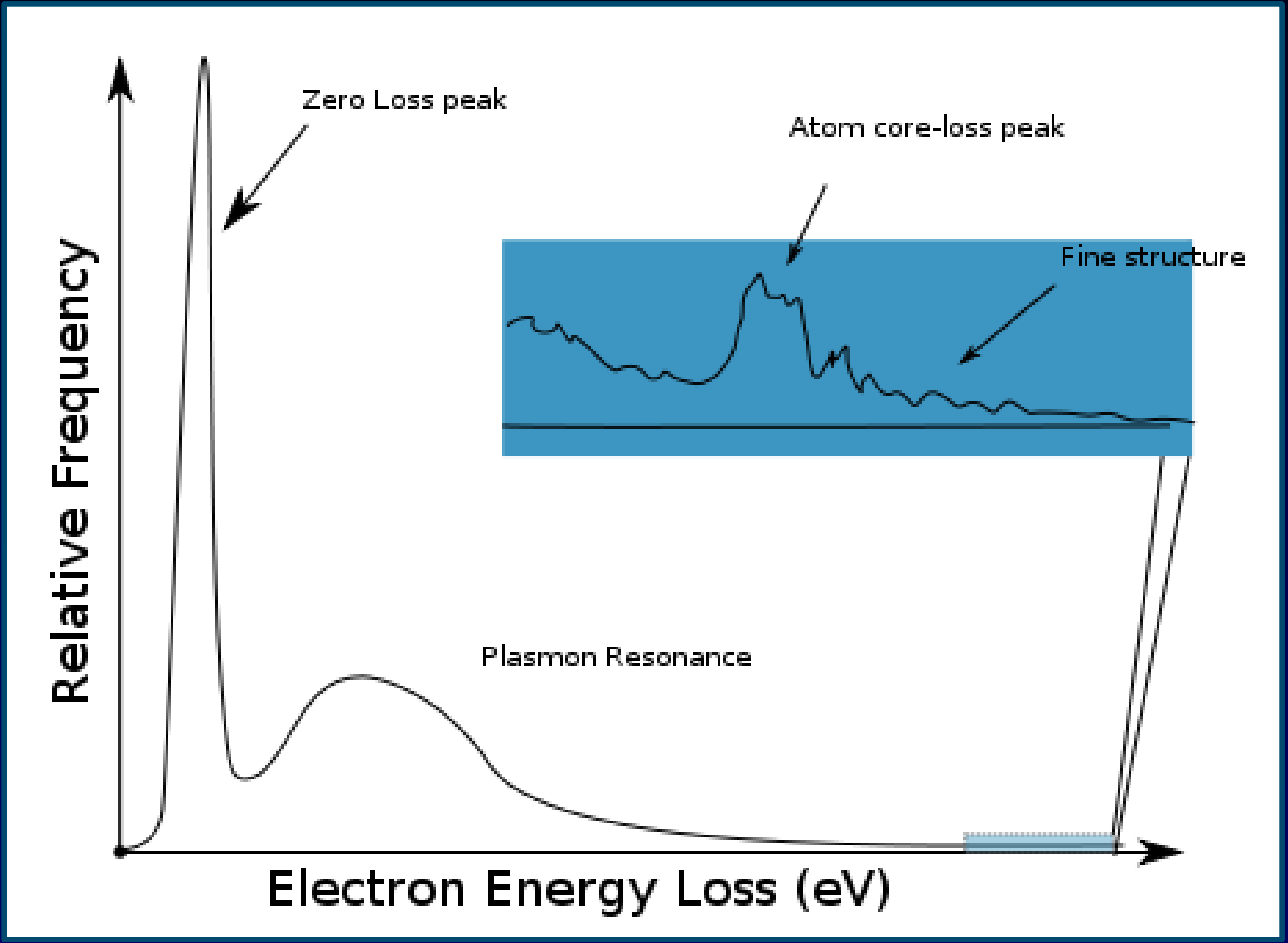
The peak positions of Amide I and II are sensitive to the protein secondary structure (a-helix, b-sheet, random coils, etc.)

(http://infrared.als.lbl.gov/)

Molecular Scale Techniques

Analytical Method	Source	Signal	Chemical Information	Notes
EELS also called PEELS or “parallel electron energy loss spectroscopy”	electrons	electrons	Oxidation state and atomic bonding geometry (similar to XANES)	Vacuum; high concentrations, crystalline and amorphous materials
XPS and Auger spectroscopy	X-rays	electrons	Oxidation state; chemical bonding info	Vacuum; surface sensitive; spatial resolution
NMR	Radio waves (+ magnetic field)	Radio waves	Sensitive to electron density (nuclear shielding); local bonding (first neighbor)	Nonvacuum; bulk liquids and solids; requires NMR-active isotope

Electron Energy Loss Spectroscopy (EELS)



A typical electron energy loss spectrum is shown below. It consists of three parts:

Zero-loss peak at 0 eV:

It mainly contains electrons that still have the original beam energy E_0, i.e., they have only interacted elastically or not at all with the specimen. [no useful info]

Low-loss region (< 100eV)

Here, the electrons that have induced plasmon oscillations occur. Since the plasmon generation is the most frequent inelastic interaction of electron with the sample, the intensity in this region is relatively high.

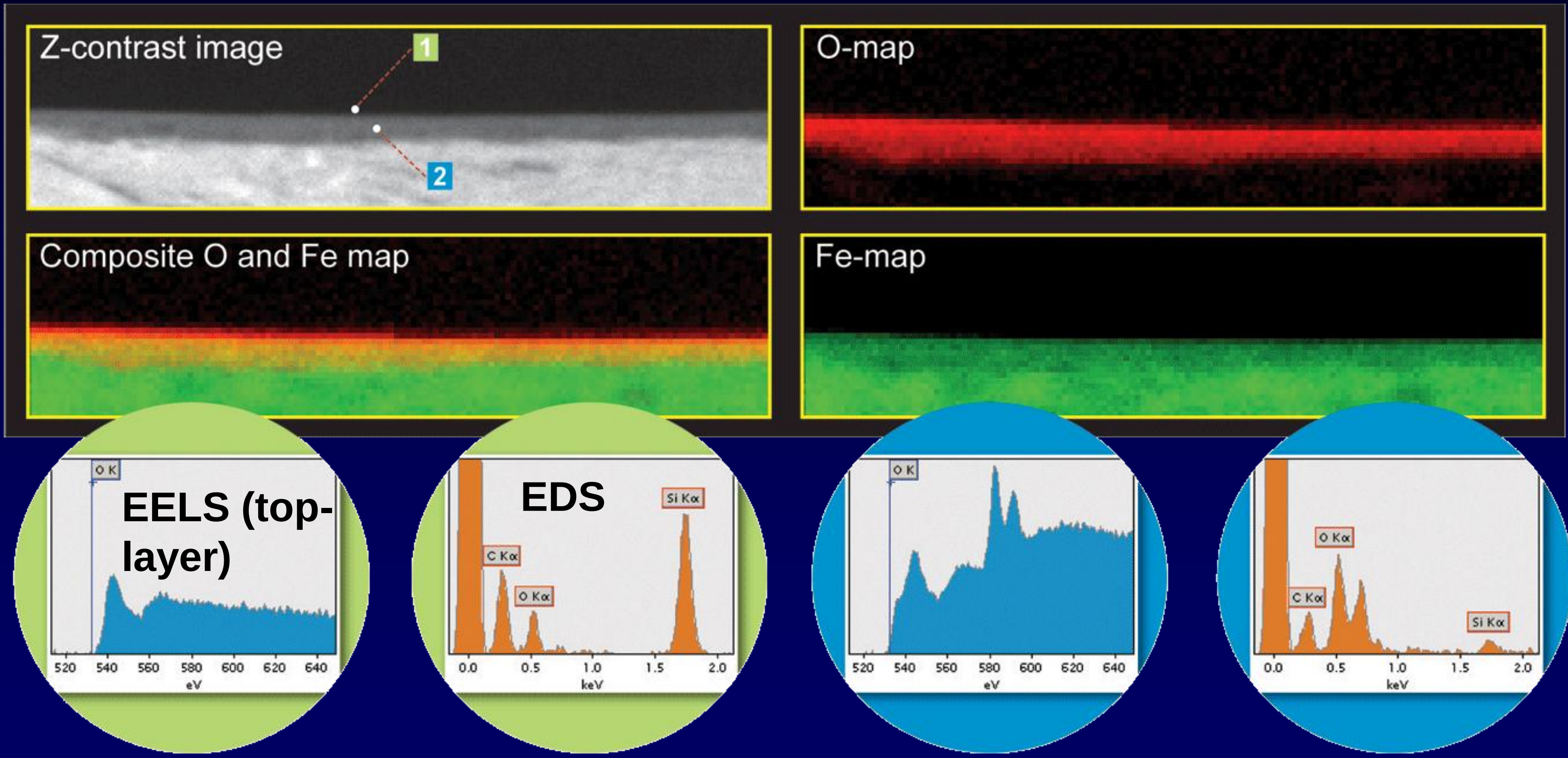
High-Loss region (> 100eV)

For the ionization of atoms, a specific minimum energy, the critical ionization energy E_C or ionization threshold, must be transferred from the incident electron to the expelled inner-shell electron, which leads to ionization edges in the spectrum at energy losses that are characteristic for an element.

In physics, a **plasmon** is a quantum of plasma oscillation. The plasmon is the quasiparticle resulting from the quantization of plasma oscillations just as photons and phonons are quantizations of light and sound waves, respectively. Thus, plasmons are collective oscillations of the free electron gas density, often at optical frequencies.

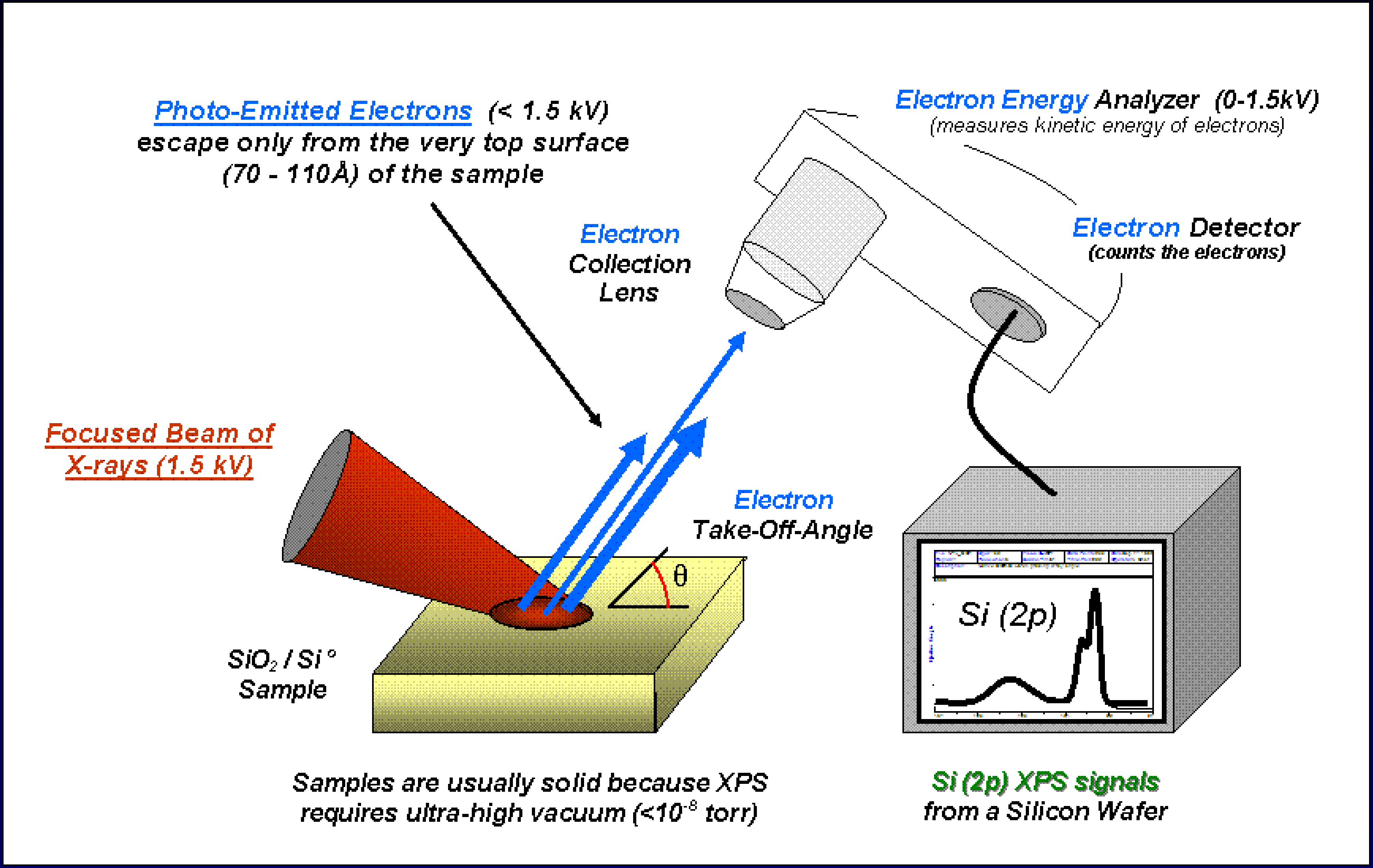
Electron Energy Loss Spectroscopy (EELS)

Imaging using a TEM with EELS and EDS capabilities



*Sample courtesy Dr. Deepak Upadhyaya of Sub-One Technology, who used these results to understand and improve coating adhesion by 150%.

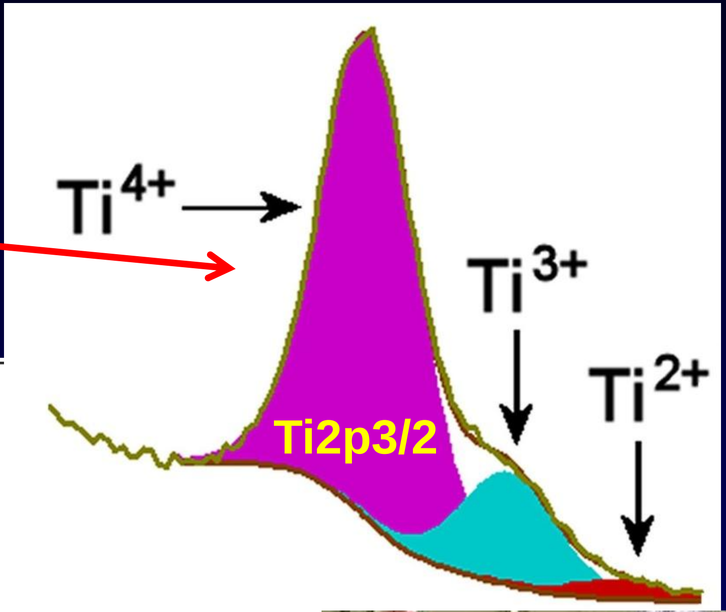
X-ray photoelectron spectroscopy (XPS)

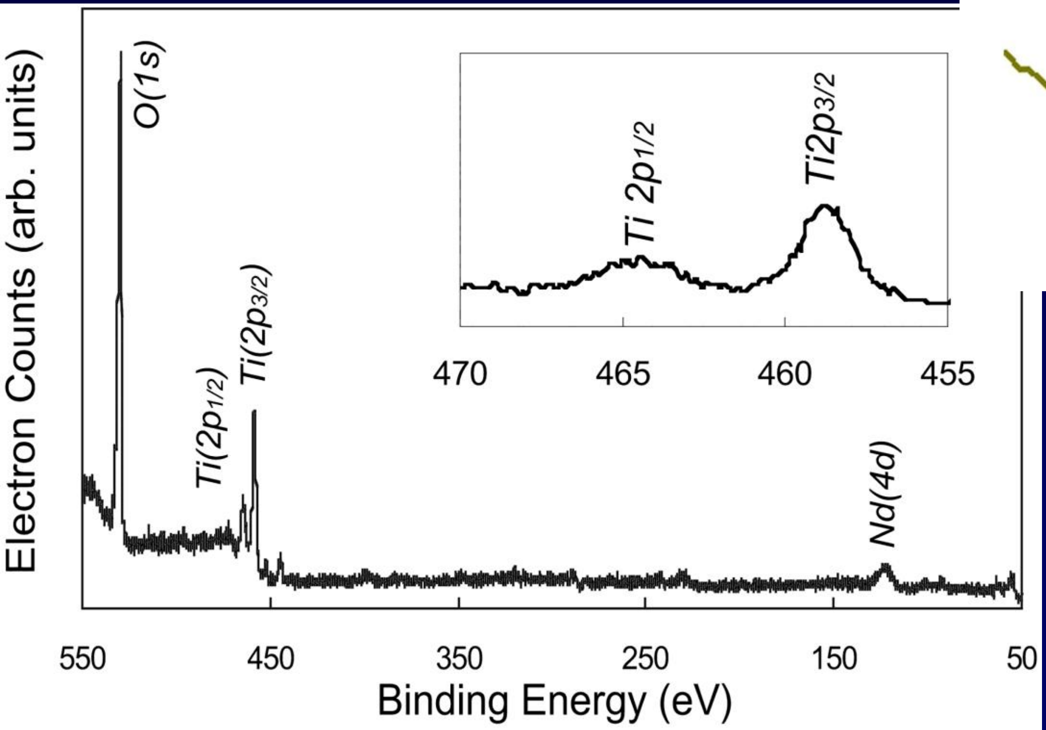


X-ray photoelectron spectroscopy (XPS)

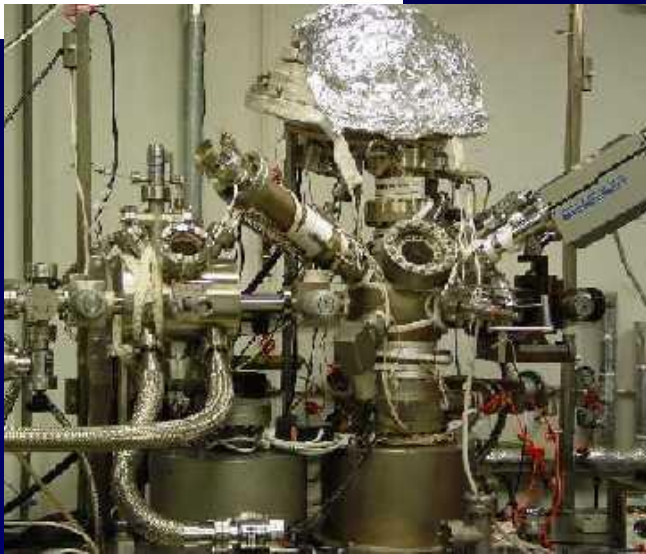
- **Has been used for sorption mechanism studies, speciation studies**

When TiO_2 is doped with Ti, the XPS spectrum shows the presence of reduced Ti ions





Wide Scan Survey of Elements



NMR

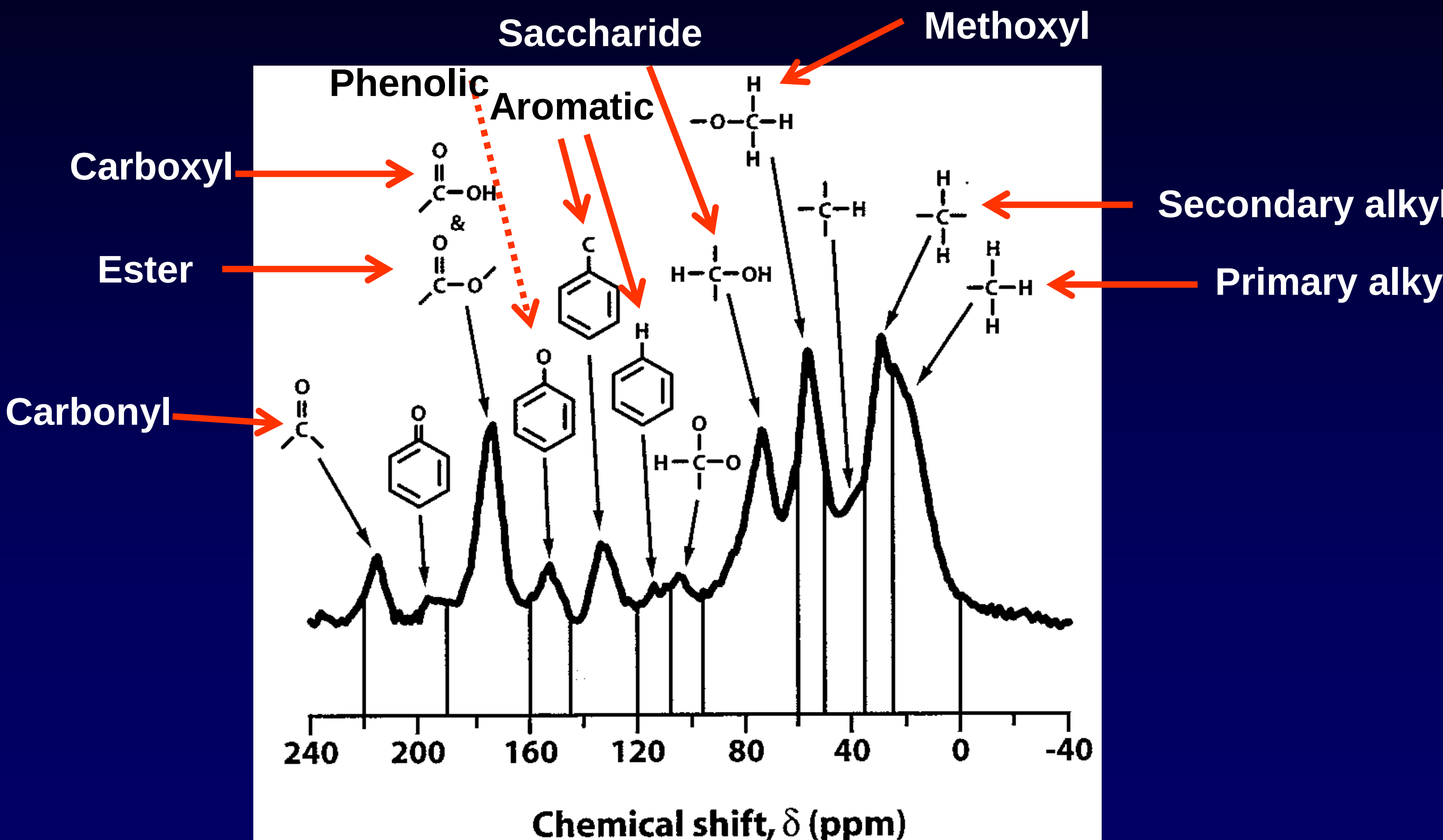
Nuclear Magnetic Resonance (NMR) spectroscopy

- **Has been used for characterization of soil organic matter and soil humification processes and ^{27}Al and ^{29}Si NMR has been used for structural identification of disordered minerals (which can not be analyzed using diffraction techniques)**

The superconducting magnet -- weighing 16 tons and standing almost three stories high – is a part of a 900 megahertz wide-bore nuclear magnetic resonance spectrometer at EMSL.

Example: Molecular Structure of Humic Acid based on CPMAS ^{13}C NMR Spectroscopy

monosaccharides have the chemical formula (CH2O)n



Molecular Scale Techniques

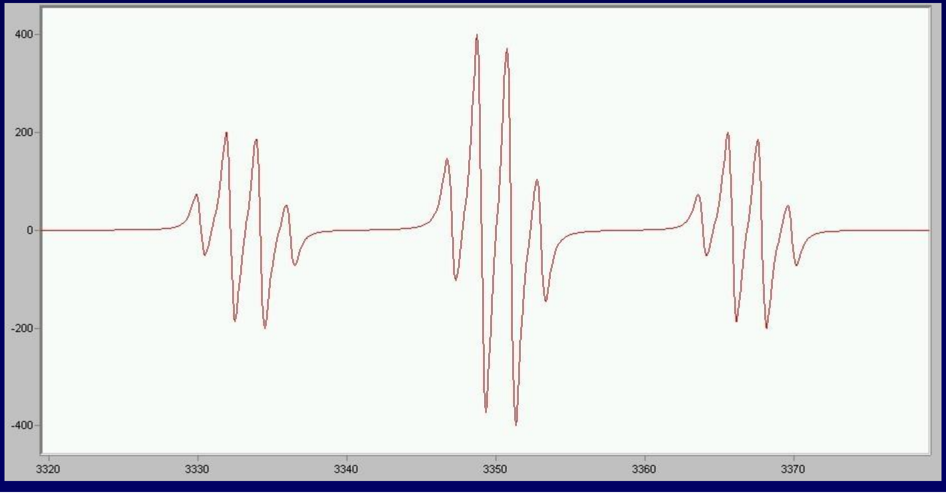
Analytical Method	Source	Signal	Chemical Information	Notes
ESR also called EPR or “electron paramagnetic resonance”	Microwaves (+ magnetic field)	Radio waves	Sensitive to electron density (electron coupling); local bonding (first neighbor)	Nonvacuum; bulk liquids and solids; sensitive to low conc.; requires paramagnetic ions
X-ray scattering (small angle, SAXS; wide angle, WAXS)	X-rays (synchrotron or laboratory)	Scattered X-rays	Quantitative structural information	Nonvacuum; crystalline and amorphous materials; microdiffraction w/synchrotron
SIMS	Charged ion beam	Atomic mass	Elemental and isotopic analysis	Vacuum; surface sensitive to low conc.; spatial resolution
LA-ICP-MS	laser	Atomic mass	Elemental and isotopic analysis	Vacuum; sensitive to low conc.; spatial resolution

Molecular Scale Spectroscopy Techniques

Electron paramagnetic resonance (EPR)

- **Has been used for sorption studies of transition metals (e.g. Fe^{3+}, Cu^{2+}) on soil minerals and soil organic matter (requires odd number of electrons)**

- EPR spectroscopy is a technique for studying chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion.



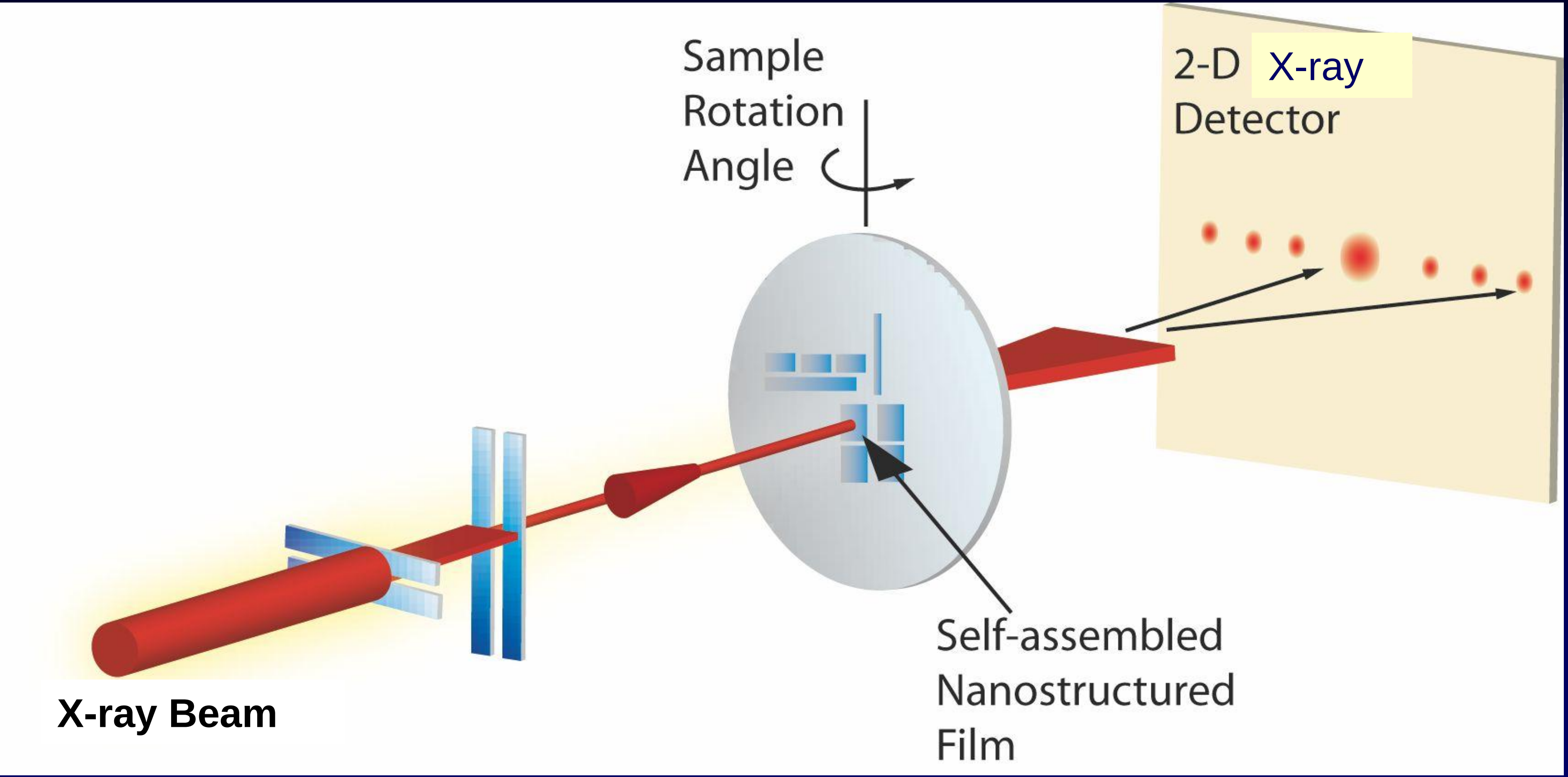
Simulated EPR spectrum of the $H_2C(OCH_3)$ radical

Small-angle X-ray scattering (SAXS)

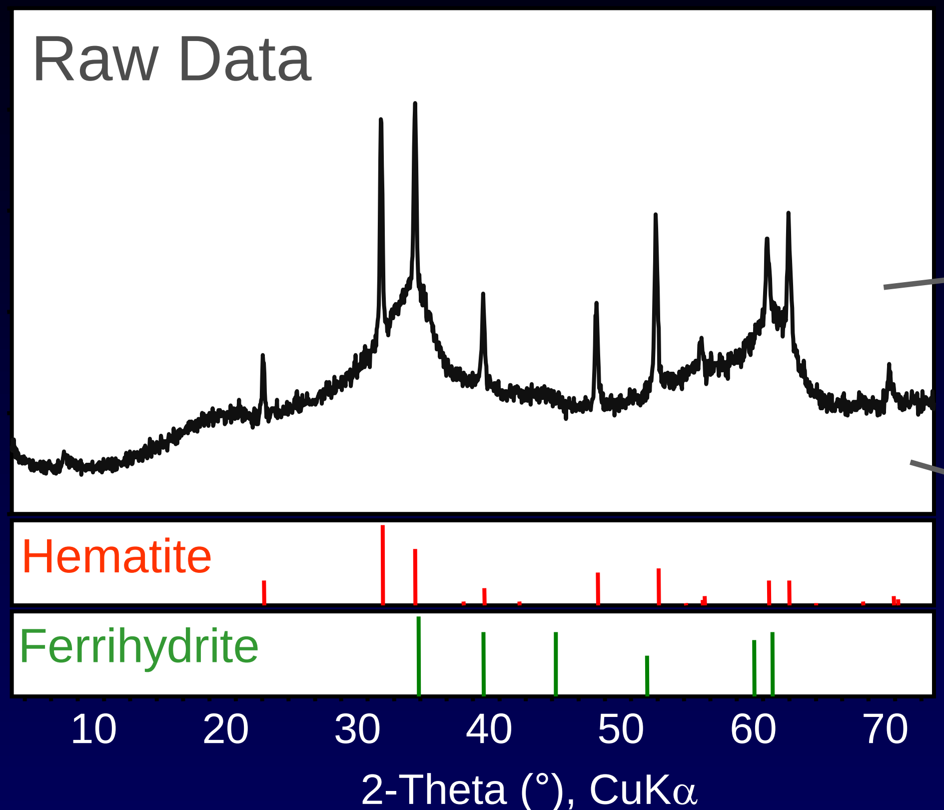
SAXS is a small-angle scattering (SAS) technique where the elastic scattering of X-rays by a sample which has inhomogeneities in the nm-range, is recorded at very low angles (typically 0.1 - 10°). This angular range contains information about the shape and size of macromolecules, characteristic distances of partially ordered materials, pore sizes, and other data. SAXS is capable of delivering structural information of macromolecules between 5 and 25 nm, of repeat distances in partially ordered systems of up to 150 nm.

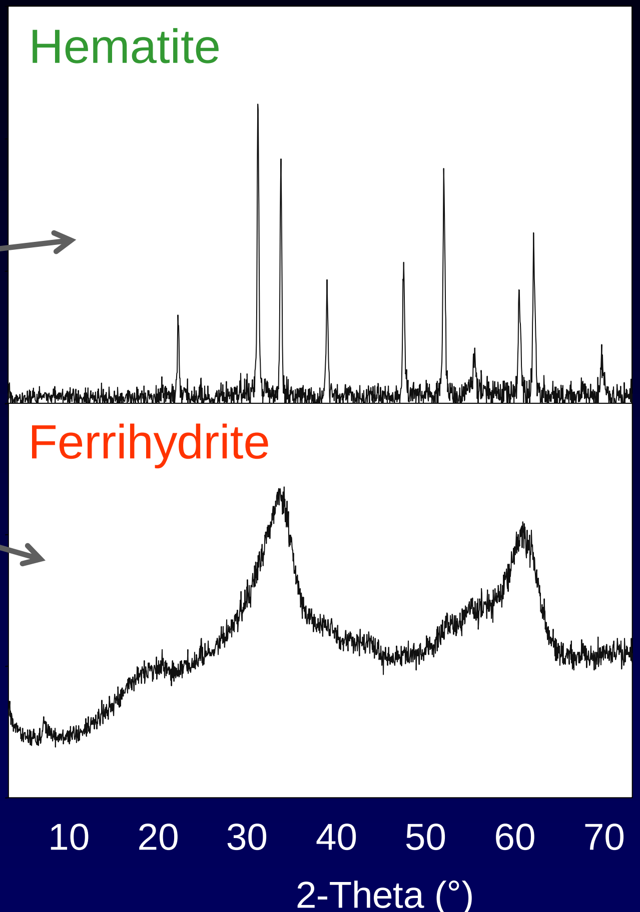
SAXS belongs to a family of X-ray scattering techniques that are used in the characterization of materials. In the case of biological macromolecules such as proteins, the advantage of SAXS over crystallography is that a crystalline sample is not needed.

Small-angle X-ray scattering (SAXS)



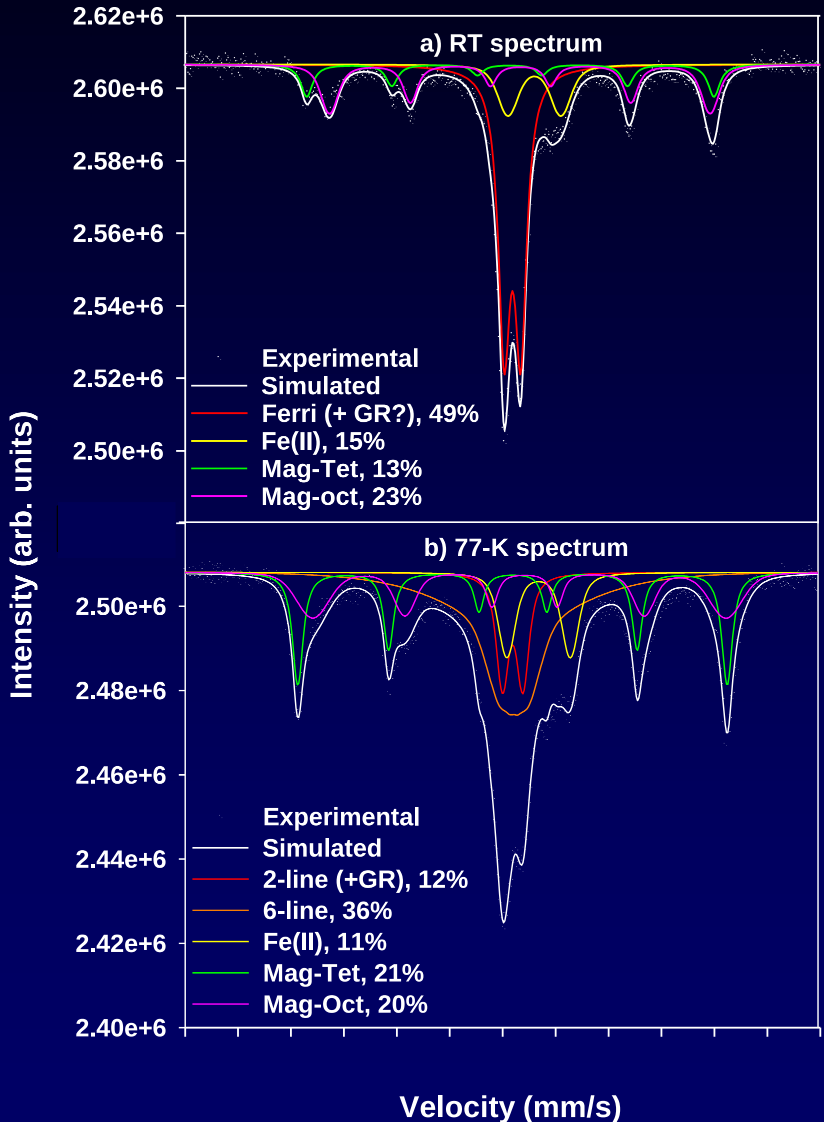
Other Techniques: X-Ray Diffraction





Transformation of Ferrihydrite; t = 14 days (Semi Quant Analysis)		
System	**Ferrihydrite**	**Hematite**
HFO + Cells	**97 %**	**3 %**
HFO + Cells + AQDS	**90 %**	**10 %**

Other Techniques: Mössbauer



Mössbauer spectroscopy is a spectroscopic technique based on the resonant emission and absorption of gamma rays in solids.

Mössbauer spectroscopy is similar to NMR spectroscopy in that it probes nuclear transitions

^{57}Fe is by far the most common element studied using this technique.

Mössbauer spectra of biomineralization products obtained at 303-K (a) and 77-K (b).

Abbreviation: Ferrihydrite (Ferri), magnetite (Mag), and green rust (Gr).

Applications of Environmental Microscopy

Field Emission Transmission Electron Microscope (TEM) with EELS

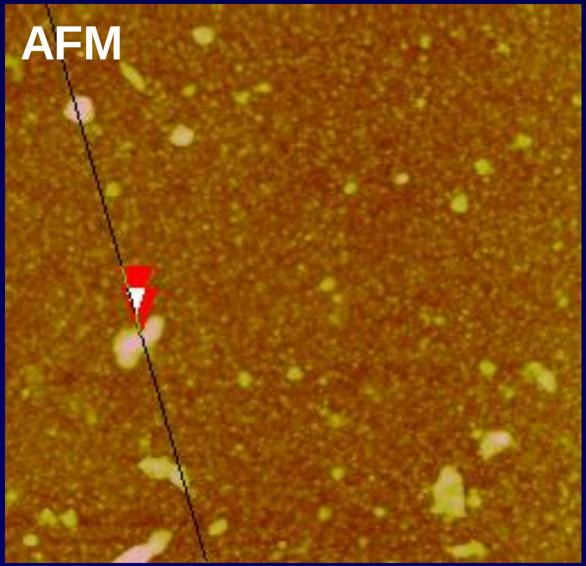
Molecular Scale Techniques

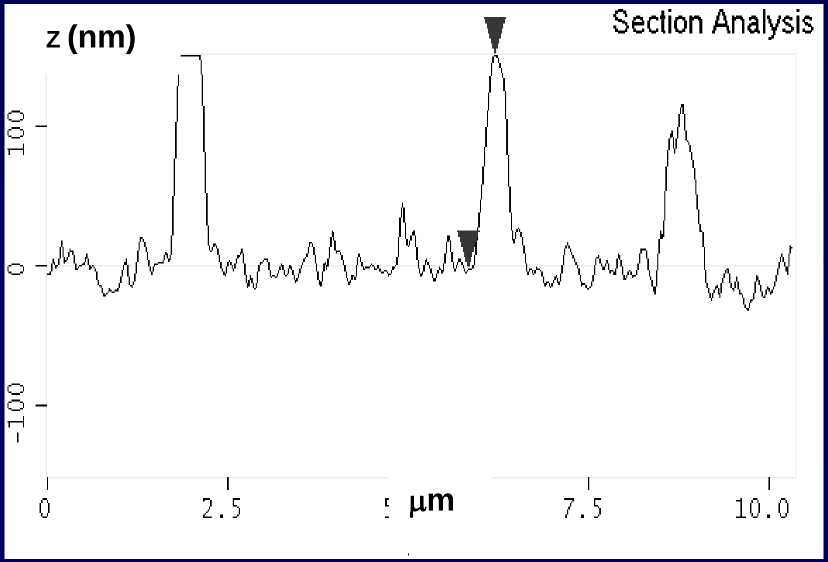
Analytical Method	Source	Signal	Chemical Information	Notes
STM	Tunneling electrons	Electronic pertuba-tions	Molecular and atomic-scale surface imaging; surface electronic structure	Vacuum and nonvacuum; conducting/semi-conducting materials only
AFM	Electronic force	Force pertuba-tions	Molecular-scale surface imaging	Nonvacuum; imaging in air or liquid

Atomic Force Microscopy

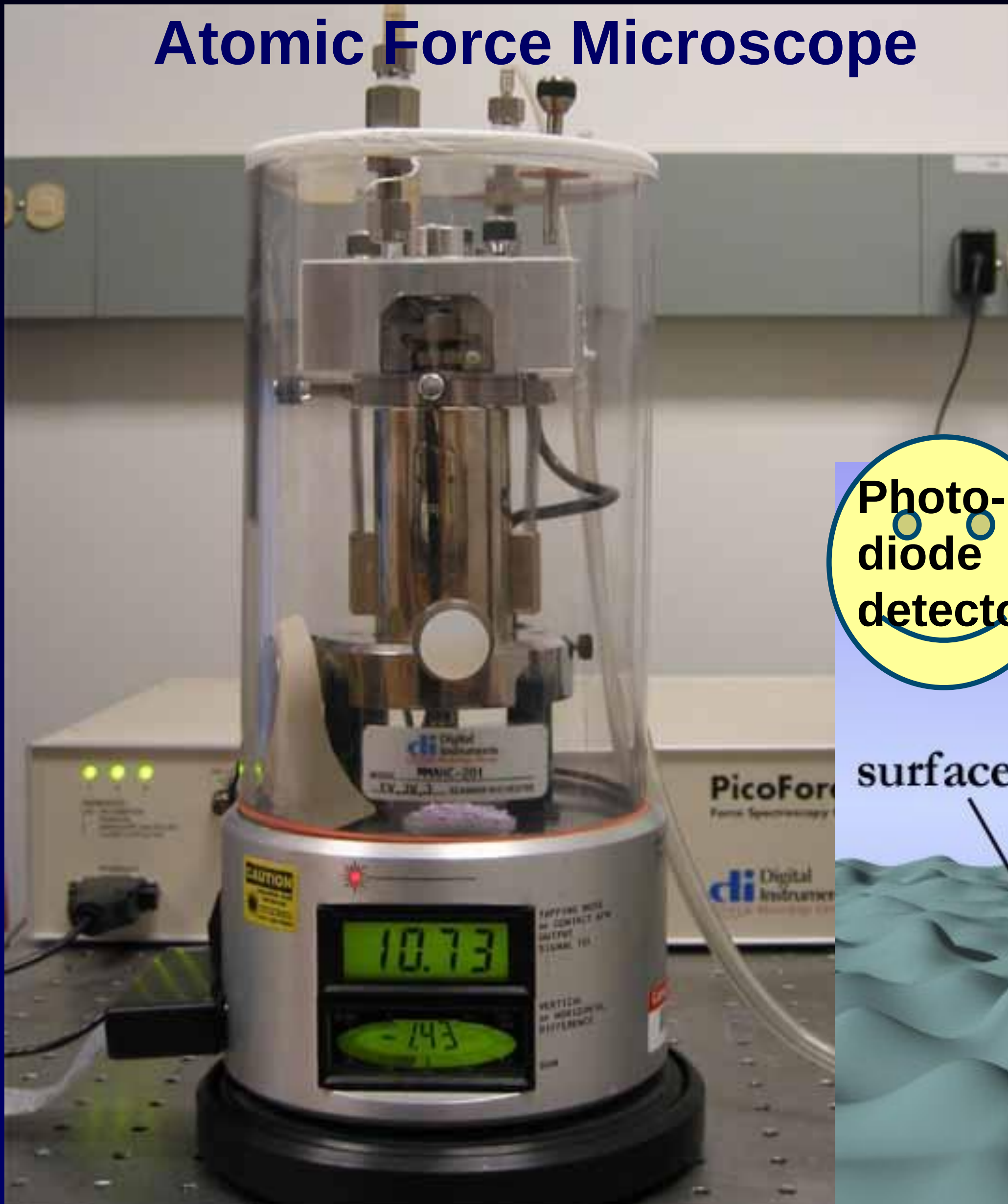
Atomic Force Microscopy (AFM)

- Allows imaging of mineral surfaces in air/water at sub-nm scale resolution
- Visualization of humic/fulvic acid structure
- Determine clay particle thickness and structure
- Measuring directly the kinetics of growth, dissolution, redox processes

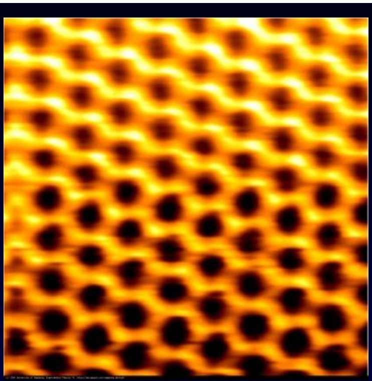




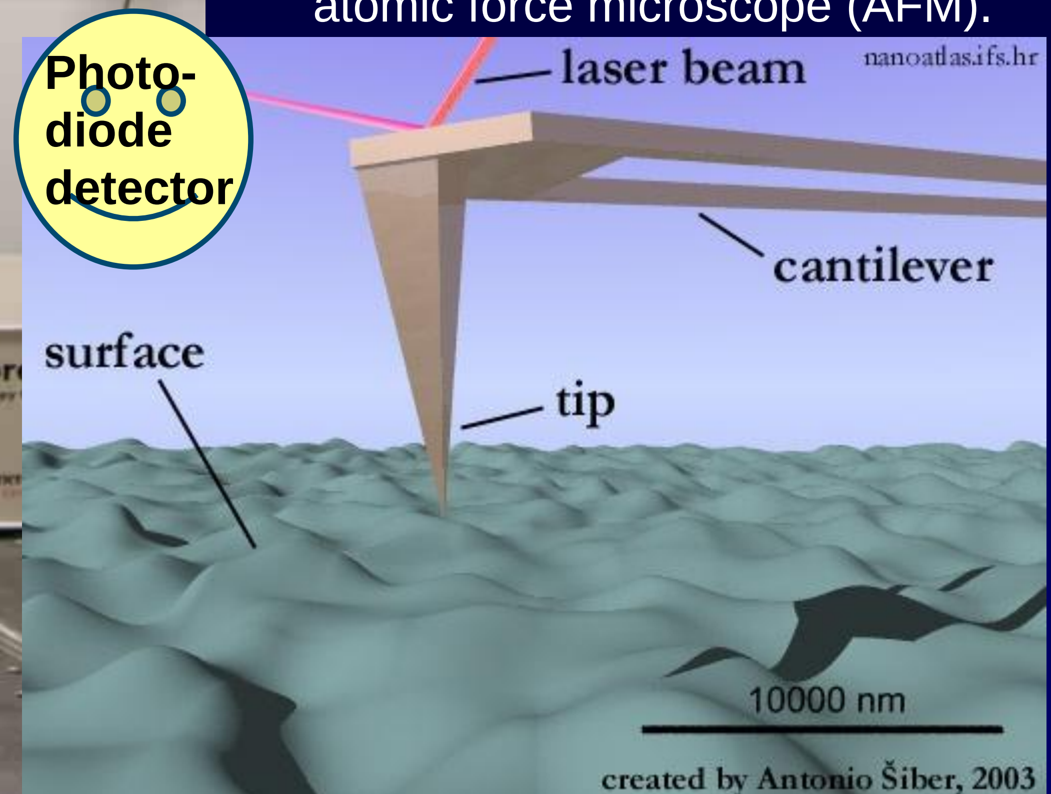
Atomic Force Microscopy



Graphite with AFM, 2×2 nm^2 (atomic resolution)

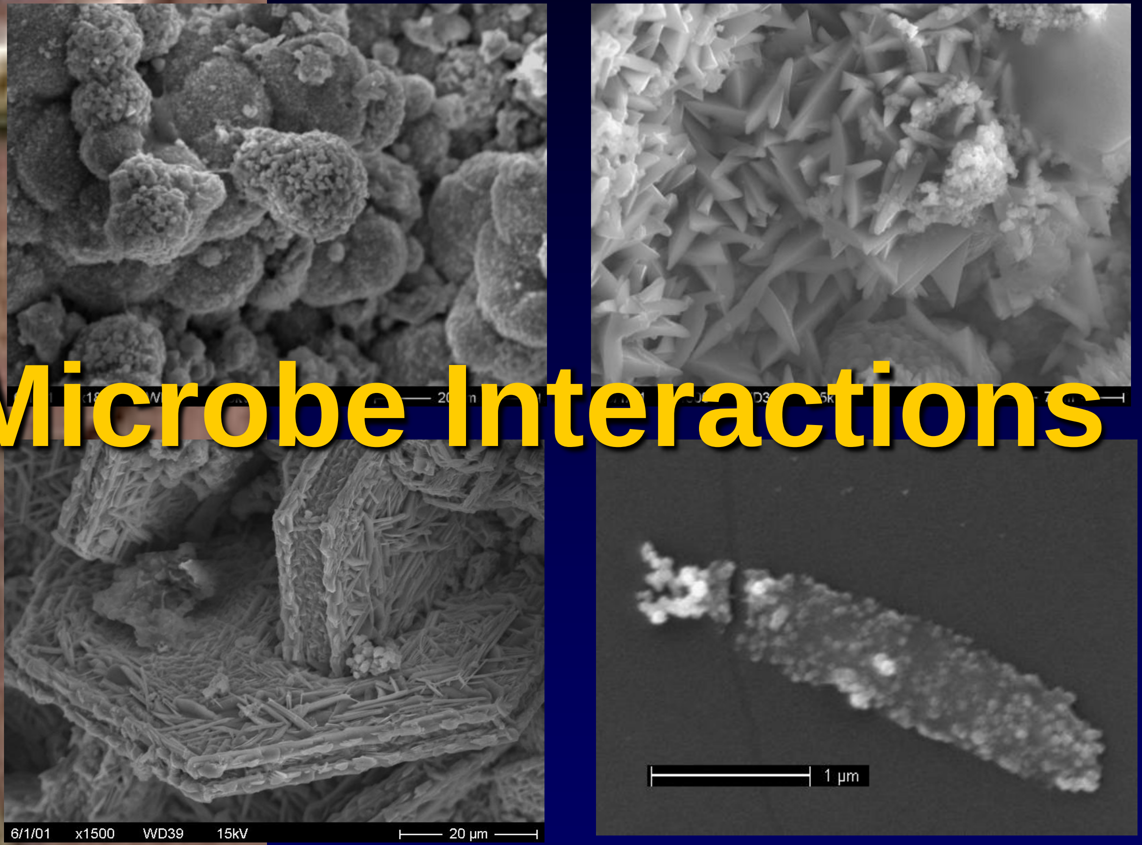


A schematic 3D description of an atomic force microscope (AFM).



Fe Oxide – Microbe Interactions

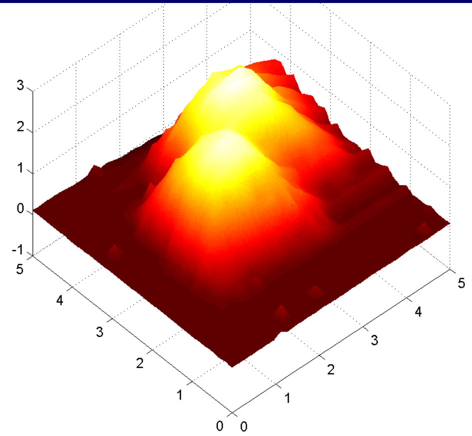
AFM Image courtesy of Fredrickson, PNNL



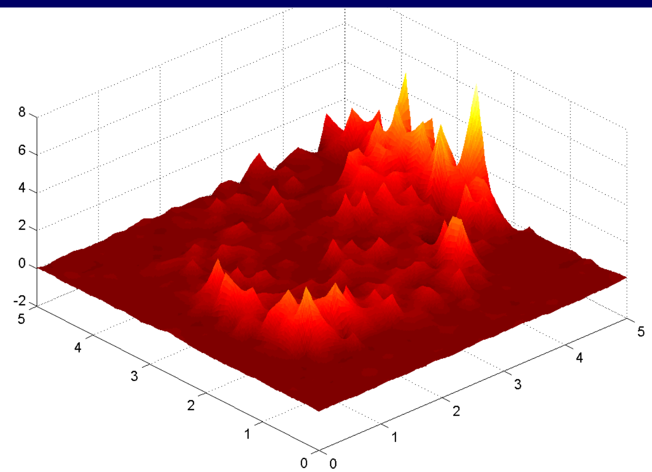
SEM Images

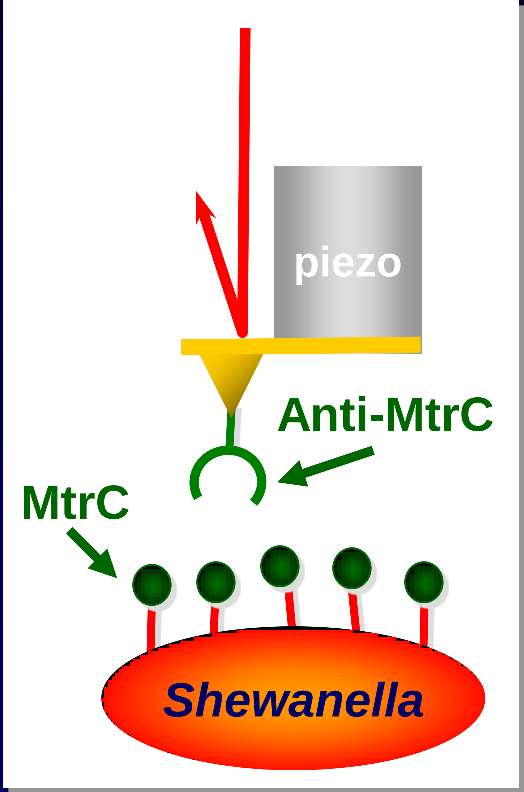
Identifying Surface Exposed MtrC on *Shewanella* Using AFM and covalently linked cytochrome-specific antibody molecules to an AFM tip

Topography of *Shewanella* cell obtained during force-volume mapping



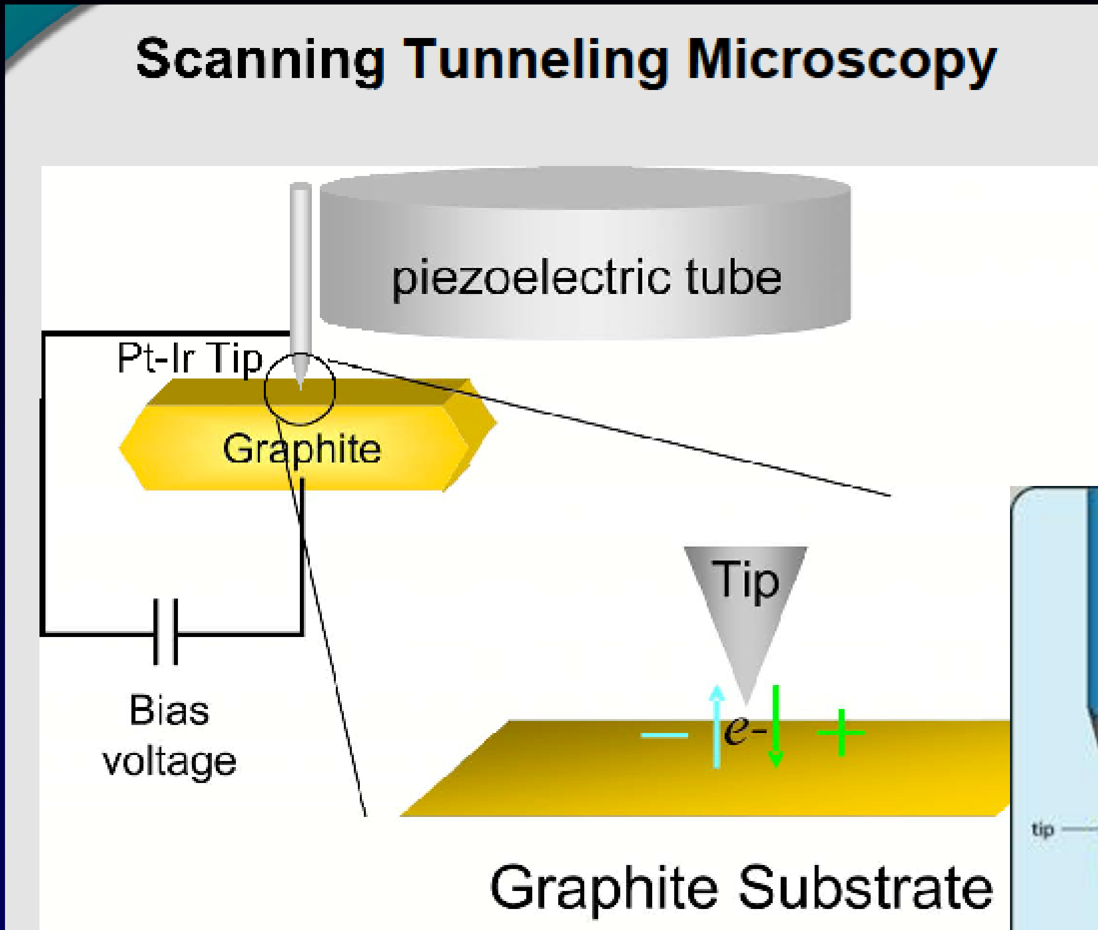
Force-Volume mapping *Shewanella* cell Using Anti-MtrC functionalized AFM tip

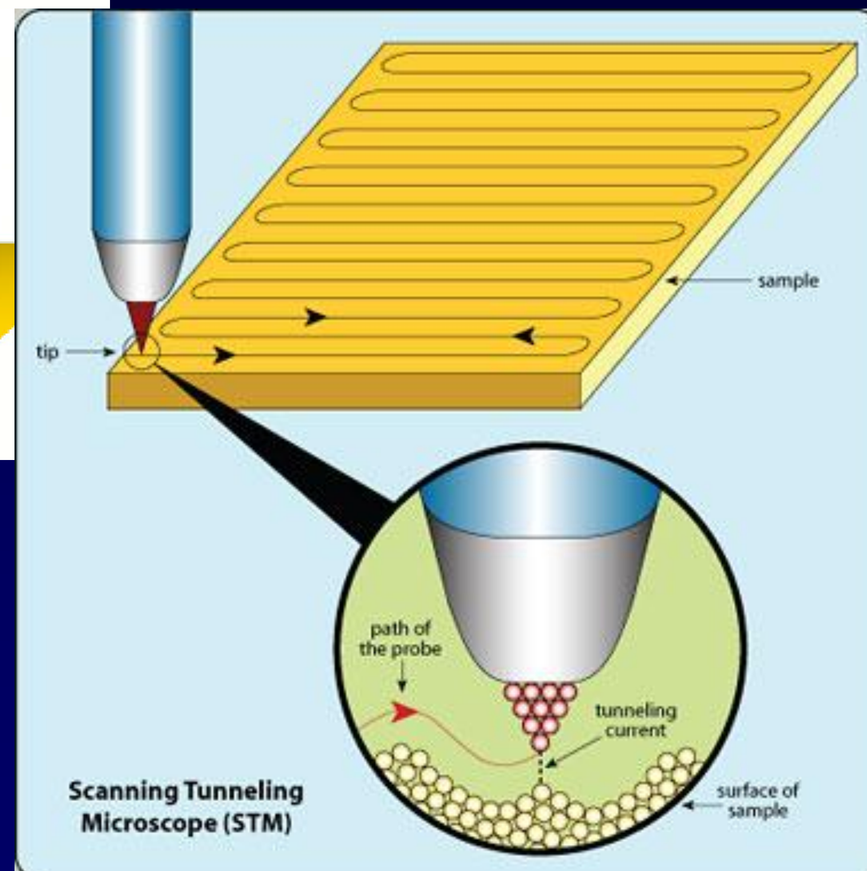




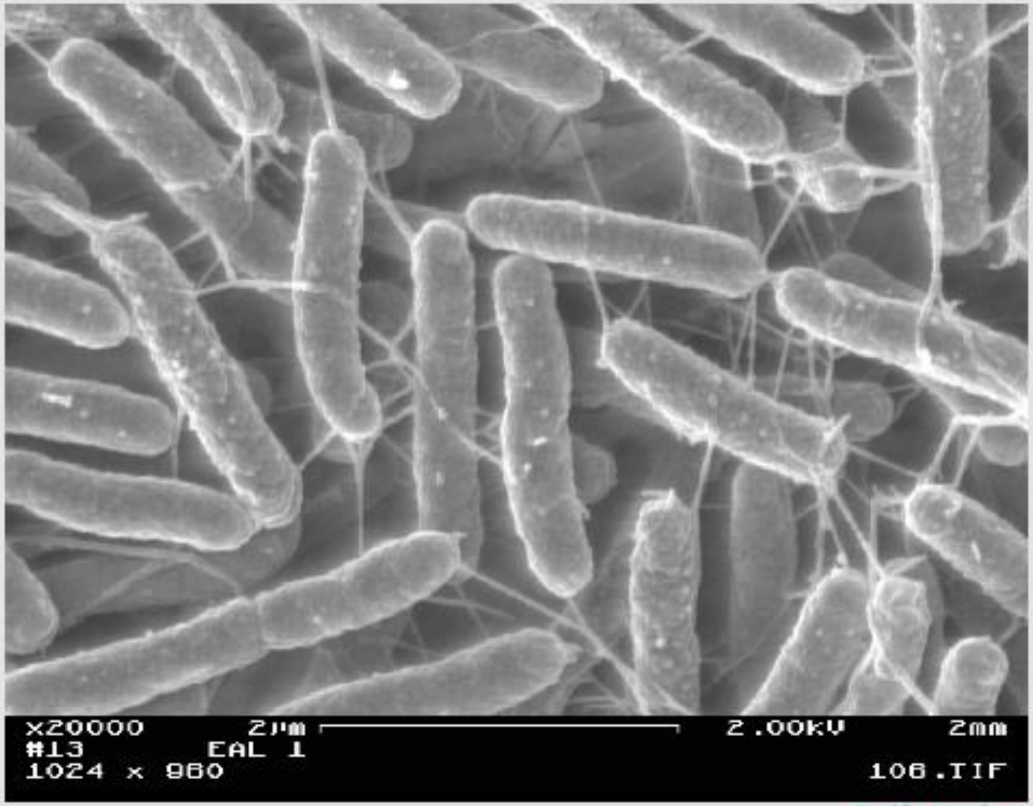
B. Lower, PNNL

STM

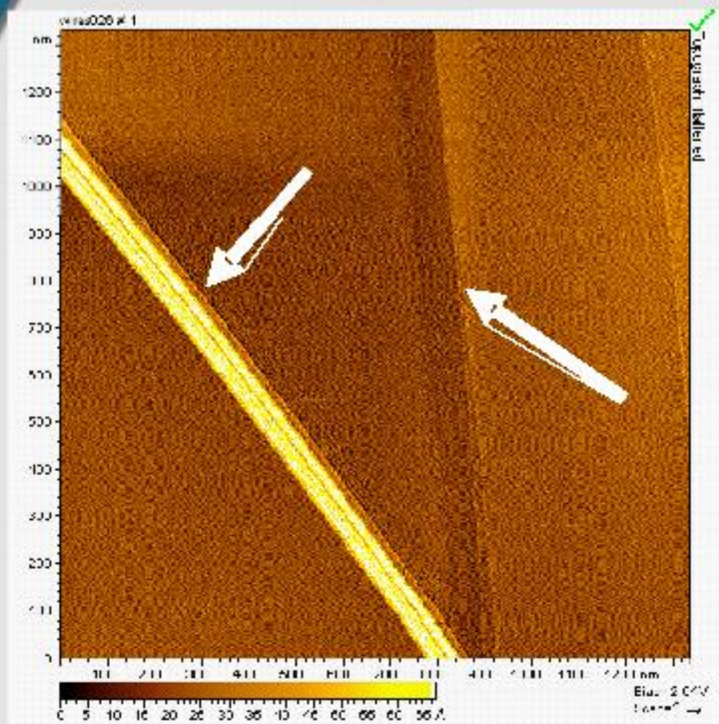

Scanning Tunneling Microscopy
piezoelectric tube
Pt-Ir Tip
Graphite
Bias
voltage
Tip
e-
Graphite Substrate

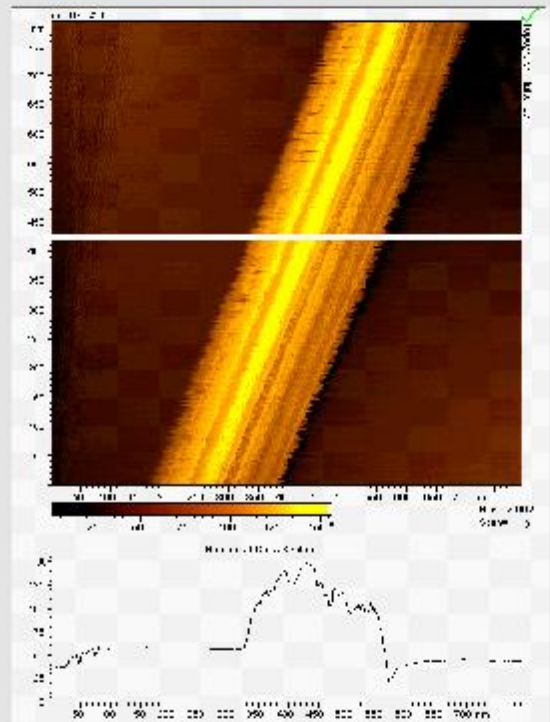

sample
tip
path of
the probe
tunneling
current
surface of
sample
Scanning Tunneling
Microscope (STM)

SEM image of MR-1 cultivated with O_2-limitation and low agitation (50 rpm)



Scanning Tunneling Microscopic images of nanowires from wild type MR-1





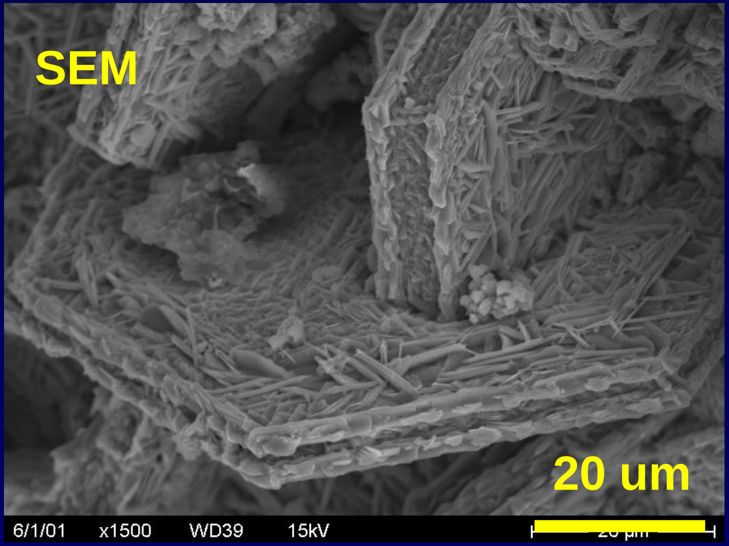
Molecular Scale Techniques

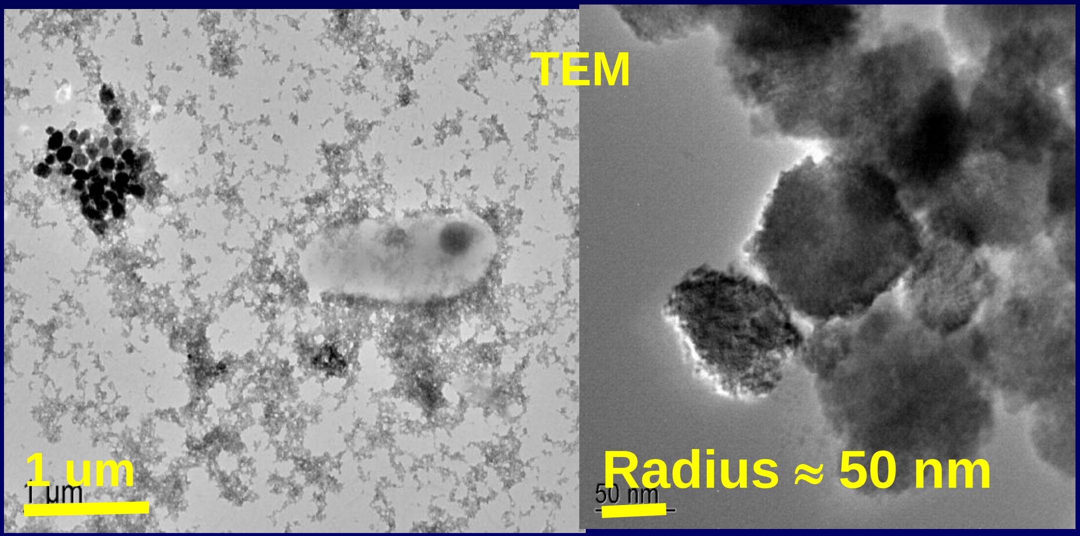
Analytical Method	Source	Signal	Chemical Information	Notes
HR-TEM and scanning transmission electron microscope (STEM)	Electrons	Transmitted or secondary electrons	Bulk morphology and crystallinity; particle- to atomic-scale spatial resolution	Vacuum or light element atmosphere
SEM/EM with EDS or WDS chemical analysis	Electrons	Secondary or backscattered electrons; fluorecent X-rays	Morphology over wide magnification; quantitative or qualitative chemical analysis (EDS/WDS)	Vacuum or light element atmosphere

TEM and SEM

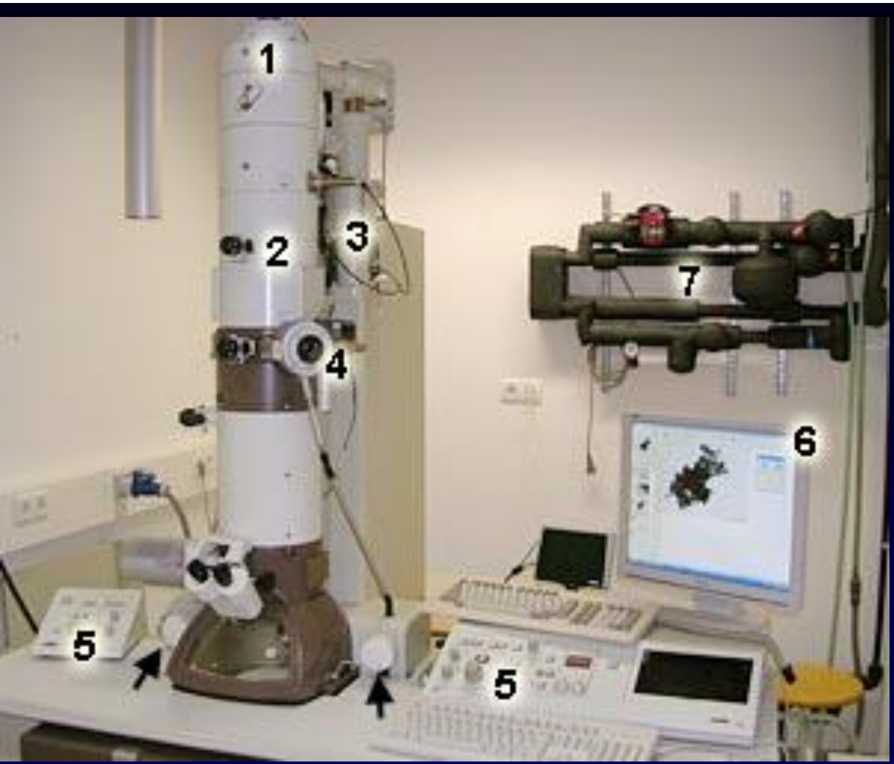
Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

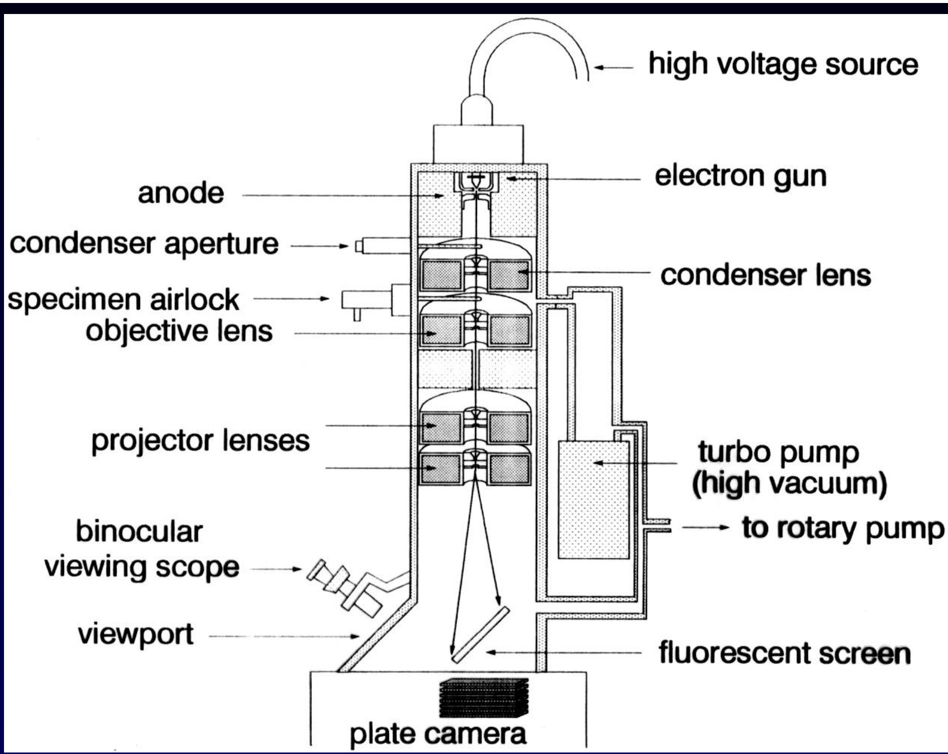
- **Can acquire both chemical and micromorphological data on soil and soil materials. TEM can provide spatial resolution (sub-nm) of surface alteration and the degree of crystallinity of sorbed species (ordering) as well as elemental analysis when combined with electron spectroscopy.**





TEM





1: Electron gun

2 Electro-magnetic lenses to direct and focus the electron beam

3: Vacuum pumps system

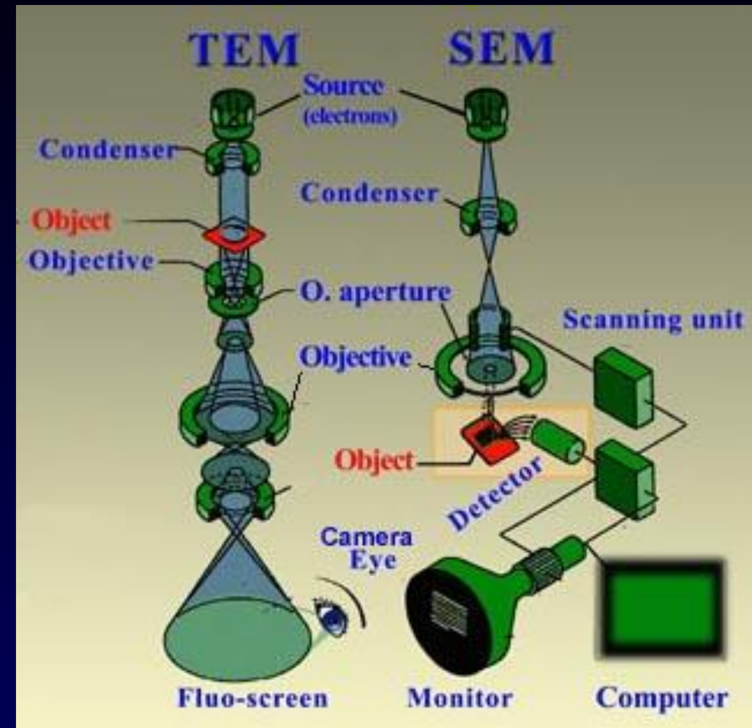
4: Opening to insert a grid with samples into the high-vacuum chamber for observation

5: Operation panels (left for alignment; right for magnification and focussing; arrows for positioning the object inside the chamber)

6: Screen for menu and image display

7: Water supply to cool the instrument.

SEM



1: Electron gun (here a so-called field-emission source)

2 Electro-magnetic lenses to direct and focus the electron beam inside the column

3: Vacuum pumps system

4: Opening to insert the sample into the high-vacuum chamber in conventional SEM mode

5: Operation panel with focus, alignment and magnification tools and a joystick for positioning of the sample

6: Screen for menu and image display

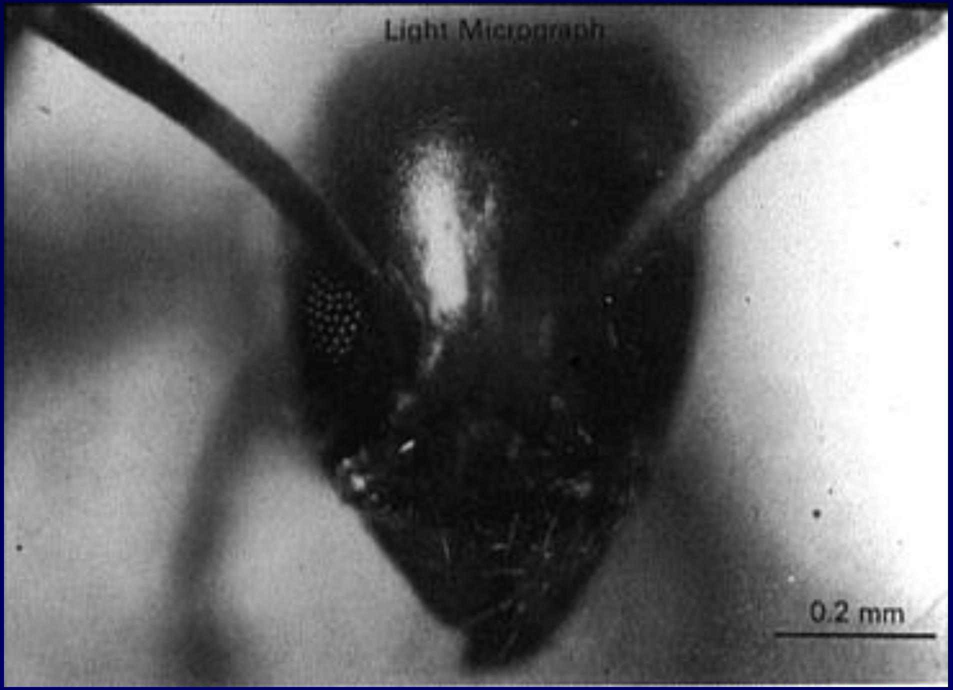
7: Cryo-unit to prepare (break, coat and sublimate) frozen material before insertion in the observation chamber in Cryo-SEM mode

8: Electronics stored in cupboards under the desk and 9: Technicians discussing a view.

Light Micrograph vs. Scanning EM

Depth of Focus with the Scanning Electron Microscope

Light Micrograph of Ant's Head



Scanning EM of Ant's Head

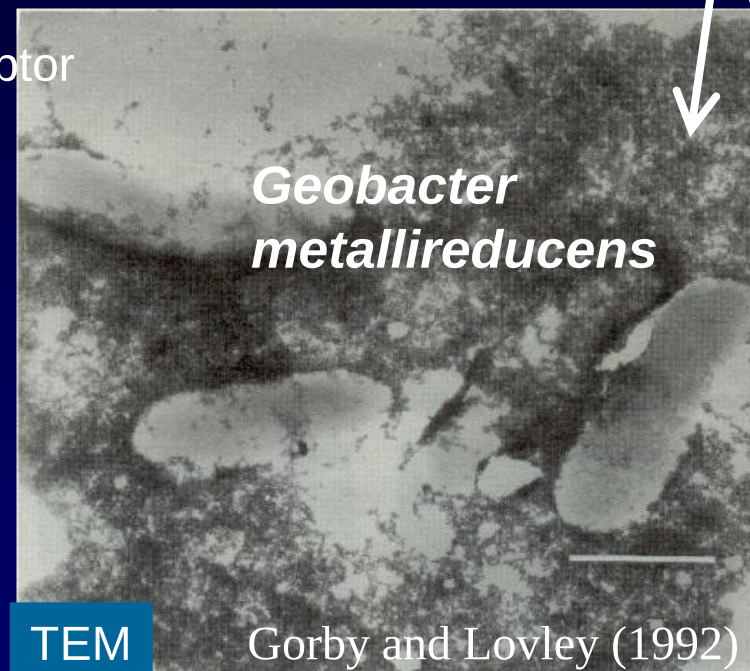
U(VI) Reduction & Immobilization by Dissimilatory Metal-Reducing Bacteria

$$CH_2O + 2U(VI) \rightarrow 2U(IV) + CO_2$$

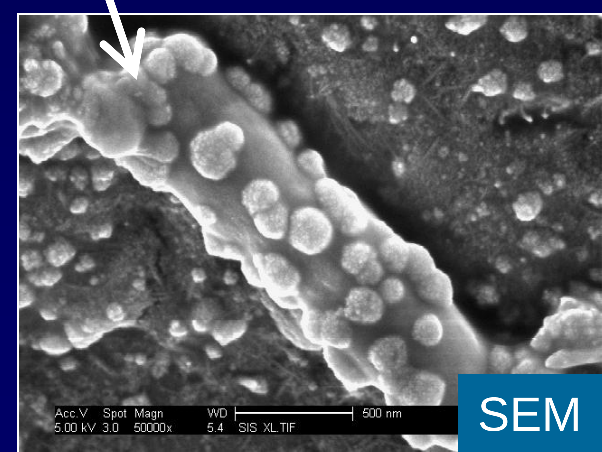
$$CH_3COO^- + 4UO_2(CO_3)_2^{2-} + 4H_2O \rightarrow 4UO_2(s) + 10HCO_3^- + H^+$$

U(VI) (e-acceptor

Acetate (e-donor)

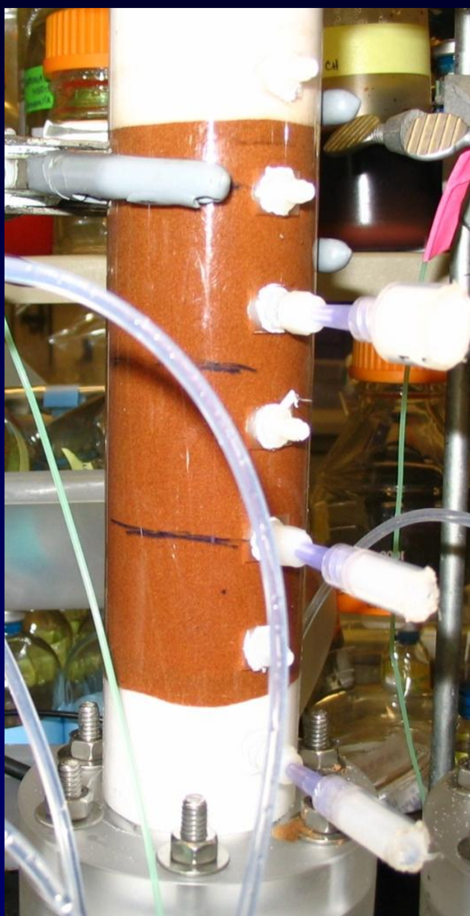


Shewanella CN32

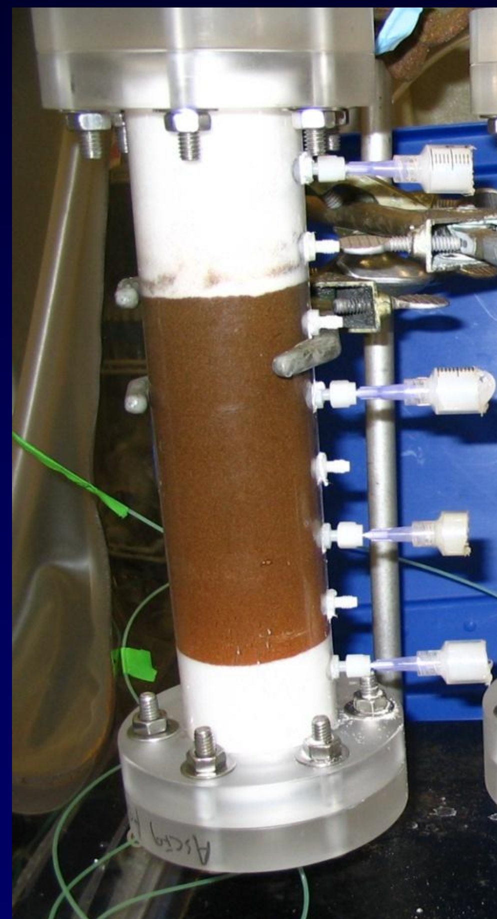


Fe Biomineralization: Impact of P

Day 1

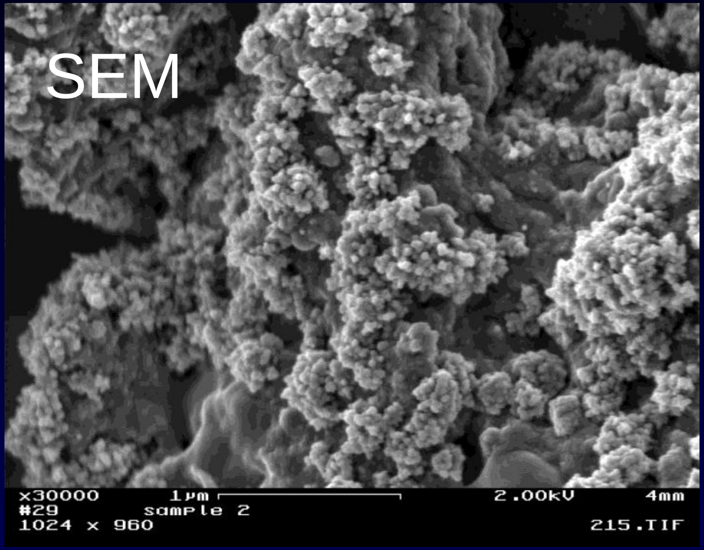


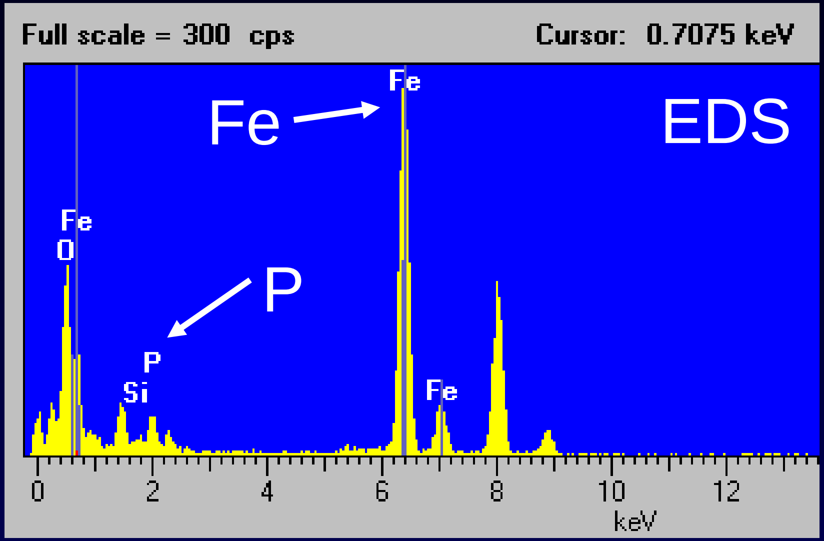
Day 17
with P

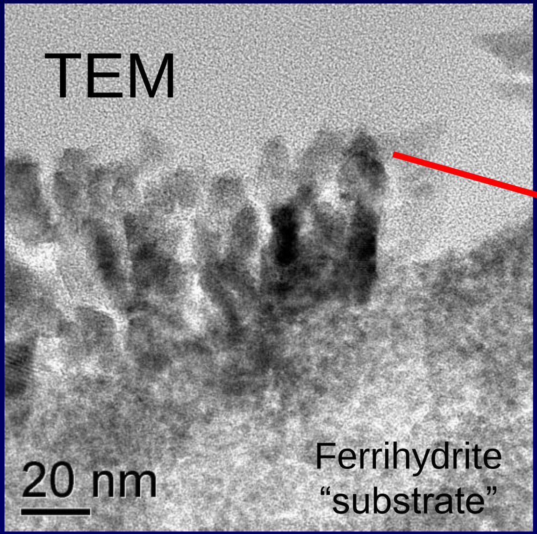


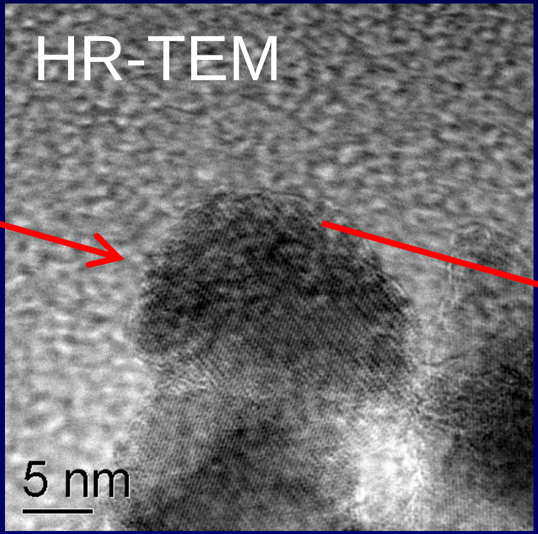
Day 17
without P

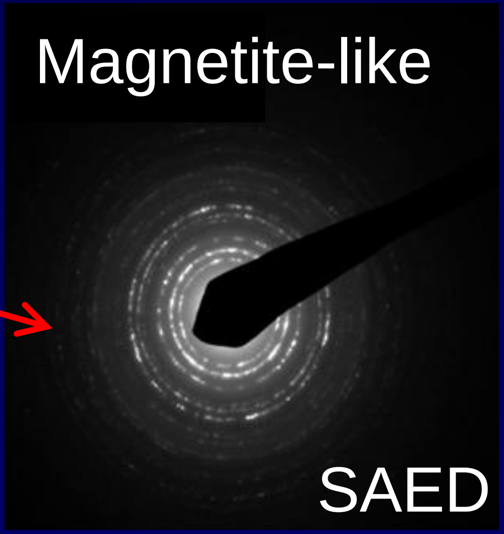
Fe Morphology Day 17 (P column)



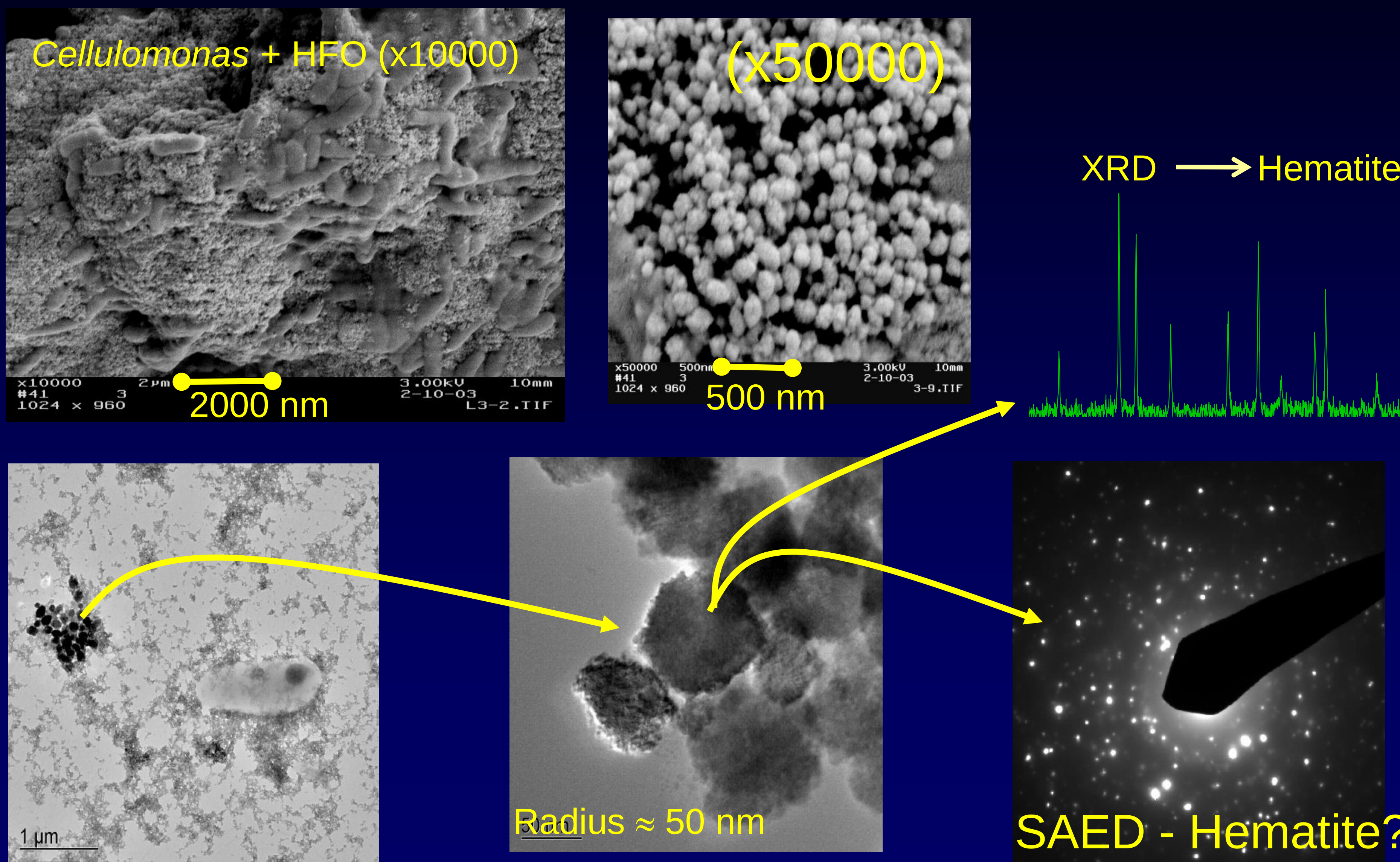




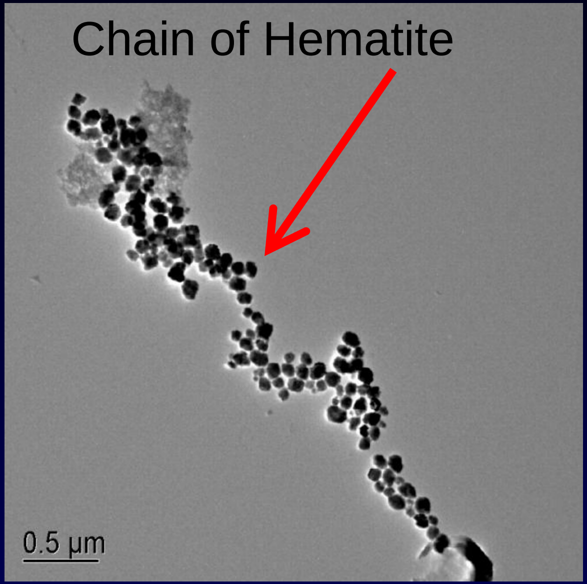


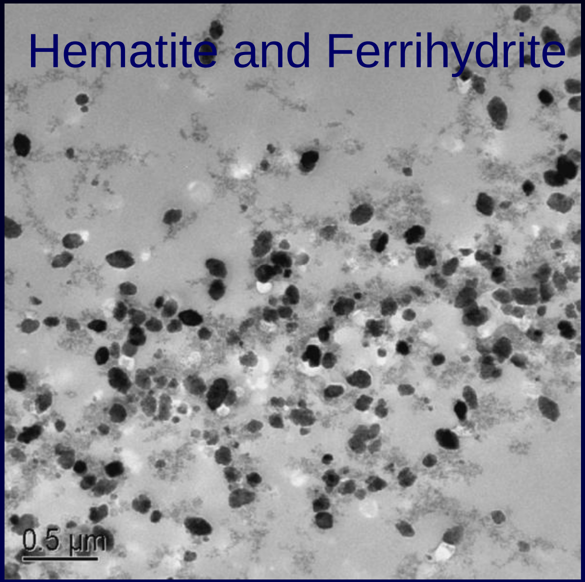


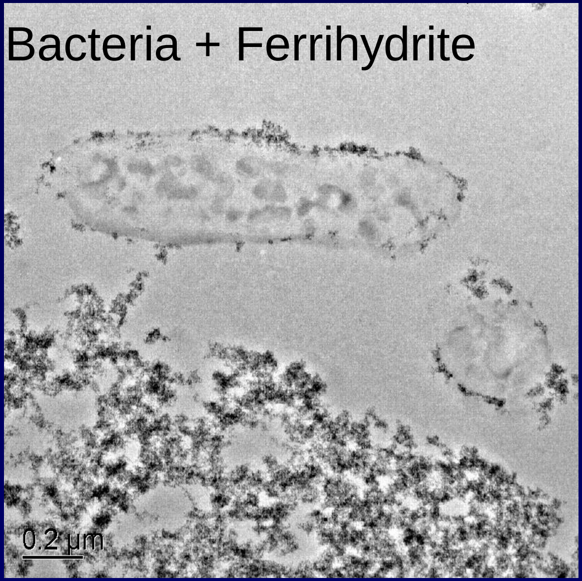
Fe-Phases Tentatively Identified by SEM/TEM/SAED and XRD in the Presence of *Cellulomonas*, Fe oxides and TNT

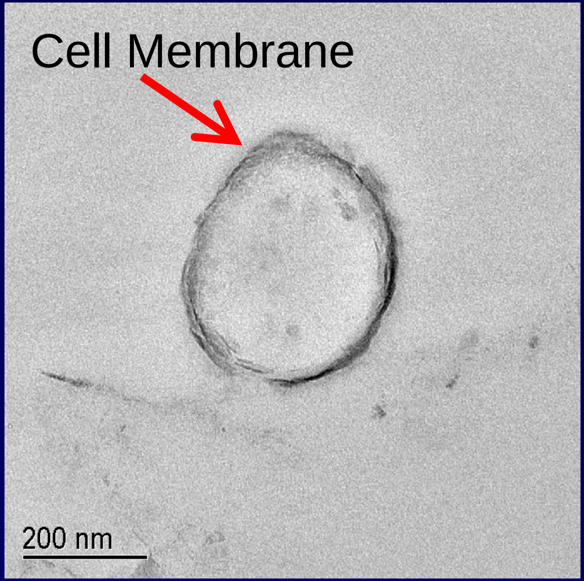


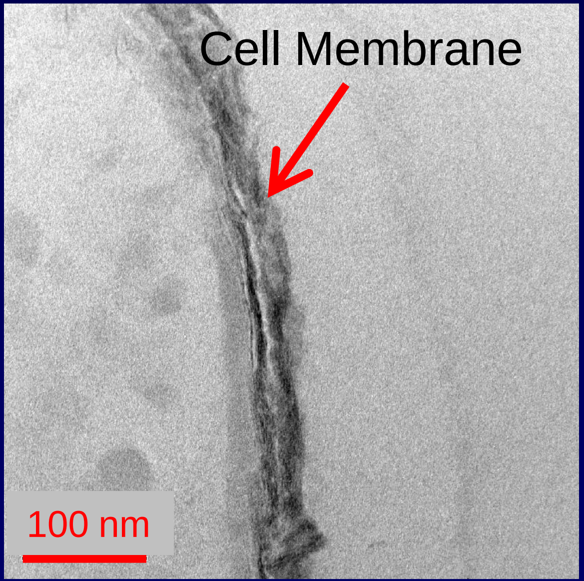
70 nm Thick Thin Sections – Fe Bioreduction



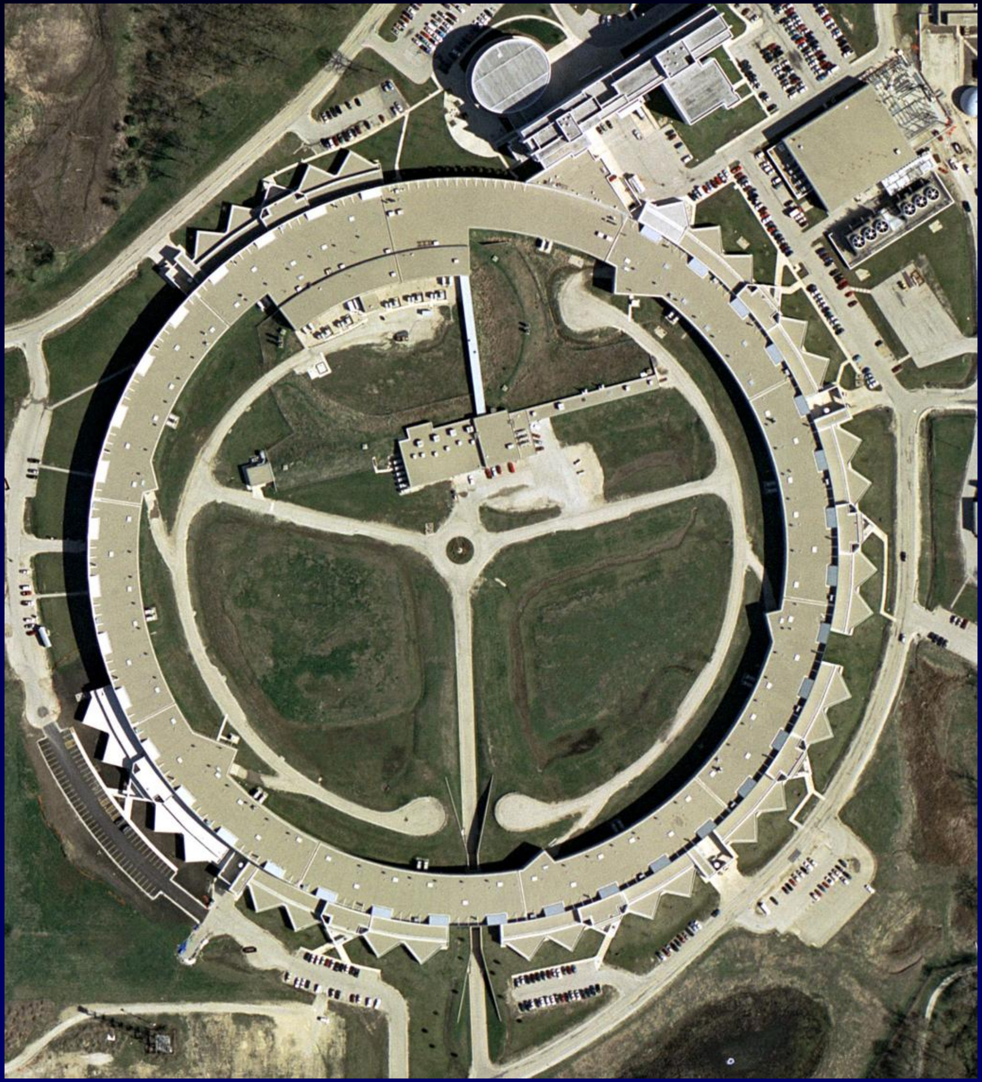








Intro to Synchrotron Radiation-Based Techniques



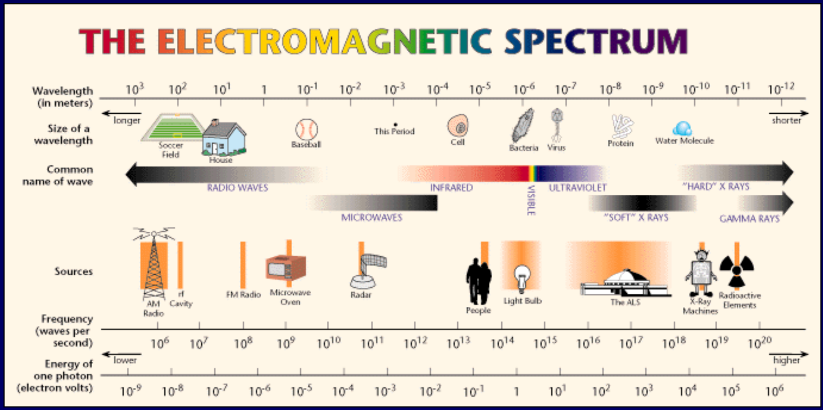
The Advanced Photon Source (APS) at Argonne National Laboratory

Detection of Molecular Properties

Wavelength from 10^{-7} – 10^{-10} meter can be used to explore the atomic structure of solids, molecules, and biological materials.

Atoms, molecules, chemical bond length, and distances between atomic planes in crystals fall within this wavelength and can therefore be detected.

The binding energies of many electrons in atoms/molecules falls within the range of photon energies of 10 to 30,000 eV.

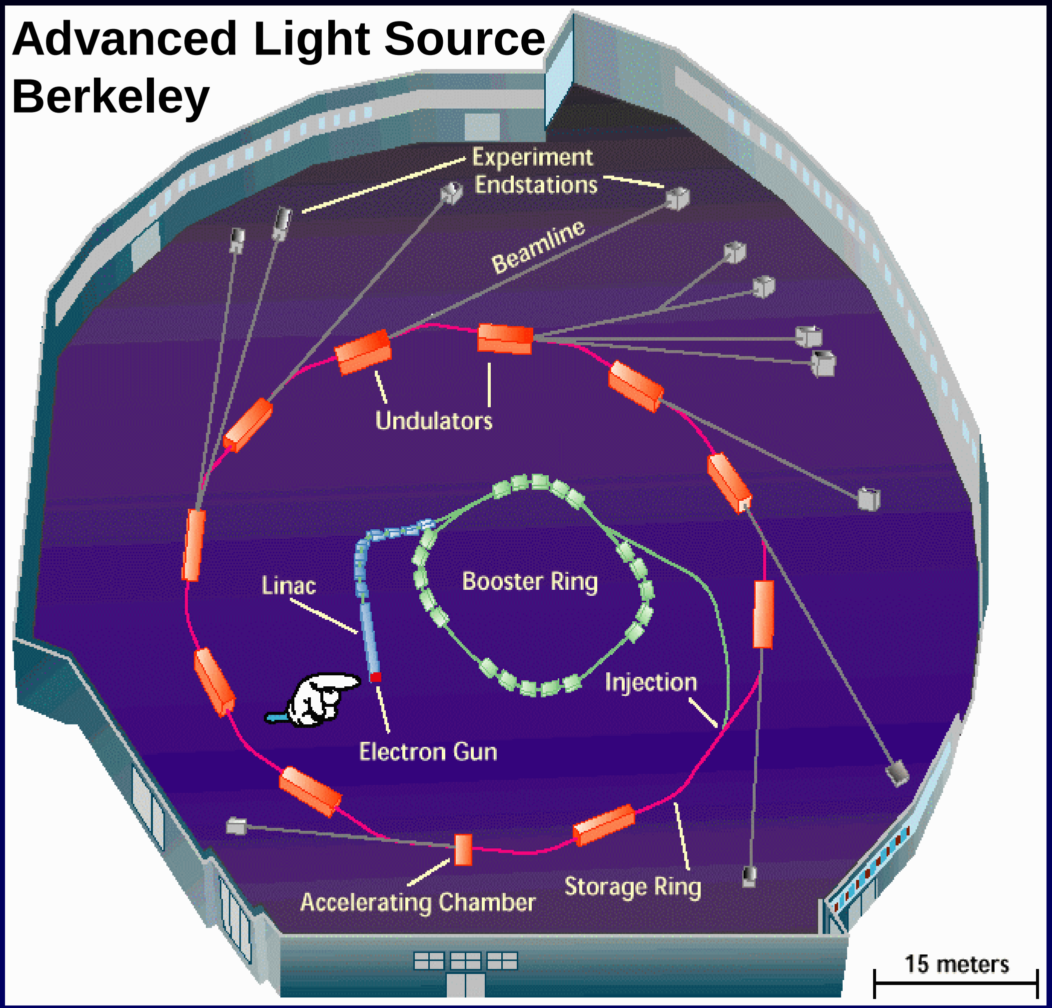


Synchrotron Radiation

- Intense light can be produced at a synchrotron facility
- Synchrotron radiation is produced from the infrared region (<1 eV) to the hard X-ray region with energies of 100 keV or more.
- There are a number of synchrotron facilities in the world:

Acronym	Facility	Location
	First-Generation Sources	
SSRL	Stanford Synchrotron Radiation Laboratory	Stanford, CA
CHESS	Cornell High Energy Synchrotron Source	Ithaca, NY
LURE	Laboratoire pour l'Utilisation de Rayonnement Electromagnétique	Orsay, France
HASYLAB	Hamburger Synchrotronstrahlungs Labor	Hamburg, Germany
	Second-Generation Sources	
SRS	Synchrotron Radiation Source	Daresbury, United Kingdom
KEK	Photon Factory	Tsukuba, Japan
NSLS	National Synchrotron Light Source	Upton, NY
BESSY	Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung	Berlin, Germany
	Third-Generation Sources	
APS	Advanced Photon Source	Argonne, IL
ALS	Advanced Light Source	Berkeley, CA
ESRF	European Synchrotron Radiation Facility	Grenoble, France
SPring-8	Super Photon ring—8 GeV	Nishi Harima, Japan

Synchrotron Radiation - Overview



Has allowed us to employ a number of spectroscopic and microscopic techniques to understand chemical reactions and processes at the molecular scale

Synchrotrons are Large Machines

e^- are injected into a ring-shaped vacuum chamber (~10^{-9} Torr) via an injection magnet

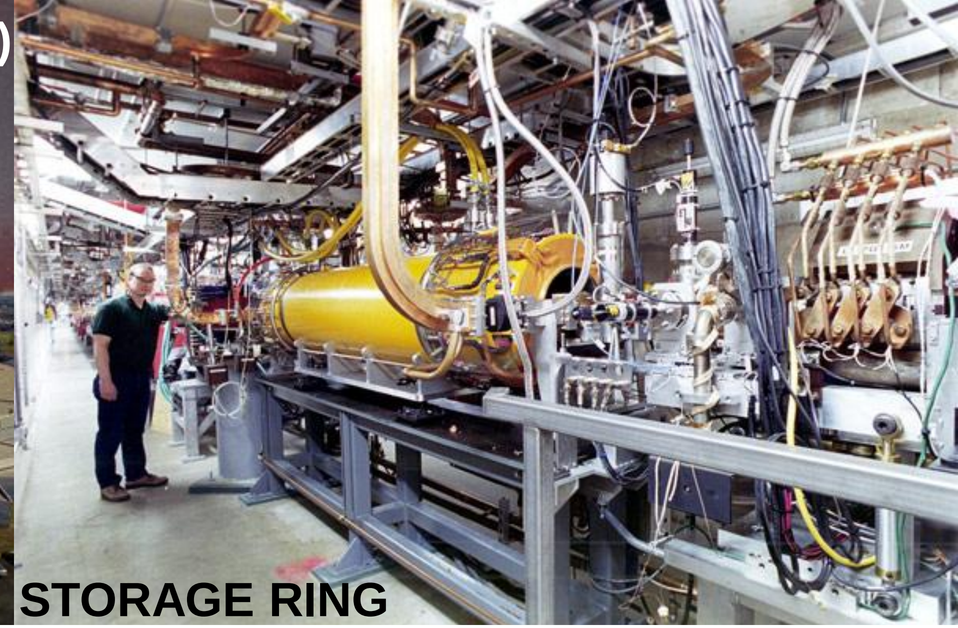
e^- are accelerated in a booster ring

e^- are injected into the storage ring (speed of light; temp of the sun)

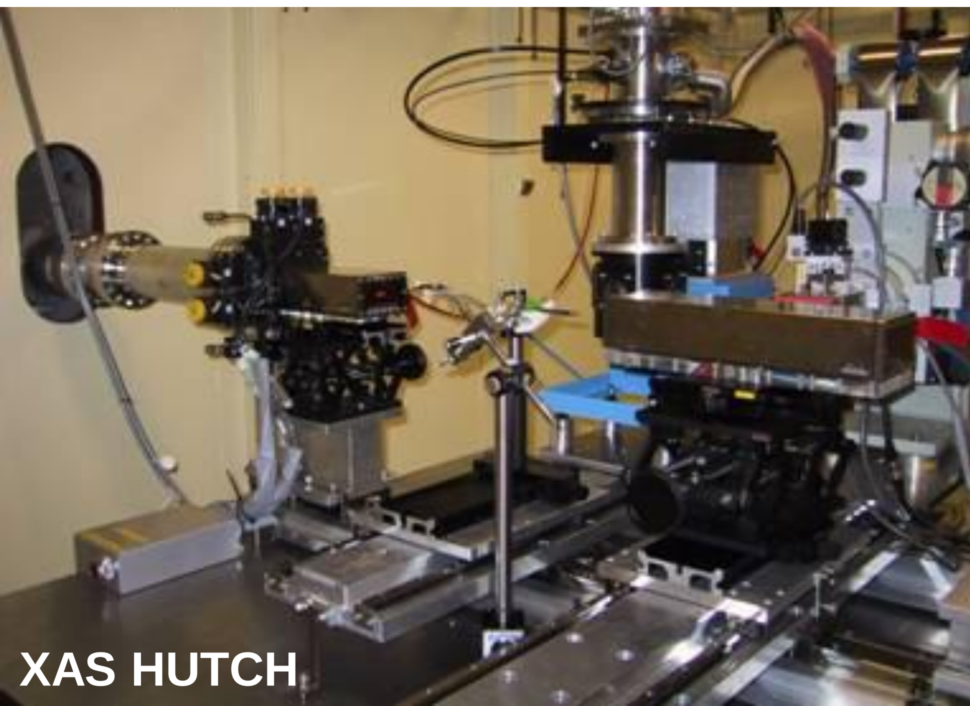
Synchrotron radiation (or light) is produced when e^- go through the bending magnets or undulators (insertion devices)

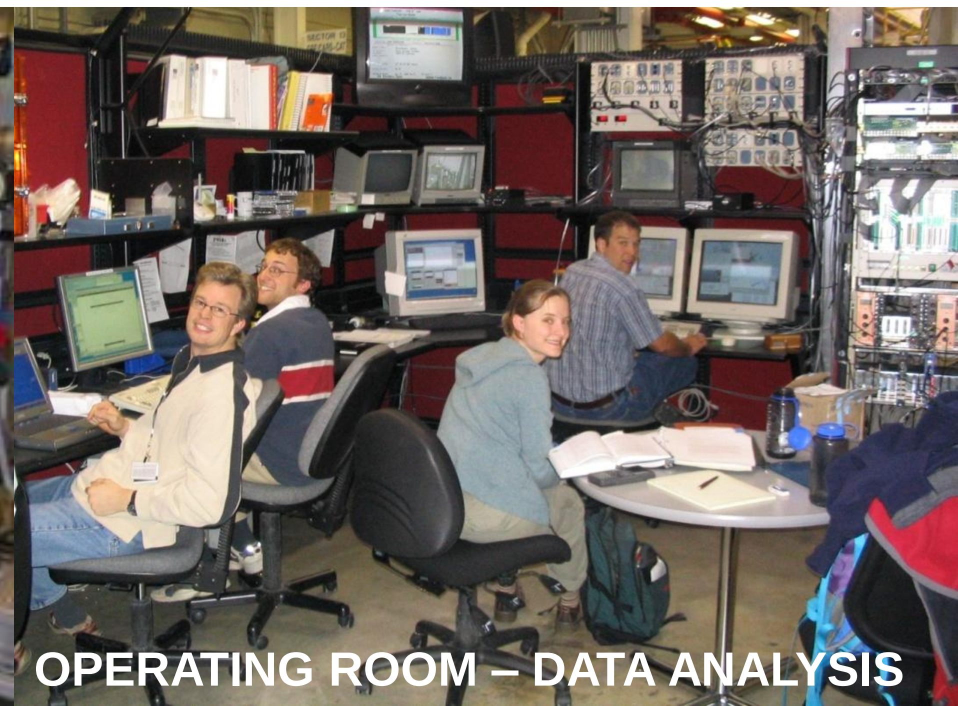
Beamlines allow the X-rays to enter shielded rooms that contain instrumentations for conducting experiments

The SPring-8 facility in Harima, Japan. This aerial view shows the existing synchrotron. The future XFEL buildings are superimposed within the red line



The Advanced Photon Source at Argonne National Laboratory



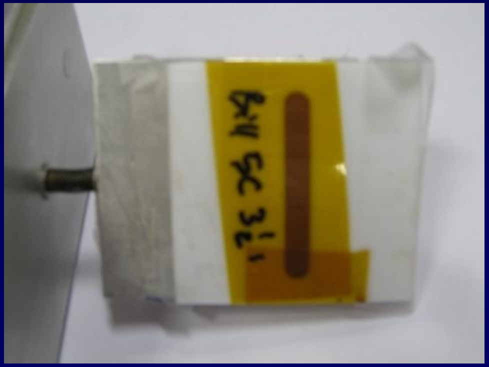


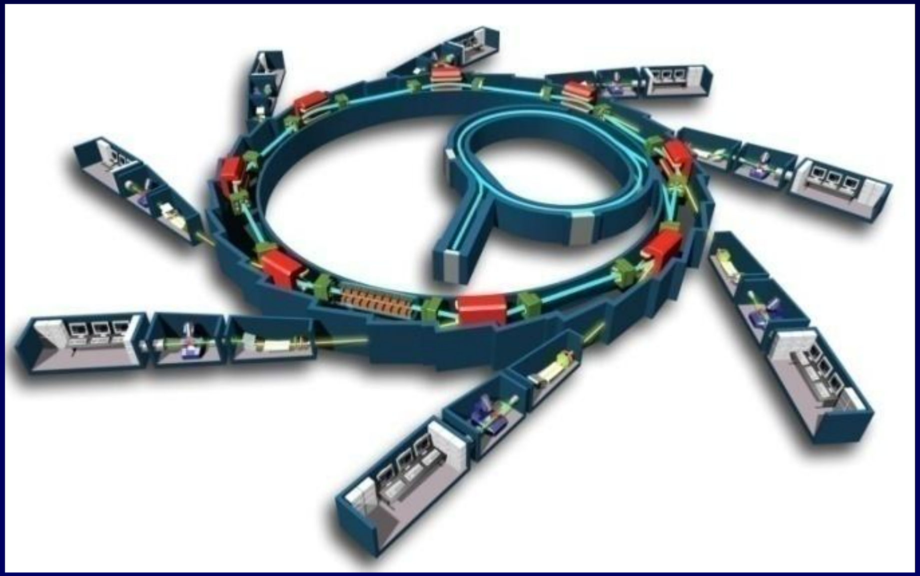
Synchrotron based techniques

A synchrotron source produces x-rays with much higher intensity than from an x-ray tube

Synchrotron produced x-rays are useful for environmental samples

- Non-destructive analysis
- Element specificity





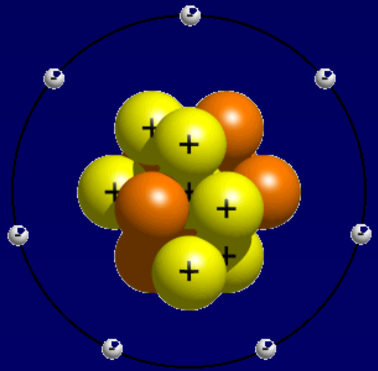
Feidenhans'l, R. (1989) *Surface Science Reports 10*, 105-188.
http://www.sync.monash.edu.au/science/index.html

X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is one of the most widely used synchrotron radiation based spectroscopic techniques for earth and environmental sciences

XAS can be used for most element both crystalline and non-crystalline solid, liquid, or gaseous states.

XAS is an in-situ technique that allows e.g. the presence of water and absence of vacuum

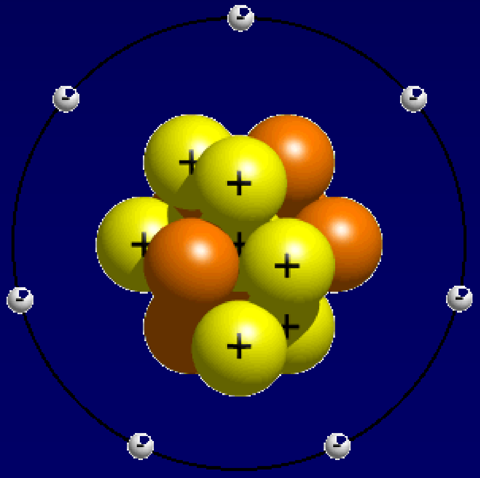


X-ray Absorption Spectroscopy

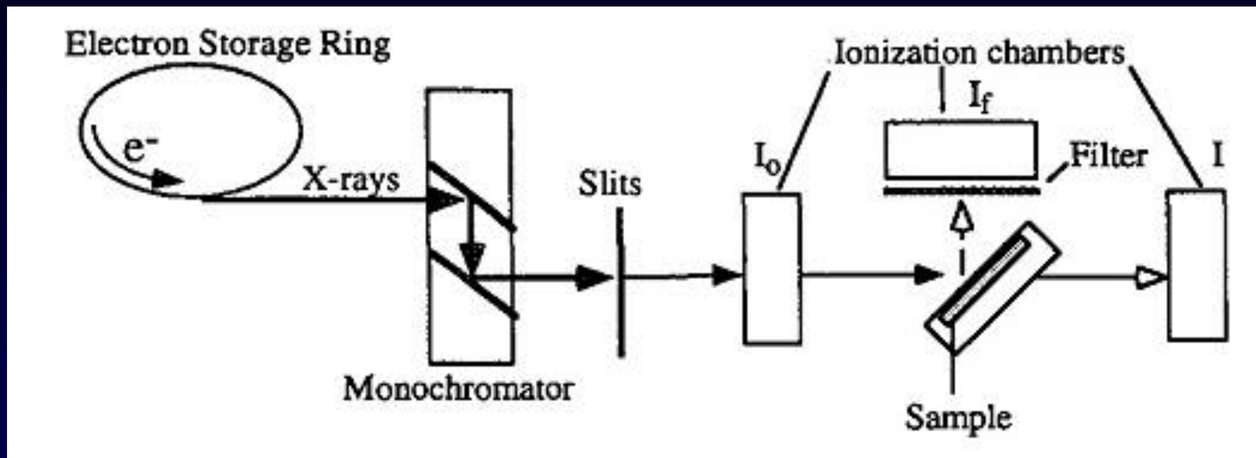
XAS is element specific method that yields information about the local structure and compositional environment of the absorbing atom.

It “sees” only the 2 or 3 closest shells of neighbors around the absorbing atom

XAS can give info on oxidation state, nearest neighbors, bond distances, and coordination numbers.



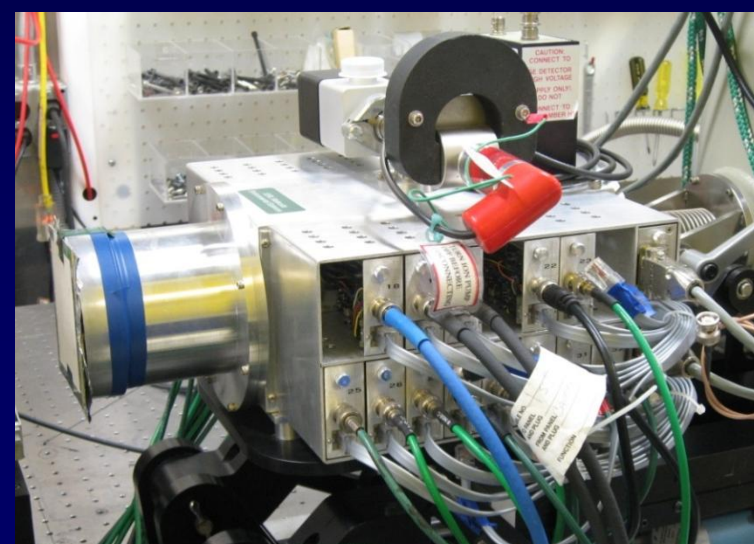
X-ray Absorption Spectroscopy



Transmission Mode

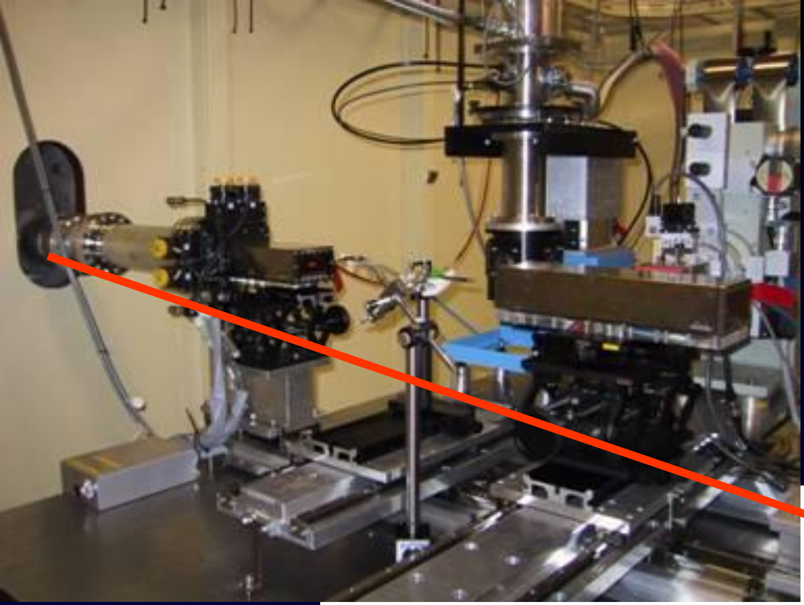
Fluorescence Mode

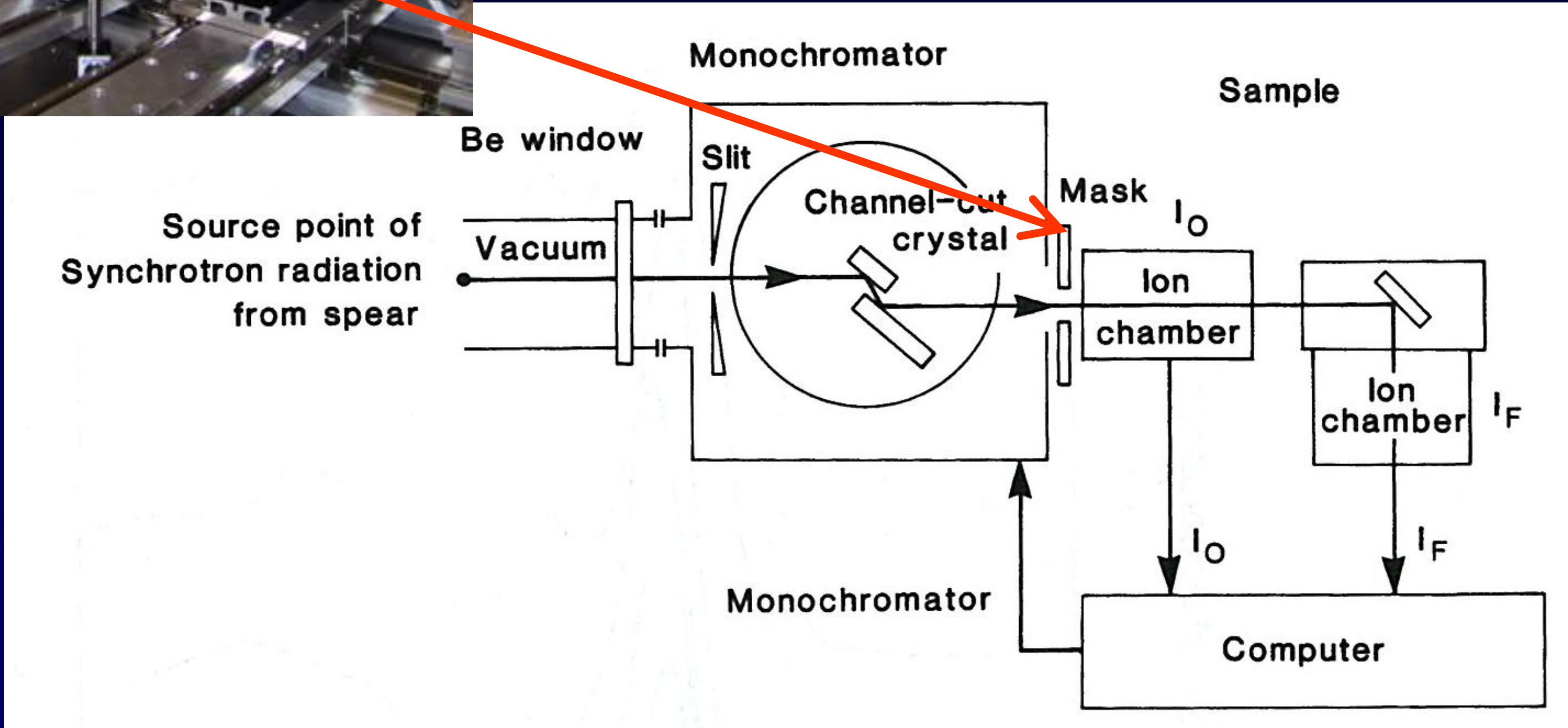
Ge Detector



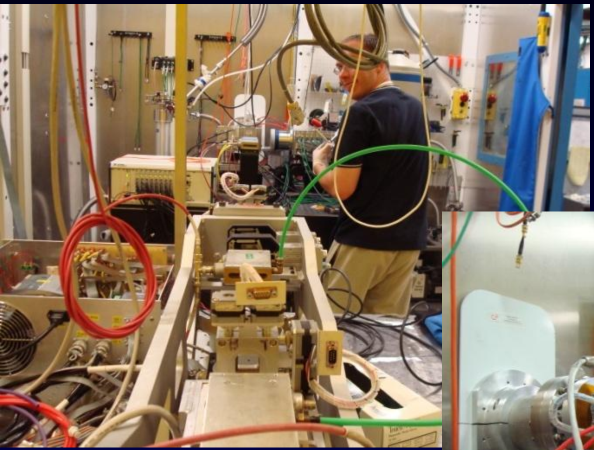
Fendorf, S.E., Sparks, D.L., Lamble, G.M. and Kelley, M.J. (1994) *Soil Sci Soc Am J* 58, 1583-1595.

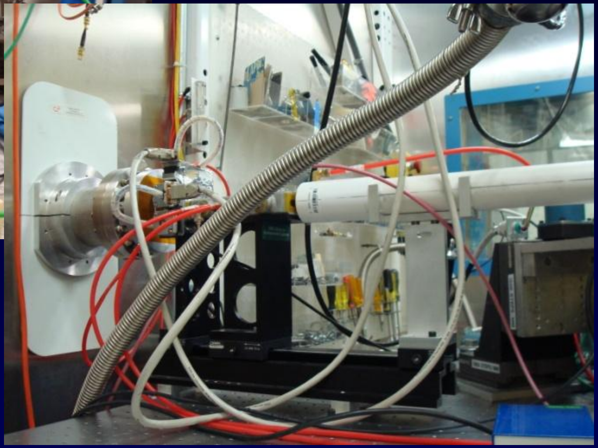
Experimental Setup for XAS Measurements

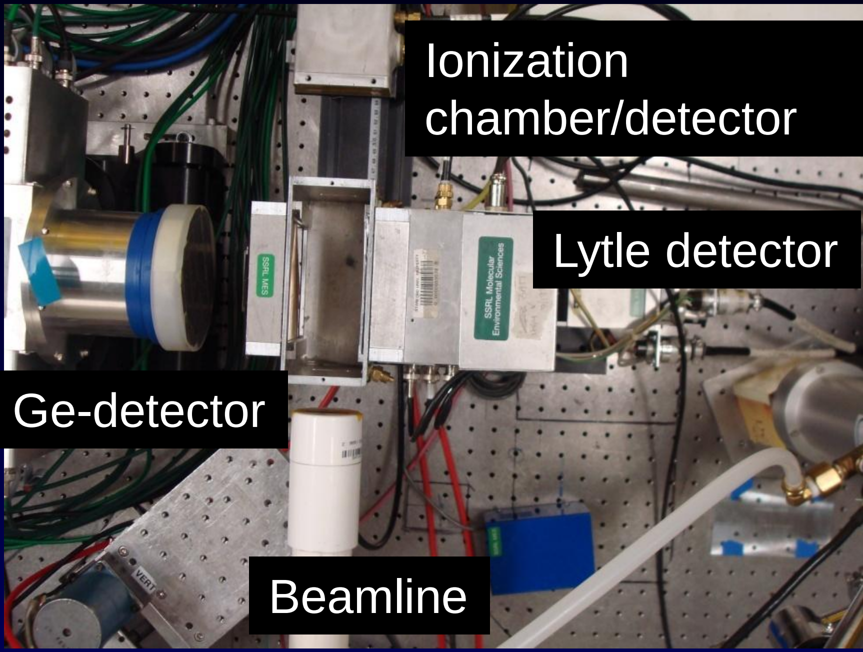


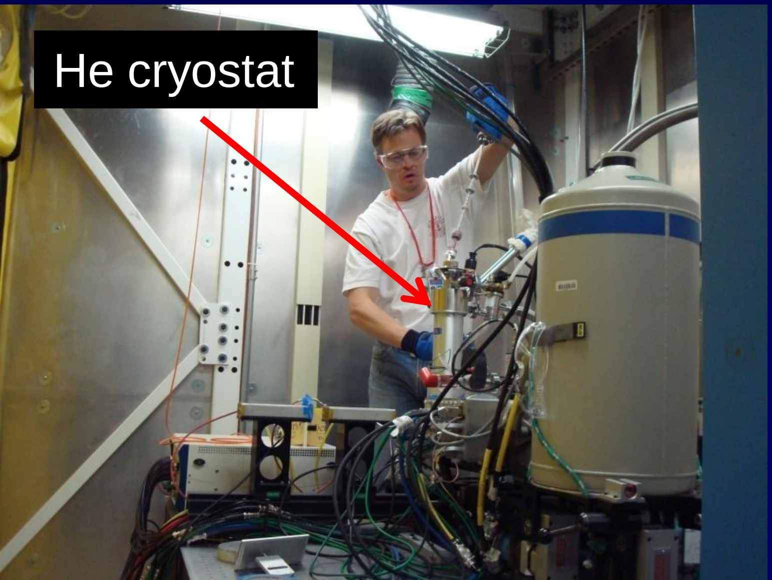


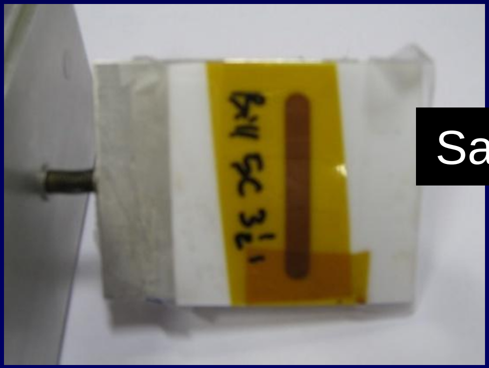
Pictures of XAS Setup







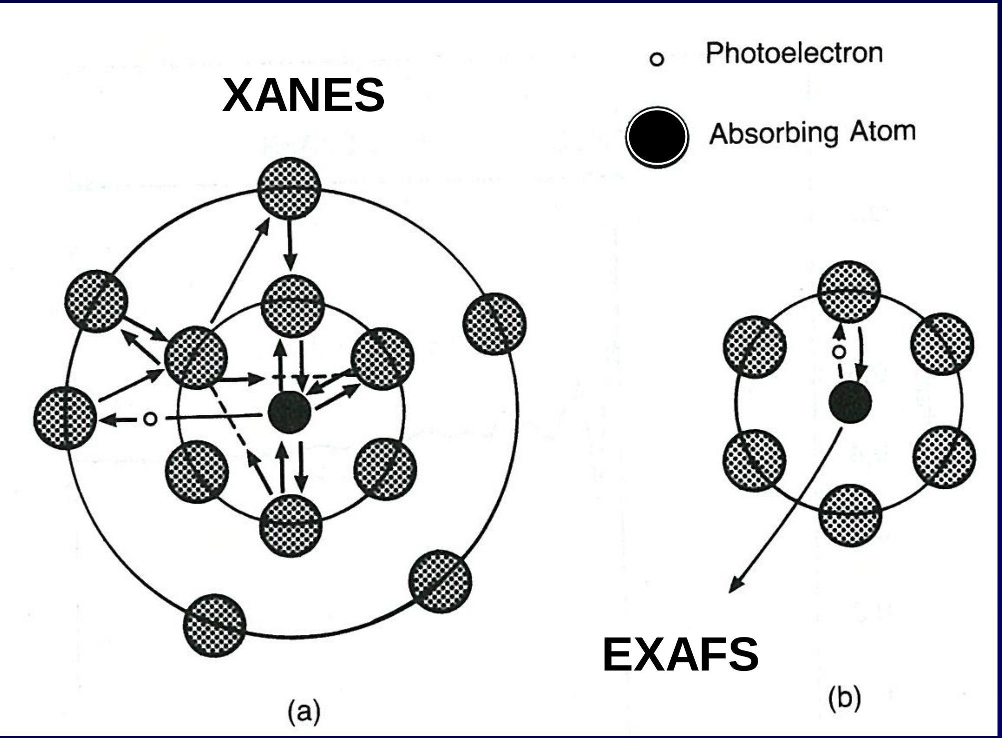


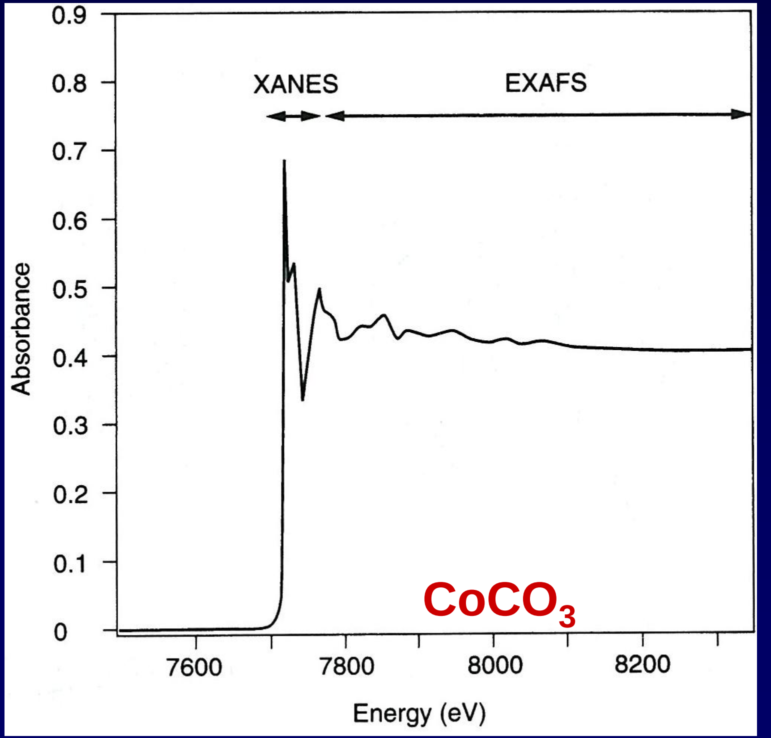


Electron Scattering (XANES)

Multiple scattering among neighboring atoms leads to the XANES portion of the spectrum

Fingerprint info such as oxidation state can be obtained from the XANES region of the spectrum.



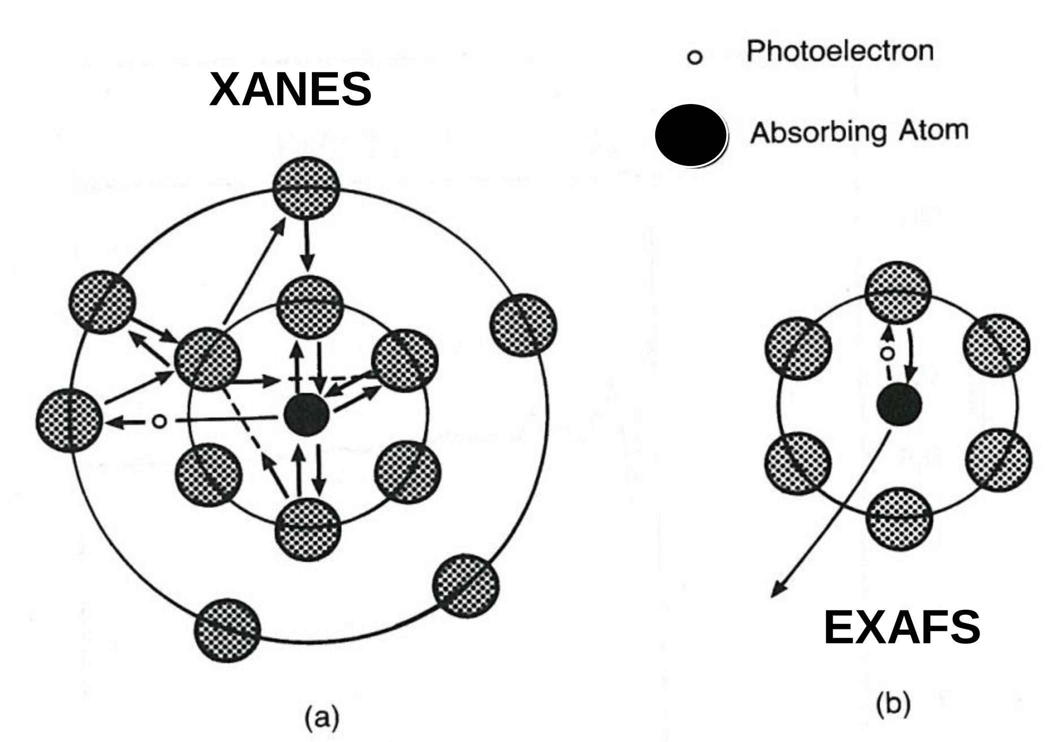


Electron Scattering (EXAFS)

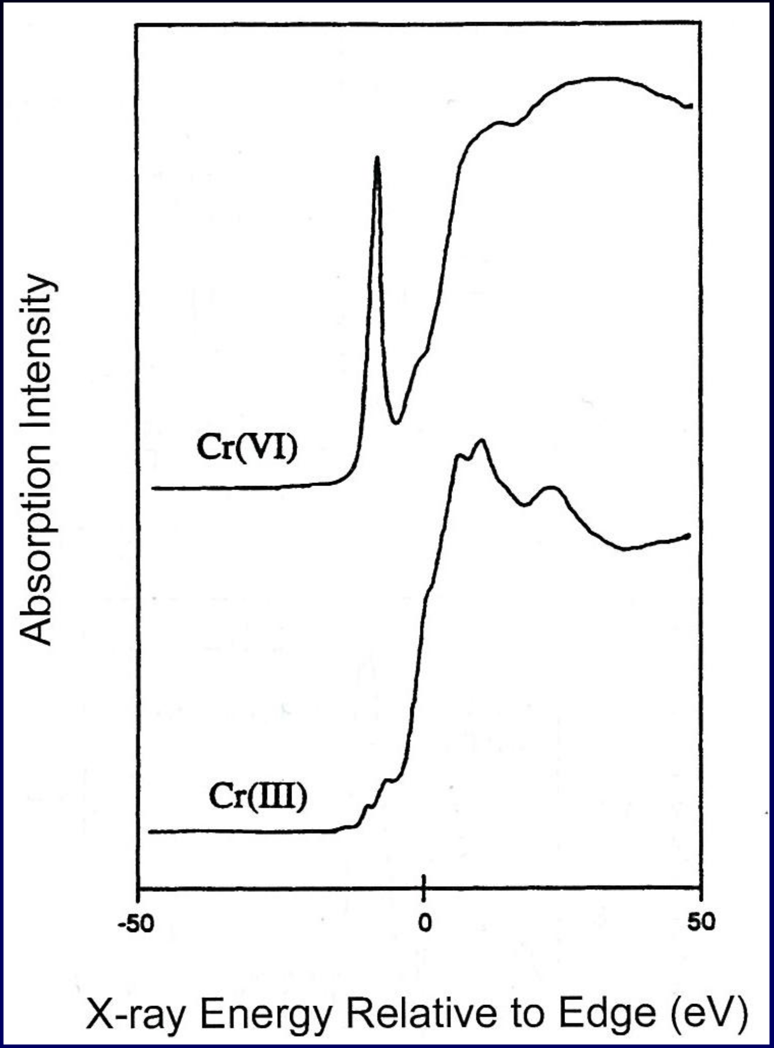
The EXAFS (extended X-ray absorption fine structure) spectrum is caused by interference between outgoing and backscattered photoelectrons, which modulates the atomic absorption coefficient (*a*).

Analysis of the EXAFS spectrum provide information on the bond distances, coordination number, and next nearest neighbors.

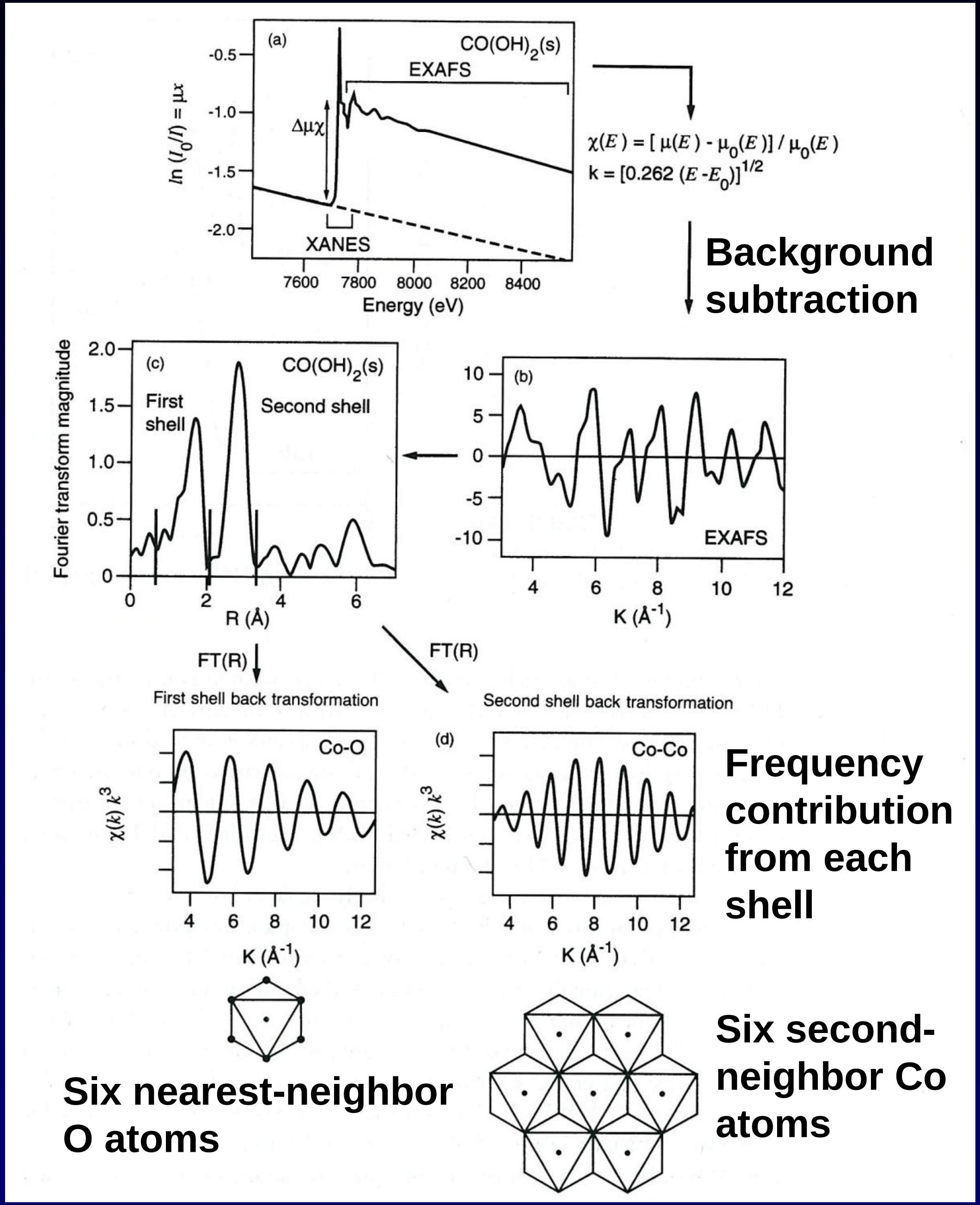
If a flux through a material decreases with distance x in proportion to e^{-ax}, then a is called the absorption coefficient.



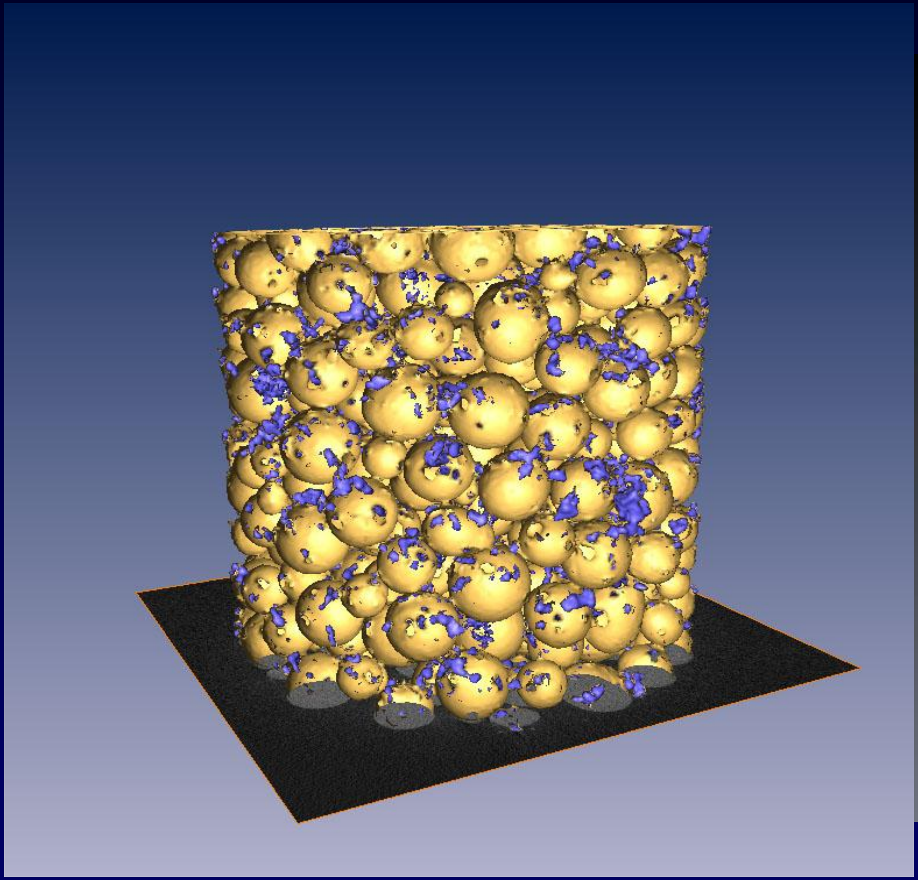
Determination of the oxidation state of Cr using XANES



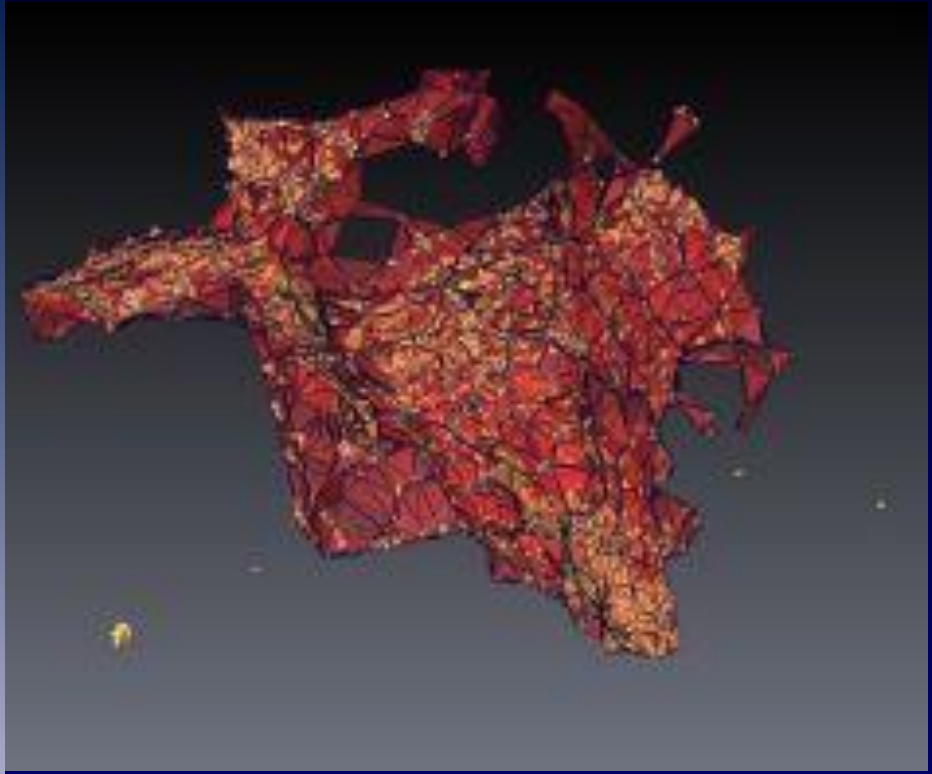
Analysis of EXAFS Spectrum



Advanced X-ray Microscopy, Tomography and Microfocused XAS



Microbially Enhanced Oil Recovery



Biofilm Structure in Porous Media

Image courtesy: http://web.engr.oregonstate.edu/~wildensd/index.html

Speciation of Metal-Contaminated Soils

TO OVERCOME THE DIFFICULTIES ASSOCIATED WITH BENCH-TOP TECHNIQUES (e.g., LOD, sample preparation/destruction)

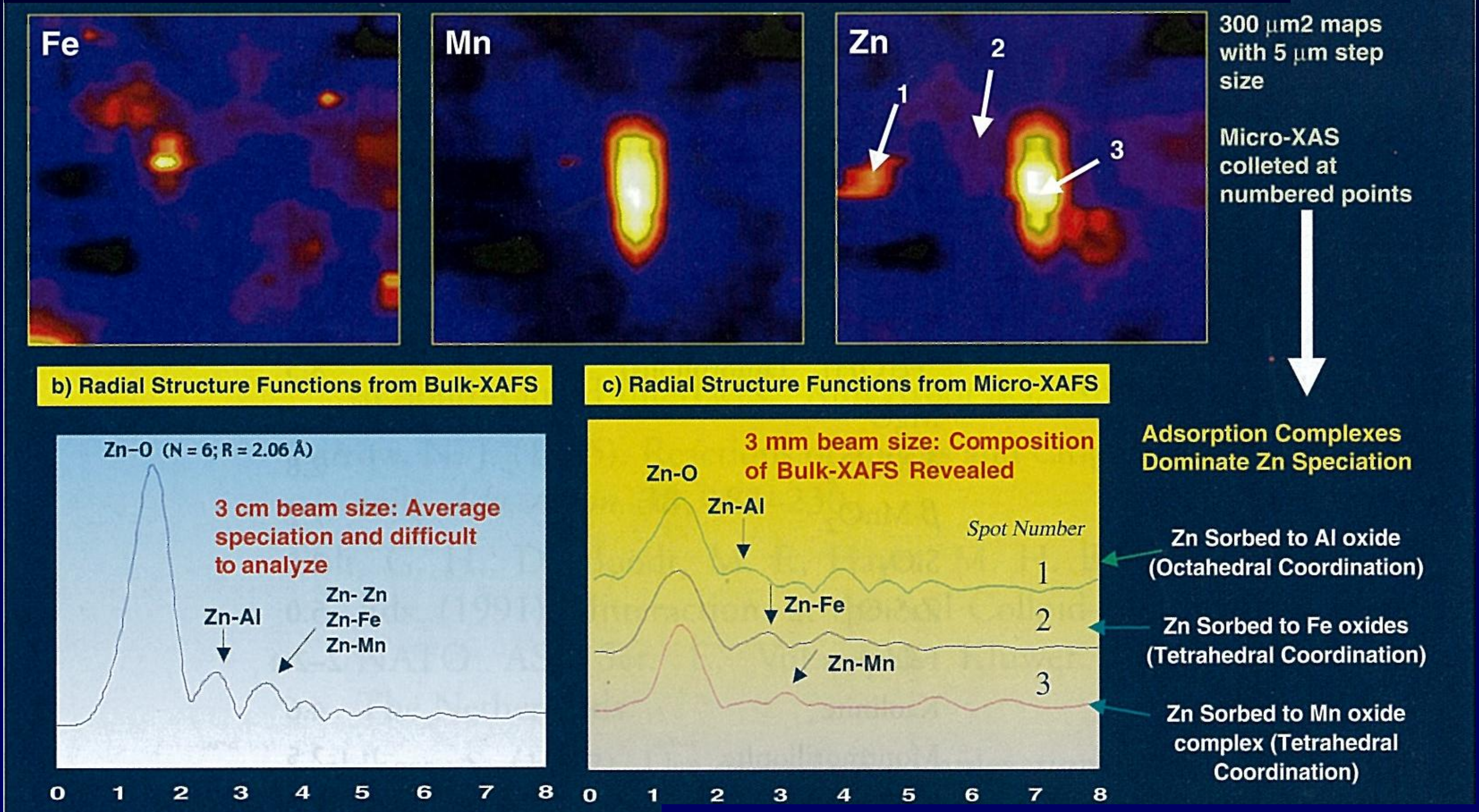
One can apply spatially resolved micro (μ)-XAFS (both μ-XANES and μ-EXAFS) combined with μ-synchrotron-X-ray fluorescence spectroscopy.

With these techniques, one can study metal speciation in soils on a micron scale (see example on WebCT "Sup. Material" chromate adsorption and reduction in arid soils: studied by (synchrotron-based) various spectroscopic and diffraction techniques.

Speciation of Metal-Contaminated Soils: Example

Example of using these techniques to speciate Zn in soils

Micro-SXRF mapping: Zn associated w. both Fe and Mn indicate that Zn could be present in different phases!

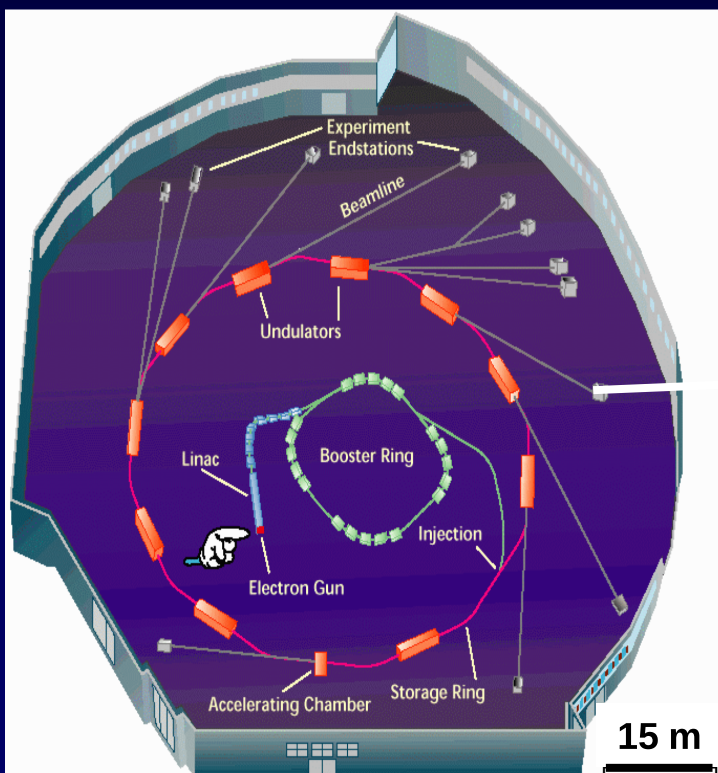


Bulk-XAFS: suggests inner-sphere complexation between Zn and Al

Micro-XAFS: Spot 1, Zn is octahedrally coordinated and sorbed to an Al phase

Scanning Transmission X-Ray Microscopy (STXM) Study of DIRB

- STXM is a new synchrotron based X-Ray SpectroMicroscopy Technique
- STXM allows us to characterize both organics (functional groups) and minerals at the nanometer scale



X-Rays

Basics of X- ray spectromicroscopy

Spectromicroscopy= Both spectroscopy and microscopy at high spatial resolution

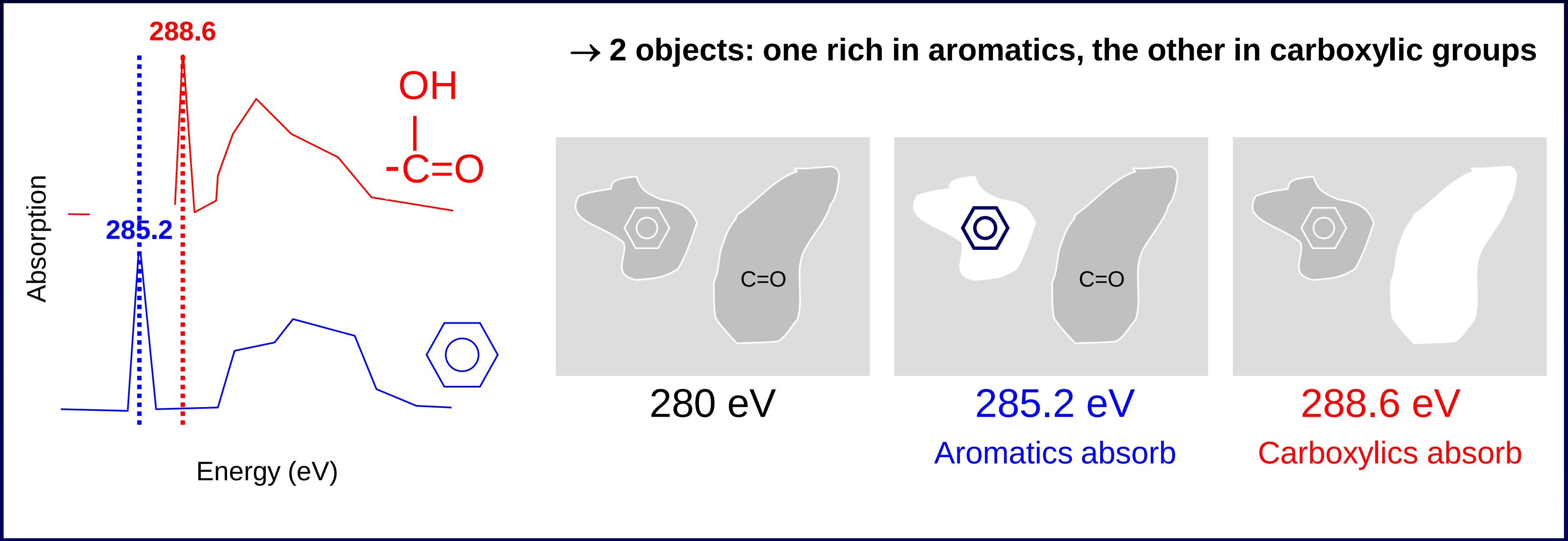
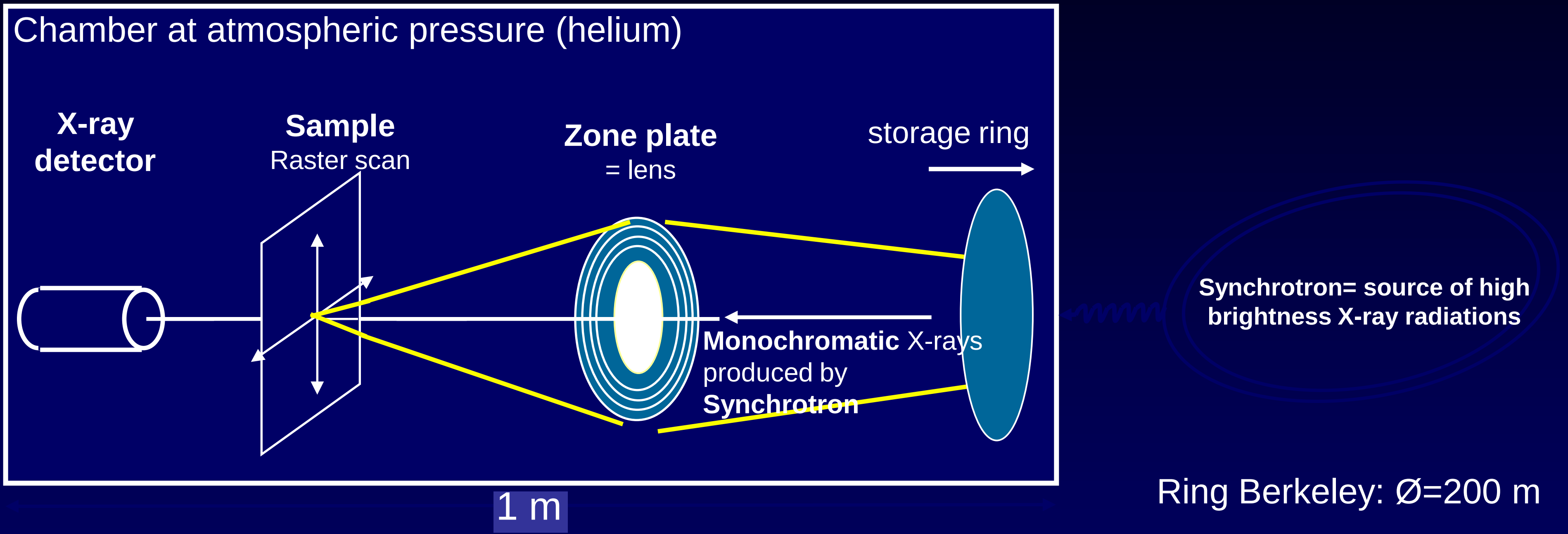


Image contrast = Differential absorption of X-rays depending on speciation

STXM= Scanning Transmission X-ray Microscopy

Advanced Light Source, Berkeley, ligne 11.0.2



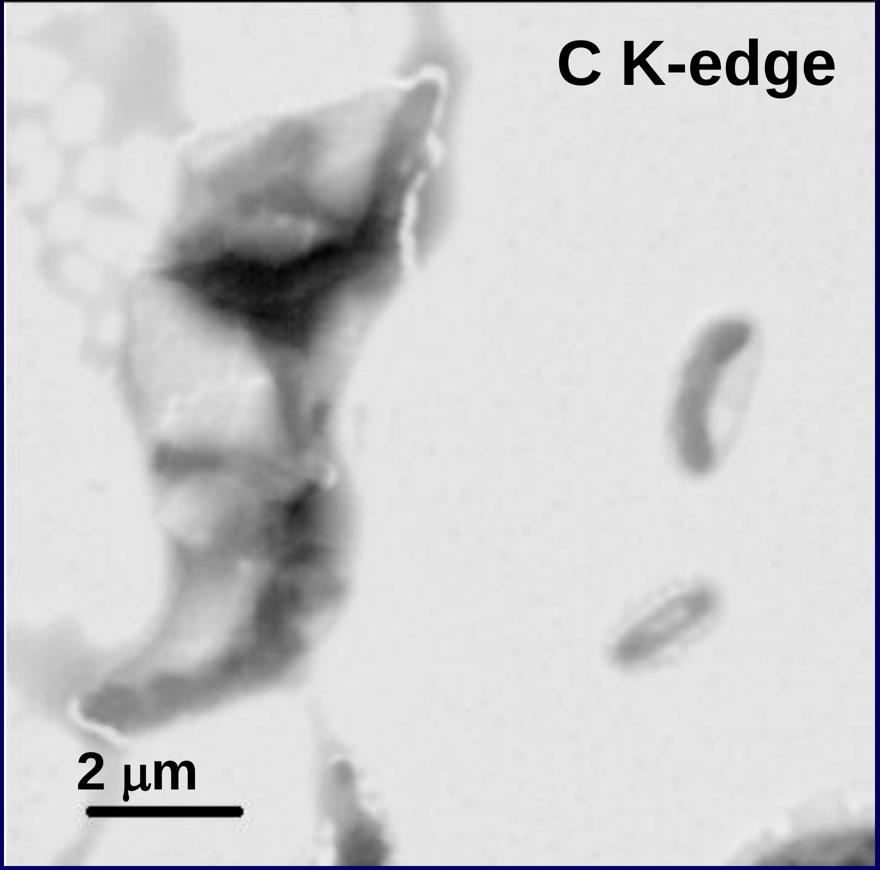
- ★ Transmission microscopy
- ★ **Spatial Resol: ~25 nm**
- ★ Spectral Resol: <0.1 eV
- ★ Energy Range: 130-2200 eV
  - K-edge: C ⇒ Si
  - L-edge: P ⇒ As

⟹

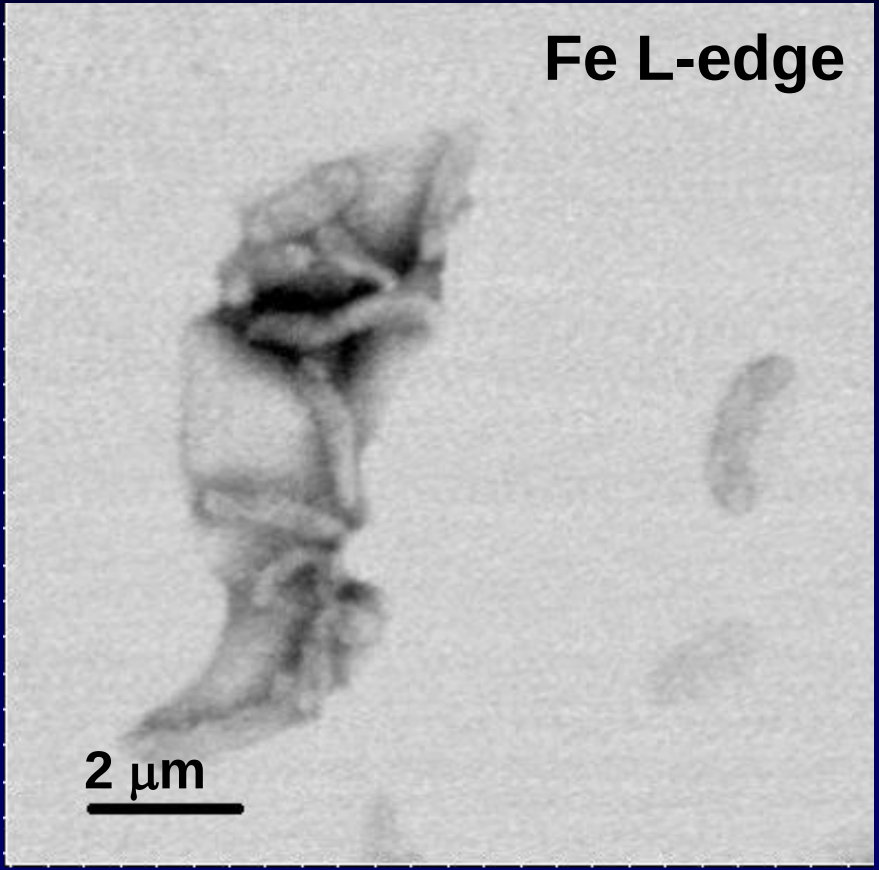
- ★ Energy-filtered Imaging
- ★ Chemical Mapping
- ★ X-ray spectroscopy (NEXAFS)

Correlation between Carboxyl Functional Groups and Reduced Iron

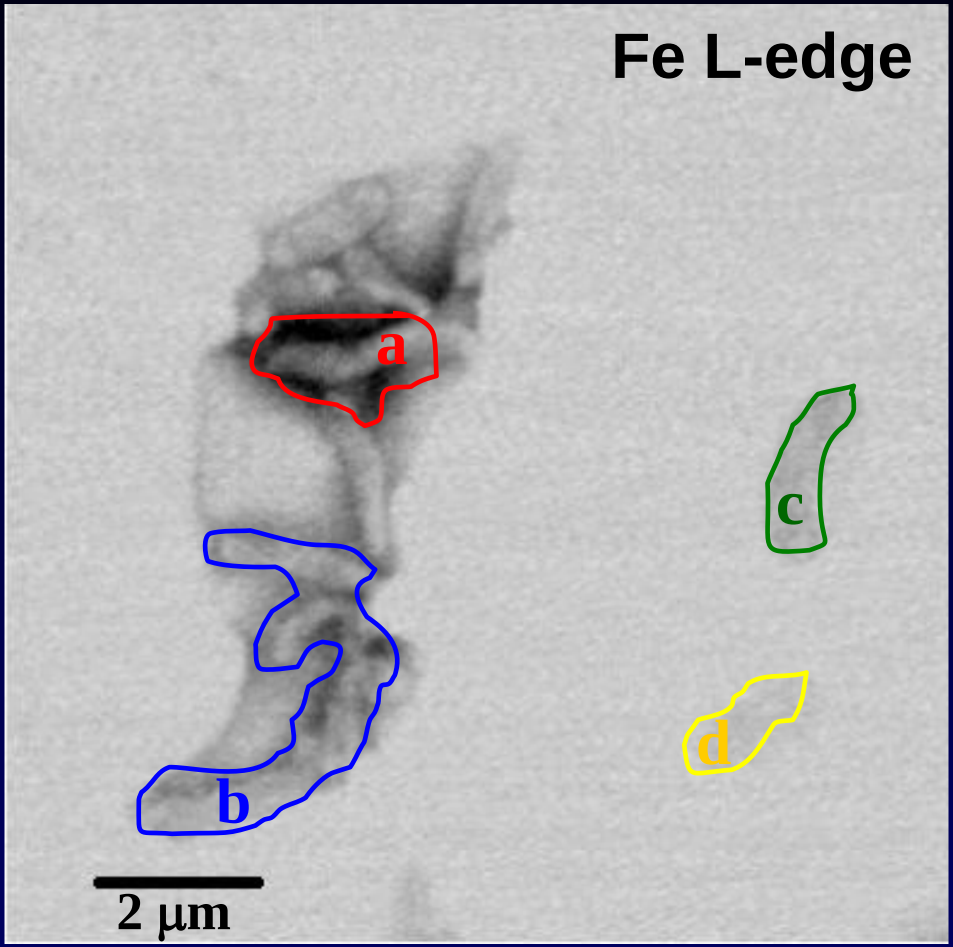
Carboxyl Map

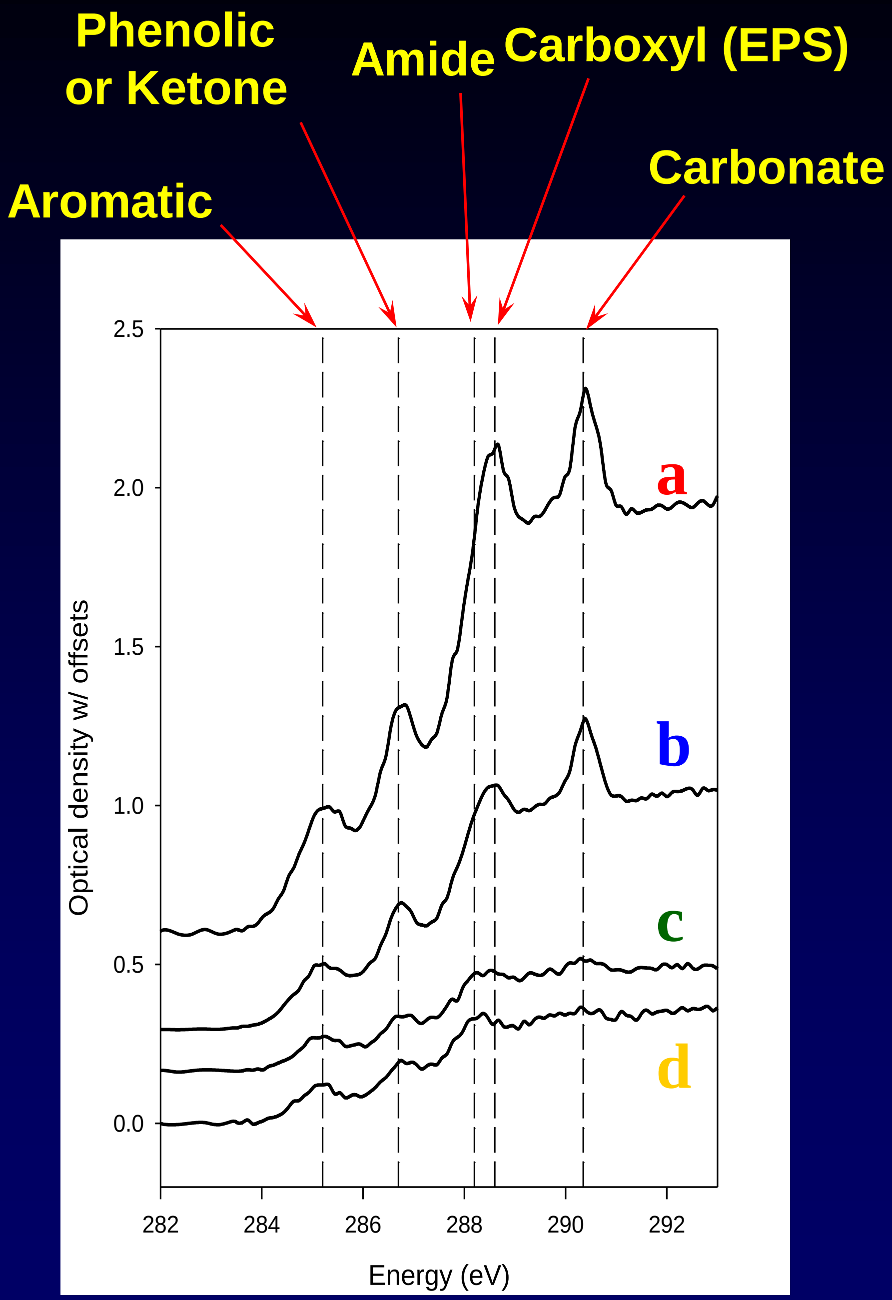


Fe(II) Map



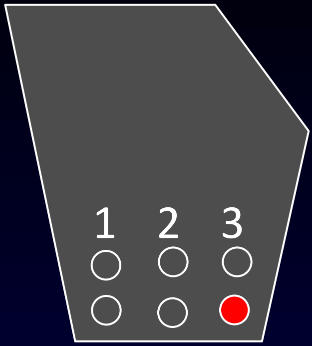
Fe(II) Map

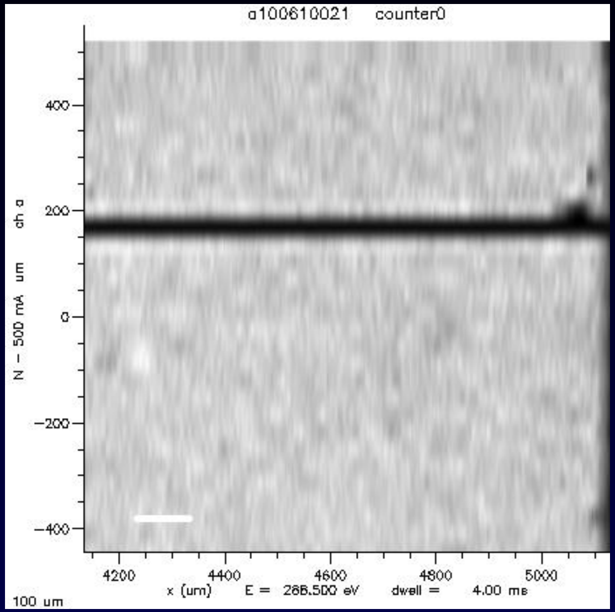


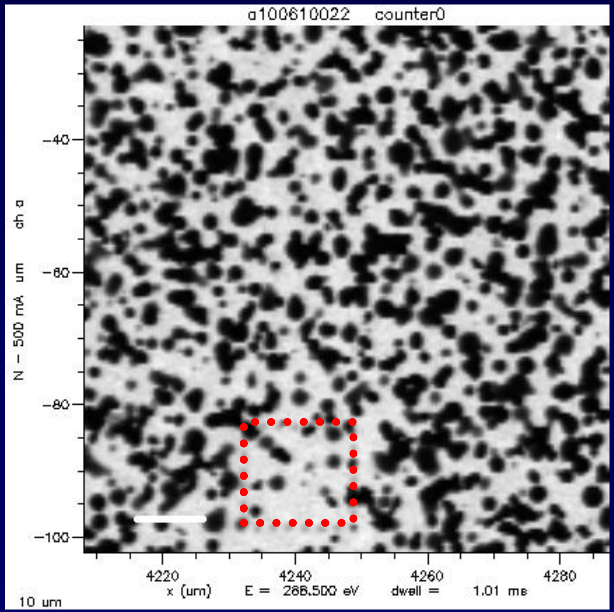


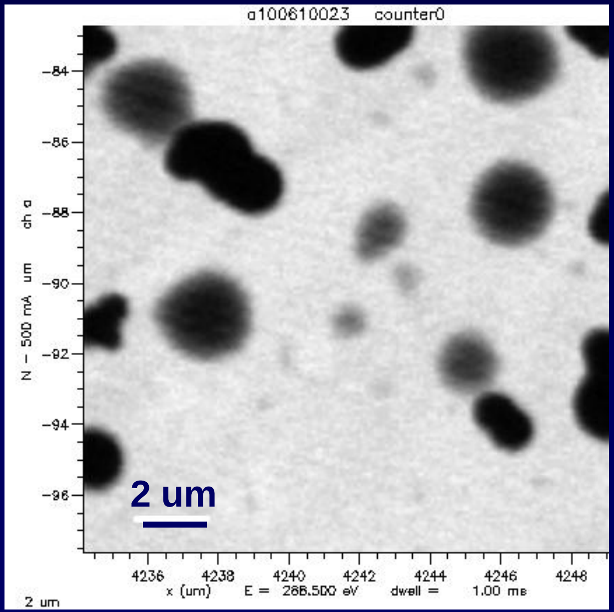
The Fe spectrum of area **a** is similar to siderite

Fulvic Acid Coated Hematite (70 nm)
STXM analysis



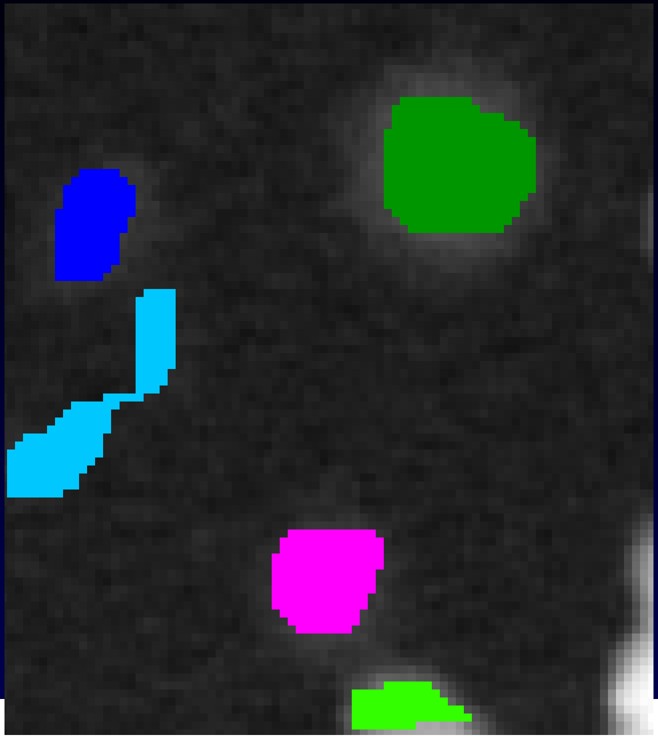


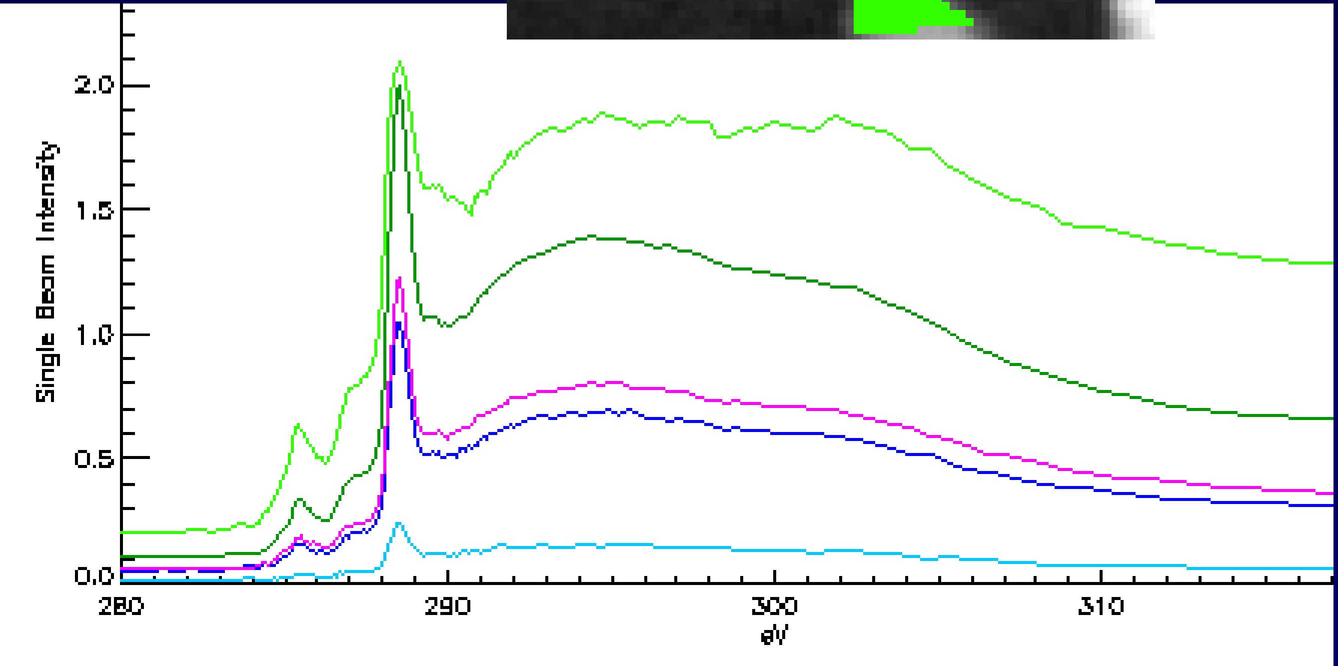




Carbon Map

C K-edge

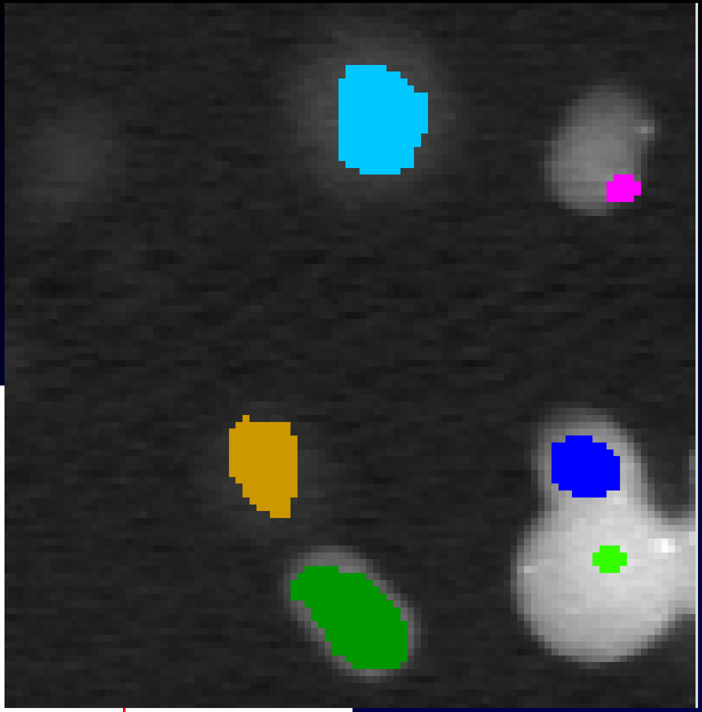


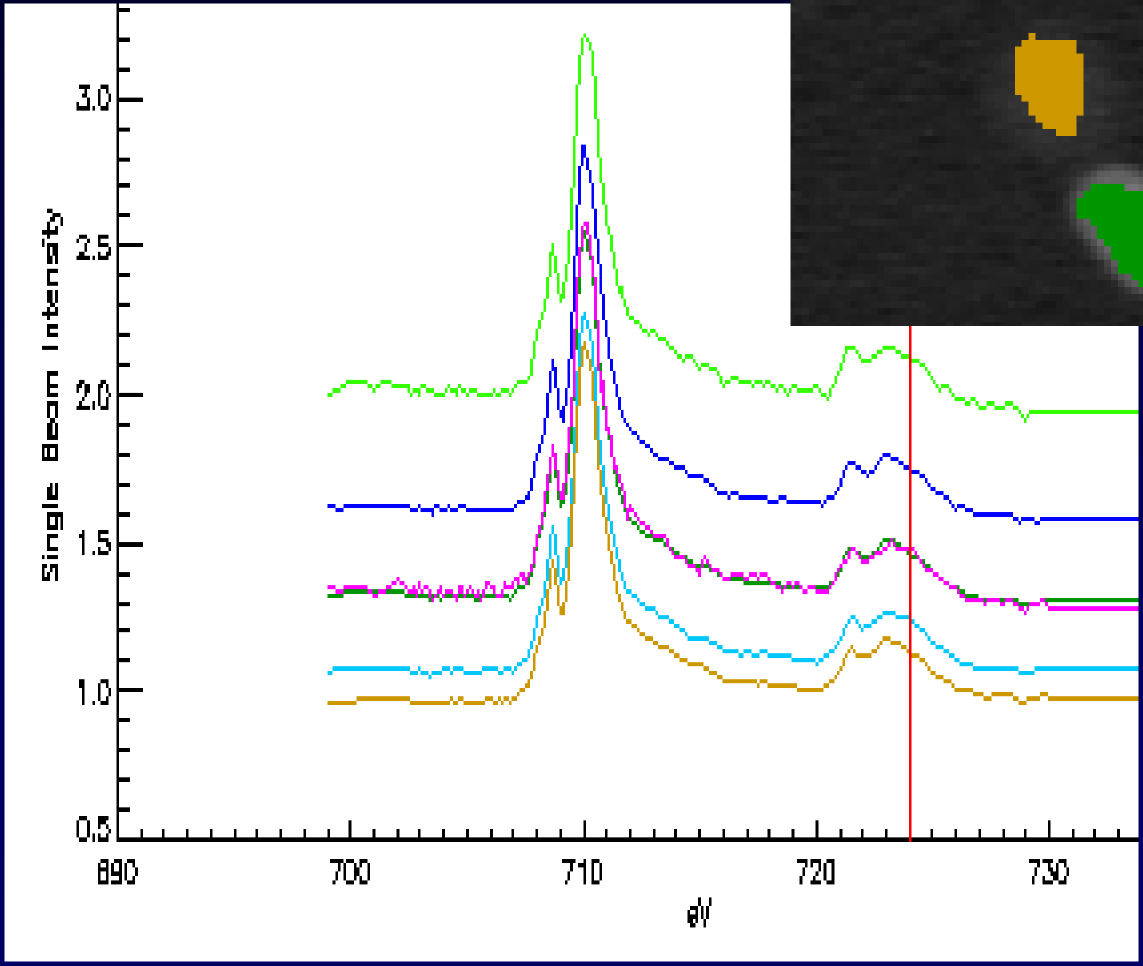


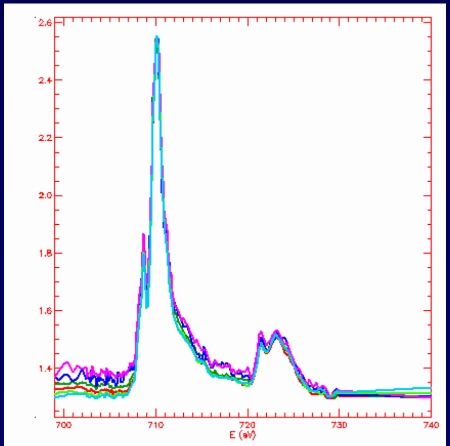
Iron (hematite) map

Fe L-edge

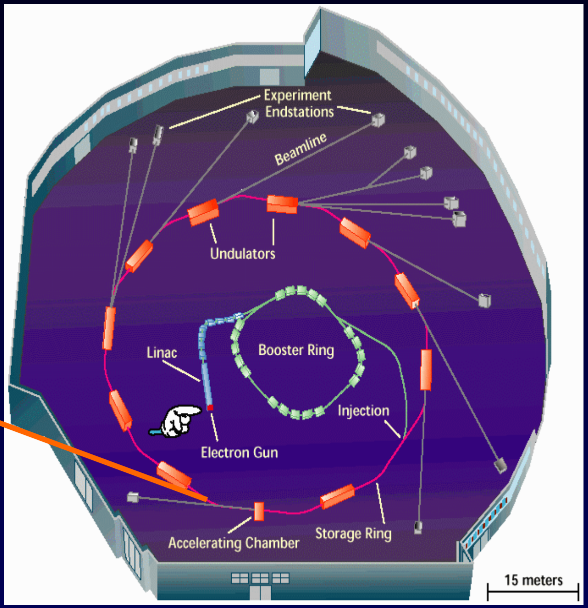
Hematite is quite homogeneous







Synchrotron-Based FTIR Spectromicroscopy

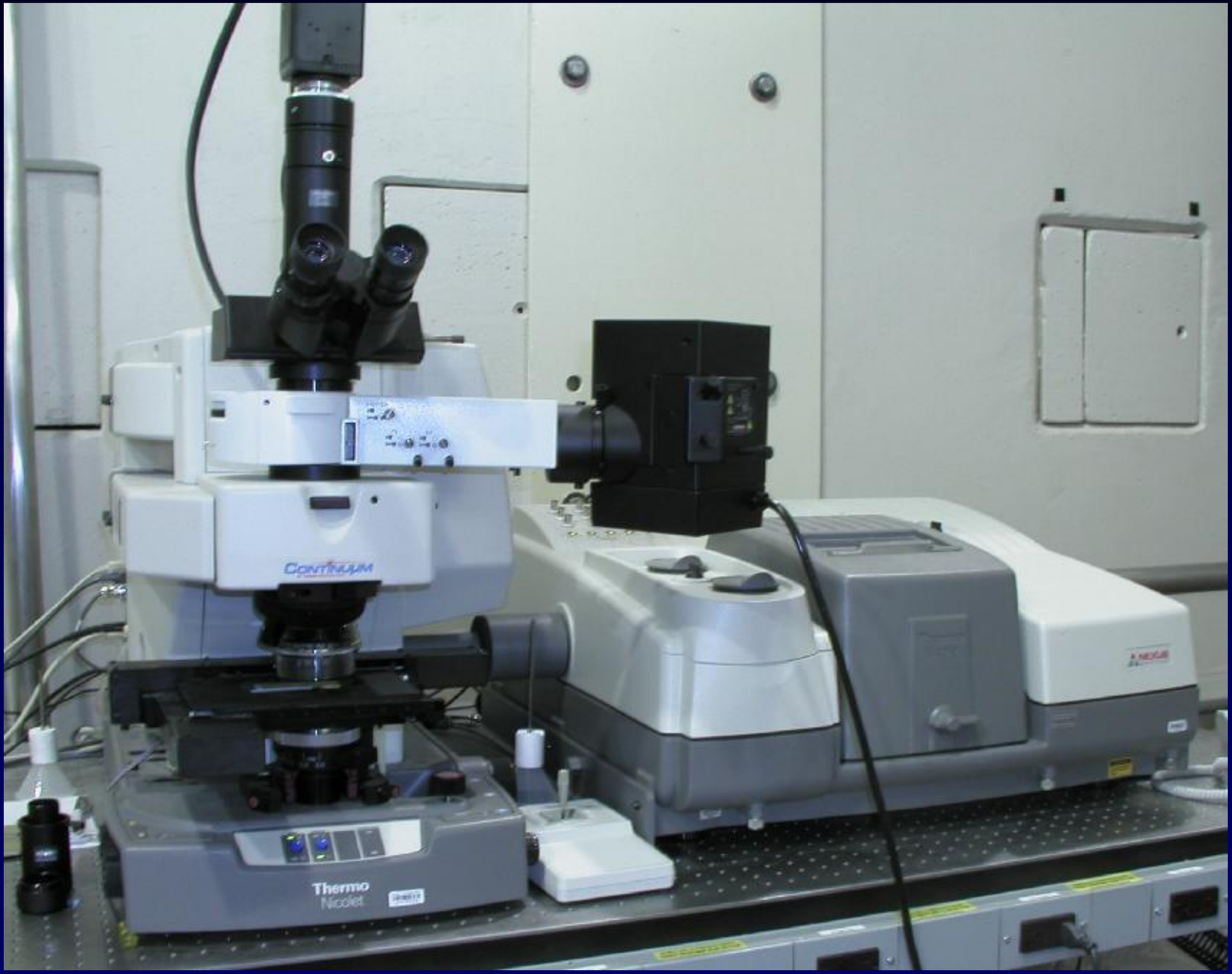


SR-FTIR facts: non-destructive to biological samples; spatial imaging resolution of 3-10 μm; high signal to noise ratio

Beamline 1.4 at The Advanced Light Source at LBNL (http://infrared.als.lbl.gov/)

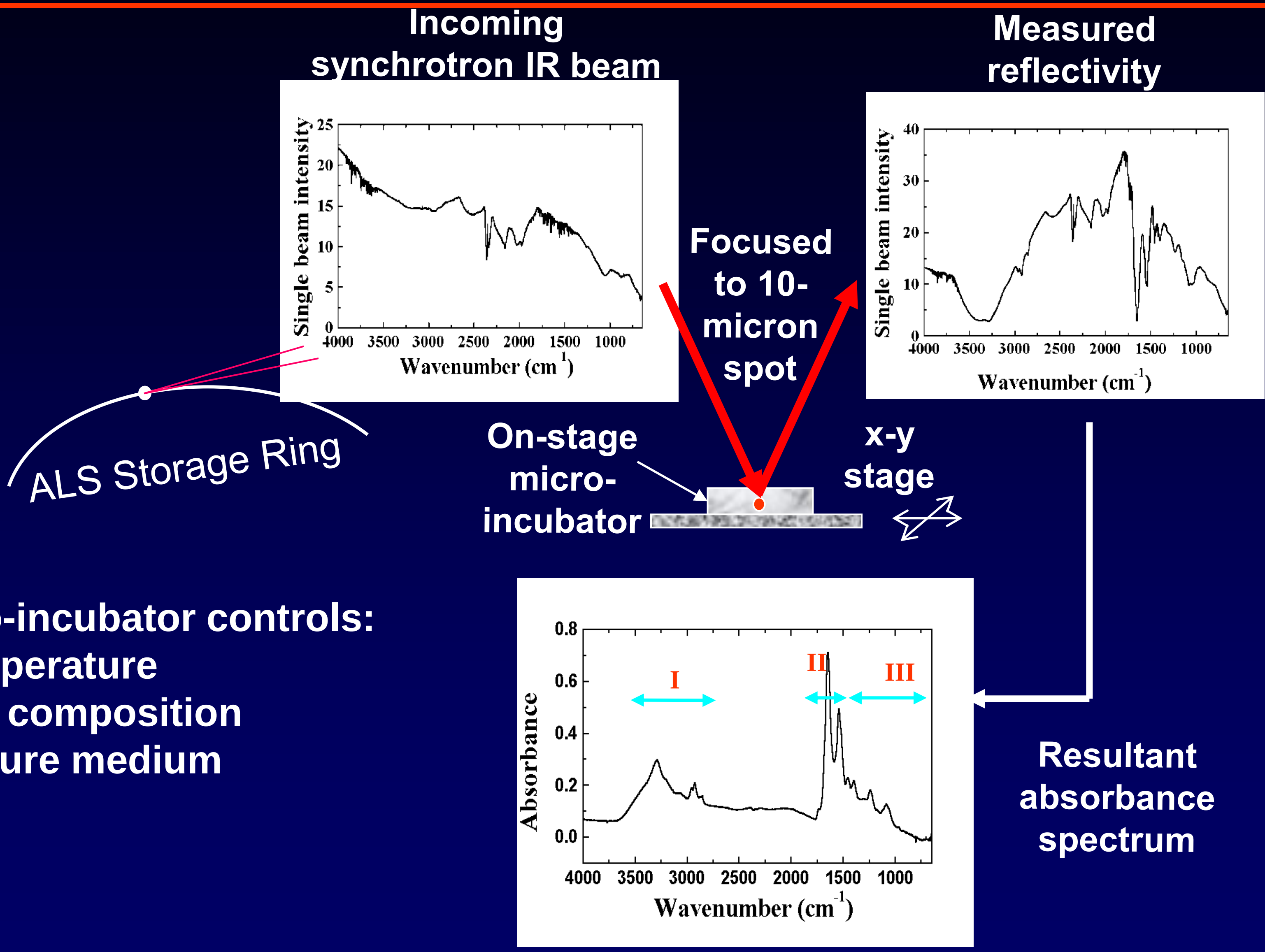
NEW SCOPE: ThermoNicolet Nexus 870

with Continuμm IR Microscope (N2 Purged)



Source characteristics	Bend magnet
Energy range	0.02-1 eV
Frequency range	200-10,000 cm^{-1}
Interferometer resolution	0.125 cm^{-1}
Endstations	Nicolet Magna 760 FTIR, Nic-Plan IR microscope (N_2 purged)
Characteristics	Motorized sample stage, micron resolution, reflection and transmission modes
Spatial resolution	Diffraction limited (~wavelength)
Detectors	Extended-range MCT (mercury cadmium telluride)
Spot size at sample	**<10 µm (diffraction limited)**

SR-FTIR Spectromicroscopy Technique

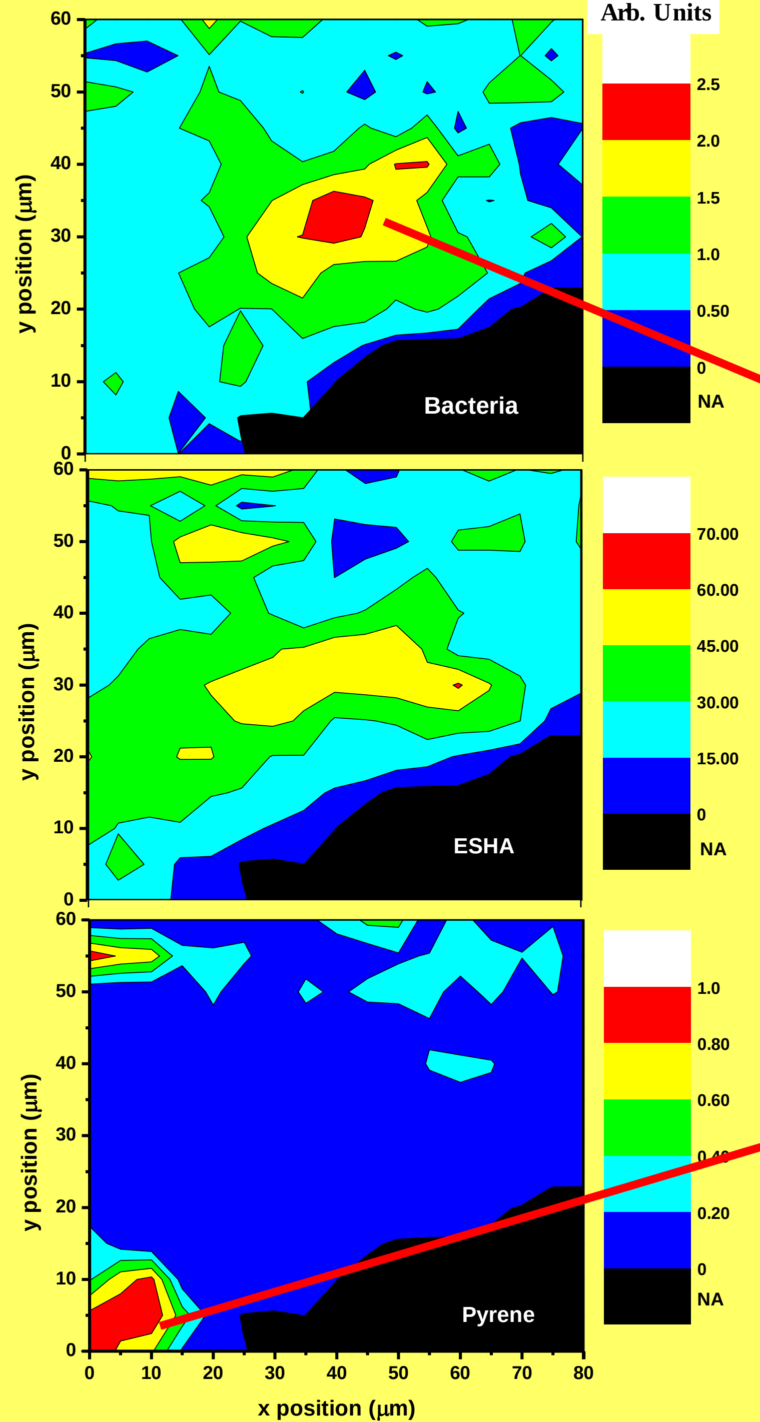


Micro-incubator controls:

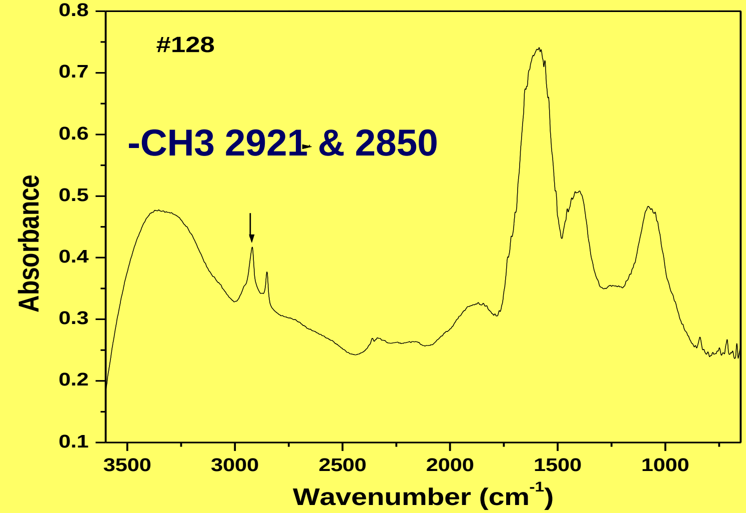
- Temperature
- Gas composition
- Culture medium

(http://infrared.als.lbl.gov/)

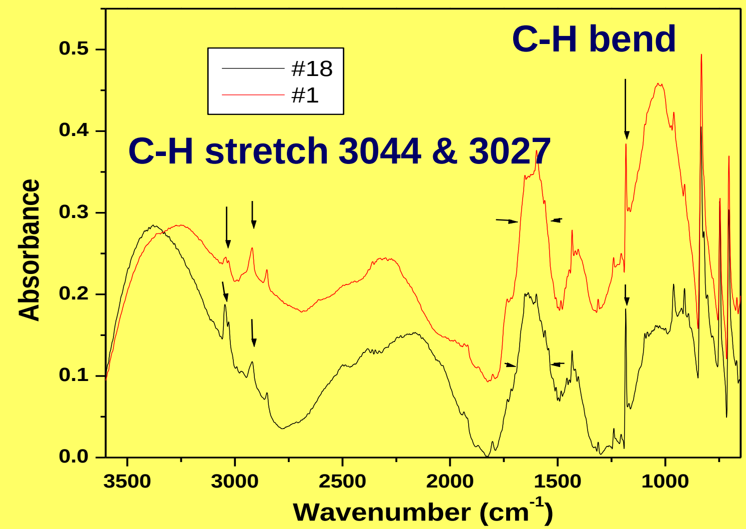
IR image at end of experiment



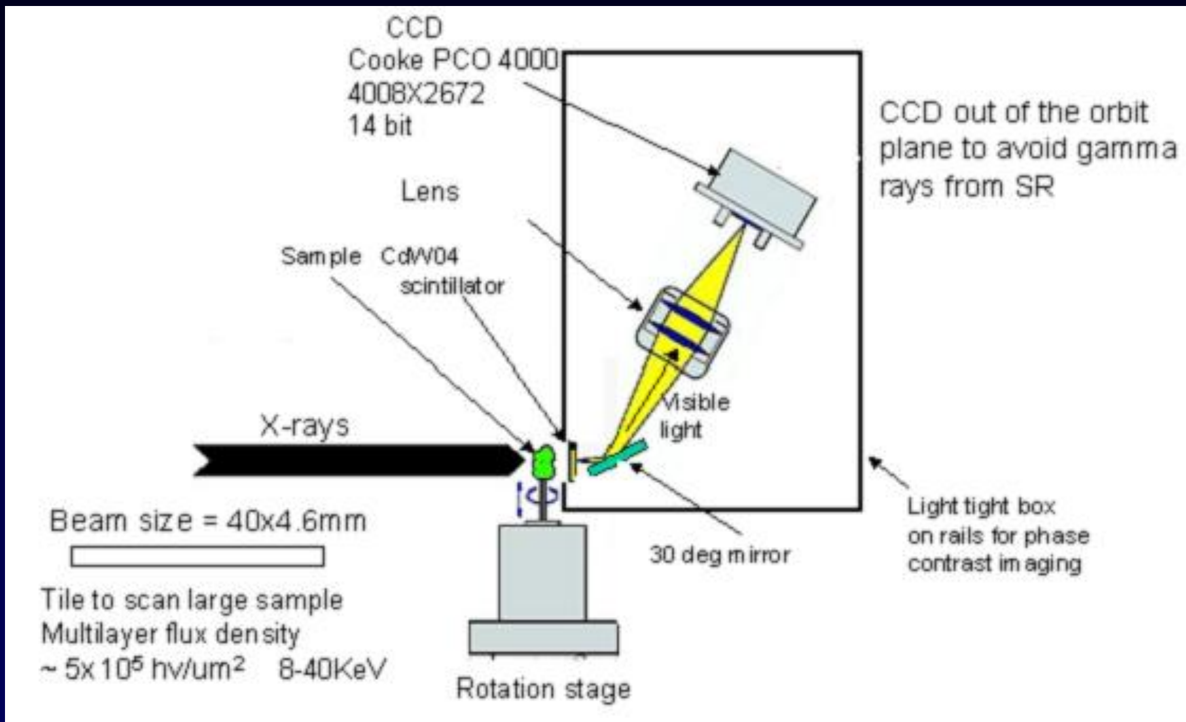
Spectrum shows bacteria:

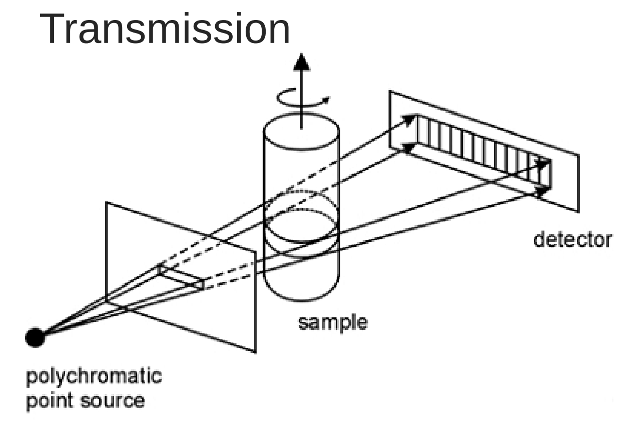


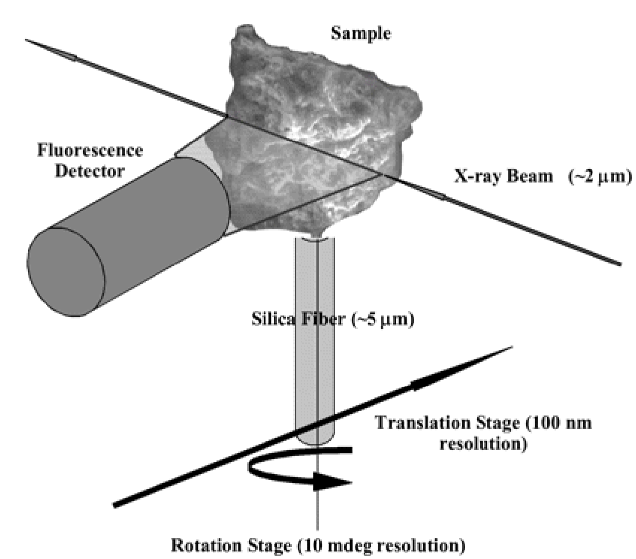
Spectra showing pyrene:



X-ray Micro-Tomography





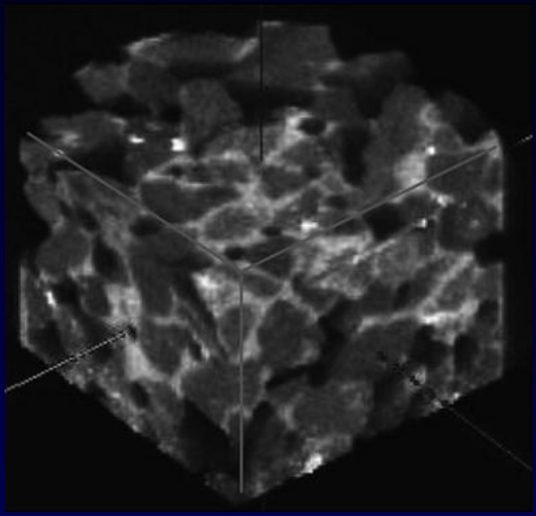


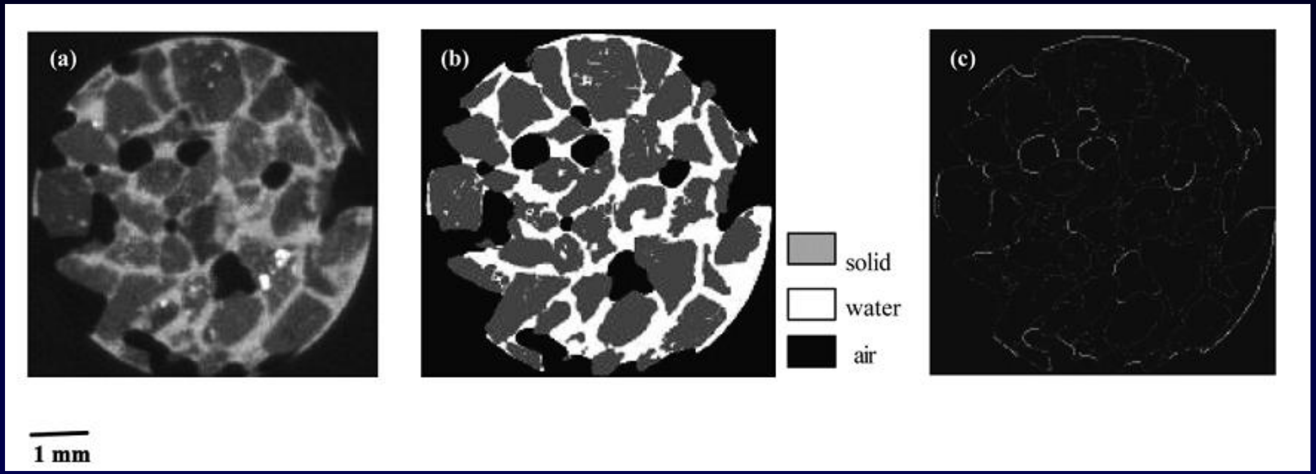
Used to obtain images of the interior of solid objects and for obtaining digital images of their 3-D geometries at a resolution of a few microns.

Images are captured by a CCD camera.

Sutton, SR, Bertsch PM, Newville M, Rivers M, Lanzirotti A, and Eng P. *Reviews in Mineralogy and Geochemistry*; January 2002; v. 49;1; p. 429-483

X-Ray Micro-Tomography





The 3-D image on the right shows a 6 mm in diameter sample of course sand.

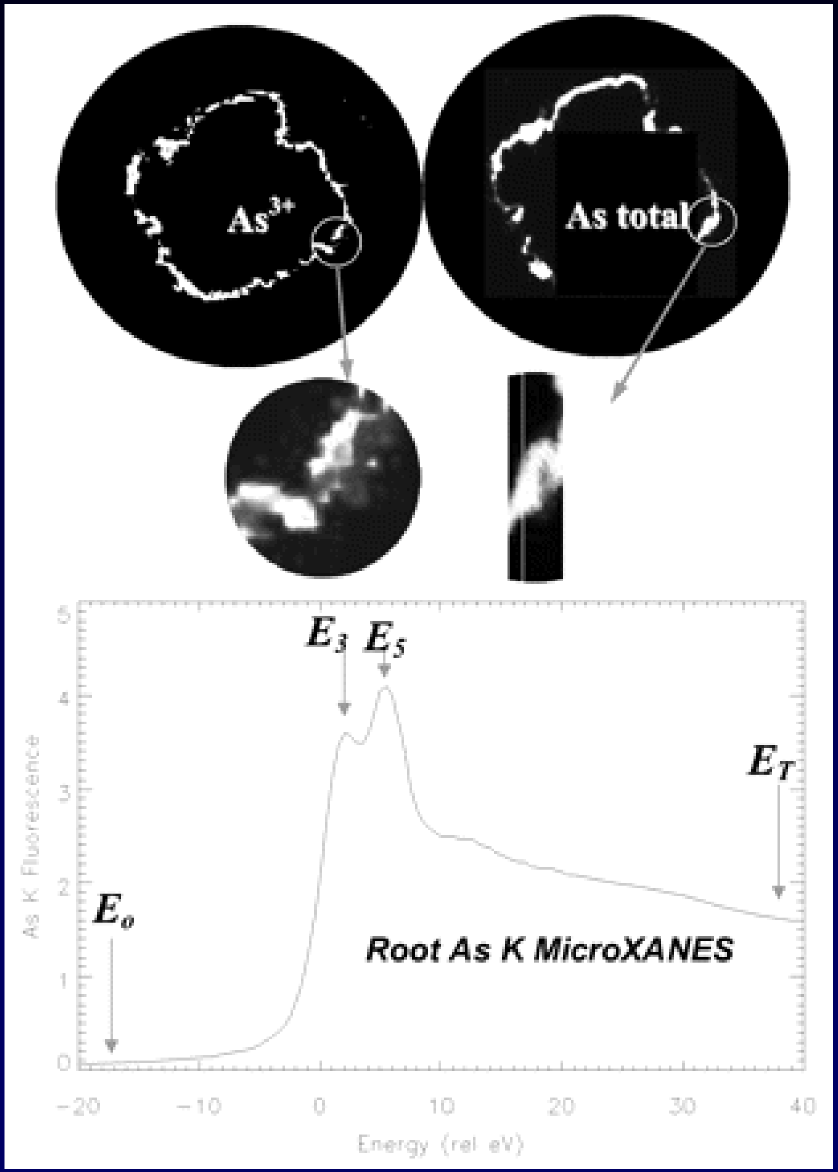
The 2-D images show the pore distribution of solid, water, and air in a sample of course sand and is correlated with flow of water through the sample. The images are also used to locate interfacial contact between water and air.

Wildenschild D, PVaz CM, Rivers ML, Rikard D, Hopmans JW, Christensen. "Using X-ray computed tomography in hydrology: systems, resolutions, and limitations ." *Journal of Hydrology* 267 (2002) 285–297.

Speciation of Metal-Contaminated Soils

XRF Tomography can be performed and then μ-EXAFS or μ-XANES can be performed on selected spots.

This example shows evidence of As (III) associated with the interior of iron plaques inside of cattails grown in As-containing wetland sediments.



Keon NE, Swartz CH, Brabander DJB, Myneni SCB, Sutton S, Newville M, Hemond HF (2002) Combined XAS and chemical extraction investigation of arsenic distribution in sediment phases and in cattail roots. Amer Chem Soc National Meeting, GEOC-127

Additional Reading

Gorby, Y. A. et al. Electrically conductive bacterial nanowires produced by Shewanella oneidensis strain MR-1 and other microorganisms. *PNAS* ***2006, 103, 11358-11363.***

O'Day, P. A., Molecular environmental geochemistry. *Rev. Geophys.* ***1999, 37, 249-274.***

Borch, T.; Camper, A. K.; Biederman, J. A.; Butterfield, P. W.; Gerlach, R.; Amonette, J. E., Evaluation of Characterization Techniques for Iron Pipe Corrosion Products and Iron Oxide Thin Films. *Journal of Environmental Engineering* ***2008, 134, (10), 835-844.***

Moberly, J.; Borch, T.; Sani, R.; Spycher, N.; Şengör, S.; Ginn, T.; Peyton, B., Heavy metal–mineral associations in Coeur d'Alene river sediments: A synchrotron-based analysis. *Water, Air, & Soil Pollution* ***2009, 201, 195-208.***

Borch, T.; Masue, Y.; Kukkadapu, R. K.; Fendorf, S., Phosphate imposed limitations on biological reduction and alteration of ferrihydrite. *Environ. Sci. Technol.* ***2007, 41, (1), 166-172.***

Download Borch papers here:

http://www.soilcrop.colostate.edu/borch/publications.html

Additional Reading

Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science

Editors: P. Fenter, M. Rivers, N. C. Sturchio and S. R. Sutton, Reviews in Mineralogy and Geochemistry, vol. 49, 221-266.

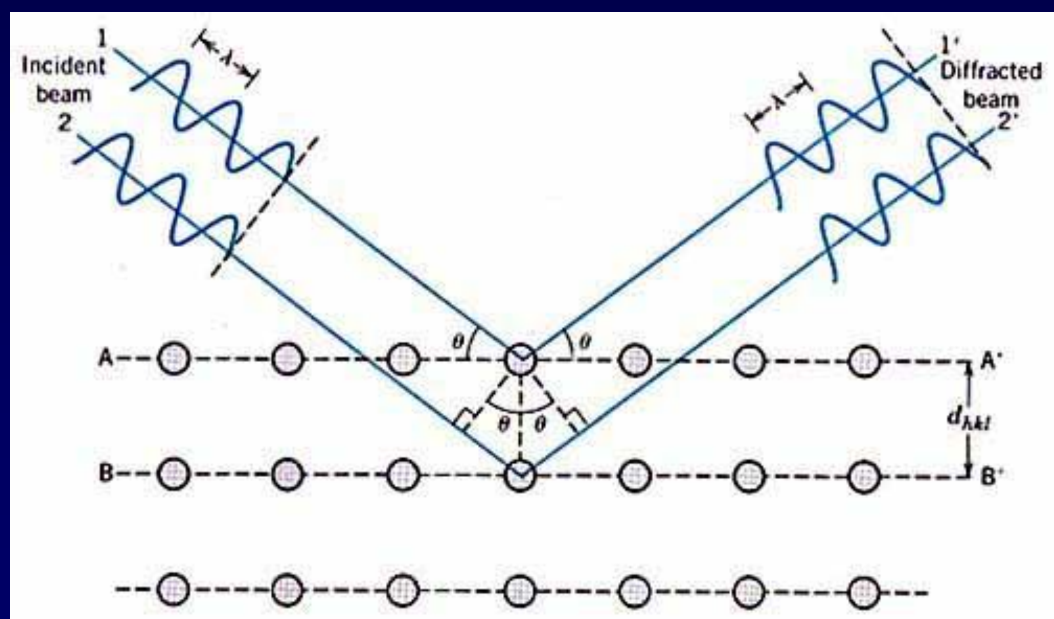
TEM-SAED provides info about D-Spacing

Bragg's law: $\lambda = 2d_{hkl}\sin\theta$

Where λ is the wavelength of the x-ray/electron beam

$$\frac{1}{d_{hkl}^2} = [hkl]G^* \begin{bmatrix} h \\ k \\ l \end{bmatrix}$$

hkl are the miller inducies of the plane and $G^* = G^{-1}$



d_{hkl} *is the inner planar spacing*

Analytical Method	Source	Signal	Chemical Information	Notes
IR and FTIR	Infrared radiation	Transmitted IR radiation	Molecular and lattice vibrations; local bonding (first neighbor)	Nonvacuum; bulk liquids, crystalline and amorphous solids
Synchrotron XAS (XANES and EXAFS)	Synchrotron X-rays	Transmitted or fluorescent X-rays; electron yield	Quantitative local structural information; oxidation state and atomic bonding geometry	Nonvacuum; element specific; liquid, crystalline, and amorphous materials
Synchrotron microanalysis (XRF, XANES)	Synchrotron X-rays	Fluorescent X-rays	Elemental analysis (XRF); oxidation state and atomic bonding (XANES)	Vacuum or nonvacuum; spatial resolution, element specific, crystalline and amorphous materials
EELS also called PEELS or "parallel electron energy loss spectroscopy"	electrons	electrons	Oxidation state and atomic bonding geometry (similar to XANES)	Vacuum; high concentrations, crystalline and amorphous materials
XPS and Auger spectroscopy	X-rays	electrons	Oxidation state; chemical bonding info	Vacuum; surface sensitive; spatial resolution
NMR	Radio waves (+ magnetic field)	Radio waves	Sensitive to electron density (nuclear shielding); local bonding (first neighbor)	Nonvacuum; bulk liquids and solids; requires NMR-active isotope
ESR also called EPR or "electron paramagnetic resonance"	Microwaves (+ magnetic field)	Radio waves	Sensitive to electron density (electron coupling)); local bonding (first neighbor)	Nonvacuum; bulk liquids and solids; sensitive to low conc.; requires paramagnetic ions
X-ray scattering (small angle, SAXS; wide angle, WAXS)	X-rays (synchrotron or laboratory)	Scattered X-rays	Quantitative structural information	Nonvacuum; crystalline and amorphous materials; microdiffraction w/synchrotron
SIMS	Charged ion beam	Atomic mass	Elemental and isotopic analysis	Vacuum; surface sensitive to low conc.; spatial resolution
LA-ICP-MS	laser	Atomic mass	Elemental and isotopic analysis	Vacuum; sensitive to low conc.; spatial resolution
STM	Tunneling electrons	Electronic pertuba-tions	Molecular and atomic-scale surface imaging; surface electronic structure	Vacuum and nonvacuum; conducting/semi-conducting materials only
AFM	Electronic force	Force pertuba-tions	Molecular-scale surface imaging	Nonvacuum; imaging in air or liquid
HR-TEM and scanning transmission electron microscope (STEM)	Electrons	Transmitted or secondary electrons	Bulk morphology and crystallinity; particle- to atomic-scale spatial resolution	Vacuum or light element atmosphere
SEM/EM with EDS or WDS chemical analysis	Electrons	Secondary or backscattered electrons; fluorecent X-rays	Morphology over wide magnification; quantitative or qualitative chemical analysis (EDS/WDS)	Vacuum or light element atmosphere