# Synchrotron based Techniques applied to Environmental Science

Daniel Grolimund

microXAS Beamline Project
SWISS LIGHT SOURCE (SLS)

PAUL SCHERRER INSTITUT





# OVERVIEW

- I. INTRODUCTION ENVIRONMENTAL SCIENCE
- ii. SYNCHTROTRON TECHNIQUES ('rough') and ENVIRONMENTAL CASE STUDIES
  - **X-Ray Absorption**
    - X-Ray Fluorescence (see presentation D. Eichert)
    - X-Ray Absorption Spectroscopy [XANES, EXAFS, Circular Dichroism] (see presentation G. Aquilanti)
  - **X-Ray Scattering**
    - X-Ray Diffration (see presentation G. Garbarino and A. Lausi)
    - [X-Ray Small Angle Scattering (see presentation S. Bernstorff)]
    - [X-Ray Reflectivity/Surface Scattering/X-Ray Standing Waves]
  - **X-Ray Imaging** (see presentation F. Zanini)
    - X-Ray Microscopy [microXRF, microXRD, microspectroscopy, (STXM)] (see presentation A. Gianoncelli)
    - X-Ray Tomography
  - **[Infrared IR, Ultraviolet VUV, ...]** (see presentation L. Vaccari)
- iii. SUMMARY & DISCUSSION

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## Environmental Science

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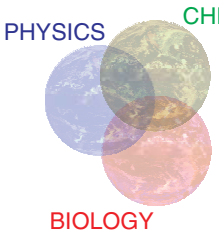
## Environmental Science: Challenge

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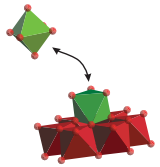
## Environmental Science: Challenge

Most fundamental problem of environmental chemistry:

**CHEMICAL SPECIATION**

(chemical speciation = description of local geometry of atoms)



**Chemical Speciation** determines:

- Chemical Reactivity
- Materials Properties
- Chemical Toxicity
- Bioavailability
- Ecological/technical Fugacity



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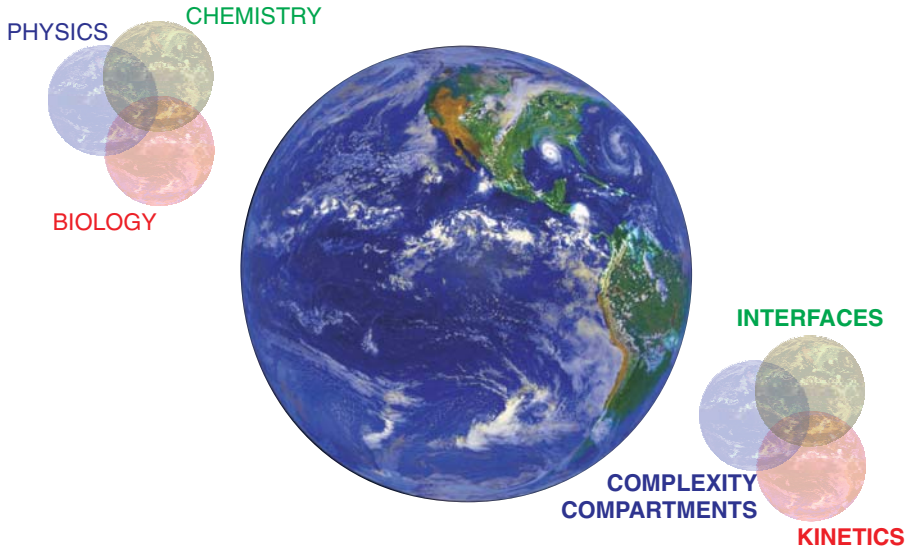
## Environmental Science: Challenge



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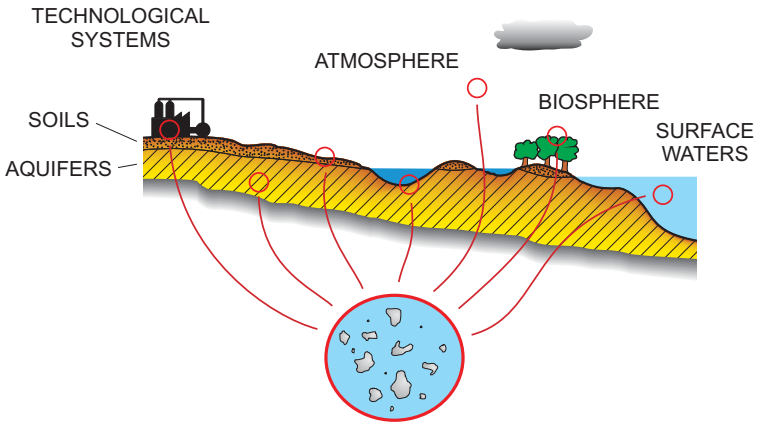
## Environmental Systems: INTERFACES



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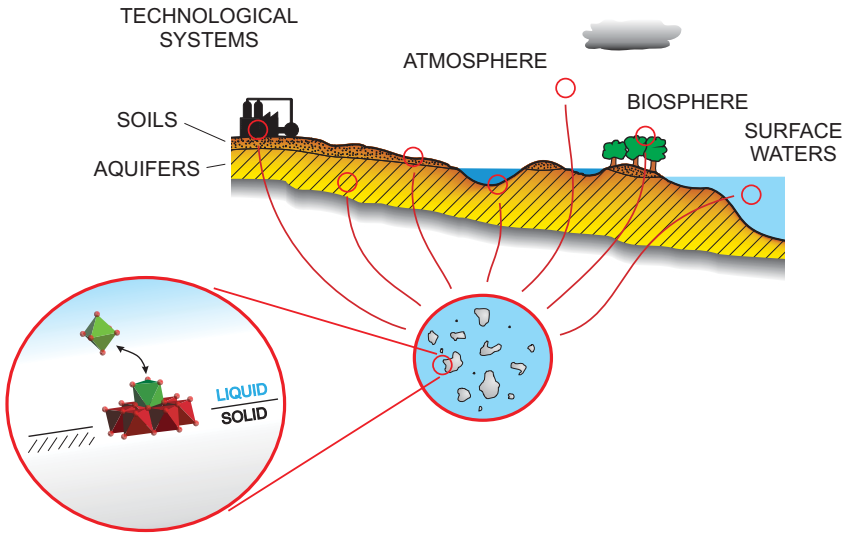
## Environmental Systems: INTERFACES



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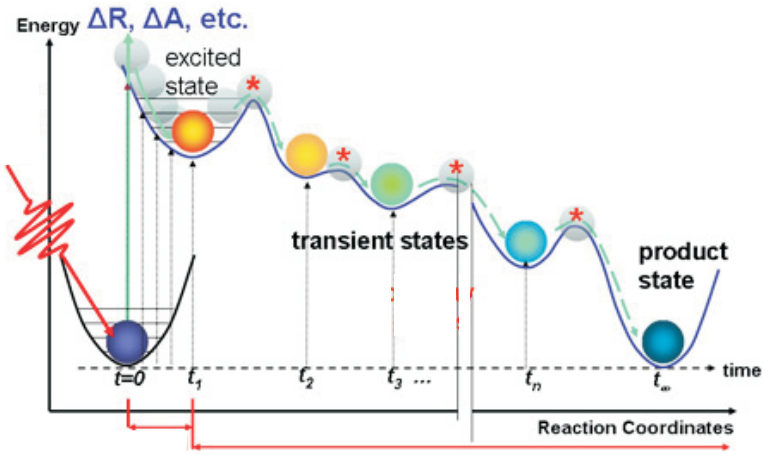
## Environmental Systems: KINETICS

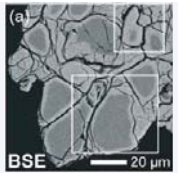
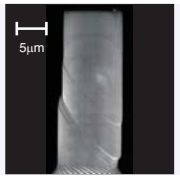





# INTRODUCTION

## Environmental Systems: DOMAINS

**Macroscopic** behavior = f(**microscopic physical** properties)

| | cells/microbes | mineral reactions | material science |
|---|---|---|---|
| physical |  |   |   |
| | BIOLOGY | CHEMISTRY | PHYSICS |
| | Finney et al. PNAS, 2007 | Geisler et al. Am. Min., 2005 | Maass et al. PRL, 2007 |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## Environmental Systems: DOMAINS

**Macroscopic** behavior = f(**microscopic chemical** and **physical** properties)

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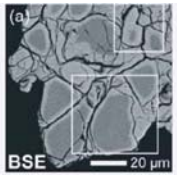
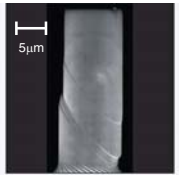
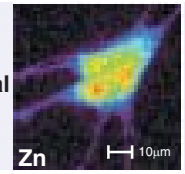
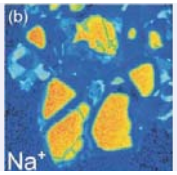
| physical |  |   |   |
| chemical |   |   |  |
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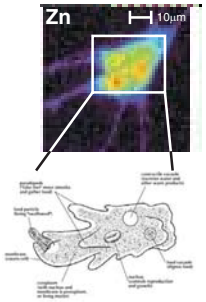
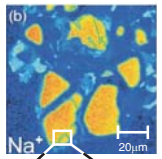
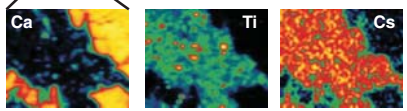
# INTRODUCTION

## Environmental Systems: DOMAINS

- importance of chemical micro/nano **DOMAINS** in science
- importance of **DOMAIN BOUNDARIES / INTERFACES**




**BOUNDARIES / INTERFACES:**
steep gradients in composition and chemical potentials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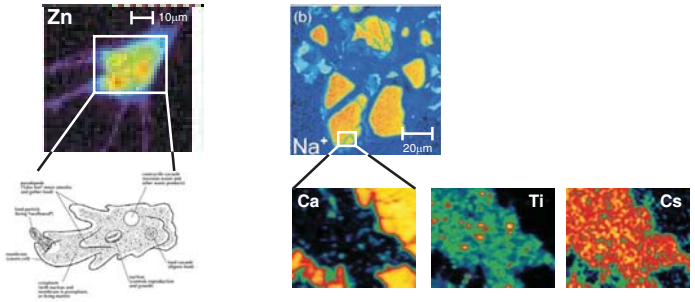


**BOUNDARIES / INTERFACES: PERTURBATION ZONES**
steep gradients in composition and chemical potentials



# INTRODUCTION

## GOAL: understand **properties** and **reactivity** of environmental 'materials' and systems

***"If you want to understand function, study structure"*** ***(Francis Crick)***

***"If you want to understand chemical reactions, study structure"*** ***('Chemist')***

***"If you want to understand physical properties, study structure"*** ***('Physicist')***


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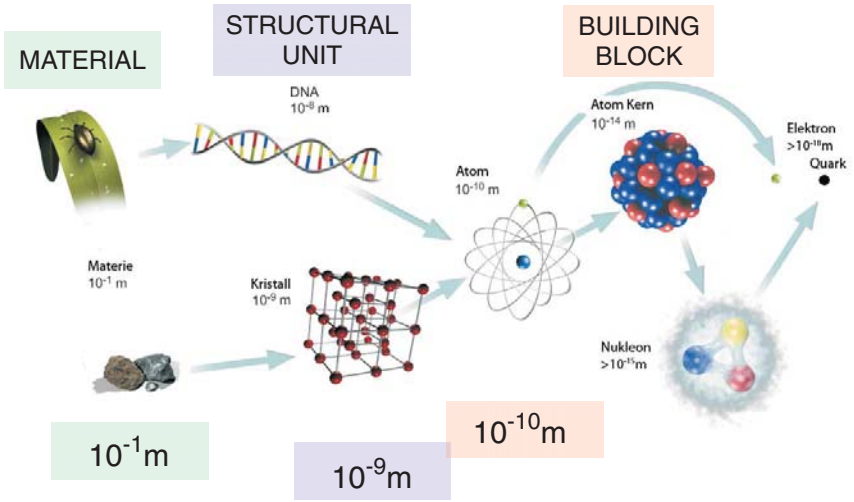



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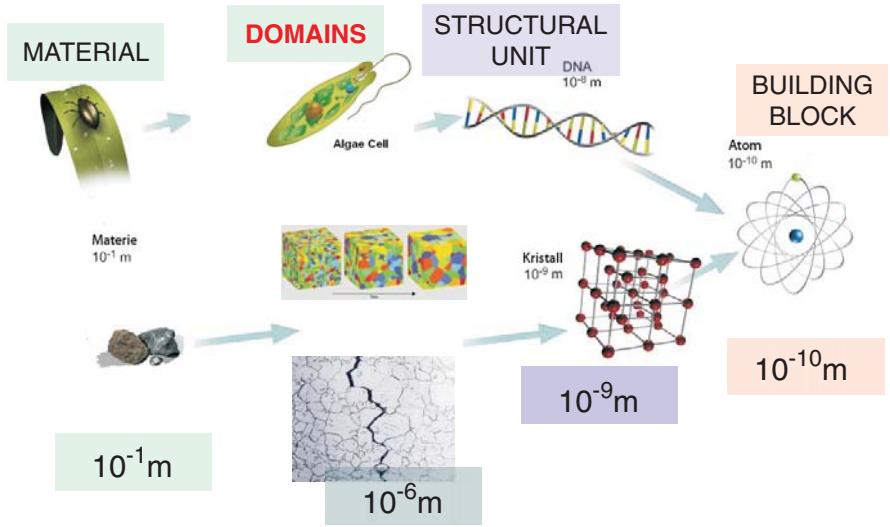



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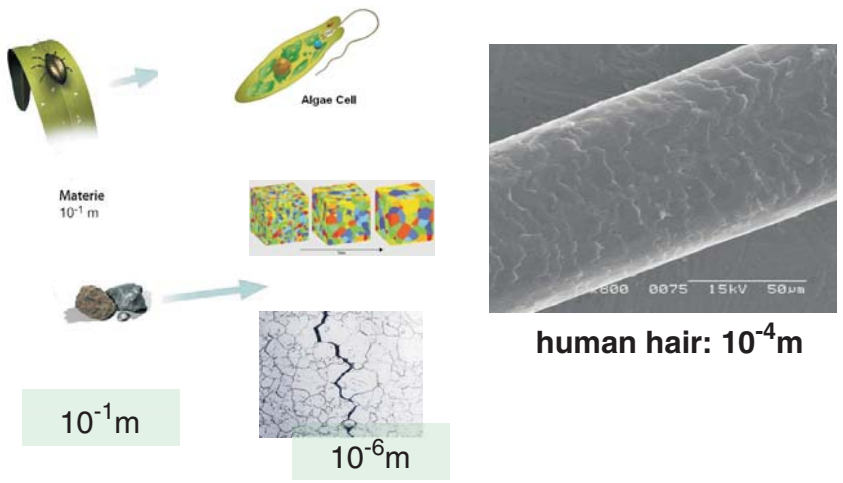






**human hair: $10^{-4}$m**

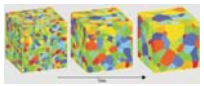


# INTRODUCTION

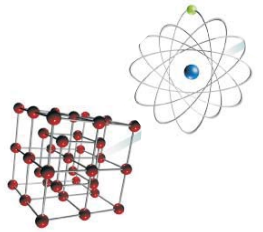
## GOAL: understand **properties** and **reactivity** of environmental 'materials' and systems

## NEED: '3-m Structural Analysis'

macrolmeso



micro



molecular



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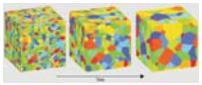
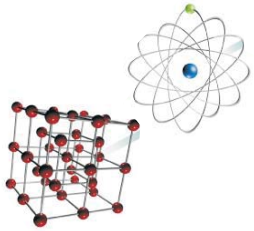


micro



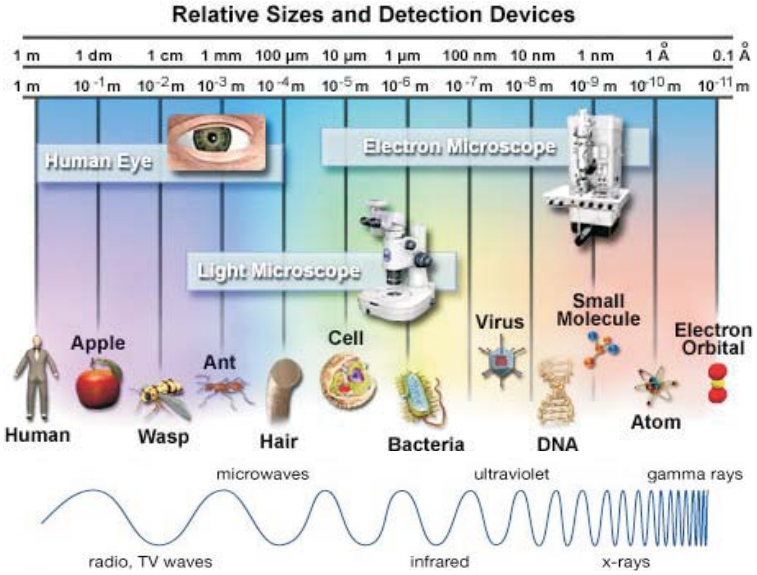
molecular

PHYSICS CHEMISTRY



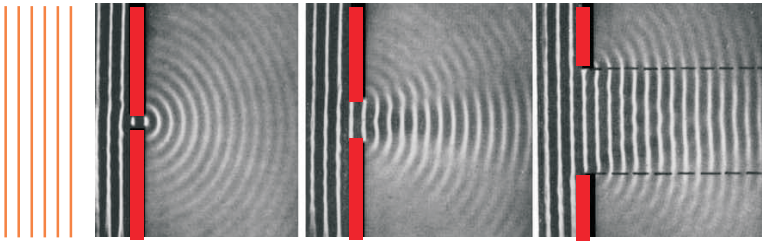
# 3m STRUCTURAL ANALYSIS

## Electromagnetic Waves



# 3m STRUCTURAL ANALYSIS

## Waves, Diffraction, and Interferences



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## Waves, Diffraction, and Interferences




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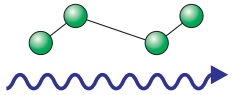

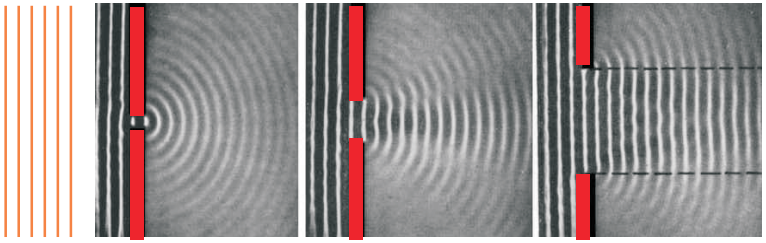


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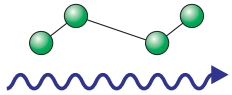

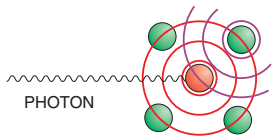


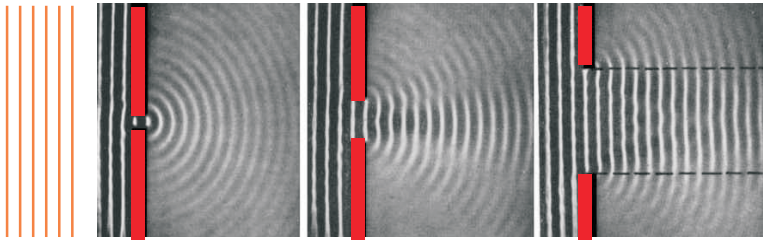


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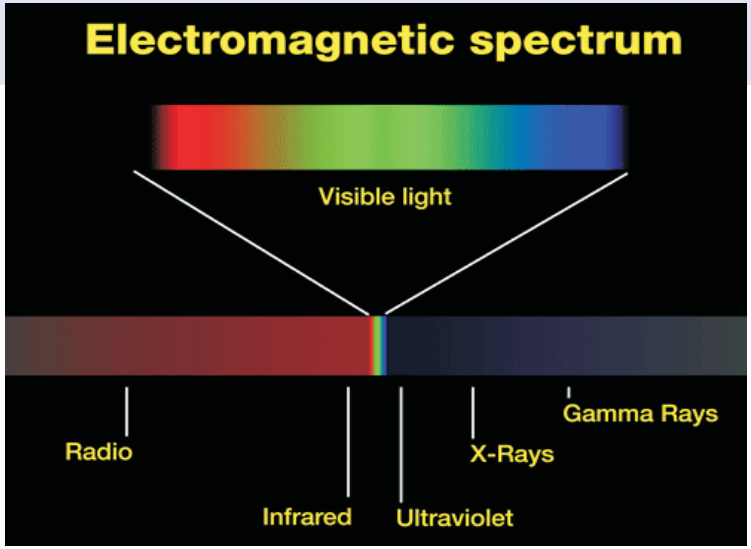


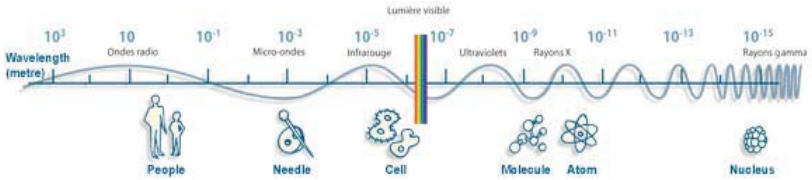




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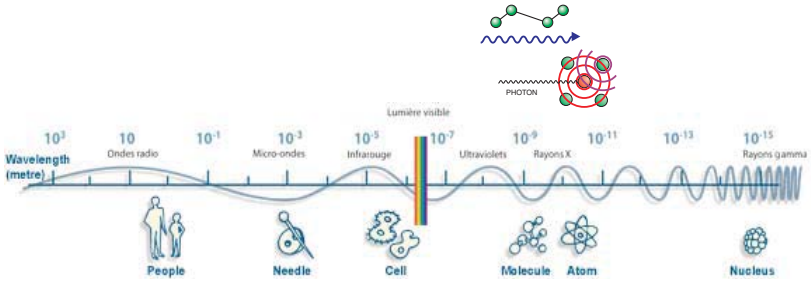



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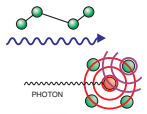
# MOLECULAR STRUCTURAL ANALYSIS

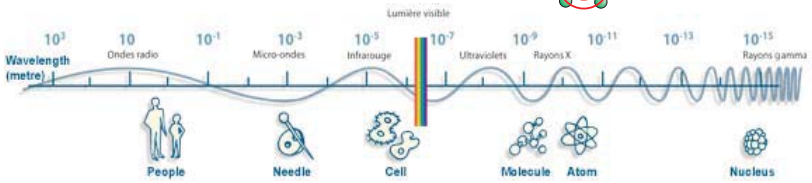
## Electromagnetic Waves

IR-vis-UV: molecular bonds

X-rays: inner electronic shells

γ-rays: nucleus





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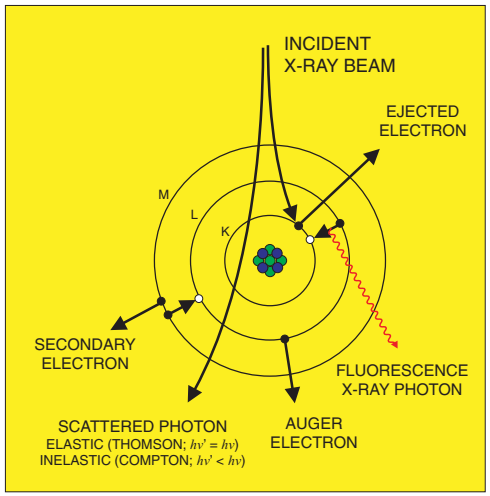
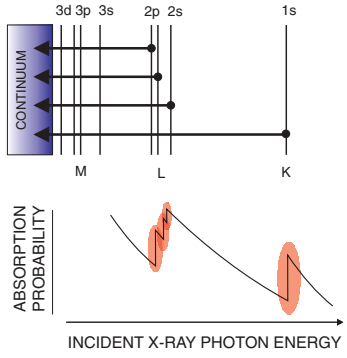
# CHEMICAL IMAGING with X-RAYS .....

## X-Ray Interactions with Atoms




**atomic photo effect**
(element selectivity)




**electronic and local structure information**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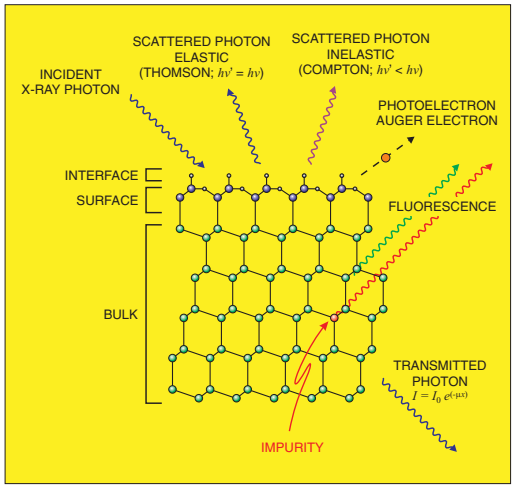
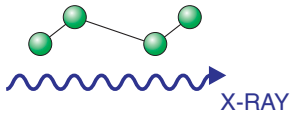
# X-RAYS .....

## X-Ray Interactions with Molecules and Matter



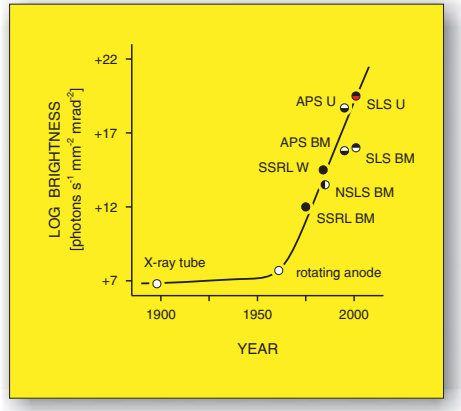

- tunable penetration power
- 'non-destructive'
- different contrast mechanisms
- λ(X-rays) ≈ inter-atomic distances






# X-RAY based ANALYTICAL TOOLS

## ANALYTICAL REVOLUTION I: SYNCHROTRON LIGHT




Röntgen: 1 year SSRL: 3 hours SLS: 1 second


SLS X05LA microXAS Beamline
Synchrotron based Techniques applied to Environmental Science
Daniel Grolimund
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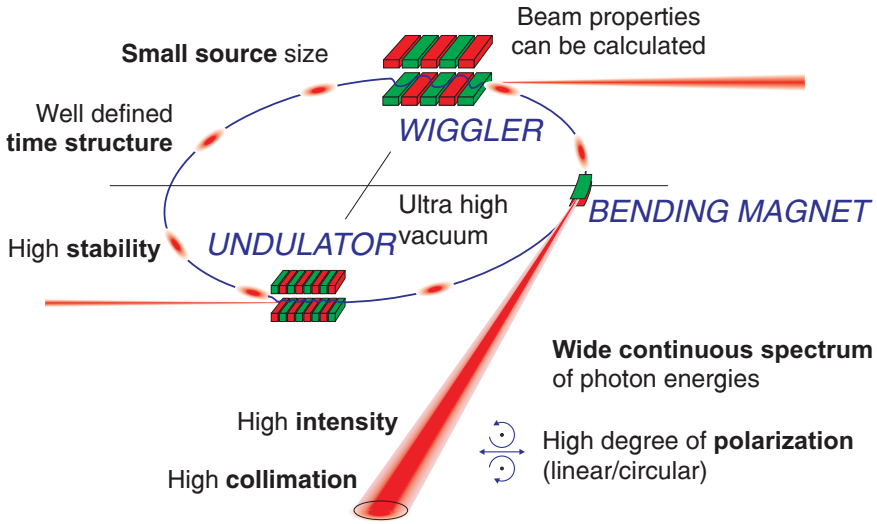
Environmental Sci.
properties and reactivity of materials
structural analysis
... with X-rays
SR TECHNIQUES and EXAMPLES
X-ray absorption
X-ray scattering
X-ray imaging
SUMMARY
PAUL SCHERRER INSTITUT PSI


# X-RAY based ANALYTICAL TOOLS

## SYNCHROTRON RADIATION: CHARACTERISTICS





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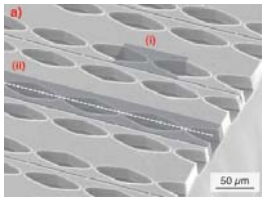
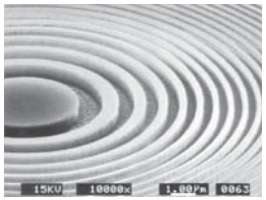
## ANALYTICAL REVOLUTION II: X-RAY OPTICS

REFRACTIVE LENSES



ANKA

BRAGG-FRESNEL LENSES

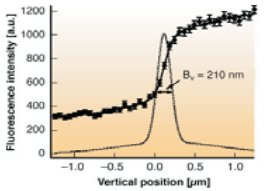


PSI

REFLECTIVE MIRRORS

ESRF

**SUB-MICRON FOCUSING of (HARD) X-RAYS:**




**Top: 10-50nm!**

**'Routine': ~1μm!**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# X-RAY based ANALYTICAL TOOLS

## ANALYTICAL REVOLUTION III: METHODS

### Phase retrieval and differential phase-contrast imaging

Pfeiffer, Weitkamp, Bunk, David
Nature *Physics*, 2, 2006

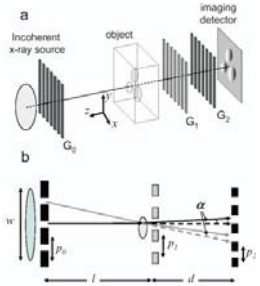



***Figure 1:*** *Talbot-Lau type interferometer.* ***a,b,*** *Principle: the source grating ($G_0$) creates an array of individually coherent, but mutually incoherent sources. A phase object causes a refraction, which is proportional to the local differential phase gradient of the object. This small angular deviation results in changes of the locally transmitted intensity through the combination of gratings $G_1$ and $G_2$. A standard x-ray imaging detector is used to record the final images*

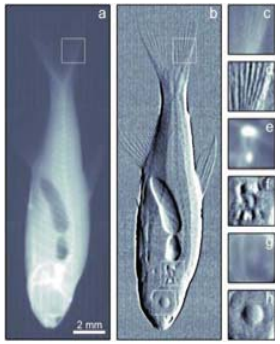



***Figure 2:*** *X-ray images of a small fish. Data recorded with a standard x-ray tube.* ***a,*** *Conventional X-ray transmission image.* ***b,*** *Differential phase contrast image.* ***c-h,*** *Two-times magnified and contrast optimized parts of the transmission (c,e,g) and the differential phase contrast image (d,f,h).*



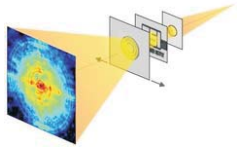

# X-RAY based ANALYTICAL TOOLS

## ANALYTICAL REVOLUTION III: METHODS

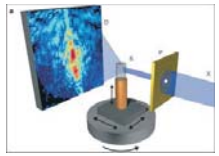
### Phase retrieval and differential phase-contrast imaging

Pfeiffer, Weitkamp, Bunk, David
Nature *Physics*, 2, 2006


Coherent Diffraction Imaging



ptychographic coherent imaging

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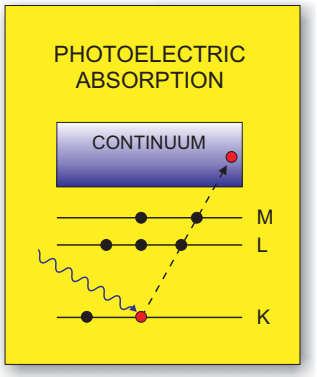
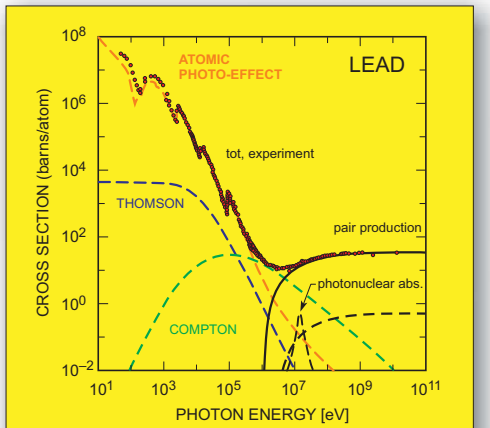
# X-RAY ABSORPTION

## X-Ray Interactions with Atoms



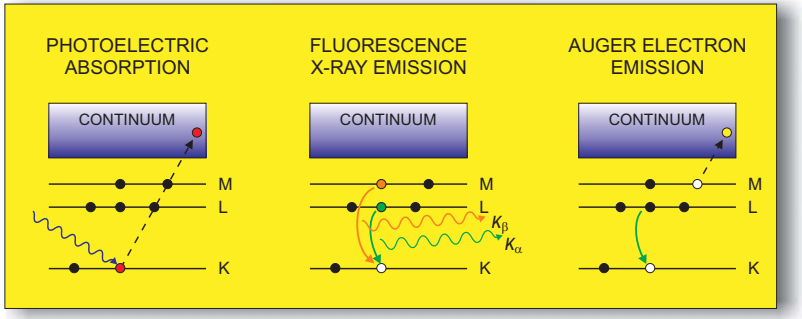

*CXRO X-RAY DATA BOOKLET (2001), figure courtesy of J. H. Hubbell.)*


# X-RAY ABSORPTION

## X-Ray Interactions with Atoms


**>> powerful SYNCHROTRON-based spectroscopic techniques:**

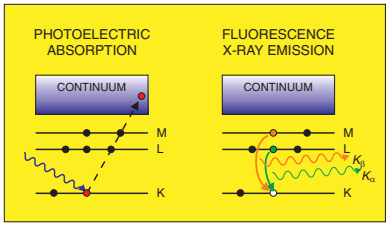
**XANES, EXAFS, GI-XAFS, etc.**



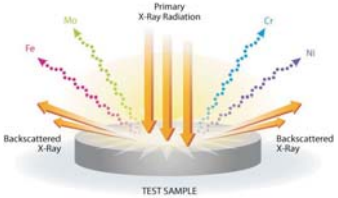
# X-RAY ABSORPTION

## X-Ray Fluorescence Analysis

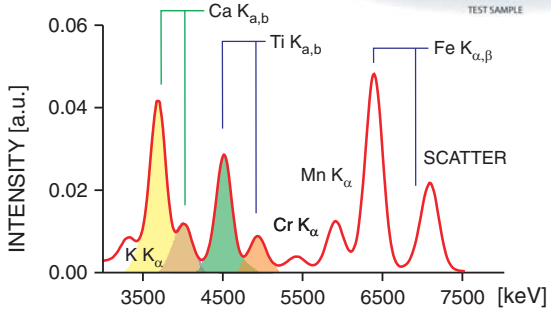
0 dimensional




### Point Analysis




ELEMENTAL QUANTIFICATION






# X-RAY ABSORPTION

## X-Ray Absorption Spectroscopy

SINGLE ATOM I 0 dim

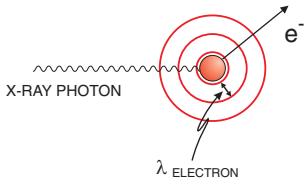
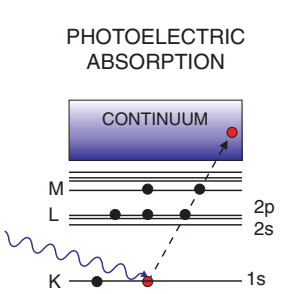
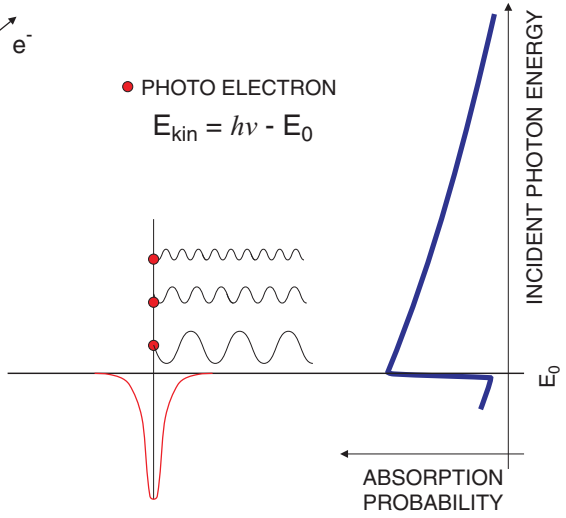



PHOTO ELECTRON

$E_{kin} = h\nu - E_0$



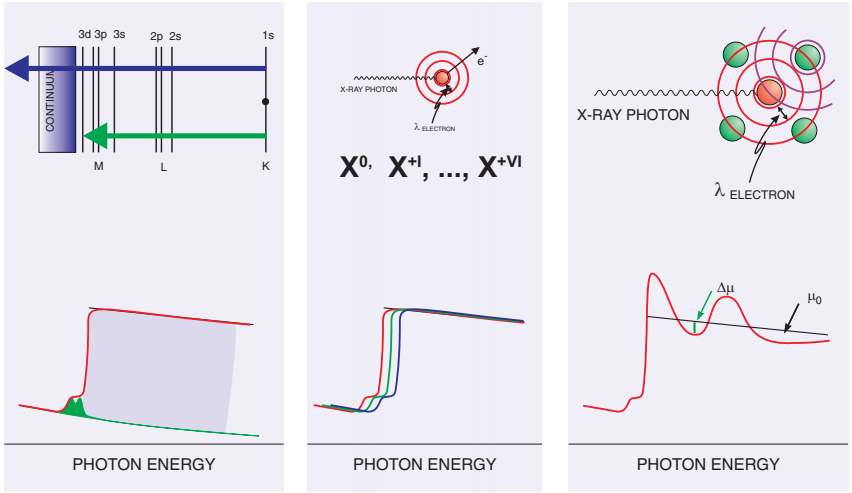






# X-RAY ABSORPTION

## X-Ray Absorption Spectroscopy

PRE-NEAR-POST EDGE



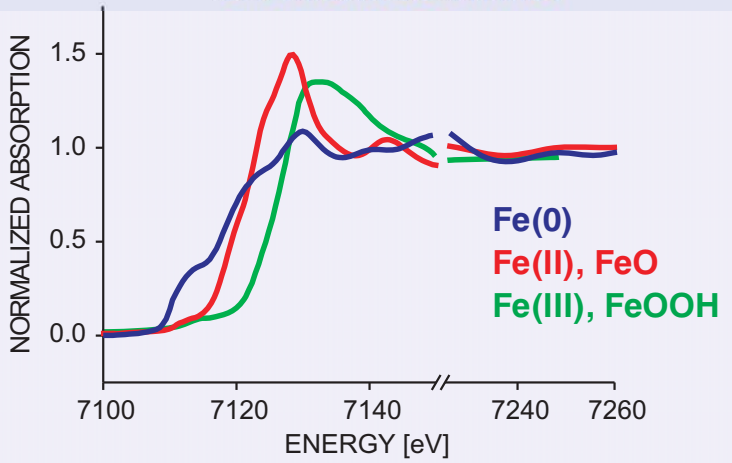



# X-RAY ABSORPTION

## X-Ray Absorption Spectroscopy

XANES

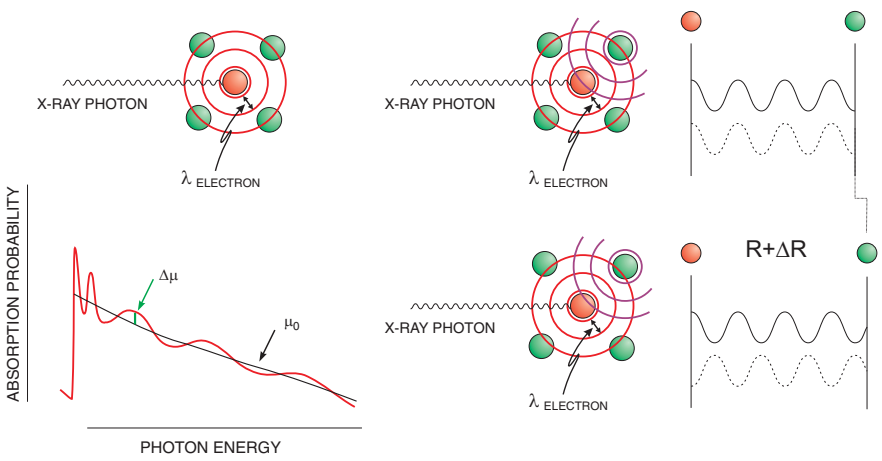
### CHEMICAL CONTRAST



# X-RAY ABSORPTION

## X-Ray Absorption Spectroscopy

MOLECULES I EXAFS



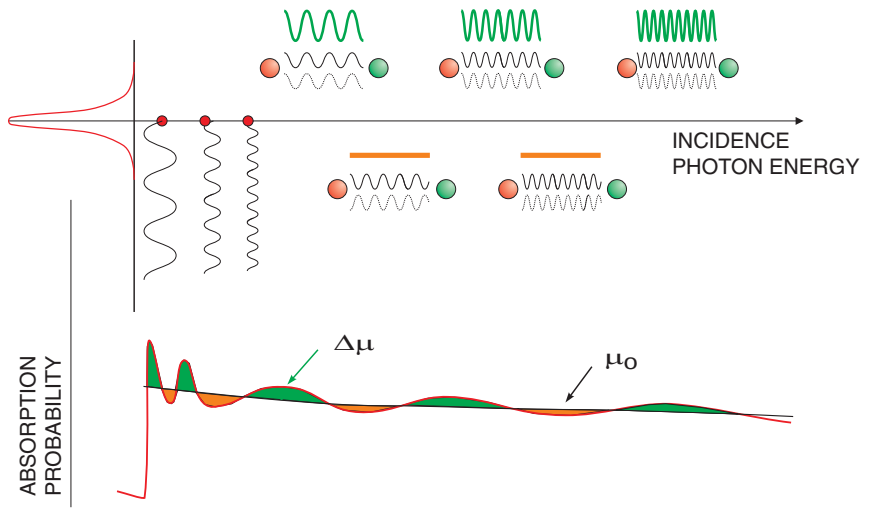

$$P \propto \left\langle \propto_{out} \propto\propto_{sc} \left| \vec{\propto} \propto \vec{R} \right| \propto_{i} \right\rangle$$




# X-RAY ABSORPTION

## X-Ray Absorption Spectroscopy

MOLECULES I EXAFS

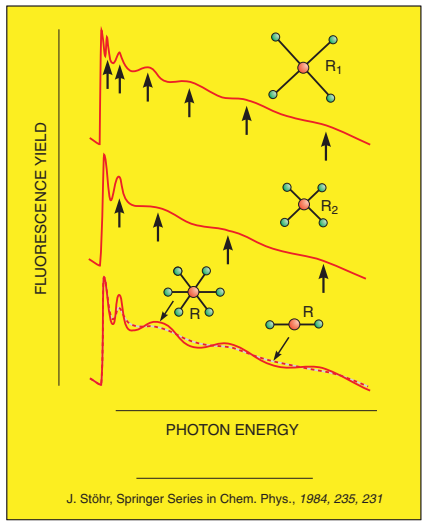





# X-RAY ABSORPTION

## X-Ray Absorption Spectroscopy

MOLECULES I EXAFS


- DETAILED **CHEMICAL** AND **STRUCTURAL** INFORMATION
  - (NON-) CRYSTALLINE SOLIDS
  - SPECIES IN SOLUTION/GAS
  - INTERFACIAL SPECIES
  - CHEMICAL STATE
  - LOCAL STRUCTURE
- *IN-SITU* PROBE
- NON-DESTRUCTIVE
- MINIMAL SAMPLE PREPARATION
- SELECTIVITY / SENSITIVITY

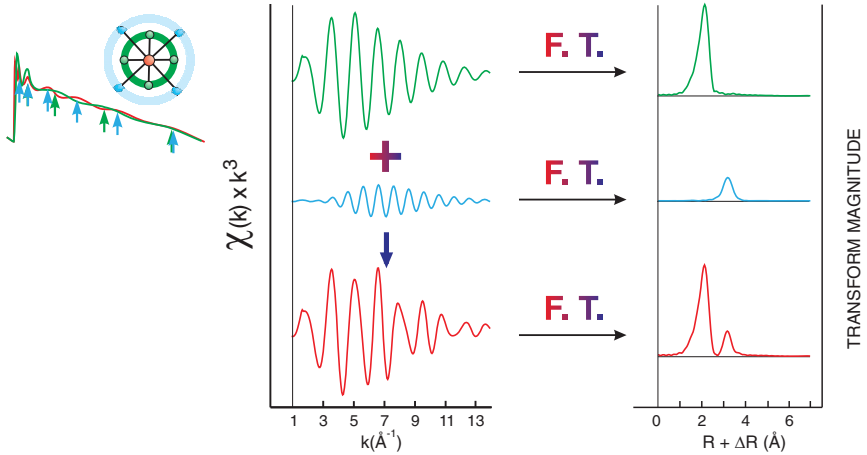

# X-RAY ABSORPTION

## X-Ray Absorption Spectroscopy

MOLECULES I EXAFS


- FOURIER TRANSFORMATION

$$\chi(k) = \Sigma\, a(k)\, \sin[2kR+\alpha(k)]$$



# CONTAMINANT TRANSPORT

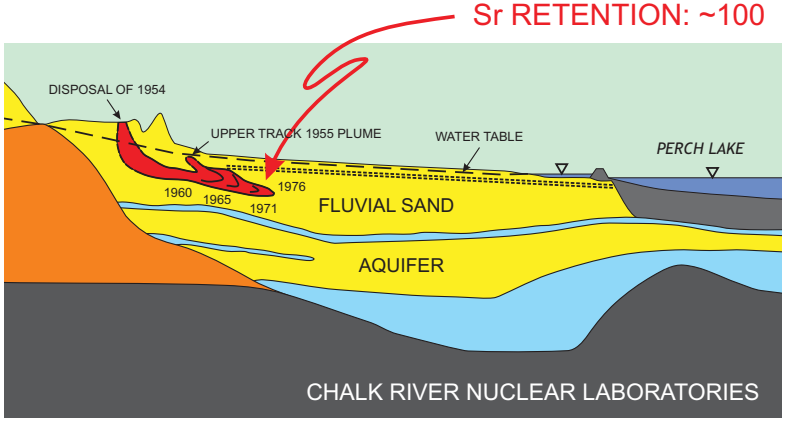



Figure adapted from Jackson and Inch, 1980

- Ewing, 1959
  - Sr Ret. ~100
- Tamura, 1972
  - Sr Ret. ~250



# CONTAMINANT TRANSPORT

## Proposed Geochemical Mechnanisms

- **MACROSCOPIC STUDIES**

| | PROPOSED MECHANISM | | CONSISTENCY FIELD - LAB | |
|---|---|---|---|---|
| Montmorillonite [1] | Cation Exchange | $K_{Sr/Ca}$ = 1.0 -1.2 | NO | Wahlberg (1965) |
| Illite [1] | Cation Exchange | $K_{Sr/Ca}$ = 1.0 -1.2 | NO | |
| Kaolinite [1] | Cation Exchange | $K_{Sr/Ca}$ = 1.1 -1.3 | NO | |
| Synth. Resin [2] | Cation Exchange | $K_{Sr/Ca}$ = 1.0 | NO | Sardin et al. (1991) |
| 'Oxides' [3] | Covalent Bonding | | ↗ | Kinniburgh et al. (1975) |
| Calcareous Soil [4] | Co-precipitation | | NO | Halevy & Tzur (1964) |

- **FIELD STUDIES**

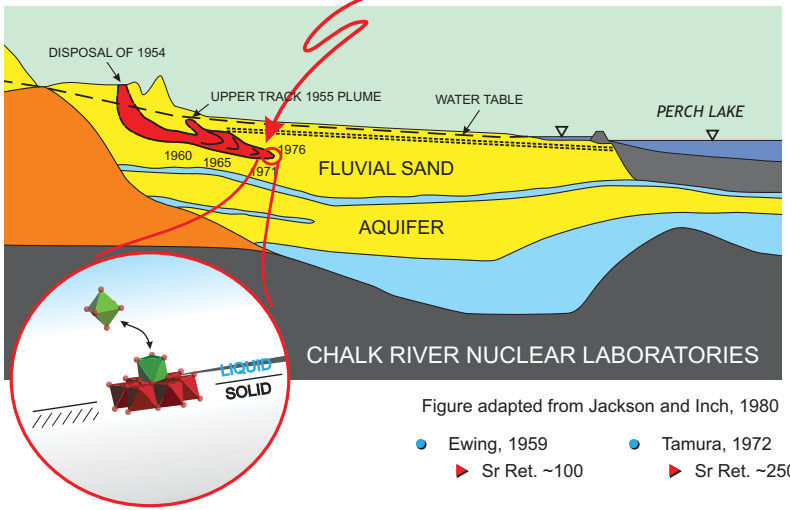
| | | | |
|---|---|---|---|
| Sediment | 'specific' (Fe/Mn Oxide Coatings) | ↗ | Cerling & Turner (1982) |
| Subsurface Material | 'specific' (Mn Oxide) | ↗ | Liszewski et al. (2000) |

- **SPECTROSCOPIC STUDIES**


# CONTAMINANT TRANSPORT INTERFACIAL CHEMISTRY

## X-Ray Absorption Spectroscopy MOLECULES | EXAFS

Sr RETENTION: ~100



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- Ewing, 1959
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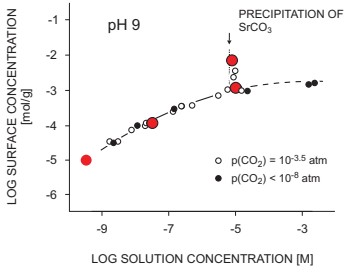
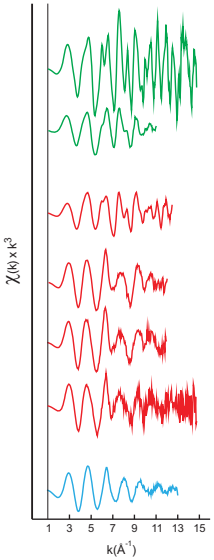
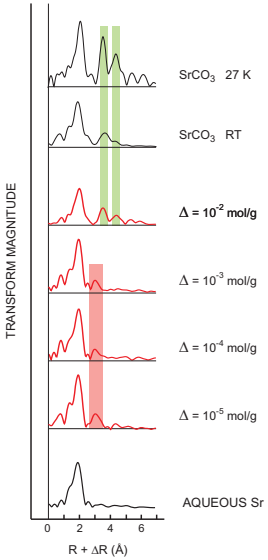
# CONTAMINANT TRANSPORT INTERFACIAL CHEMISTRY

## X-Ray Absorption Spectroscopy MOLECULES | EXAFS


### STRONTIUM EXAFS SORPTION SAMPLES





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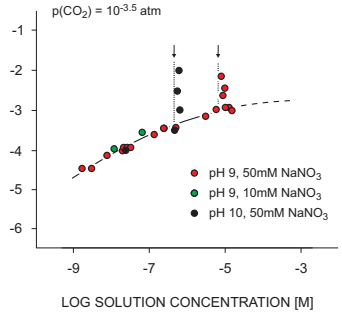
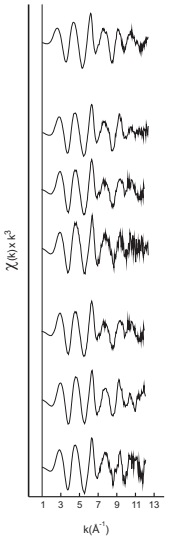
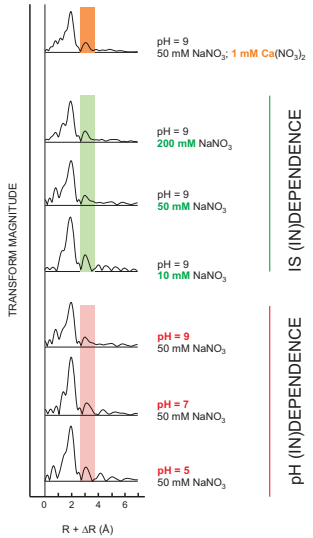
## X-Ray Absorption Spectroscopy

MOLECULES | EXAFS

### STRONTIUM EXAFS SORPTION SAMPLES

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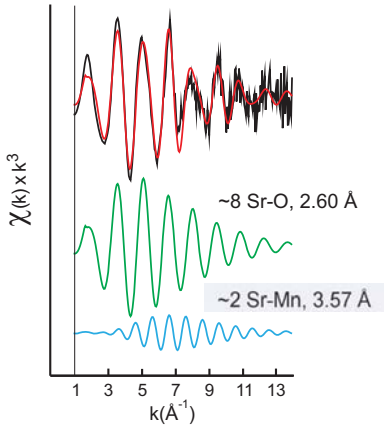
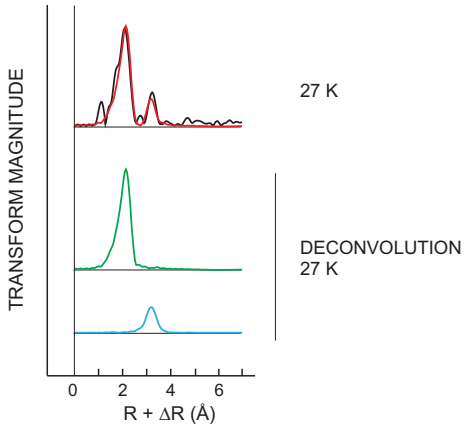
X-Ray Absorption Spectroscopy MOLECULES | EXAFS

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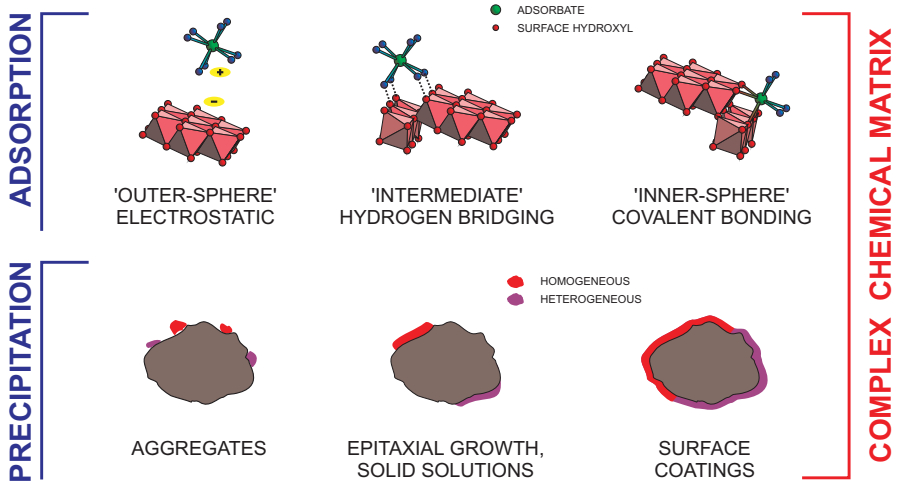


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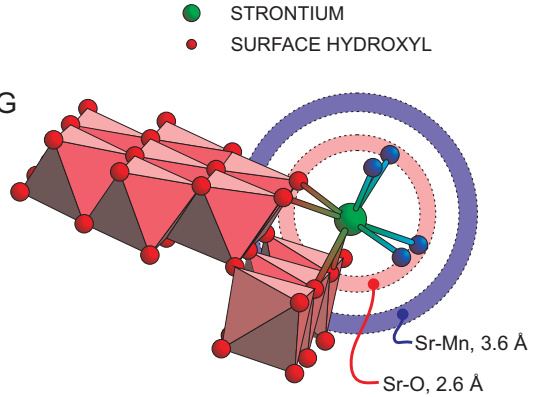
X-Ray Absorption Spectroscopy MOLECULES | EXAFS

### Proposed Interfacial Complex

'INNER-SPHERE' COVALENT BONDING




" … vernadite [δ-$MnO_2$] contains as many **corner-sharing octahedra** as todorokite."

Manceau et al., 1992

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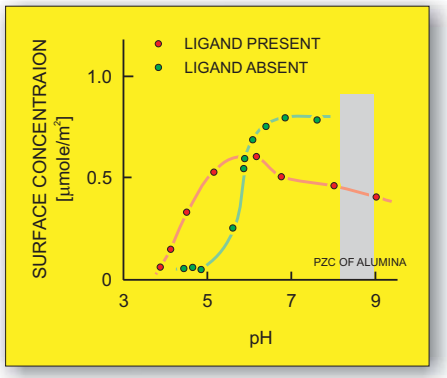
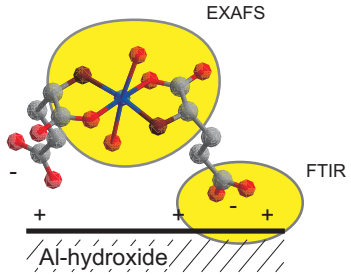
# TERNARY COMPLEXES

INTERFACIAL CHEMISTRY

## X-Ray Absorption Spectroscopy

MOLECULES I EXAFS




J. Fitts et al., *1999*, J. Colloid Interface Sci.

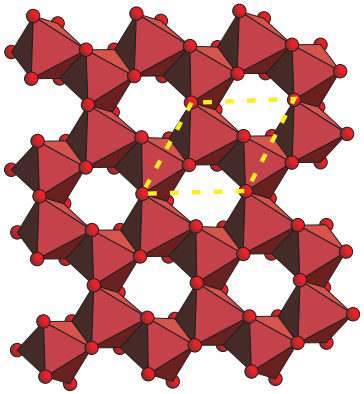


# INTERFACIAL REACTIVITY

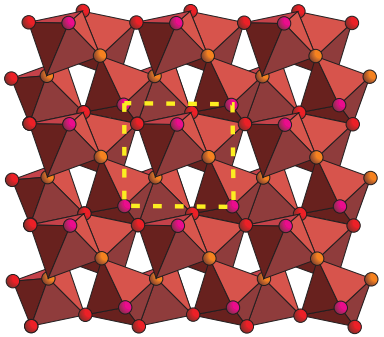
## SINGLE CRYSTAL SURFACES

$\alpha$-$Al_2O_3$ SURFACES

C-CUT SURFACE (0001)



R-CUT SURFACE ($1\bar{1}02$)



DOUBLY COORDINATED OXYGENS

SINGLY COORDINATED OXYGENS

TRIPLY COORDINATED OXYGENS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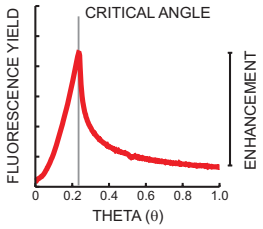
# INTERFACIAL REACTIVITY

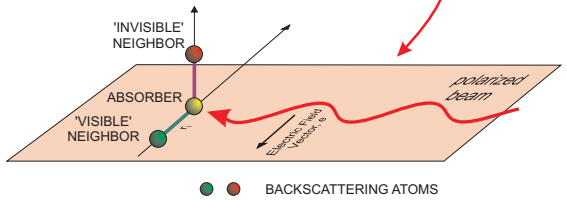
## GRAZING-INCIDENCE XAFS

$\alpha$-$Al_2O_3$ SURFACES

### Advantages:

- ENHANCED SURFACE SENSITIVITY (SMALL PENETRATION DEPTH)
- IMPROVED DETECTION LIMIT
- POLARIZATION DEPENDENCE
- ORIENTED SINGLE CRYSTAL SUBSTRATES





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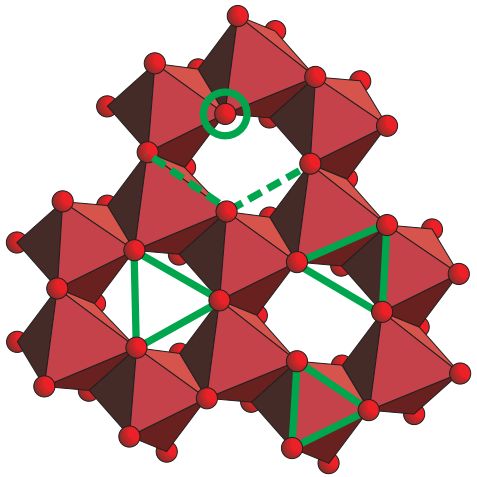
# INTERFACIAL REACTIVITY

SINGLE CRYSTL SURFACES

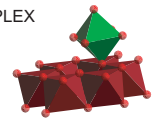
## Well Defined Surface Sites

$\alpha$-$Al_2O_3$ SURFACES

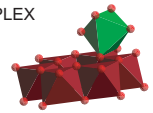
$\alpha$-$Al_2O_3$ (0001) SURFACE



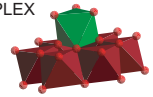
MONODENTATE COMPLEX



BIDENTATE COMPLEX



TRIDENTATE COMPLEX

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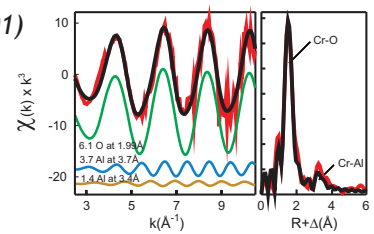
# INTERFACIAL REACTIVITY

SINGLE CRYSTL SURFACES

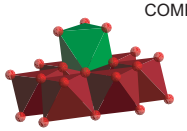
## Interfacial Cr(III) Species

$\alpha$-$Al_2O_3$ SURFACES

*a-$Al_2O_3$ (0001)*

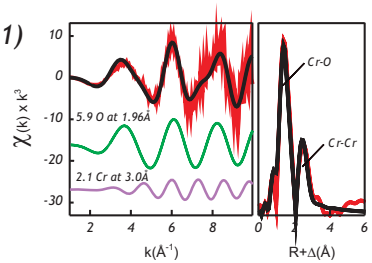



TRIDENTATE COMPLEX

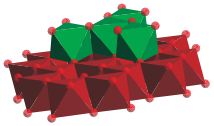


Cr - Al DISTANCE: ~3.4 Å (<3)
~3.7 Å (<3)

*a-$Fe_2O_3$ (0001)*




MULTI-NUCLEAR SURFACE COMPLEX OR PRECIPITATE



Cr - Cr DISTANCE: 3.0 Å
APPROX. 2 NEIGHBOURS

D. Grolimund et al., 1999, J. of Synchrotron Radiation, 6, 612ff.

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# INTERFACIAL REACTIVITY

SINGLE CRYSTL SURFACES

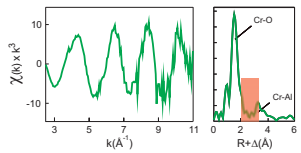
## Interfacial Cr(III) Species

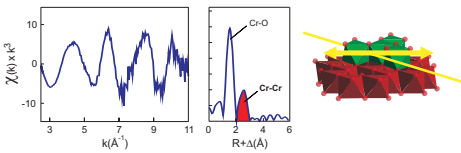
$\alpha$-$Al_2O_3$ SURFACES


Cr(III) on $\alpha$-$Al_2O_3$ (0001)
2 hours exposure time

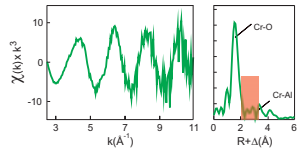
Cr(III) on $\alpha$-$Al_2O_3$ (0001)
**1 month exposure time**

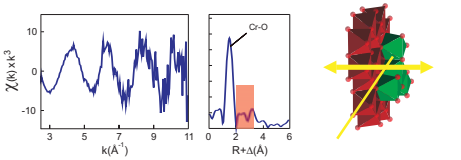
Horizontal



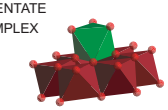




Vertical

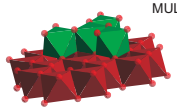



TRIDENTATE COMPLEX



MULTI-NUCLEAR SURFACE COMPLEX OR PRECIPITATE




# INTERFACIAL REACTIVITY

SINGLE CRYSTL SURFACES

## Interfacial Cr(III) Species

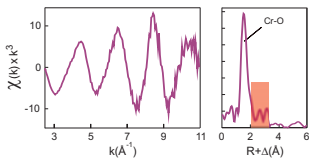
$\alpha$-$Al_2O_3$ SURFACES

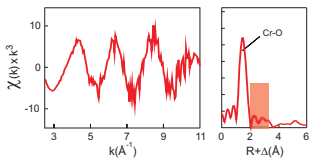

Cr(III) on $\alpha$-$Al_2O_3$ ($1\bar{1}02$)
2 hours exposure time

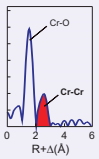
Cr(III) on $\alpha$-$Al_2O_3$ ($1\bar{1}02$)
1 month exposure time

$\alpha$-$Al_2O_3$ (0001)
1 month

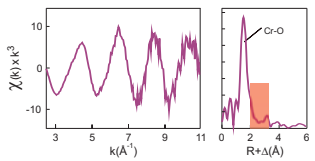
Horizontal

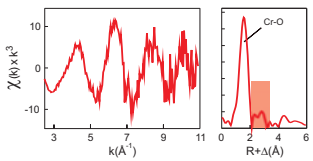


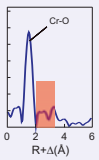




Vertical



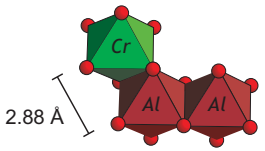


# INTERFACIAL REACTIVITY

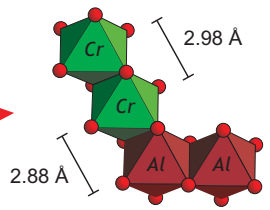
SINGLE CRYSTL SURFACES

## Interfacial Cr(III) Species

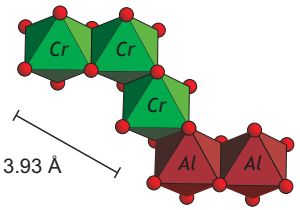

I. EDGE-SHARING BIDENTATE MONOMER

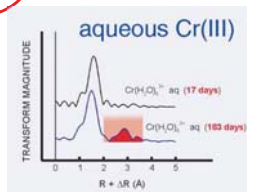



II. EDGE-SHARING DIMER




III. EDGE-SHARING POLYMER

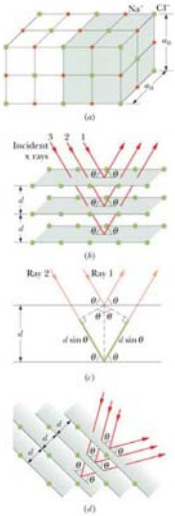


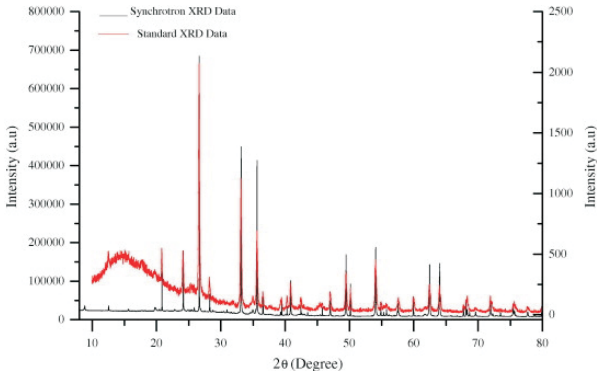
# X-RAY SCATTERING

## X-Ray Diffraction

powder | 0 dimensional



$2d \sin\theta = m\lambda$ for m = 0,1,2,.... Bragg's law



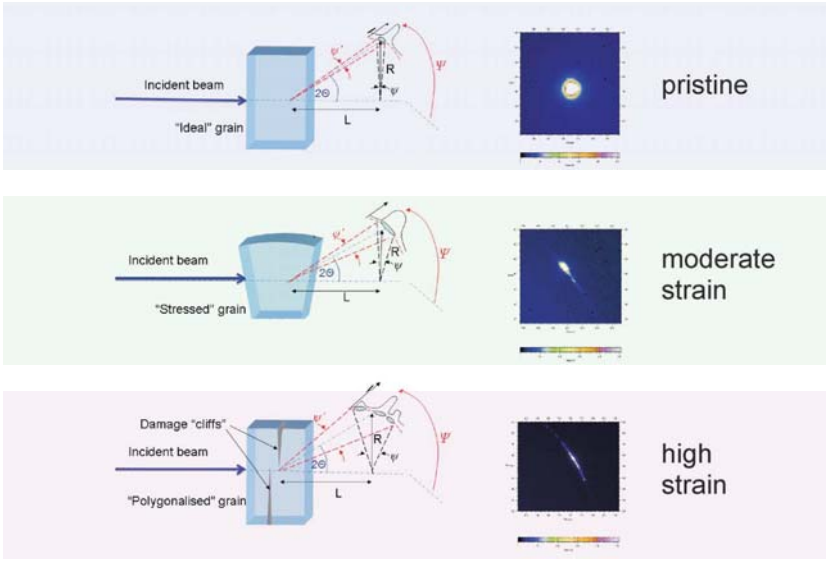

Reynolds et al., Minerals Engineering, 23(9), 2010



# X-RAY SCATTERING

## X-Ray Diffraction

single cystal | 0 dim. | oriented





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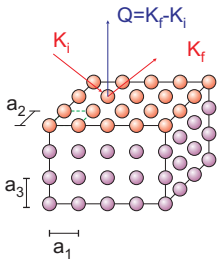
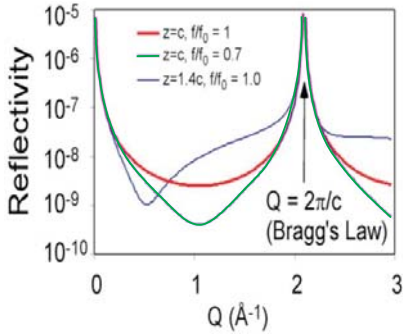
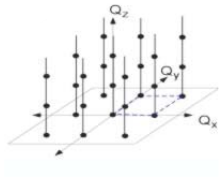
# X-RAY SCATTERING

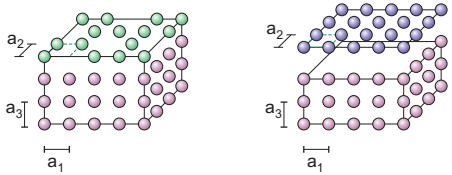
## X-Ray Surface Diffraction

Crystal Truncation Rods




*P. Fenter, "X-ray Reflectivity as a Probe of Mineral-Water Interfaces: A User Guide", Reviews in Mineralogy and Geochemistry, Vol. **49**, 149-220 (2002).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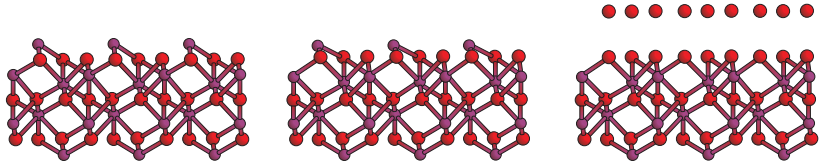
# X-RAY SCATTERING

## Interface Structure

Crystal Truncation Rods

$\alpha$-$Al_2O_3$ (0001) SURFACE



| TRUNCATED BULK | SOLID - VACUUM INTERFACE | SOLID - SOLUTION INTERFACE |
|---|---|---|
| | • Al TERMINATED<br>• RELAXED SURFACE | • HYDROXYL TERMINATED<br>• RELAXED SURFACE<br>• 'STRUCTURED' OVERLAYER |
| | P. Guenard, G. Renaud, A. Barbier, M. Gautier-Soyer, *1997*, *Mat. Res. Soc. Symp. Proc. Vol. 437* | T.P. Trainor, P. Eng, S. Sutton, G.E. Brown, Jr., *1999*, *submitted* |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## Interface Structure

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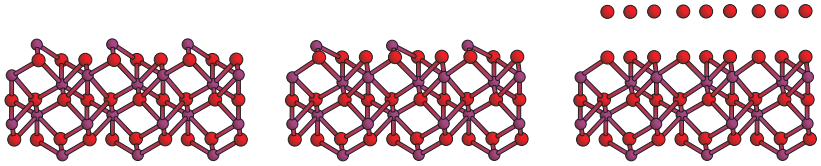
$\alpha$-$Al_2O_3$ (0001) SURFACE



| TRUNCATED BULK | SOLID - VACUUM INTERFACE | SOLID - SOLUTION INTERFACE |
|---|---|---|
| | • Al TERMINATED<br>• RELAXED SURFACE | • HYDROXYL TERMINATED<br>• RELAXED SURFACE<br>• 'STRUCTURED' OVERLAYER |
| | P. Guenard, G. Renaud, A. Barbier, M. Gautier-Soyer, *1997*, *Mat. Res. Soc. Symp. Proc. Vol. 437* | T.P. Trainor, P. Eng, S. Sutton, G.E. Brown, Jr., *1999*, *submitted* |

Resonant Anomalous X-ray Reflectivity (RAXR)

X-ray Reflection Interface Microscopy (XRIM)

P. Fenter et al., ANL | APS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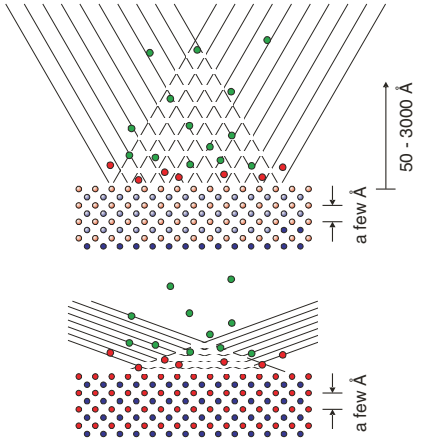
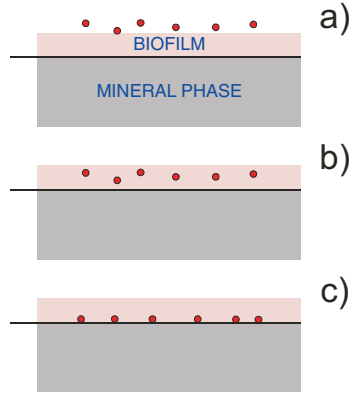
# X-RAY SCATTERING

## X-Ray Standing Waves





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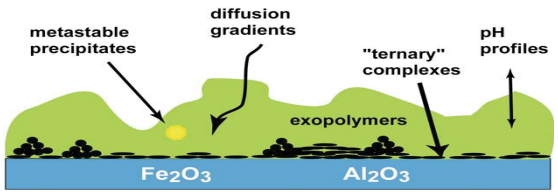
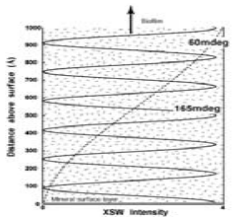
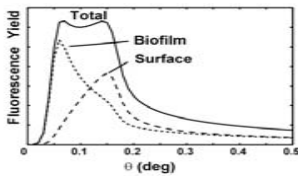
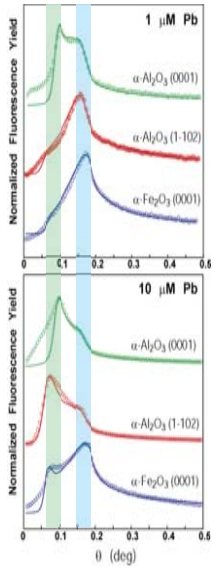
# MULTI-COMPONENT INTERFACES

## Mineral | Biofilm | NOM Composites




A.S. Templeton et al. (2001), *Proc. Natl. Acad. Sci., 98, 11897*
T.P. Trainor, et. al. (2006), J. Electr. Spectr. Relat. Phenom., 150, 66-85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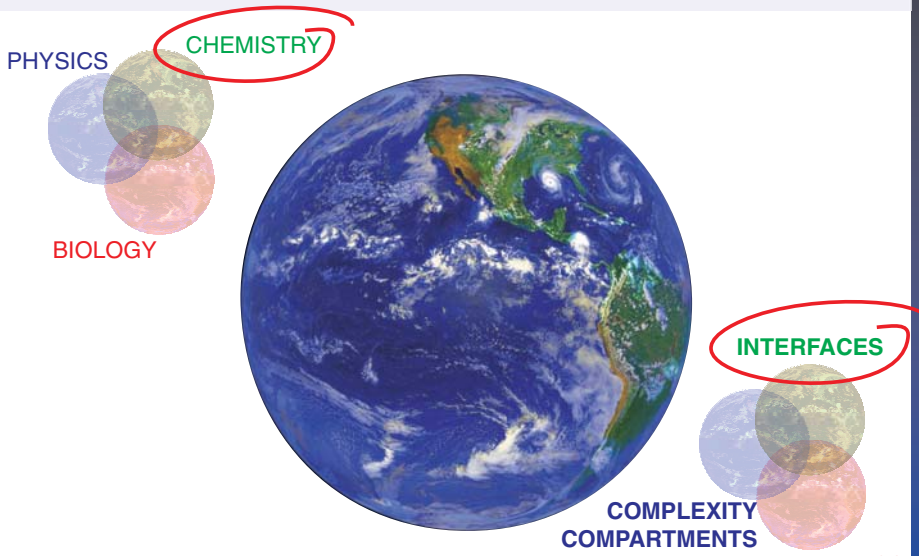
# ENVIRONMENTAL SCIENCE

## Environmental Science: Challenge





SLS X05LA microXAS Beamline
Synchrotron based Techniques applied to Environmental Science
Daniel Grolimund
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structural analysis
... with X-rays
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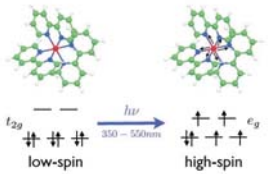
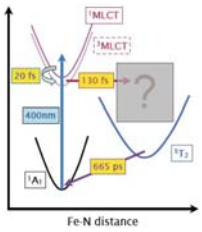
PAUL SCHERRER INSTITUT PSI

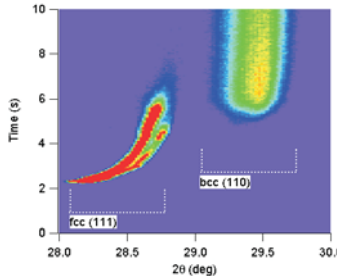
# ENVIRONMENTAL SYSTEM ANALYSIS

## KINETICS

X-Rays: Up to Ultrafast Temporal Resolution,
non-invasive ....




.... not yet fully explored in Environmental Science, e.g.
Atmospheric Chemistry, Geochemistry, Redox, ....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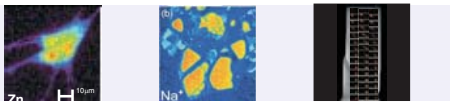
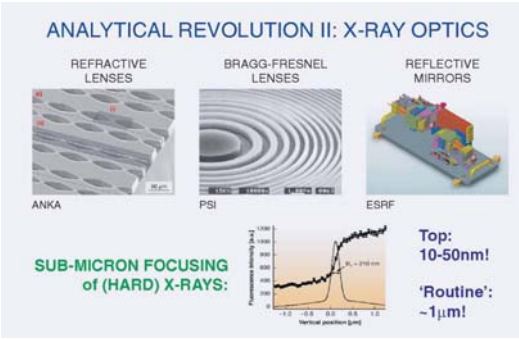
## COMPARTMENTS



## HIGH SPATIAL RESOLUTION IMAGING





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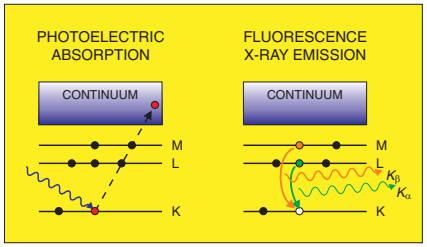
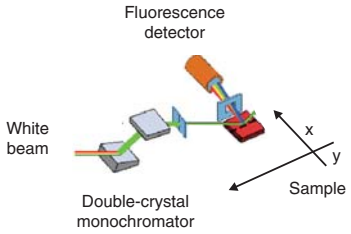
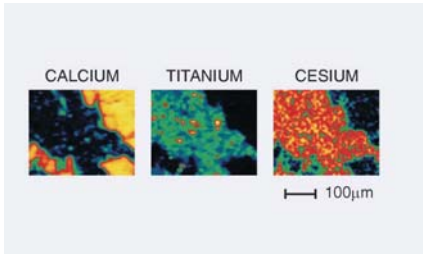
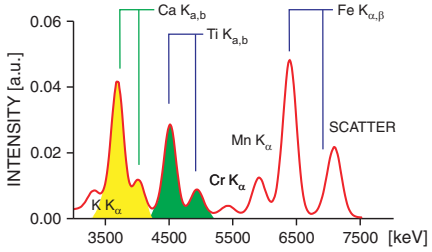
## microXRF: CHEMICAL IMAGING

2 dimensional





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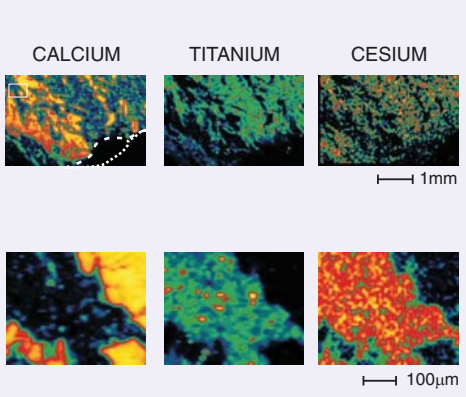
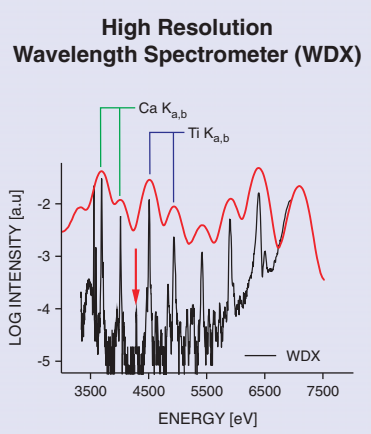
## microXRF: CHEMICAL IMAGING

INTERFERENCES I 2D




H.A.O. Wang, et. al., 2011, Analytical Chemistry, 16, 6259–6266.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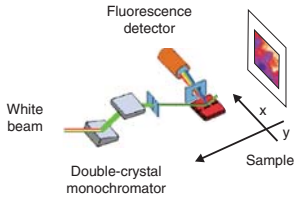
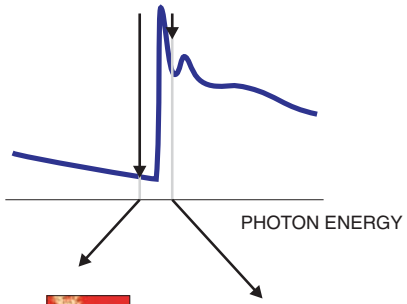
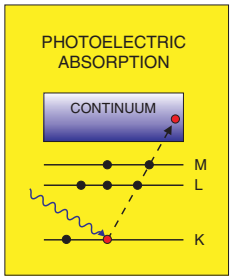
## microXRF: CHEMICAL IMAGING

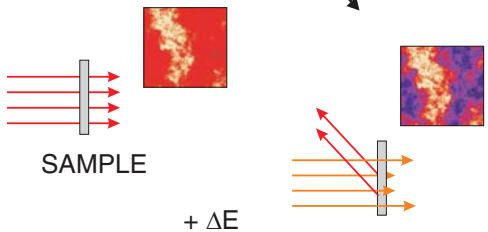
INTERFERENCES | 2D

**MONOCHROMATIC LIGHT**



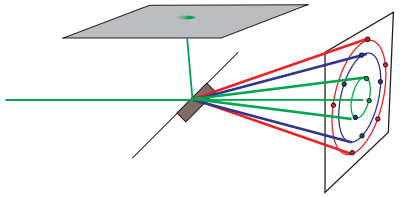


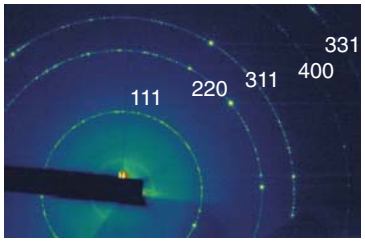

# ENVIRONMENTAL SYSTEM ANALYSIS

## microXRD: CHEMICAL IMAGING

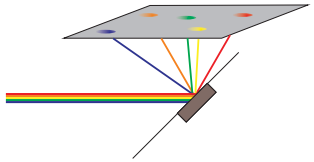
2D

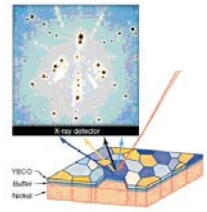
**MONOCHROMATIC LIGHT**






**"PINK" BEAM**







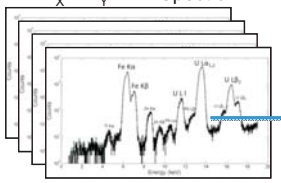
# ENVIRONMENTAL SYSTEM ANALYSIS

## microXRF | microXRD: CHEMICAL IMAGING

2D

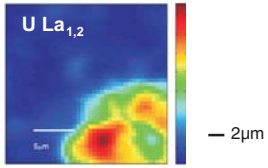
- Per pixel XRF spectrum
- Per pixel 2D diffraction pattern

$N_X$ x $N_Y$ XRF Spectra



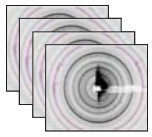
Track ROI in original spectra

Fluorescence Counts Map



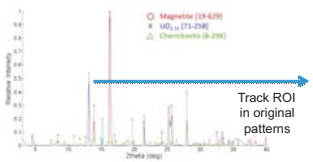

— 2μm

$N_X$ x $N_Y$ 2D XRD Patterns



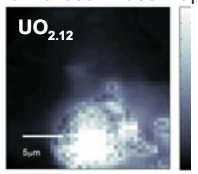
Sum and azimuthal integration

Sum 1D Pattern – Phase ID



Track ROI in original patterns

Normalised Phase Map

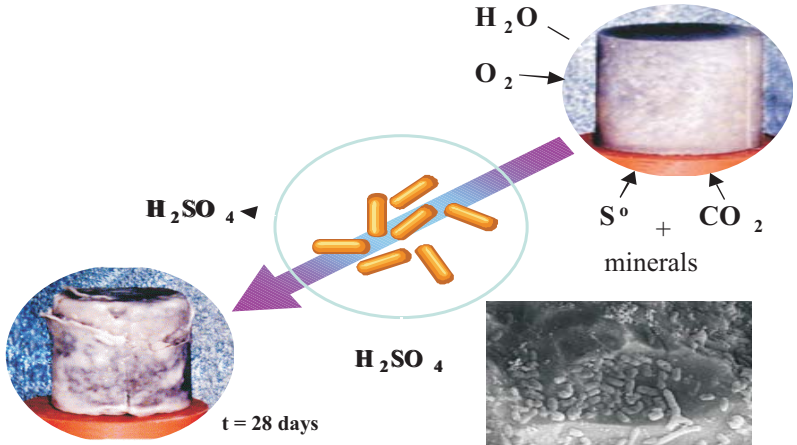



Crean et al., Uni. Sheffield & Manchester



# CHEMICAL IMAGING

## Degradation of Solidified Cementitious Waste

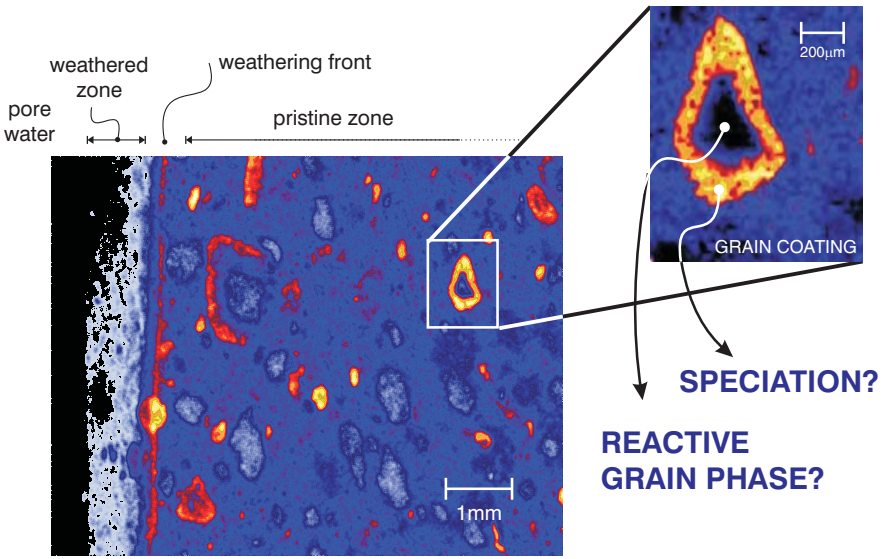



collaboration with C.R. Cheeseman, Imperial College London, UK

*Thiobacilli thiooxidans*

# CHEMICAL IMAGING

## Degradation of Solidified Cementitious Waste





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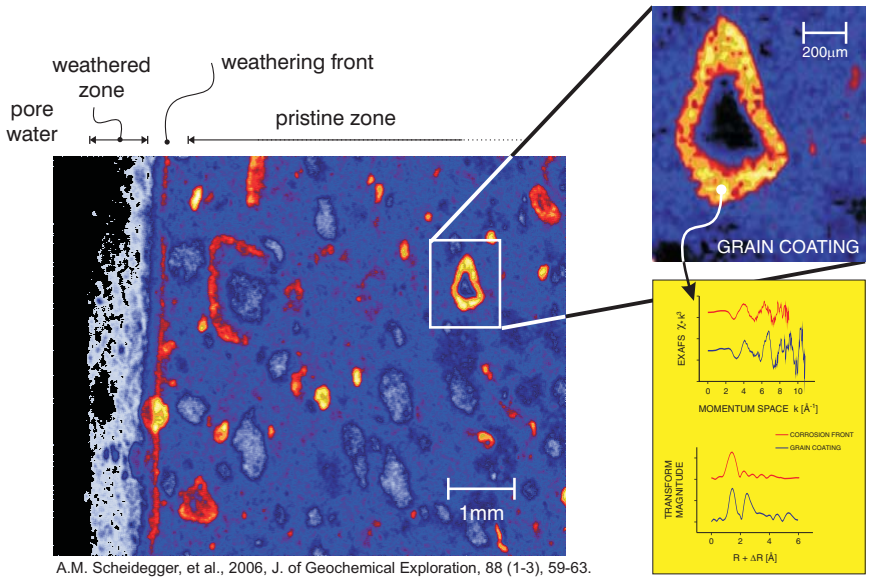


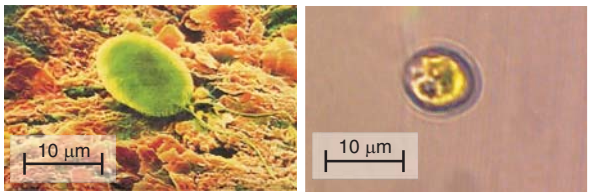

A.M. Scheidegger, et al., 2006, J. of Geochemical Exploration, 88 (1-3), 59-63.


# CHEMICAL IMAGING

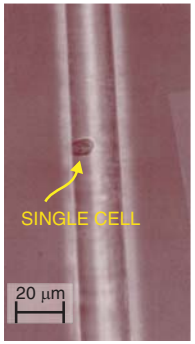
## Biogeochemistry: BIOSENSORS

SINGLE ALGAE CELLS


- microXRF:
  ELEMENTAL DISTRIBUTION WITHIN CELL
- microXANES/EXAFS:
  CHEMICAL SPECIATION WITHIN CELL COMPARTMENTS




CAPILLARY TECHNIQUE





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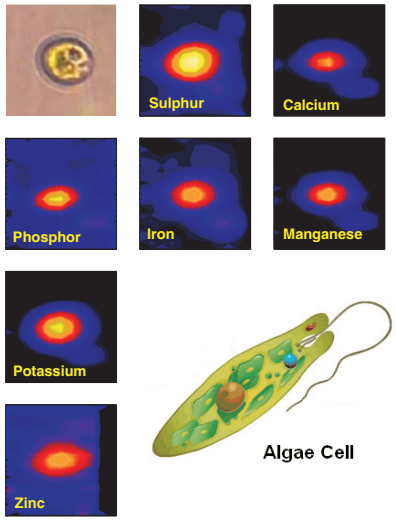
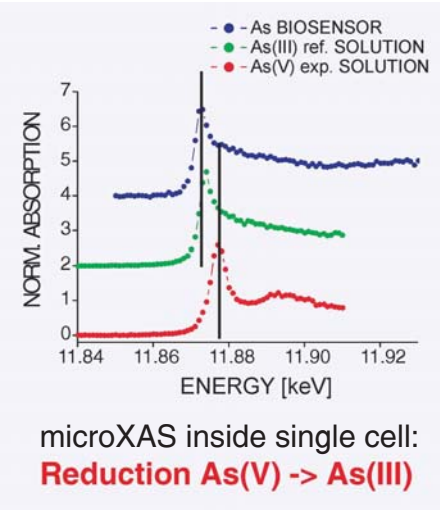
## Biogeochemistry: BIOSENSORS

SINGLE ALGAE CELLS

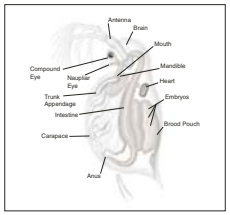



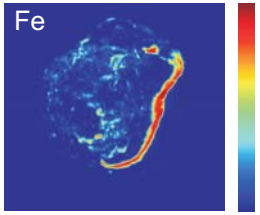

microXAS inside single cell:
**Reduction As(V) -> As(III)**

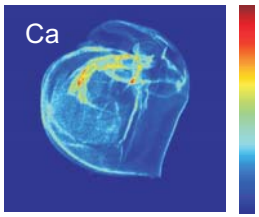
# CHEMICAL IMAGING

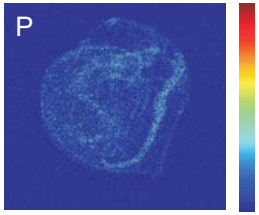
## Exposure to Nano-Particles

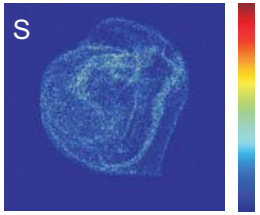
DAPHIA




collaboration with T.H. Yoon et al., Hanyang University, Korea

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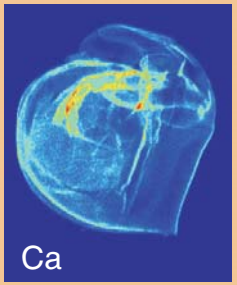
# CHEMICAL IMAGING

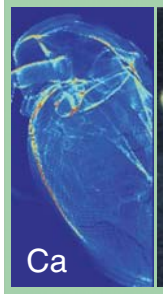
## Exposure to Nano-Particles

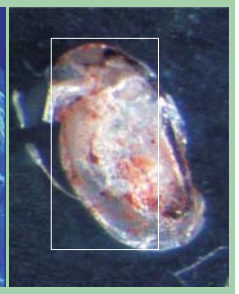
DAPHIA

### micro - X-Ray Imaging




### hard X-Ray nanoImaging



even for large overview images nanoImaging provides additional minute details

- head area
- carapace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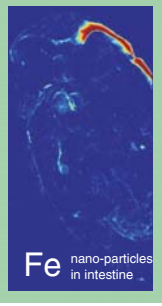
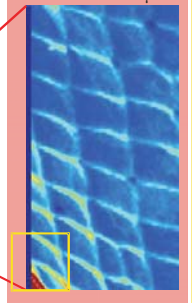
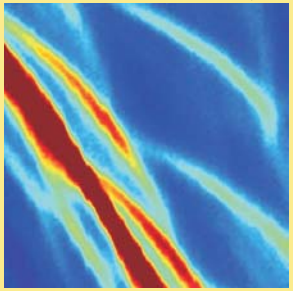
### hard X-Ray nanoImaging








nanoImaging: collaboration with C. David, P. Karvinen, PSI, Switzerland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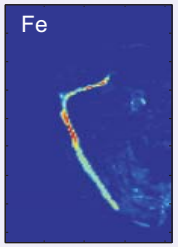
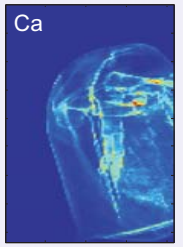
# CHEMICAL IMAGING

## Exposure to Magnetite Nano-Particles

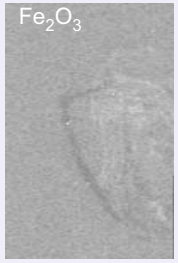
DAPHIA

XRF mapping




XRD mapping
17keV







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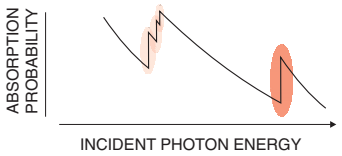
# CHEMICAL IMAGING

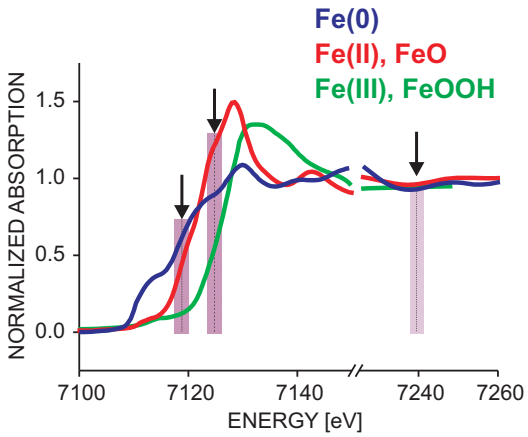
## Spectromicroscopy: Imaging Speciation in 2D




**electronic and local structure information**

| ENERGY [eV] | Fe(0) | Fe(II) | Fe(III) |
|---|---|---|---|
| 7119 | 0.6 | 0.4 | 0.1 |
| 7125 | 0.9 | 1.2 | 0.6 |
| 7240 | 1.0 | 1.0 | 1.0 |

**CHEMICAL CONTRAST !**



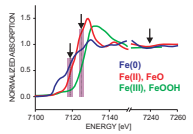



# CHEMICAL IMAGING

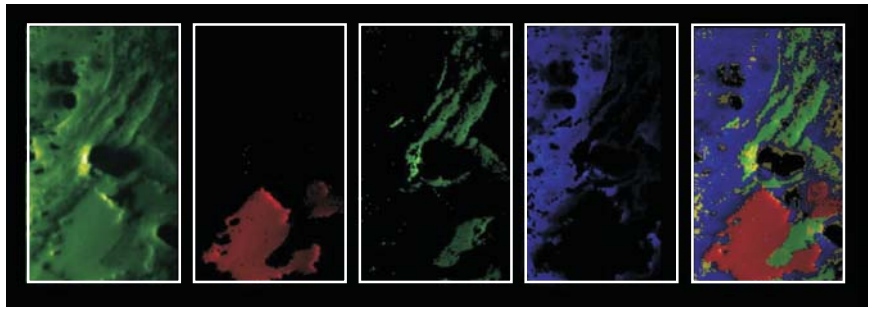
## spectromicroscopy: Imaging speciation in 2D

### Historic Iron Slag: Reconstruction of Smelter Operation

ANCIENT IRON SLAG




$Fe_{tot}$ Fe(0) Fe(II) Fe(III)



D. Grolimund, et al., Spectrochim. Acta B (2004)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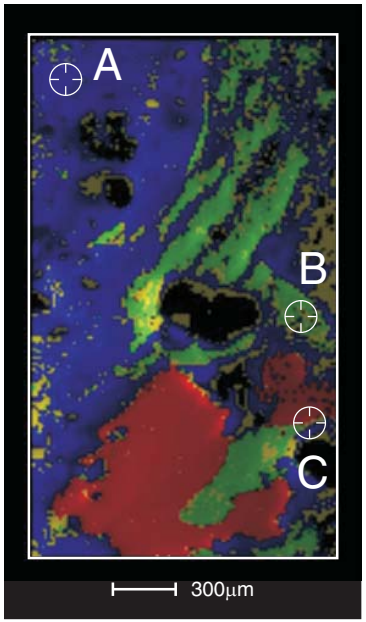


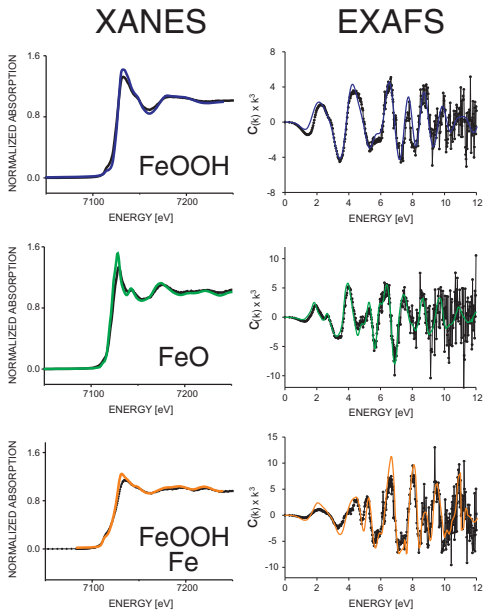



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# CHEMICAL IMAGING

## Depleted Uranium in the Environment

Crean et al.
Uni. Sheffield & Manchester

**Armoured Target**
Pyrophoric Interaction
Temperature ~3000°C*


## Goals:

Provide knowledge on environmentally aged DU residues as input to

- Long term management of soil and associated risk
- Remediation based on understanding of properties of the contaminant


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## Depleted Uranium in the Environment

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$N_X$ x $N_Y$ XRF Spectra

Track ROI in original spectra

Fluorescence Counts Map

U $La_{1,2}$

— 2µm

$N_X$ x $N_Y$ 2D XRD Patterns

Sum and azimuthal integration

Sum 1D Pattern – Phase ID

Track ROI in original patterns

Normalised Phase Map

$UO_{2.12}$

n XRF maps $E_1$ $E_2$ $E_3$

Redox Map

U(VI)

U(IV)




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## Depleted Uranium in the Environment

Crean et al.
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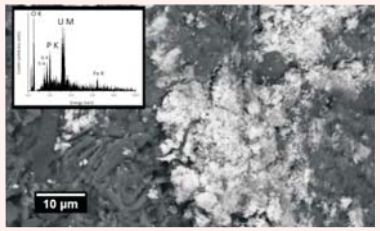


— 10µm


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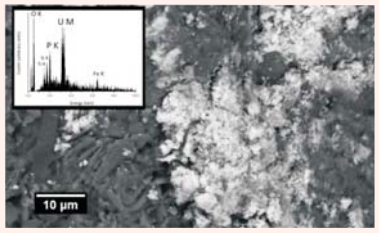
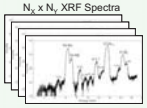
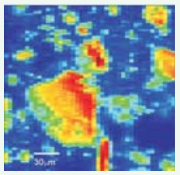


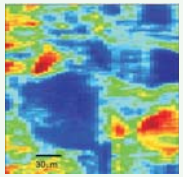

— 10µm



U Fluorescence Map



Fe Fluorescence Map



— 30µm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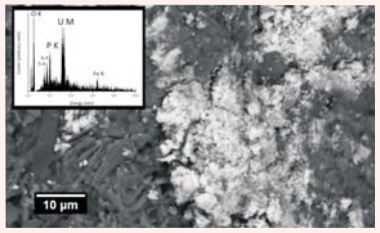
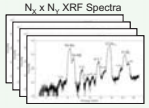
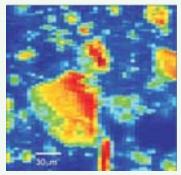


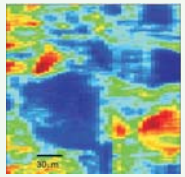

— 10µm



U Fluorescence Map

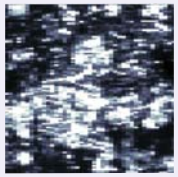


Fe Fluorescence Map



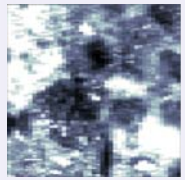
$N_x$ x $N_y$ 2D XRD Patterns





$UO_{2.34}$

$U_3O_8$



$Fe_3O_4$

— 30µm

# CHEMICAL IMAGING

## Depleted Uranium in the Environment

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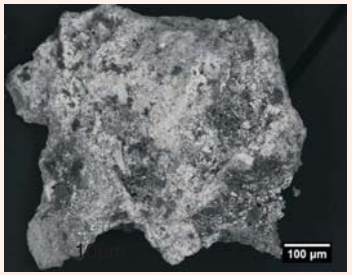
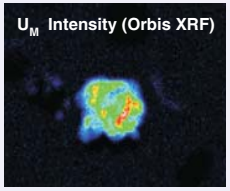
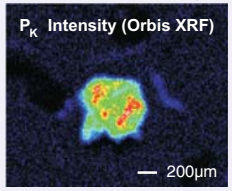
Uni. Sheffield & Manchester




100µm

### Complementary, lab-based XRF (30µm)





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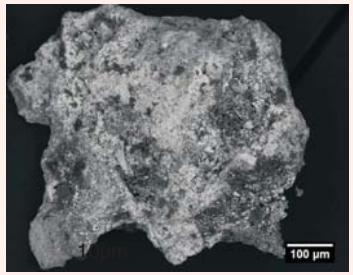
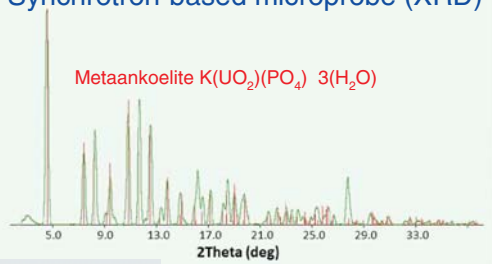
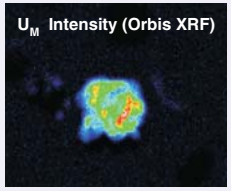
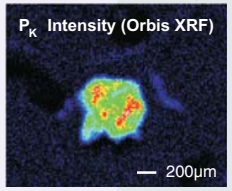


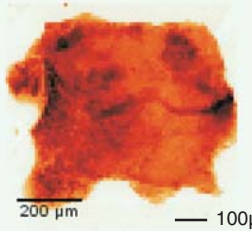

### Synchrotron-based microprobe (XRD)




### Complementary, lab-based XRF (30µm)





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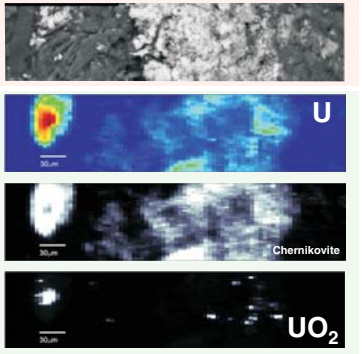
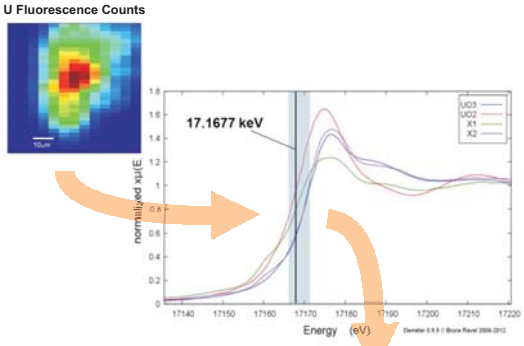
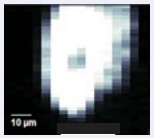


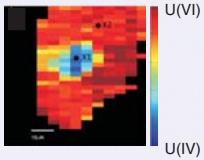




**U(IV)** $UO_2$




**U(VI)** Chernikovite

**Average Uranium Oxidation State**




D.E. Crean, F.R. Livens, M. Sajih, M.C. Stennett, D. Grolimund, C.N. Borca, N.C. Hyatt, J. Hazard. Mat.,submitted ( 2013).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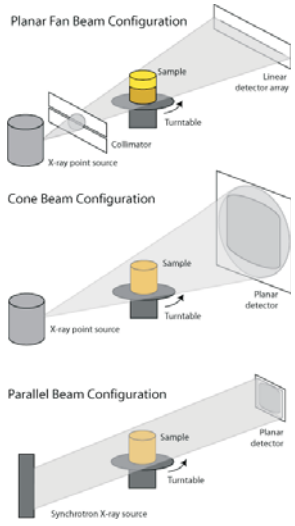
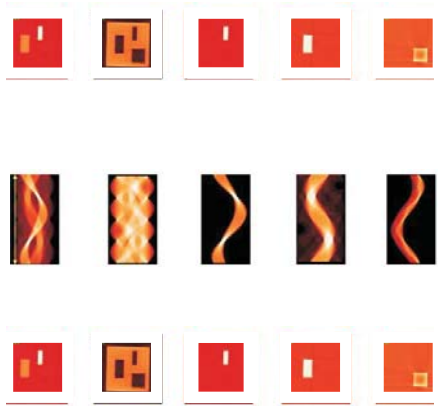
## X-Ray Tomography



V. Scot , J.E. Fernandez , L. Vincze , K. Janssens, 2007, NIM B, 263 (1), 204-208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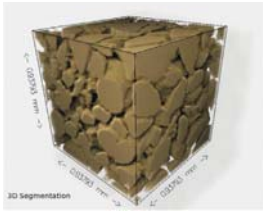
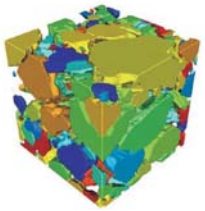
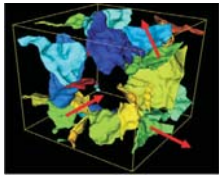


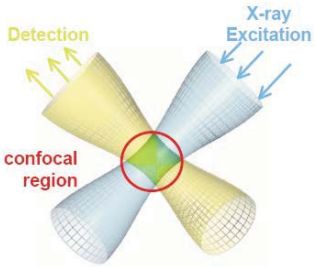


Arad, A., Mahdadi, M., Christy, A.G., Sheppard, A.P., Averdunk, H., Knackstedt, M.A., 2010, Petrophysics (in press).



# CHEMICAL IMAGING

## Confocal Microscopy




+ use microXAS microprobe
+ bulk samples
+ no projections
+ 'no' reconstruction
+ single voxel analysis (XRF, XANES, ...)

- spatial resolution

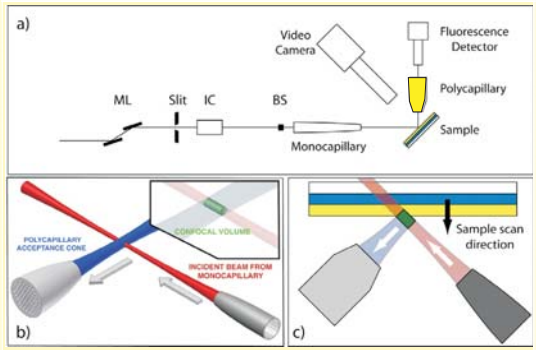



**Fig 1:** Schematic illustrations of the confocal X-ray fuorescence geometry. (a) shows the experimental setup, indicating the multilayer optics (ML), slit, ion chamber (IC), beamstop (BS), focusing and collecting optics, and the detector. (b) shows a 3D view of how the confocal active volume is formed from the focal regions of the two optics. (c) indicates, in cross-section, how the sample is scanned through the confocal volume, so that fuorescence from individual layers is resolved.

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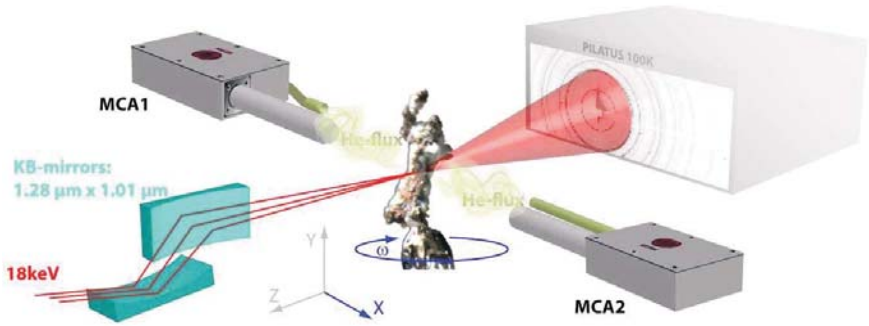
# CHEMICAL IMAGING

## Chemical micro-Tomography

microXRF | microXRD




W. deNolf, University Antwerp @ microXAS

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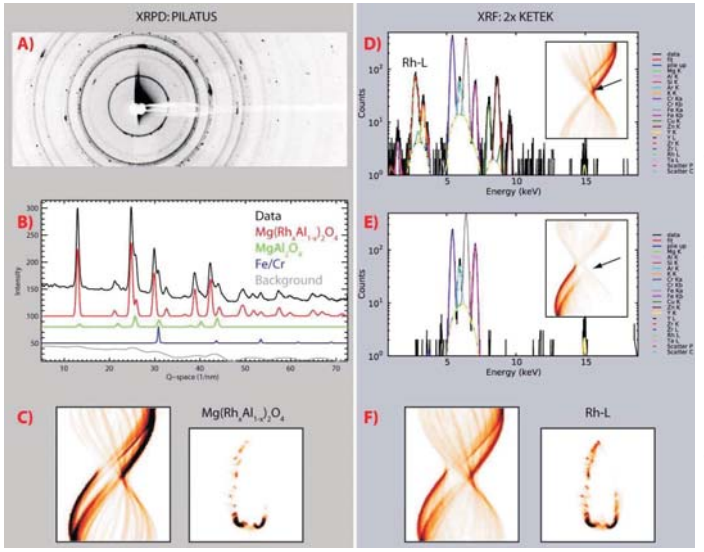


W. deNolf, University Antwerp @ microXAS

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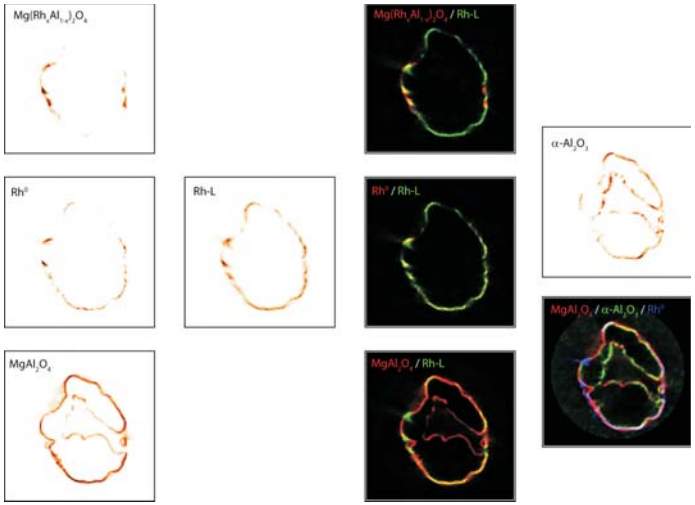


W. deNolf, University Antwerp @ microXAS



# SUMMARY

## Env. Sci.: Need for Mechanistic, Molecular-level Information

- IDENTIFICATION OF CHEMICAL SPECIES INVOLVED
- DEVELOPMENT OF CHEMICAL CONCEPTS
- ENHANCED PREDICTIVE CAPABILITIES
  - EXTRAPOLATION
  - DESIGN (!) OF REACTIVE INTERFACES
  - INDUSTRIAL/ENVIRONMENTAL (DE)CONTAMINANTION
- NATURAL SYSTEMS ARE 'N-DIMENSIONAL'
  - COMPETITION
  - HETEROGENEITY
- KINETICS
  - PROCESS IDENTIFICATION | VALIDATION
  - UP-SCALING 'LAB - FIELD' (SPACE + TIME)


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## Crucial Mechanistic Information in Interfacial Chemistry

| | |
|---|---|
| STRUCTURE OF INTERFACE | DIFFRACTION, CTR, SPECTROSCOPY, STANDING WAVE TECHNIQUES |
| REACTIVE SURFACE GROUPS | (SURFACE SENSITIVE) SPECTROSCOPY |
| INTERFACIAL SPECIES | SPECTROSCOPY |
| DISTRIBUTION OF SPECIES | STANDING WAVE TECHNIQUES |
| REACTION PATHWAYS | TIME RESOLVED SPECTROSCOPY |
| SPACIAL HETEROGENEITY | MICRO ANALYSIS |


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# SUMMARY

## Imaging Chemistry (and Physics) with X-rays

| | |
|---|---|
| **CHEMISTRY** | → chemical sensitivity<br>→ atomic/molecular-level information |
| **SPACE** | → microscopic (nanoscopic) spatial resolution<br>→ penetration power (→3D) |
| **TIME** | → 'non-destructive'<br>→ 'fast' |


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# SUMMARY

- **Chemical micro-Imaging** is fundamental to understand structure and **chemical reactivity** of complex systems
  - → ... evolution, degradation, toxicity, bioavailability, metabolism, ...
- Synchrotron-based **X-rays** have a pronounced imaging and spectroscopic 'power'
  - → ... suite of techniques: XRF, **XAS**, XRD, **cSAXS**, ..
  - → ... enormous potential: spatial and temporal resolution, 3D, 4D, quantification, ...
- Complementary Approach:
  - ... different microscopic & (micro)-spectroscopic tools & macroscopic & theoretical tools
  - → **Quantitative Chemical (and Physical) Imaging of Environmental Systems in Space and Time**



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... with X-rays
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X-ray absorption
X-ray scattering
X-ray imaging
SUMMARY