Nanotechnology for cement-based materials

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Collaborators

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• Prof. David Attwood	U.C. Berkeley and ALS
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• Dr. Mauricio Mancio	Postdoc at U.C. Berkeley
• Dr. Jae Oh	Postdoc at U.C. Berkeley
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• Seyoon Yoon	PhD student
• Cagla Meral	PhD student
• Pierre Itty	PhD student
• Ju-hyuk Moon	PhD student
• Kamel Celik	PhD student

World demand/year

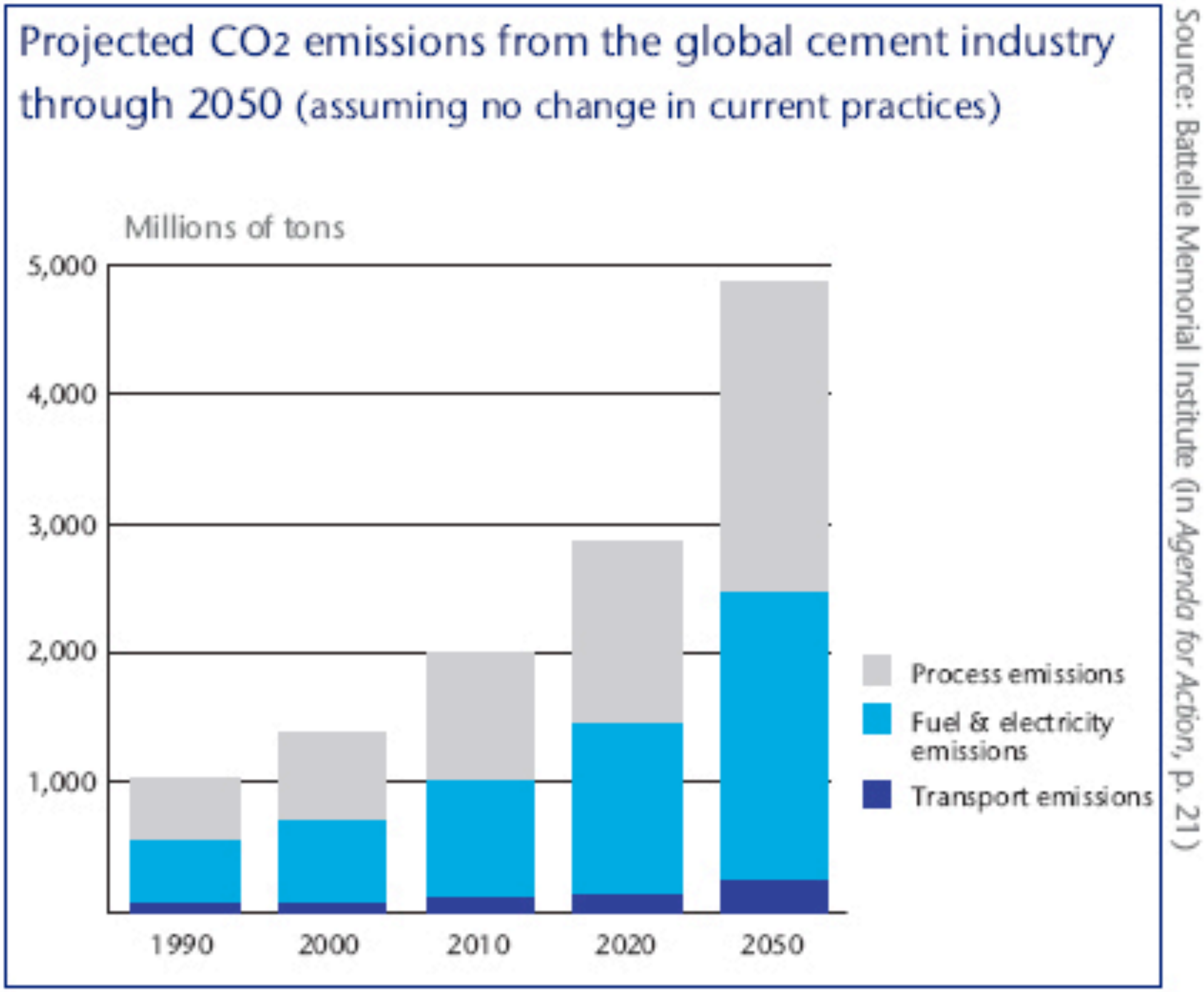
- 16 billion ton of concrete
- 1.5 billion ton of water
- 12.4 billion ton of aggregate
- 2.1 billion ton of cement

Production of portland cement

Environmental Impact:
1 ton of cement generates 0.8 ton of CO_2

Consequence:
The production of cement →5-8% of CO_2 generation in the world

Business as usual is not an option!



Fundamental Question:

Exciting opportunities with disruptive impact have been identified. Why somebody has not taken advantage of them?

BECAUSE IT IS <u>REALLY </u>HARD:

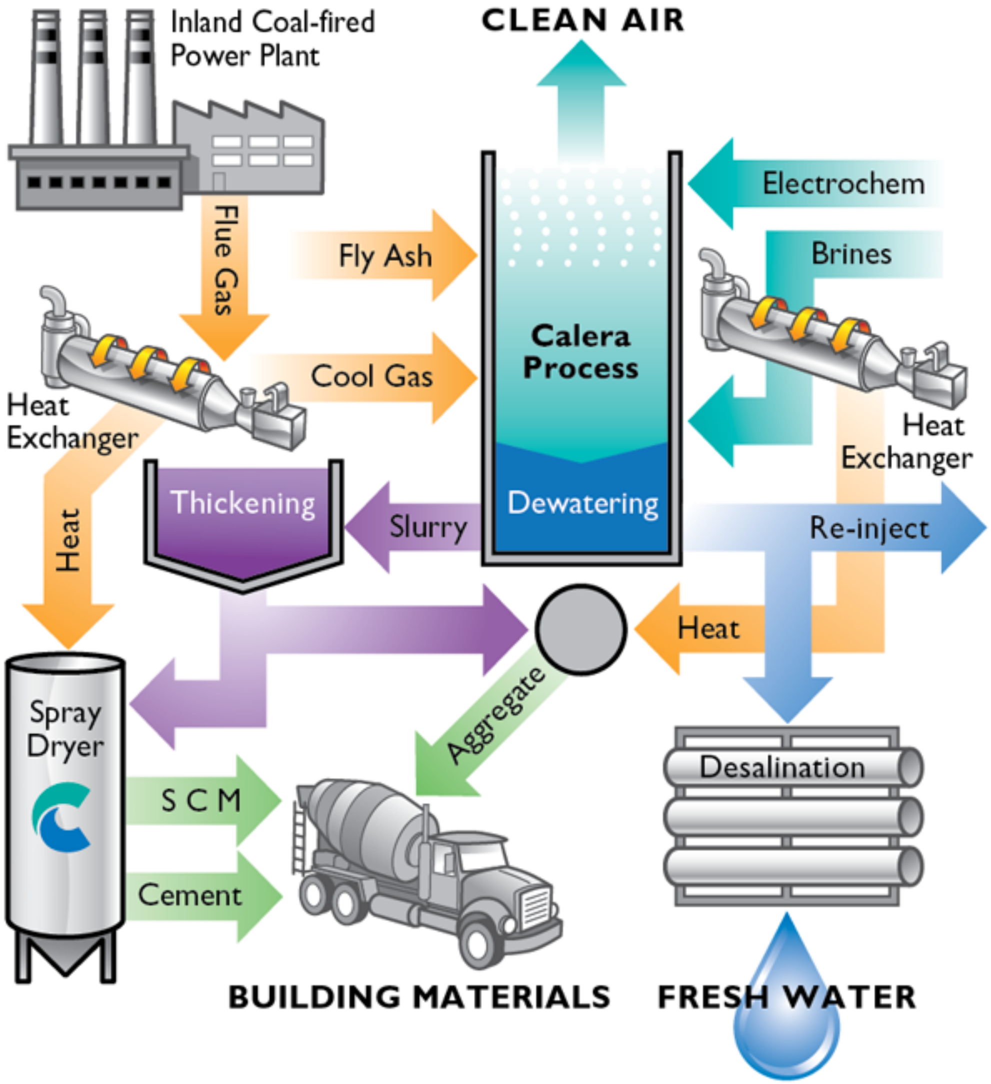
120 years of development for portland cement.

It requires science, technology, and resources.

Fantastic opportunity

- 16 billion ton of concrete
- 12.4 billion ton of aggregate
- 2.1 billion ton of cement

Thinking really big...

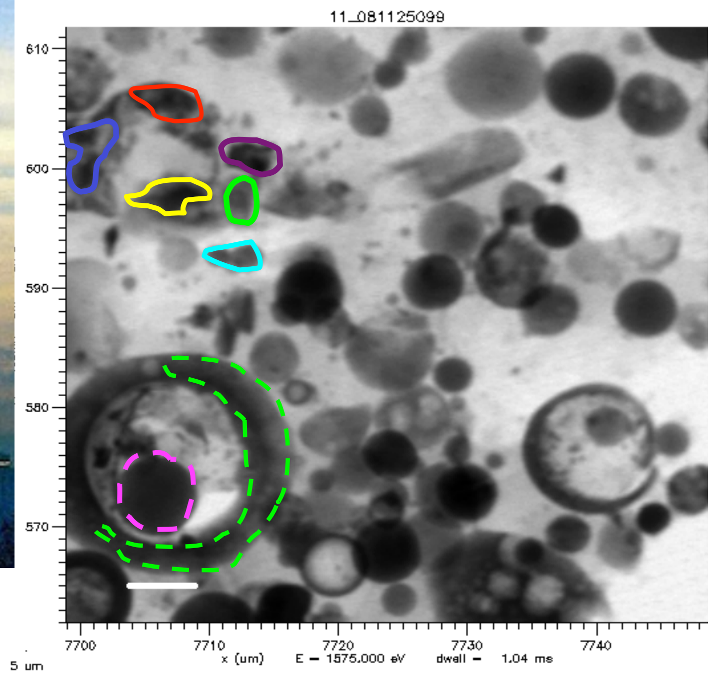


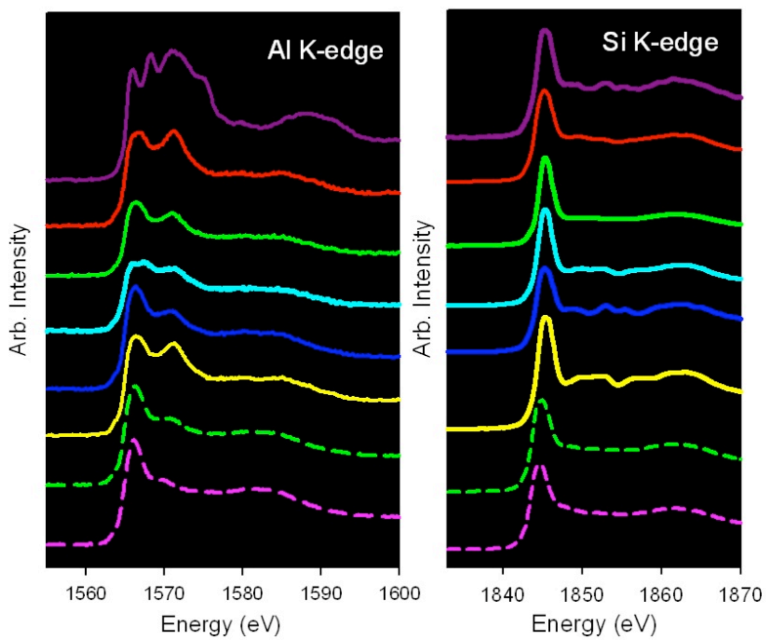
Moss Landing, Ca

<u>Products:</u>

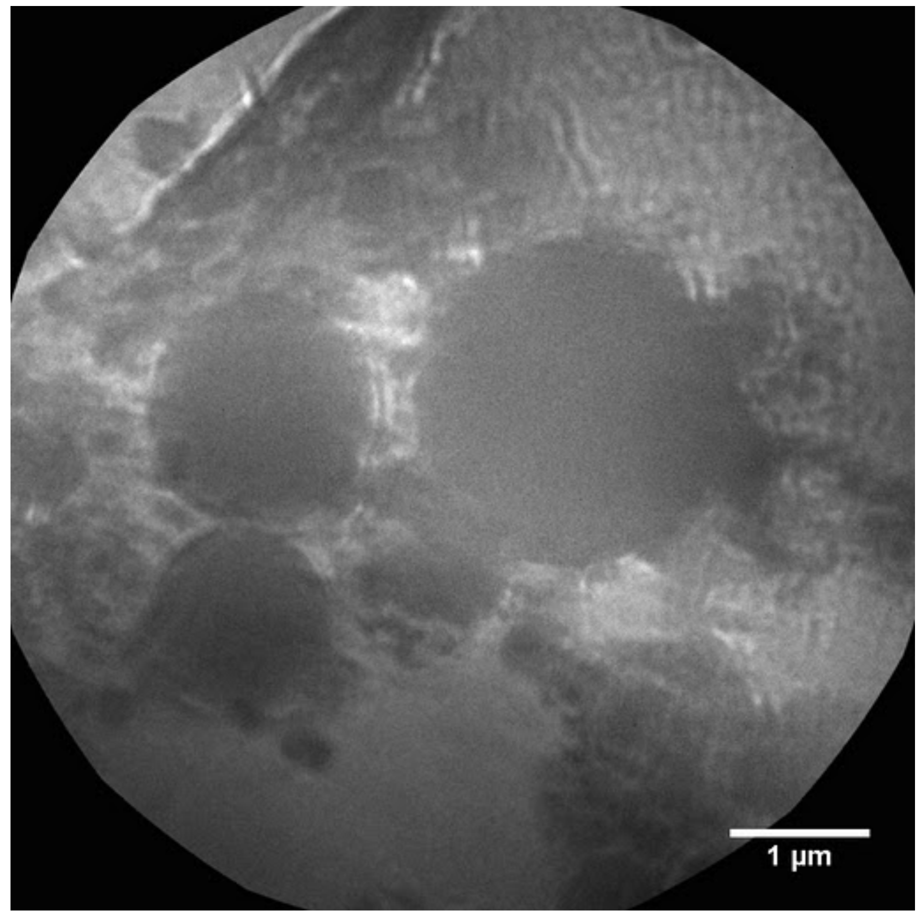
Amorphous Calcium Carbonates
Vaterite
Aragonite
Calcite

Geopolymers (no cement!)

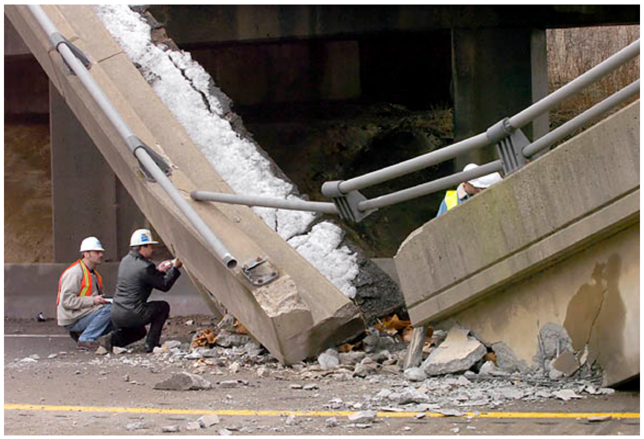




10 M NaOH solution

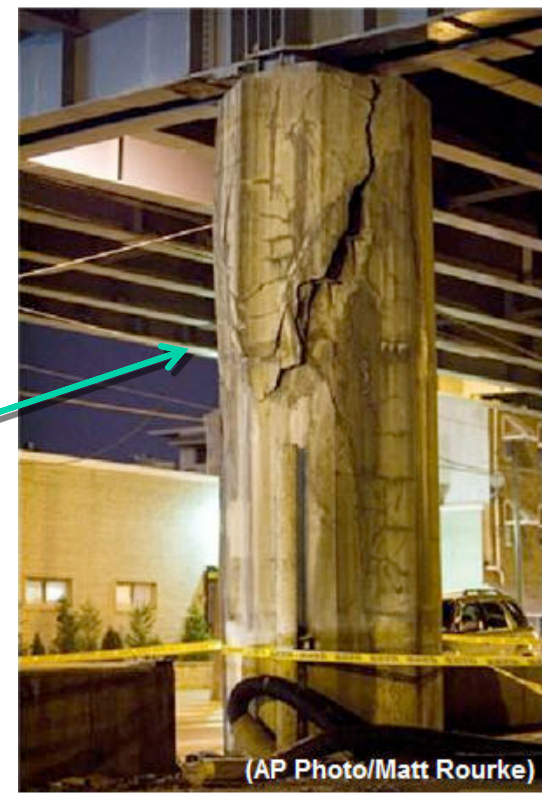


Conservative Industry



Corrosion (from MATCO's)

March 17, 2008,
I-95 in Philadelphia



Multi-scale approach

Macro

Mix Design
Geopolymers
Durability

Micro

Interfaces
Reduction of pores
micromechanics

Nano

X-ray microscope
Neutron diffraction
High pressure

Integrated research

Advanced Light Source

Soft x-rays microscopy, Small Angle Scattering, High-Pressure, Microdiffraction, Microtomography, Ambient XPS.

Advanced Photon Source

Total scattering methods (pdf), Nanotomography, Small Angle Scattering.

BESSY

Nanotomography

… more at Los Alamos

Nanotechnology

The purposeful engineering of matter at scales of less than 100 nanometers _to achieve size-dependent properties _and functions.

Matthew Nordan, 2005

We need the ability to measure the properties at this scale

Advanced Light Source

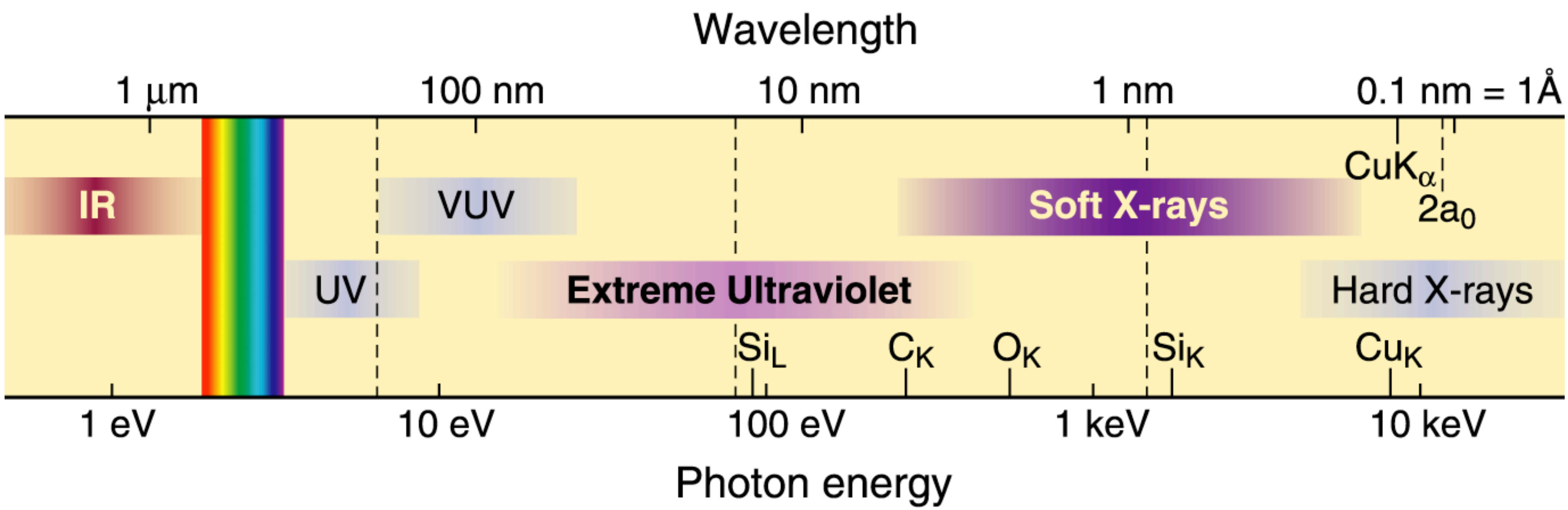
Location

the world's first third-generation synchrotron light source in its energy range

Location, location, location

Our office ALS

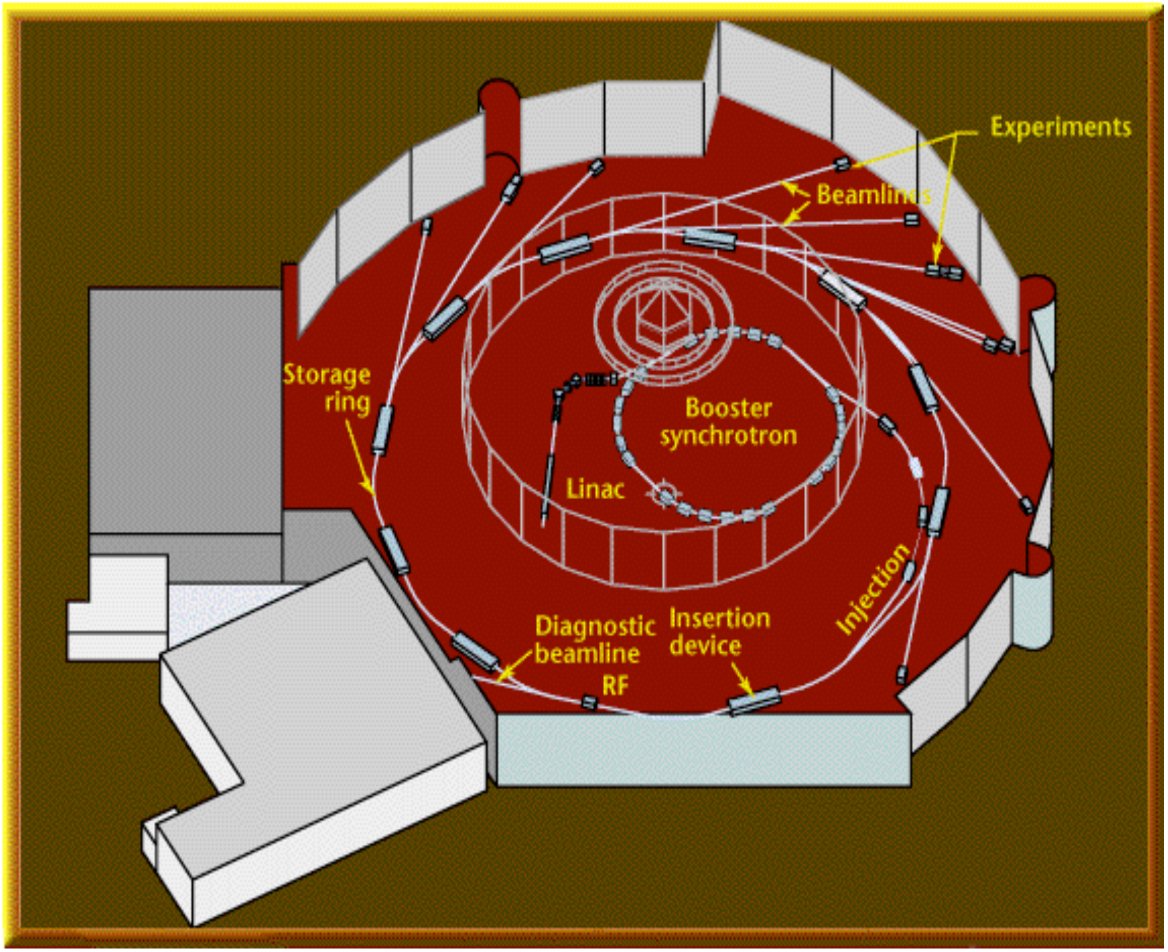
The Short Wavelength Region of the Electromagnetic Spectrum



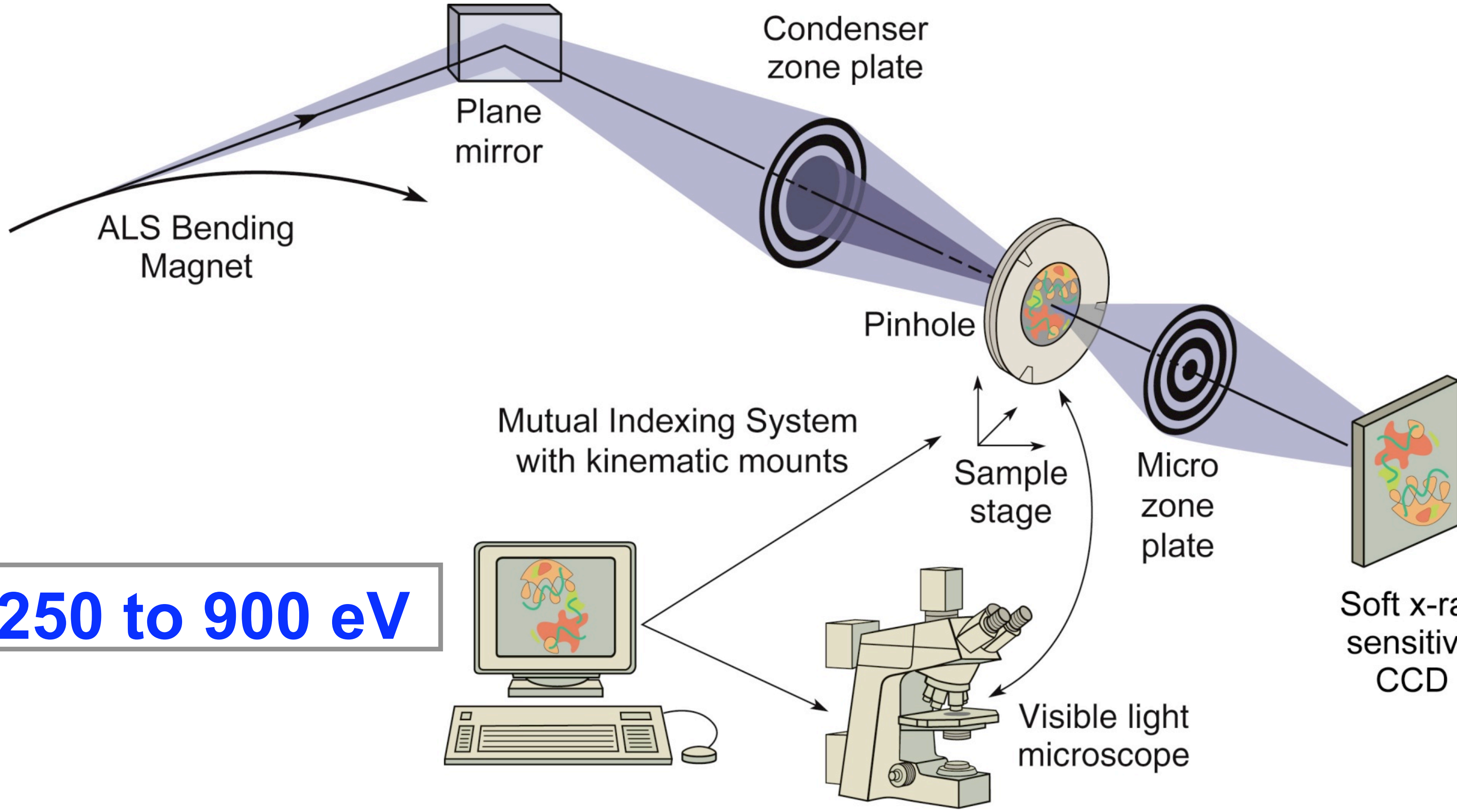
- **See smaller features**
- **Write smaller patterns**
- **Elemental and chemical sensitivity**

Courtesy from David Attwood

Advanced Light Source at Berkeley



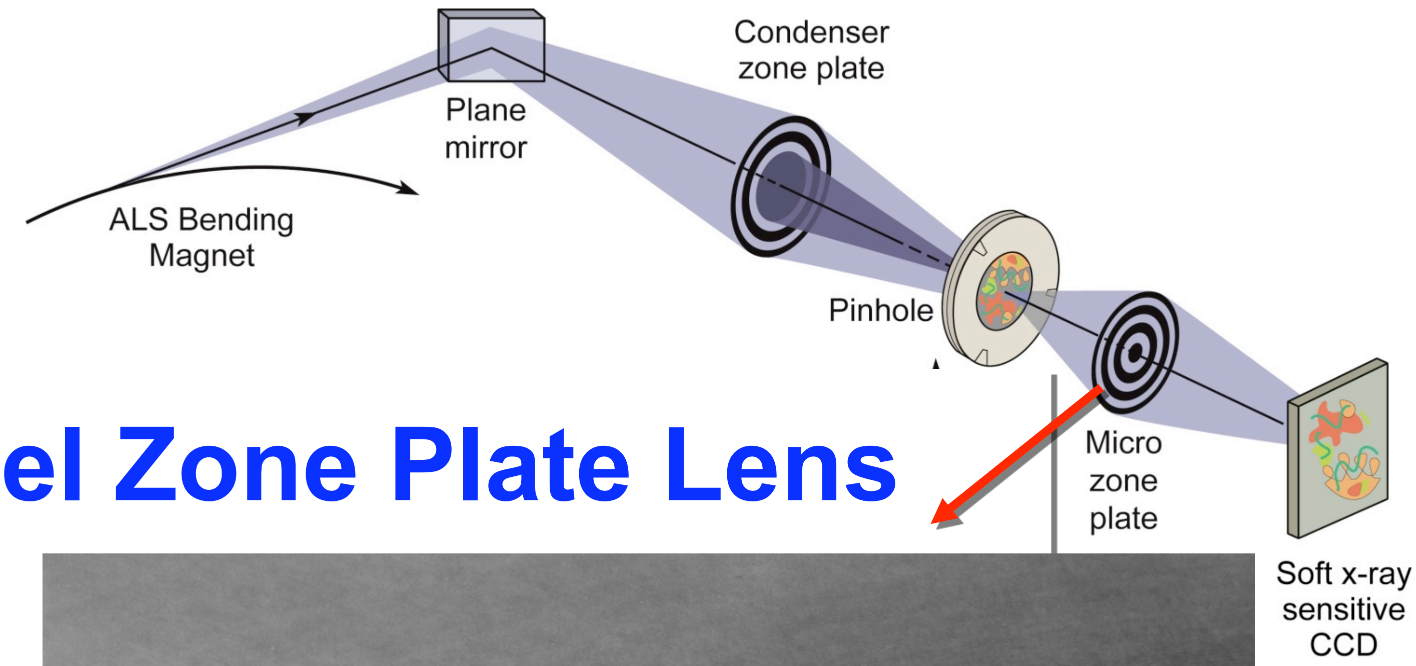
Imaging the chemical reactions with soft x-ray microscopy



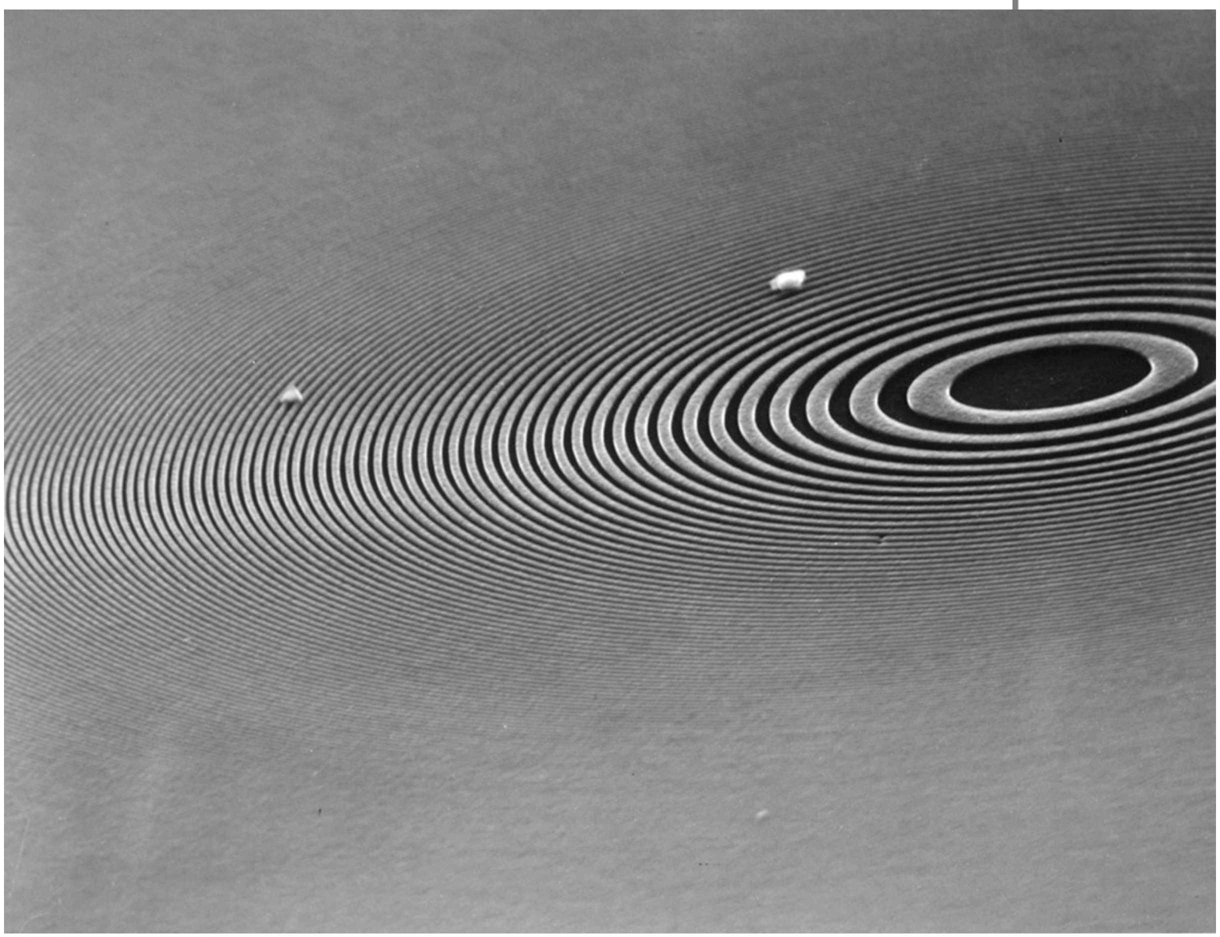
250 to 900 eV

Resolution: 15 nm

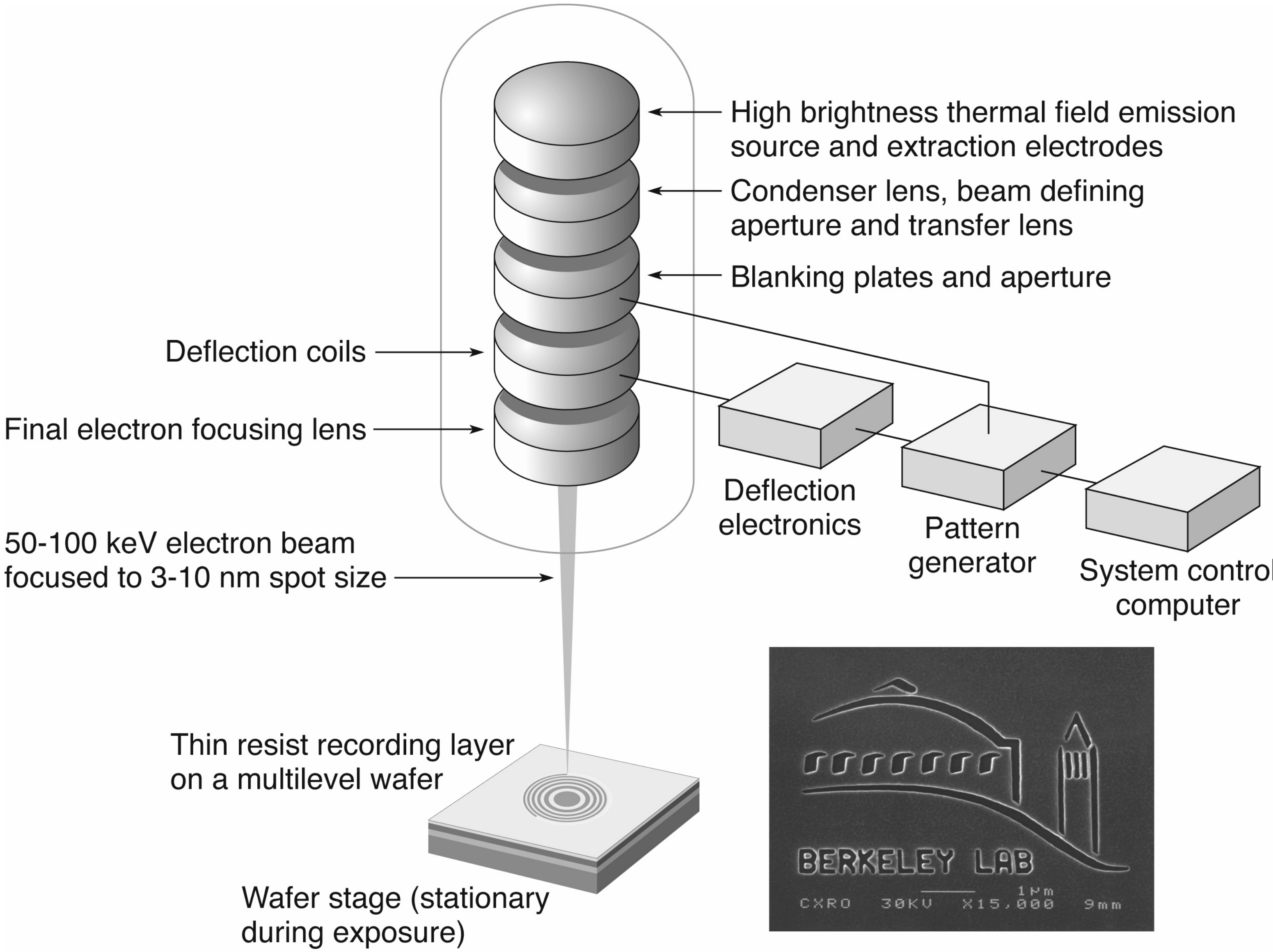
Magnification: 1600 to 2400 times



Fresnel Zone Plate Lens



The Nanowriter: High Resolution Electron Beam Writing With High Placement Accuracy

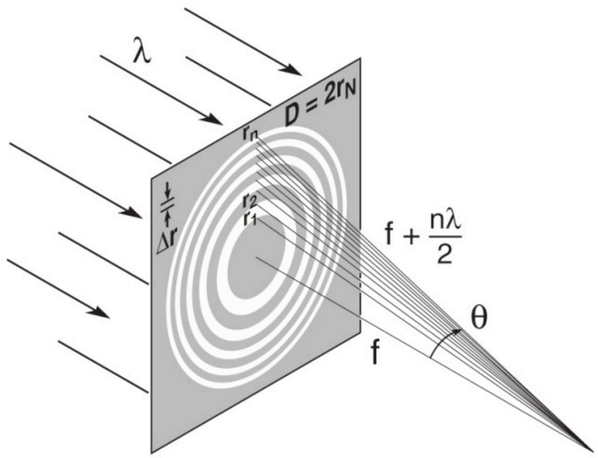


Ch09_F43VG.ai

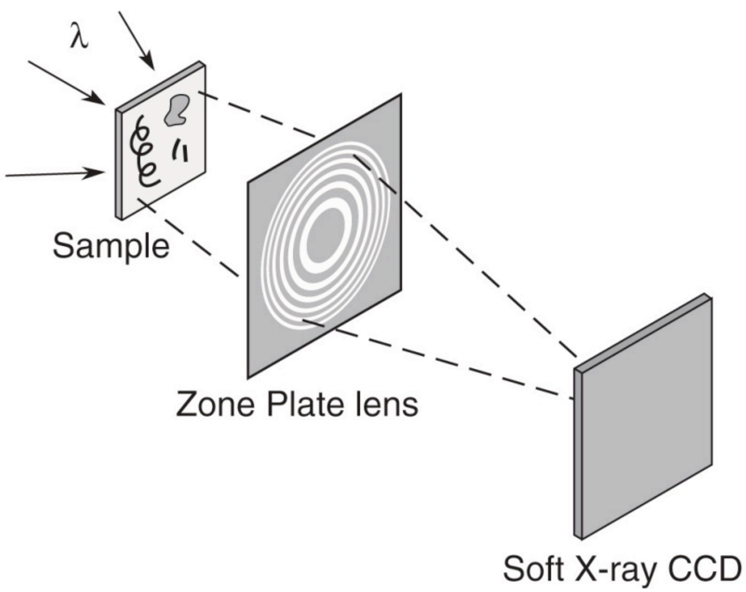
Courtesy of E. Anderson (LBNL)

Zone Plates for Soft X-Ray Image Formation

Zone Plate Lens



Soft X-Ray Microscope



Zone Plate Formulae

$$r_n^2 = n\lambda f + \frac{n^2\lambda^2}{4} \qquad (9.9) \qquad \lambda = 2.5\text{ nm},\ \Delta r = 25\text{ nm},\ N = 618$$

$$D = 4N\Delta r \qquad (9.13) \qquad 63\ \mu\text{m}$$

$$f = \frac{4N(\Delta r)^2}{\lambda} \qquad (9.14) \qquad 0.63\text{ mm}$$

$$NA = \frac{\lambda}{2\Delta r} \qquad (9.15) \qquad 0.05$$

$$\text{Res.} = k_1 \frac{\lambda}{\text{NA}} = 2k_1\Delta r \begin{cases} k_1 = 0.61\ (\sigma = 0) & 1.22\Delta r = 30\text{ nm} \\ k_1 = 0.4\ (\sigma = 0.45) & 0.8\Delta r = 19\text{ nm} \end{cases}$$

$$\text{DOF} = \pm\frac{1}{2}\frac{\lambda}{(\text{NA})^2} \qquad (9.50) \qquad 1\ \mu\text{m}$$

$$\frac{\Delta\lambda}{\lambda} \le \frac{1}{N} \qquad (9.52) \qquad 1/700$$

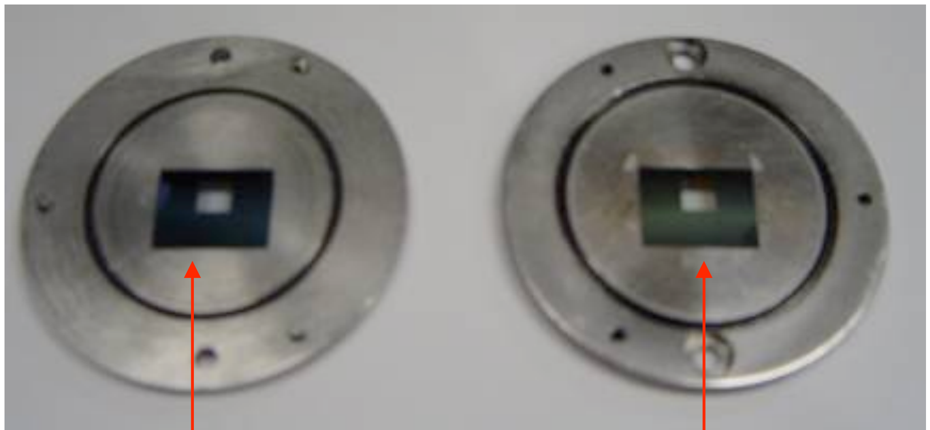
Cement Hydration

Experimental challenges:

- Samples must be studied wet
- Able to observe and record reactions in *real time*
- Identify areas of elemental concentrations
- High resolution
- No artifacts from drying or pressure change
- Characterization of internal structure

Sample Preparation and Positioning

<u>Restriction</u>: sample thickness (less than 10 μm)

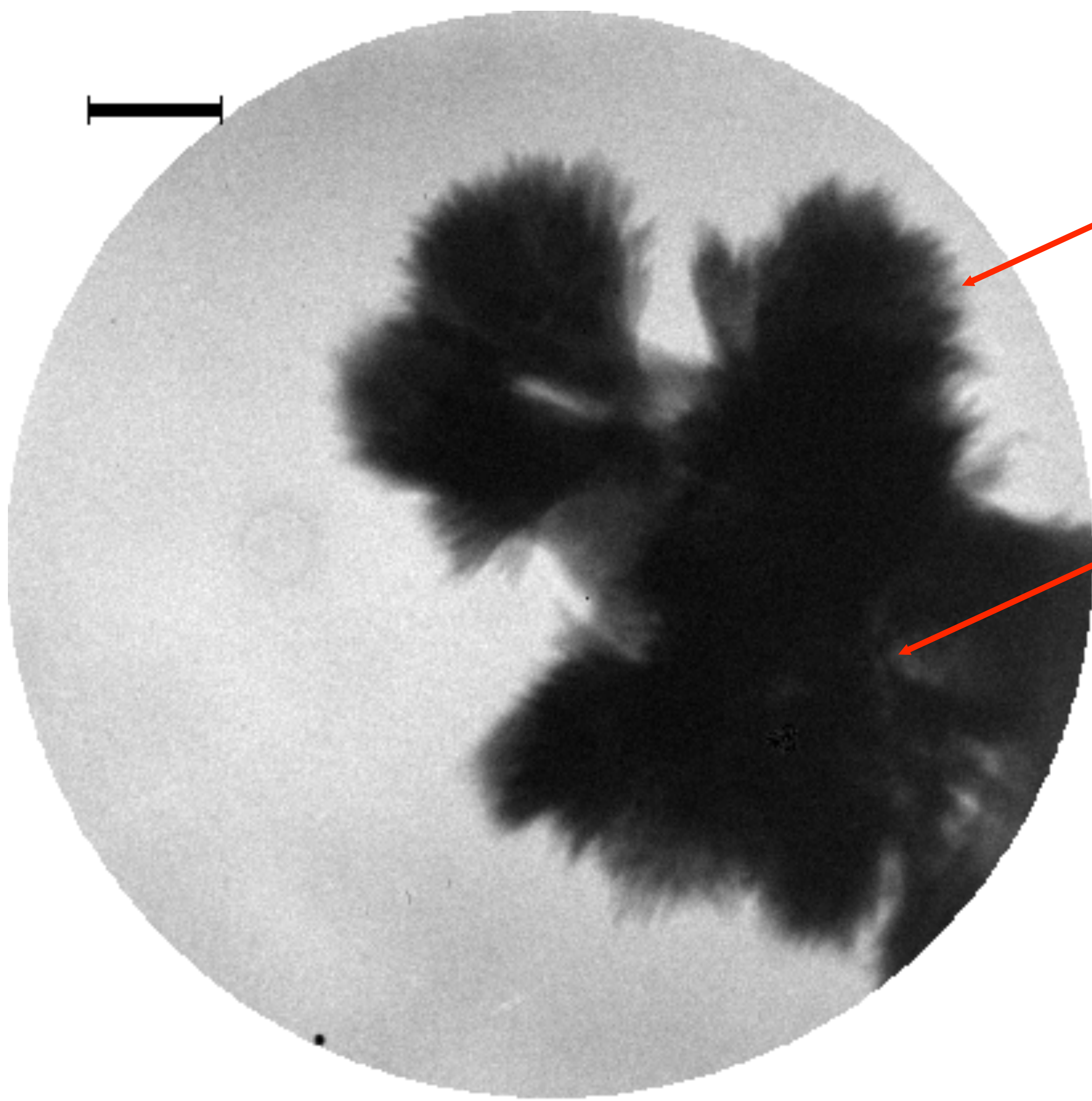


Silicon nitride windows

Highly diluted samples (water/cement is 5 before centrifugation)

Imaging as soon as 6 minutes after mixing

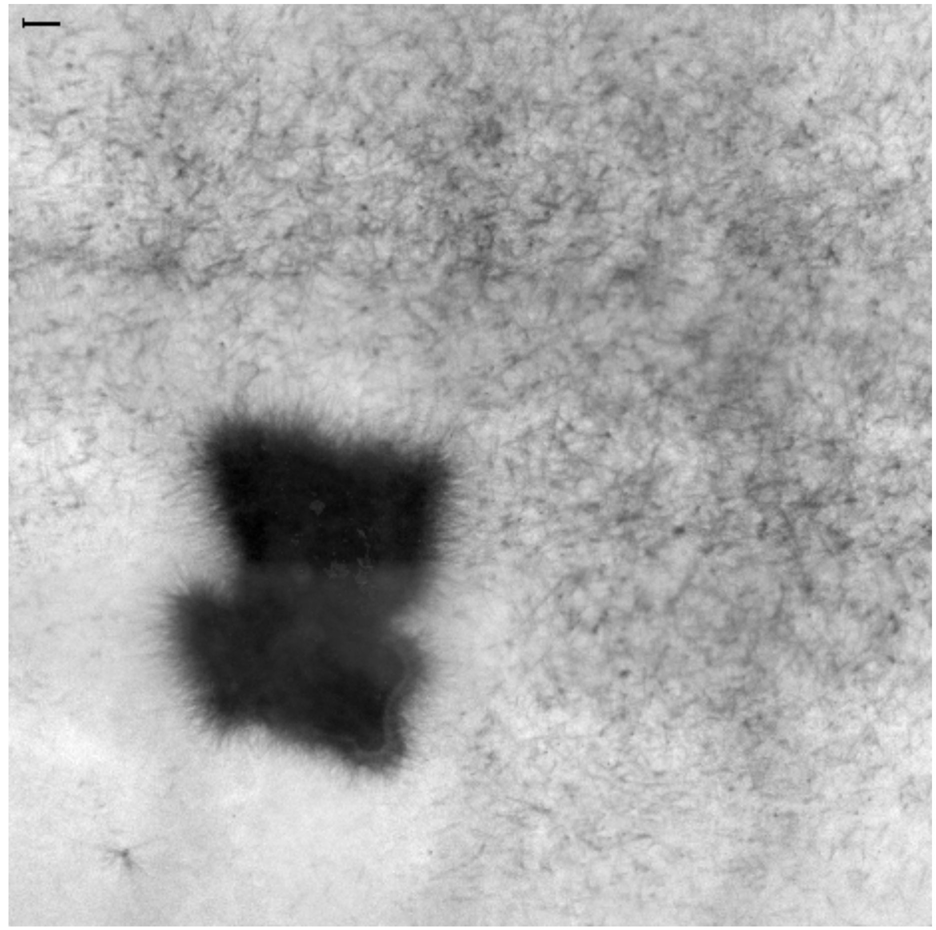
Early hydrates forming during the pre-induction period



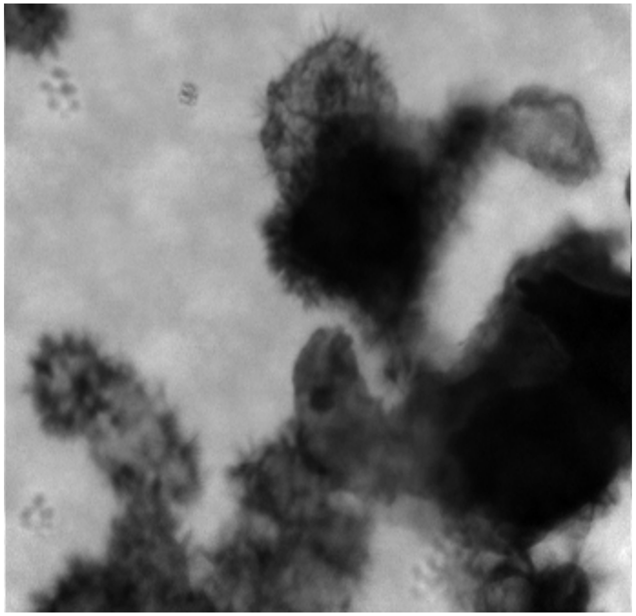
C3S hydrated for 34 min. in saturated lime and calcium sulfate at w/c=5, 1s exposure time, 516eV, scale bar 1μm.

In-situ Massive precipitation

8h 30min.

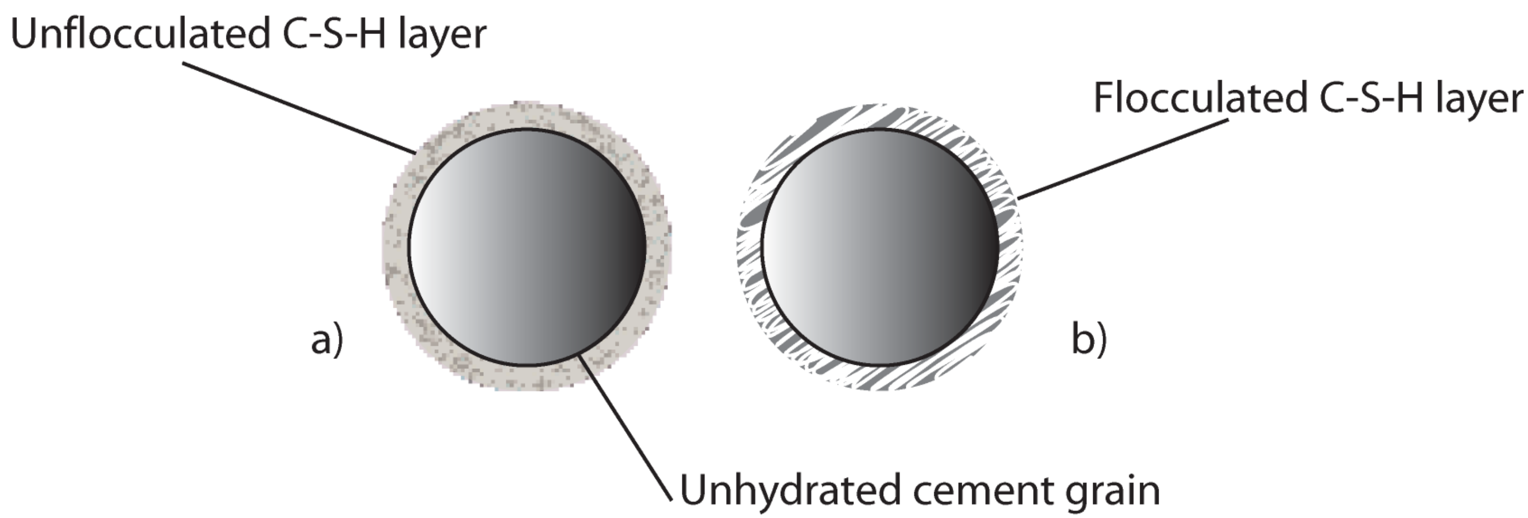


Admixtures: C_3S + Accelerators ($CaCl_2$)



M.C.G. Juenger, P.J.M. Monteiro, E.M. Gartner, G.P. Denbeaux, Cement and Concrete Research 25 (2005) 19-25.

The effectiveness of $CaCl_2$ may be connected to the ability of Ca^{2+} and Cl^- ions to flocculate hydrophilic colloids, leading to a permeable C-S-H shell and favoring Ca^{2+} leaching from inside the boundaries of the original grain.

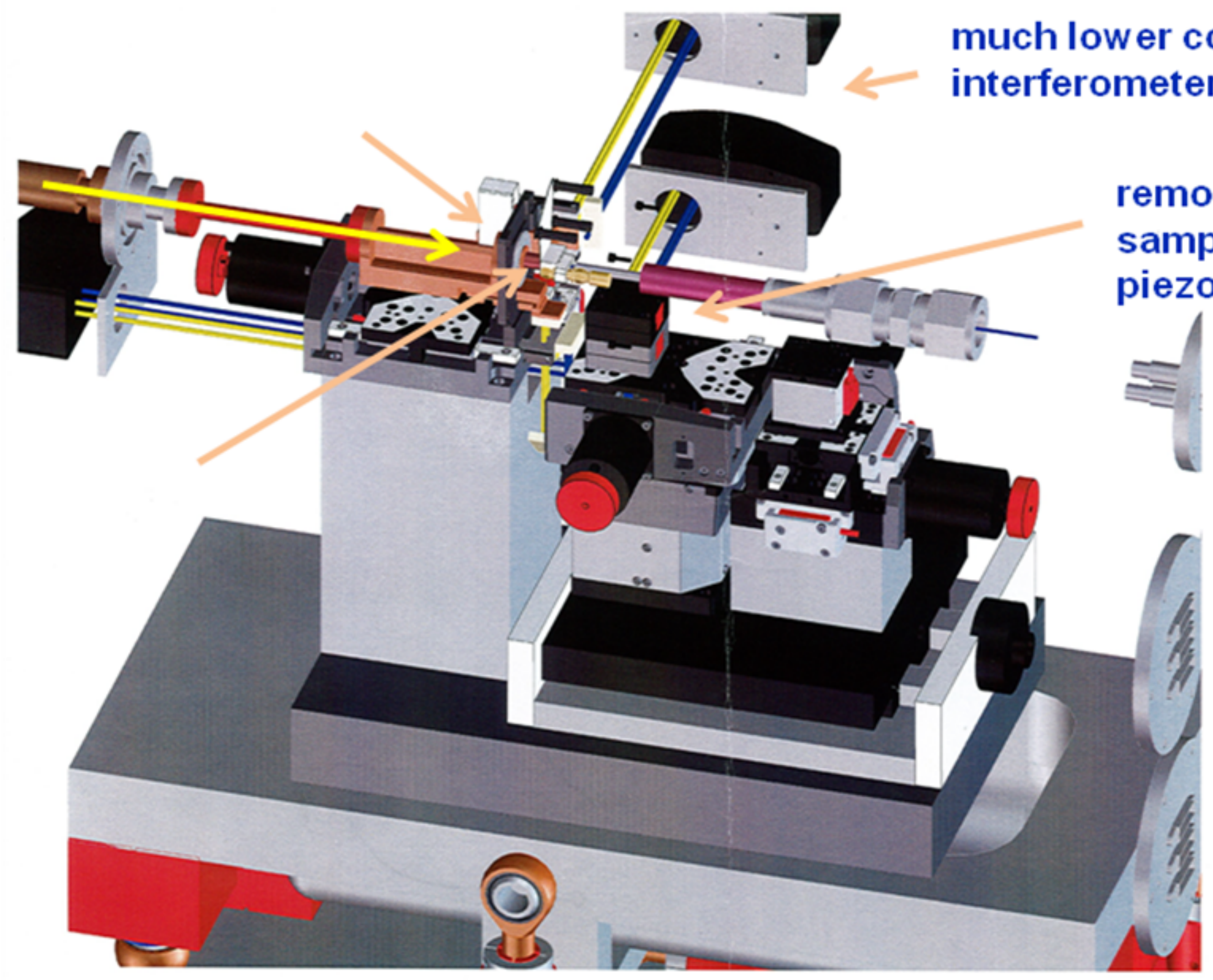


Two Limitations:

- No chemical information
- Two-dimensional images

Characterizing the chemical speciation at the nanolevel with x-ray spectromicroscopy (STXM)

New Microscope Design

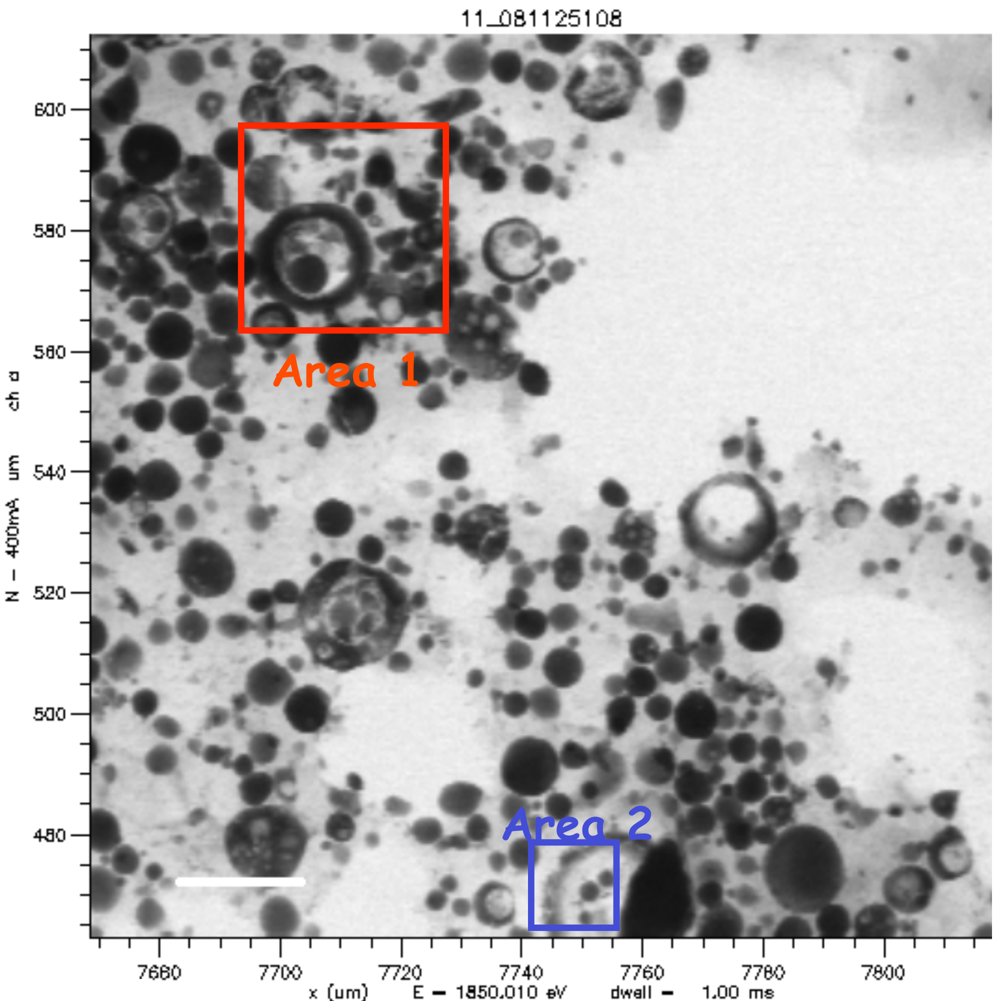


much lower cost for better interferometers, these days

removable sample-scan piezo-stack

Fly ash characterization - STXM

- Fly ash: important binder for geopolymers
  - Not much is known

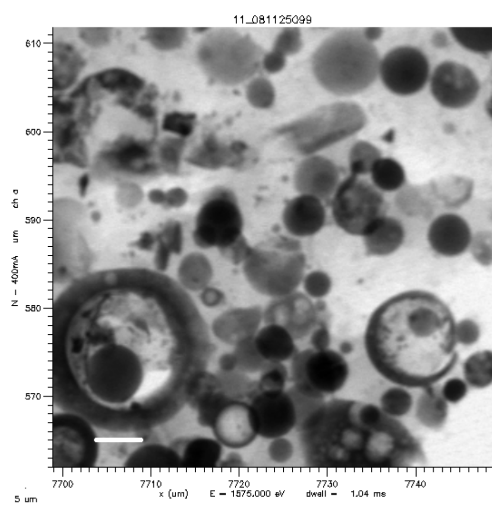


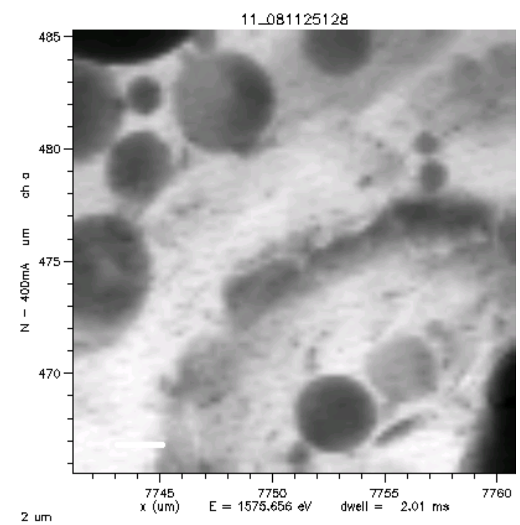
20 µm

- Fe L-edge
- Al K-edge
- Si K-edge

❖ Identify different phases

❖ Probe spatial correlation

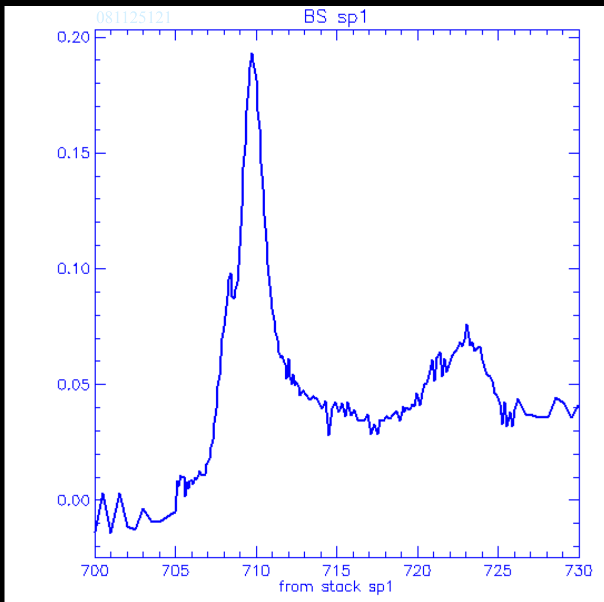




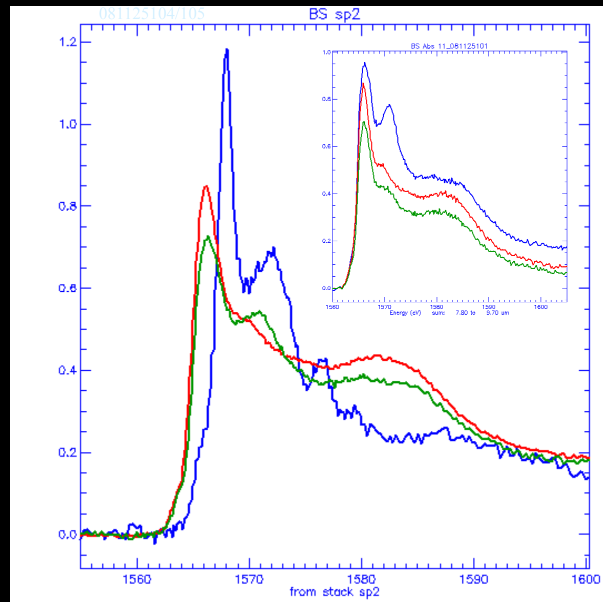
Area 1 Area 2

fly ash F

Fe L-edge

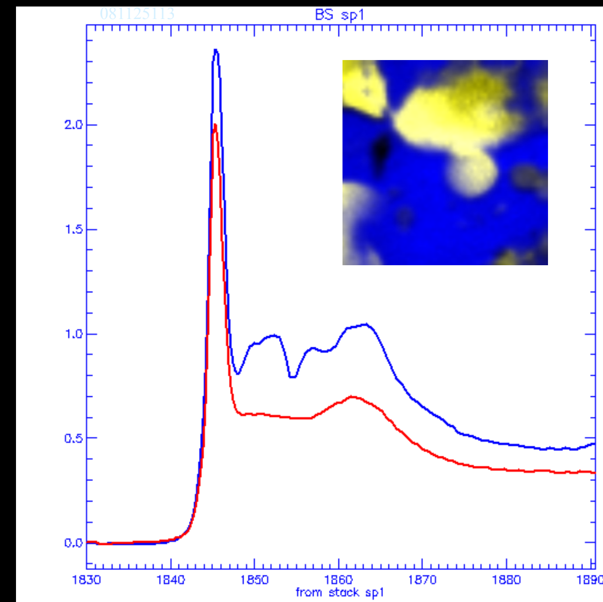


Al K-edge

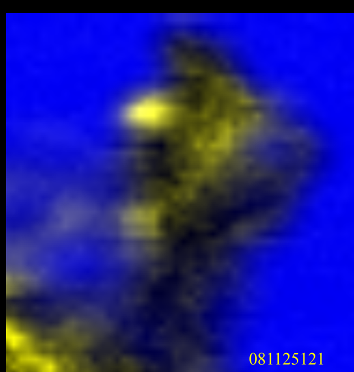


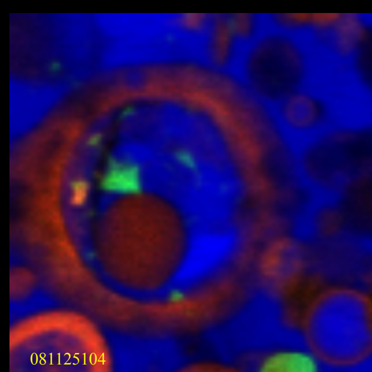
red – red curve 1566.38 eV
green – blue curve 1567.9 eV
blue – sample
green curve from other stack

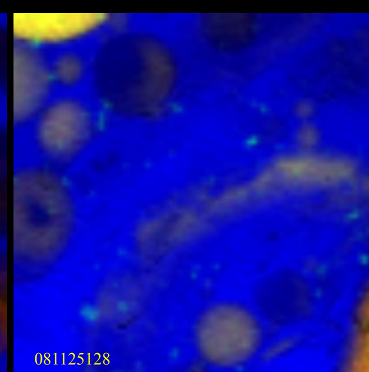
Si K-edge

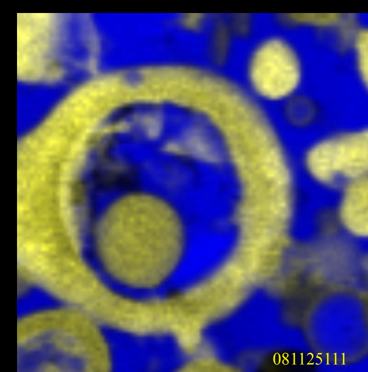


different Si spectra



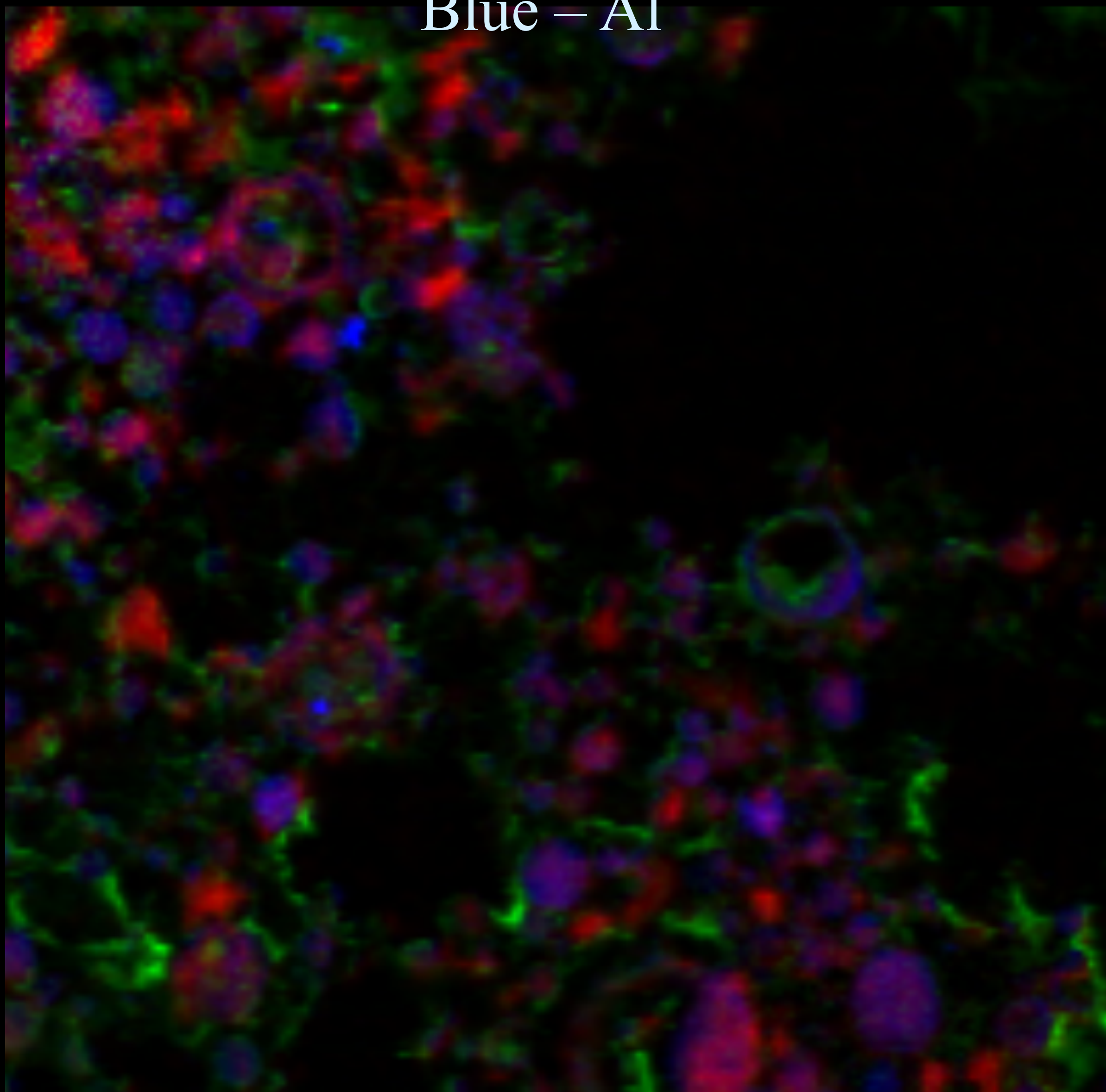


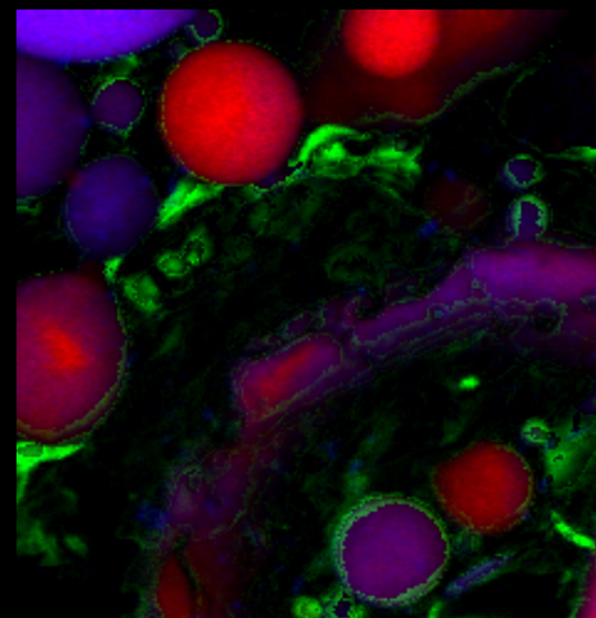




fly ash F

Red – Si
Green – Fe
Blue – Al





Red – Si
Green – Fe
Blue – Al

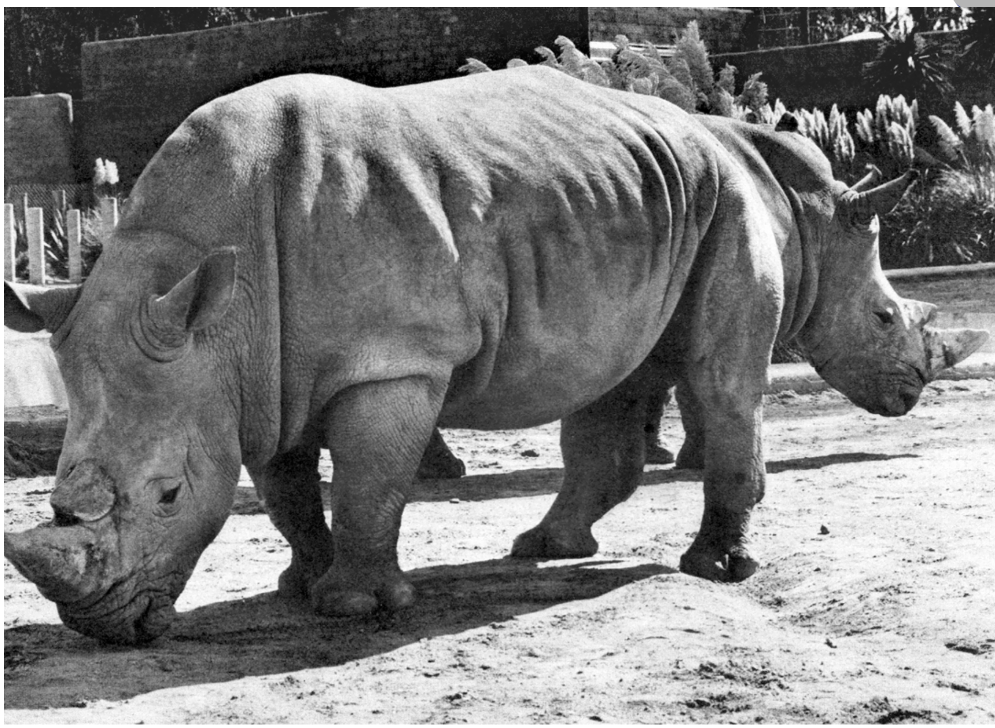
Two Limitations:

- ~~No chemical information~~
- Two-dimensional images

Use of X-rays for imaging

Wilhelm Conrad Roentgen
first Nobel prize in physics (1901)

Compressing 3-d information into a 2-d image



Development of tomography

Sir Godfrey N. Hounsfield

Allan M. Cormack

Nobel Prize in Physiology or Medicine 1979

Backprojection of Filtered Projections

$$f(x,y)=\int_0^{2\pi}\int_0^{\infty} e^{i2\pi(\omega_x x+\omega_y y)}F(\omega_x,\omega_y)\,d\omega_x d\omega_y$$

Inverse Fourier Transf.

First we do cartesian-to-polar coordinate transform:

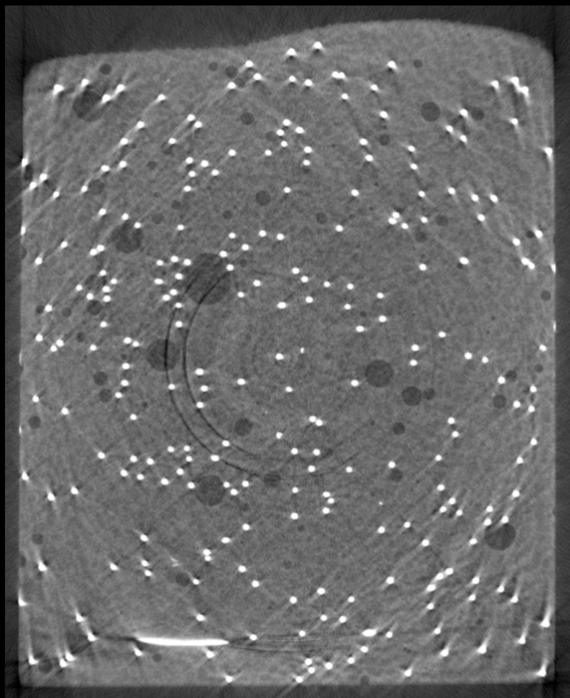
$$\omega_x=\omega_s\cos\theta,\omega_y=\omega_s\sin\theta \qquad d\omega_x d\omega_y=\omega_s d\omega_s d\theta$$

and we get:

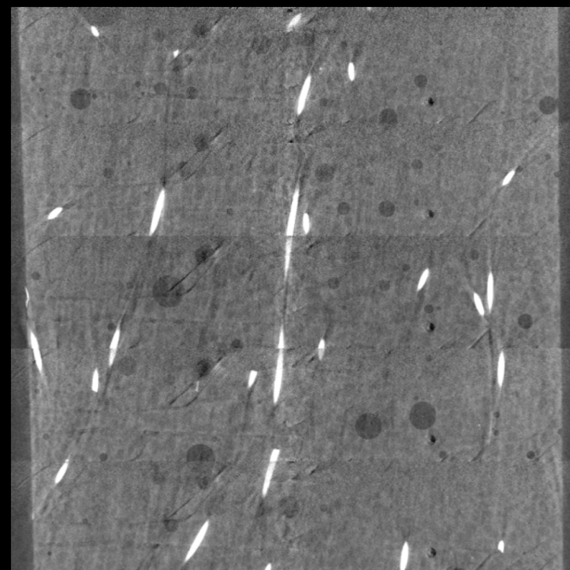
$$f(x,y)=\int_0^{2\pi}\int_0^{\infty} e^{i2\pi\omega_s(x\cos\theta+y\sin\theta)}F(\omega_s\cos\theta,\omega_s\sin\theta)\omega_s d\omega_s d\theta$$

$$=\int_0^{\pi}\int_{-\infty}^{\infty} e^{i2\pi\omega_s(x\cos\theta+y\sin\theta)}P(\omega_s,\theta)|\omega_s|\,d\omega_s d\theta$$

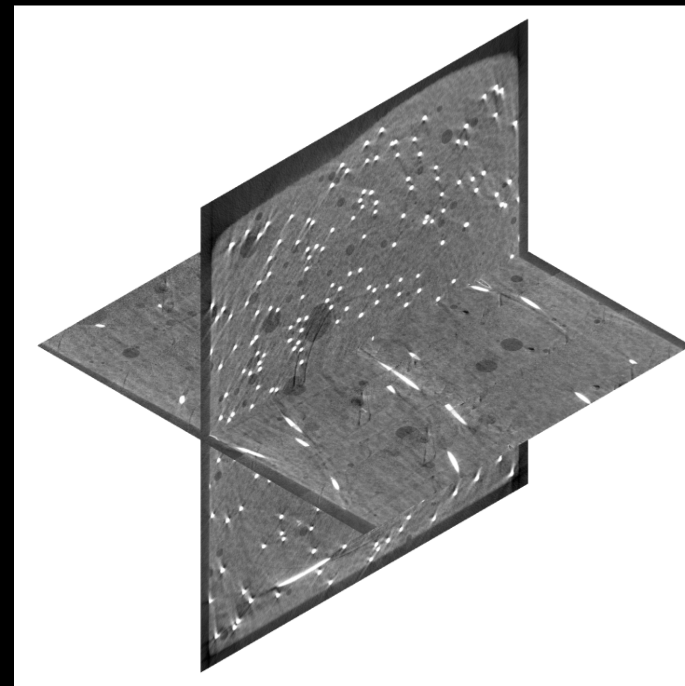
Synchrotron XCMT



xy plane tomogram



yz plane



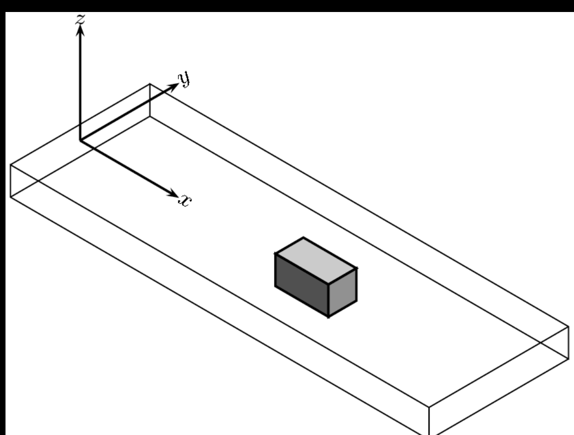


Image courtesy of S. Brisard

- Smaller sample size used (20 mm x 20 mm)
- Scanned volume (approximately 20mm x 20mm x 25 mm)
- White light absorption mode with filtered x-rays (E>30keV) using metal filters
- 11.55 x 2 = 23 μm/pixel resolution

Fiber isolation

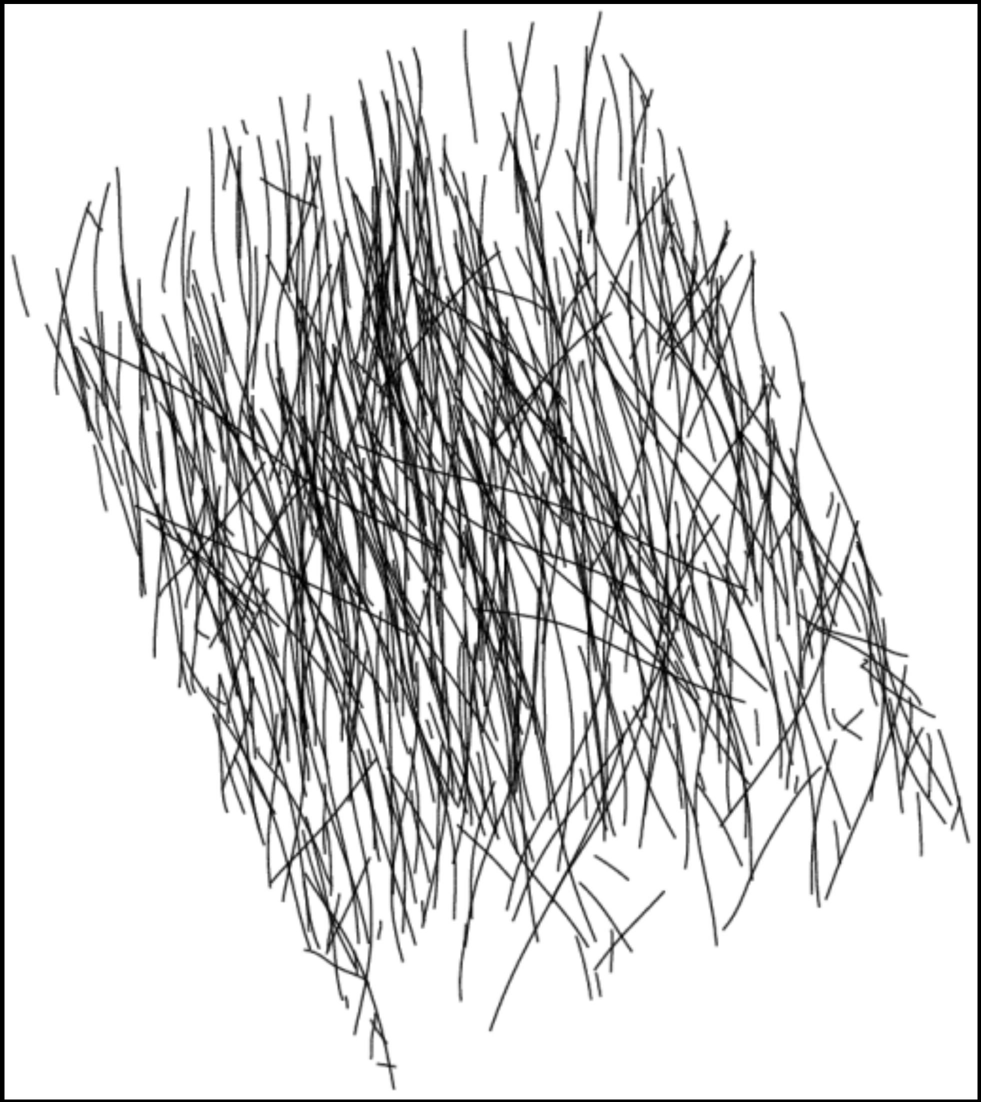


Image courtesy of S. Brisard

Nanotomography

- Life gets more challenging and exciting
- Goals: Obtain 3-d images with resolution of resolution of 20 nm or better

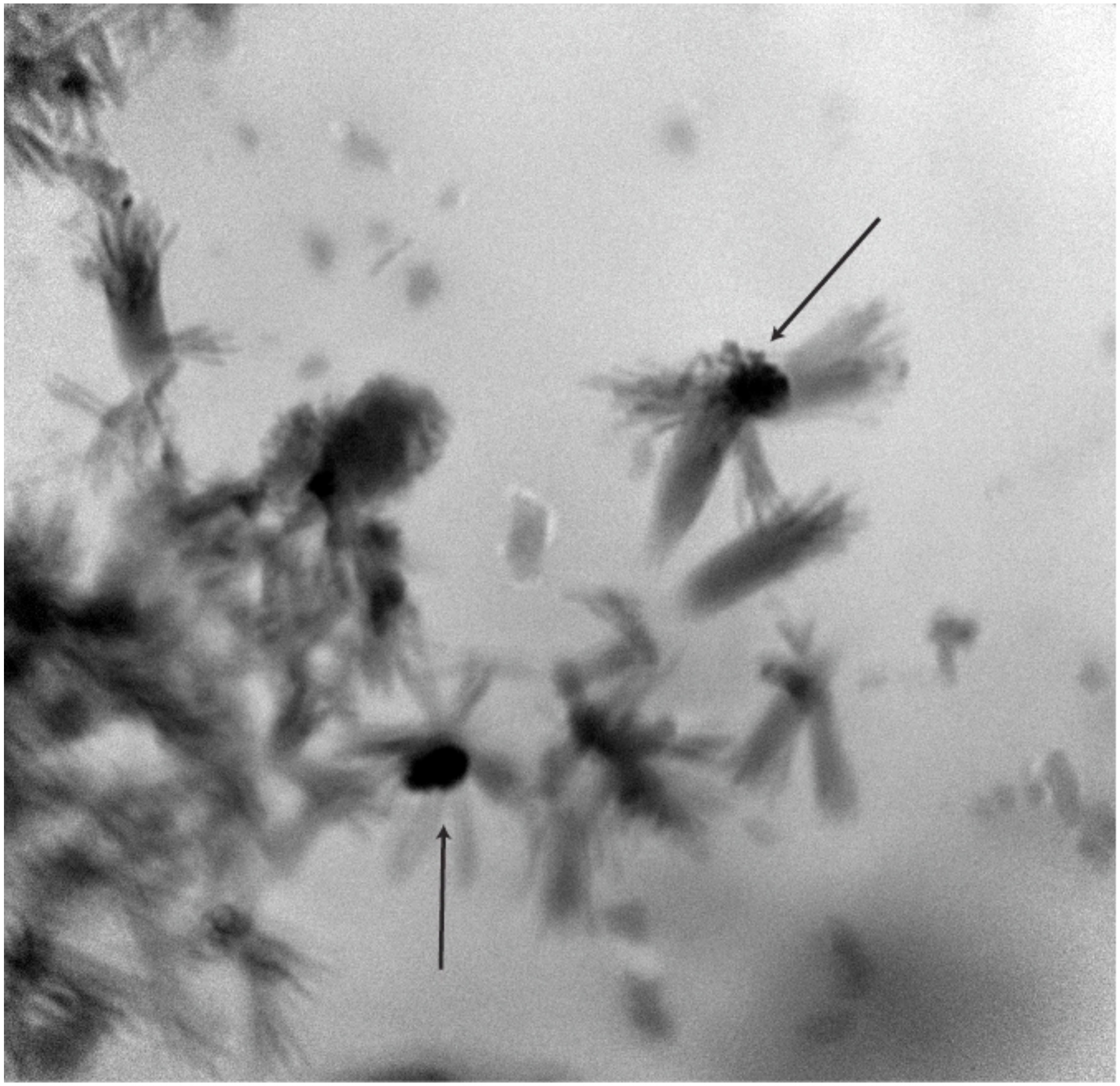
Major centers of excellence

- BESSY (soft x-rays)
- APS (hard x-rays)
- Stanford (hard x-rays)
- Berkeley (soft x-rays, under development with the KAUST project)

Challenges

- Alignment of the images
- Stability of the system
- Limited angle tomography when using flat sample holders

Why nanotomography?



Work at Bessy

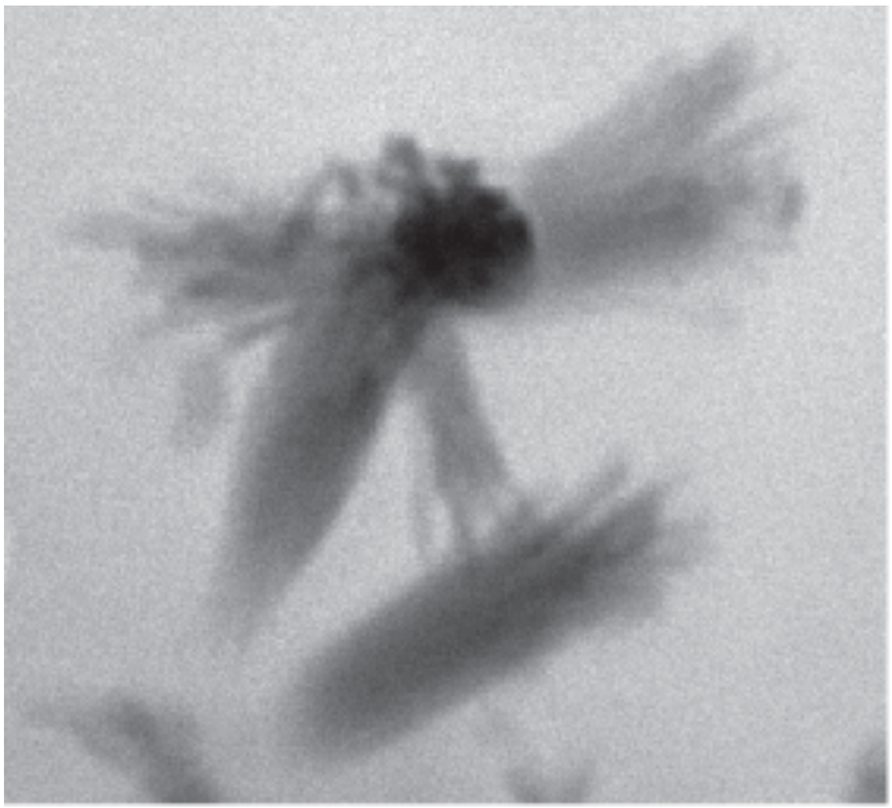
- This transmission image seems to show that the "sheet of wheat" (or "stars") have a core which acts as a nucleation point (see arrows)

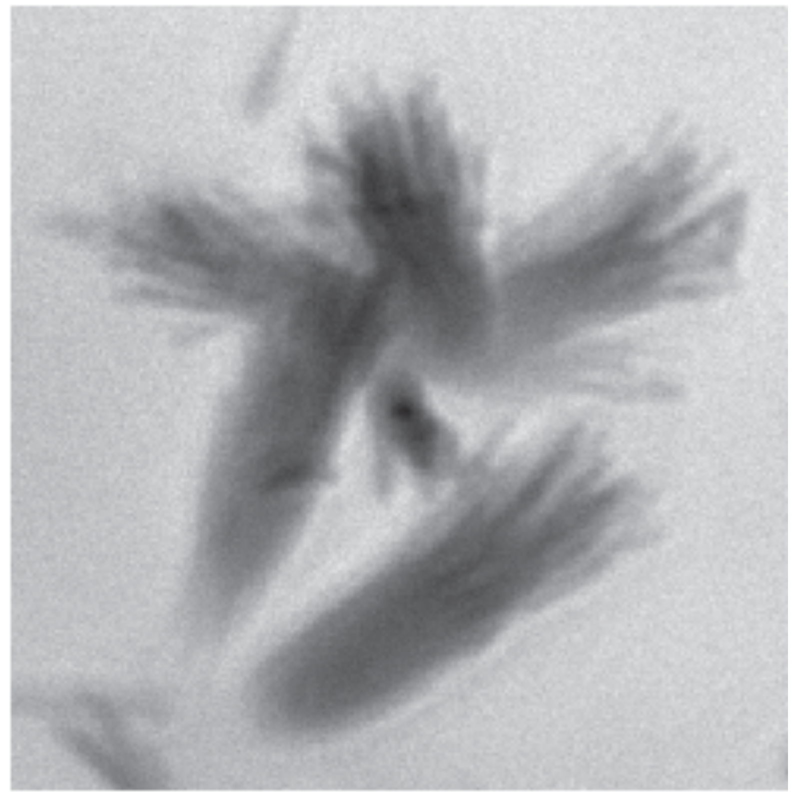
Work with Brisard, Levitz and Chae

Wrong assumption!

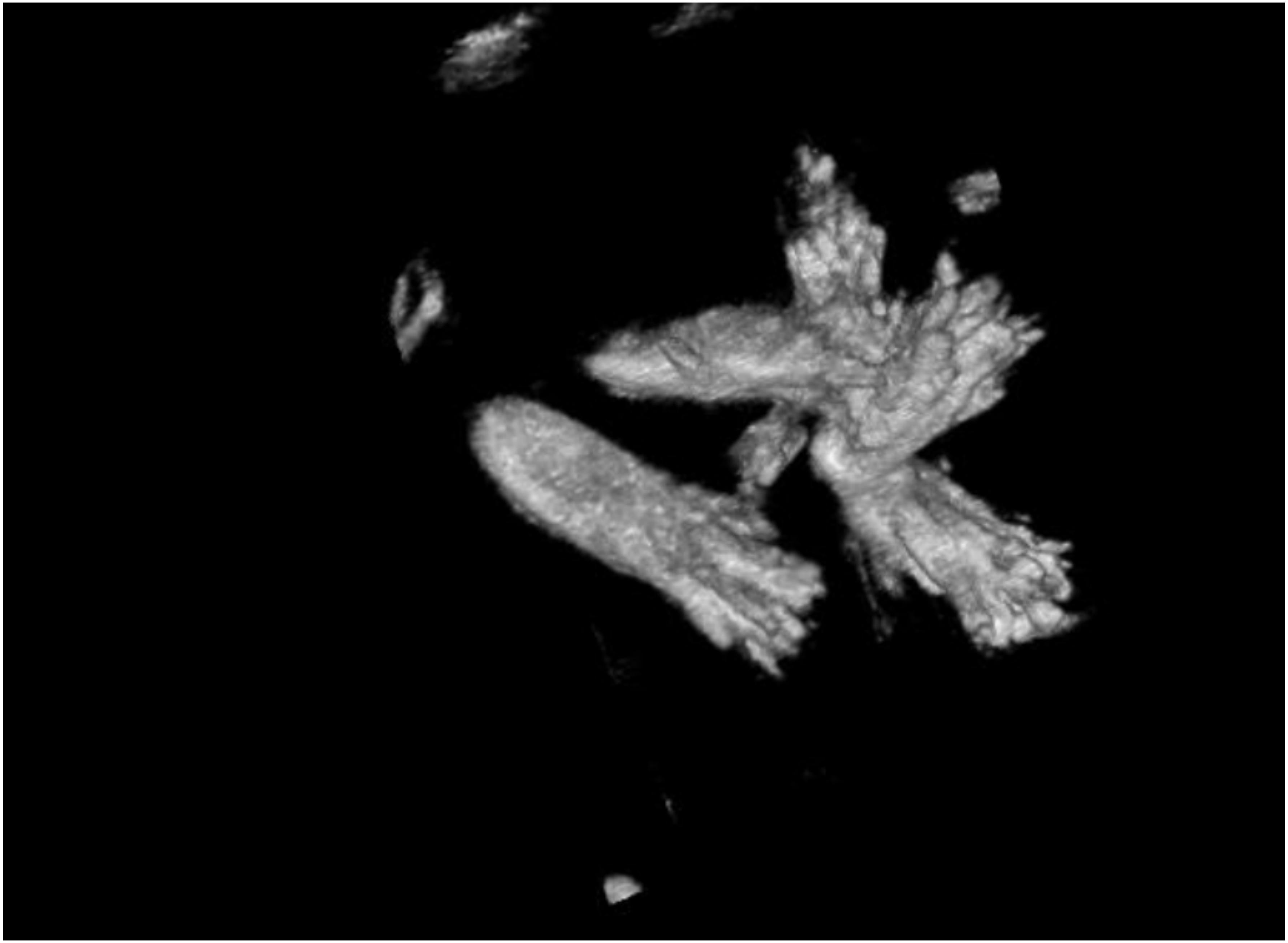
Work with Brisard, Levitz and Chae

Comparisons





Work with Brisard, Levitz and Chae



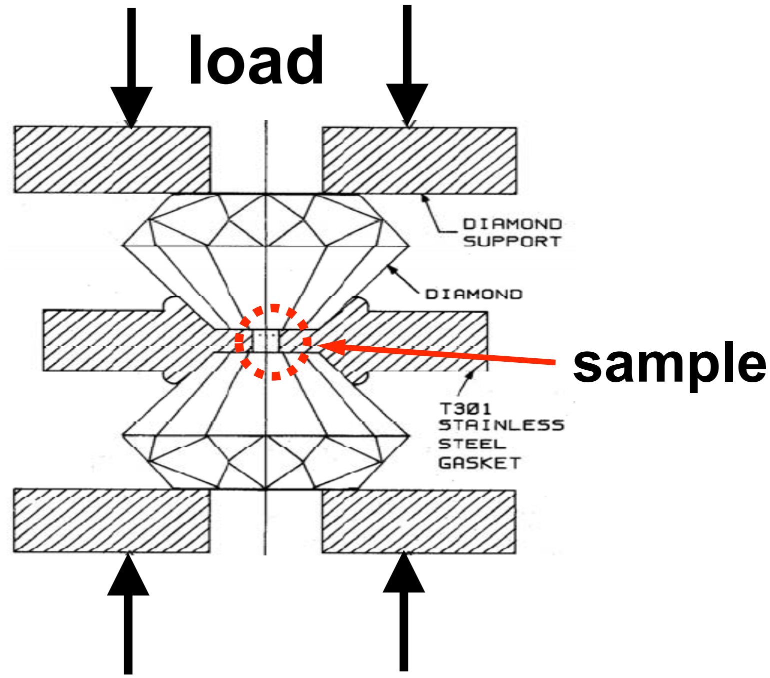
Work with Brisard, Levitz and Chae

Question:

- How can we measure the mechanical properties of very small crystals?

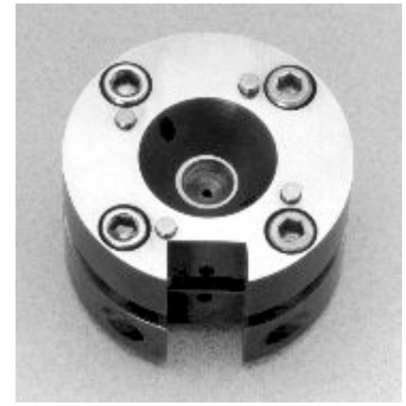
High Pressure X-ray Diffraction

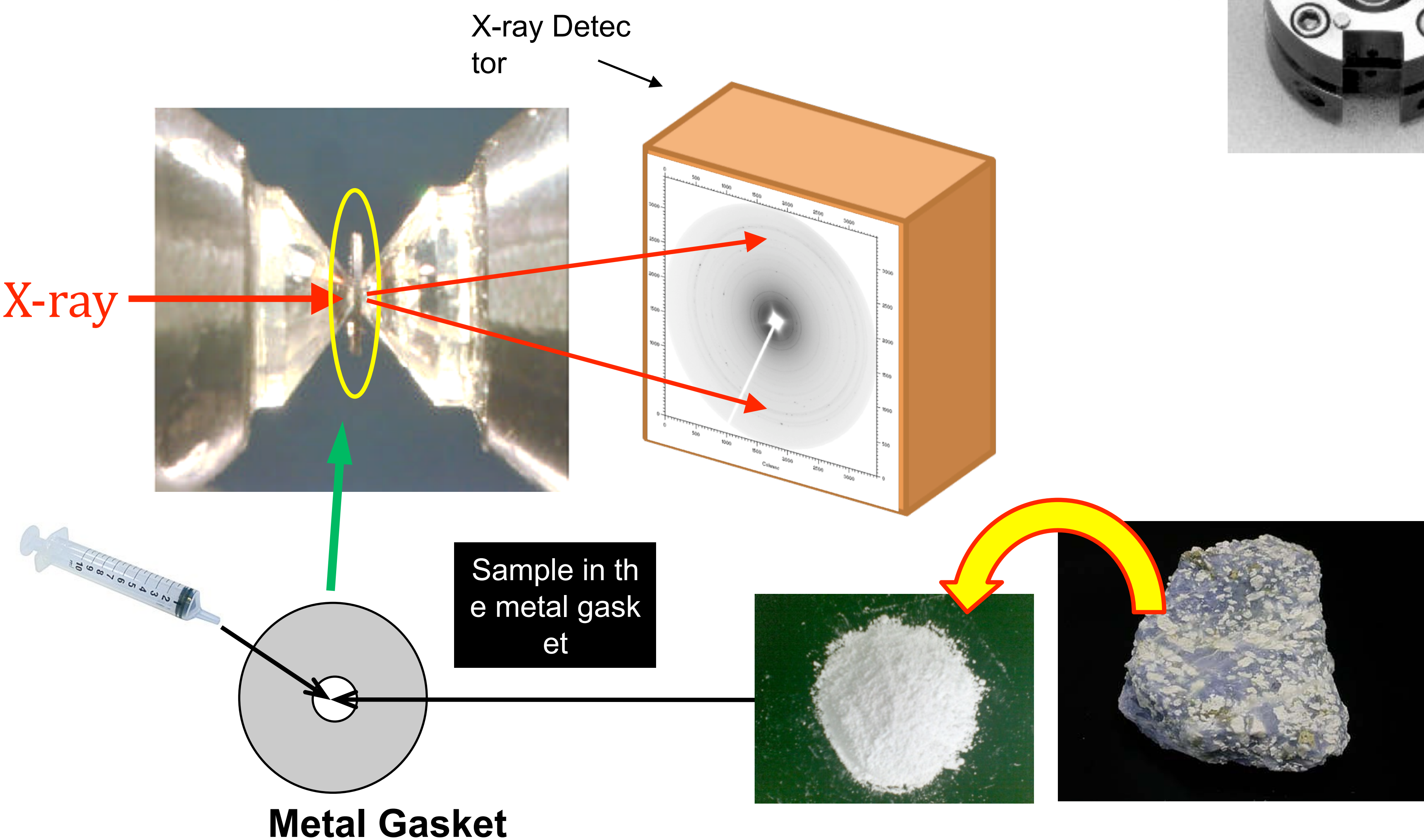
- Able to apply high pressure
- High pressure generating device:
  - Diamond Anvil Cell (Ko=~440GPa)
  - Theoretically, possible over 500GPa, but usually ~50GPa
  - Extremely small sample size
- Hydrostatic pressure Medium
  - 4:1 Methanol/Ethanol solution
  - Up to ~20GPa, nearly hydrostatic pressure
- Measurement of pressure inside of anvil cell: Ruby fluorescence technique



Schematic of Diamond Anvil Cell

DAC (Diamond Anvil Cell)





Experimental Procedures of XRD

- As the pressure increases, the unit cell shrinks.
- Unit cell dimensions (a, b, c, α, β, γ) at a certain pressure can be calculated from X-ray diffraction pattern
- $P(V/V_o)$ can be obtained
- Bulk modulus = $K_T = -V\frac{dP}{dV}$

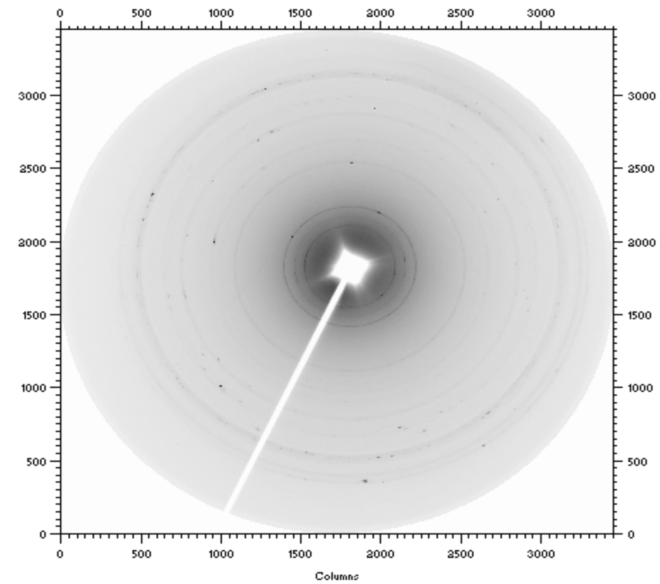
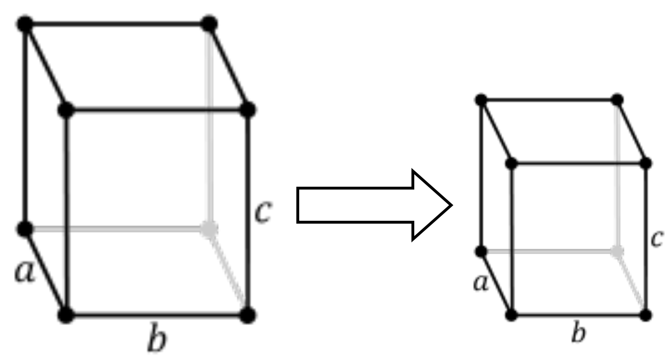
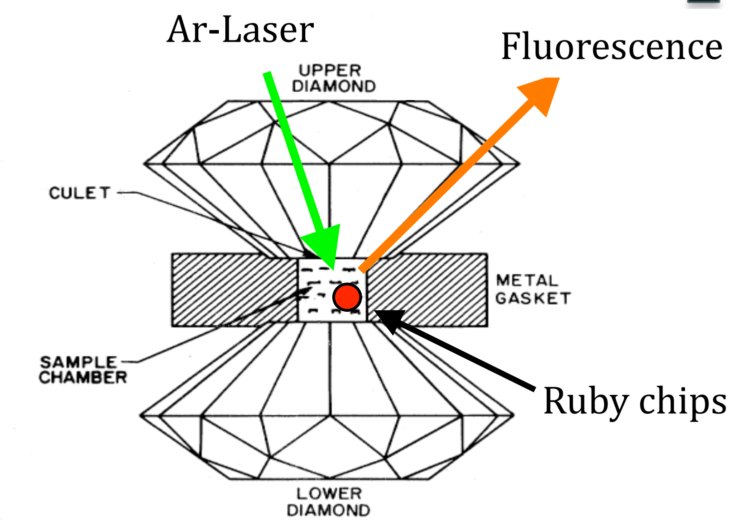


Figure. X-ray diffraction Pattern in beamline 12.2.2 (tobermorite)

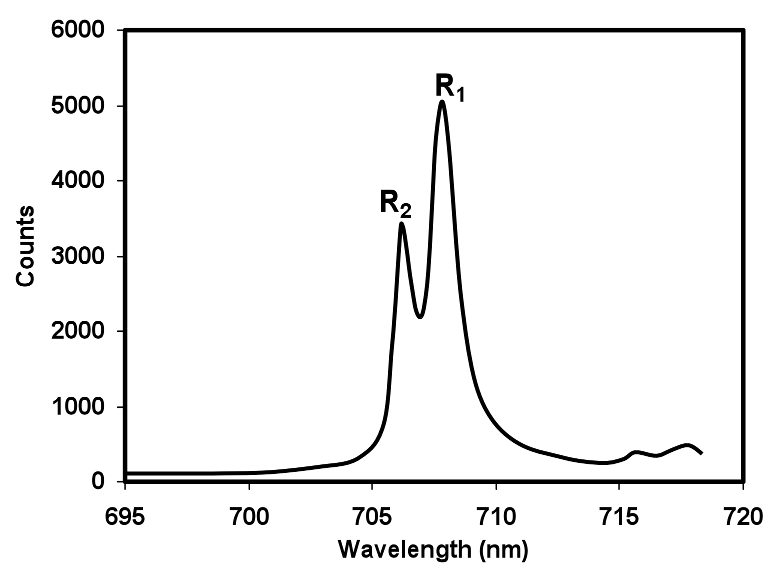


At low pressure **At high pressure**

Ruby Fluorescence Technique



- Pressure Measurement
- ~5-10μm ruby chips in sample chamber
- R_1 and R_2 peaks in spectrum ➔ shift with increasing pressure
  - Linear up to 30GPa
  - Available up to 200GPa



Birch Murnaghan Equation of State

- Equation of State (EOS): V = *f* (P,T)
- EOS of condensed material
  - Volume vs. Hydrostatic Pressure
  - Isothermal Equation
- **3rd order Birch Murnaghan EOS**

Simple Definition of BULK MODULUS

$$K = -V\frac{dP}{dV}$$

$$P = \frac{3}{2}K_o\left[(V/V_o)^{-\frac{7}{3}} - (V/V_o)^{-\frac{5}{3}}\right]\left[1+\frac{3}{4}(K_o'-4)\left((V/V_o)^{-\frac{2}{3}}-1\right)\right]$$

where,

1. Ko=bulk modulus at zero pressure
2. Ko'=the derivative of bulk modulus at zero pressure

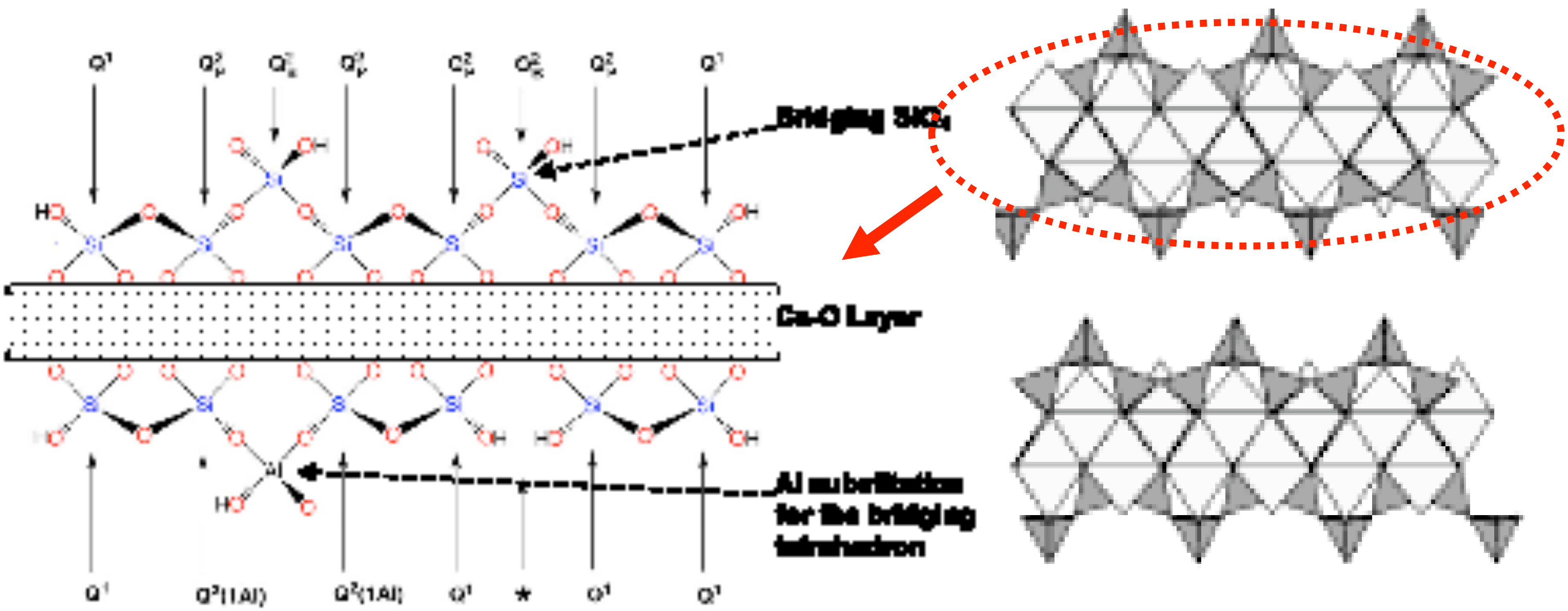
Nanoquestion:

Does the Al substitution change the mechanical behavior of CSH?

Alkali-activated Slag C-S-H (I) vs. synthetic C-S-H (I)

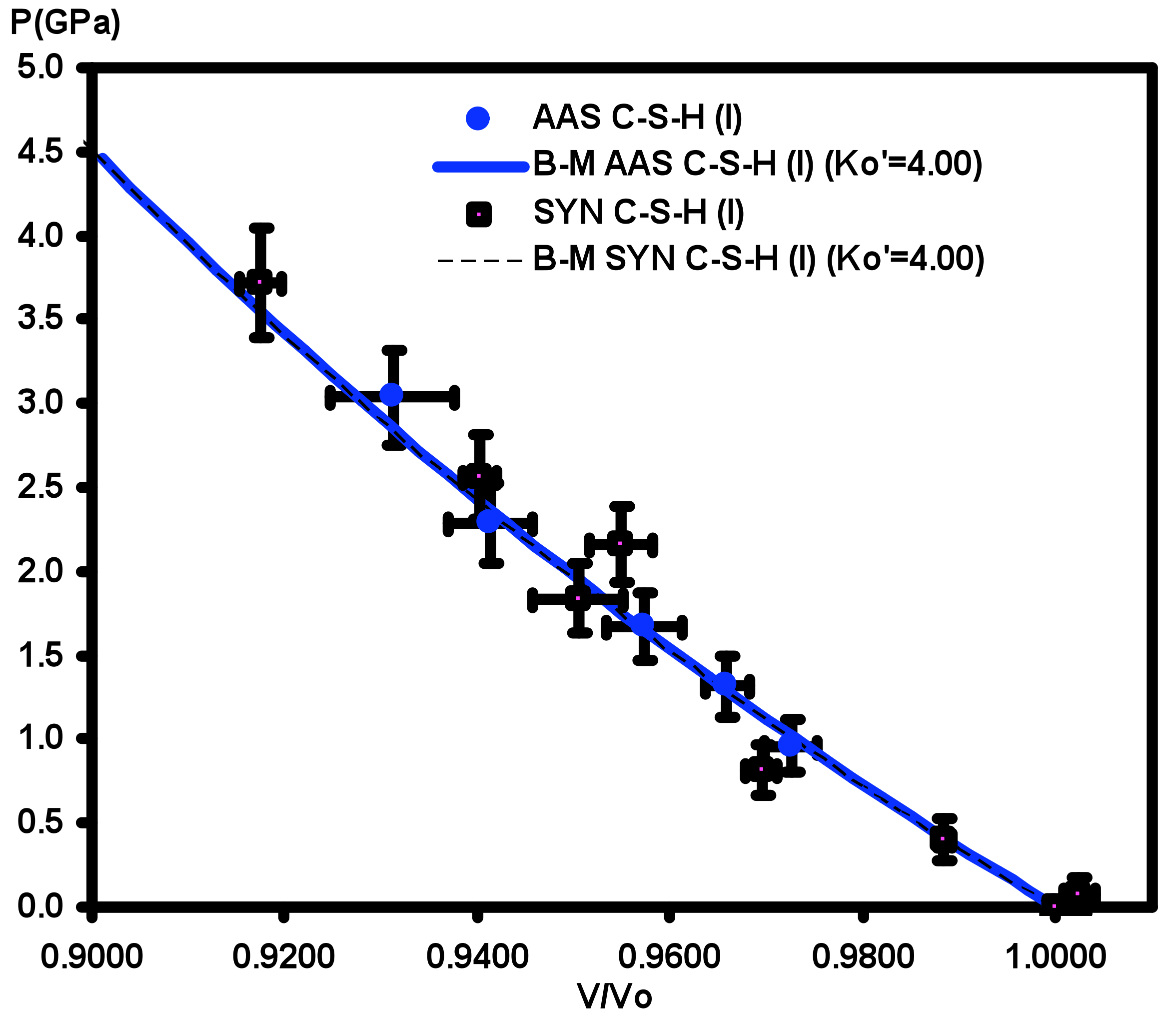
What's the structural difference betw een them?

- **Al substitution:**
  - The synthetic C-S-H (I) does not contain Al in its structure
  - The alkali-activated slag C-S-H (I) contains Al in i ts structure



Result

- There is no difference in bulk modulus due to



Results

- There is no difference in bulk modulus due to the Al substitution.

Class	Phase	bulk modulus K_o (GPa)	pressure derivative K'_o	R-squared value (R^2) of EOS to the data
C-S-H♪	SYN C-S-H (I)	**34.73 ± 4.98**	4.00 (assumed)	0.9722
	AAS C-S-H (I)	**34.70 ± 1.48**	4.00 (assumed)	0.9920

Summary

Exciting developments in x-ray microscopy are permitting to image highly complex chemical reactions. This can lead the way to development of sustainable construction materials.