X-ray microscopy
The Short Wavelength Region of the Electromagnetic Spectrum

- See smaller features
- Write smaller patterns
- Elemental and chemical sensitivity
A highly recommended book

David Attwood, Soft X-Rays and Extreme Ultraviolet Radiation: Principles and Applications
Cambridge University Press
Third Generation Synchrotron Facilities

- Bright radiation for spatially resolved studies
- Important coherence properties at very short wavelengths
Beamlines at the Advanced Light Source in Berkeley
X-ray Imaging

Undulator

Monochromator and refocusing optics

Pinhole

Zone plate lens

Sample

Raster scanned sample stage

FigI_Monteiro.ai
Two Common Soft X-Ray Microscopes

Full-Field Microscope
- Sample
- Zone Plate lens
- Soft X-ray CCD
- Best spatial resolution
- Modest spectral resolution
- Shortest exposure time
- Bending magnet radiation
- Higher radiation dose
- Flexible sample environment (wet, cryo, labeled magnetic fields, electric fields, cement, ...)

Scanning Microscope
- Aperture (OSA)
- Sample scanning stage
- Detector
- Least radiation dose
- Good spatial resolution
- Best spectral resolution
- Requires spatially coherent radiation
- Long exposure time
- Flexible sample environment
- Photoemission (restricted magnetic fields), fluorescence imaging

Courtesy from David Attwood
Zone Plates for Soft X-Ray Image Formation

Zone Plate Formulae

\[ r_n^2 = n\lambda f + \frac{n^2\lambda^2}{2} \]  \hspace{1cm} (9.9)

\[ D = 4N\Delta r \]  \hspace{1cm} (9.13)

\[ f = \frac{4N(\Delta r)^2}{\lambda} \]  \hspace{1cm} (9.14)

\[ NA = \frac{\lambda}{2\Delta r} \]  \hspace{1cm} (9.15)

\[ \text{Res.} = k_1 \frac{\lambda}{NA} = 2k_1\Delta r \]

\[ \begin{align*}
   \text{Res.} &= k_1 \frac{\lambda}{NA} = 2k_1\Delta r \\
   k_1 &= 0.61 \\
   (\sigma &= 0) \\
   k_1 &= 0.4 \\
   (\sigma &= 0.45)
\end{align*} \]

\[ \text{DOF} = \pm \frac{1}{2} \frac{\lambda}{(NA)^2} \]  \hspace{1cm} (9.50)

\[ \frac{\Delta \lambda}{\lambda} \leq \frac{1}{N} \]  \hspace{1cm} (9.52)

\[ \lambda = 2.5 \text{ nm,} \]  \hspace{1cm} \Delta r = 25 \text{ nm}

\[ N = 618 \]

\[ \lambda = 63 \text{ \mu m} \]

\[ 0.63 \text{ mm} \]

\[ 0.05 \]

\[ 1.22\Delta r = 30 \text{ nm} \]

\[ 0.8\Delta r = 19 \text{ nm} \]

\[ 1 \text{ \mu m} \]

\[ 1/700 \]

Courtesy from David Attwood
A Fresnel Zone Plate Lens Used for X-Ray Microscopy

Courtesy of E. Anderson (LBNL)
The Nanowriter: High Resolution Electron Beam Writing With High Placement Accuracy

- High brightness thermal field emission source and extraction electrodes
- Condenser lens, beam defining aperture and transfer lens
- Blanking plates and aperture

Deflection coils

Final electron focusing lens

50-100 keV electron beam focused to 3-10 nm spot size

Deflection electronics

Pattern generator

System control computer

Thin resist recording layer on a multilevel wafer

Wafer stage (stationary during exposure)

Courtesy of E. Anderson (LBNL)
Full View Soft X-Ray Microscope at the Advanced Light Source (ALS)

- High spatial resolution (20 nm)
- Modest spectral resolution ($E/\Delta E \sim 700$)
- Thick, hydrated samples (10 µm)
- Short exposure time (~1 second)
- Well engineered, pre-focused
- Mutually indexed visible and x-ray microscopes
- High throughput (hundreds of samples per day)
- Large image fields by tiling
- Easy access, user friendly
- Cryotomography

$E = 250 - 1.8$ keV
$\lambda = 0.7$ nm - 5 nm

Courtesy from David Attwood
Full-View X-ray Microscope

- ALS Bending Magnet
- Plane mirror
- Condenser zone plate
- Pinhole
- Microzone plate
- Sample stage
- Mutual Indexing System with kinematic mounts
- Visible light microscope
- Soft x-ray sensitive CCD
The Water Window for Biological X-Ray Microscopy

Absorption length ($\mu$m) vs. Photon energy (eV)

Typical protein:
- Carbon 52.5%
- Oxygen 22.5%
- Nitrogen 16.5%
- Hydrogen 7.0%
- Sulfur 1.5%

Courtesy from David Attwood
Sample Preparation and Positioning

**Restriction**: 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, under atmospheric pressure and room temperature
Sample Preparation and Positioning

Sample holder
Hydration of $\text{C}_3\text{S}$

- 33 min
- 49 min
- 1 h 10 min

$0.7 \mu\text{m}$
C$_3$S + 2% CaCl$_2$ (%wt C$_3$S)

Very few needle or fiberlike hydration products grow in the first minutes.

Some hydration products form outside of the original grain, bridging the space between grains.

An amorphous, less dense phase begins to form mostly within the boundaries of the original C$_3$S particle.

Discussion: $C_3S + 2\% \text{ CaCl}_2$

- The effectiveness of $\text{CaCl}_2$ as an accelerator may be connected to the ability of $\text{Ca}^{2+}$ and $\text{Cl}^-$ ions to flocculate hydrophilic colloids, leading to a permeable C-S-H shell and favouring $\text{Ca}^{2+}$ leaching from inside the boundaries of the original grain.

Cement + 0.1% sucrose (SS/c=50)

It takes around 1 hour for the first hydrated crystals to grow on the surface of the cement particles.

Inner and outer products are formed. Inner C-S-H results from the leaching process of calcium.

“delayed accelerator” as shown by the rapid growth of inner products

Cement + 0.1% lignosulfonate (SS/c=50)

- Thin C-S-H fibers covers the cement particles after almost 3 hours.
- Rapid growth of inner products is not seen.

Cement + 0.1% gluconate (SS/c=50)

- C-S-H fibers are absent.
- Rapid growth of globular hydrated products from the solution and on the surface of the cement grains.
- The apparent volume of solids increases over time.
- Changes to the nano-structure of C-S-H?

The following slides are from a joint work with Dr. Denise Silva


C₃S + 2% EVA (%wt SS)

Scale bar is 0.7 µm
$\text{C}_3\text{A} + 2\% \text{ EVA (\%wt SS)}$

Scale bar is 0.7 $\mu$m
Cellulose ether
C₃S + 0.2% HPMC (%wt SS)

C₃S + HPMC

PURE C₃S

Scale bar is 0.7 µm
$C_3S$ and $C_3A + 0.3\%$ Welan gum

$C_3S + \text{WG}$
- 8 min
- 1 h 10 min
- 2 h 45 min

$C_3A + \text{WG}$
- 35 min
- 1 h 17 min
- 2 h 17 min

Scale bar is 0.7 $\mu$m
Siloxane surface modified nano-SiO₂ for cements

In-situ imaging