Applications of *in-situ* X-ray Scattering Techniques

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SSRL Scattering Workshop

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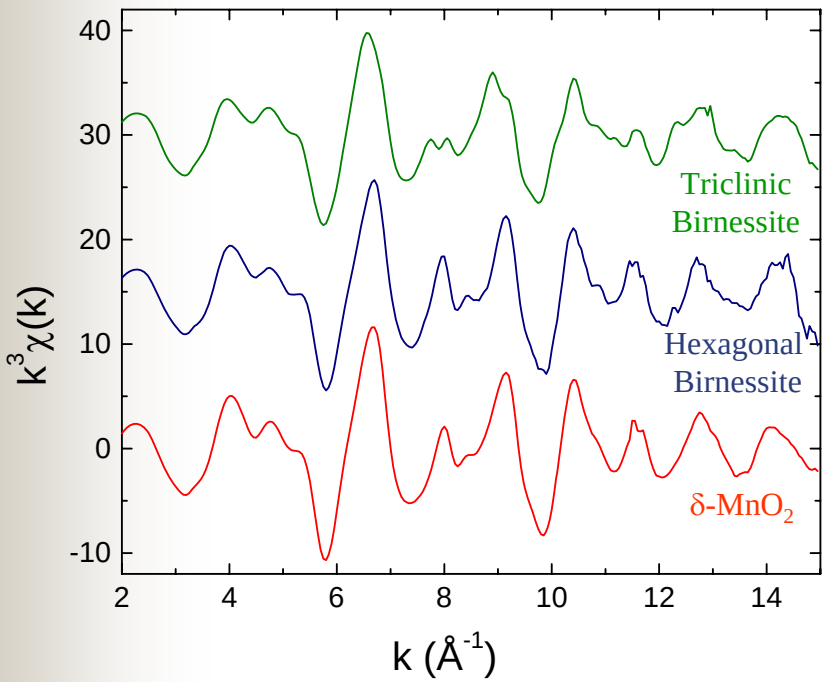
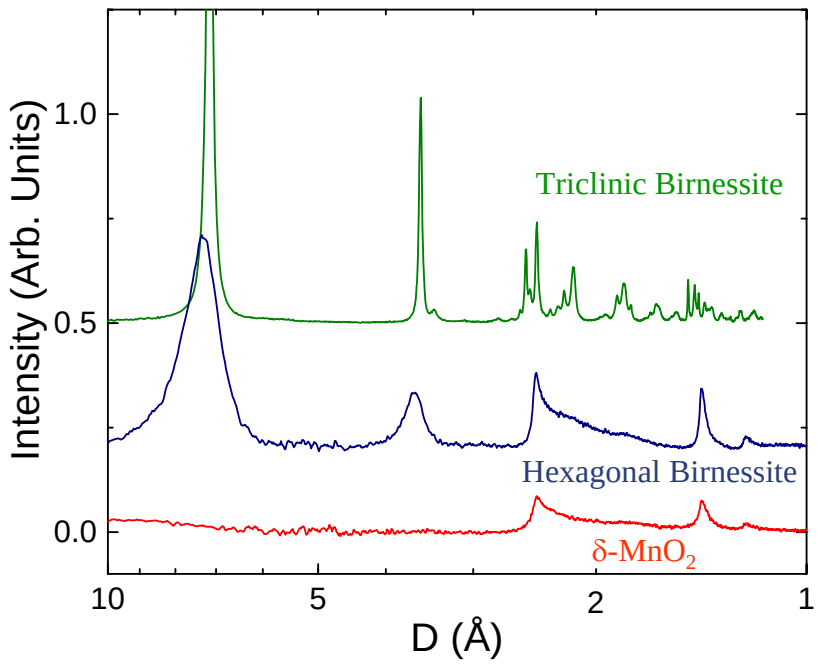
Overview

- Why in situ?
- Experimental Design
  - Beamlines
  - Sample prep
  - Analysis
- Reactions with x-ray scattering
- Example(s)

Why Should I Do Scattering When I Have EXAFS Data?





EXAFS = *Local Structure*
WAXS = *Long-Range Structure*

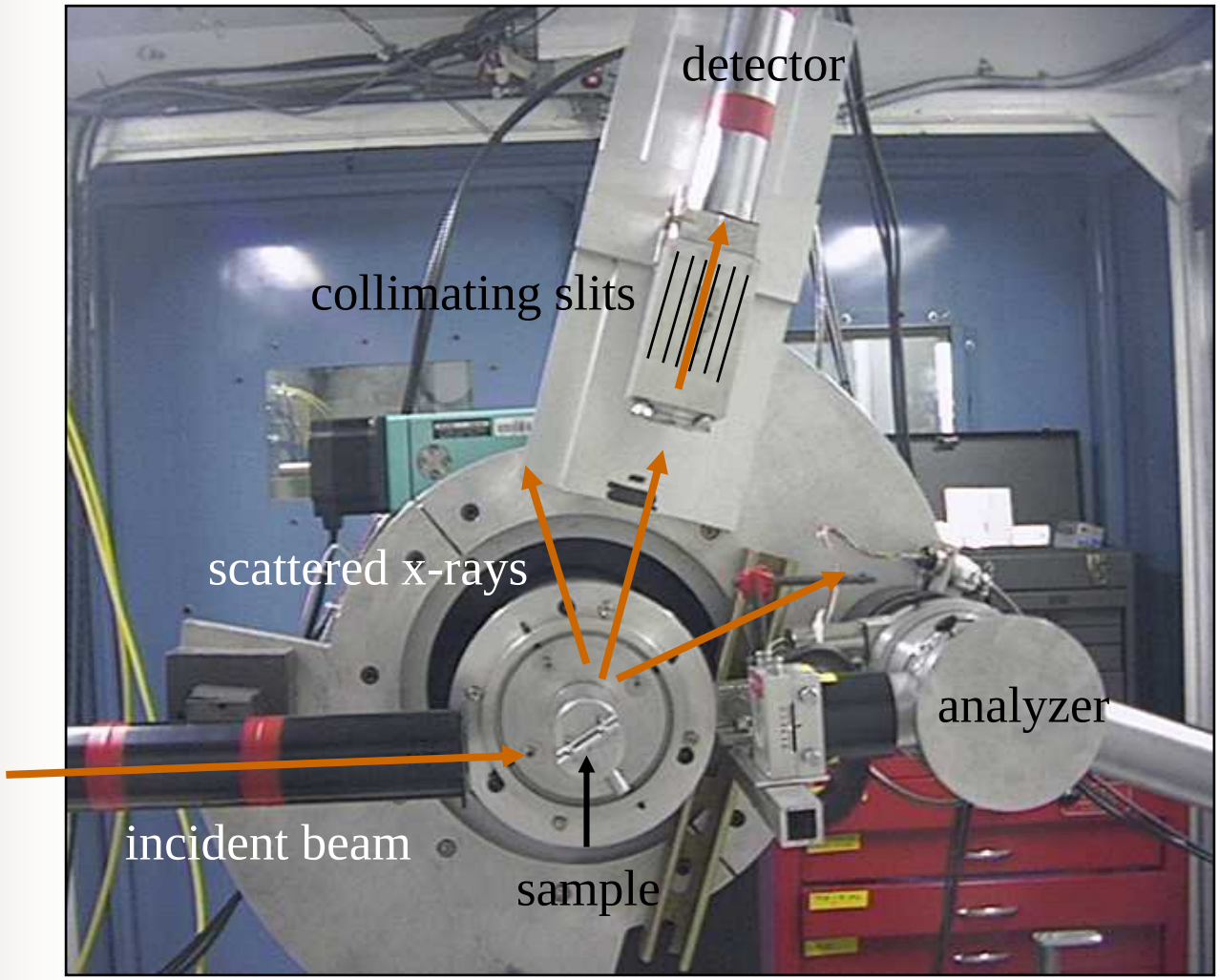
Why In-situ

- Traditional powder diffraction experiments require dry, fine powders as samples
- For many biological and environmental samples:
  - Drying = artifact
    - Dehydration, exposure to air
  - Powder = artifact
- Other thoughts to consider…
  - Sample throughput
  - Sample textures
  - Timing/Reactions

Experimental Design

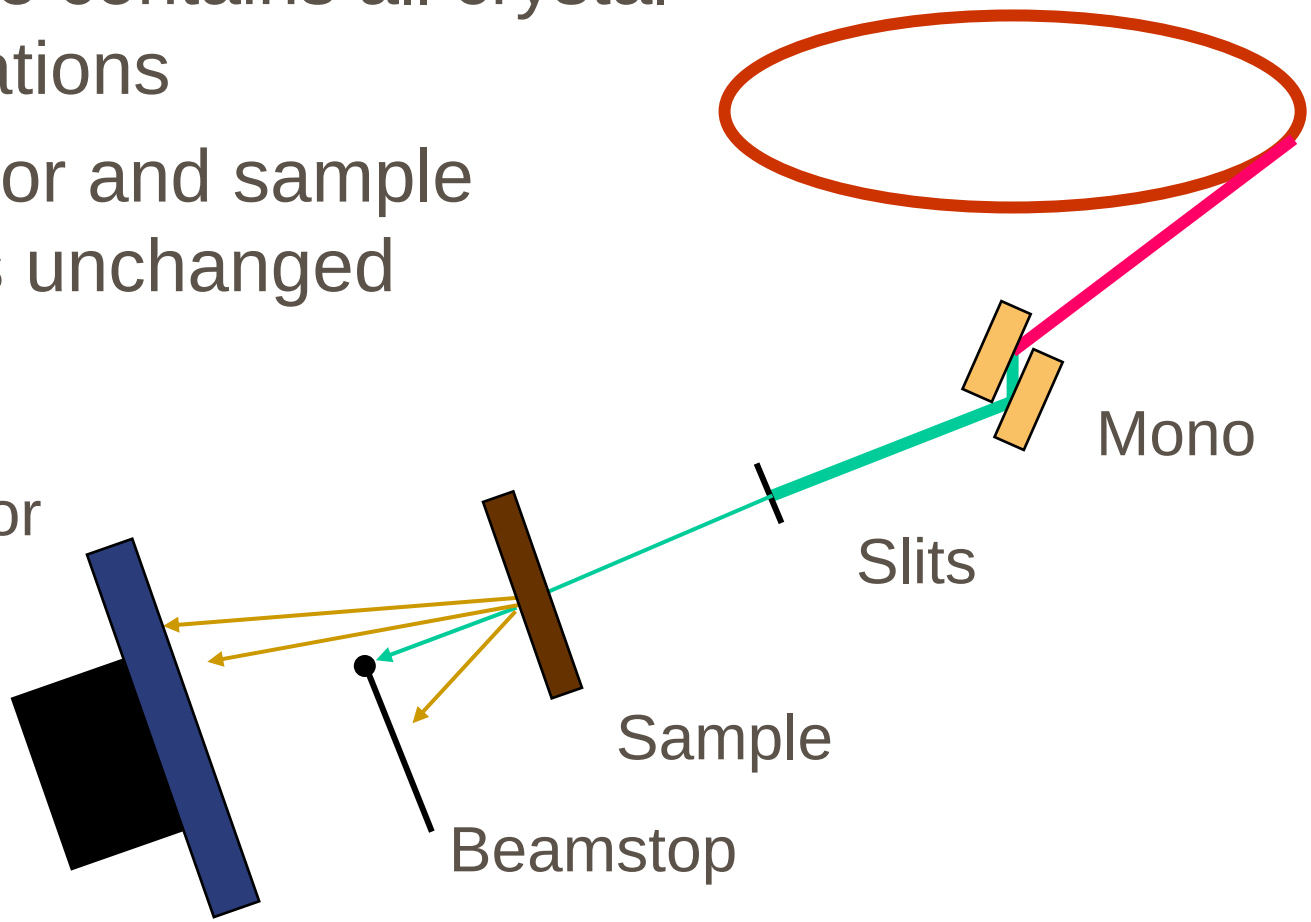
- Does my sample need to be wet?
  - Transmission vs. reflection
  - Tradeoffs due to backgrounds of sample holder and water
- High resolution vs. low
  - Soller slits vs. analyzer vs. area detector
- Data range
- Exposure to beam?
- Exposure to air?

Diffractometer (SSRL BL 2-1)

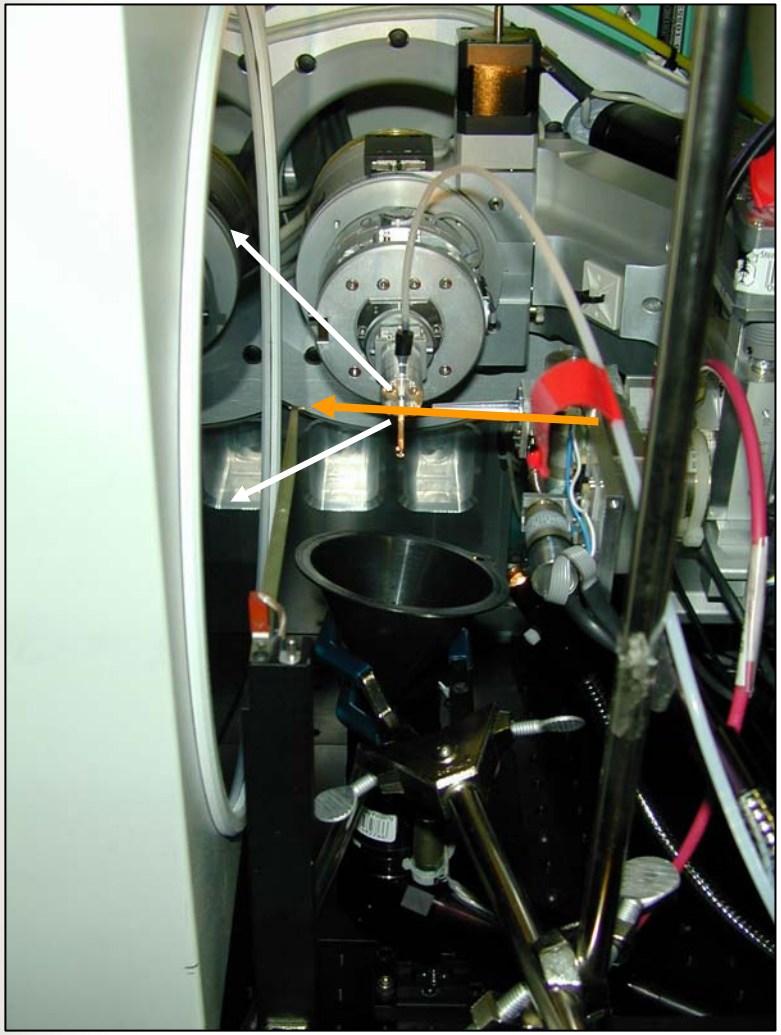


Powder Scattering Experiment

- Monochromatic
- Sample contains all crystal orientations
- Detector and sample angles unchanged

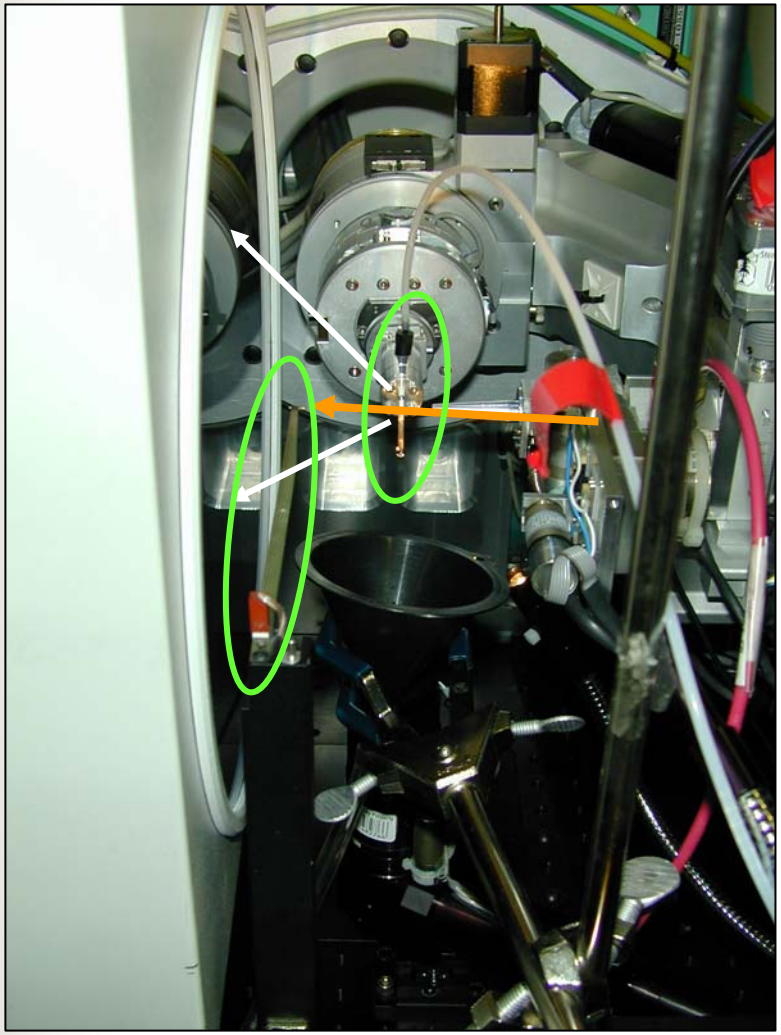


Diffractometer (SSRL 11-3)



- Tight spaces in hutch
- Samples:
  - Flat plate transmission
  - Reflection (half of area detector)
  - Capillary
- BL software (Blu-Ice)
- 5-10 MB per picture

Diffractometer (SSRL 11-3)



- Tight spaces in hutch
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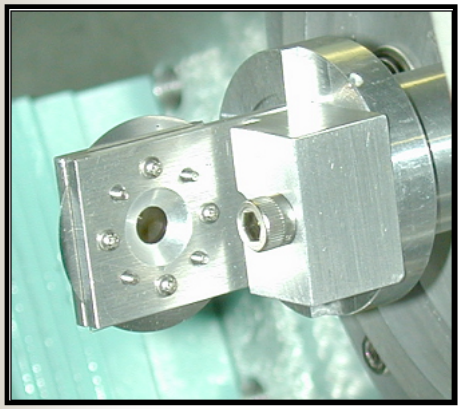
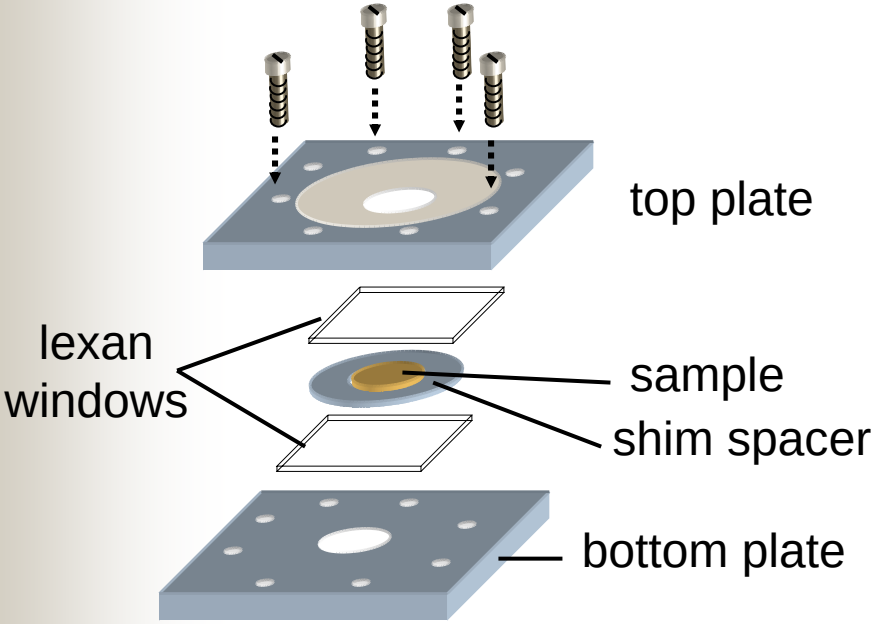
Sample Preparation (Flat plate)



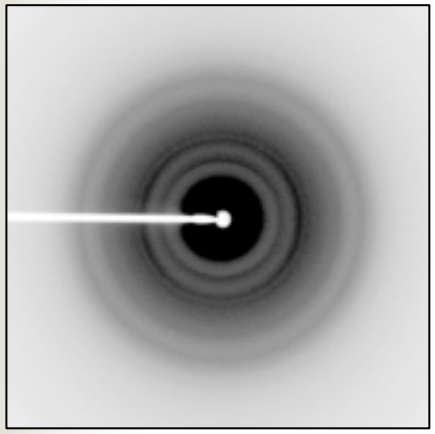
- Keep sample hydrated to avoid artifacts!
  - Change in oxidation state/mineralogy
  - Collapse of hydrated structures
- Use transmission geometry
  - Why? - Better subtraction of background scattering (water, windows)
    - Window material important
      - Lexan is a good material for background removal (WAXS)
      - Water peaks in similar places as silica
  - Optimize sample thickness depending on λ and sample composition. Sample should absorb ~ 20-50% of incident beam. One "μ" is about max.
  - Other sample holders – goniometer head – sample distance ~ 37 mm (11-3, 7-2)

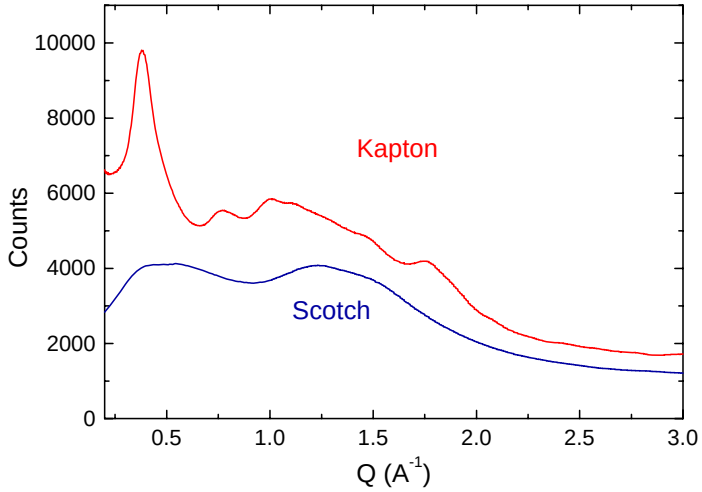


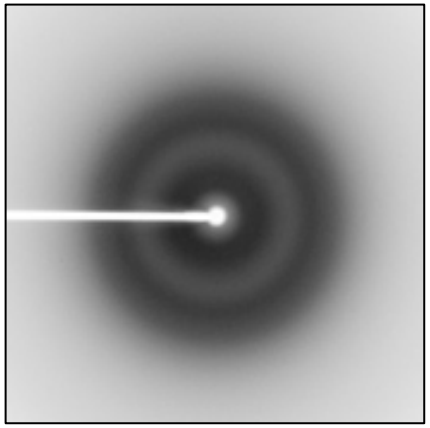
What if I have a powder for transmission?

- Flat plate is poor for dry samples
  - Particles are not generally stable and settle – even out of beam!
- Need a better support – tape!

- Kapton *not* ideal
- Scotch Magic tape (translucent)



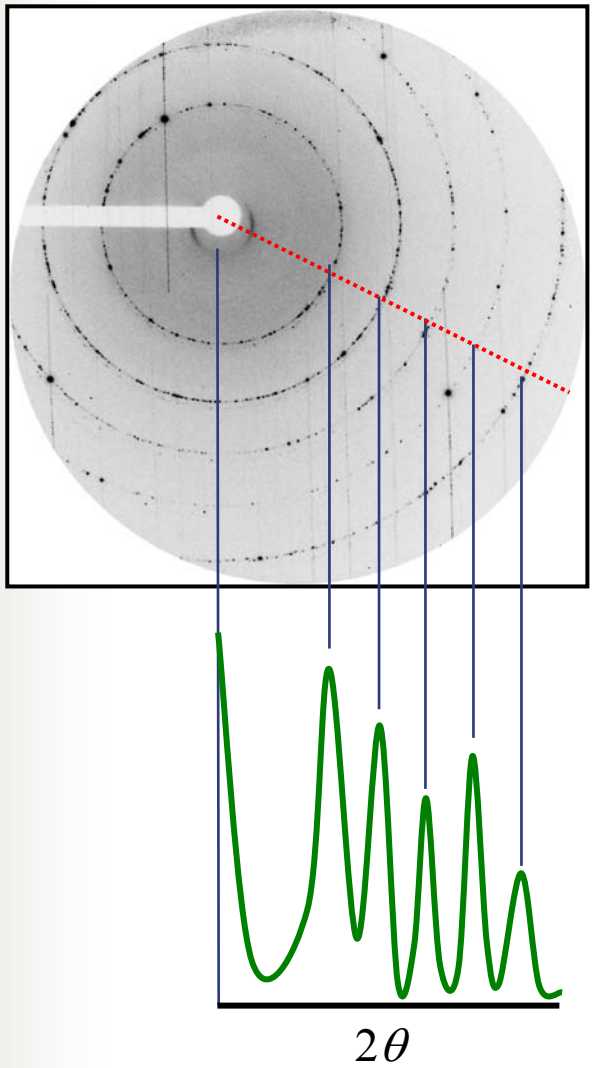




Data Analysis

- CCD to diffractogram (2D to 1D)
- Geometry corrections
- Background subtraction
  - Windows, capillary, tape
  - Water
  - Other interferences (cotton, etc)

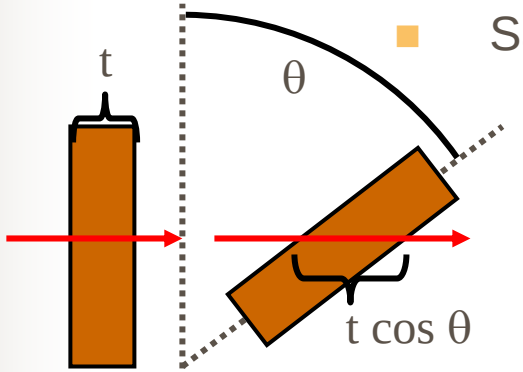
Integration of Powder Pattern



- What Can it Tell?
  - Peak Positions:
    - Phase identification
    - Lattice symmetry
  - Peak Shape & Width:
    - Crystallite size
    - Textures (preferential orientation, multiple phases, etc.)
  - Peak Intensity:
    - Crystal structure
- FIT2D
  - http://www.esrf.fr/computing/scientific/FIT2D/

Theta Dependent Effects

- **Absorption**



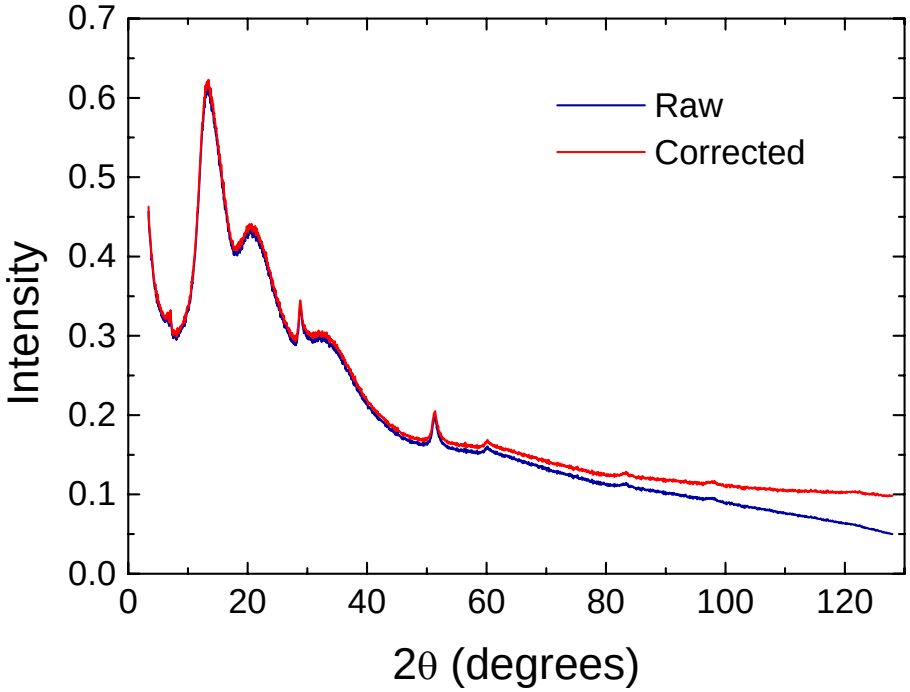
  - Samples absorb the incident and transmitted beams

$$\mathrm{Abs} = (t / \cos\theta)\exp(-\mu t/\cos\theta)$$

  - Measure sample absorption at the beamline!

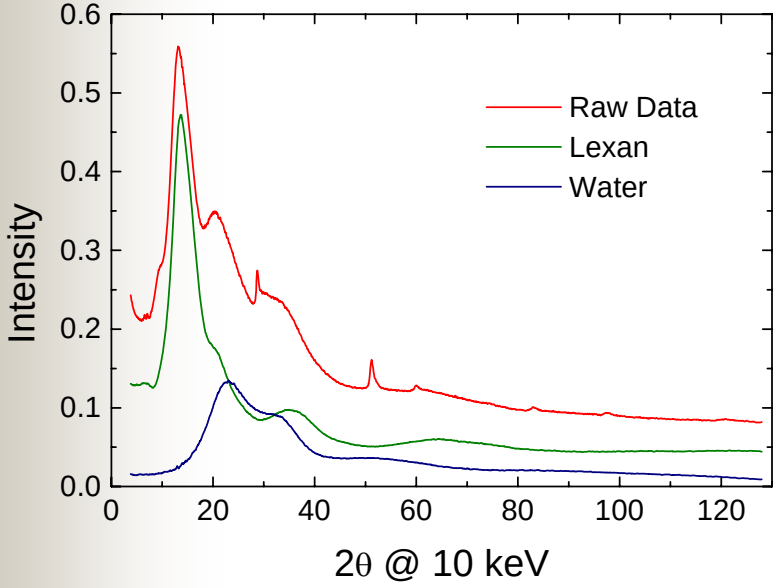
- **Volume effect**
  - 1/cos θ dependence
- **Compton Scattering**
  - Highest at large θ

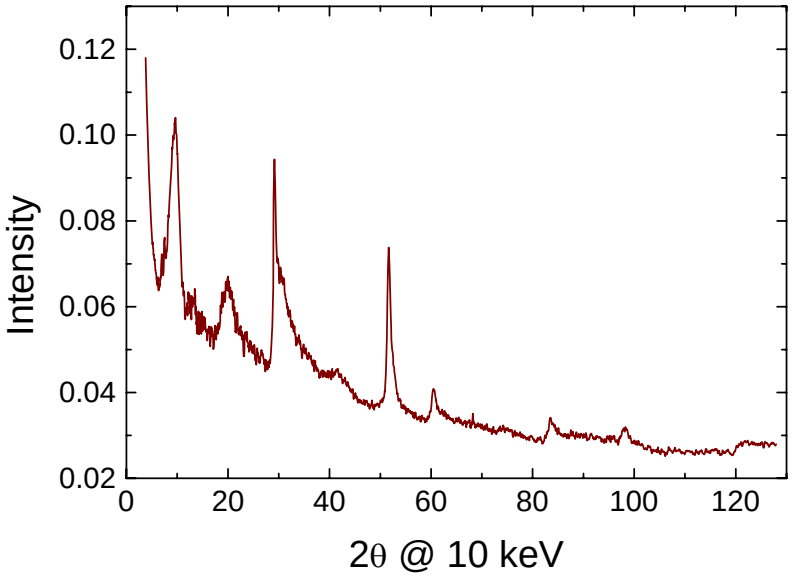
In order to get proper removal of background (windows, water) these corrections must be made. *Critical for thicker samples!*



Background Subtraction

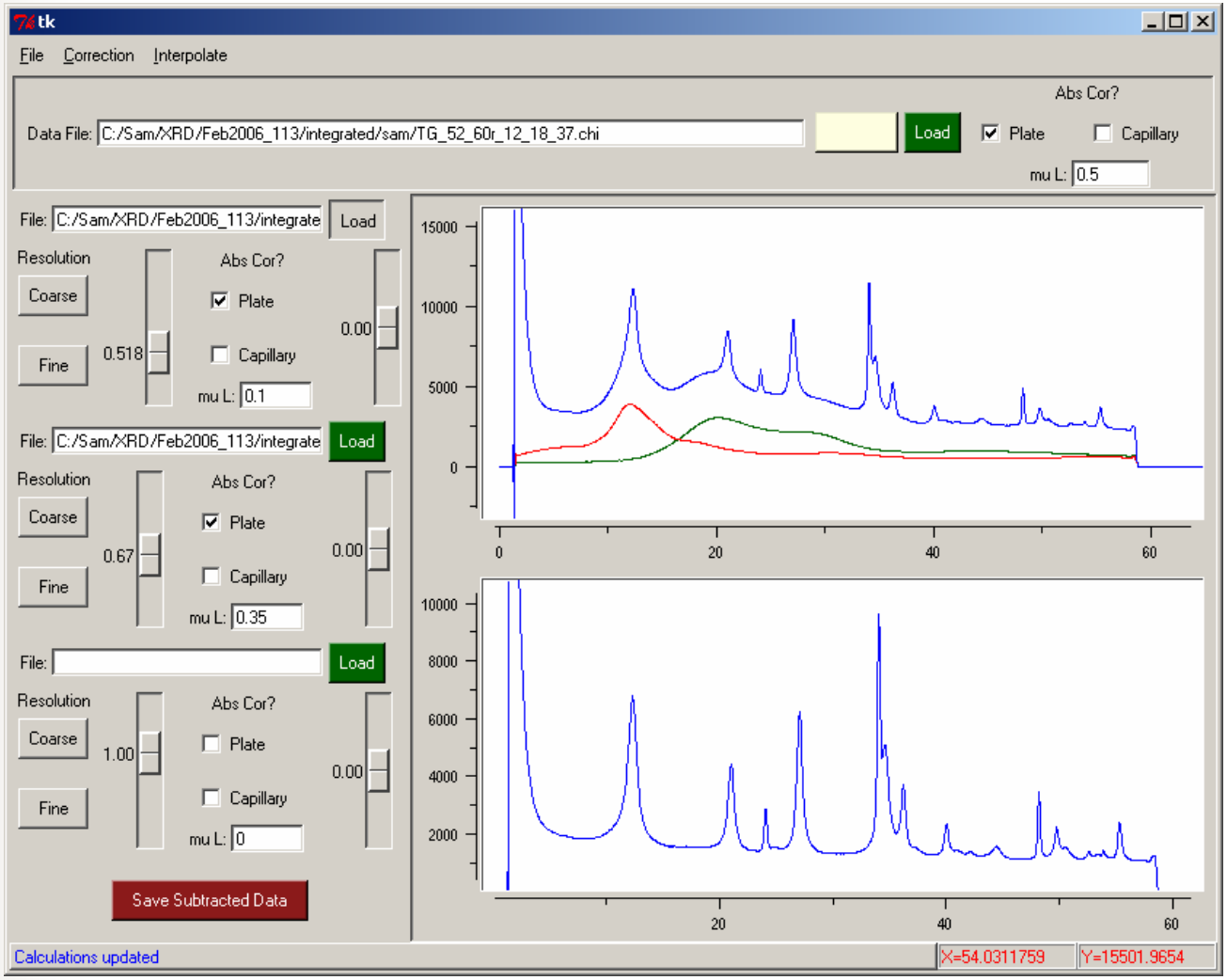
- Background in experiments consists of lexan windows and water





XRD-BS

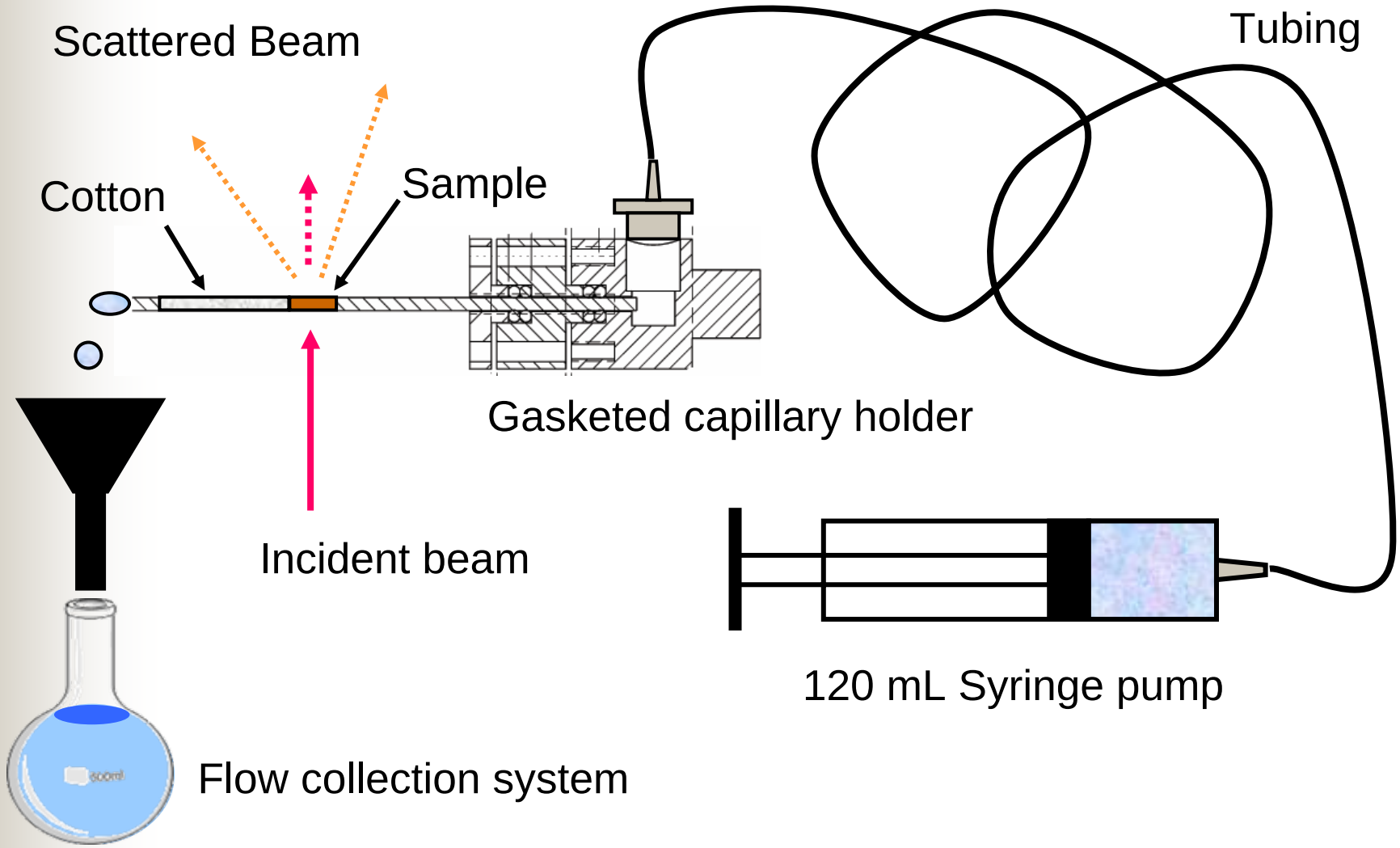
- GUI for removal of background and thickness corrections
  - http://www-ssrl.stanford.edu/~swebb/xrdbs.zip
  - http://www-ssrl.stanford.edu/~swebb/xrdbs.htm (coming soon)



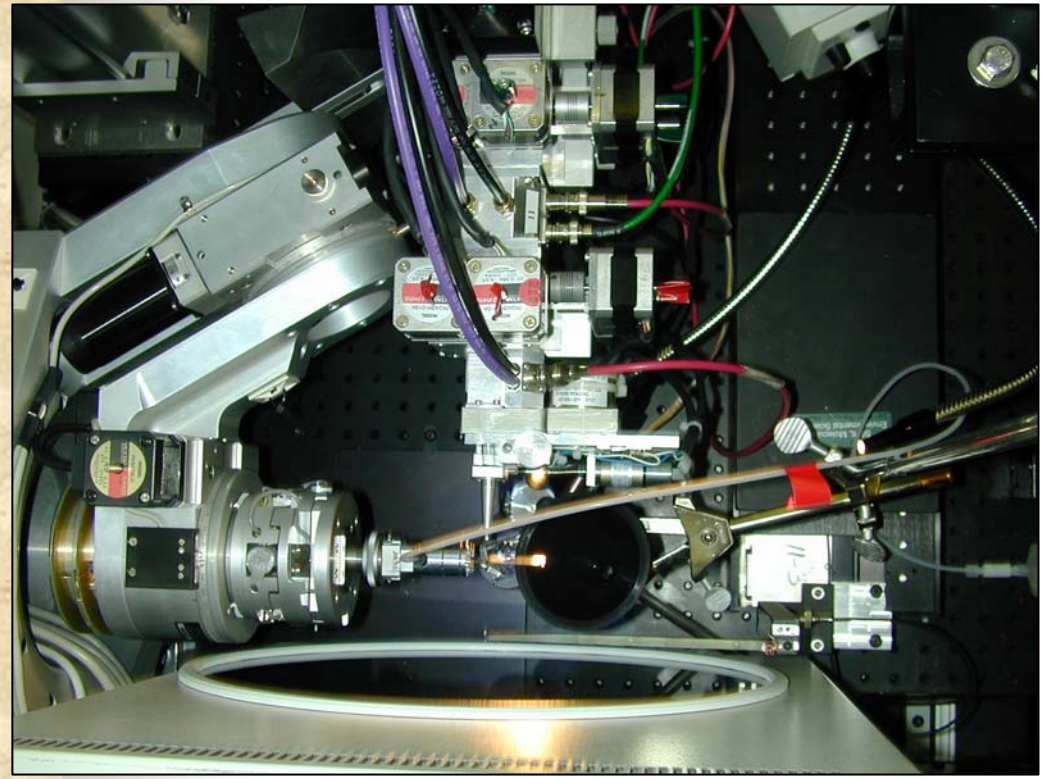
Reactions

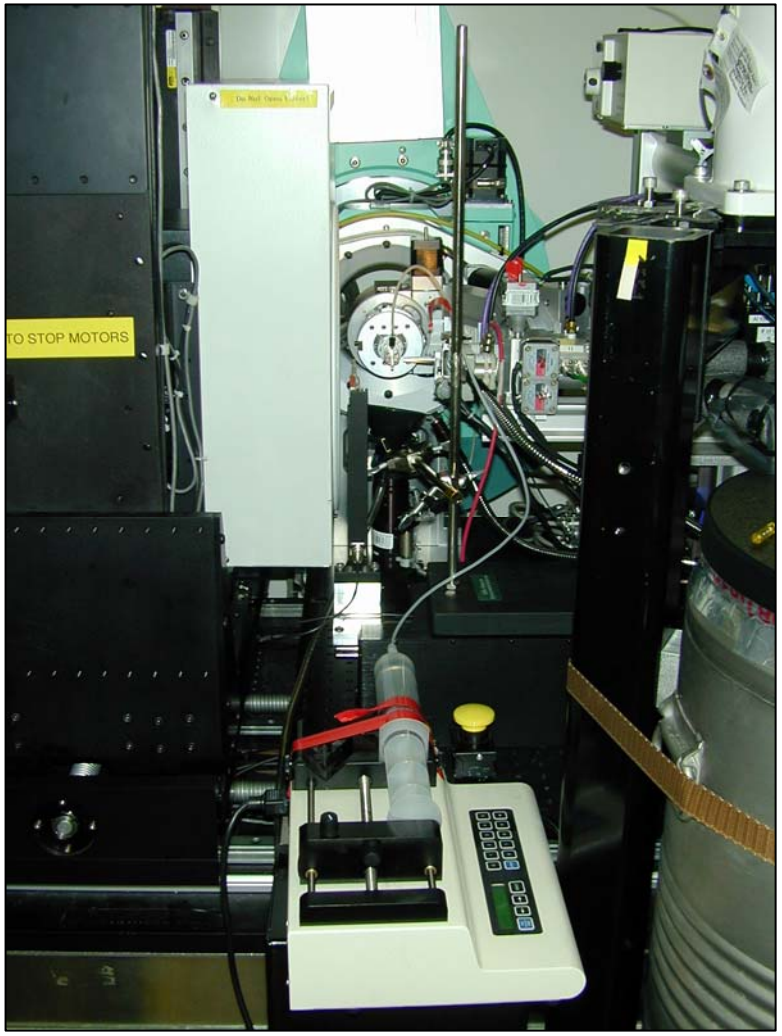
- Mineral-solution reactions
  - Time scale of minutes to hours
  - Redox reactions
  - Cation exchange
  - Colloid transport
- Sample prep = miniaturized “columns” (i.e., particles packed in a capillary)
  - Lexan capillary
    - Better background (no overlap with water like silica)
    - Doesn’t break!
  - Particle size and porosity
    - Clogging
  - Flow rate
    - Stalling of pump

Reaction Flow Setup (not to scale)



Beamline Setup (BL 11-3)





Future Improvements…

- Peristaltic pump vs. syringe pump
  - Better flow and ability to change reactant solutions
- Gas impermeable tubing
  - Improve anaerobic conditions
- Injection loop
  - Easy loading of capillary
- Fraction collector
  - Analysis of post-reaction fluids
- Fluorescence detector
  - Monitor elemental changes in sample if reactions lead to deposition / removal of compounds

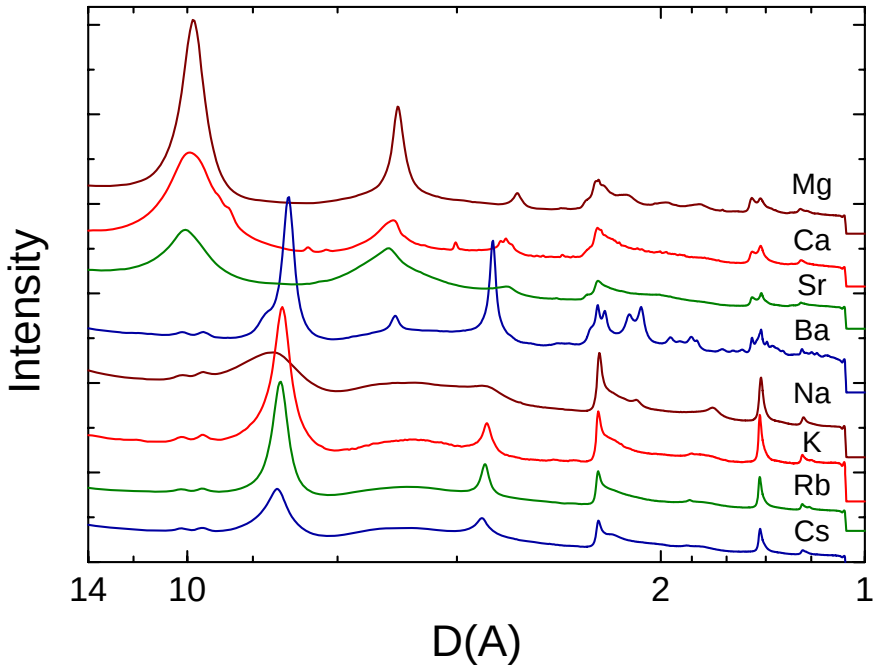
Examples

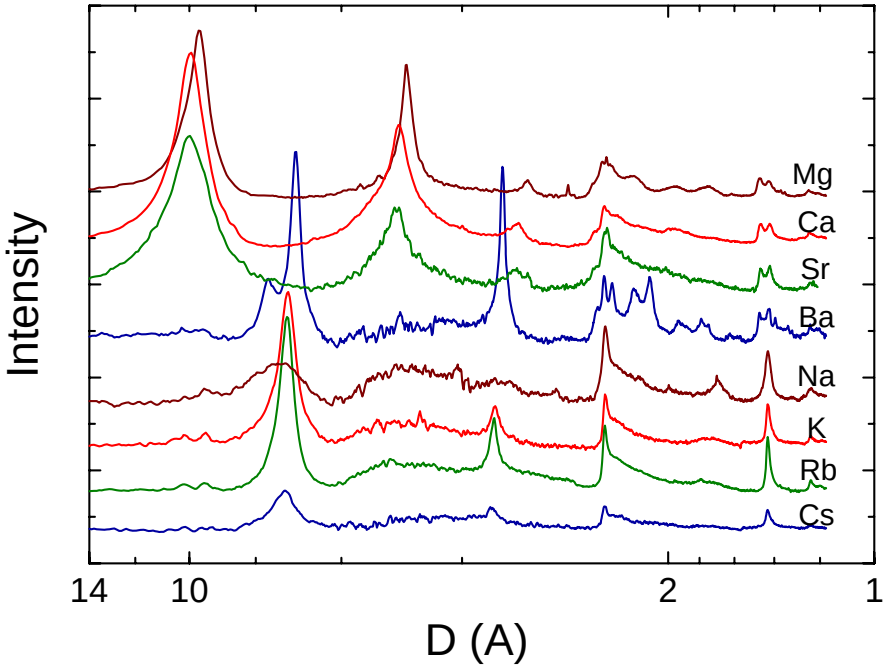
- Mn biomineral structures
  - Compare 2-1 and 11-3 data quality
- Real time biogenic Mn oxidation
  - Area detectors in reactions
- MnOxide reactions with metals
  - Area detectors in reactions
- Sulfide mineral oxidation
  - Wet-dry artifacts for air sensitive minerals
  - Air exposure

Mn Oxide Biomineral Structure

- BL 11-3
- 2 minute exposure
  - 360 degrees are better than 1!

- BL 2-1
- Sum of 4 to 5 scans, ~8 hours total

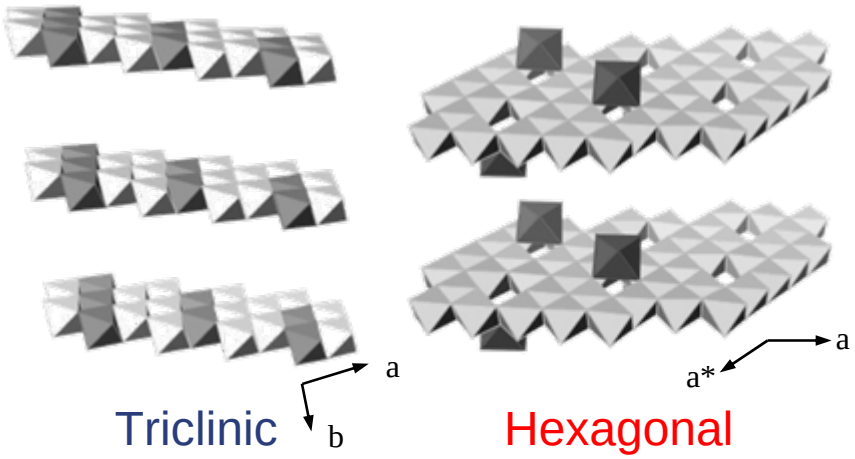


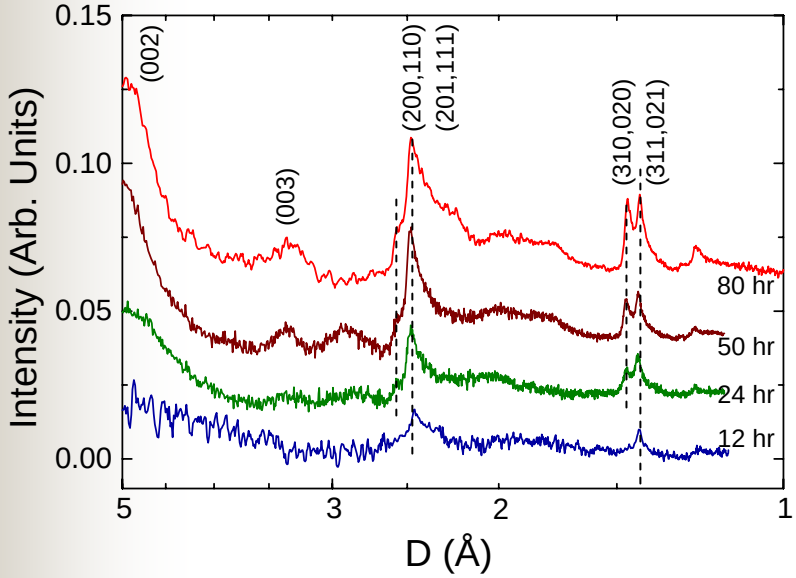


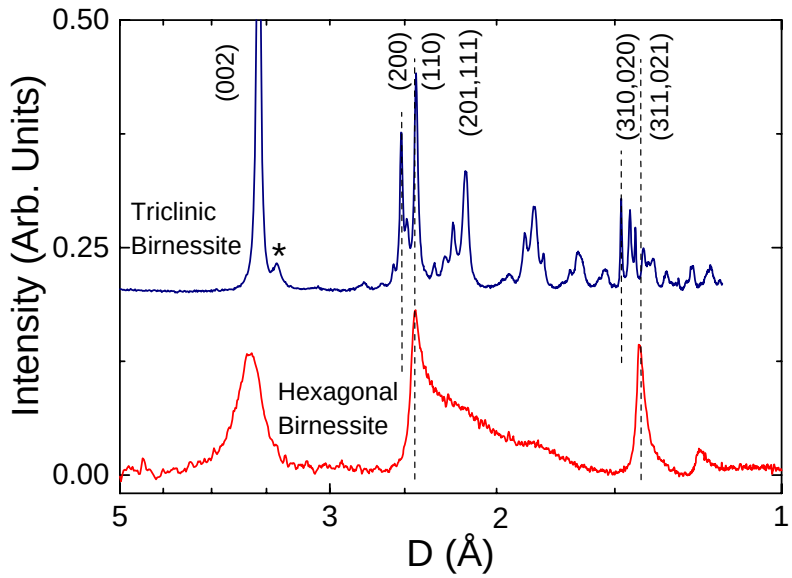
Tradeoff between noise-resolution-time

Biogenic Mn Oxidation

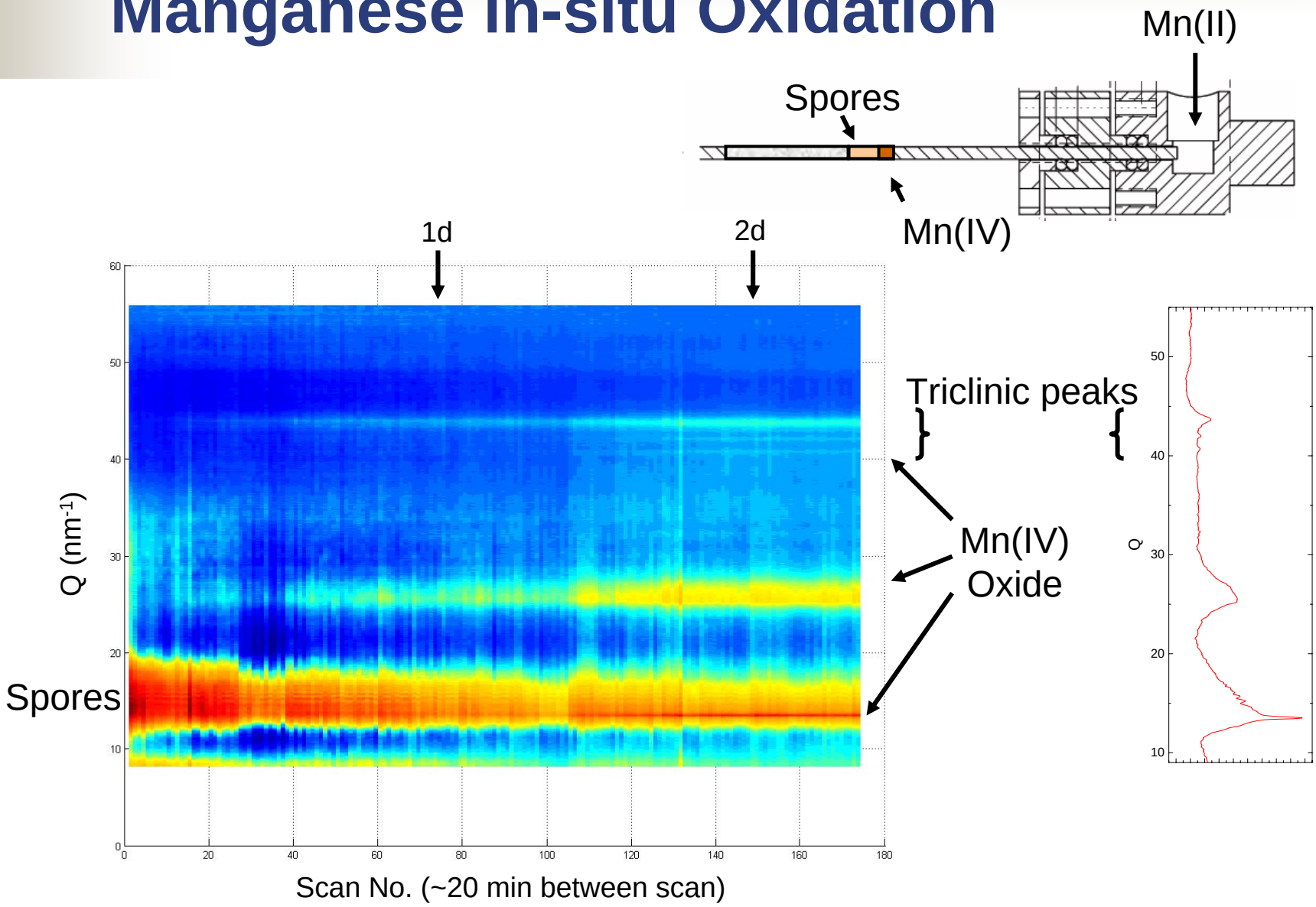
- Mn oxidation in seawater progresses through symmetry changes in oxide structure
- Due to the effect of Ca present in interlayers



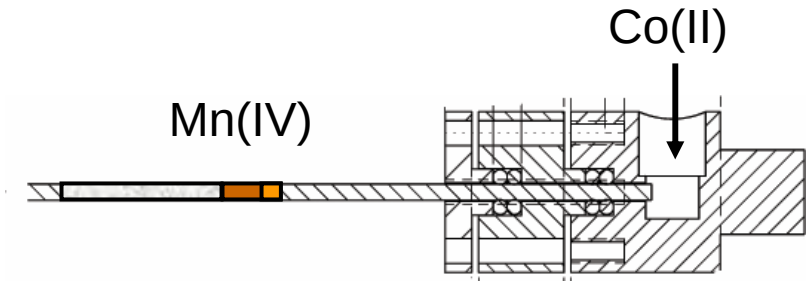


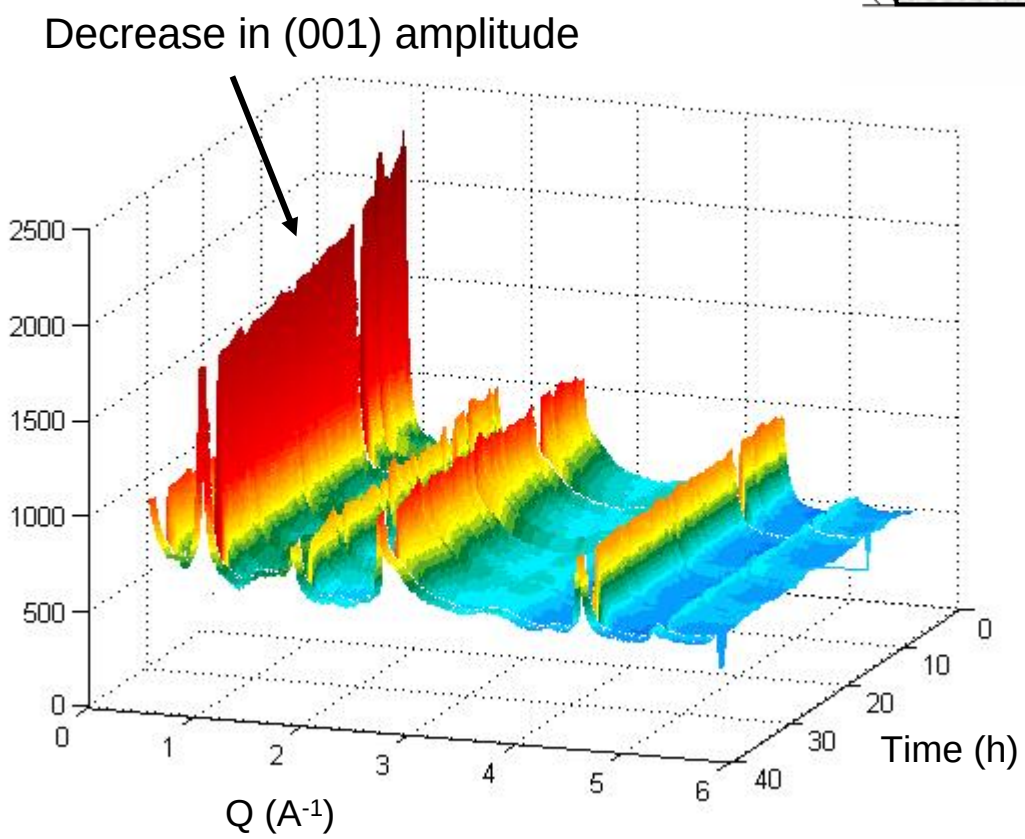


Manganese in-situ Oxidation



Manganese oxide reaction with metals

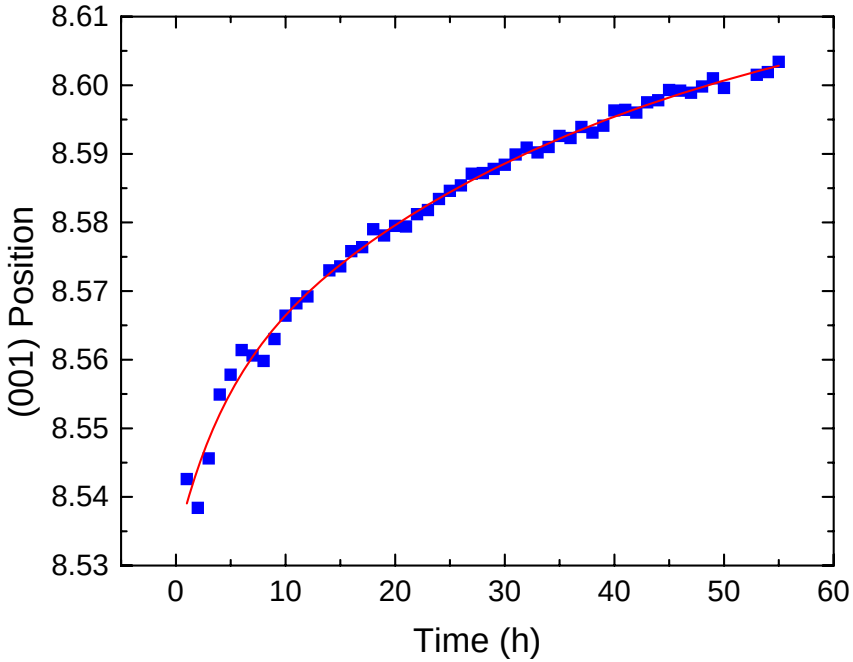


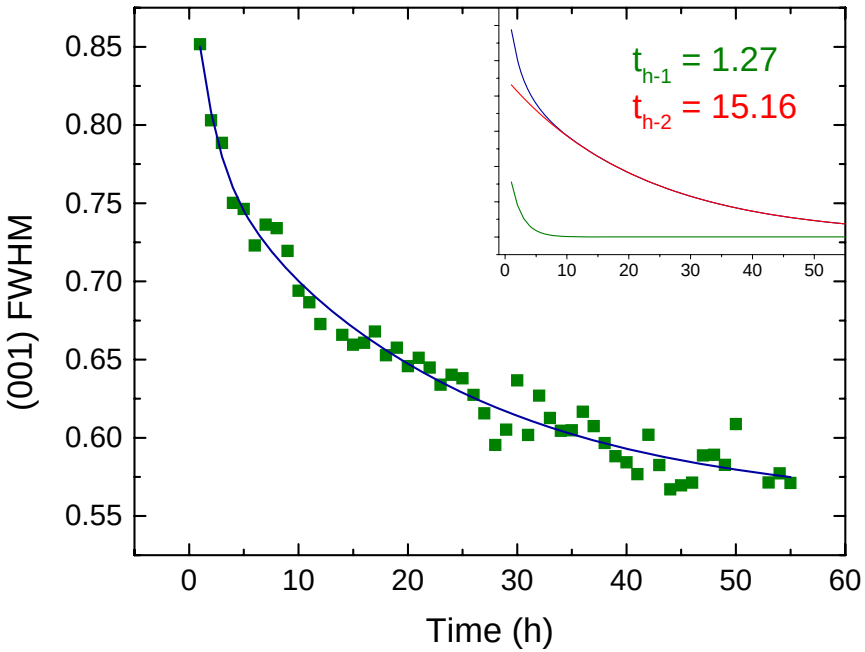


- Co(II) reacts with pre-formed biogenic oxides to oxidize to Co(III). Mn-oxides are reduced
- No evidence of new Co(III) minerals

Biogenic MnOxides + Co(II)

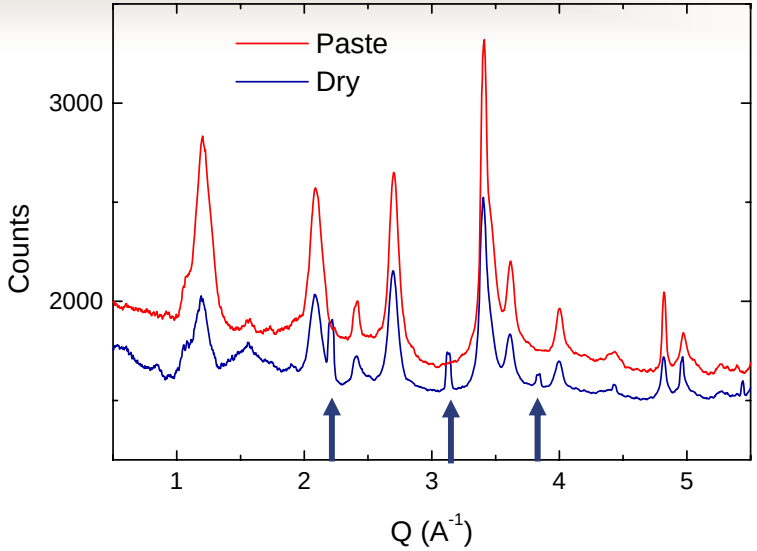
- 001 peak broadens with reaction and shifts to larger d-spacings
- Changes follow pseudo-first order reaction kinetics
  - Slow and fast steps of Co(III) incorporation



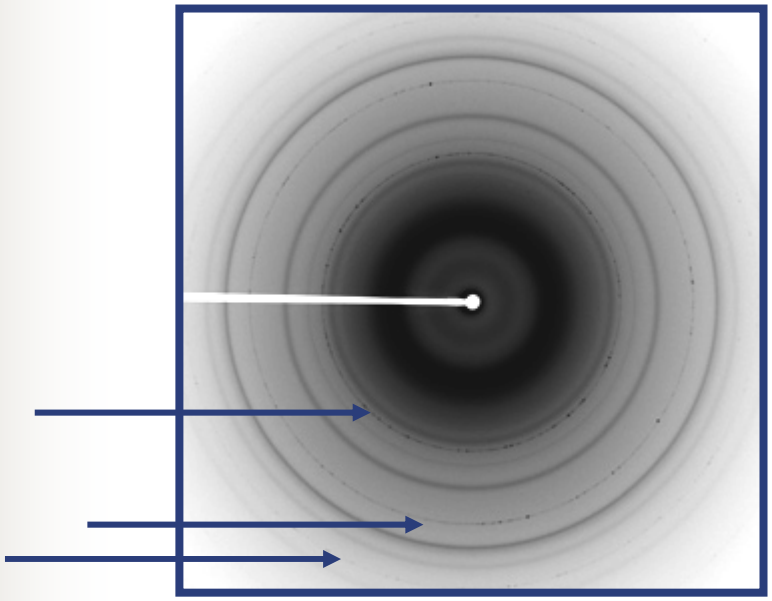


Wet-Dry Artifacts

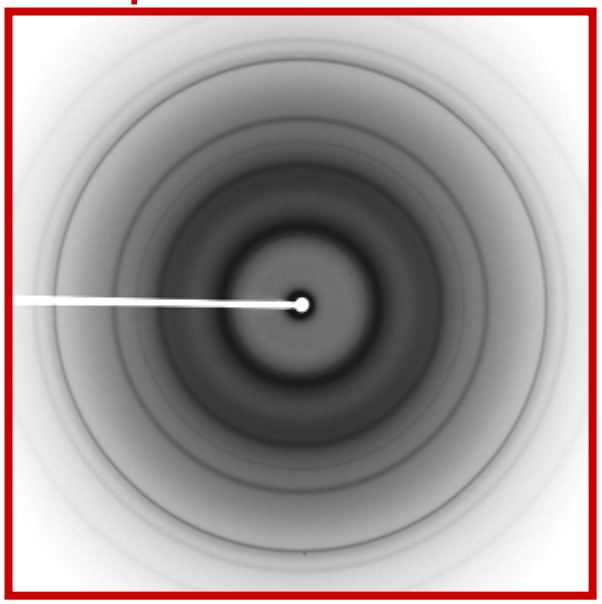
- Measurements of anaerobic, dried sample lead to formation of peaks with different texture



FeS dried

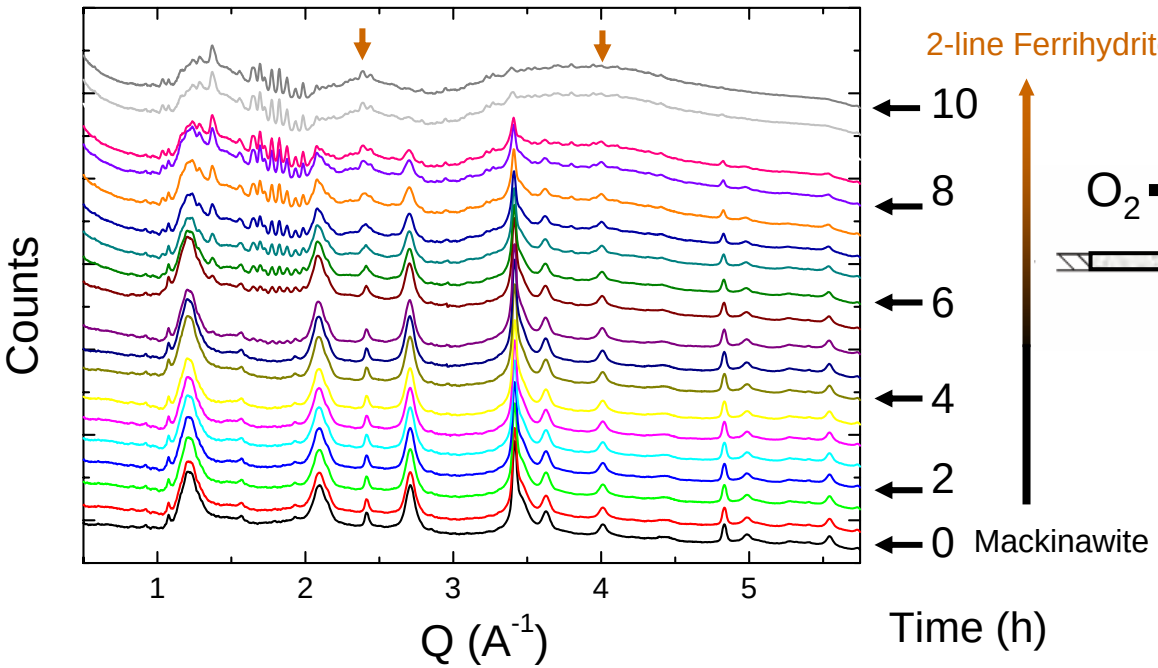


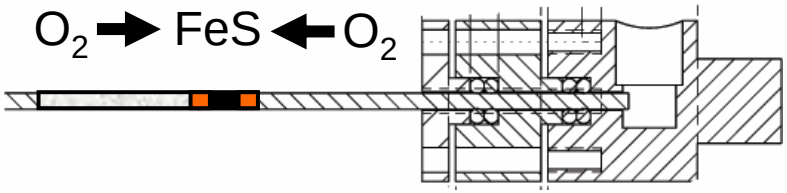
FeS paste, anaerobic

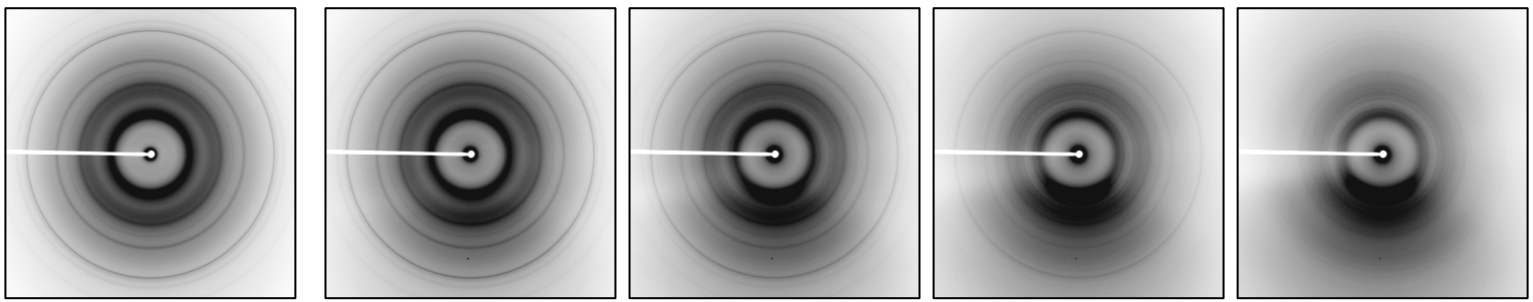


Fe-Sulfide oxidation reactions

~1.2 mm from end







t=0 t=7 t=8 t=9 t=10

Acknowledgements

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R/V Knorr, Black Sea, 2003