New scientific directions and possibilities for environmental and geosciences scattering research (PDF, surface scattering, microdiffraction), technical requirements to achieve next generation capabilities, instrumentation and detector trends

John Parise

Including a summary of the Materials Diffraction Draft White Paper (and PING BAT; Jan 17-18 2008) - surfaces especially need input from EMS group!

What basic science do agencies expect will under-pin future environmental science?

I wish I knew

- *Some grand challenges - inherently multi-discipline/ multi agency that scattering will impact*
  - *(1) Sequestration*
    - *E.g. Carbon sequestration*
  - *(2) Role of Geo-nano-materials (inc. Bio-produced)*
    - *surface scattering, PDF, in situ, joint XAS-PDF*
  - *(3) Reinventing manufacture, use & recycling of materials*
    - *Understanding the consequences of processes*

Many of these missions involve scattering

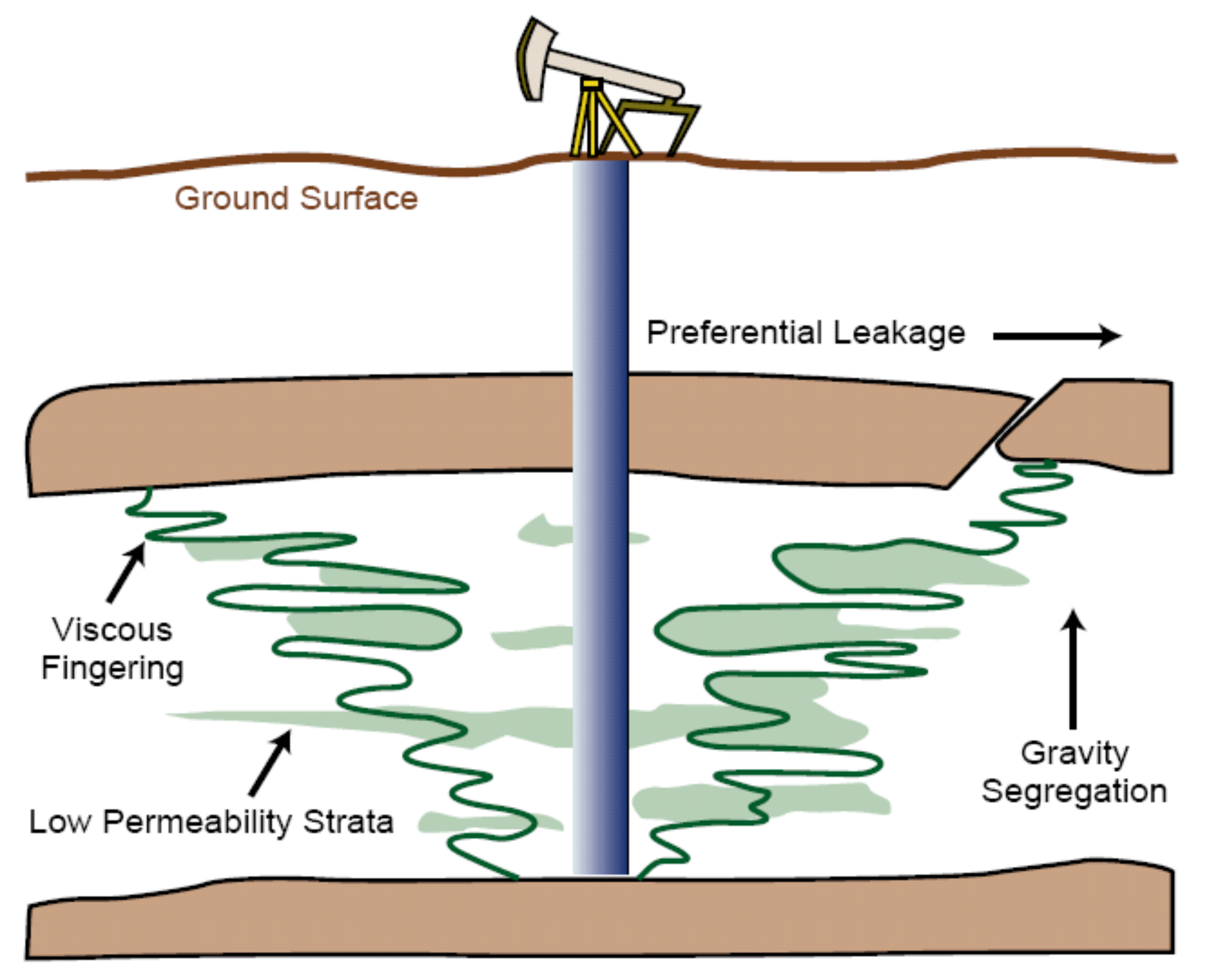
- **Most will require observations *in operando***
- **Many involve poorly crystalline materials**
- **Need capabilities for in situ at high energies**

- **No such instrument in DOE inventory**

- **No instrument optimized for in situ work**
  - **optics, detectors, environmental cells designed as a package**
  - **Design of standard mechanical coupling to instrument available to users designing and building their own cells, at least 2 years before availability to outside users (preferably before)**

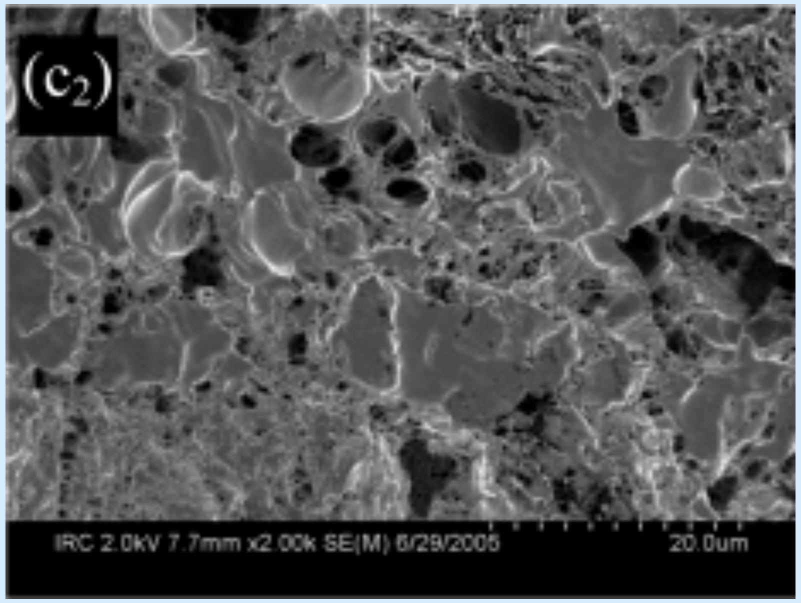
(1&3) Potential research areas – CO_2 Sequestration, green chemistry

- Materials processing in supercritical CO_2
  - Polymers, extraction, etc
- CO_2 sequestration mineralogy studies
  - Rock/ CO_2 interactions
- Flammable gases
  - CO_2/CH_4 mix
- No Be corrosion
  - CO_2/H_2O mix



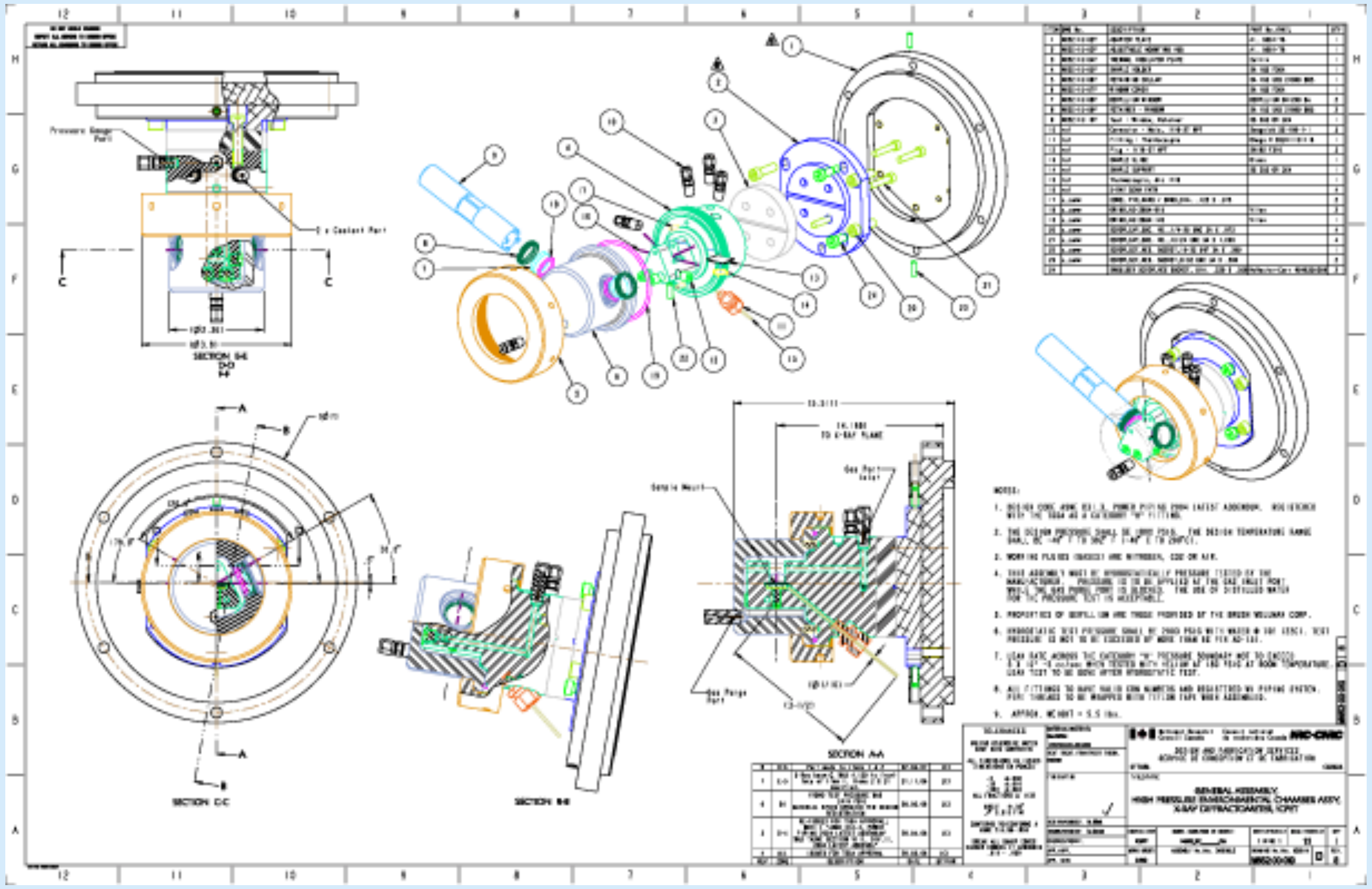
What should be our interest?

- Interested in the use of sub and supercritical CO_2 for polymer processing / microstructure control (crystallization, foaming, etc)
- Compact lab XRD in-situ gas cell designed and built for CO_2/inert gases up to 125 bar (-40 to 200ºC)



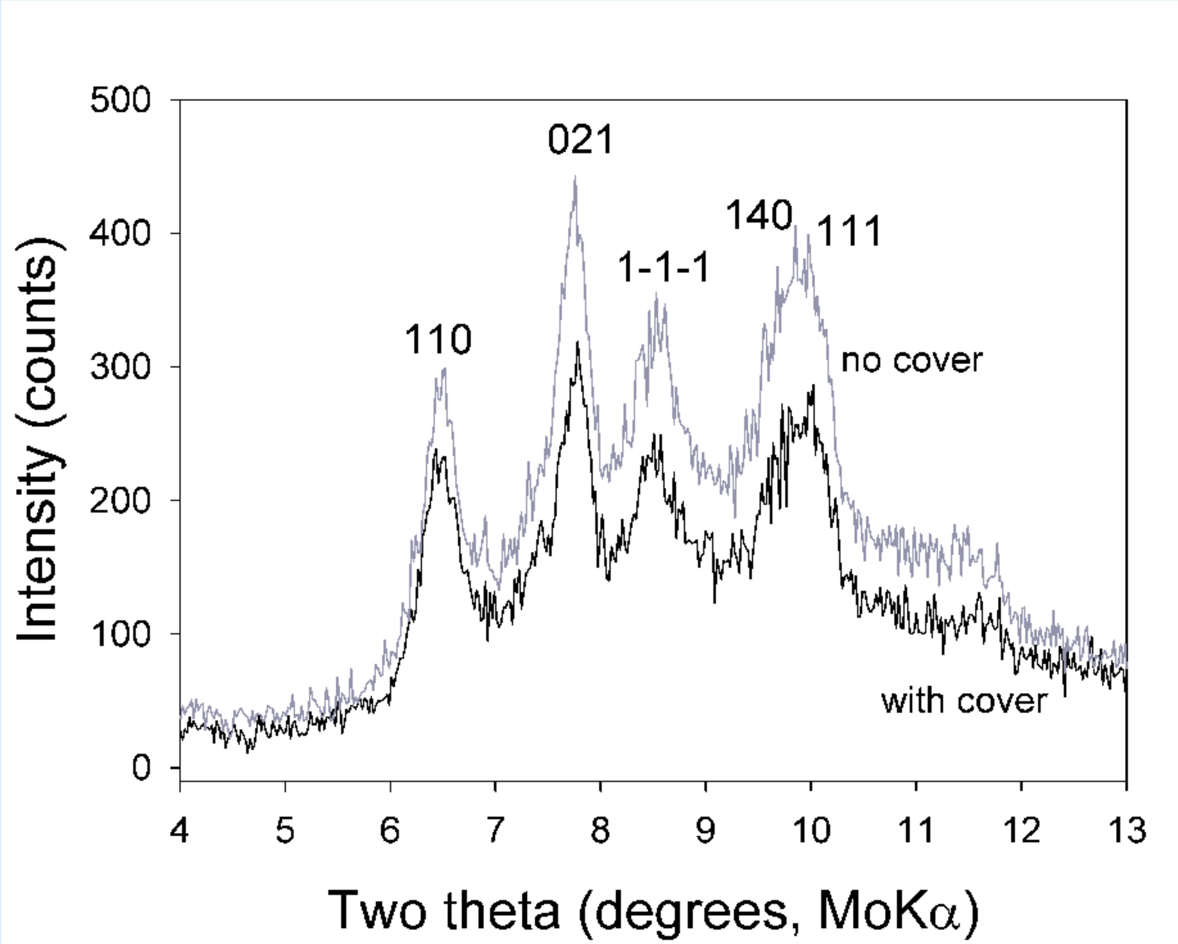
Foamed PLLA produced using 5.5 MPa CO_2 at 90ºC for 5 mins

CAD drawing of the cell

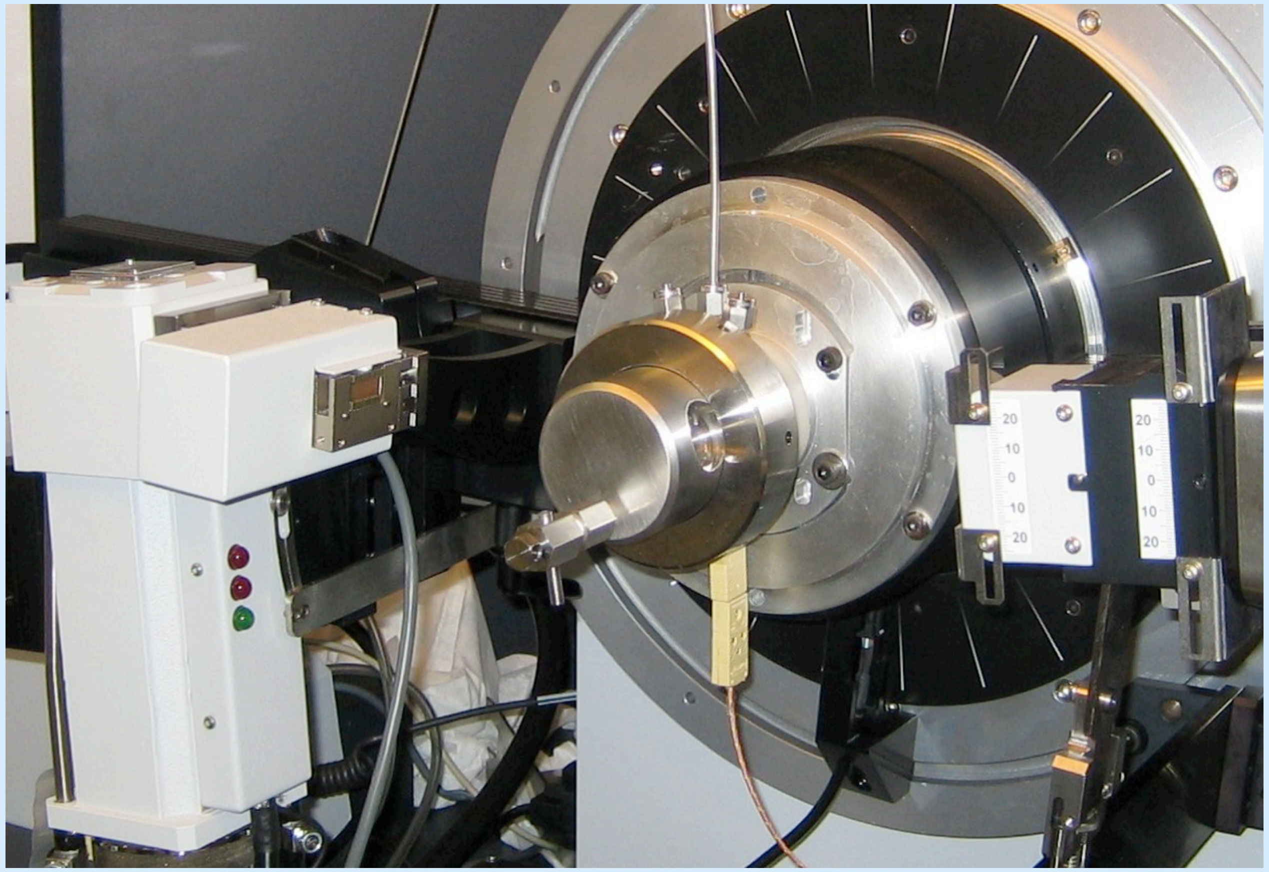


How far can I go in the lab?

- Coupled with Mo tube and Vantec PSD detector in fixed scan mode can do kinetic studies with time resolutions of the order of seconds
- Haven’t had chance to hook up recirculating fluid heating/cooling yet



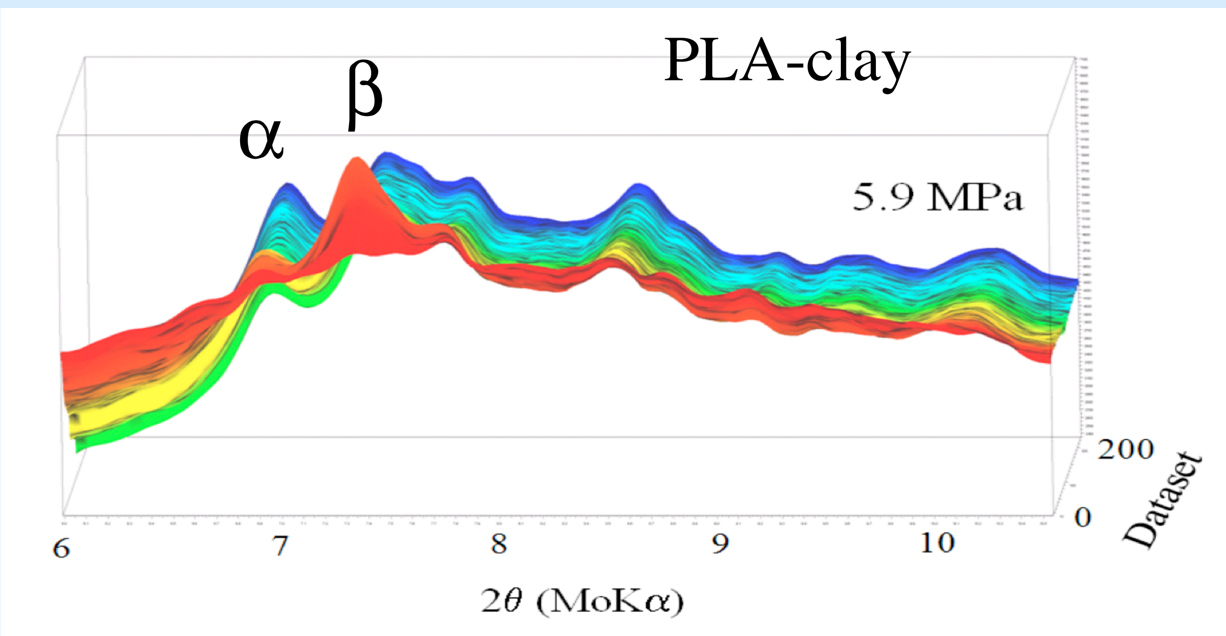
1s snapshots of polypropylene at 1atm

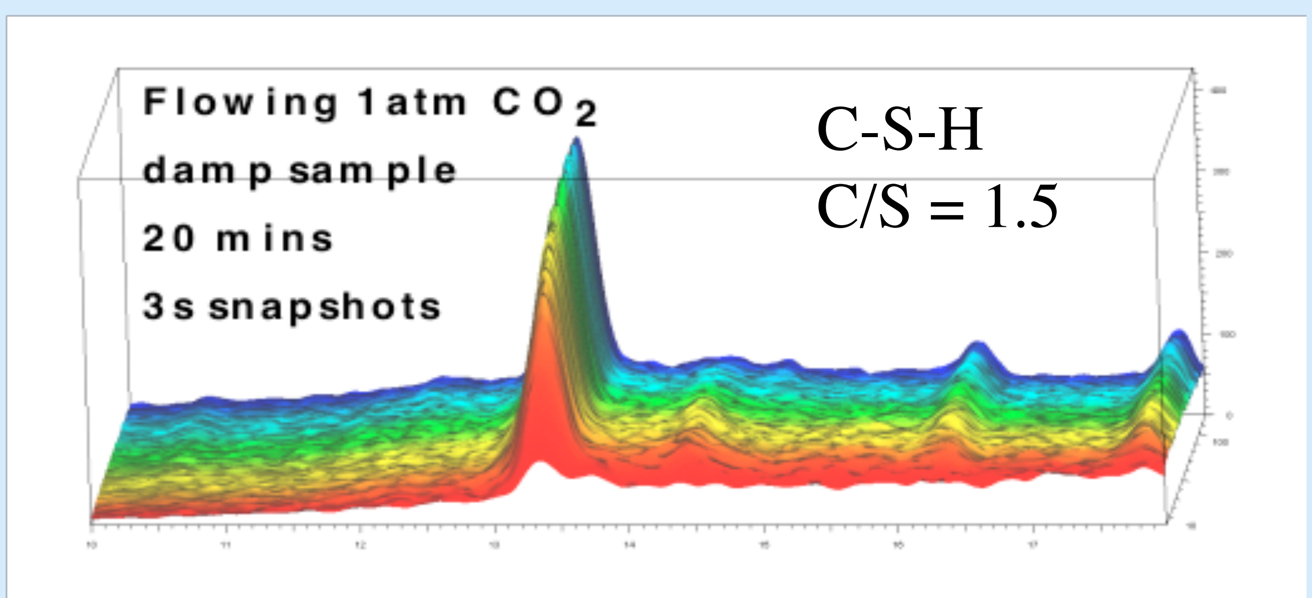


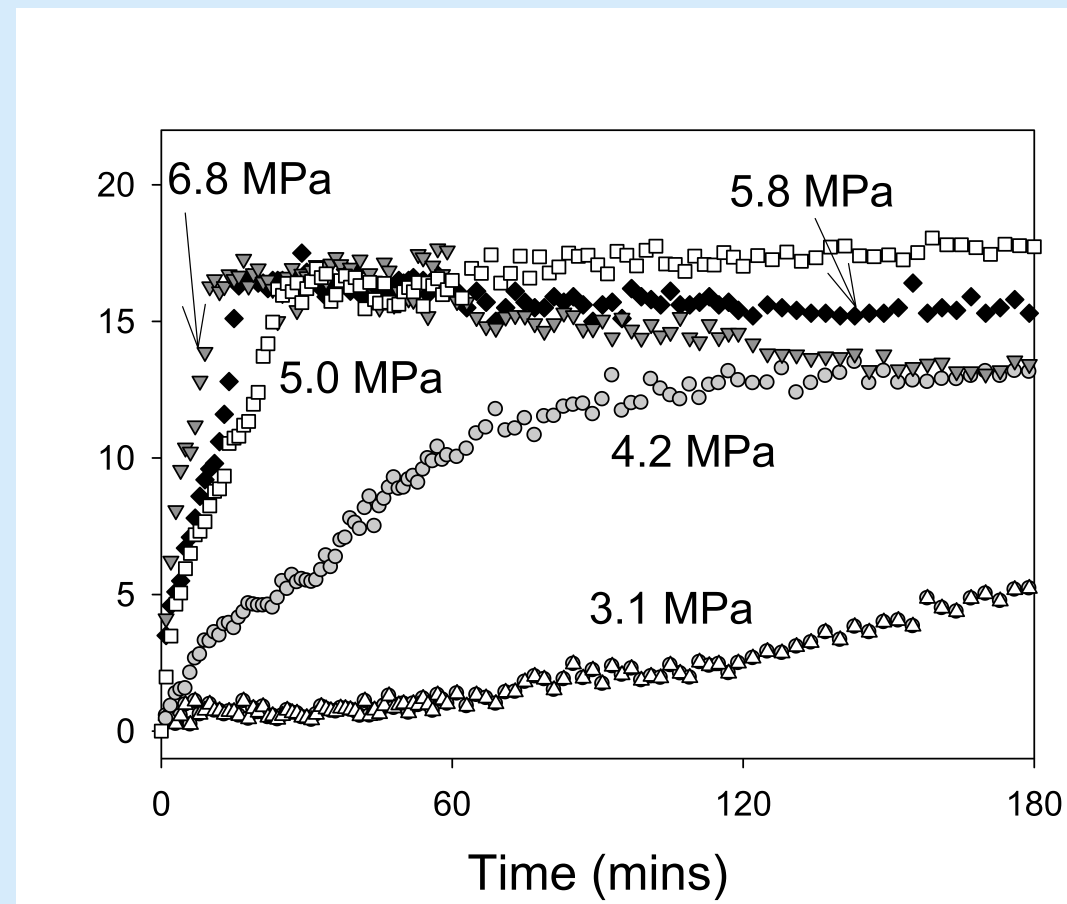
Cell mounted on Bruker D8

What's been done in the lab so far…

- Crystallization of polylactic acid (PLA) and PLA-clay composites
- Carbonation of calcium silicate hydrate (cement binding phase)



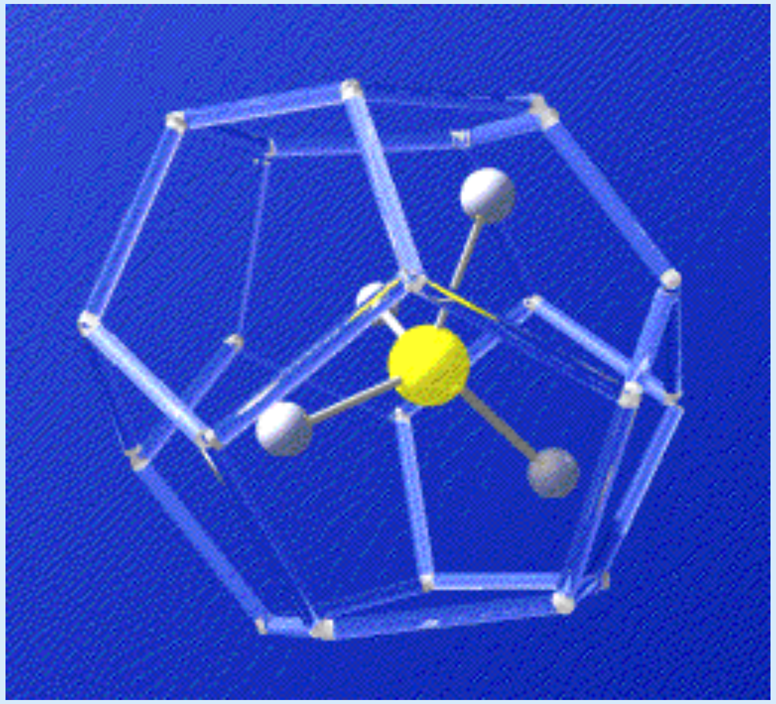




Crystallization over the first hour for PLA-clay nanocomposite at different CO_2 pressures @29ºC

(1 &3) Other systems

- Hydrogen storage (low/medium pressure, 100-400ºC)
- Gas hydrates (low pressures, sub-ambient temps)

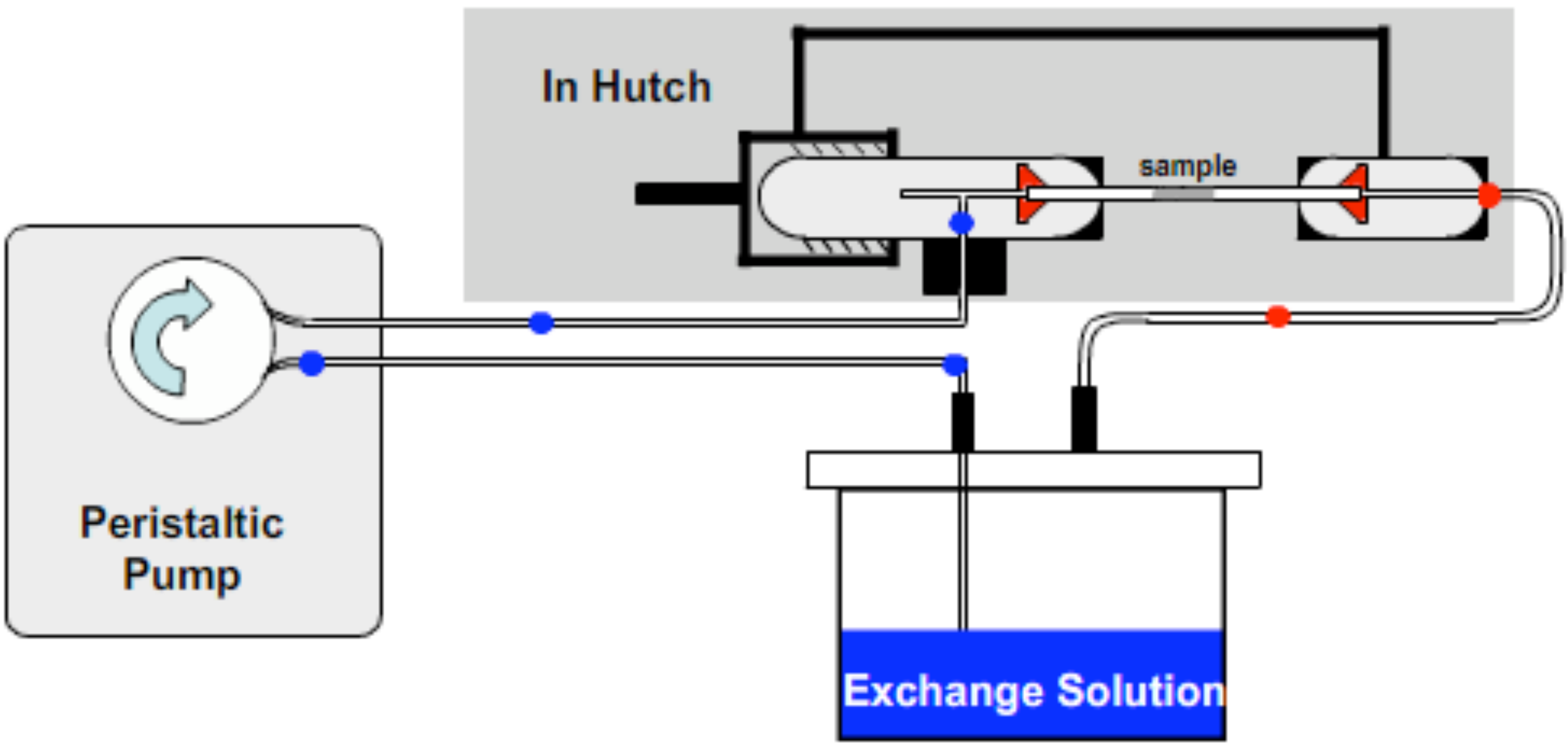


Clathrate structure

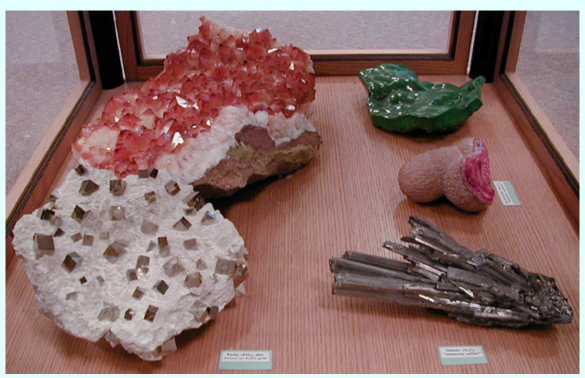
- Organic magnets (would need kilobar pressure?)
- Anything anyone else can think of…

- Suggestions?

(1,2 &3) Time-resolved studies



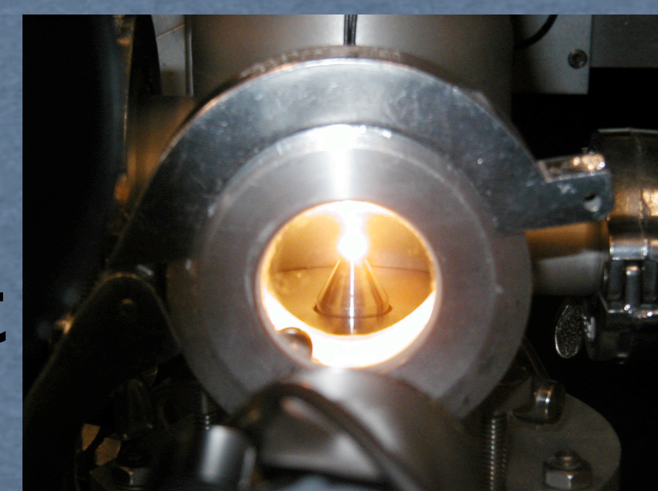
(2) Geo-materials: What we work on and what we wished we worked on



Fe/AlOOH flocs

vernadite

STRUCTURE
of solute/solvent
(inc. @ surface)

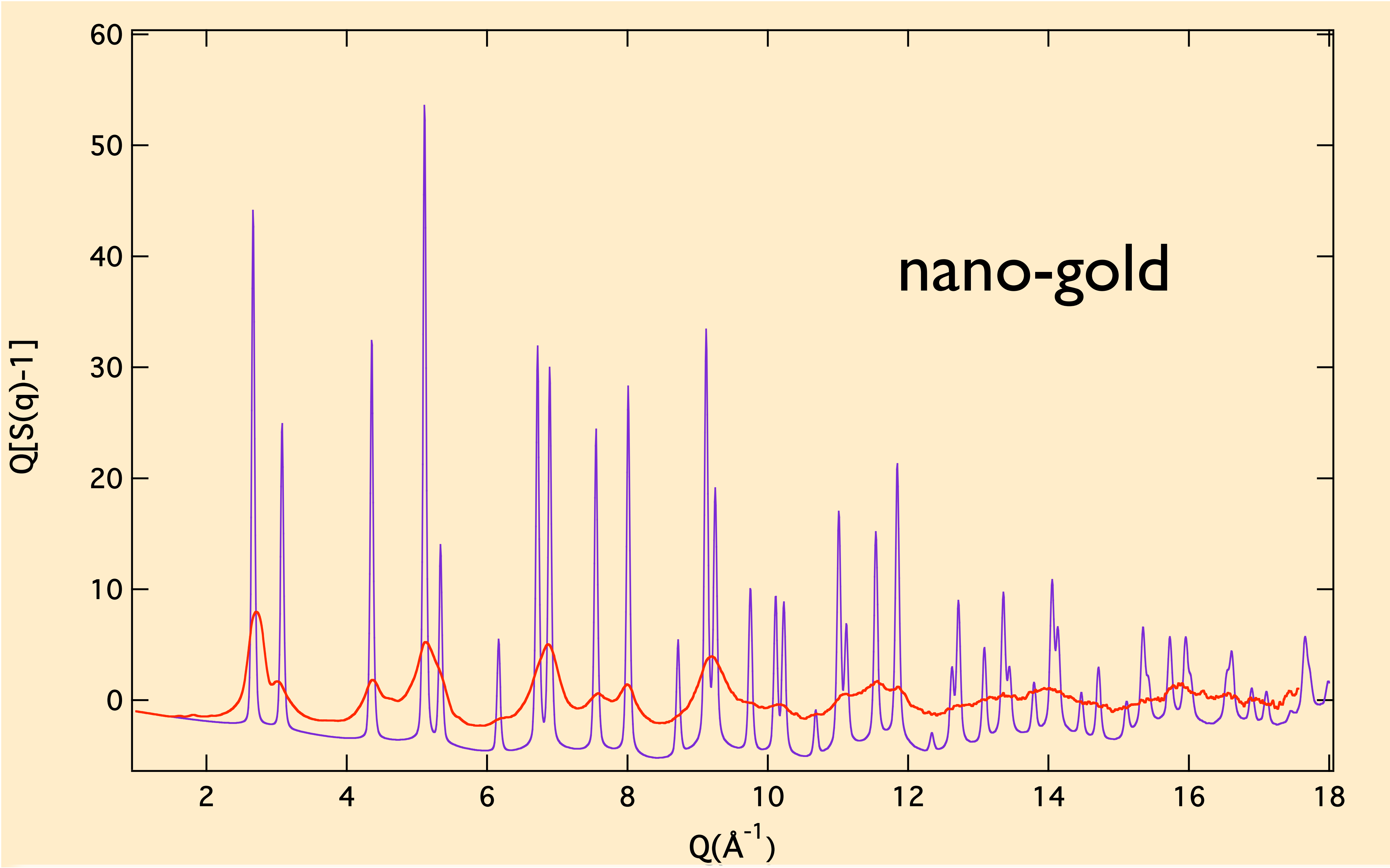


forsterite glass

Bulk elastic X-ray scattering with new tools

Where the atoms are .... nano materials (~ < 2 - 20 nm)

Information loss - broadened peaks, build-up of diffuse scattering



XRD of Ferrihydrite

LONG-RANGE PERIODICITY

116 Eggleton and Fitzpatrick *Clays and Clay Minerals*

“2-line”

“6-line”

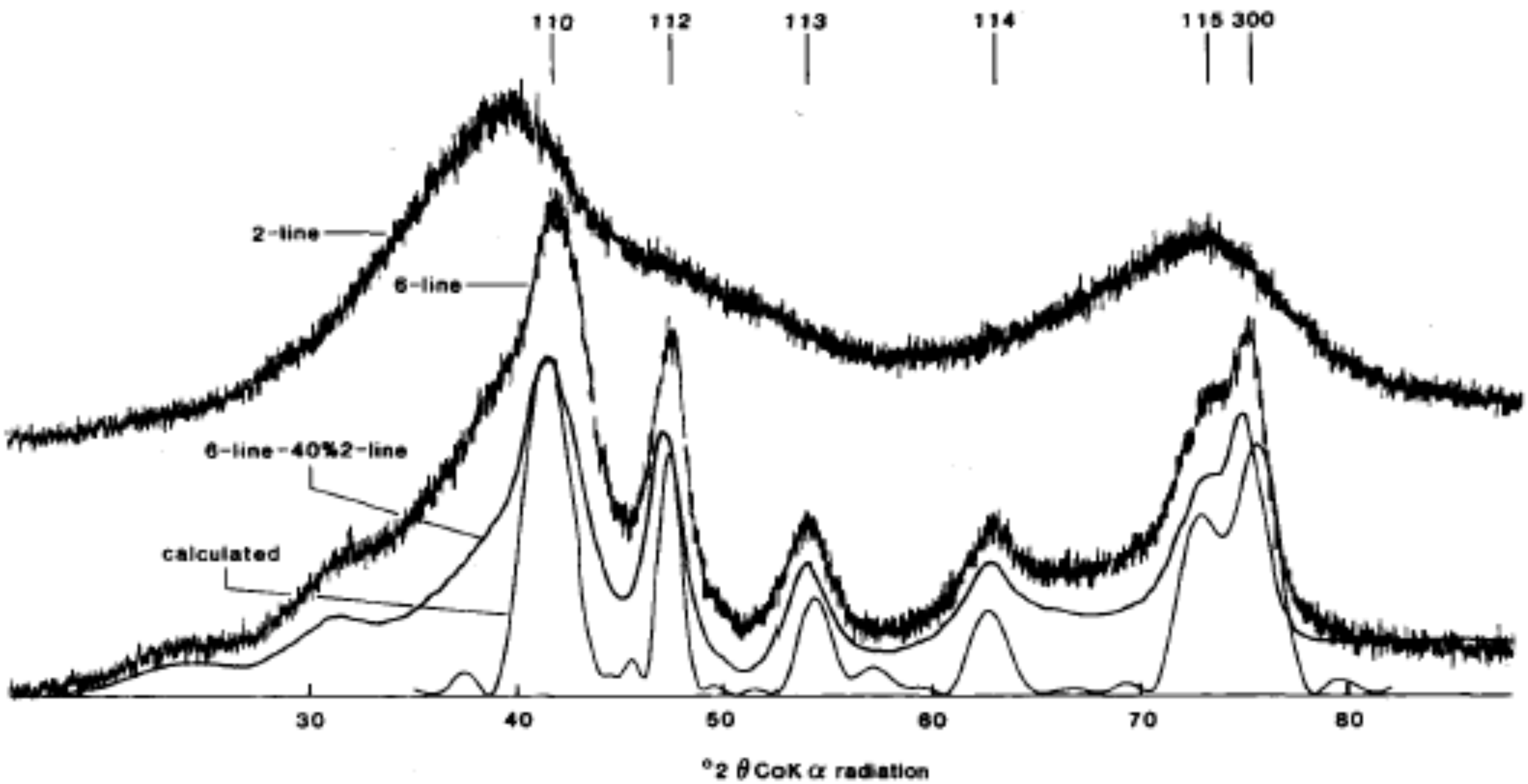


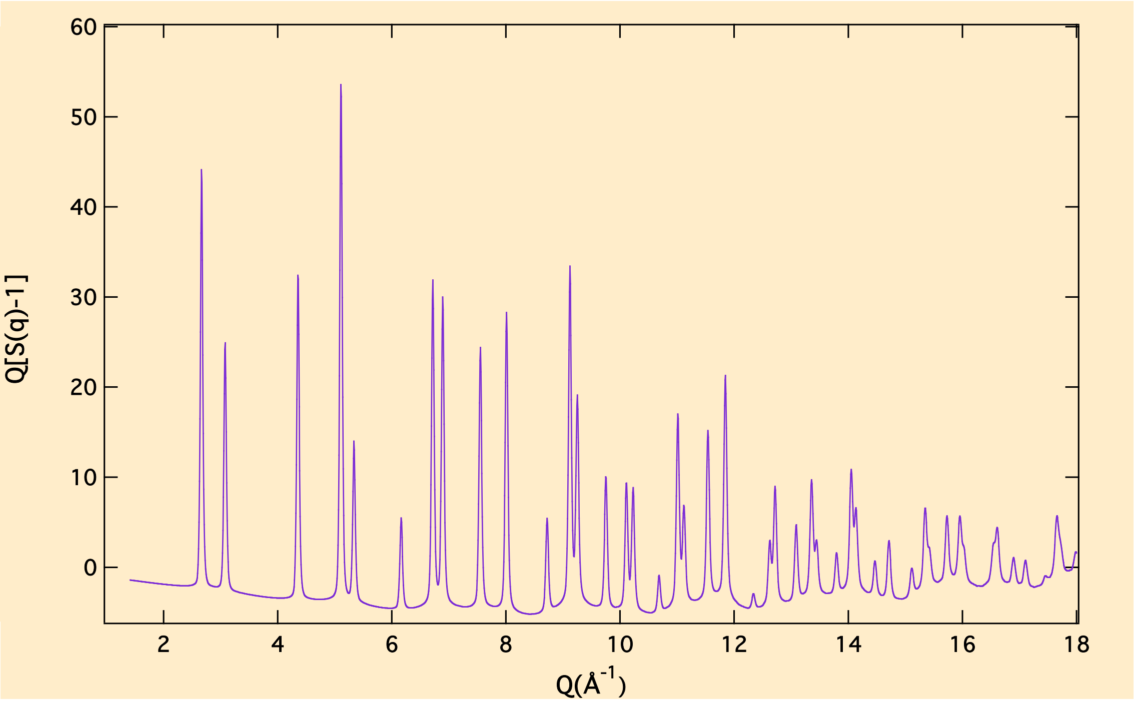
Figure 2. X-ray powder diffraction data: observed traces for 2-line and 6-line ferrihydrites, smoothed trace for 6-line with 40% 2-line ferrihydrite subtracted, and pattern calculated from parameters of Table 3, assuming 40-Å-size crystals.

From: Eggleton and Fitzpatrick, *Clays and Clay Minerals,* **36**, 2, 111-124 (1988).

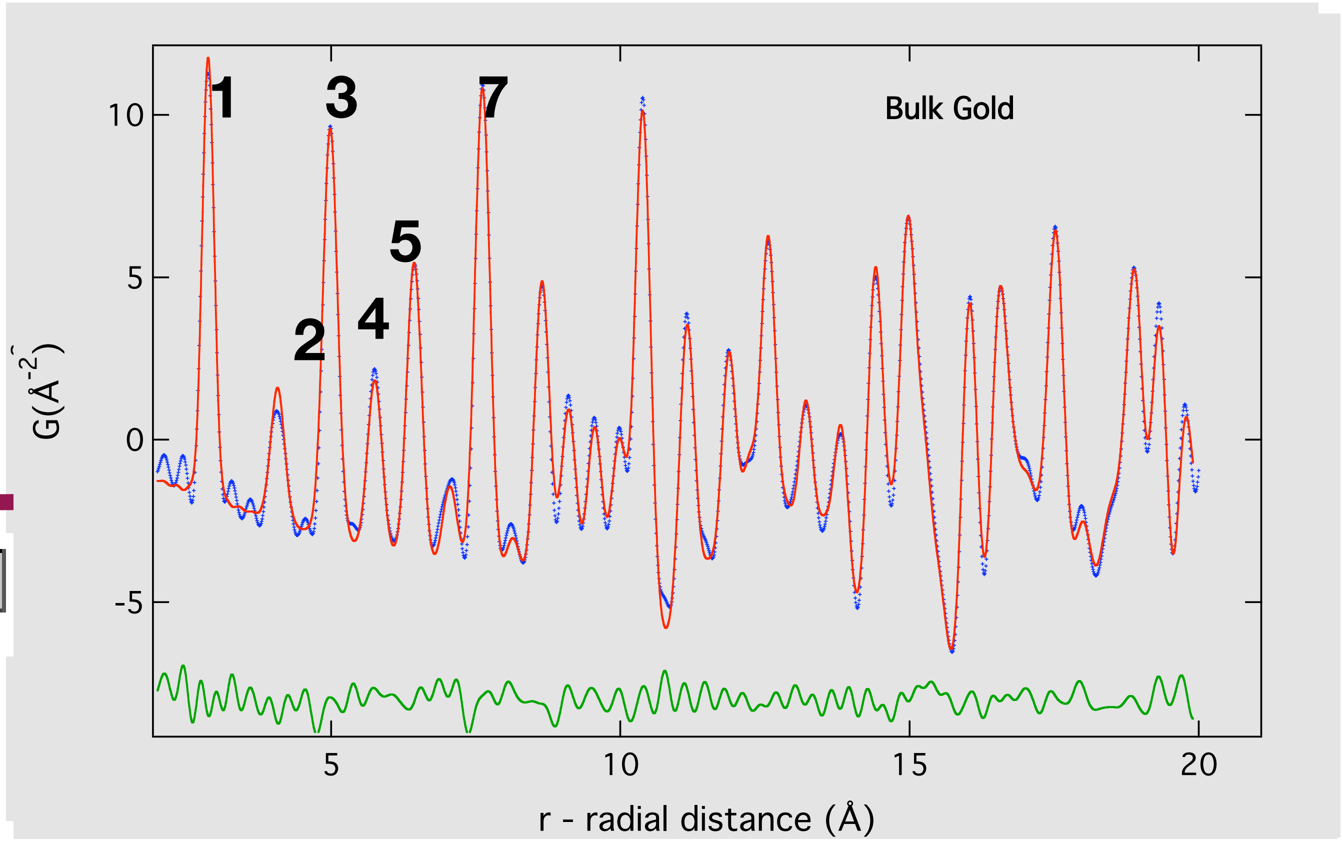
Pair Distribution Function analysis (PDF) *FROM TOTAL (BRAGG +DIFFUSE) SCATTERING*

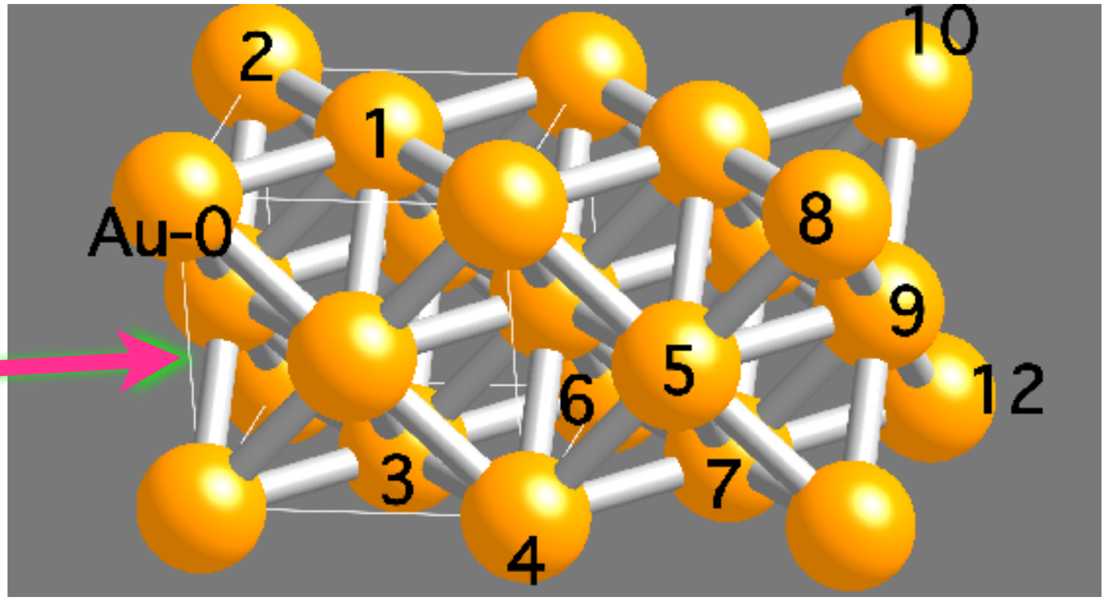
scattering (S(Q) - what we observe)

(G(r) + fit



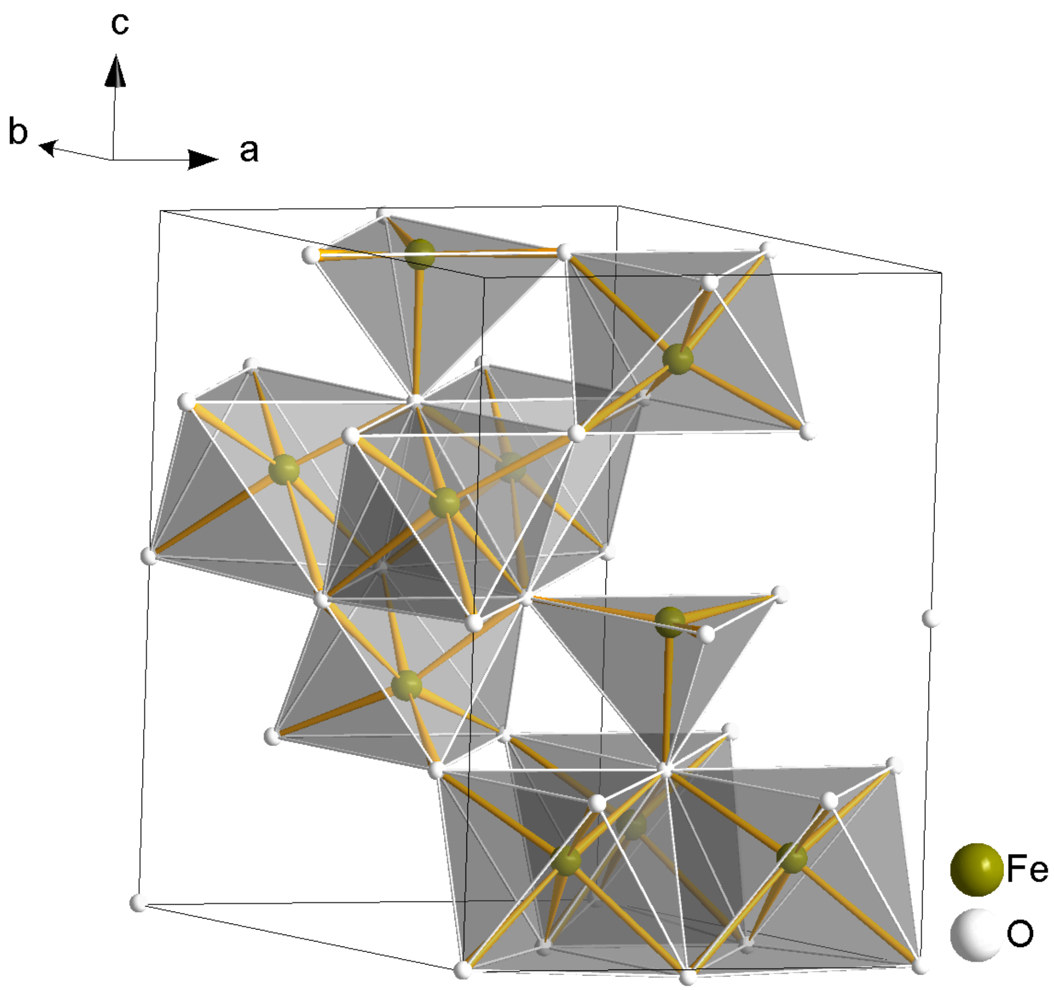
$\mathcal{F}_x[f(x)]$





Adjust this model, calculate the red curve to minimize difference with "observed" G(r) - the green curve

Synthetic Ferrihydrite (Stony Brook, X17A, APS, Temple)



Hexagonal Unit Cell

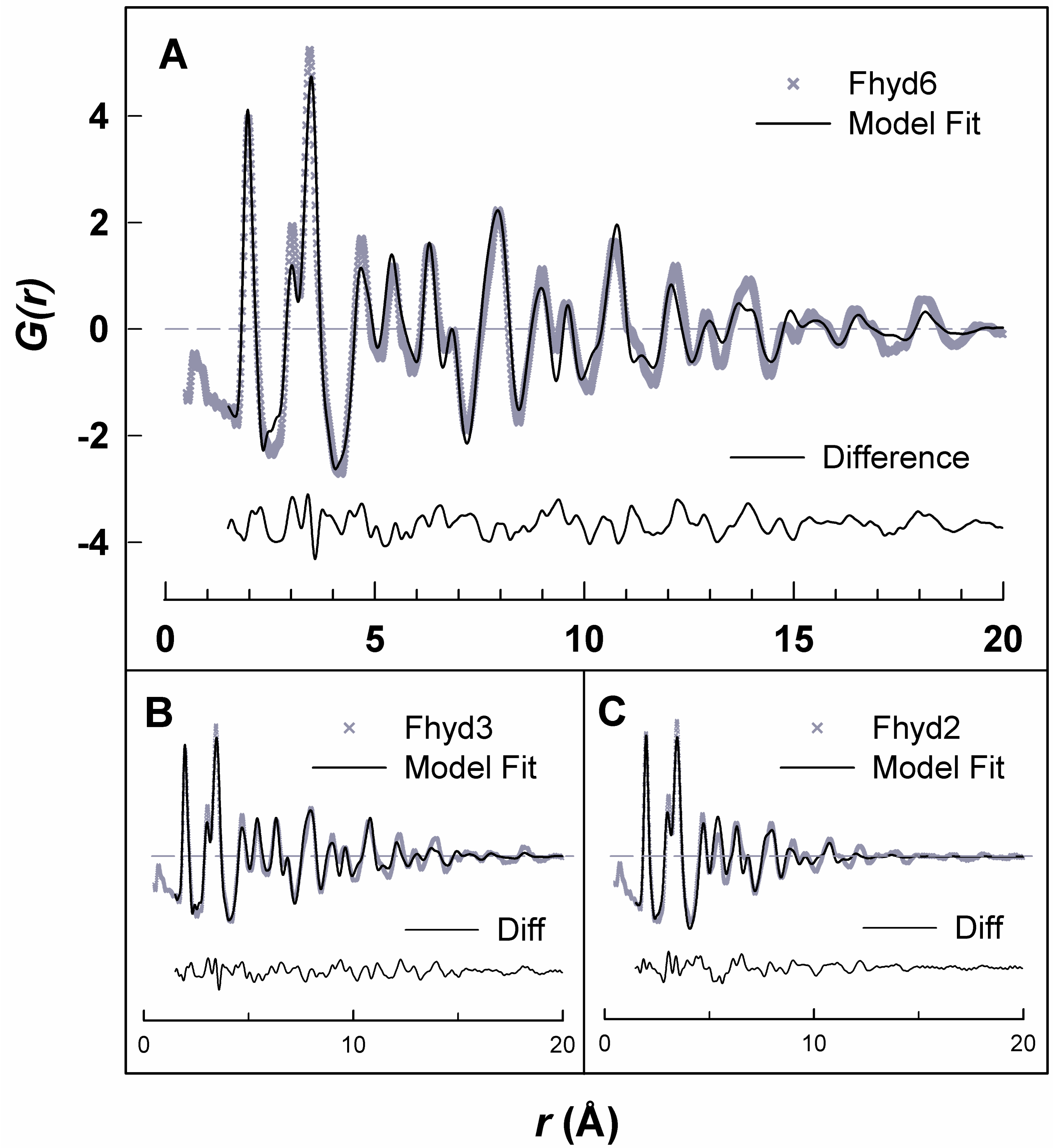
a = ~5.97 Å

c = ~9.03 Å

* *Particle size dependence*

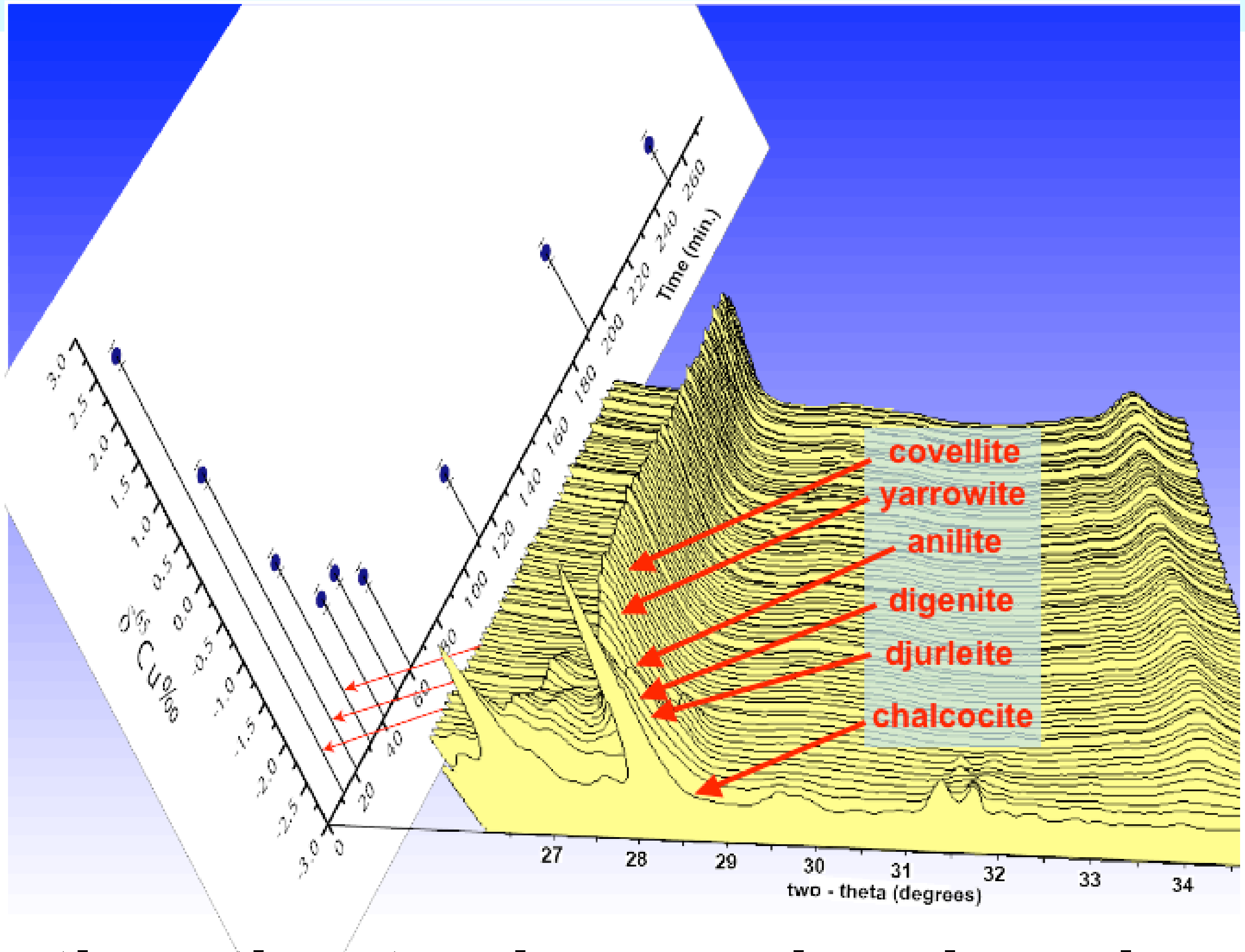
20% tetrahedral Fe

80% octahedral Fe



Michel et al., *Science*, **2007**, 316, 1726 - 1729.

(3) Reinventing materials cycles: Link Isotope Fractionation and Structure (Heaney, Post; Penn State/Smithsonian - X7B.

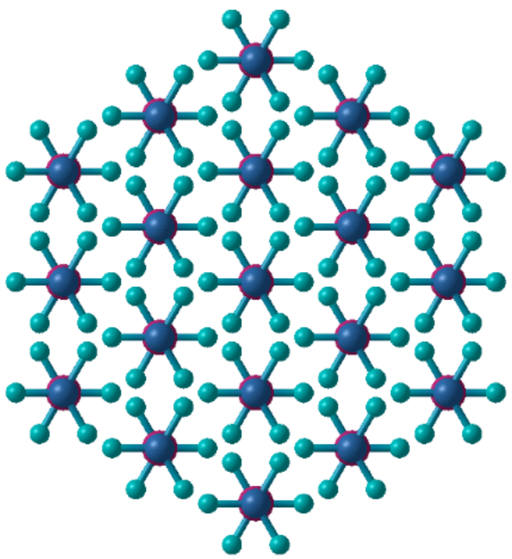


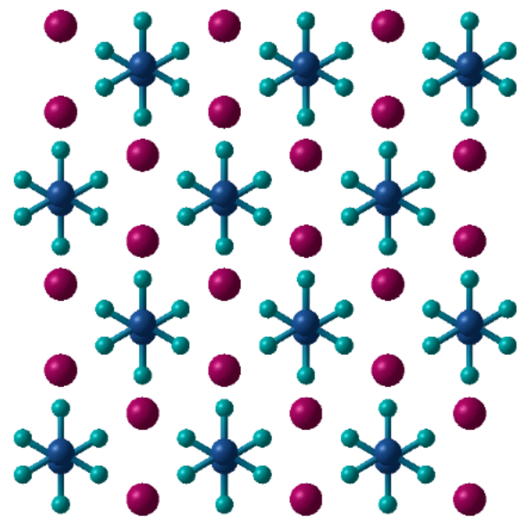
– Tie isotopic fractionation to changes in mineralogy with reactions (Cu ore distribution, role of organisms generation of acid mine waste). Cu extracted from chalcocite by leach, replaced by digenite ($Cu_{1.96}S$), anilite ($Cu_{1.75}S$), etc. Large change during chalcocite ⇒ digenite ⇒ crystal structure influences isotope fractionationation

(3) Reinventing materials cycles: Transformative Materials - decreasing the discovery-utility cycle

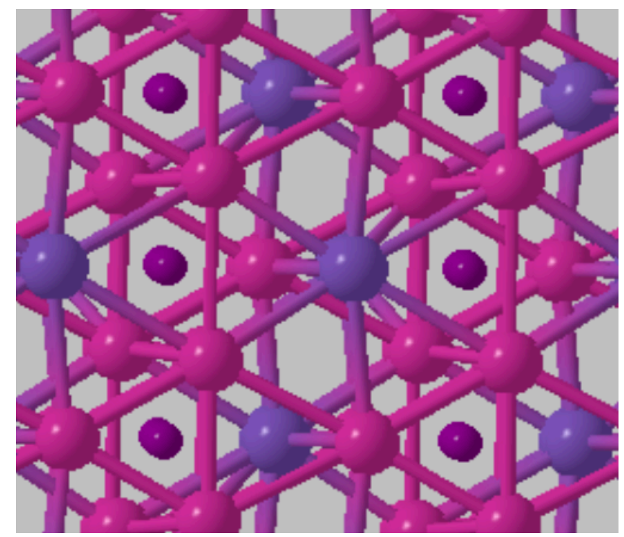
Joint computational - diffraction approaches

Well known and tested in cases where polymorphs (same composition different crystal structure) or polytypes are investigated

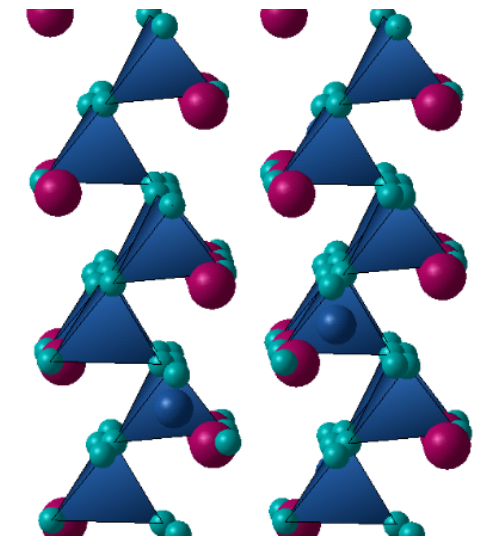




$CaCO_3$- calcite Aragonite (known)



post-aragonite > 42 GPa(verified)



$C222_1$ (140 GPa) (verified)

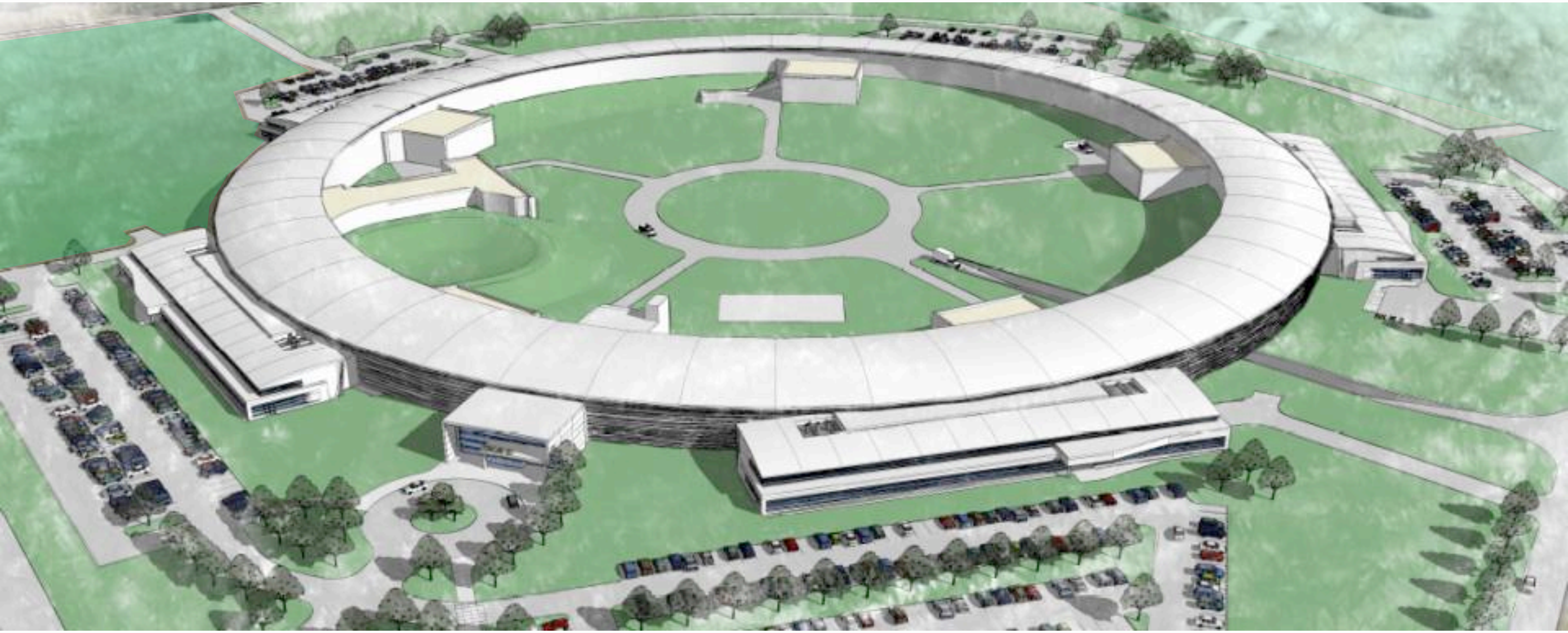
New methods of crystal structure prediction at modest pressures (Oganov, ETH): novel chemistry of carbonates. Joint computational - diffraction approaches

BNL with Blue Gene (next generation) and NSLS-II well placed to explore possibilities for variable composition

At NSLS NOW ......and getting ready now for NSLS - II

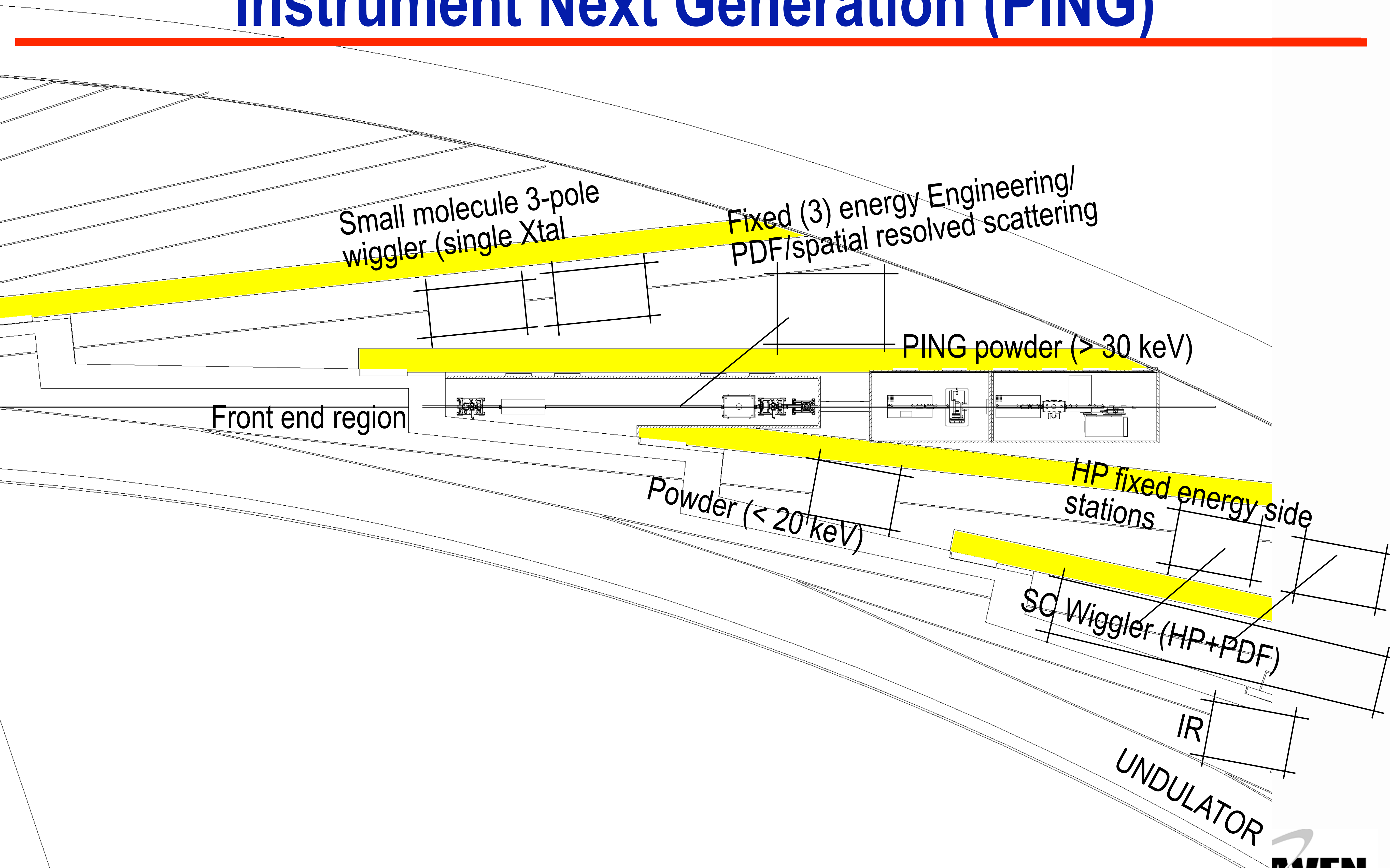
- ***Build-out of 17 - B - 1 including more experience with strip detector***
- ***continued development of next generation detection (X16, X7A/B- Siddons)***
- ***continued support for ancillary equipment for time resolved in situ studies (X7B/A)***
- ***testing the ideas of consistent mechanical coupling for environmental cells (gas pressure)***
- ***A core group devoted to in situ studies - volenteers?***
- ***Your input HERE please***

Powder Diffraction Beamlines: including Powder Instrument Next Generation - PING



Parts lifted directly or slightly adapted from Andy Broadbent, NSLSII PD Workshop, 16 Jan 2008.
Courtesy of J.M. Ablett & D.P. Siddons, ACCEL Instruments, and others.
Largely based on material presented at the NSLS-II CD-2 DOE Review November 7, 2007

A FLUID beamline suite anchored on Powder Instrument Next Generation (PING)



Scientific Mission of NSLS-II Powder Instrument Next Generation (PING)

PING - tunable, high-resolution (angular, spatial) high E (30 - 100 keV), fast (milli-second)

Energy range make Unique in US inventory; With couple sample environment unique in world!! Plans to engage wider community in sample environment design (standard mechanical coupling

Some Scientific Thrusts:-

- Structural studies – crystal structures, atomic PDF analysis, glasses, geo-nanomaterials.
- *In-situ* studies – phase changes, solid-state chemistry, adsorption / desorption, electrochemistry, etc.; temperature, pressure measurements.
- High throughput – many samples, varied compositions, preparation conditions, etc.
- Quantitative analysis – many phases, trace phases.
- Microstructure – detailed analysis of peak shapes.
- Residual strain – mapping peak positions in components.

Powder Instrument Next Generation (PING) Beamline Advisory Team (BAT) -

Billinge, Chupas, Ehm, Hanson, Kaduk, Parise, Stephens

Materials Physics, Materials Chem., HP/crystallography, Catalysis, Industry, Enviro, Diffraction Physics

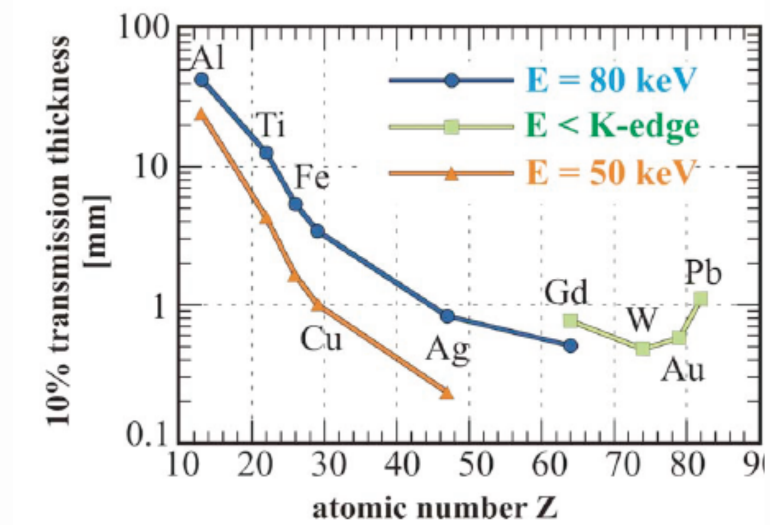
Geography: mostly NE + 2 MW

National Lab, Academia, Industry stake holders, DOE, NSF, NASA...

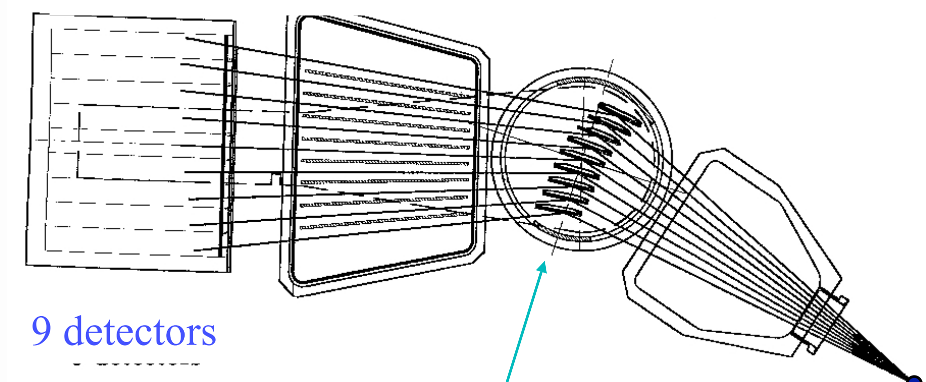
More diverse participation welcome

PING 1 - detectors

Environmental Cells
High-q (Atomic PDF,
DAC). Thick/ High-Z materials → High- Energy (> 40 keV)



Accurate Peak detection
& profile measurements → High- Resolution (analyzer)



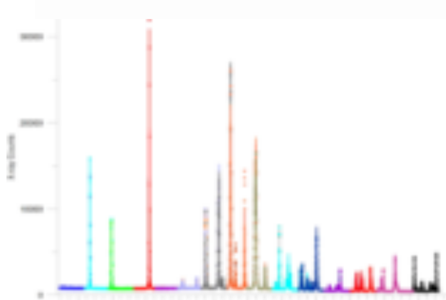
9 detectors

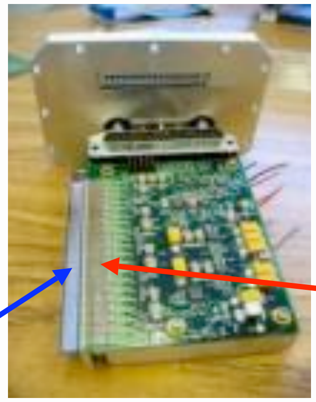
9 Si 111 analyser crystals

Sample

Kinetics → Fast (msec)

BNL 7000-element silicon strip array detector





sensor
640 strips
125um pitch

20 ASICs
low-noise preamplifiers + discriminators + counters

Office of Science
U.S. DEPARTMENT OF ENERGY

BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES

2.3 Power Load Considerations

How can reduce the 65kW incident power load to something reasonable?

- by means of a tight aperture (1mrad H, x 0.1mrad V), we can reduce the heat load to 5kW, and
- by including heavy filters (~5mm carbon) to remove low energy x-rays we can reduce the heat loads on the Laue mono to manageable values.

This restricts the beamline to >20keV operations.

WORKSHOP DISCUSSION

removal of the mirror and insertion of more filters

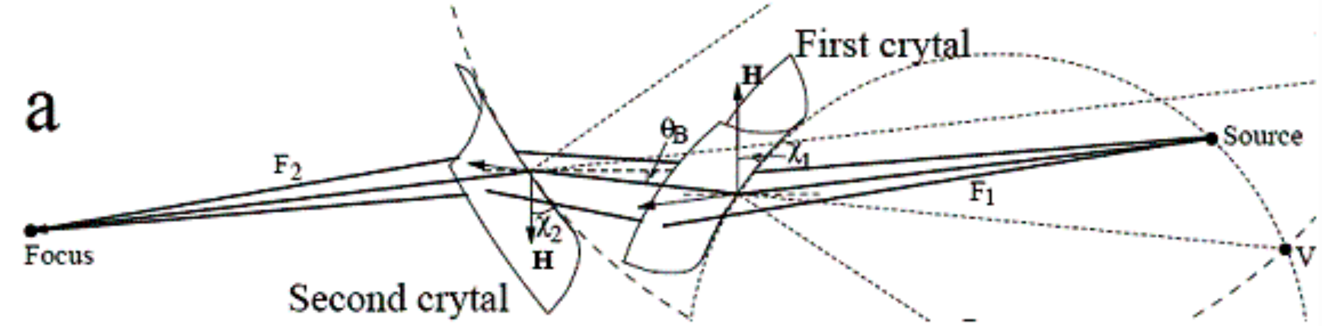
bring out side station for fixed (say 3) energy

low heat on Laue-Laue mono, focus CRL, H & V

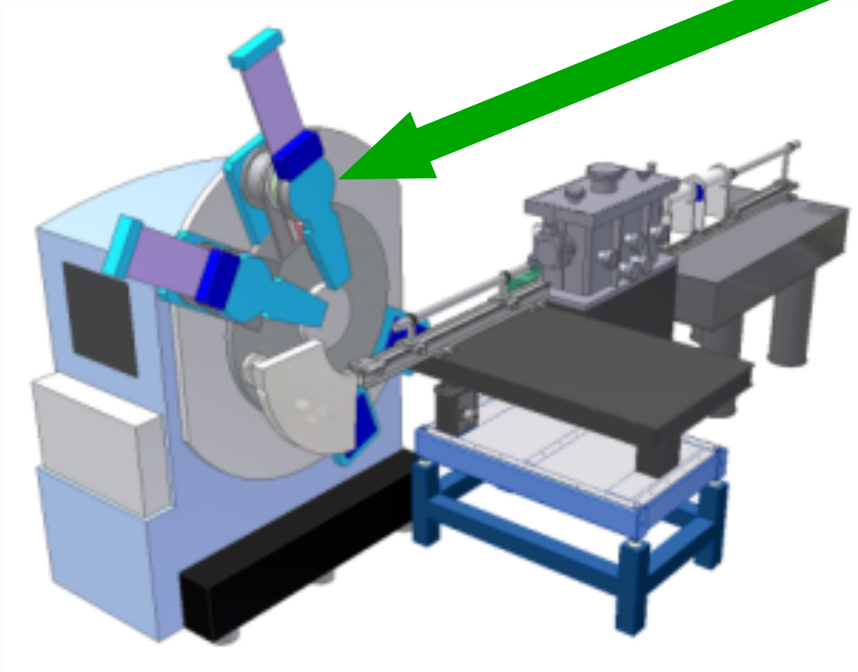
Restricts operations to (say) > 30 keV

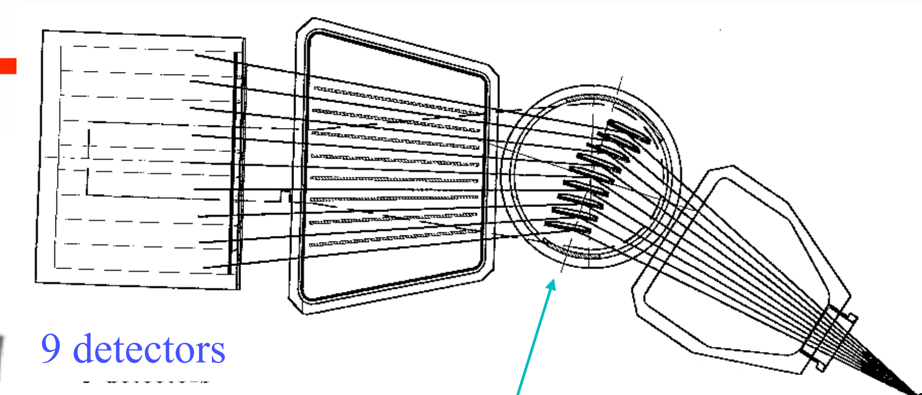
2.5 Sagitally Focusing Double-Crystal Laue Monochromator

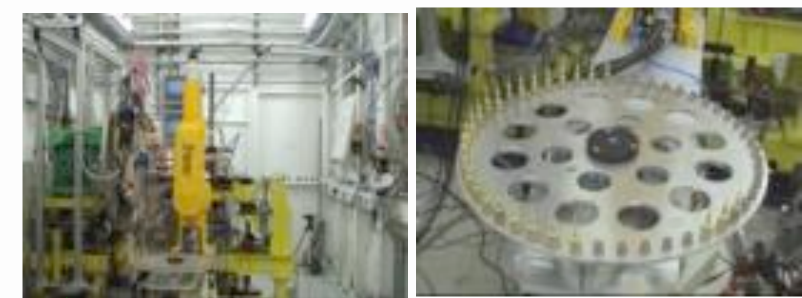
- In use at NSLS X17, (tested for X7B)
- Can take a large horizontal fan (> 3 cm) and focus it down to a few hundred microns
- Fixed Exit - modified boomerang style design
- Asymmetric Bent Si (111), Si (311)
- Band-Width (in focusing mode)
dE/E ~ few x 10^{-3} for Si(111) ~$1x10^{-4}$ for Si(311)
- Energy Range: 20 to 100 keV
- Side-water cooling works at X17, but
more power on NSLS-II damping wiggler



PING - Front Hutch







ESRF robot

Key Features

High resolution diffractometer

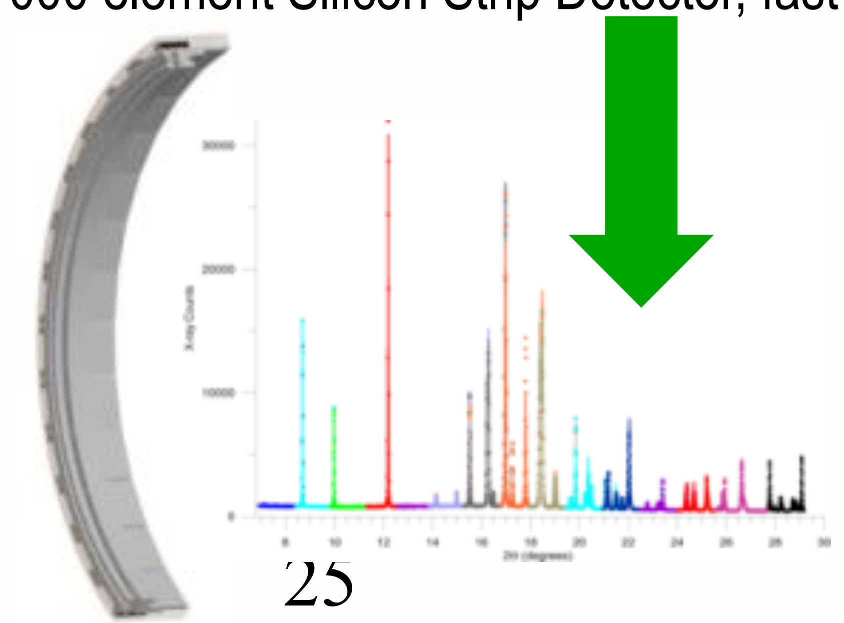
Graded Multilayer Focusing

Robot Sample Changer * not shown

Sample environments (furnaces, DACs, cryostats)* not shown

Laue Analyser Crystals

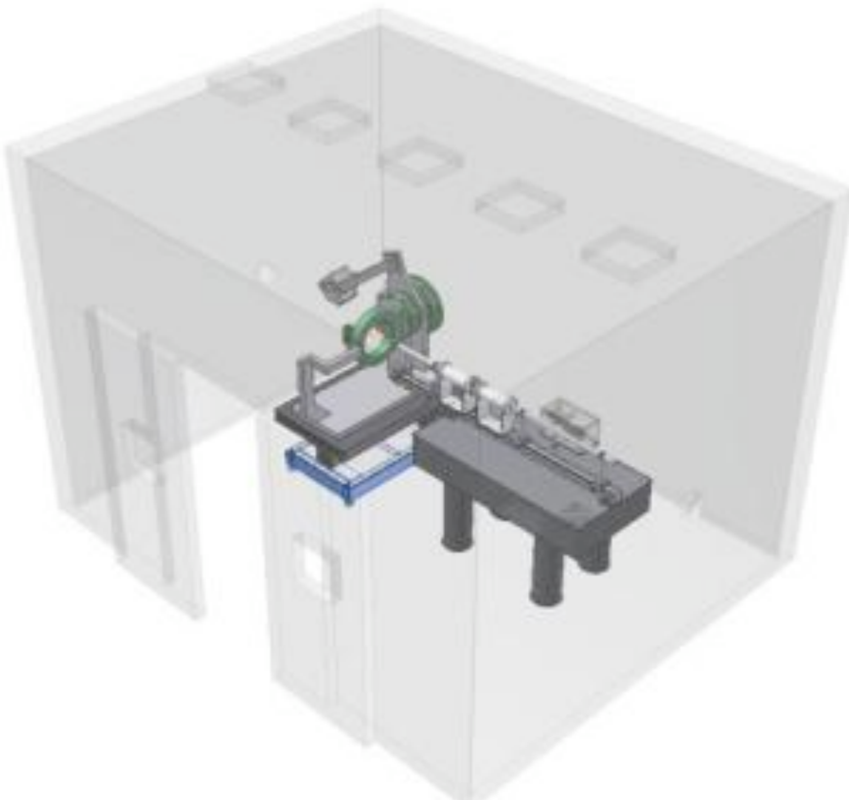
7000 element Silicon Strip Detector, fast read out (msec)

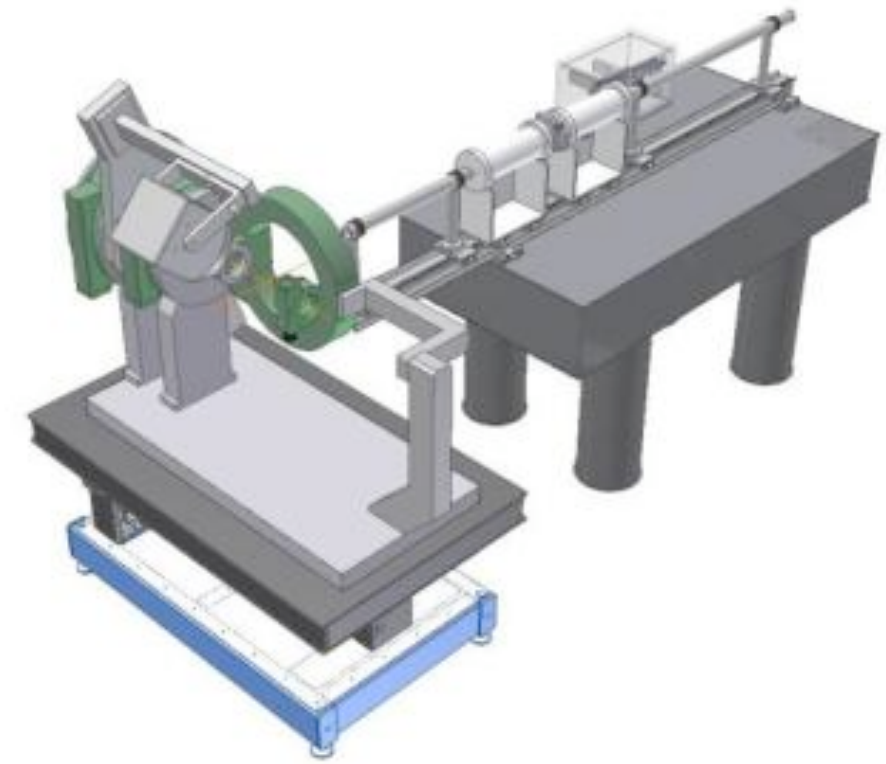


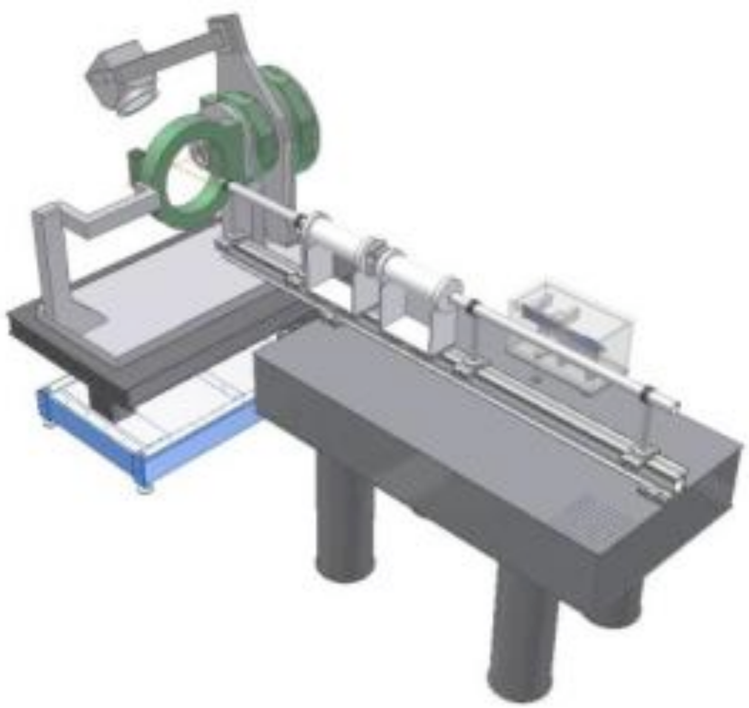
Funding OPPORTUNITY

Combined SAXS/WAXS with 2 area detectors

PING - Back Hutch funding opportunity







<u>Enclosure *only* costed, equipment to be used from NSLS-I</u>

<u>Key Features</u>

CCD area detector, SAXS/WAXS??

Graded Multilayer Focusing * not shown,

Robot Sample Changer * not shown

Sample environments (furnaces, DACs, cryostats)* not shown

Breakout V (Materials): Surface and Interface Science - need input from this group

- One beamline with as many stations as possible will accommodate multiple generic types of systems. The stations will be configured to maximize beamline productivity and throughput.
    - Large instruments customized for various materials growth and processing techniques require extensive support facilities and are not easily moveable. Requires dedicated hutch.
    - Medium instruments also require significant support facilities. Can be moved, e.g. to swap processing systems, but significant setup time (days) is required.
    - Small systems that can be mounted on a four circle diffractometer or other standard piece of equipment. Modest setup time.
    - Ex-situ measurements. No significant setup time.

Preliminary Beamline Specifications

- High brightness undulator source.
- Energy range 2 - 25 keV.
- Choice of bandwidth: 1%, 0.01%, 2eV.
- Focussing elements for ~30 micron to ~50 nm at sample inside processing environment.
- Multiple end stations with various size/complexity growth and processing equipment.
- Ventillation, gas handling, fume hood, etc.
- Close proximity and easy access to LOB.
- Desks for students.

Uniqueness

- Many materials and condensed matter systems have inhomogenous structures on the scale of ~1 micron. Structures through lithography and patterning.
- Use the high brightness of the NSLS-II source to provide small beams in-situ; examine surfaces and films on this scale. Best resolution compatible with processing environment is ~20-50 nm.
- Simultaneously maintain highly parallel beams for diffraction contrast imaging.
- Capability of 0.2 eV energy resolution for chemical or magnetic contrast through resonance.
- Possible opportunities to partner with industry.

Beamline Layout

- Part or all of beamline external to NSLS-II building in order to accomodate large equipment, multiple hutches.
- Connection to LOM preferred.
- Other configurations (canted undulators, etc.) need to be considered.

R&D Needs

- Endstation design. Collaborate with APS?
- Phase retrieval for surface/interface structure determination.
- Detector development: Strip detectors, area detectors with special capabilities such as microsecond time resolution, energy resolution.