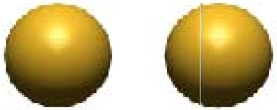
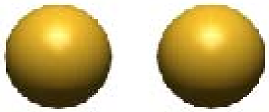
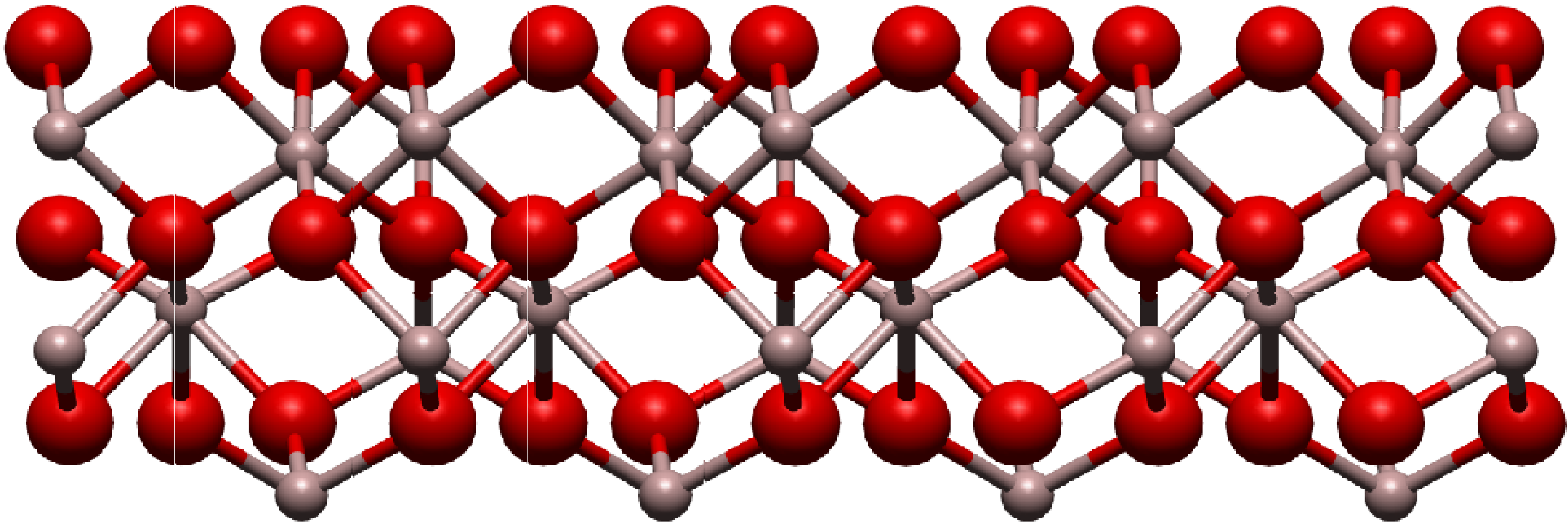
The GeoSoilEnviroCARS APS Sector 13: From the Surface to the Core



Peter J. Eng
Consortium for Advanced Radiation Sources (CARS)
and The James Franck Institute (JFI)
University of Chicago

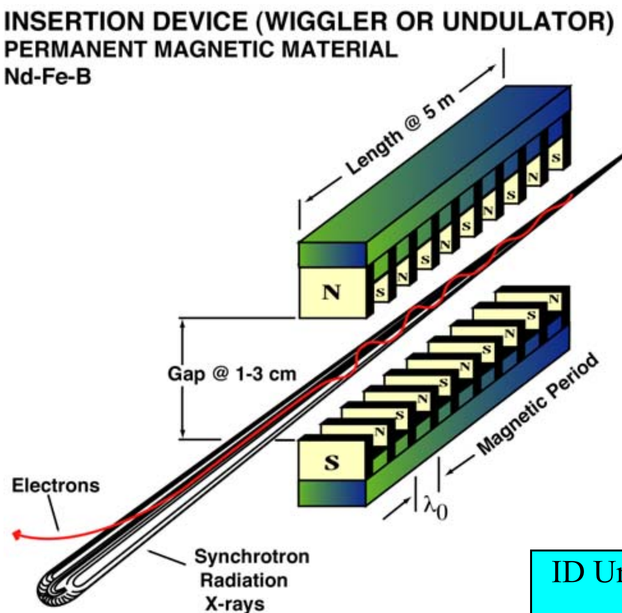


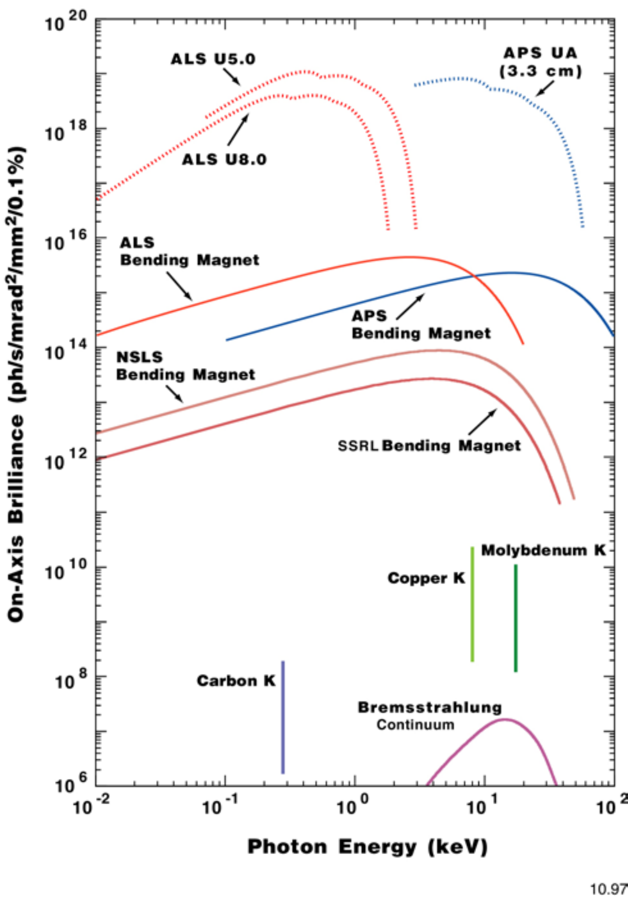


- Consortium for Advanced Radiation Sources (CARS) operates beamlines at the APS and NSLS
- Operated by faculty and staff from the University of Chicago
- Seeded by funds received from University of Chicago in 1992 (Joe Smith)
- Distributed over three sectors (with individual PI's) in 1993:
  - GeoSoilEnviroCARS – sector 13
  - BioCARS -- sector 14
  - ChemMattCARS – sector 15
- Phase one construction fully funded for all three sectors by 1995.
- First beam 1996
- Presently CARS has nine operating end stations (two more soon) with nearly 100% of the available beamtime allocated through the APS general user proposal system.

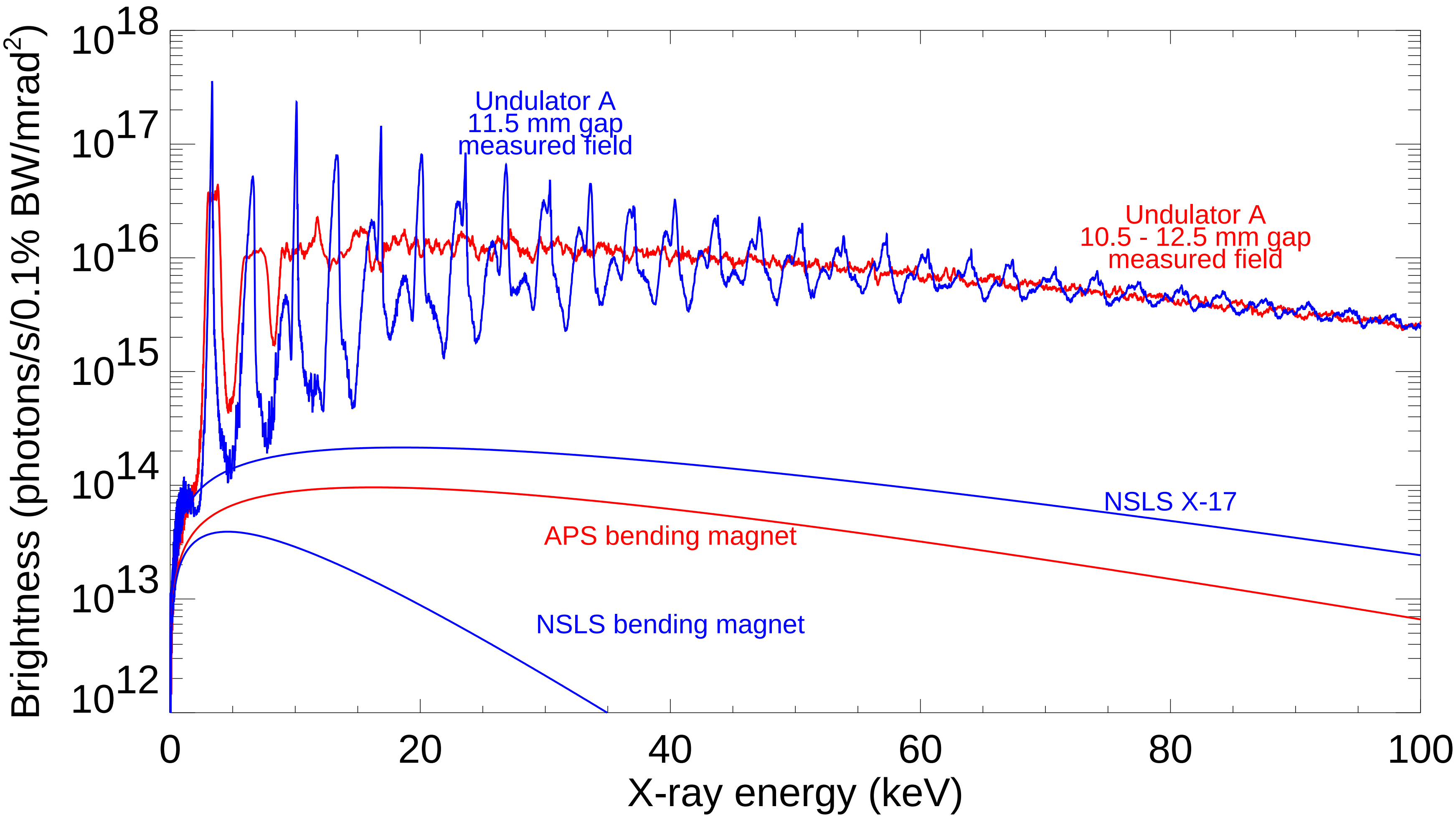
- Scientific objective: Operate a national user facility at the APS to conduct experiments in earth, planetary, soil, and environmental sciences.
  - Since 1998 we have received 709 beam time proposals from 443 independent investigators resulting in 225 peer-reviewed publications and are 2 ½ times over subscribed.
- Experimental techniques include:
  - Diffraction at high pressure and high temperature using both diamond anvil cell (DAC) and large volume press (LVP) apparatus.
  - Single crystal diffraction studies of micro crystals and surfaces
  - Spectroscopic studies including surfaces, interfaces, and microspectroscopy
  - X-ray fluorescence (XRF) microprobe studies of trace element distributions
  - Micro Tomographic imaging, adsorption and fluorescence
  - Inelastic x-ray (IXS) scattering at high pressure and in liquid environments
- Why we need the APS?
  - Extremely small and / or heterogeneous samples require a source with high brilliance
  - Samples contained in highly absorbing apparatus require a large flux of high energy photons

Introduction - APS



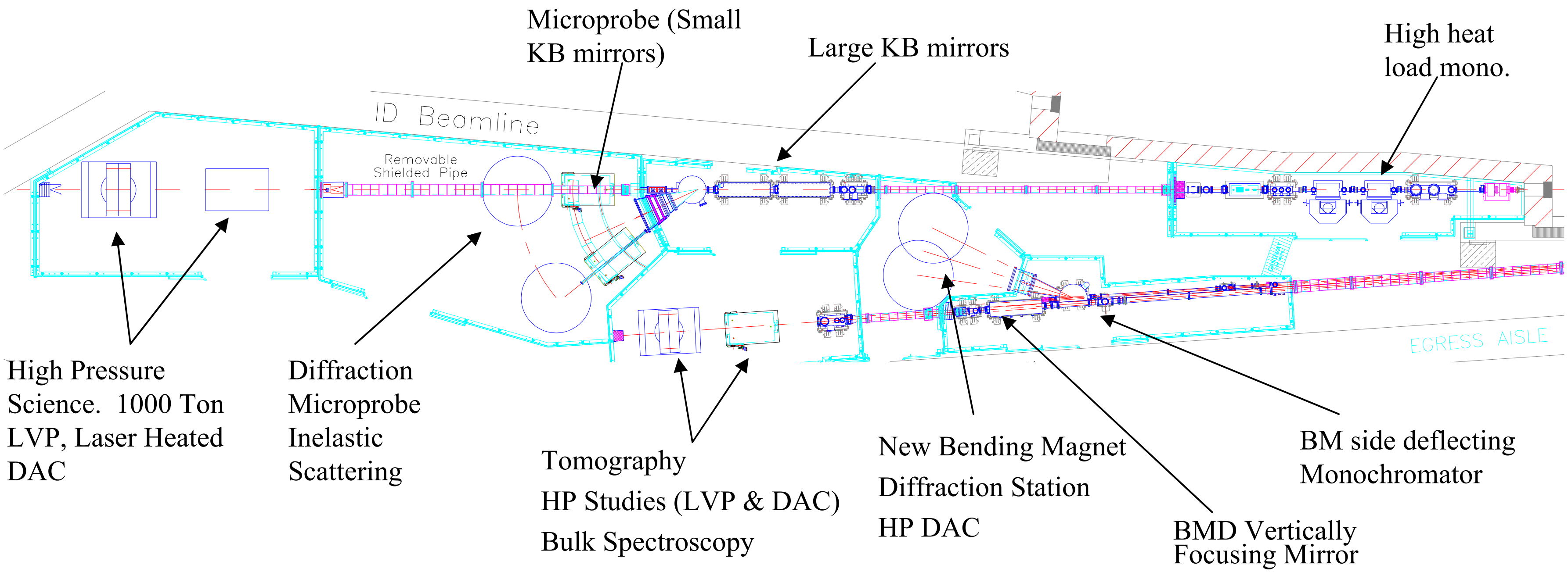


ID Undulator A Characteristics (2% Coupling)	
Horizontal Size [σ]:	208 μm
Vertical Size [σ]:	17 μm
Horizontal Divergence [σ]:	15 μrad
Vertical Divergence [σ]:	6 μrad
BM Characteristics	
Horizontal Size [σ]:	74 μm
Vertical Size [σ]:	35 μm
Vertical Divergence [σ]:	59 μrad



For XAFS (requiring ~ 1 keV scannable range), the undulator is scanned in unison with the monochromator. For energy-dispersive diffraction the undulator is run in tapered mode, where the spectrum is quite smooth above 20 keV.

Experiment setup – Beamline Layout and Optics



- All hutches are white beam capable
  - Two operating ID stations
  - One operating BM station
  - Second BM station planned to start commissioning 3rd Quarter 2004

- X-ray Optics
  - ID line
    - Cryo Cooled Si 111 (4.5 to 45 keV
    - Large KB mirrors Demag ~ 10:1
    - Small KB mirrors Degmag ~500:1
  - BM line
    - Water Cooled Si 111 (4.5 to 70 keV)
    - Side Deflecting monochromator
    - Vertical focusing mirror

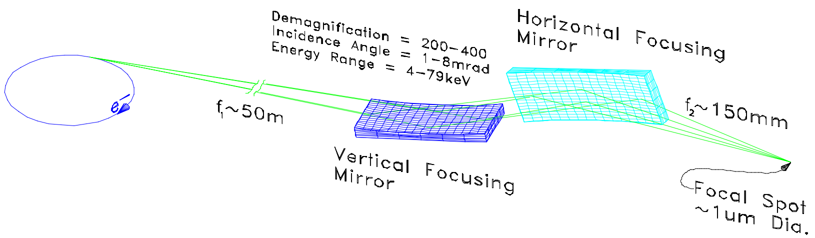
Experiment setup - Beamline Layout and Optics - Scientific Requirements

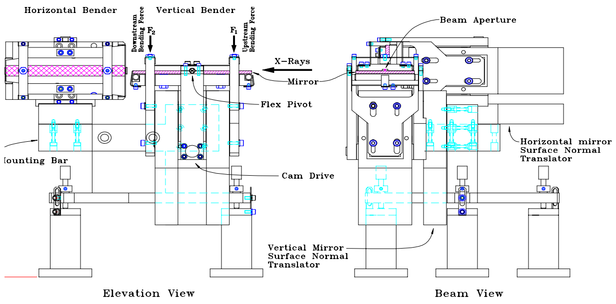
- Many earth science problems involve heterogeneous systems on length scales ranging from 500μm to 0.5μm.
- The high brilliance of the APS undulater allows us to strongly focus the beam while keep the divergence to levels acceptable to most of our measurements.
- Achromatic focusing needed to support spectroscopy, and multi wave length scattering experiments.

- Techniques:
  - Micro-crystal diffraction
    - Ambient conditions mounted on tapered glass fiber
    - DAC single crystals up to 20Gpa
  - Surface Scattering
    - CTR
    - Reflectivity
  - Surface Spectroscopy
  - Micro-Probe
    - Elemental mapping
    - Spectroscopy
    - Tomography
  - Inelastic scattering

Experiment setup – Beamline Layout and Optics –- KB Microfocusing Optics

Double Focused Beam using Two Grazing incidents Elliptical Figured Mirrors





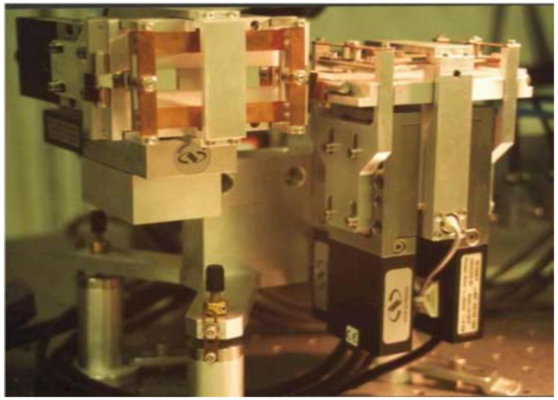
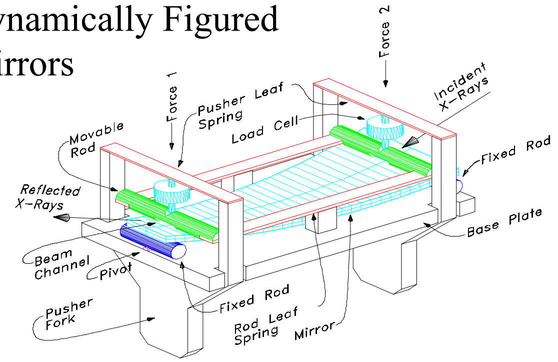
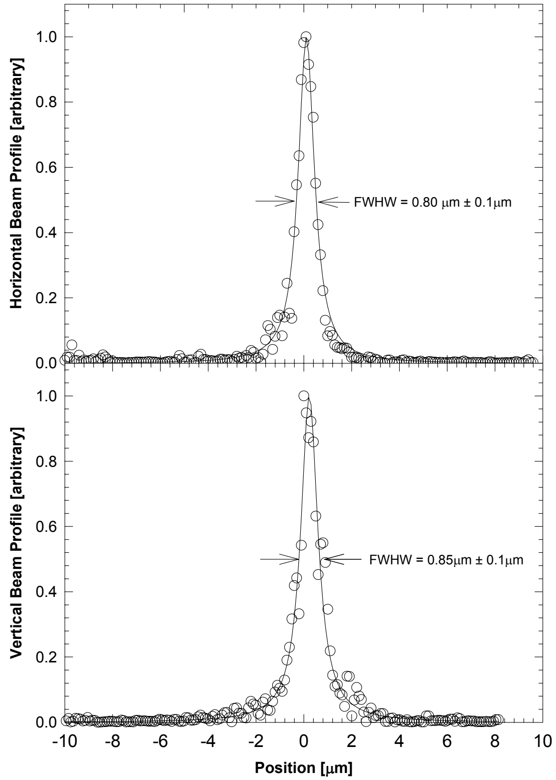


Fig 3. GSECARS KB micro-focusing system. The top panel shows the horizontal and vertical benders mounted on a on mounting bar with their beam apertures aligned. The lower panel shows a photo of the system installed on the probe table (beam enters from the right.)

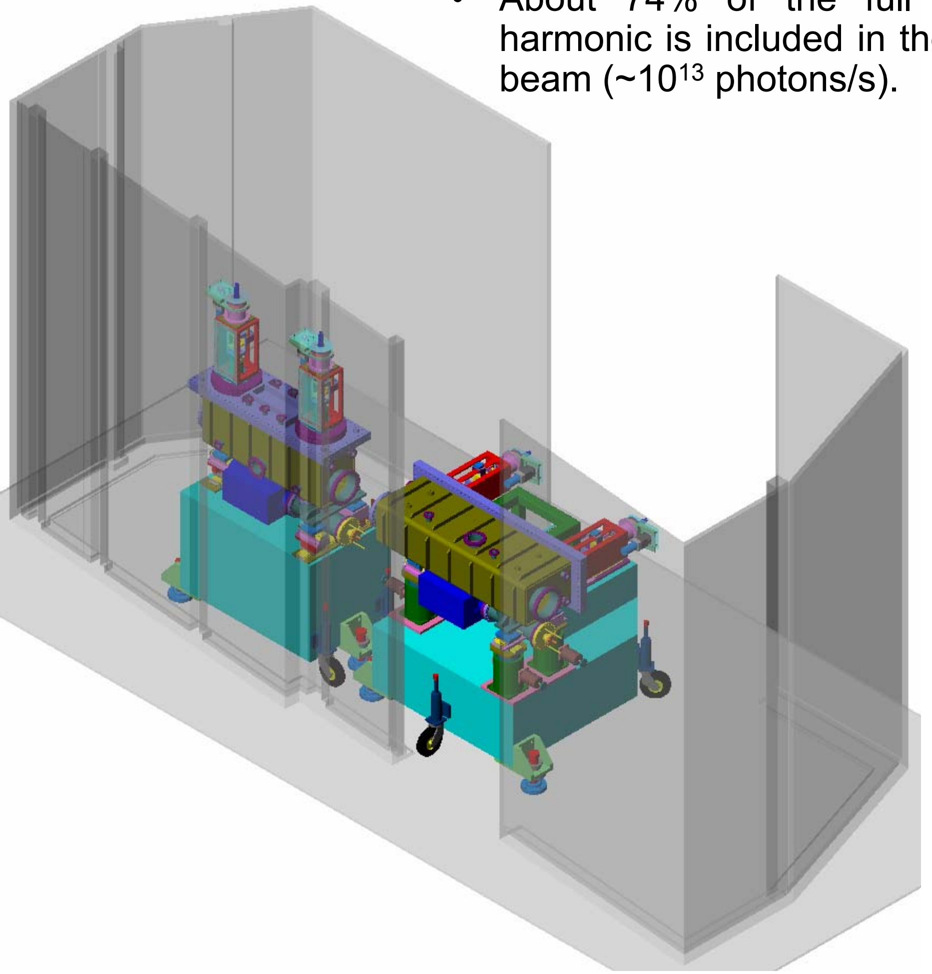
Dynamically Figured Mirrors

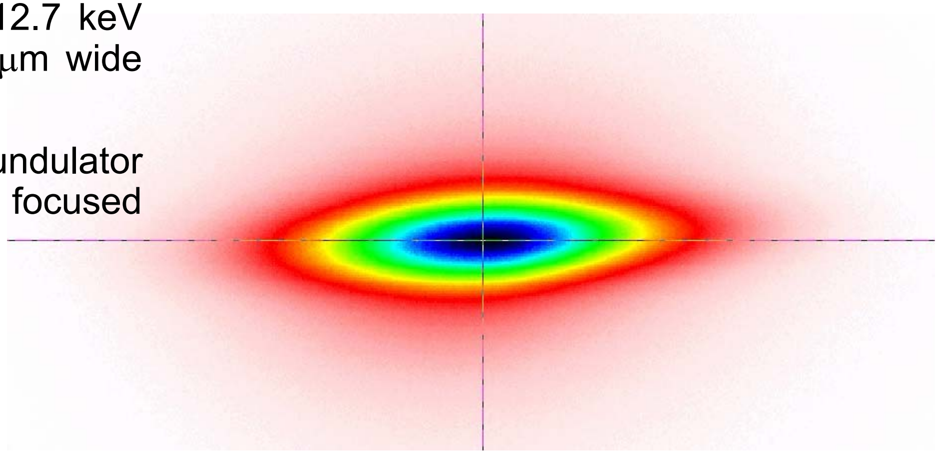


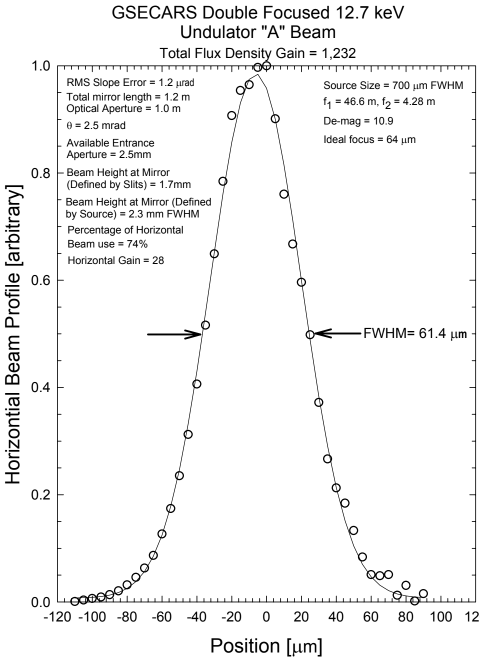


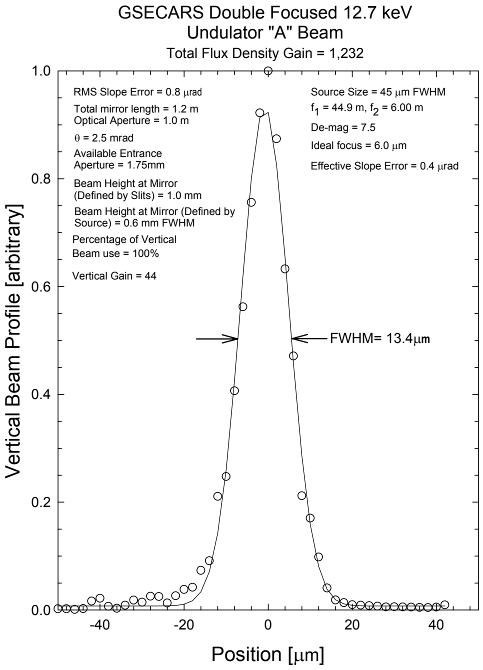
Experiment setup – Beamline Layout and Optics – Large KB Mirrors

- Image of double focused 12.7 keV Undulator “A” beam: 61.4 μm wide by 13.4 μm tall.
- About 74% of the full undulator harmonic is included in the focused beam (~10^{13} photons/s).

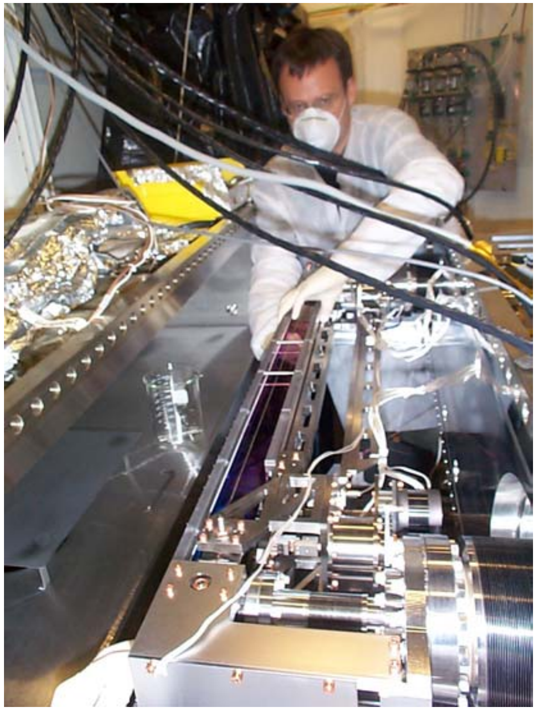


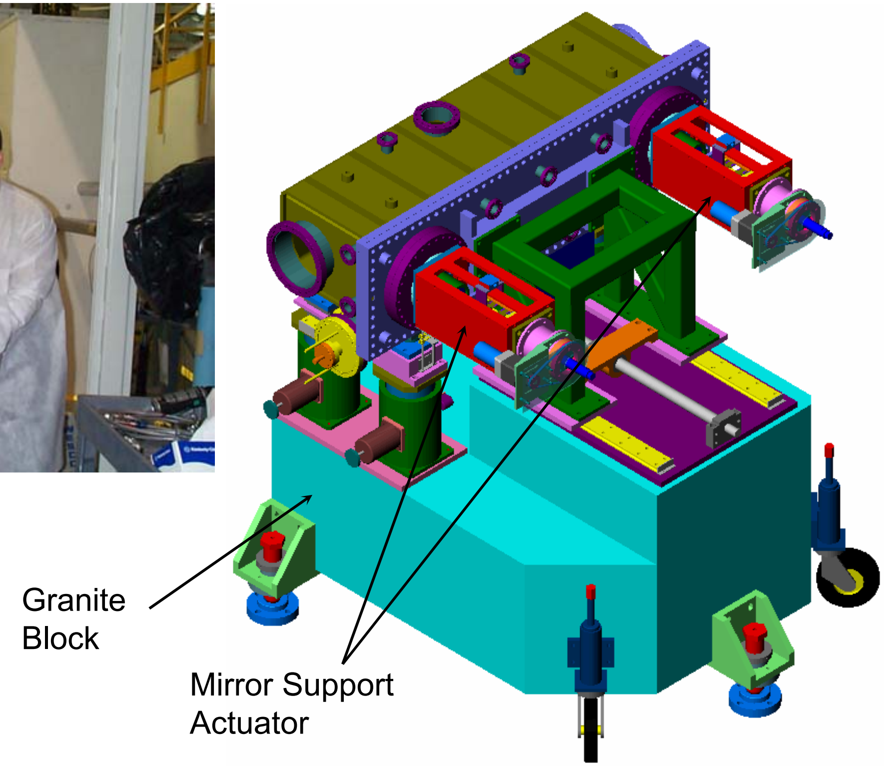


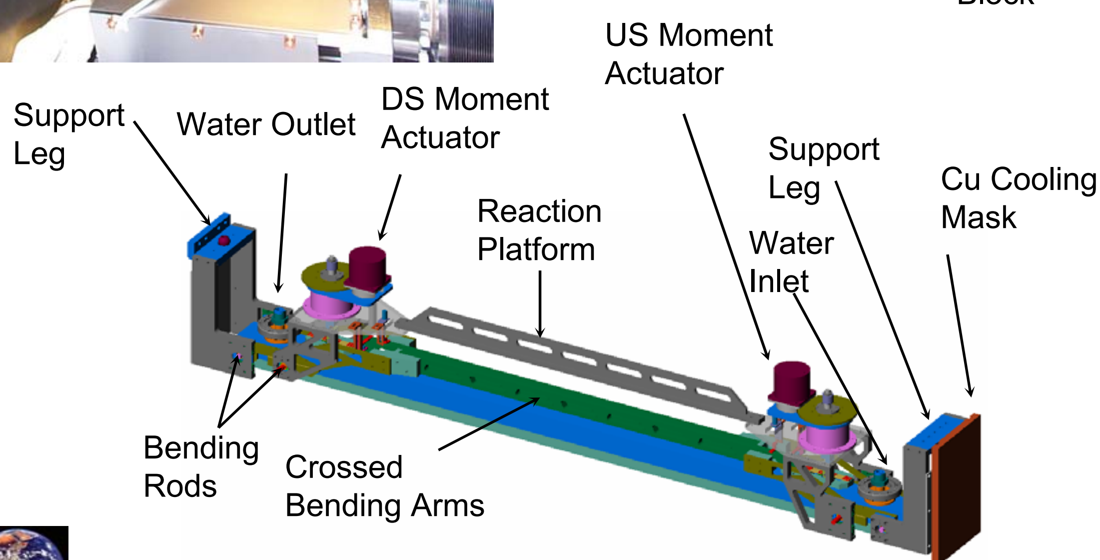




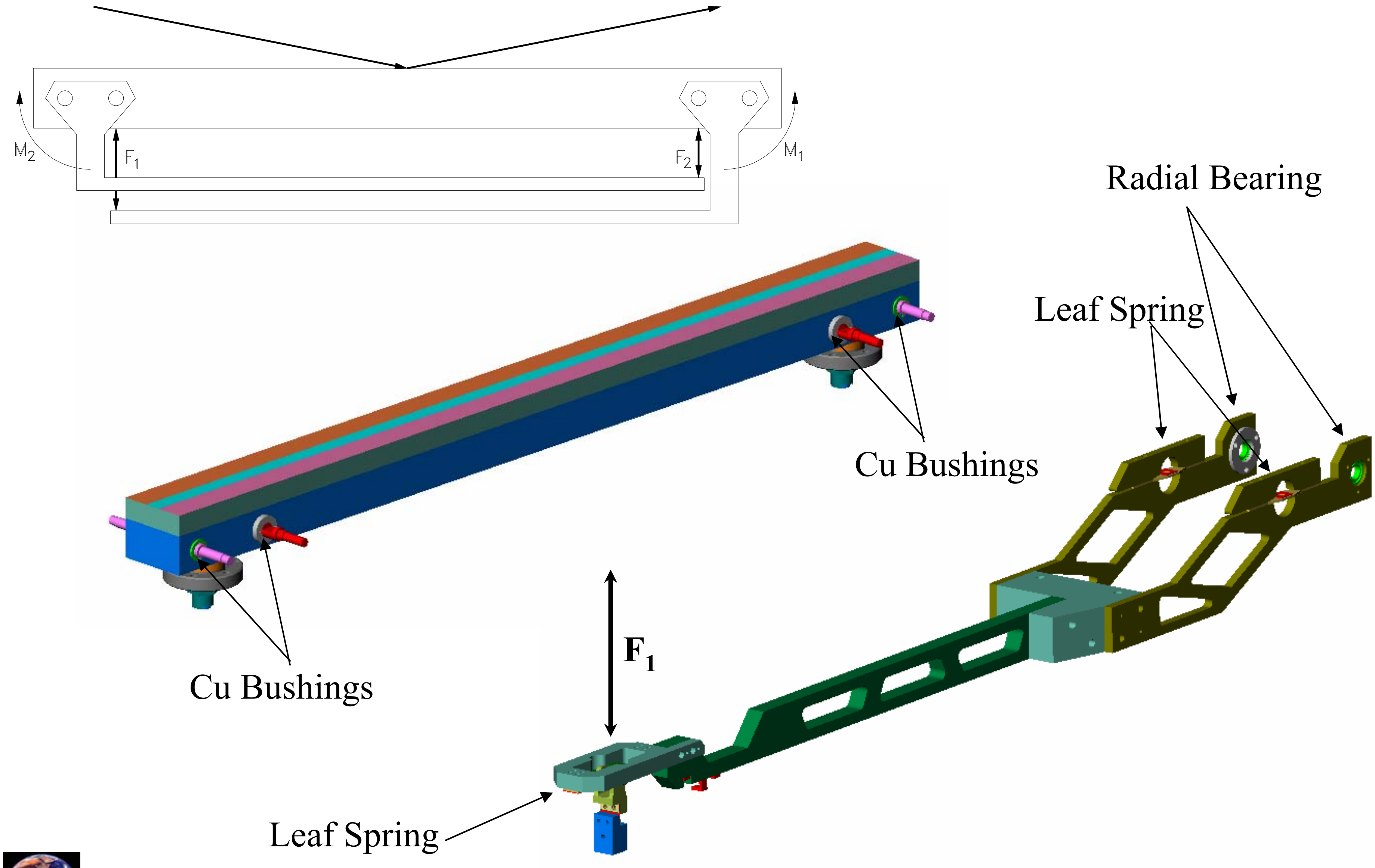
Bender Design – Vertical and Horizontal Mirrors Systems Installed in SOE



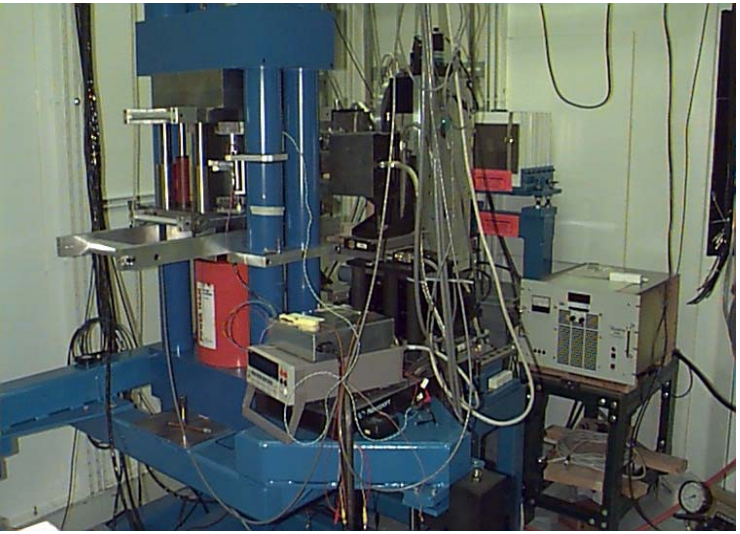




Bender Design – Stable Two Moment Mirror Bender

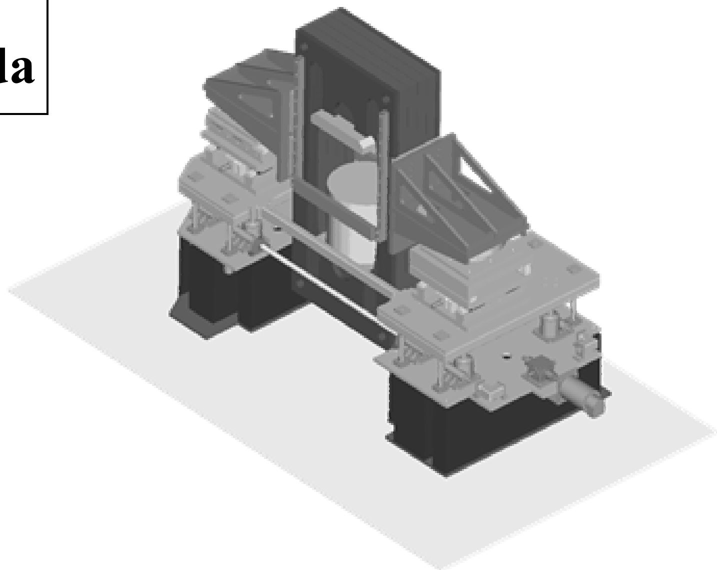


250 T LVP: BM Line

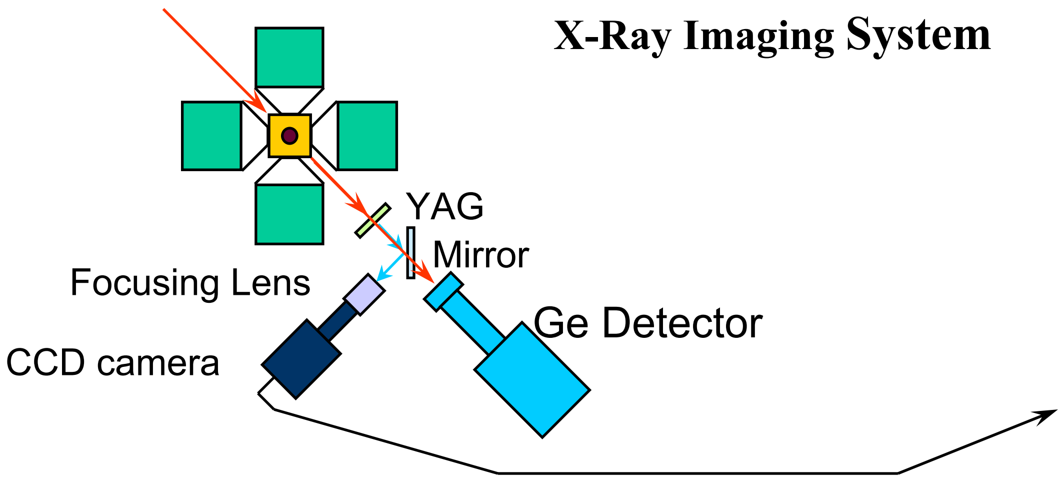


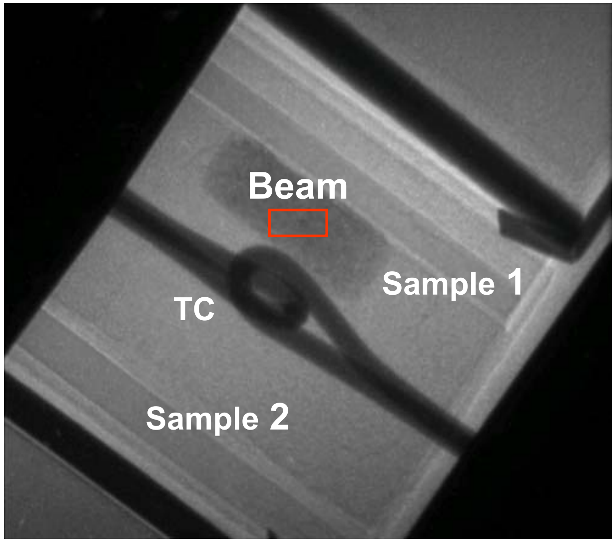
Yanbin Wang
Takeyuki Uchida

1000 T LVP: ID Line

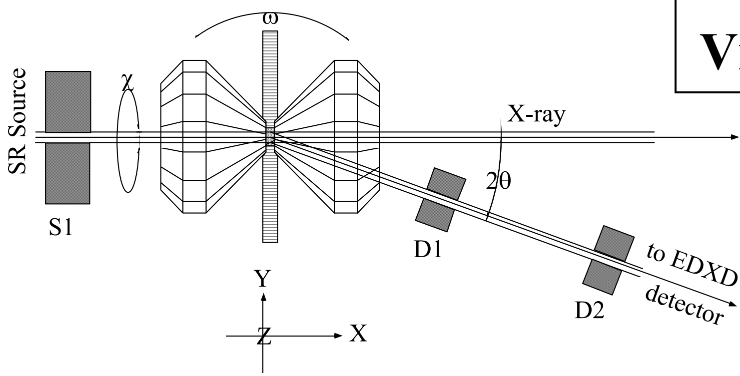


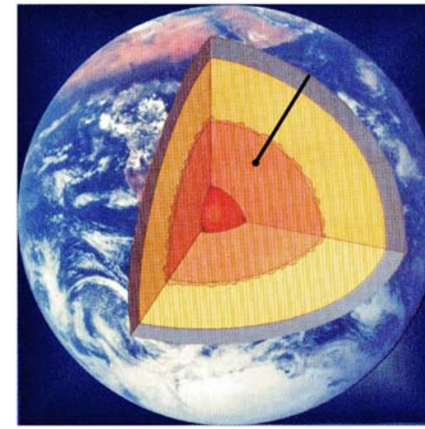
X-Ray Imaging System





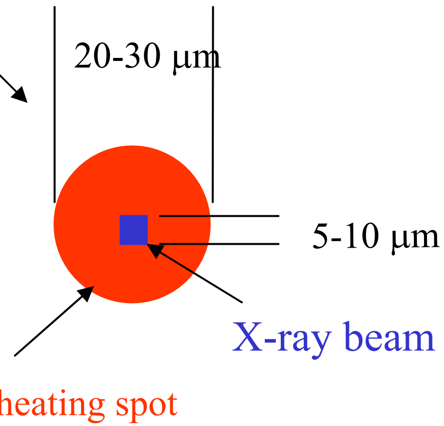
Guoyin Shen
Vitali Prakepenka

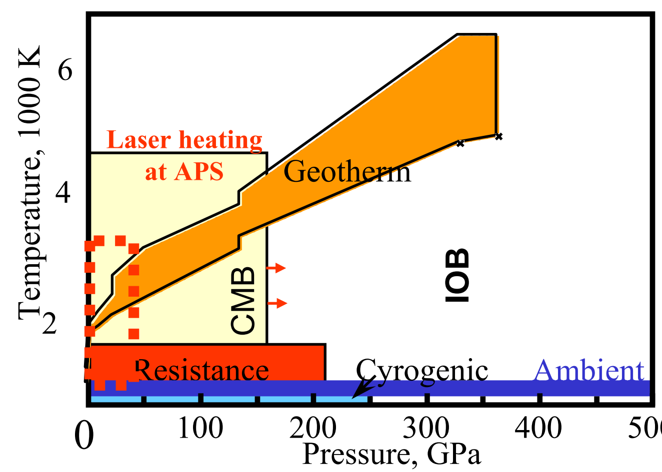




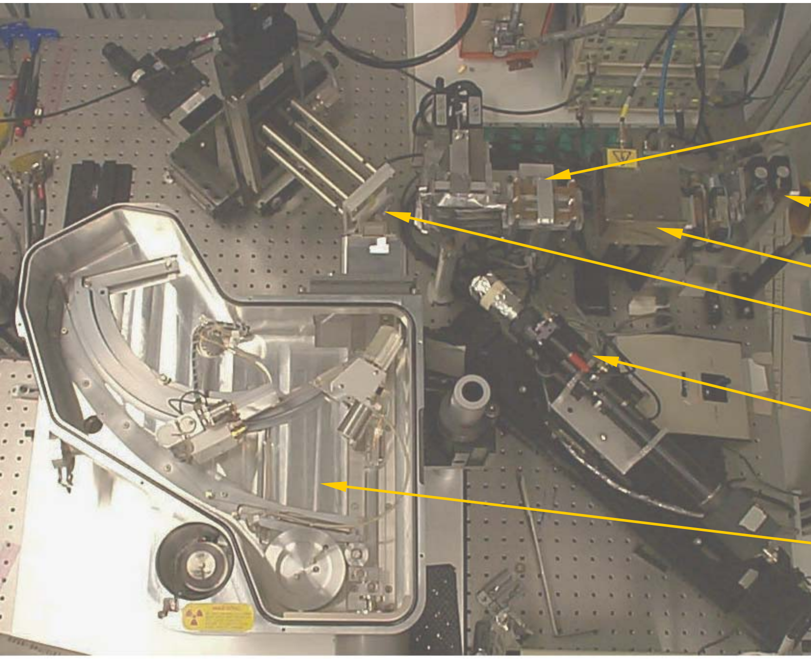
High P **High T**

P	*d*	*Volume*
50 GPa	~200 μm	~10 nl (10^{-9} l)
200 GPa	~20 μm	~1 pl (10^{-12} l)





Overview of the GESCARS Beamline - Station Equipment - X-ray Microprobe



Kirkpatrick-Baez focusing mirrors

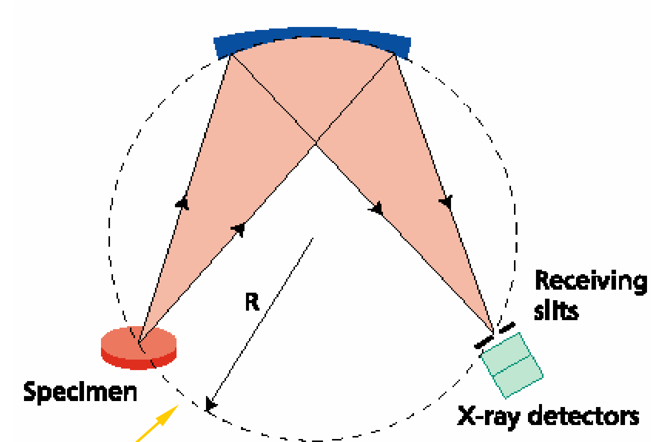
table-top slits

ion chamber

sample positioner (x-y-z stage)

optical microscope (10x to 50x) with video system

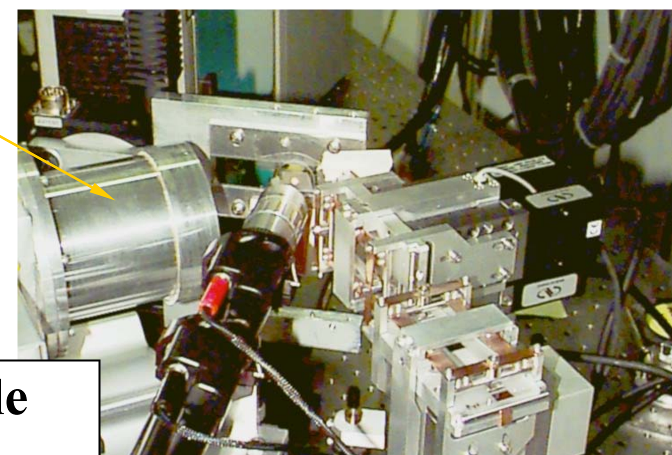
fluorescence detector Wavelength Dispersive Spectrometer (Oxford WDX-600)



Johansson geometry
bent to radius 2R and
ground to radius R

fluorescence detector

Multi-Element Ge



- Undulator source
- Monochromator (< 1 eV resolution)
- Beam defining slits
- KB microfocusing mirrors (0.8 μm)
- X-Y-Z sample stage (0.1 μm step)
- Optical viewing microscope (50-500x)
- XRF detectors: Si(Li), multi-element Ge, WDS

Matt Newville

Steve Sutton

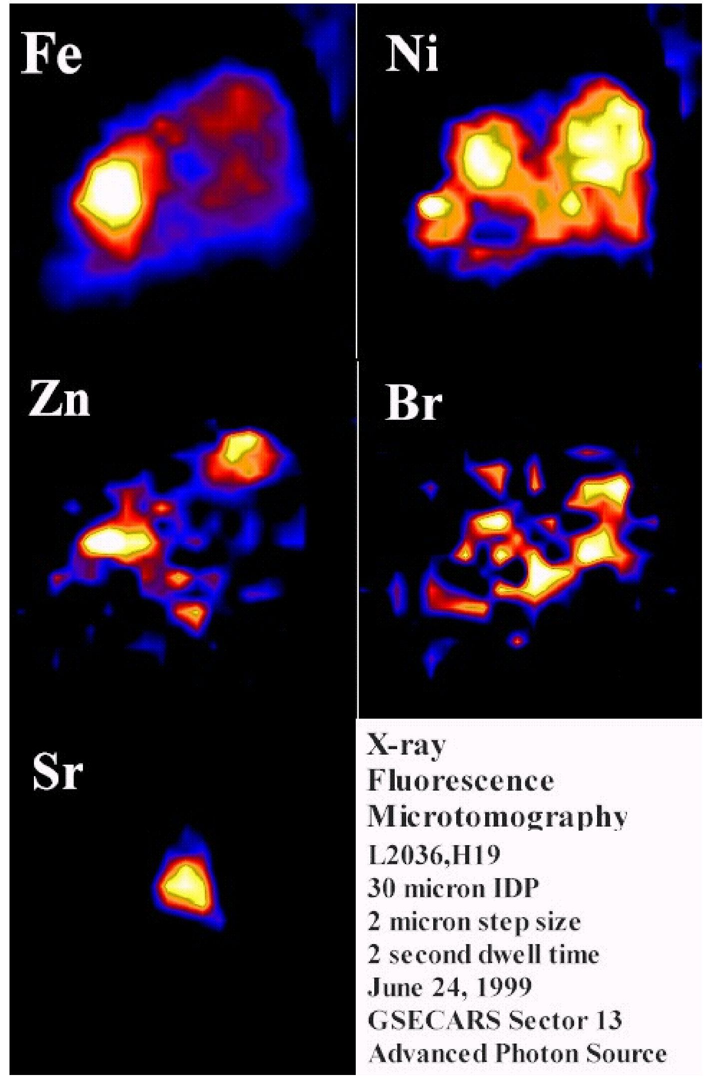
Microprobe – Fluorescence Microtomography

Interplanetary Dust Particles collected in the Stratosphere (Matt Newville, Steve Sutton and George Flynn, SUNY-Plattsburgh)

Mark Rivers

Matt Newville

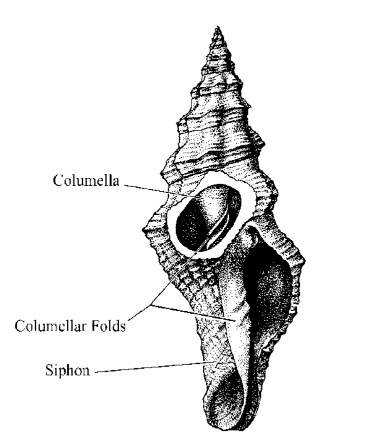
Steve Sutton



Evolution of Marine Snails
(B. Price, M. Rivers; U. of Chicago)

Latirus lynchi (Basterot), a Miocene fasciolariid from France

Fusinus exilis



Mark Rivers

Peter Eng

Earths surface

Water's effect the structure and reactivity of mineral surfaces

In-situ CTR measurements and analysis of hydrated:

α-Al_2O_3 (0001)

α-Fe_2O_3 (0001) (Natural oxide from Bahia Brazil)

Thomas P. Trainor, Mathew Newville, Mark L. Rivers Steven R. Sutton
Anne M. Chaka, Gordon E. Brown, Jr., Glenn A. Waychunas

Deep below the earths surface

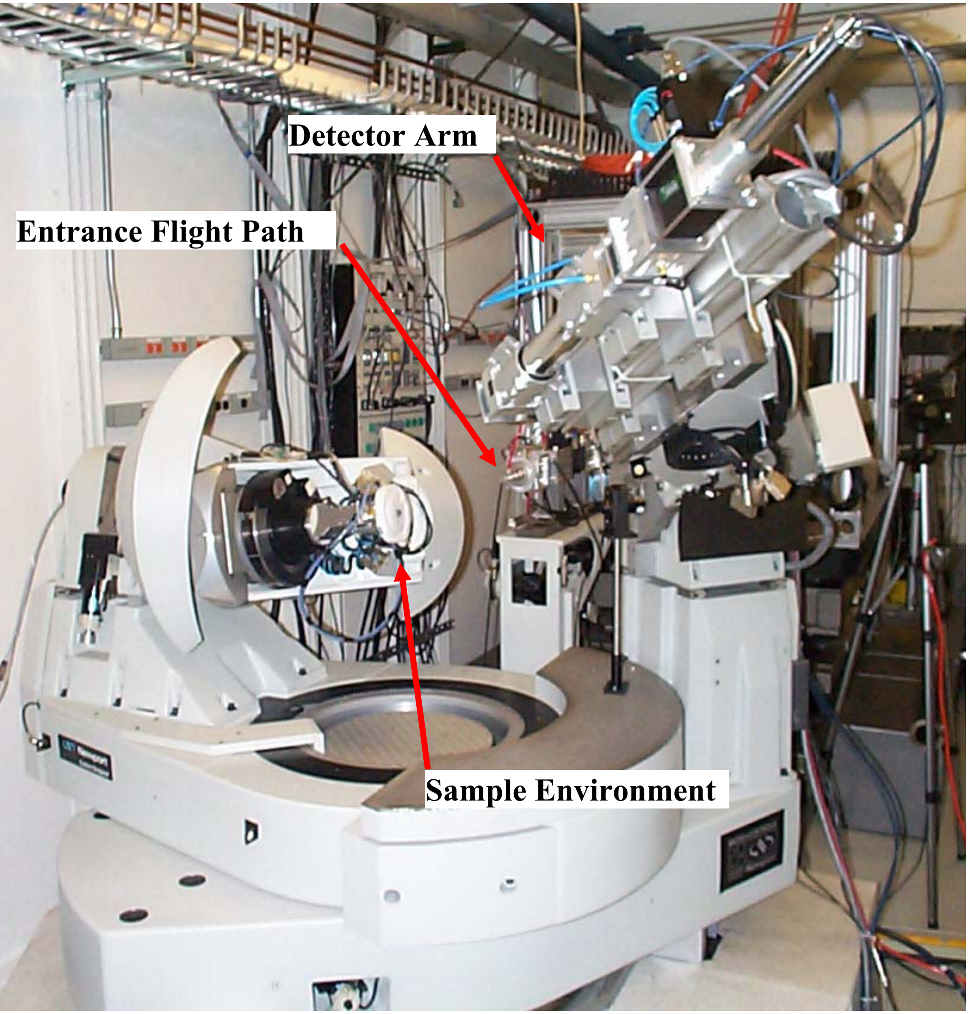
High pressure DAC near K-edge spectroscopy using inelastic x-ray scattering (IXS)

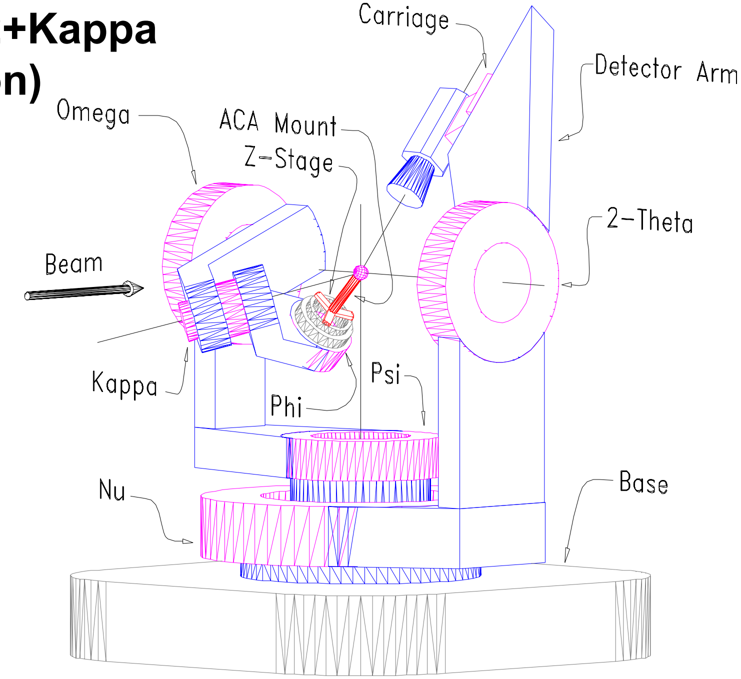
Graphite up to 24 GPa

Boron Nitrite up to 18 GPa

Wendy Mao, David Mao, Yue Meng, Tom Trainor, Matt Newville
Michael Hu Chi-Chang Kao and Wolfgang Caliebe

General Purpose Diffractometer 2+2+Kappa (CARS – Newport Collaboration)



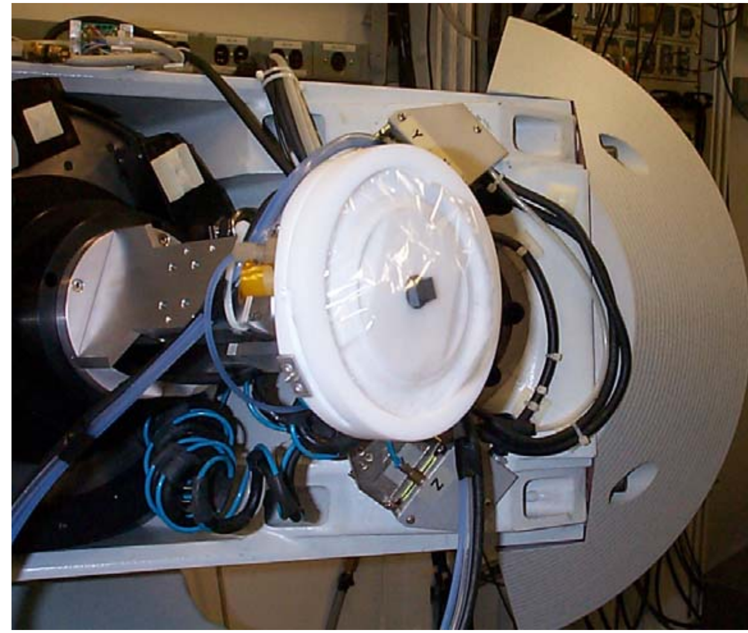


Open sample cradle, capable of supporting large sample environments weighting up to 10kg.

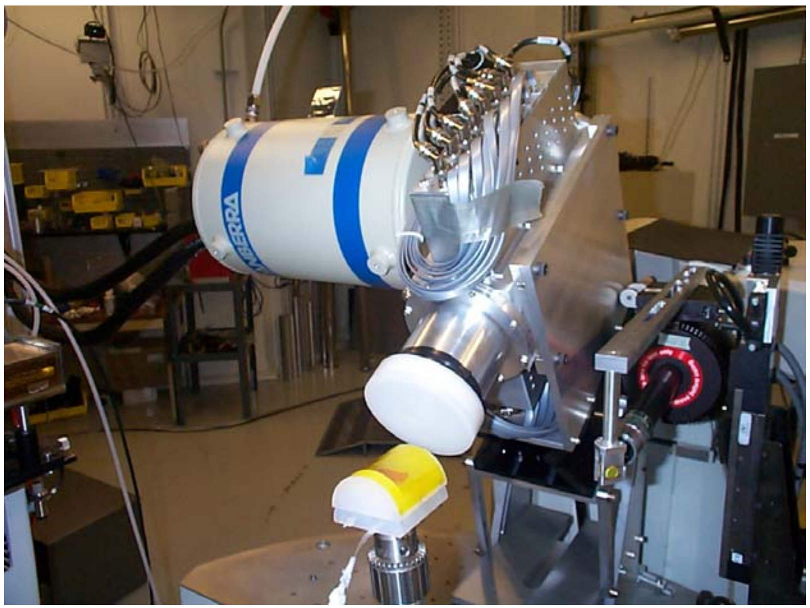
- High temperature furnace.
- Liquid solid environment cells.
- Closed loop refrigerator.
- Diamond Anvil Cell (DAC)
- High power liquid He and LN2 cryostat
- Small UHV Chamber with Hemispherical Be window

Water Mineral Interface - Experiment setup – Diffractometer

- High angle velocity 8^o/sec
- Multi axis synchronization, complex coordinated trajectories
- On the fly scanning capability
  - Rapid data collection and improves integrated intensity quality.
  - Captures sharp features since detector is always counting.
- Combined measurements
  - Point detection for Diffraction measurements
  - 16 element florescence detector for surface spectroscopy XSW



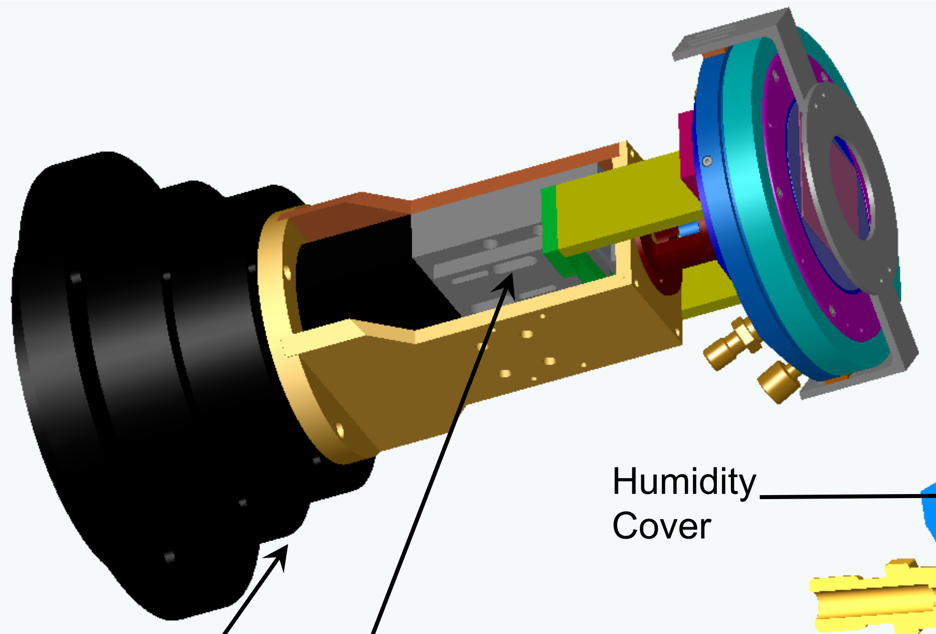
New Liquid Cell Mounted onto the Diffractometer with Hematite under Humidity Cover

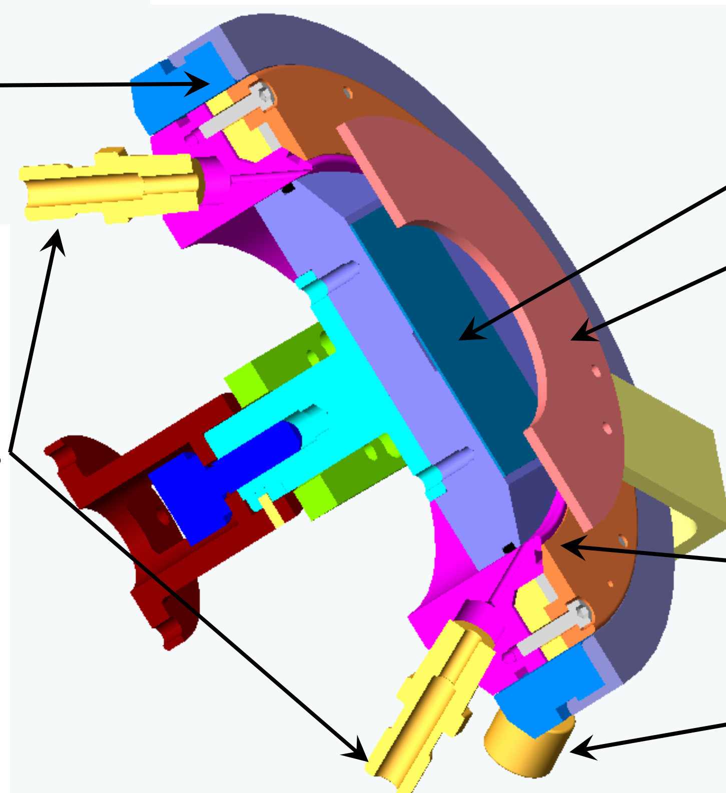


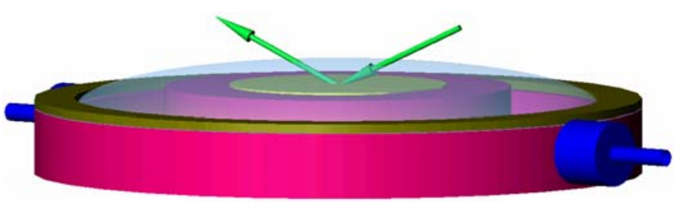
Standing Waves and GIAFS Setup

Water Mineral Interface - Experiment setup – Sample Cell

- In-situ Liquid cell with thin membrane.
  - Adjustable membrane gap for rapid changes in bulk chemistry and flow experiments.
  - Traps 1 μm or less of liquid for scattering and spectroscopy measurements.



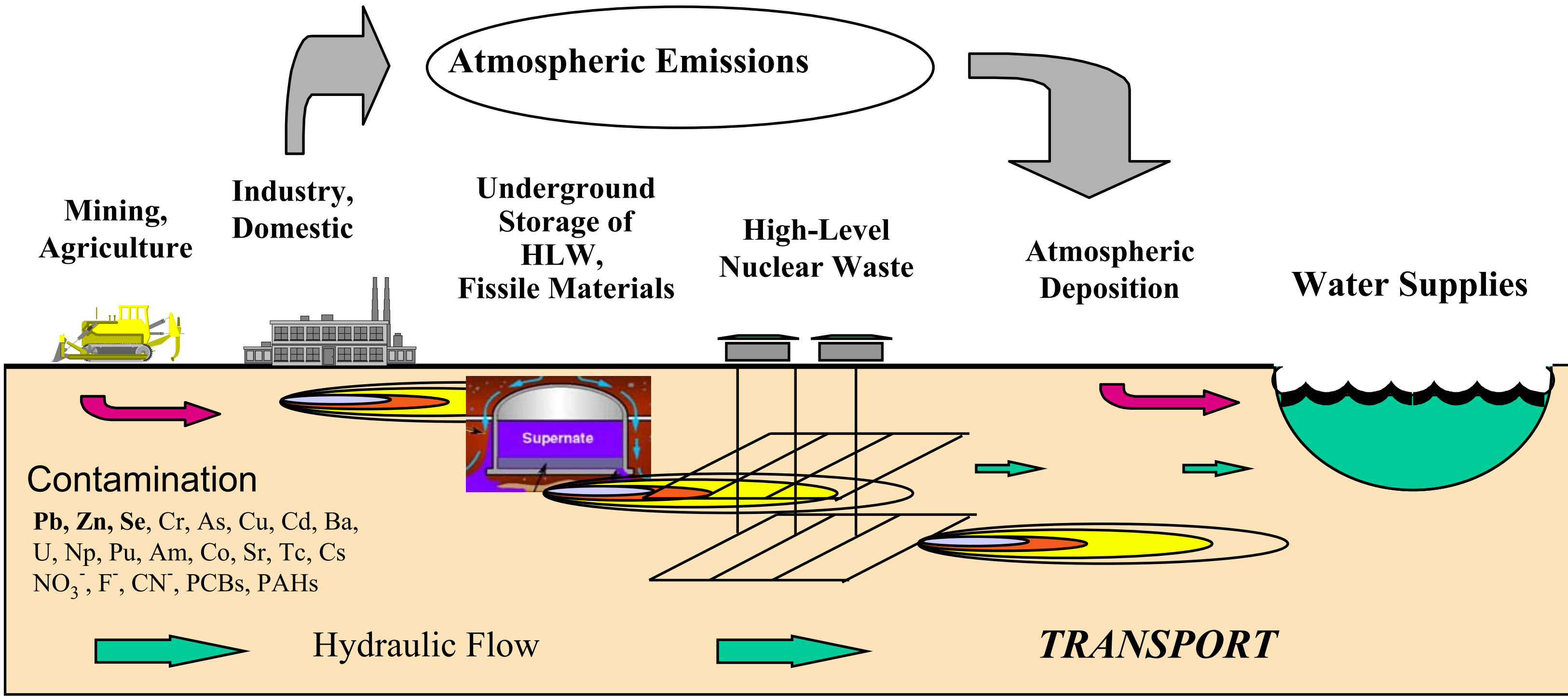




- The interaction of liquid water with the surfaces of natural solids is one of the most fundamental chemical reactions occurring in nature.

- Geochemical processes such as mineral dissolution and sorption/desorption reactions play major roles in:
  - Chemical weathering
  - Contamination of ground waters
  - Environmental restoration
  - Biogeochemical cycling of elements

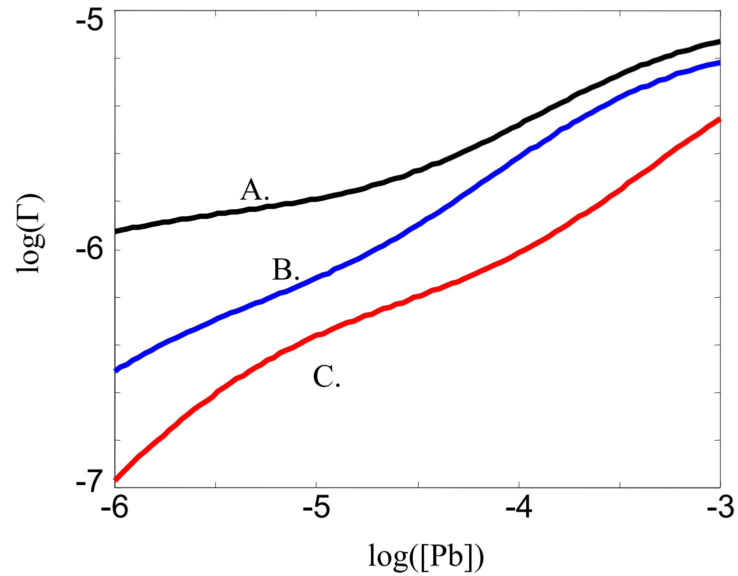
Water Mineral Interface - Contaminants In Aquatic Systems



- The transport, fate and bioavailability of contaminants are influenced by the chemical reactions that occur in the aqueous environment
- Goal is to understand the chemical speciation of contaminants in order to model/predict:
  - **transport**
  - **assess risk**
  - **design remediation schemes**

- Surface reactions play important role in speciation
- Multiple factors influence surface reactions
  - Structure and composition of surfaces
  - Presence of coatings
  - Solution conditions
- Studies focus on model systems
  - Simplified analog of natural system
  - Use to constrain and interpret reactions in natural systems

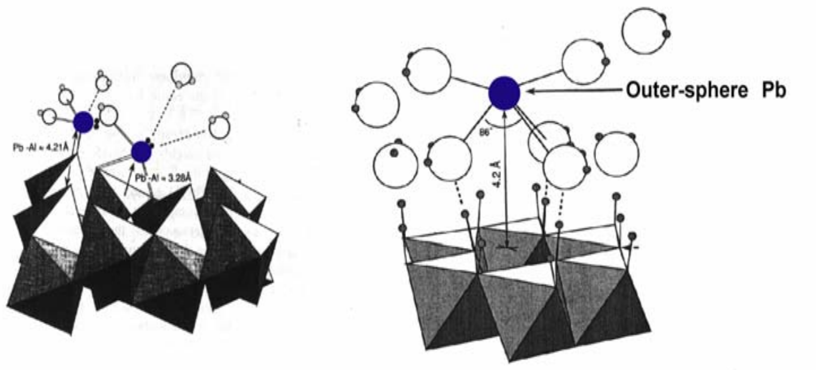
- Using crystal truncation rod (CTR) diffraction we provide details of the structure of hydrated oxide surfaces to aid in the understanding of:
  - Reactivity
  - Local Structure of sorbate geometry



Pb^{2+} sorption isotherms

A. α-Fe_2O_3 (0001)
B. α-Al_2O_3 (1-102)
C. α-Al_2O_3 (0001)

After: A.S. Templeton, *et al.* (2001). *Proc. Nat. Acad. Sci*. **98,** 11897-11902.



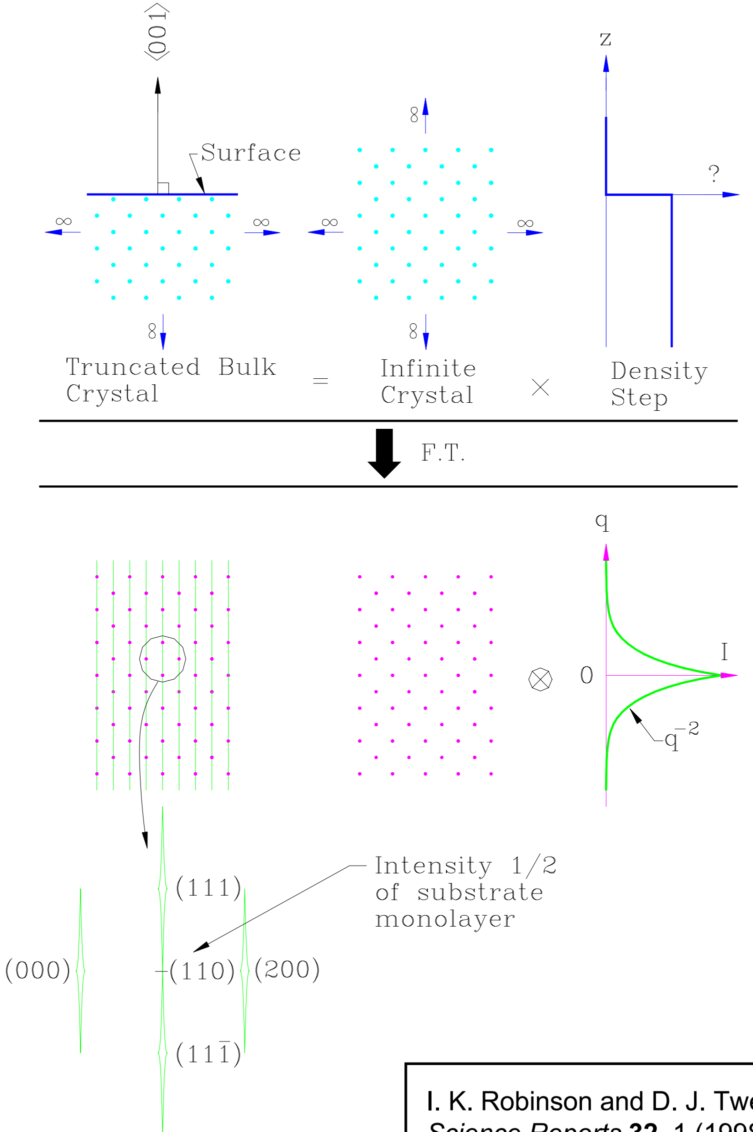
From: J. Bargar, *et al.* (1997) *J. Colloid Inter. Sci*. **185,** 473-492.

Water Mineral Interface - Hydrated α-Al_2O_3 and α-Fe_2O_3 surfaces

- Important model system for understanding the reactivity of naturally abundant phases of Al and Fe containing (hydr)oxides such as gibbsite, hydrous aluminosilicate clays, goethite and magnetite.
  - The Al and Fe in these phases have similar coordination chemistry with many natural minerals and act as a good analogs.

- The reaction of water with the α-Al_2O_3 and α-Fe_2O_3 has recently received a lot of attention, both experimentally and theoretically.

Water Mineral Interface - Measurements – Crystal Truncation Rod Diffraction

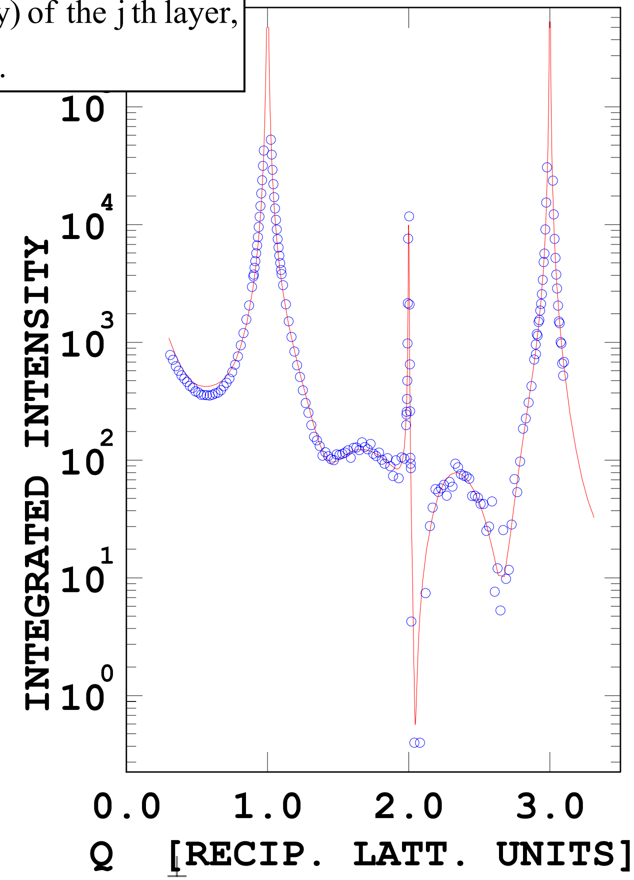


$$F(q) = f(q)\sum_{j=0}^{\infty}\rho_j e^{iqz_j}$$

z_j = position of the j th layer,

ρ_j = density (occupancy) of the j th layer,

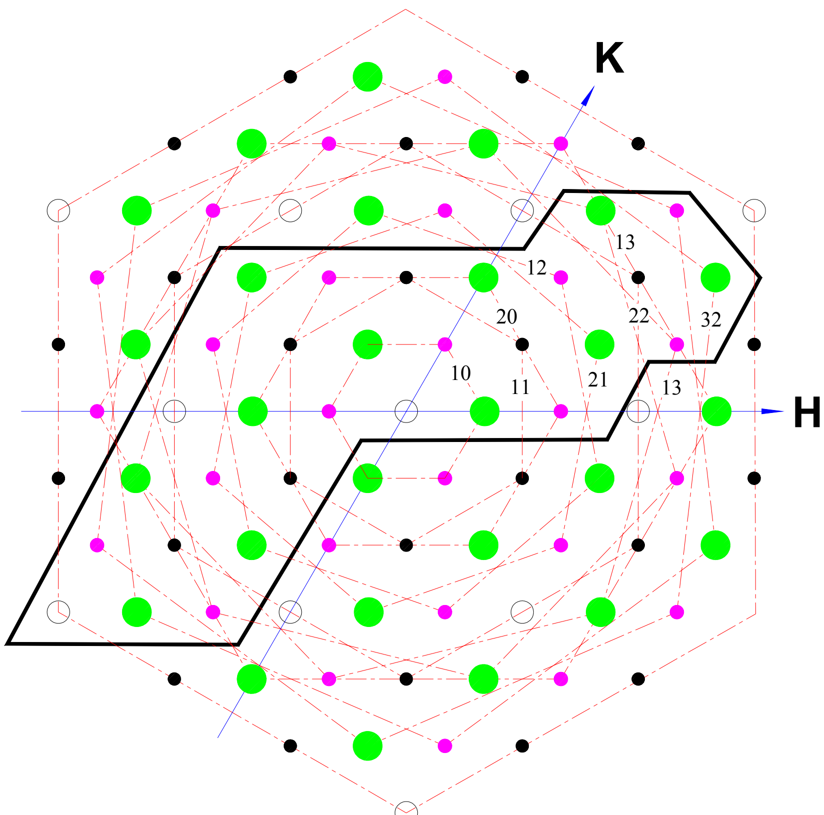
$f(q)$ = atomic form factor.

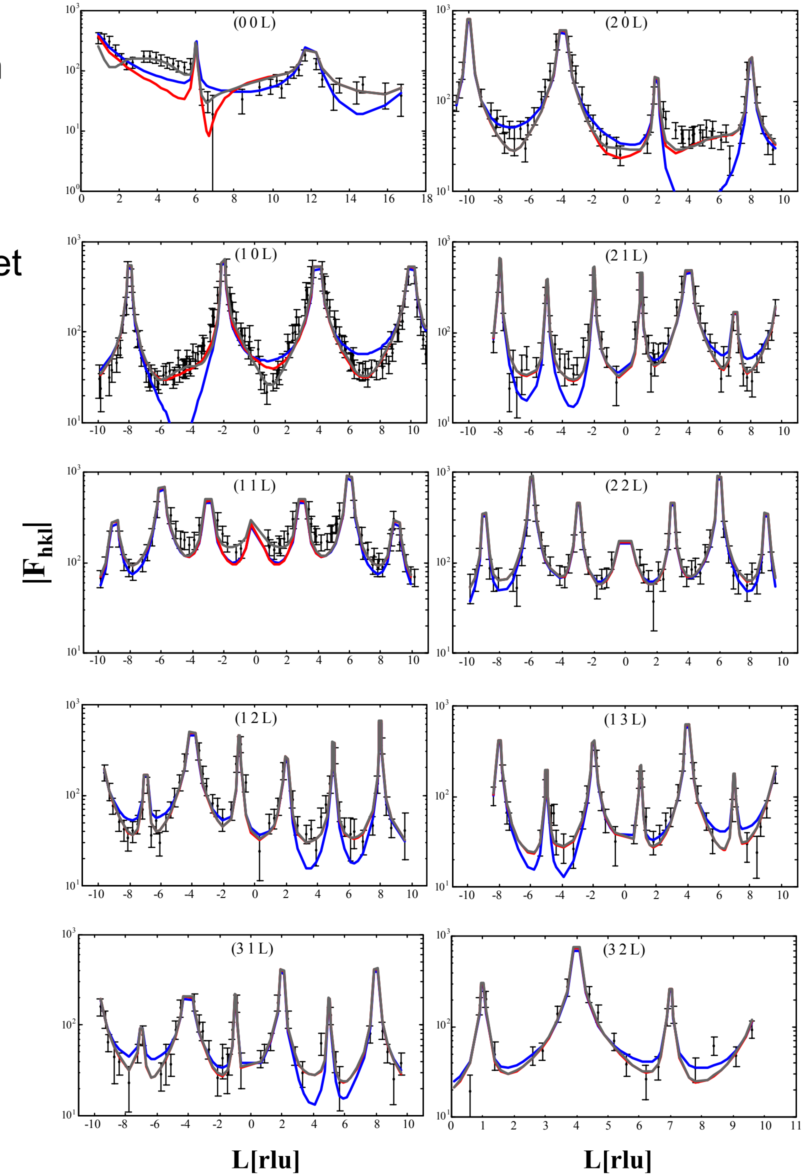


I. K. Robinson and D. J. Tweet, *Rep. Prog. Phys.* **55**, 599 (1992); G. Renaud, *Surface Science Reports* **32**, 1 (1998); P. Fenter *et al.*, *Geochem. Cosmochim. Acta* 64, 1221 (2000).

Water Mineral Interface - Measurements – Data collection and reduction – α-Al_2O_3

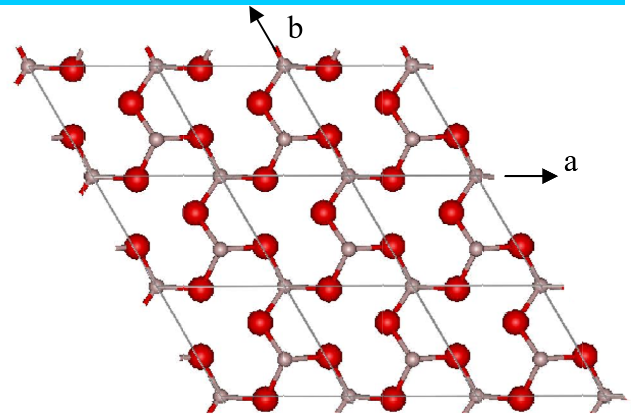
- A total of 882 structure factors were determined by integrating rocking scans through the crystal truncation rods.
- The integrated intensity is corrected for: active area, polarization, step size and Lorentz factor.
- After symmetry equivalents were averaged, the data set consisted of 525 unique data points from 10 crystal truncation rods.

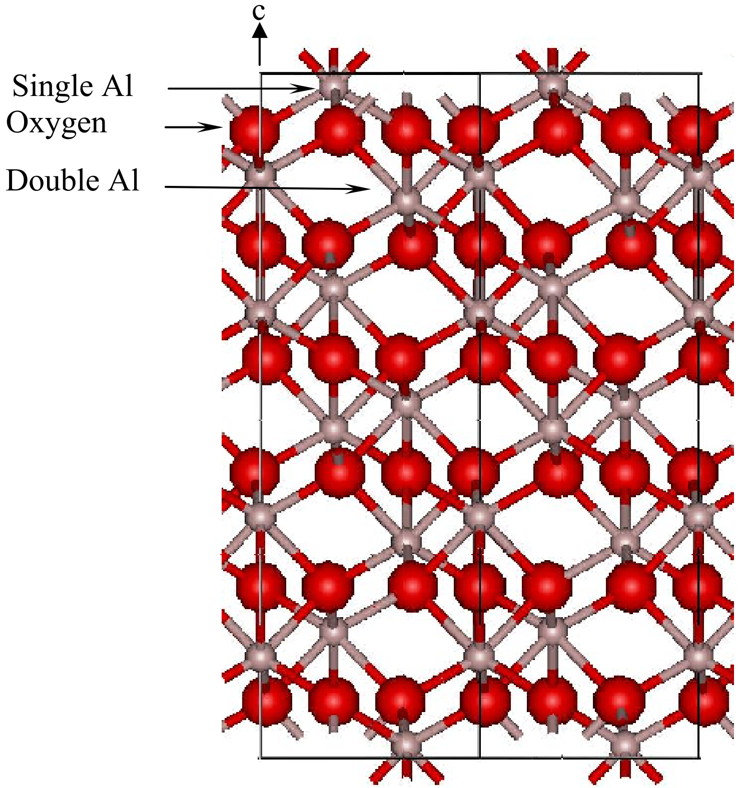




Water Mineral Interface - Analysis – Fitting and Model Details – α-Al_2O_3

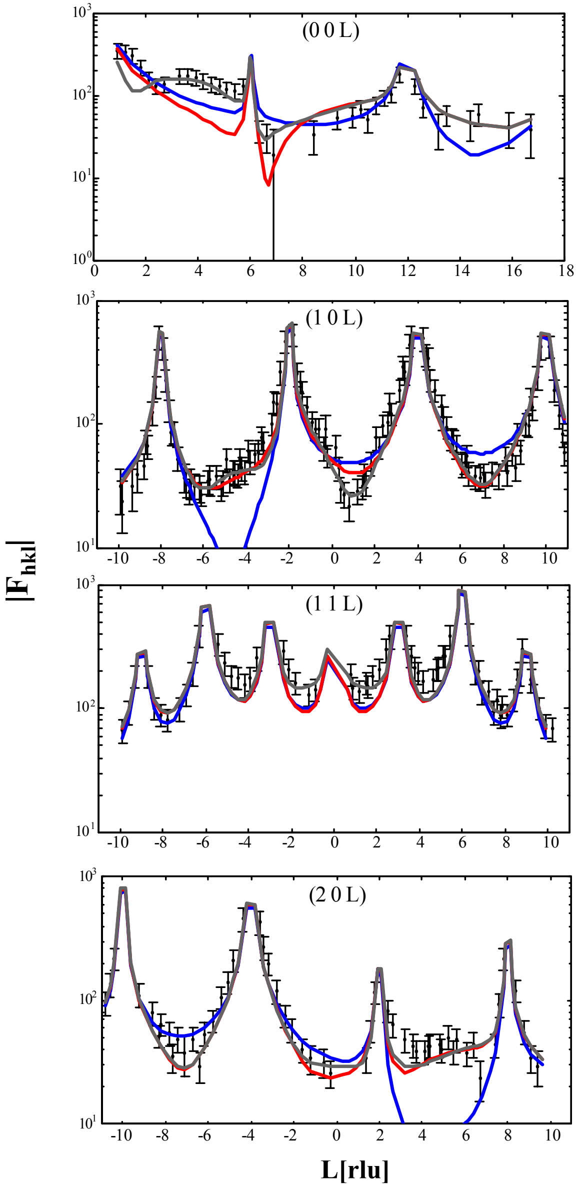
- Non-linear least squares fits of the full data set to a model consisting of a fixed bulk structure of α-Al_2O_3 and an adjustable surface region were determined.
- The Bulk structure
  - Three chemically distinct terminations: a double Al termination, a single Al termination, and an oxygen termination
  - For each chemical termination there are six crystallographically distinct terminations that are equally probable
- Surface Model
  - Six equal weighted terminations
  - Same fit parameters: displacement, Debye-Waller factors and occupancies
  - Surface has p3 symmetry, Al atoms centered on 3-fold axis, oxygen's arranged about 3-fold axis
  - To maintain symmetry: Al atoms only displaced in z-direction, and oxygen atoms must maintain trigonal symmetry





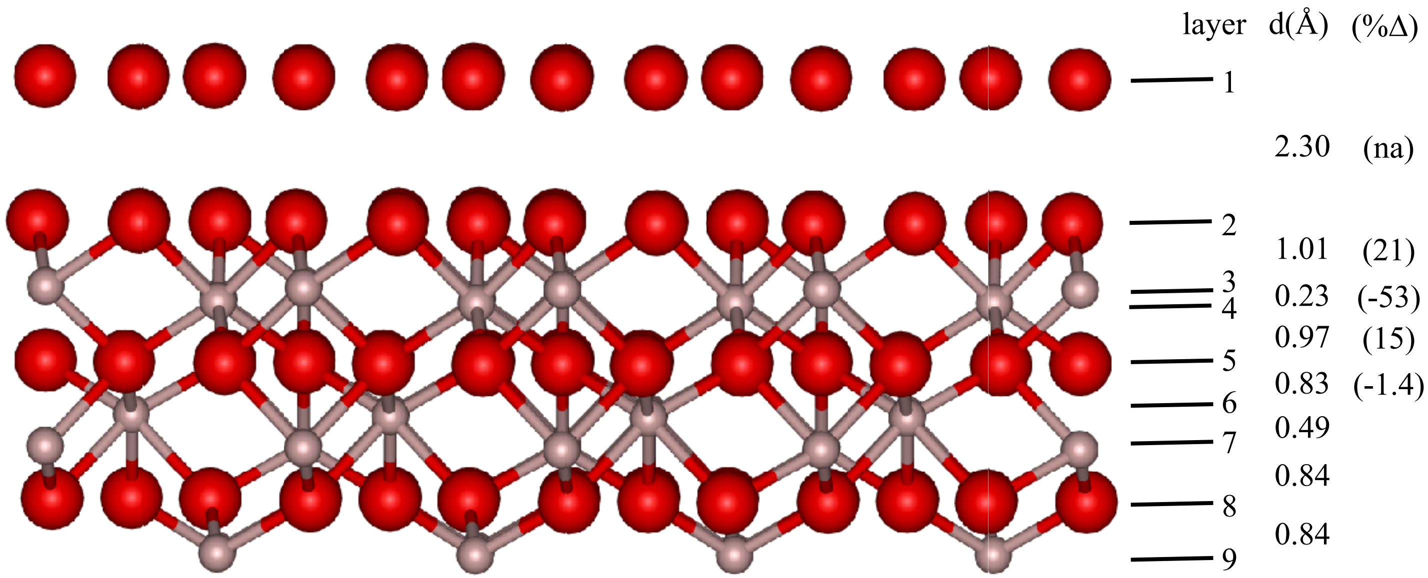
Water Mineral Interface - Analysis – Fit results – α-Al_2O_3

- Oxygen terminated.
- Poor fit for (10L) and (20L) rod for the Unrelaxed Oxygen terminated surface.
- Relaxing surface atoms: $\chi^2 = 1.58$
- Something still missing from model. Poor fit on Specular rod, and deviations at small L on off specular rods.
- Added an Oxygen overlayer with its own disorder term. Represents a partly ordered physisorbed (hydrogen-bonded) water layer.
- Significantly better fit to the (00L) rod with an overall improvement in the fit: $\chi^2 = 1.37$
- Layer order exists for approximately one of the adsorbed layers.



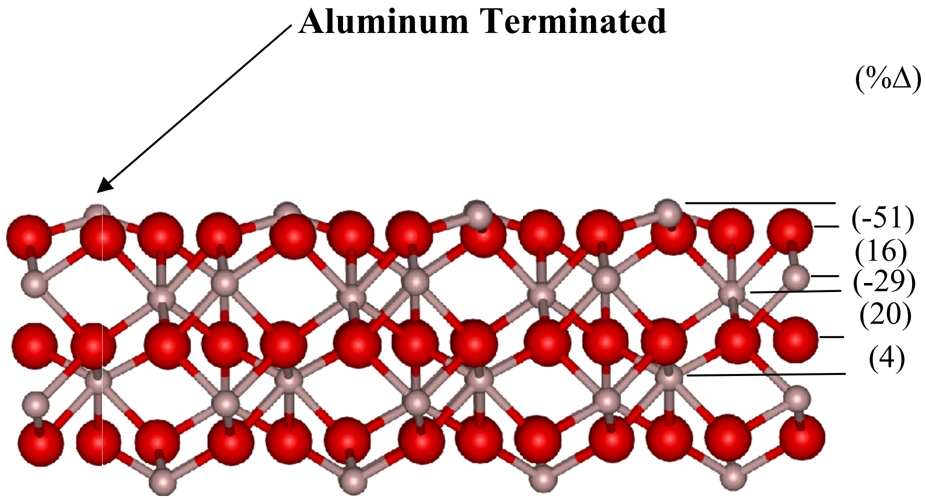
Water Mineral Interface - Analysis – Fit results – α-Al_2O_3

- Overlayer
  - Layer 1 oxygens: d-spacing of ≈ 2.3 ± 0.4 Å. Reasonable for hydrogen bonding of water to surface hydroxyl groups
  - Overall fit is improved by adding layer, but has an insignificant effect on the relaxed surface structure.

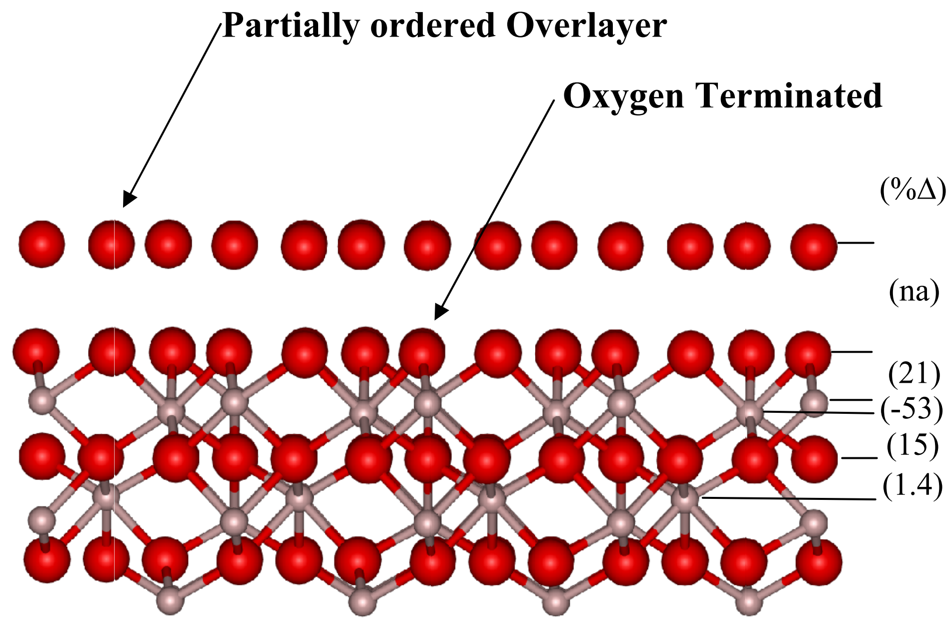


P.J. Eng, T.P. Trainor, G.E. Brown Jr., G.A. Waychunas, M. Newville, S.R. Sutton, M.L. Rivers, *Science* **288**, 1029 (2000)

Water Mineral Interface - Analysis – Fit results – Interface Structure – α-Al_2O_3



UHV Clean Surface



Hydrated Surface

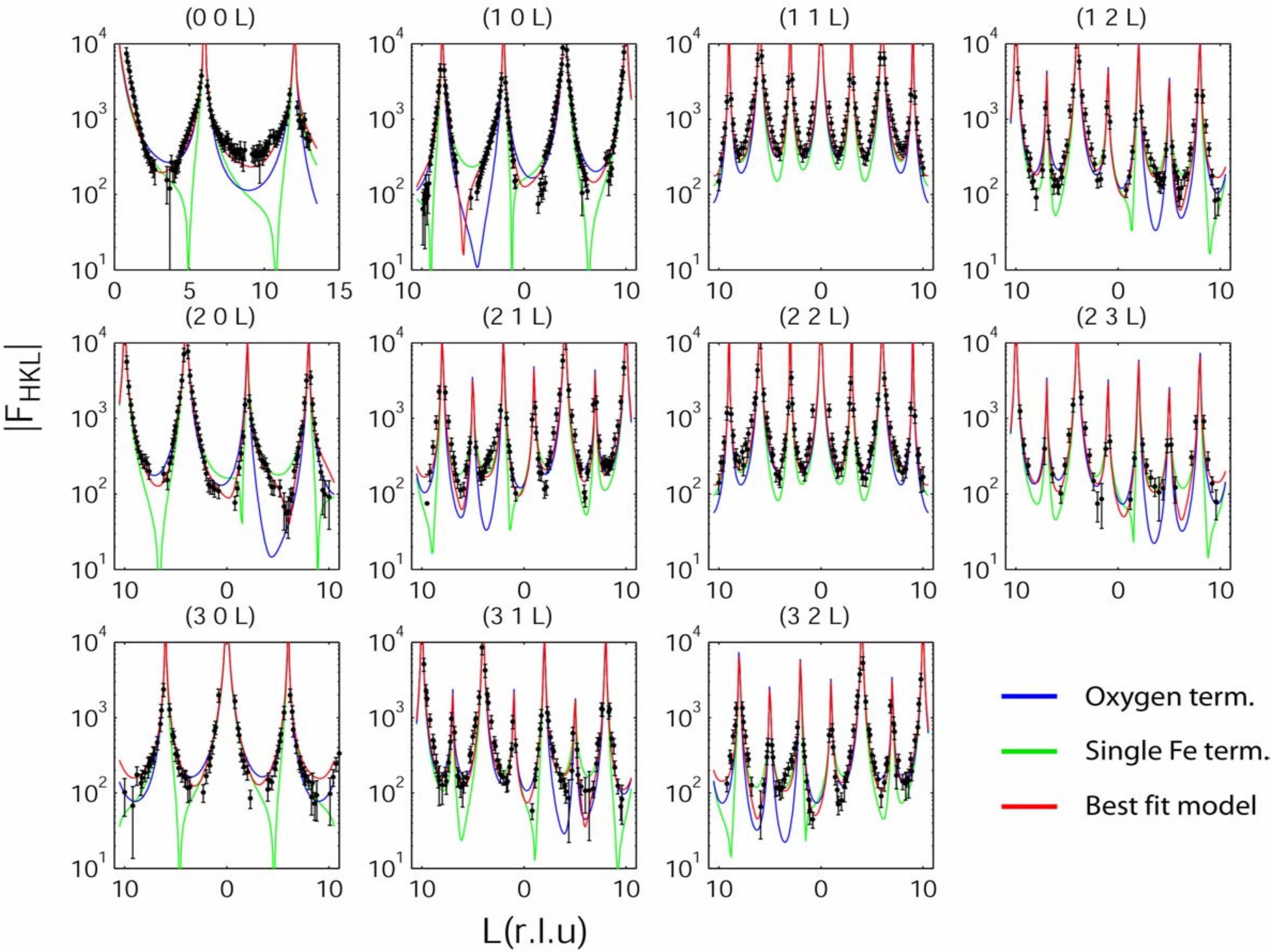
Water Mineral Interface - Conclusion – α-Al_2O_3

- Hydrated Alumina is essentially passivated as compared to the very reactive Al-terminated UHV-clean surface
- Al sites in Al-terminated model are strong Lewis acid sites
- OH groups in the OH-terminated surface are Lewis bases
- Fully hydroxylated α-Al_2O_3 (0001) has a lower reactivity to water but enhanced reactivity to metals such as Pb, increasing its metal wettability and supporting smooth overlayer growth.

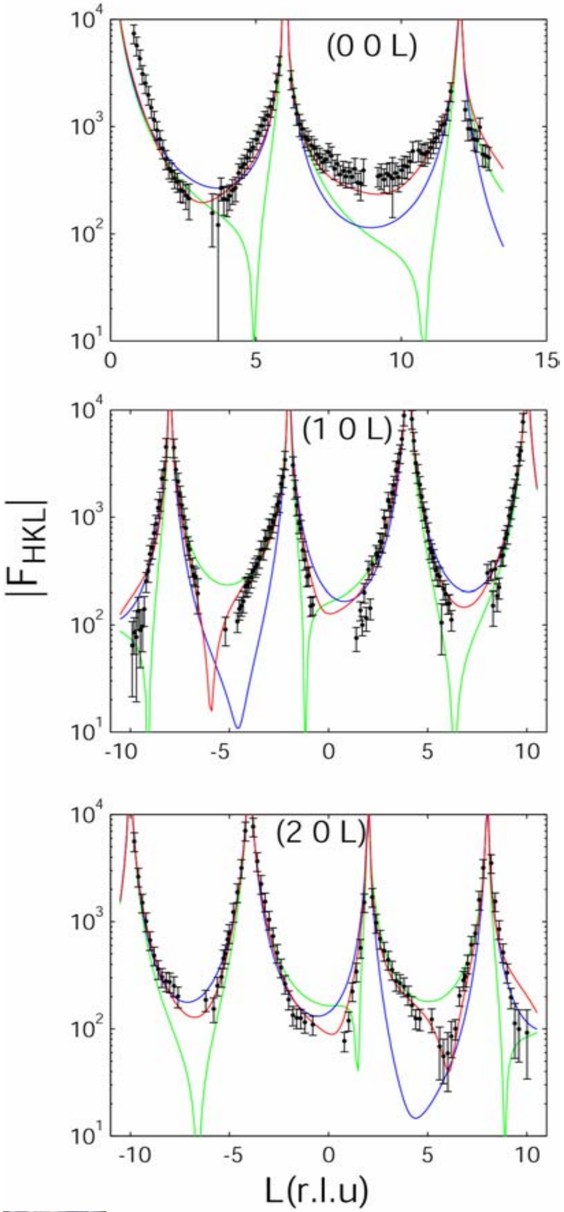
Water Mineral Interface - Natural Hematite α-Fe_2O_3 (0001)

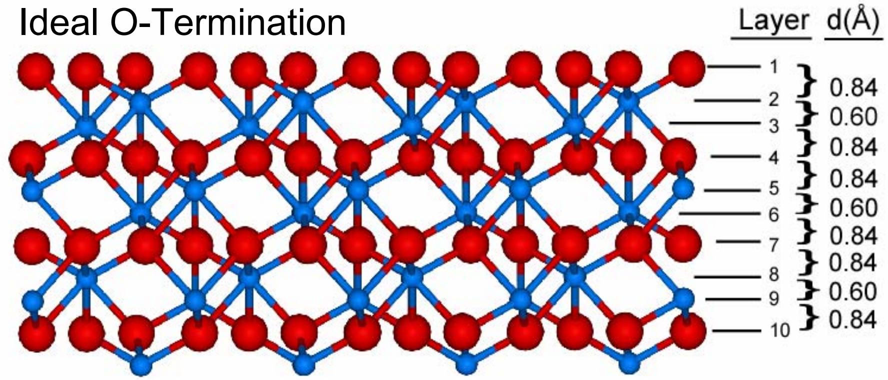
- Natural single crystal sample from Bahia Brazil **Glenn A. Waychunas**
- The α -Fe_2O_3 (0001) has the same structure as α - Al_2O_3 (0001)
- Data Collection and Analysis
  - Measured 1641 individual structure factors
  - ~800 unique structure factors on 11 CTR's

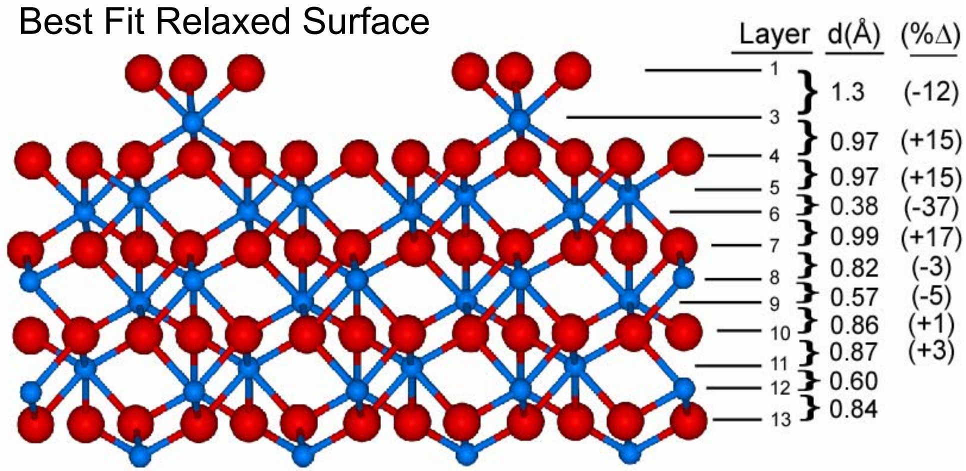
Water Mineral Interface - Measurements – Hydrated α-Fe_2O_3 (0001)



Water Mineral Interface - Analysis – Fit Results – Hydrated α-Fe_2O_3 (0001)







Oxygen term.

Single Fe term.

Best fit

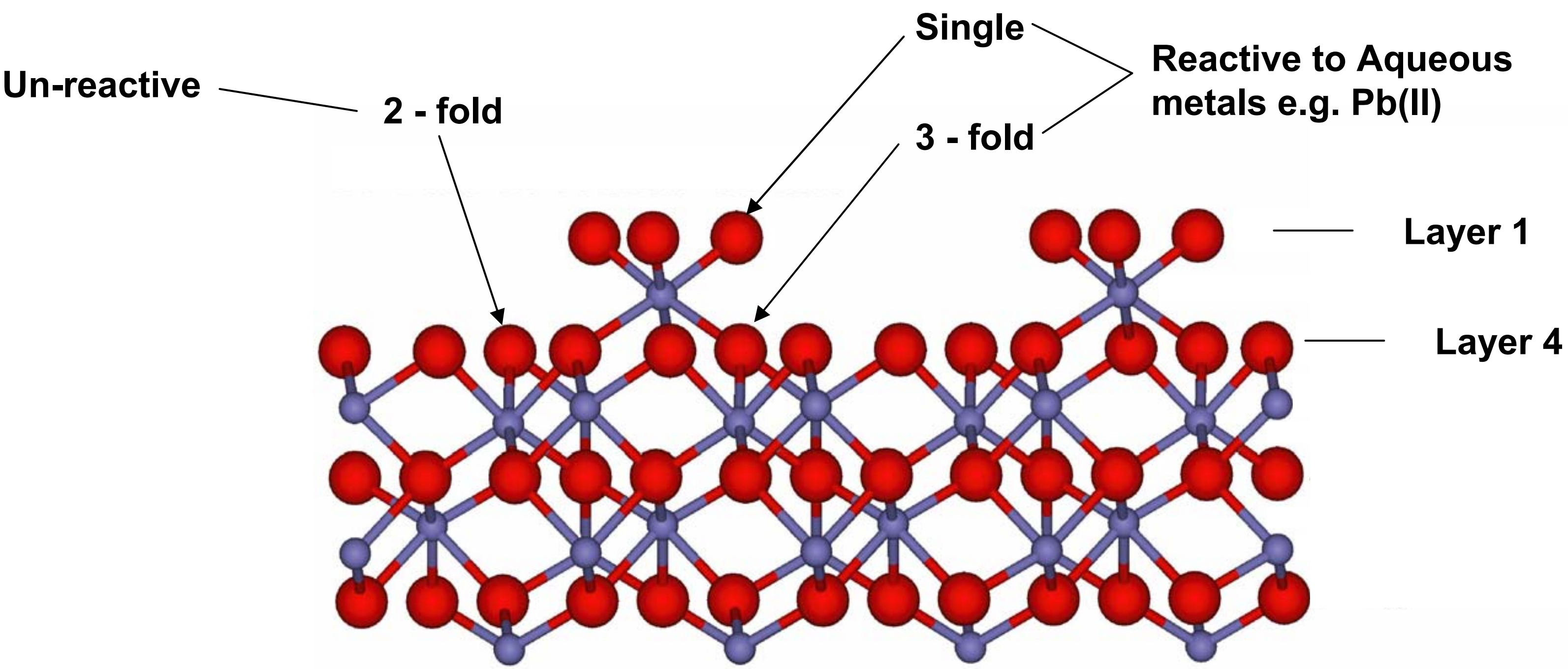
- Occupancy of layer-1 O and layer-3 Fe ~1/3
- Layer-2 Fe consistently rejected from the fit
- Large relaxation of Fe double layer
- Expansion of layer-3 Fe

- Three types of surface (hydr)oxo functional groups:

  -Layer 4 oxygen: 2 - fold and 3 - fold coordinated

  -Layer 1 oxygen: singly coordinated

Simple Pauling bond valence analysis shows:



Analysis – *ab initio* thermodynamic calculations – Hydrated α-Fe_2O_3 (0001)

Teamed up with

Anne Chaka (INST)

- Conducted *ab initio* thermodynamic calculations
  - To better understand surface hydration / hydroxylation (H is not visible due to its weak scattering power)
  - Provide energy minimized structural models to test consistency with our measurements
- Examined two dissociation mechanisms of surface water
  - Heterolytic (ionic) dissociation

$$H_2O \leftrightarrow HO^- + H^+$$

  - Homolytic dissociation

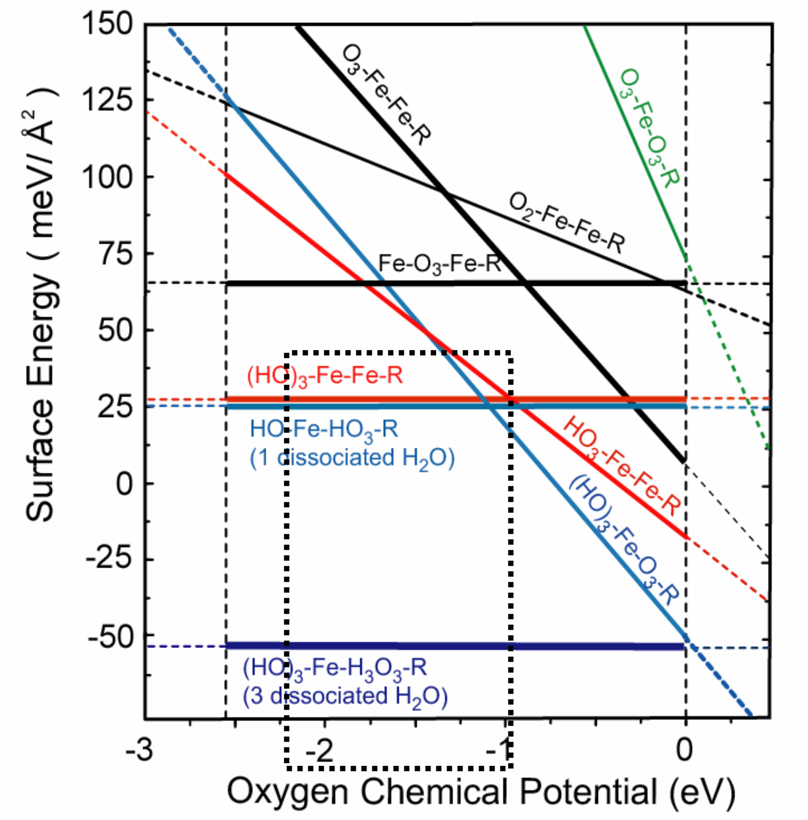
$$H_2O \leftrightarrow HO\bullet + 1/2H_2\uparrow$$

Neutral OH radical binds to surface cations (HO•)

Released as gas (H_2)

Analysis – Surface Energy Diagram - DFT Calculations– Hydrated α-Fe_2O_3 (0001)

DFT calculations @ 0K and 1 bar H_2O



When water is added we see a lowering of the surface energy!

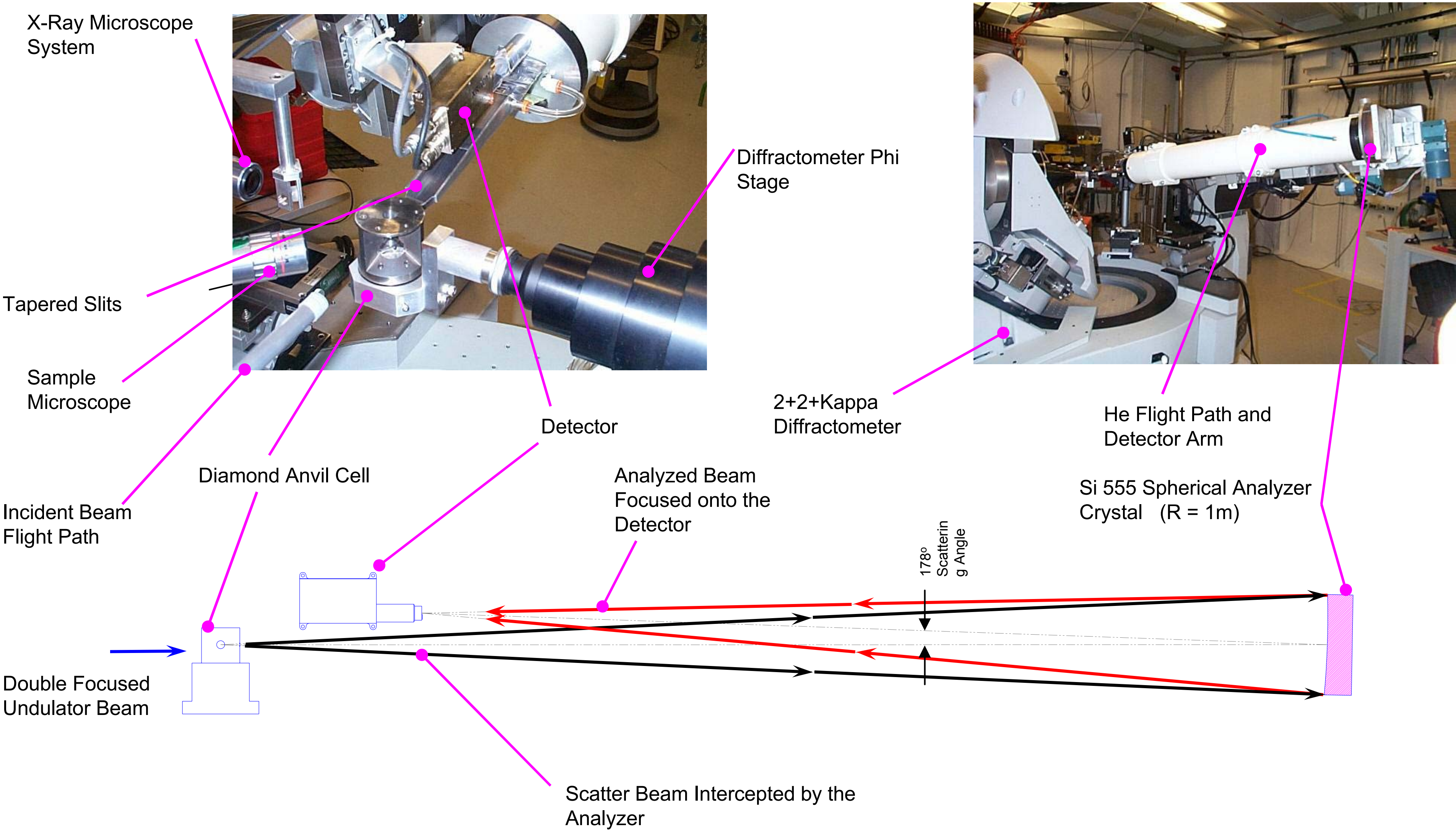
Water Mineral Interface - Summary – Hydrated α-Fe_2O_3 (0001)

- Hematite (α-Fe_2O_3) is significantly more reactive to water and metal ions than its isostructure corundum (α-Al_2O_3)
- CTR diffraction and DFT calculations show that the stable hydrated hematite (0001) surface consisting of two domains:
  - Iron-rich regions terminated by singly coordinated hydroxyls
  - Oxygen-rich regions terminated by doubly coordinated hydroxyls
- The presence of singly coordinated hydroxyls on hydrated α-Fe_2O_3(0001) and their absence on hydrated α-Al_2O_3(0001) explain the higher reactivity of hematite.
- DFT calculations indicate that water reacts with hematite both heterolytically and homolytically at a threshold pressure orders of magnitude lower on α-Fe_2O_3(0001) than on α-Al_2O_3(0001), which is consistent with experimental findings.

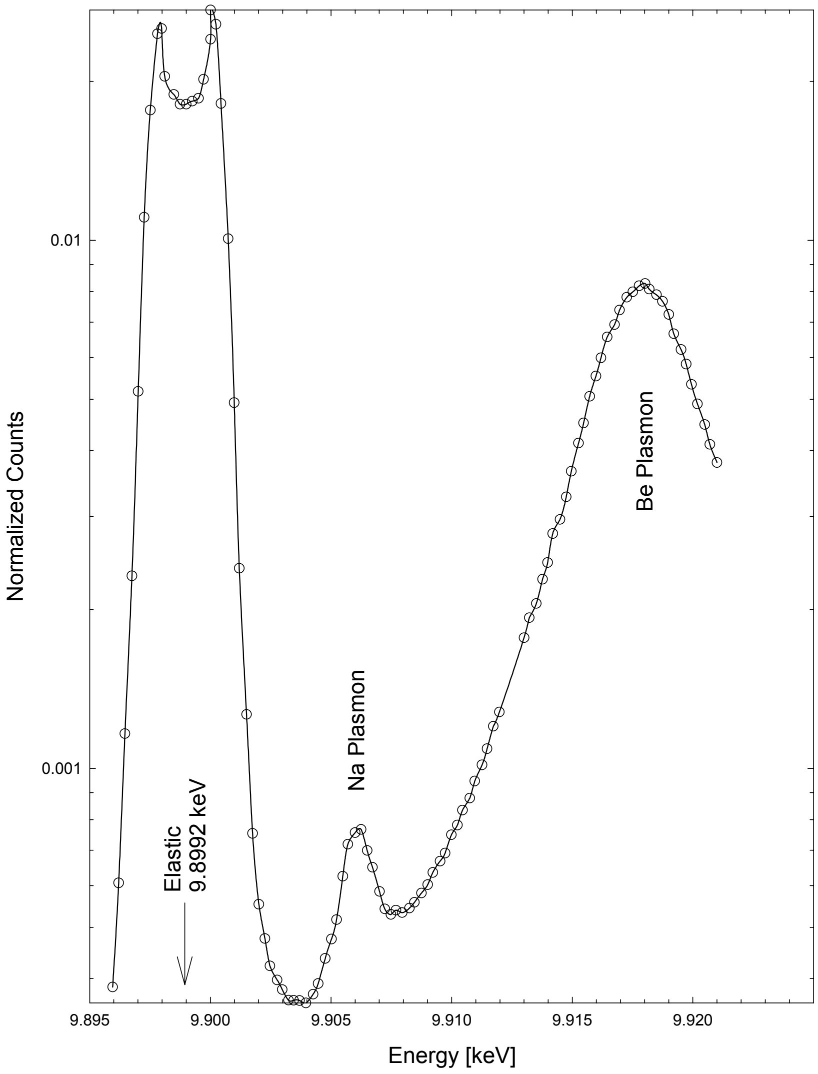
Future Direction

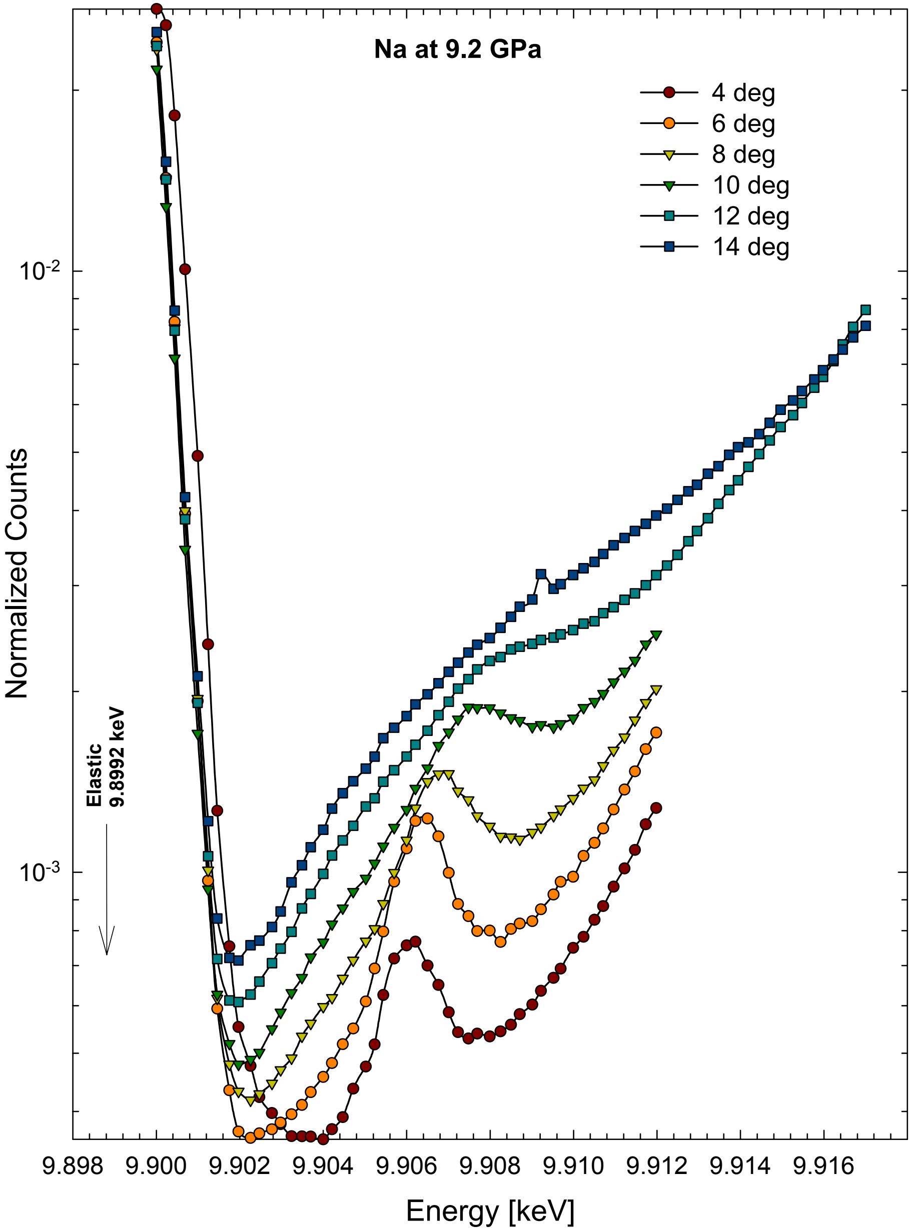
- Explore variation in structure and reactivity as function of surface orientation and defects.
- Continue sorption studies of aqueous metal Ions on our model surfaces.
- Bio-films and their role in surface dissolution and reactivity.
- Develop in-situ computer control of pH, ion concentration, film thickness and temperature in our liquid cell.
- Light portable UHV scattering chamber with hemispherical Be window.

High Pressure - Inelastic X-ray Scattering – Experimental Setup

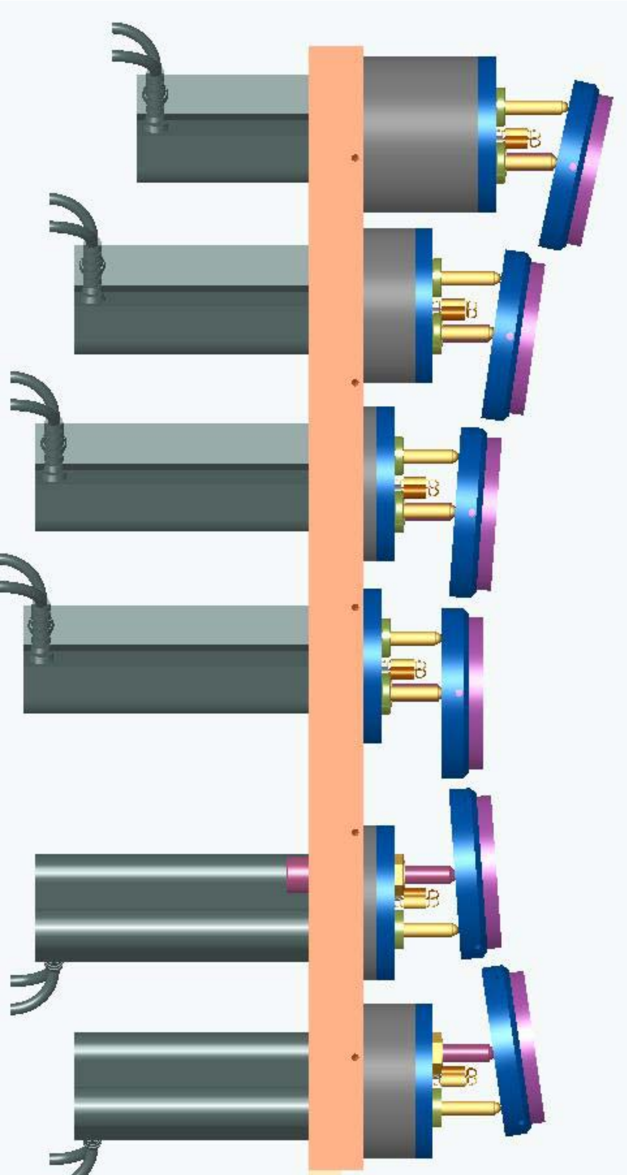


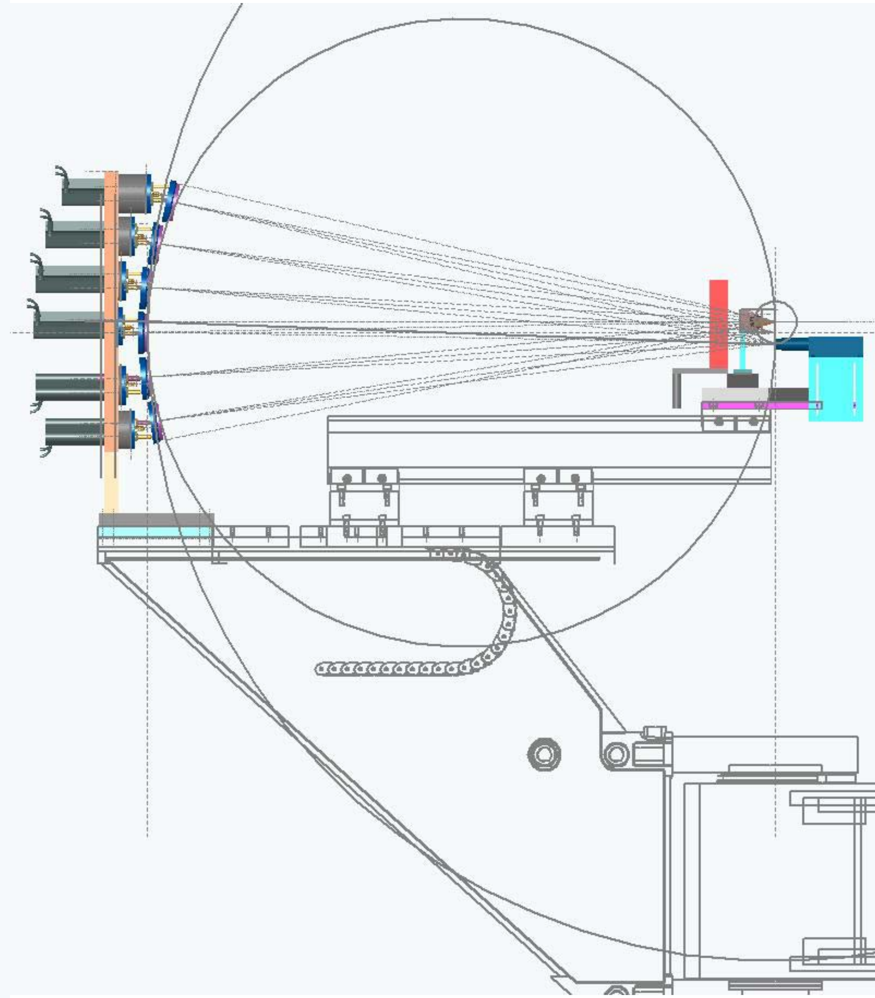
High Pressure - Inelastic X-ray Scattering – Experimental Setup



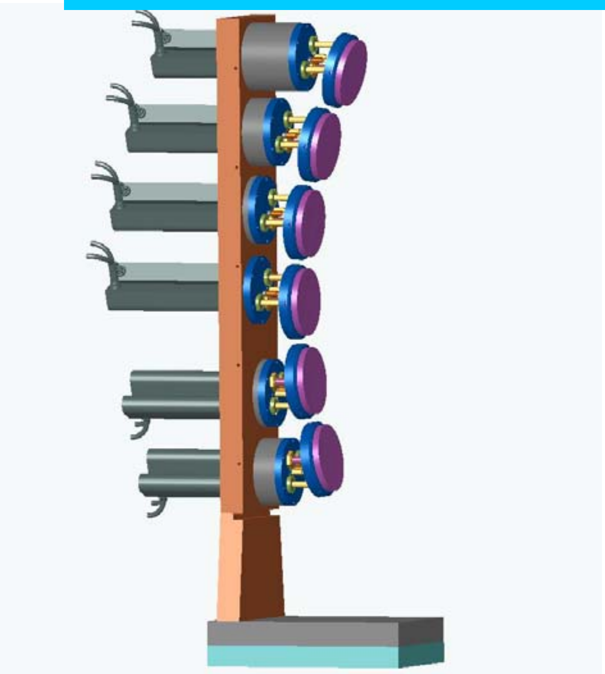


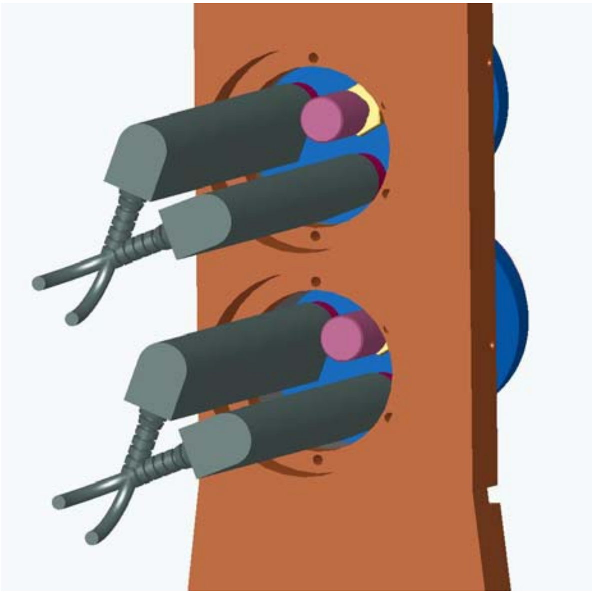
High Pressure - Inelastic X-ray Scattering – Six Element Array

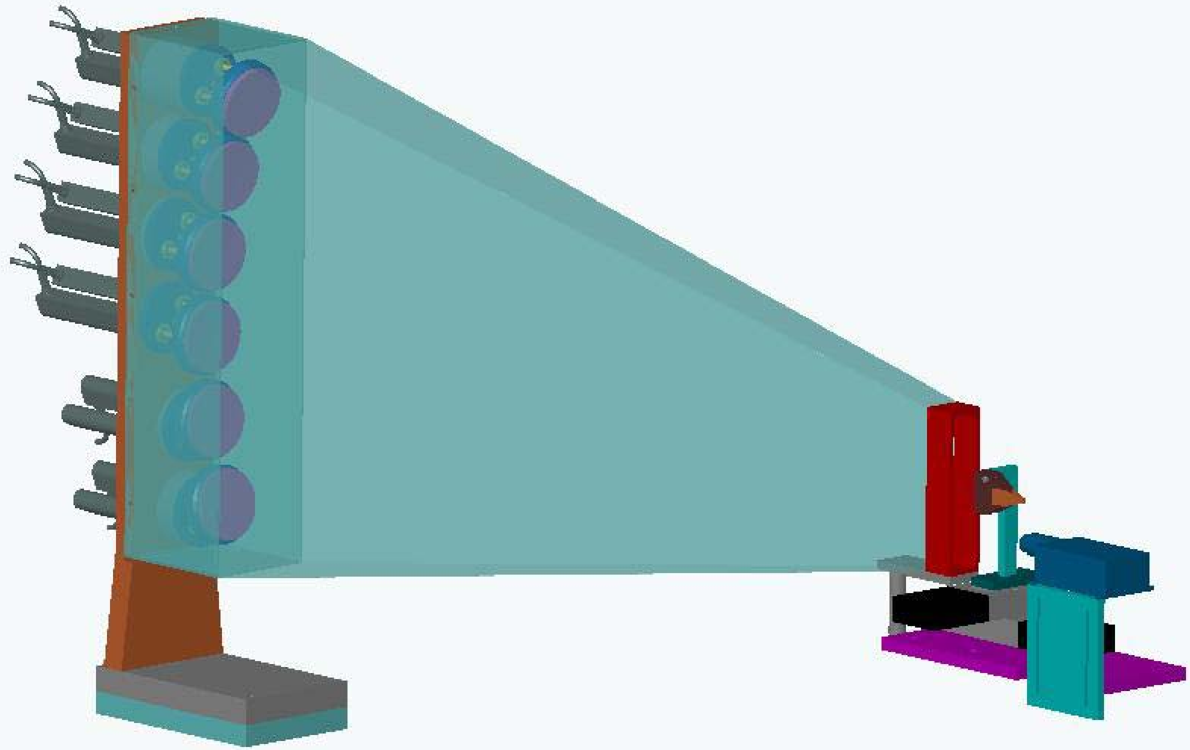




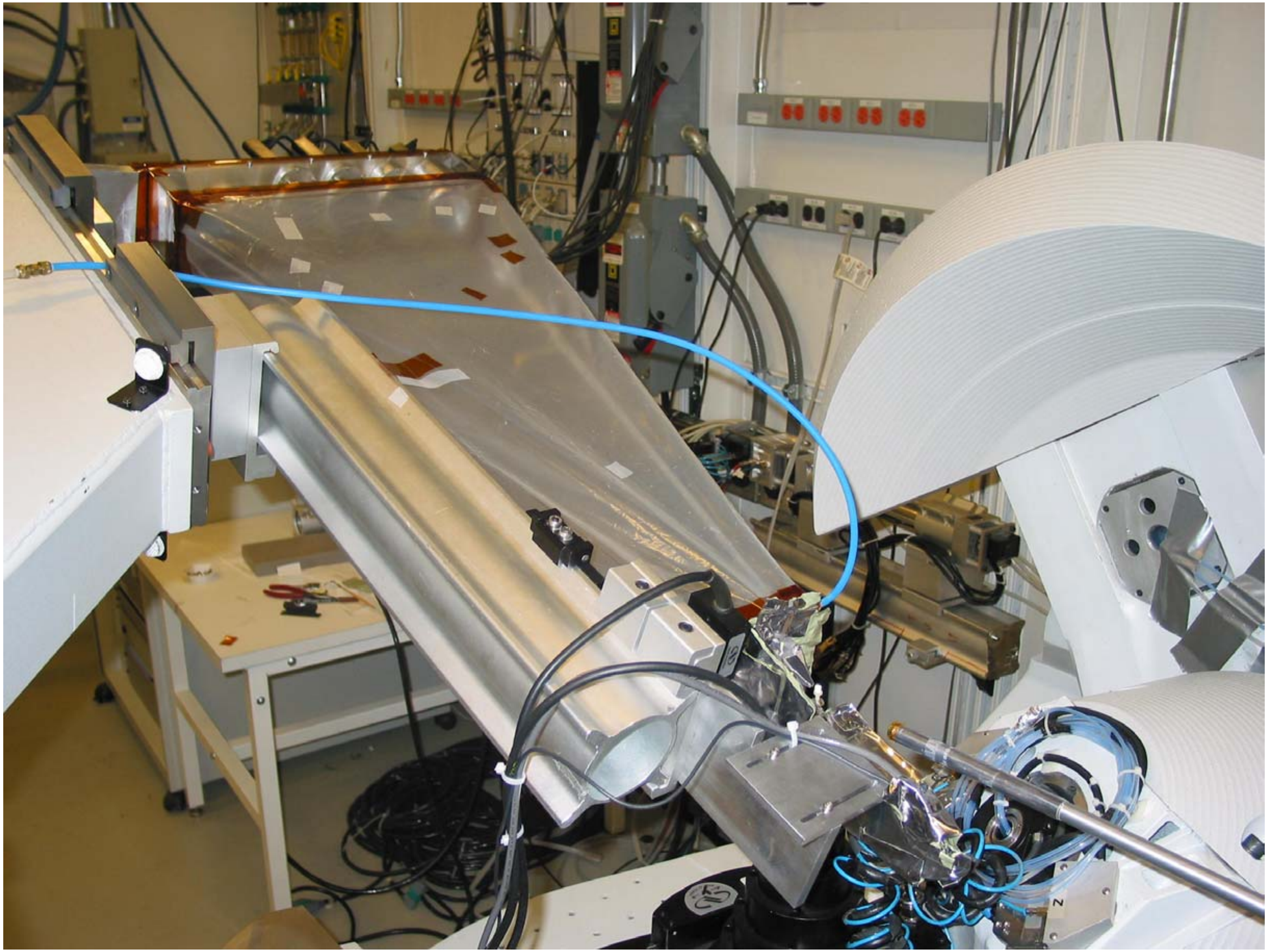
High Pressure - Inelastic X-ray Scattering – Experimental Setup



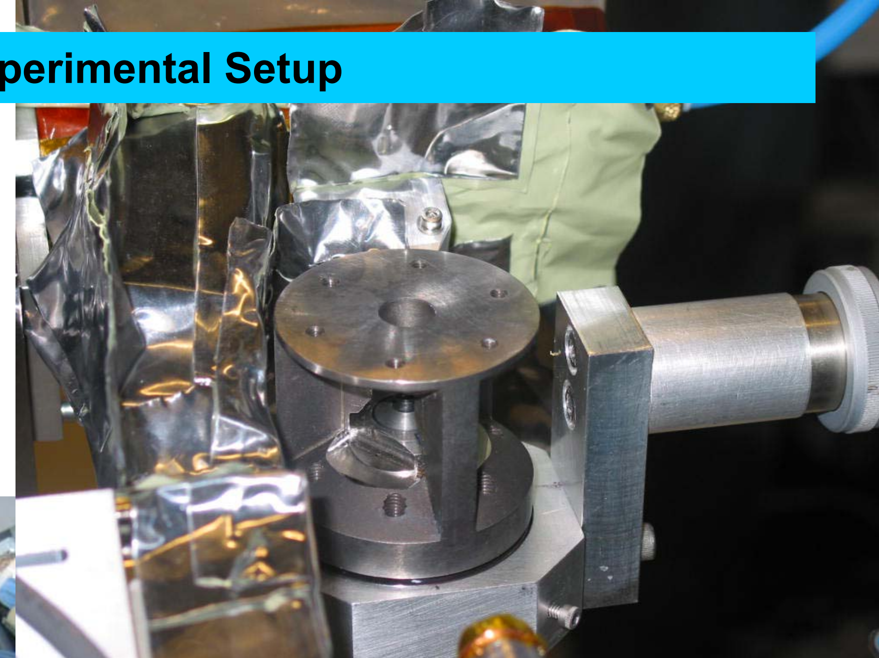


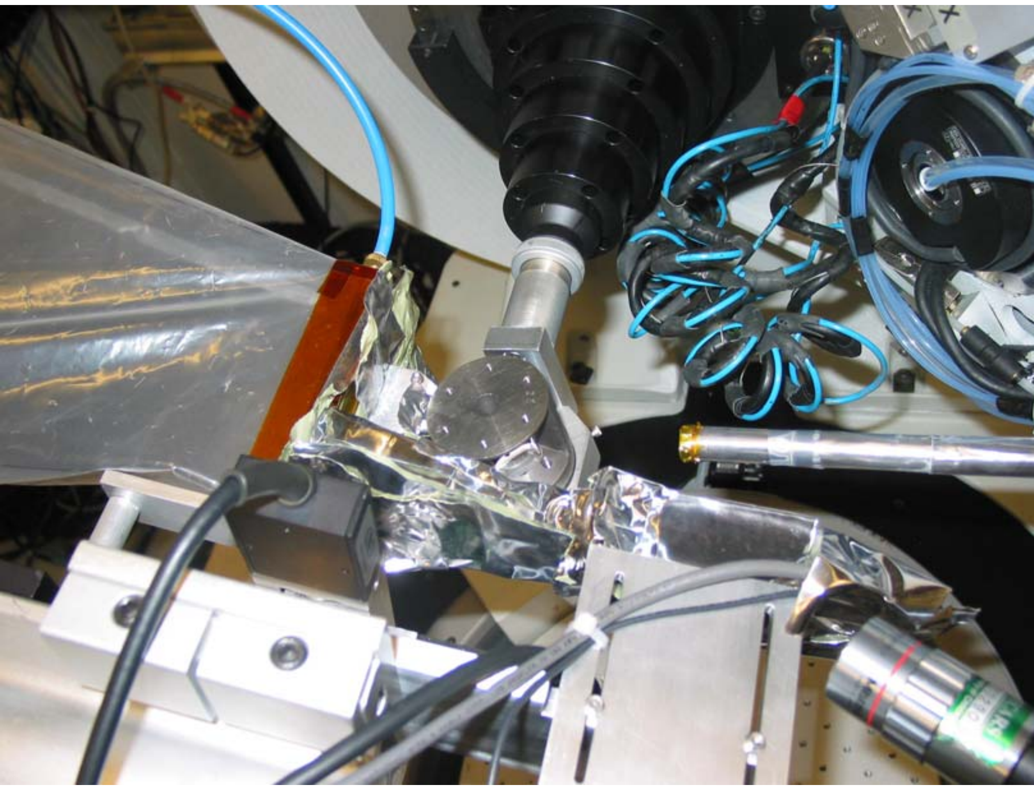


High Pressure - Inelastic X-ray Scattering – Experimental Setup

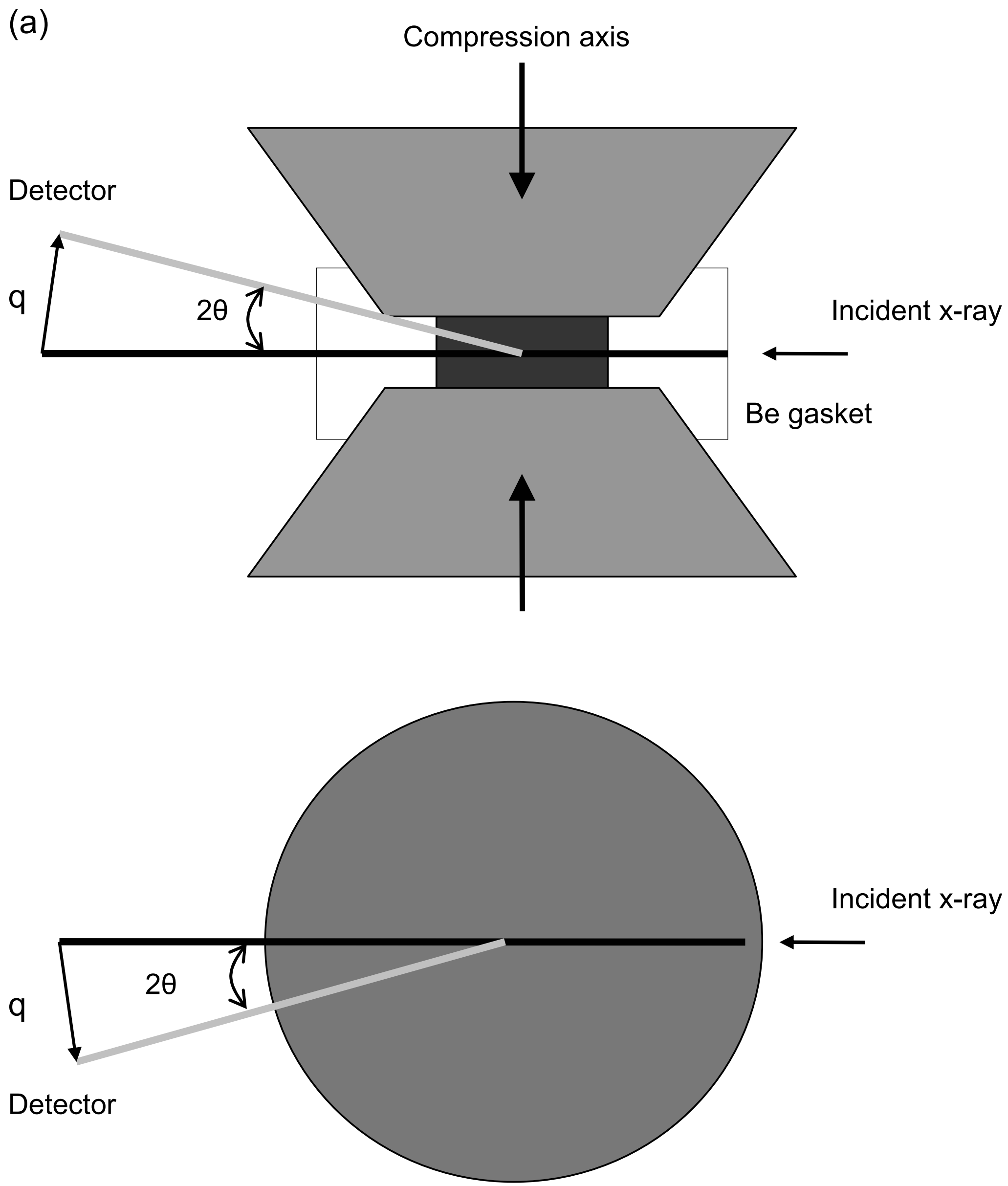


High Pressure - Inelastic X-ray Scattering – Experimental Setup





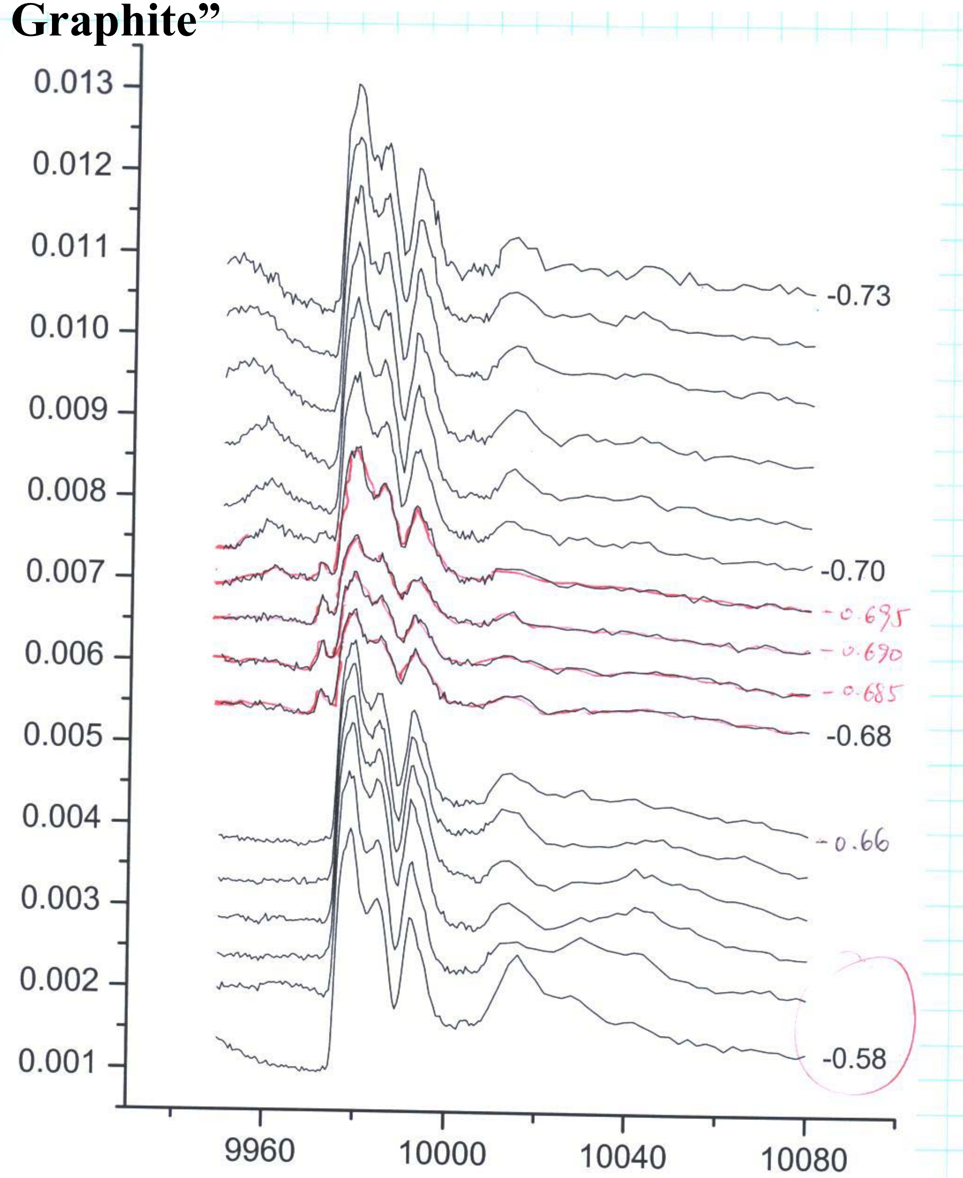
High Pressure - Inelastic X-ray Scattering – Experimental Setup



“Bonding Changes in Compressed Superhard Graphite”

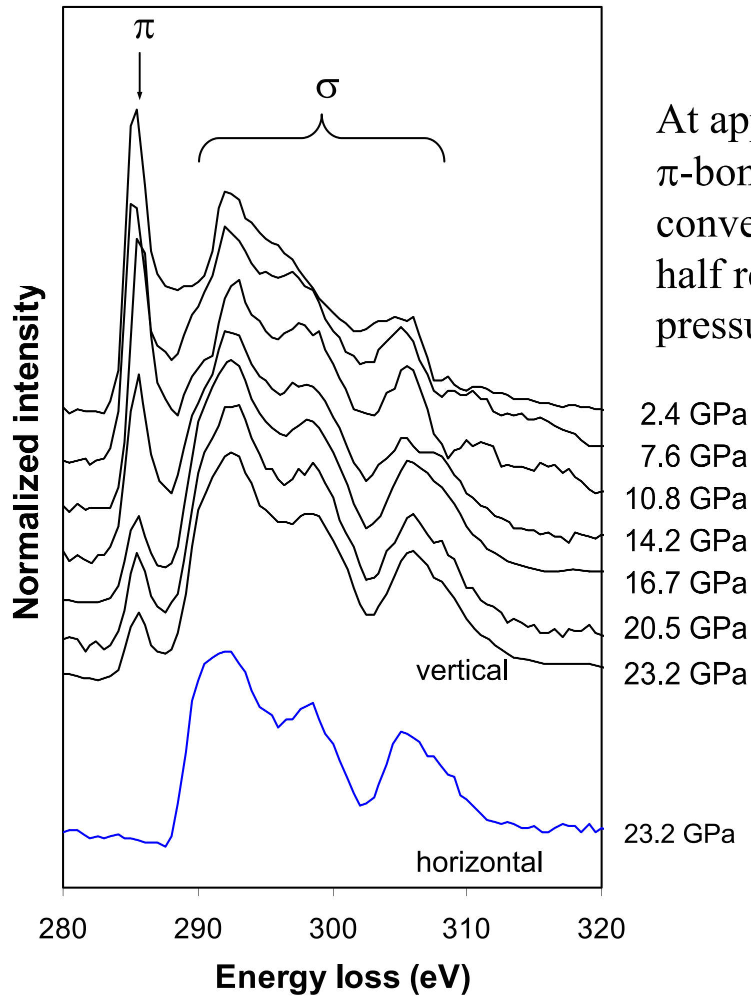
Wendy L. Mao et al.

Science ***302*** *425-427 (2003)*

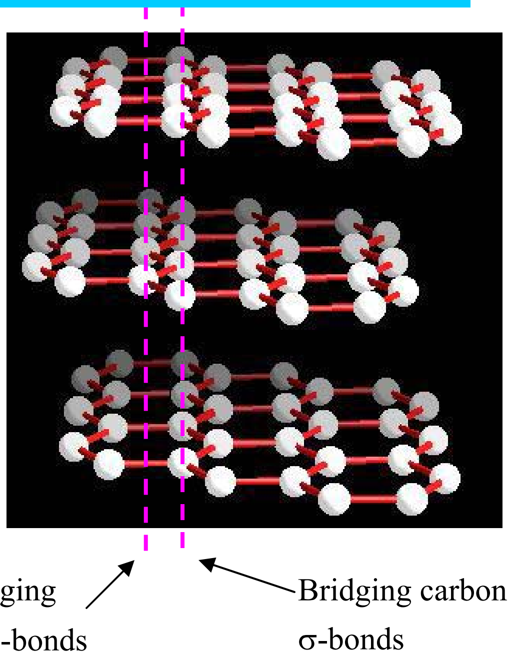


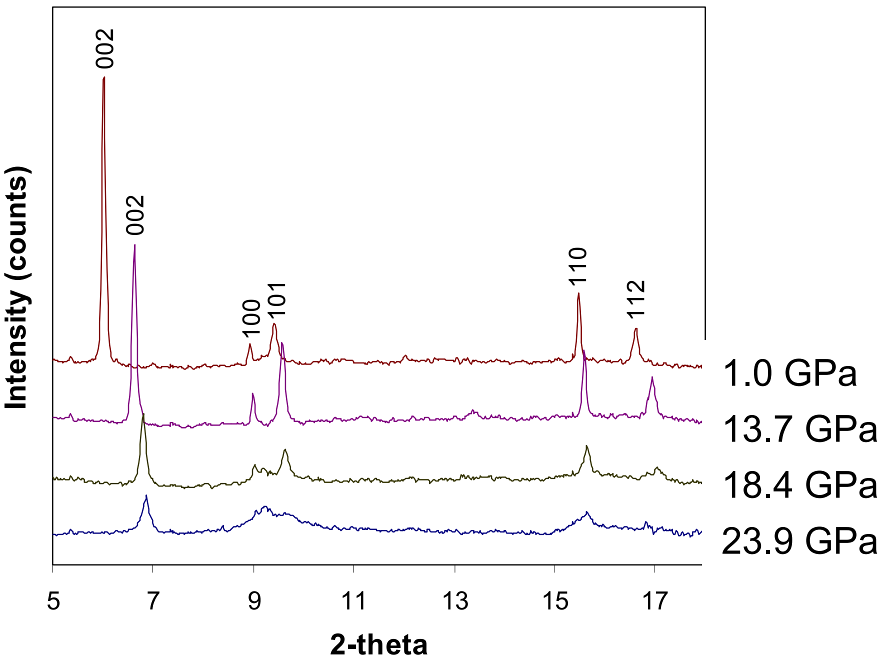
High Pressure - Inelastic X-ray Scattering – Superhard Graphite

Carbon K-edge



At approximatly 17 GPa half of the π-bonds between graphite layers convert to σ-bonds while the other half remain as π-bonds in the high-pressure form.

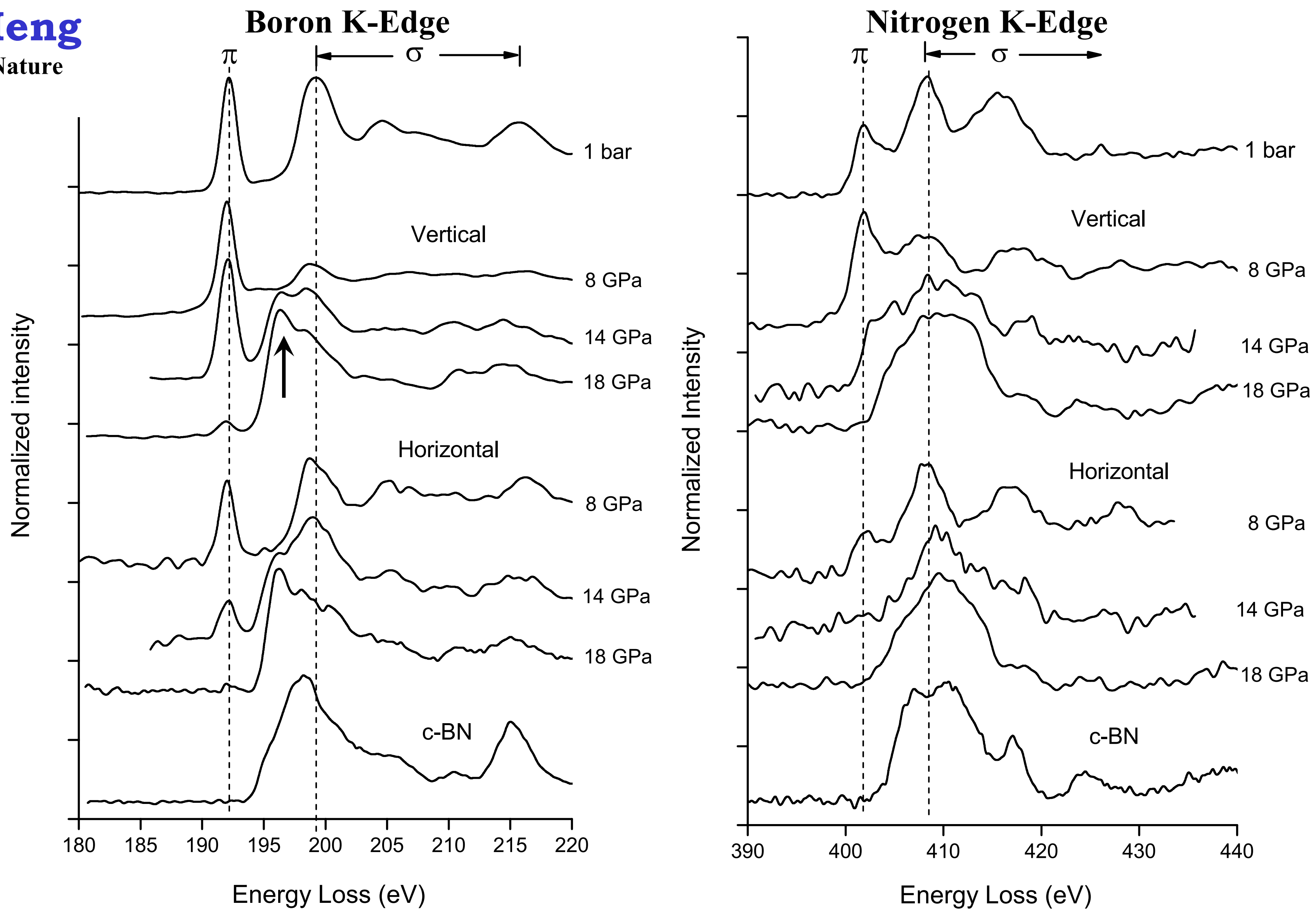




High Pressure - Inelastic X-ray Scattering – Boron Nitrite

Yue Meng

Accepted "Nature Material"



Nancy Lazarz, Fred Sopron, Clayton Pullins, Kevin Westman, Mike Jagger, Joy Talsma, Jim Ciston, Paul Murray, Patrick Dell, Leo Gubenko, Yifei Jaski,

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