X-Ray Diffraction

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Wednesday, June 29, 2005

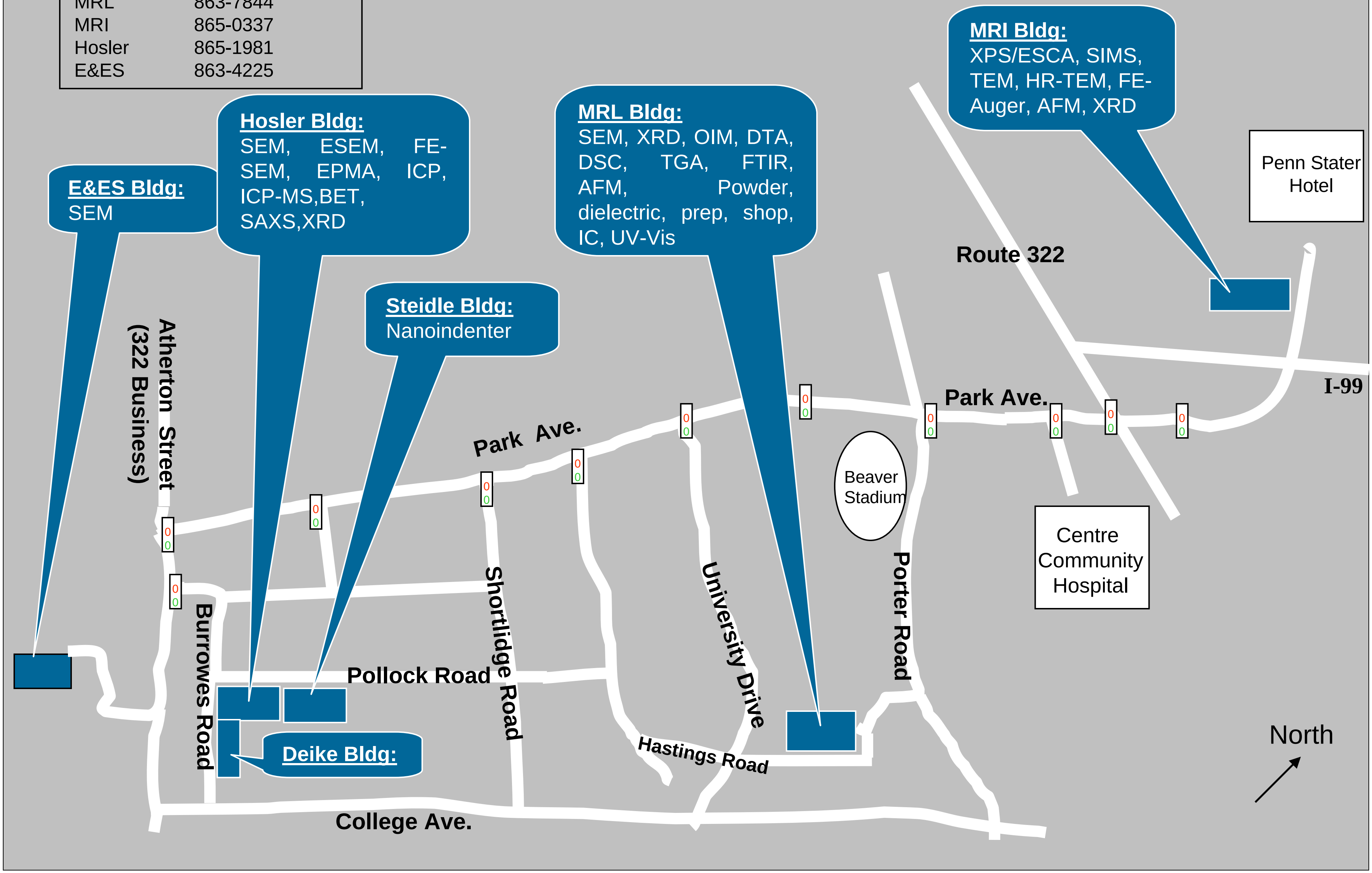
Summer Characterization Open Houses

Technique	Time	Date	Location
Thermal analysis (TGA, DTA, DSC)	9:45 AM	June 8	250 MRL Bldg.
Transmission Electron Microscopy (TEM/STEM)	9:45 AM	June 15	114 MRI Bldg
Scanning electron microscopy (SEM)	9:45 AM	June 22	541 Deike Bldg.
Analytical SEM	11:00 AM	June 22	541 Deike Bldg.
X-ray Diffraction (XRD)	9:45 AM	June 29	250 MRL Bldg.
Dielectric Characterization (25 min lecture only)	9:45 AM	July 6	250 MRL bldg.
High temperature sintering lab (20 min lecture only)	10:15 AM	July 6	250 MRL Bldg.
Focused Ion Beam (FIB)	9:45 AM	July 13	114 MRI Bldg
TEM sample preparation	11:00 AM	July 13	114 MRI Bldg
Orientation imaging microscopy (OIM/EBSD)	9:45 AM	July 20	250 MRL Bldg.
Chemical analysis (ICP, ICP-MS)	9:45 AM	July 27	541 Deike Bldg.
Atomic Force Microscopy (AFM)	9:45 AM	August 3	114 MRI Bldg
Small angle x-ray scattering (SAXS)	9:45 AM	August 10	541 Deike Bldg.
Particle Characterization	9:45 AM	August 17	250 MRL
X-ray photoelectron spectroscopy (XPS/ESCA)	9:45 AM	August 24	114 MRI Bldg
Auger Electron Spectroscopy (AES)	11:00 AM	August 24	114 MRI Bldg

NOTE LOCATIONS: The MRI Bldg is in the Innovation Park near the Penn Stater Hotel; MRL Bldg. is on Hastings Road.
More information: www.mri.psu.edu/mcl

Materials Characterization Lab Locations

Bldg	Telephone
MRL	863-7844
MRI	865-0337
Hosler	865-1981
E&ES	863-4225

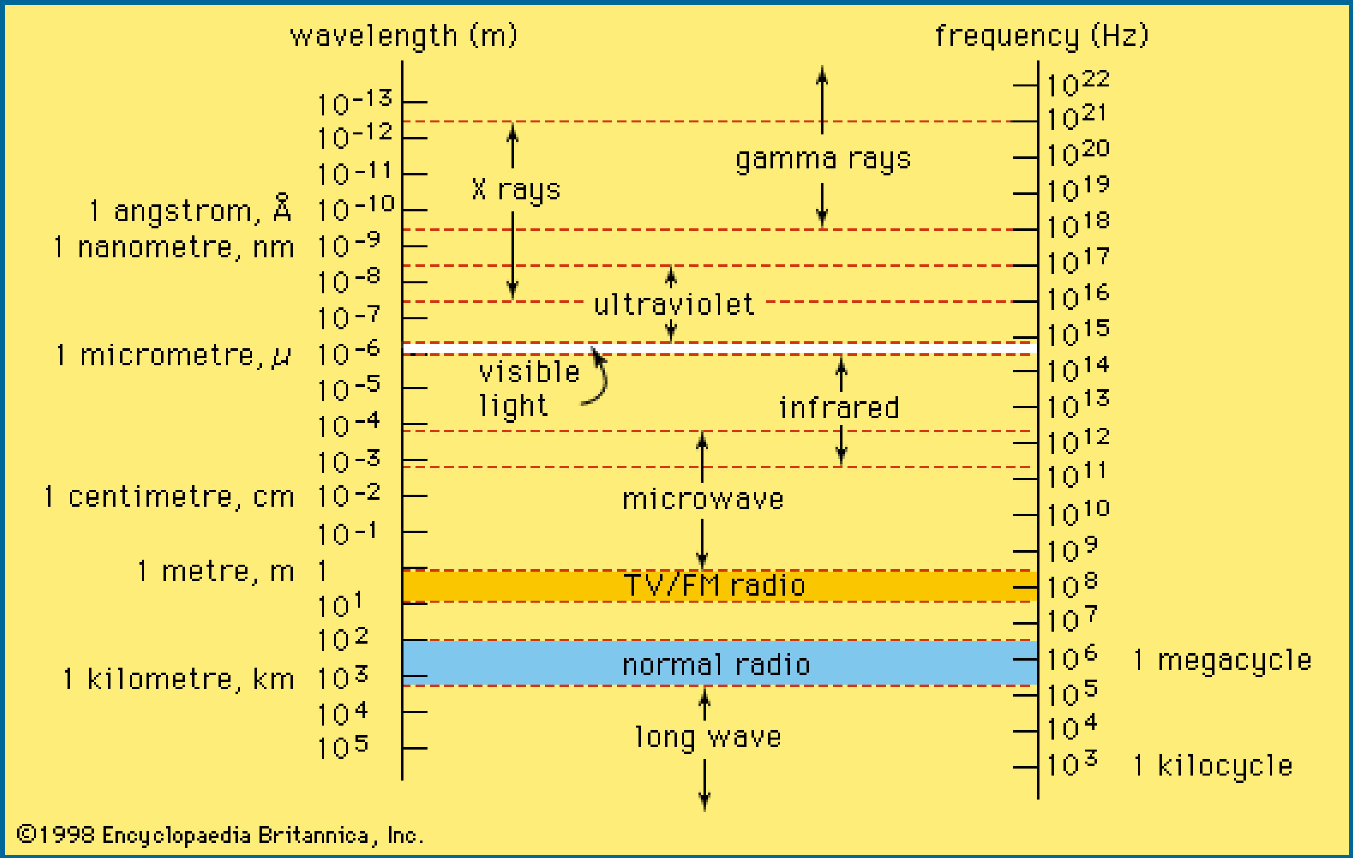


Outline

History / Theory
Instrumentation
Strengths / Limitations
MCL Instruments /Capabilities
Applications at PSU
Software
How to Get Started
Sample Prep
Campus and Other Resources
Lab Tour

HISTORY

Wavelength Range of X-rays



Encyclopedia Britannica, Inc.

The Discovery of X-Rays

- On 8 Nov, 1895, **Wilhelm Conrad Röntgen** (accidentally) discovered an image cast from his cathode ray generator, projected far beyond the possible range of the cathode rays (now known as an electron beam). Further investigation showed that the rays were generated at the point of contact of the cathode ray beam on the interior of the vacuum tube, that they were not deflected by magnetic fields, and they penetrated many kinds of matter.

- A week after his discovery, Rontgen took an X-ray photograph of his wife's hand which clearly revealed her wedding ring and her bones. The photograph electrified the general public and aroused great scientific interest in the new form of radiation. Röntgen named the new form of radiation X-radiation (X standing for "Unknown").

http://inventors.about.com/library/inventors/blxray.htm

It was the Rage……..

An x-ray "studio"

Get your bone portrait!

Laue - 1912

Showed that if a beam of X rays passed through a crystal, diffraction would take place and a pattern would be formed on a photographic plate placed at a right angle to the direction of the rays.

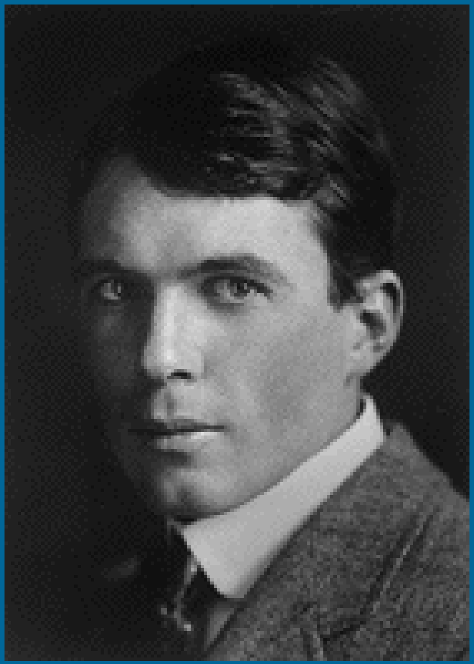
Today, known as the Laue pattern

Max von Laue

A few months later – Two Braggs

Father
Sir William Henry Bragg

Son
Sir William Lawrence Bragg



http://www.britannica.com/nobel/micro/83_18.html

THEORY

Young Bragg

- Believing that Laue's explanation was incorrect in detail, he carried out a series of experiments, the result of which he published the Bragg equation –

He was 15 years old when he did this!

$$n\lambda = 2d\sin\theta$$

Bragg's Law - defined

$$n\lambda = 2d\sin\theta$$ Bragg's Law

Assume n=1 for the first order reflection (hkl=111)

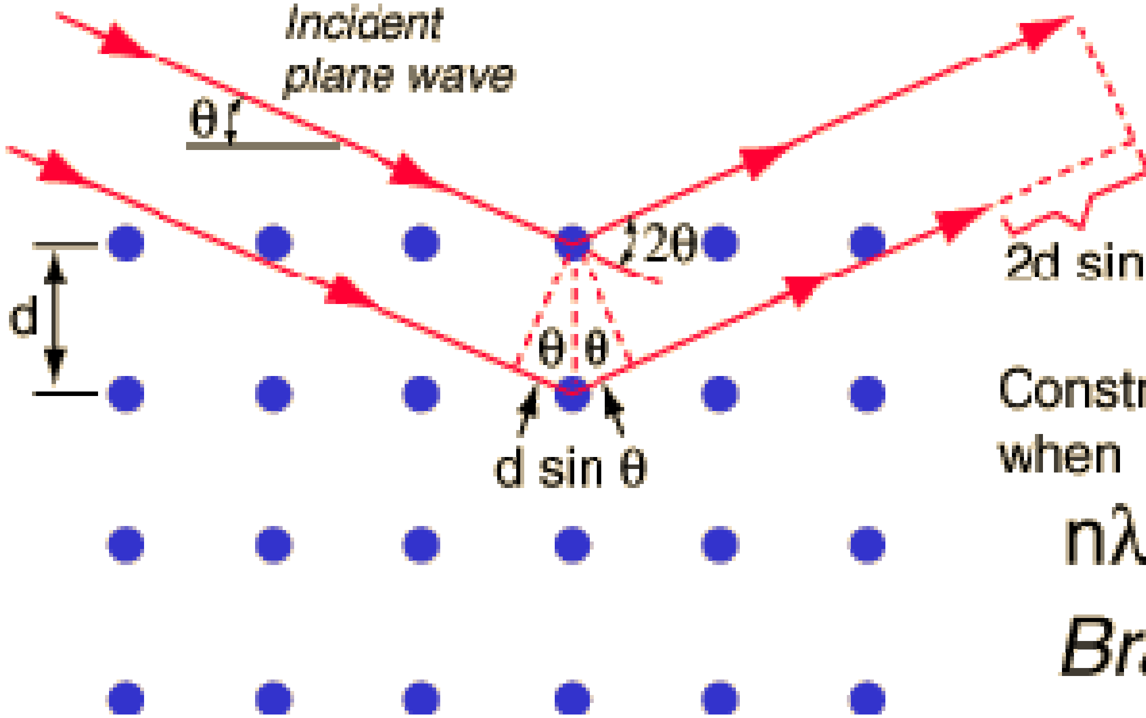
Tells us at what angles X rays will be diffracted by a crystal when the X-ray wavelength and distance between the crystal atoms are known

λ = Wavelength
1.54 A for Cu
(known value)

θ = X-ray incidence angle
(known value)

d = Lattice inter-planar spacing of the crystal *(calculate)*

Bragg's Law



Assumptions:
Monochromatic beam
Parallel beam

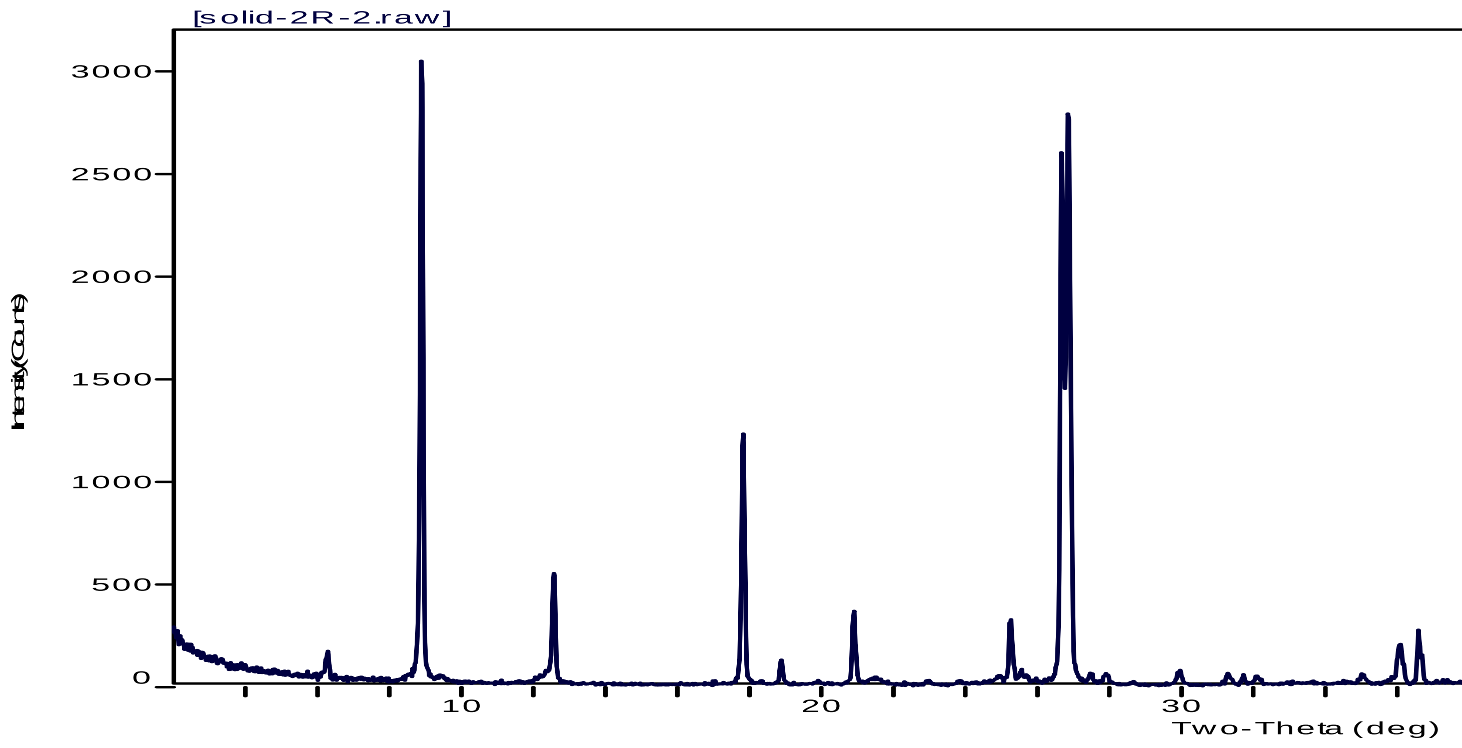
Constructive interference when

$$n\lambda = 2d \sin\theta$$

Bragg's Law

http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html

Eventually……… Bragg-Brentano Diffractometer and The Diffraction Pattern



Development of Modern Spectrometers

Invention of the X-ray Tube

- William D. Coolidge's name is inseparably linked with the X-ray tube-popularly called the 'Coolidge tube.'

  This invention completely revolutionized the generation of X-rays and remains to this day the model upon which all X-ray tubes are patterned.

- Ductile Tungsten

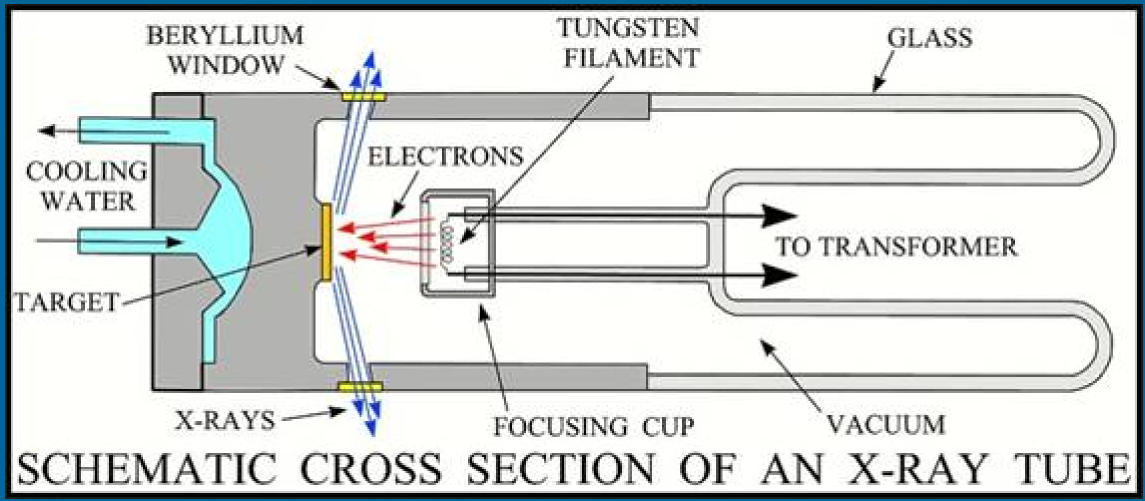
  at General Electric

http://inventors.about.com/gi/dynamic/offsite.htm?site=http://www.invent.org/hall%5Fof%5Ffame/1%5F1%5F6%5Fdetail.asp%3FvInventorID=33

Modern X-Ray Tube

Cross Section

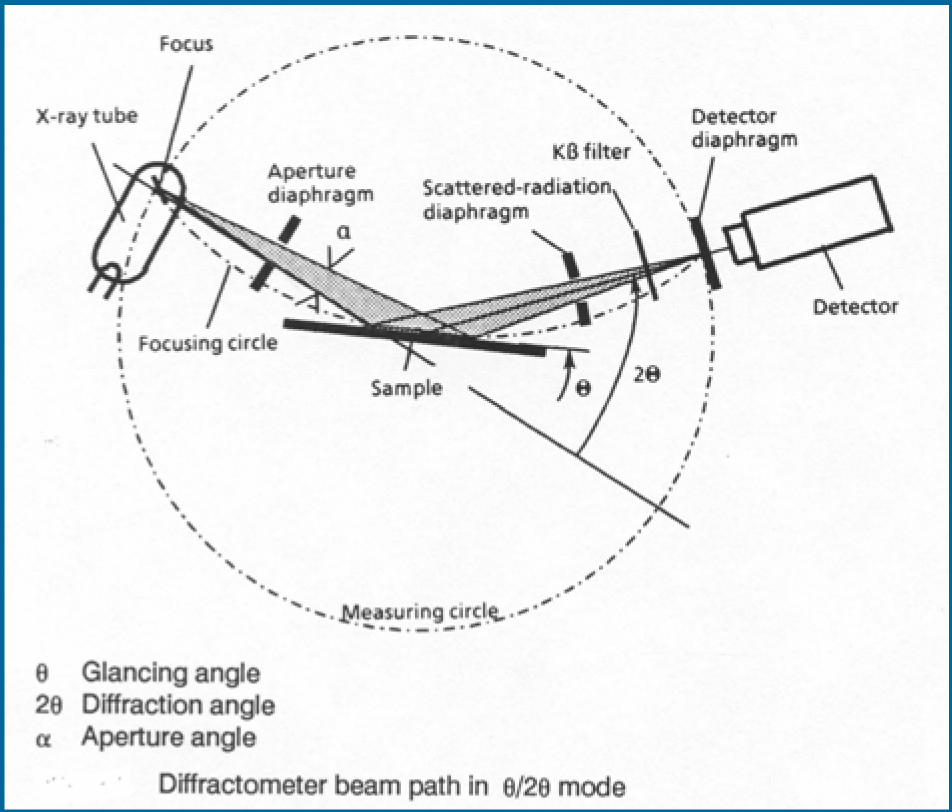
- In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions.



SCHEMATIC CROSS SECTION OF AN X-RAY TUBE

http://pubs.usgs.gov/of/of01-041/htmldocs/xrpd.htm

Schematic of Bragg-Brentano Diffractometer



From the Siemens (now Bruker AXS) manual for the D5000

First was introduced by North American Philips in 1947

Construction and geometry today differ little today from the early diffractometers

BUT.....Significant advances in:
detection and counting systems, automation, and analysis of the data (computers)

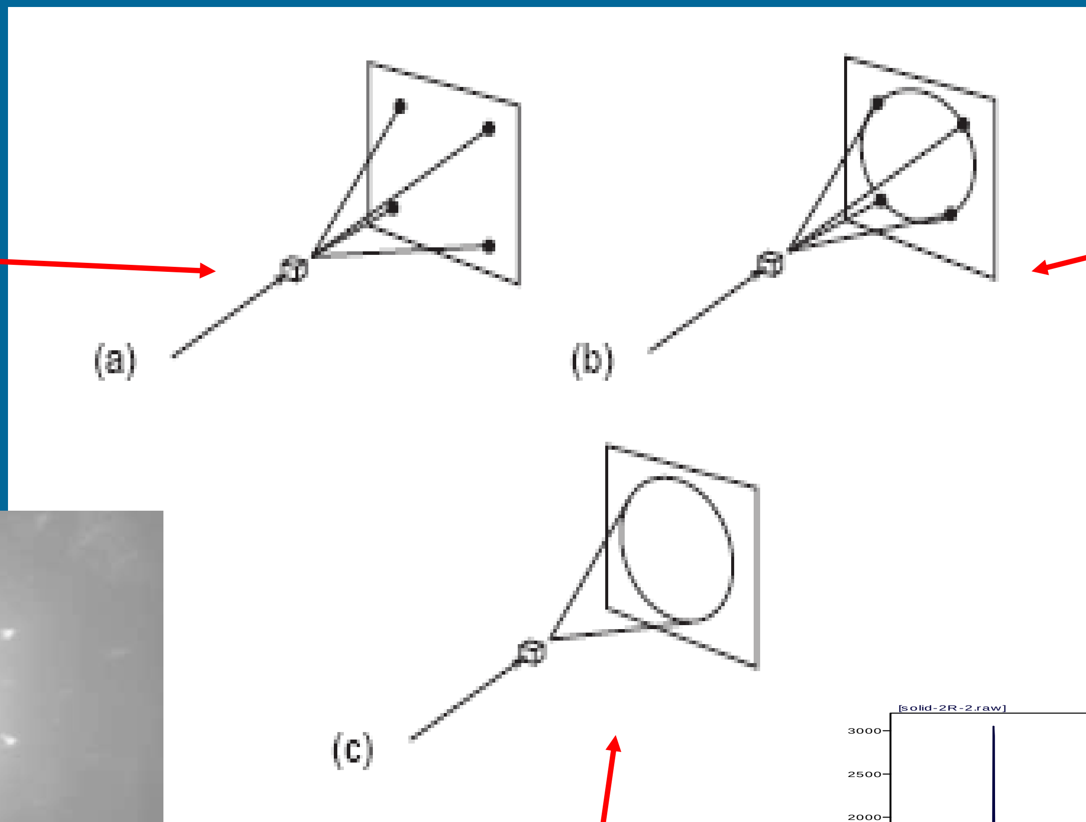
Types of X-ray Diffraction Instruments

Two Types of Instrumentation

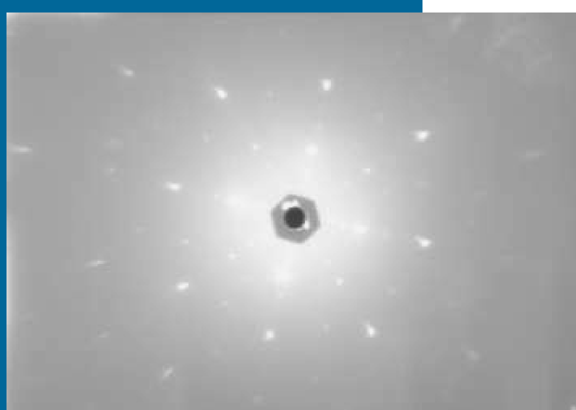
- Powder
- Single Crystal

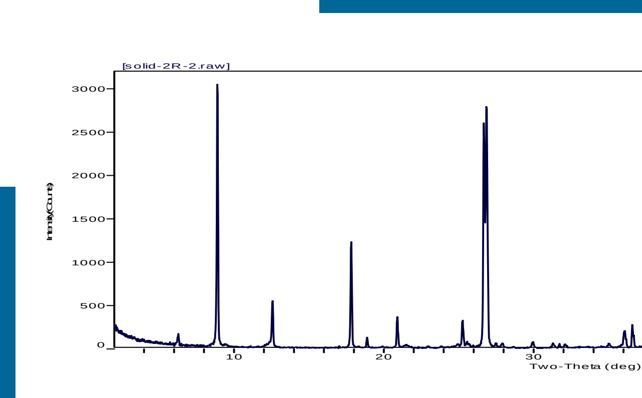
Types of Patterns

From a Single crystal



From an Oriented powder





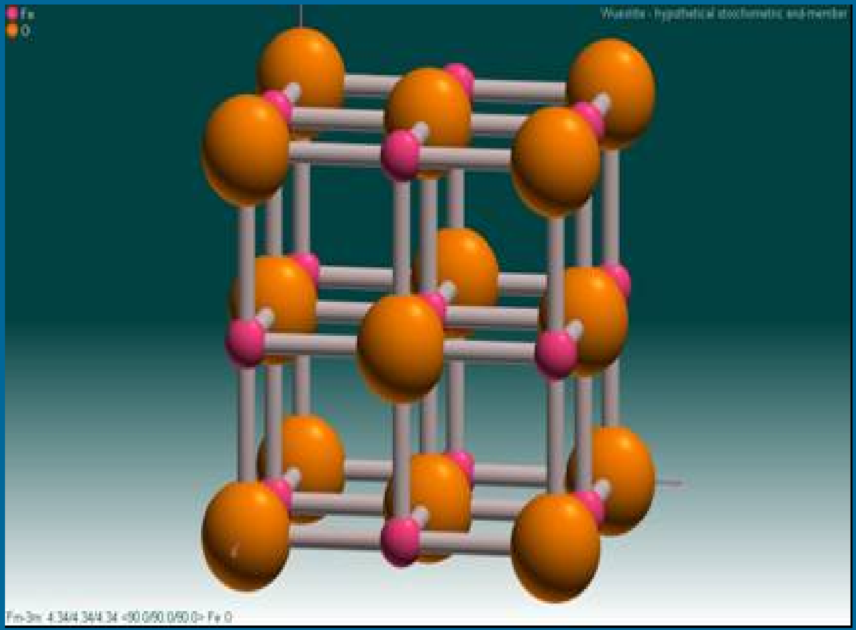
From a randomly Oriented powder

Powder Diffraction

- Use Powder when working with:
  - Essentially anything that can be ground to a powdered form
    - Rocks, cements, pharmaceuticals, etc
  - Materials for which you wish to know the compounds present – not just the elements - (and perhaps how much of each compound if a mixture)

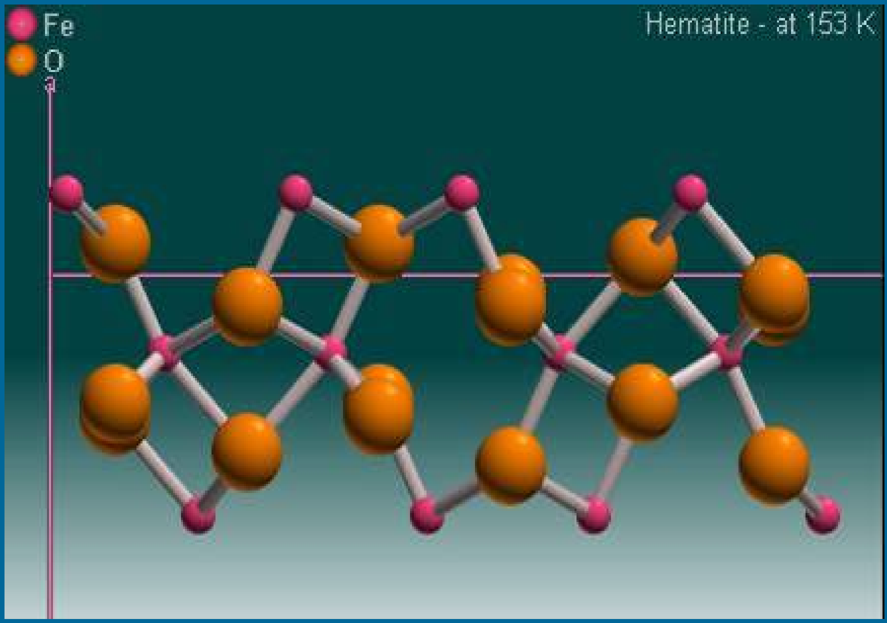
Compounds

"I have iron oxide. I want to know if it is in the form of FeO (wuestite) or Fe2O3 (hematite)."



Wuestite - cubic

FeO



Hematite - hexagonal

Fe_2O_3

Single Crystal Diffraction

- Use Single Crystal when working with:
  - Obviously when you have "single crystals"
  - When you want to know the structure of a crystal – information such as
    - bond lengths
    - bond angles
    - atom positions

Strengths / Limitations of Powder Diffraction

Strengths of Powder X-ray Diffraction

- Non-destructive – small amount of sample
- Relatively rapid
- Identification of compounds / phases – not just elements
- Quantification of concentration of phases – (sometimes)
- Classically for powders, but solids possible too
- Gives information regarding crystallinity, size/strain, crystallite size, and orientation

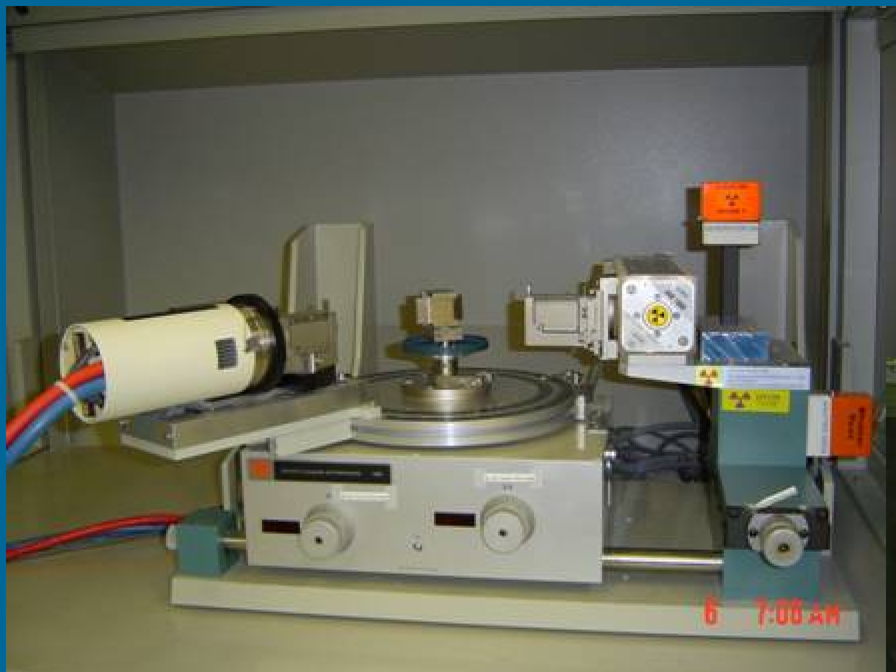
Limitations of Powder X-ray Diffraction

- Bulk technique – generally – unless a camera is uses
- Not a “stand-alone” technique – often need chemical data
- Complicated spectra – multiphase materials – identification / quantification can be difficult

MCL Instruments / Capabilities

Powder Diffraction

Scintag



……Scintag 1

Both horizontal θ/2θ geometry
-tube is stationary
- detector and sample move

Both used for basic powder Diffraction.

Scintag 2………

Both located in 158 MRL building

Scintag (cont'd)

……..Scintag 3

Vertical θ/θ geometry
- sample is stationary
- tube and detector move

Hot (up to 1500C), Cold (to Liquid nitrogen -196C), and sample rotation stages available

Located in 158 MRL

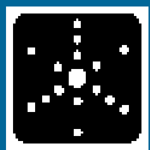
Philips X'Pert

Has both focusing and parallel beam optics.

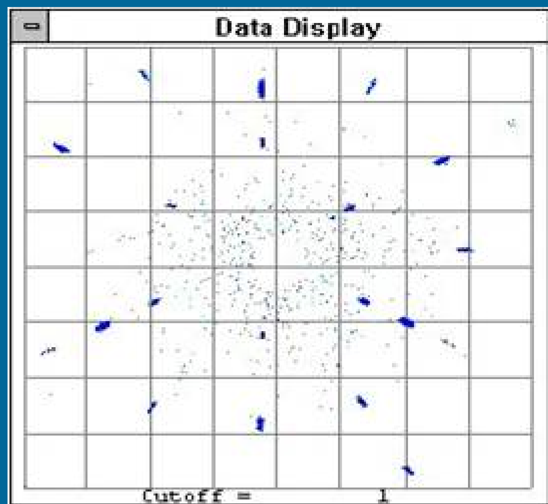
Located in Room 158 MRL building

Single Crystal Diffractometers

Laue



Multiwire Laboratories



Located in 156 MRL

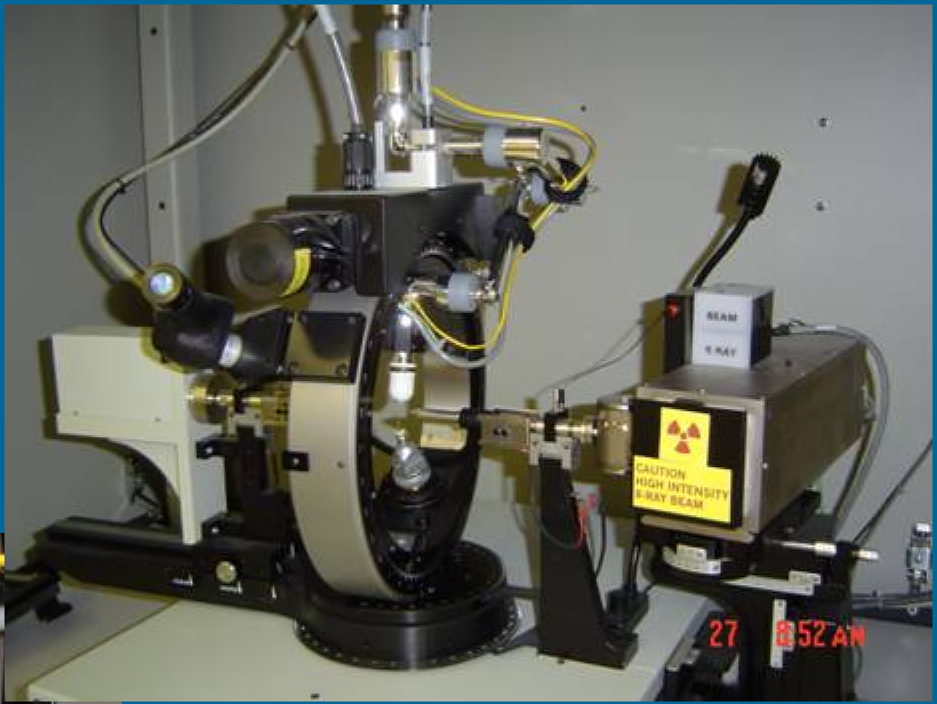
Consists of a position sensitive x-ray proportional counter connected to a computer system - orients and characterizes single crystals quickly in real-time.

Laue patterns can be easily stored, displayed, and printed - completely avoiding the use of film.

Philips High Resolution 4-Circle

Located in room   MRI building

Bruker 4-Circle

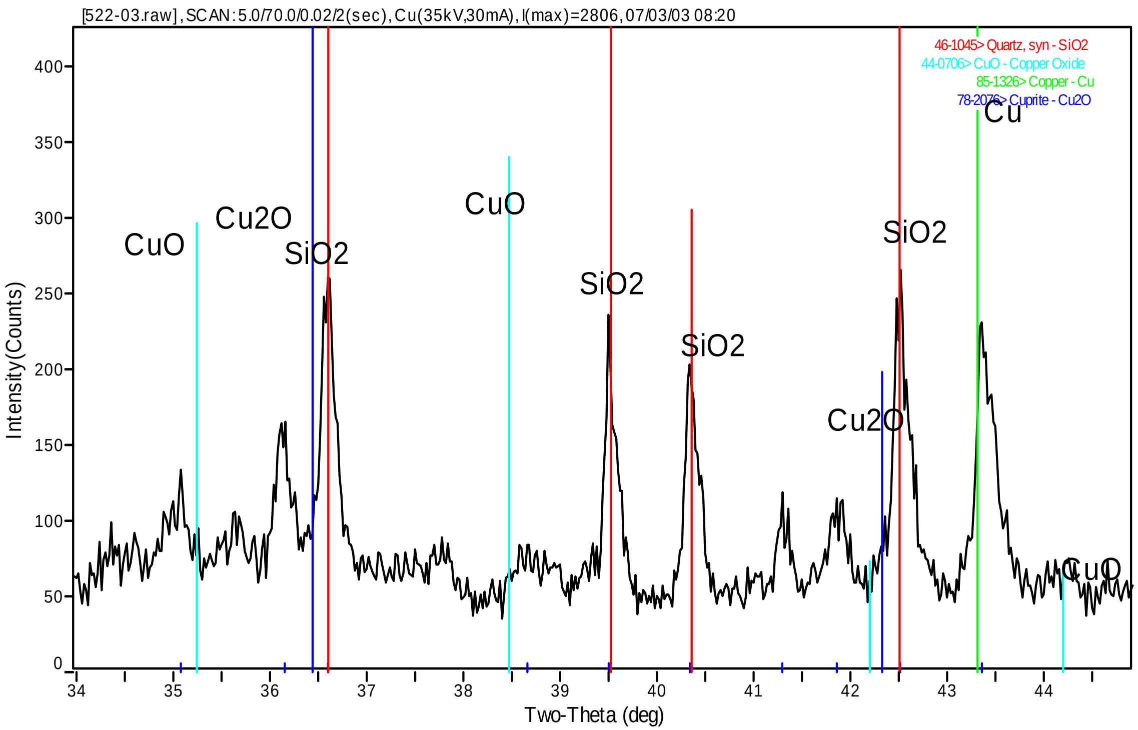


Located in 156 MRL

Applications at PSU

Oxidation States of Copper

As a fungicide on roofing materials



The major phase is quartz, (red) also a significant amount of Cu, (green).

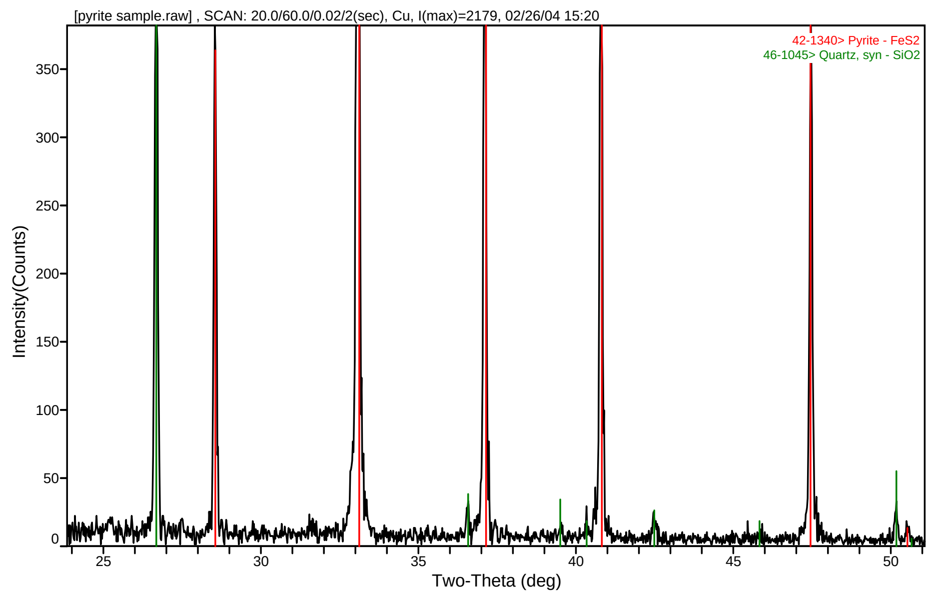
Perhaps, some Cu2O, (blue), but Cu2O directly overlaps the SiO2 lines.

There is no CuO detected.

Other unidentified phases also present.

Pyrite

- Example of the mineral pyrite, FeS_2, that was found at a local road construction site.



(Eq. 1) $FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$

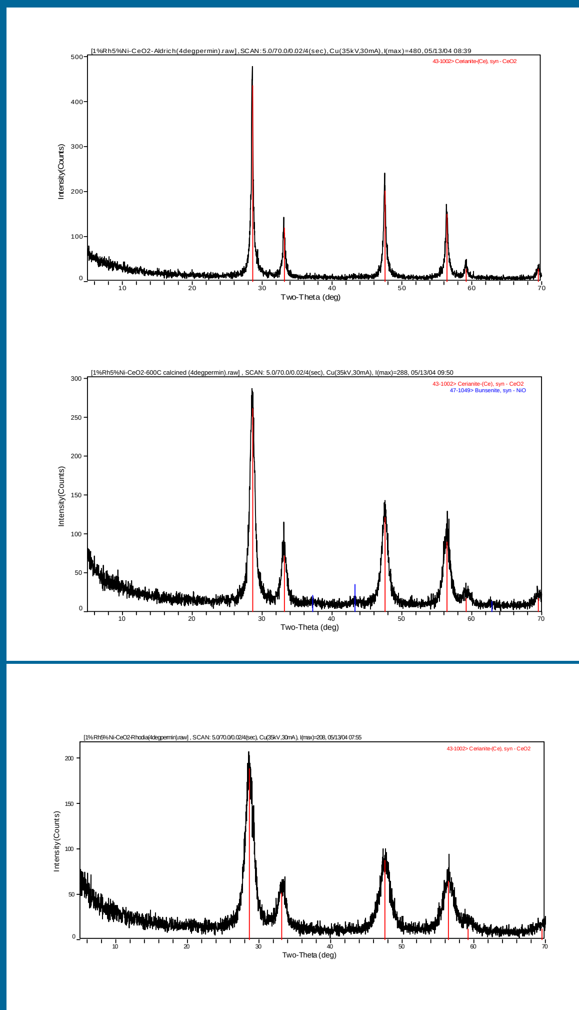
(Eq. 2) $Fe^{2+} + 1/4O_2 + 3/2H_2O = FeOOHppt + 2H^+$

(Eq. 3) $FeS_2 + 15/4O_2 + 7/2H_2O = Fe(OH)_3ppt + 2SO_4^{2-} + 4H^+$

Crystallite Size Measurement

Rh-Ni CeO2 powders

Decreasing crystallite size



$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

τ = particle size

K = shape factor (typically 0.85-0.9)

λ = wavelength (Angstroms)

β = corrected FWHM (radians)

θ = ½ 2θ (peak position)

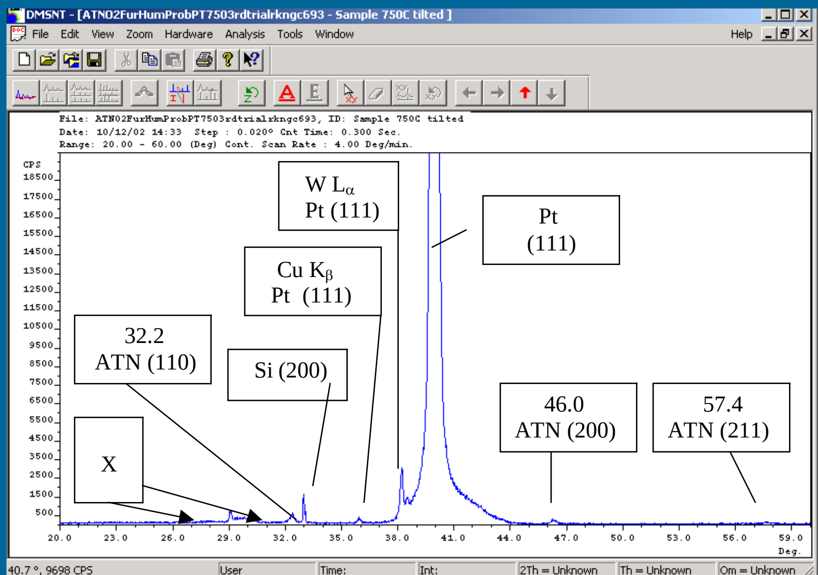
Good for particle sizes < 500A and no strain.

If strain, other Methods:

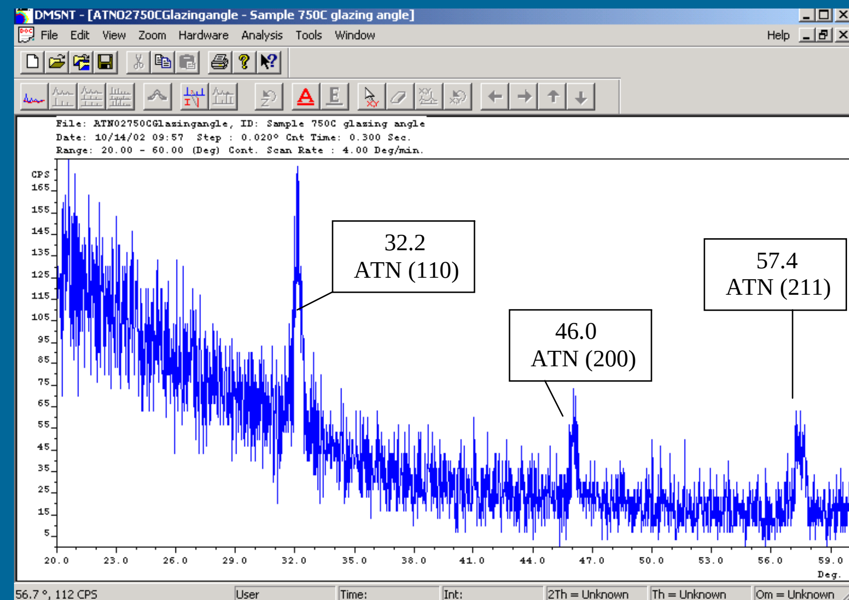
Warren / Averbach

Williamson-Hall plot

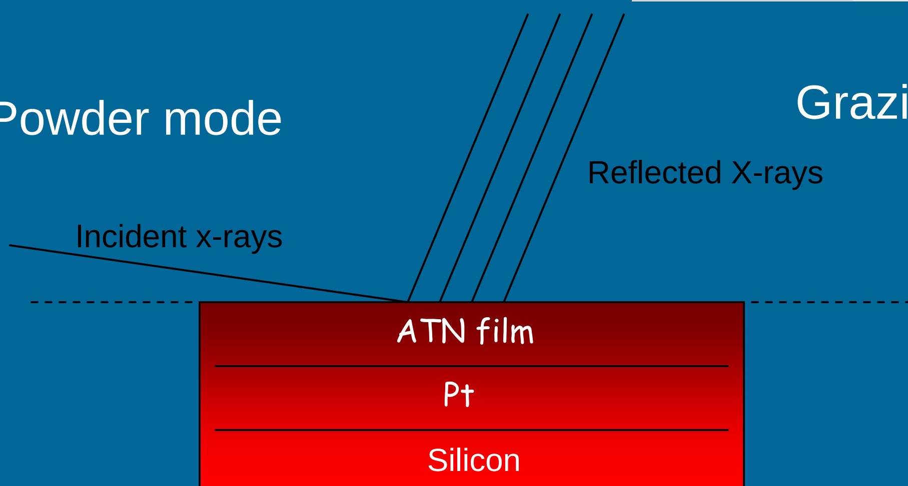
Grazing Angle Geometry



Normal Powder mode



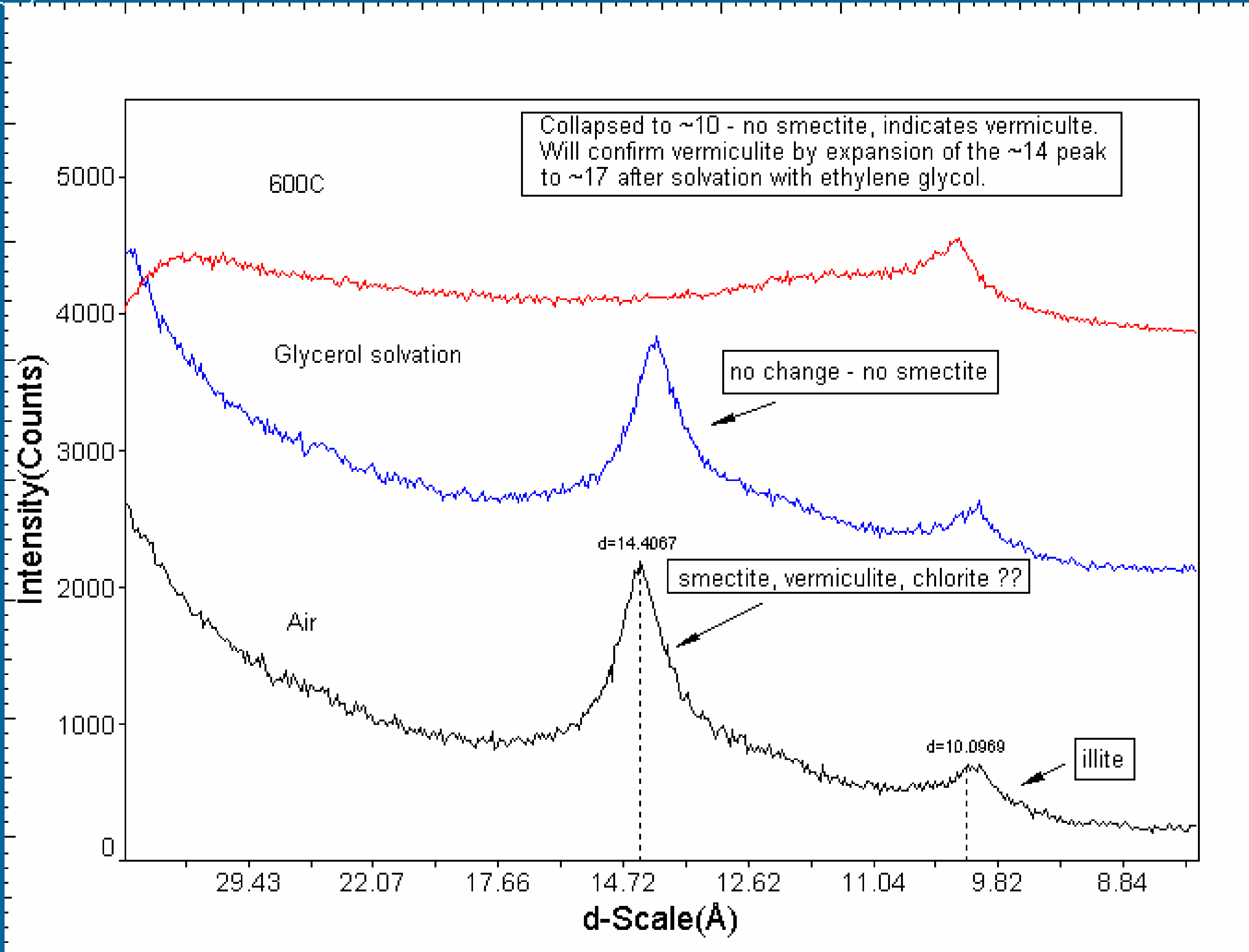
Grazing angle mode



PENNSTATE

Materials Research Institute

Materials Characterization Lab
www.mri.psu.edu/mcl

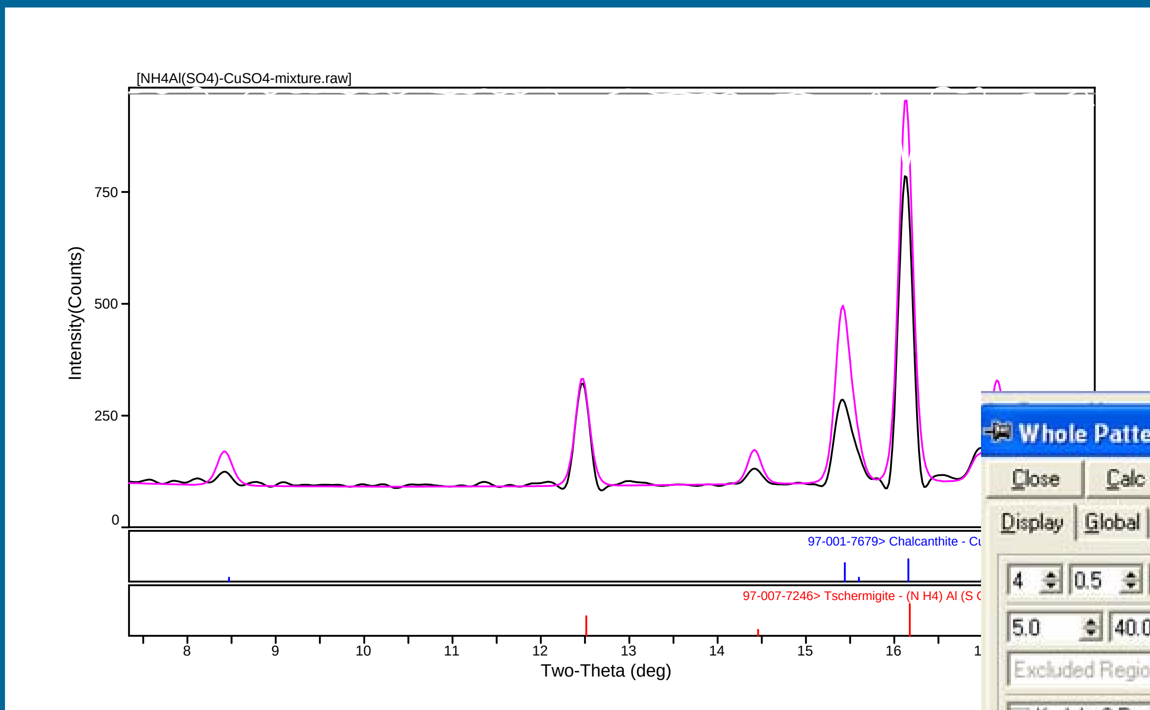


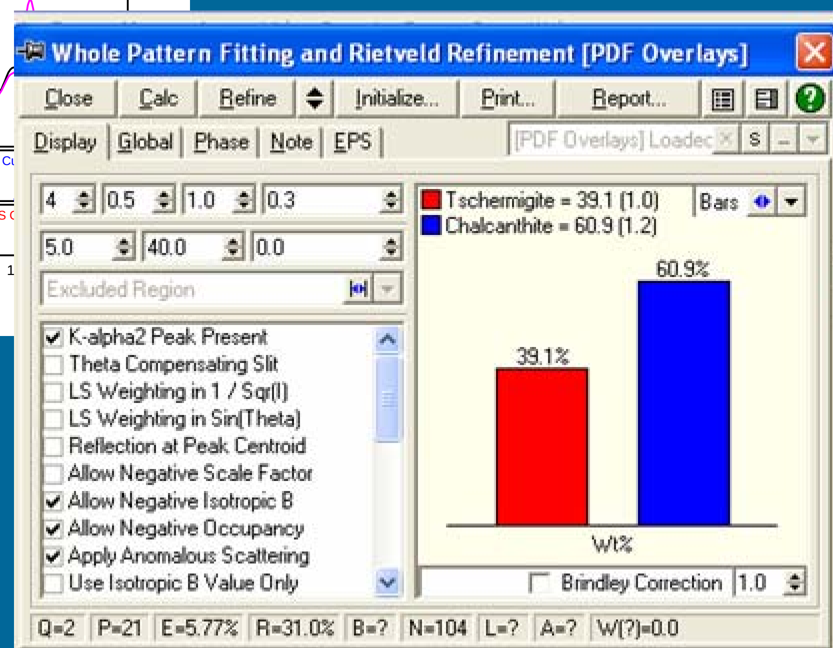
Software

Jade

- Currently using Jade 7.1+ software manufactured by MDI, Inc.
  - Capabilities include (not inclusive):
    - Full Search / Match of current ICDD (2004) and ICSD (2005) databases for phase ID
    - Whole Pattern Profile Fitting / Rietveld Refinement
    - RIR Quantitative (Easy Quant)
    - Crystallite Size Estimate / Strain
    - 3-D Crystal Structure Viewer

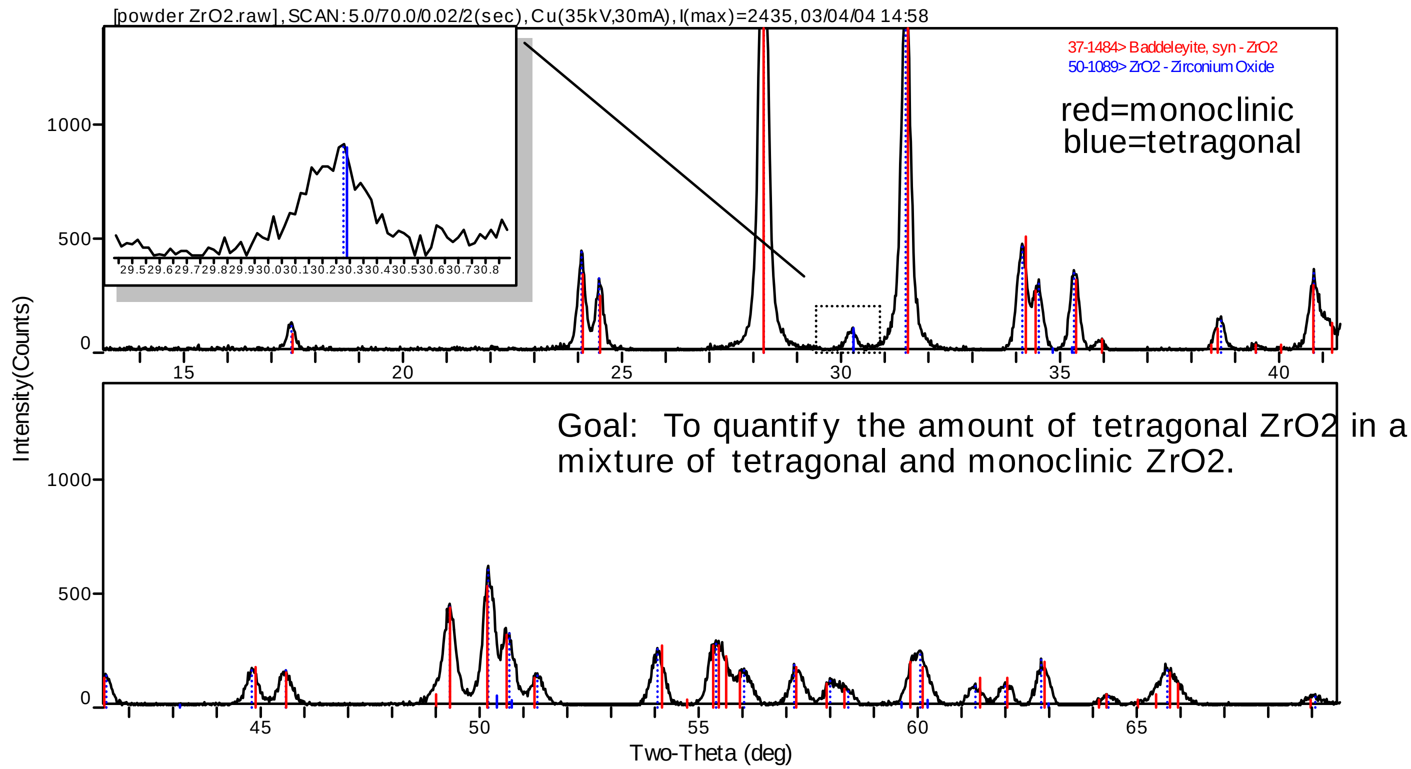
Quantitative Analysis – by Rietveld





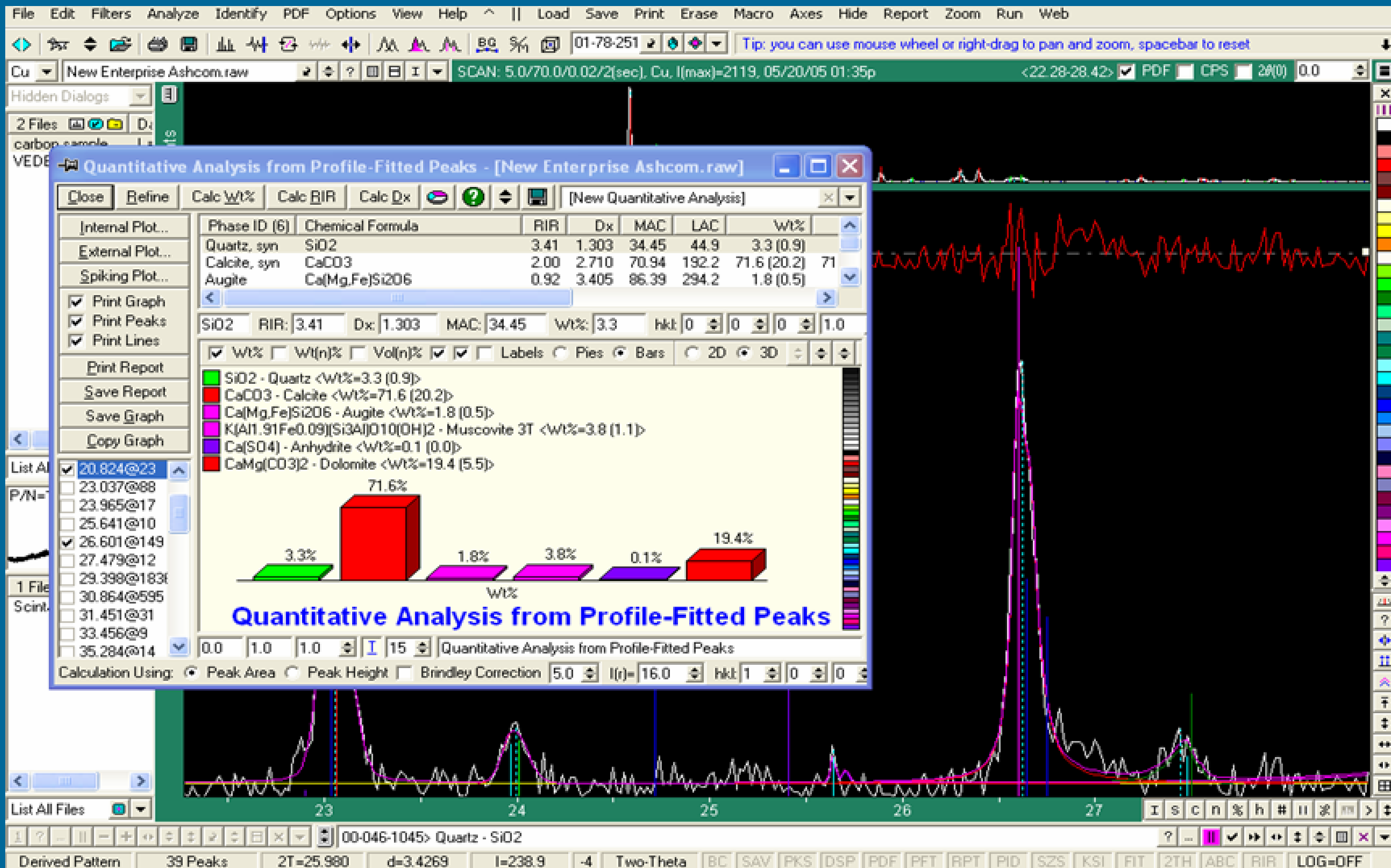
Rietveld Refinement

- Quantify monoclinic and tetragonal zirconia – only the 100% tetragonal peak visible / clear from overlap



Quantitative Analysis – RIR Method

Jade's "Easy QUANT"



How to Get Started

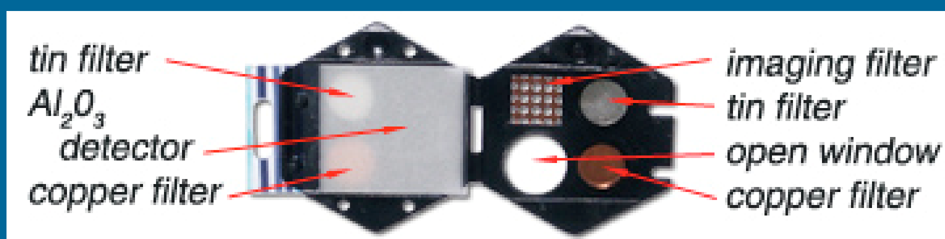
Environmental Health and Safety X-ray safety training course

PENNSTATE
Environmental Health and Safety

http://www.ehs.psu.edu/radprot/x-ray_safety_training.cfm

Dosimetry

- Worn on the wrist closest to the x-ray source (varies by instrument) – issued once each quarter



Thin strip of specially formulated aluminum oxide (Al2O3) crystalline material. During analysis, the Al2O3 strip is stimulated with selected frequencies of laser light causing it to luminesce in proportion to the amount of radiation exposure.

Who Do I Contact to use X-ray Diffraction Equipment at PSU?

MCL Contacts

(For equipment in the MRL building)

Nichole Wonderling
nmw10@psu.edu
159 MRL Building
863-1369

(For equipment in Hosler and MRI buildings)

Mark Angelone
msa3@psu.edu
310 Hosler Building
883-9350

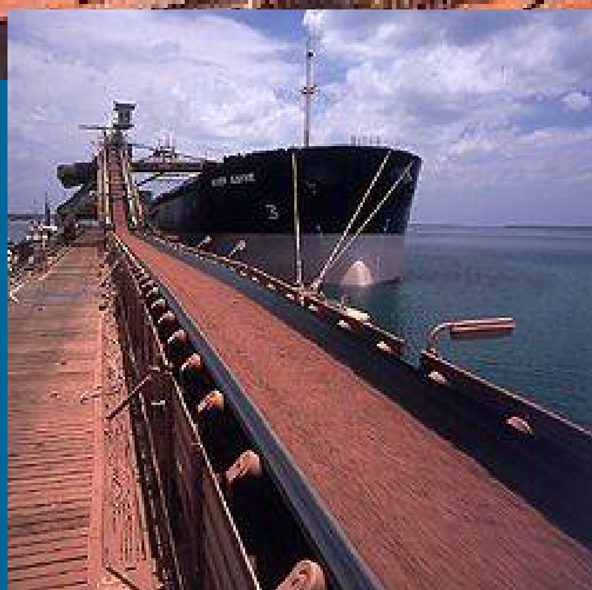
John Cantolina
jjc16@psu.edu
310 Hosler Building
883-8358

Sample Preparation

In Search of the Elusive "Perfect" Powder Sample

- A "Representative" sample

The Elusive "Perfect" Powder Sample



How do I get a "representative" sample?

The Elusive "Perfect" Powder Sample

- A "Representative" sample
- Sufficient number of crystallites
  Particle Size

POWDER ?

Make mine a powder……

You may be lucky and have one of these…….. a SPEX Shatterbox

Picture of SPEX Shatterbox from Georgia State, Geology dept. web site
http://www2.gsu.edu/~wwwgeo/pages_03/lab/xRayFluorescence.htm

Or maybe You have…

the XRD's Best friend………

The trusty mortar and pestle.

The Elusive "Perfect" Powder Sample

Particle Size

< 325 mesh or < 400 mesh (38-44 micron) – for *Qualitative Work*

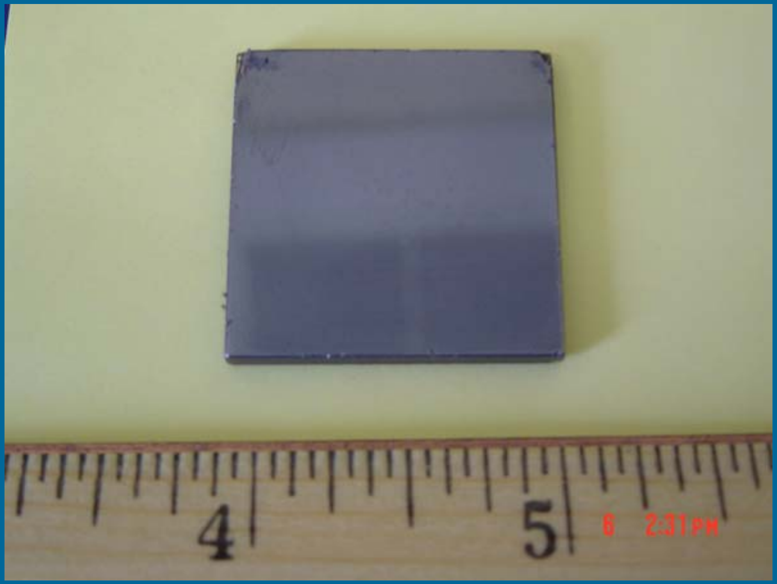
10 micron or less for *Quantitative Work* – very difficult if not impossible by hand!

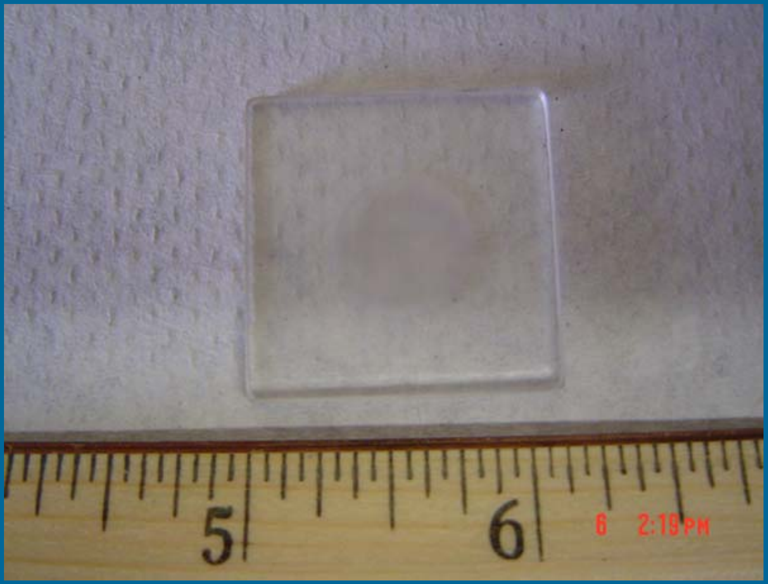
Somehow…….it needs to go through here!

The Elusive "Perfect" Powder Sample

- A "Representative" sample
- Sufficient number of crystallites
  - Particle Size
- Total randomness of the crystallite orientations
  - How the Sample is Introduced to the Instrument

Zero Background Holders (ZBH)



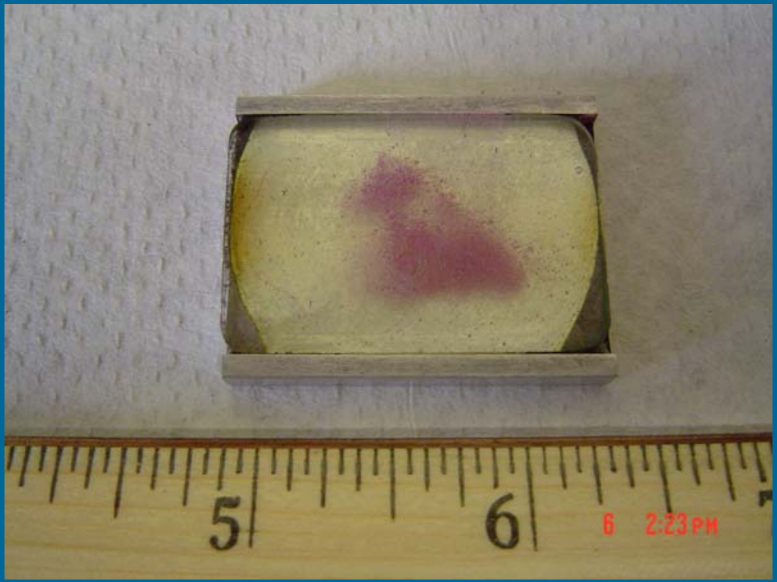


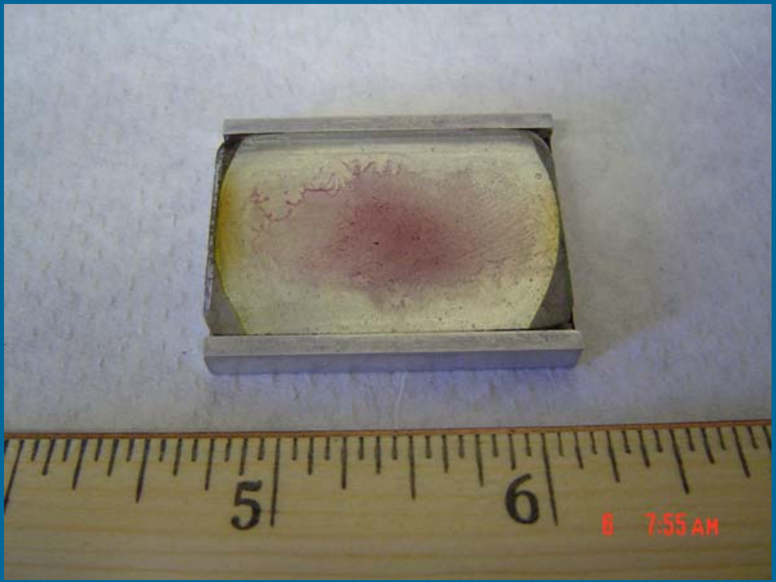
Flat Silicon ZBH
Cut parallel to Si (510)
Si (511) – *also available, but has peak at 96ºθ*

Quartz ZBH with cavity
Cut 6 º from (0001)

See www.gemdugout.com for additional information

Flat Quartz ZBH



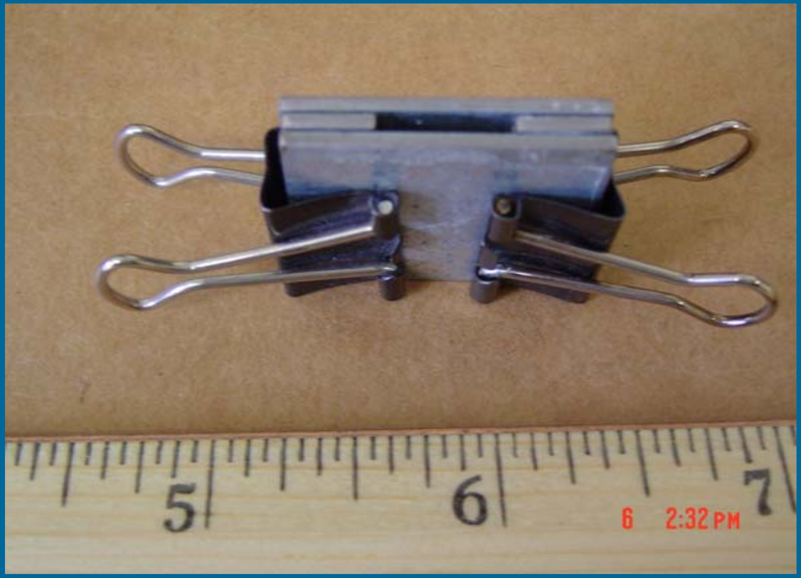


Vaseline Mount

Smear Mount

Back Filled Sample Holder

Side Drift Mount



Assembled

Disassembled

Designed to reduce preferred orientation – great for clay samples, (and others with peaks at low 2-theta angles)

The Elusive "Perfect" Powder Sample

- A "Representative" sample
- Sufficient number of crystallites

  Particle Size

- Total randomness of the crystallite orientations

  How the Sample is Introduced to the Instrument

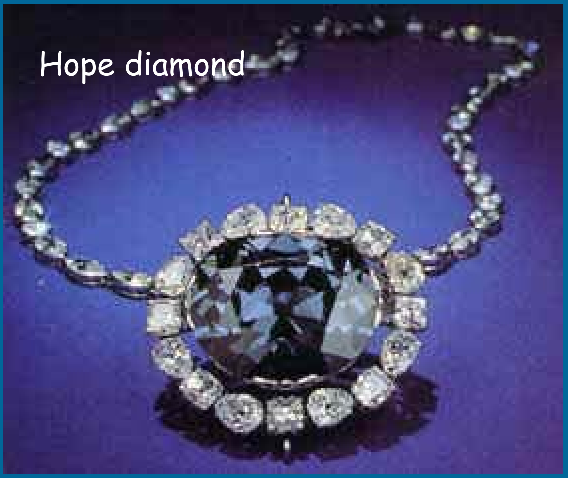
- Sufficient intensity – limit of detection ~5%

  Enough sample area presented to the beam and enough of the phase of interest present

"Real World" Samples

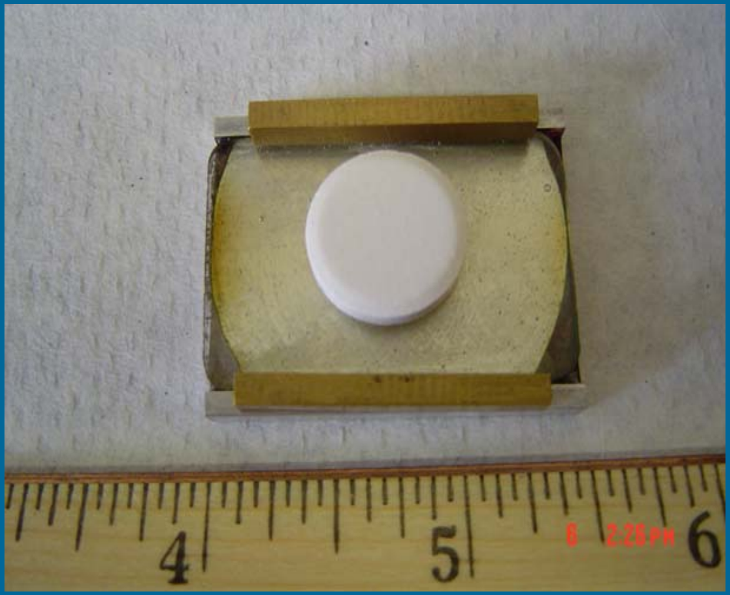
Some things can't practically be powders:

films
pellets
crystals
mineral specimens



There are techniques available to deal with many of these – ask!

Shimmed Pellet Mount



Plastic box - Pellet Mount

Campus and Other Resources

Courses

- MATSE 430 Materials Characterization
  - Fall semester only, 3 credit course, instructor Elizabeth Dickey

Books

"Elements of X-ray Diffraction," Cullity and Stock

"Introduction to X-ray Powder Diffractometry," Jenkins and Snyder

"Fundamentals of Powder Diffraction and Structural Characterization of Materials," Pecharsky and Vitalij

"A Practical Guide for the Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis," Buhrke, Jenkins, Smith

Journals

"Powder Diffraction"
"Acta Crystallographica"
"Zeitschrift für Kristalographie"

On-line

http://www.ccp14.ac.uk/

http://www.icdd.com/

Faculty Experts at PSU

- Elizabeth Dickey, 195 MRI
- Peter Heaney, 309 Deike Building
- Gerald Johnson, Jr.; Prof. Emeritus, 153 MRL
- Earl Ryba, 304B Steidle Building
- Barry Scheetz, 107 MRL

Lab Tour