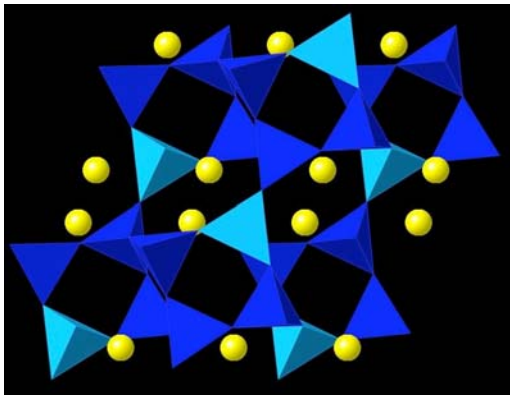
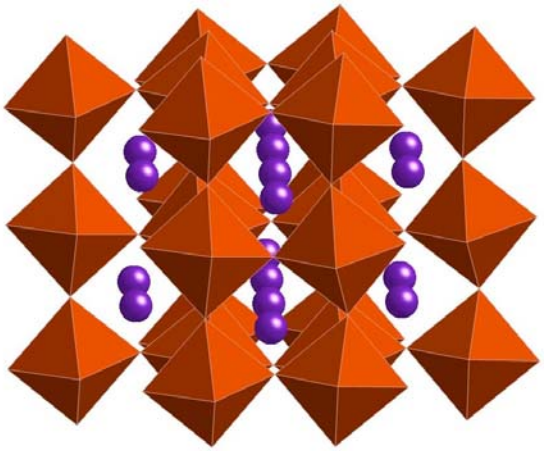
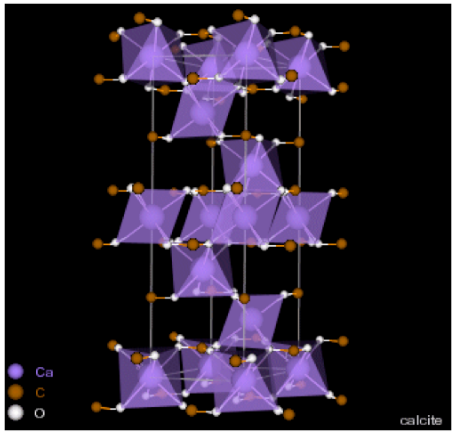




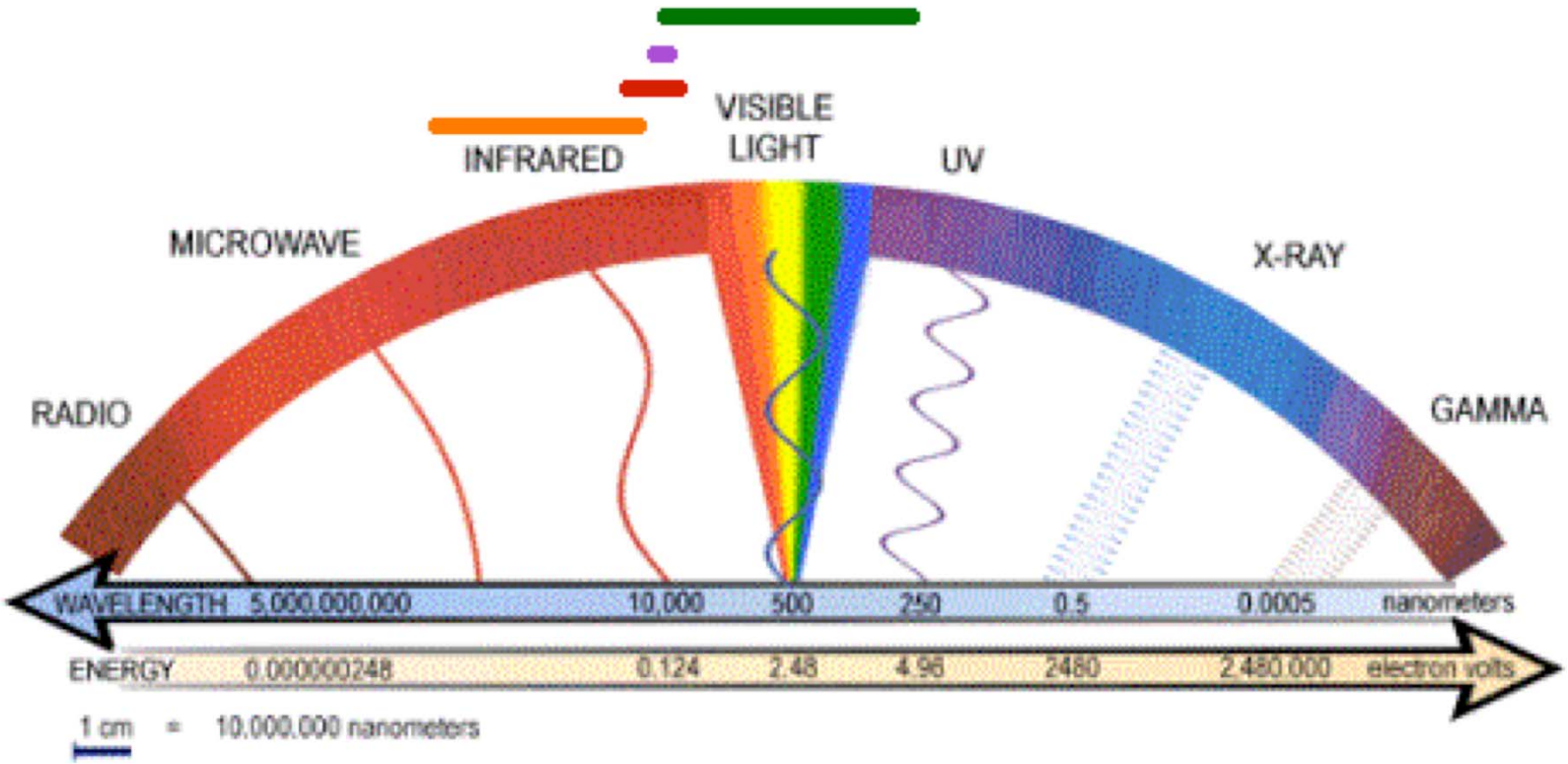


X-ray Powder Diffraction, Part 2: Review & Applications

February 22, 2010

Jennifer Jackson

Electromagnetic spectrum



X-rays: λ ~0.5 nm

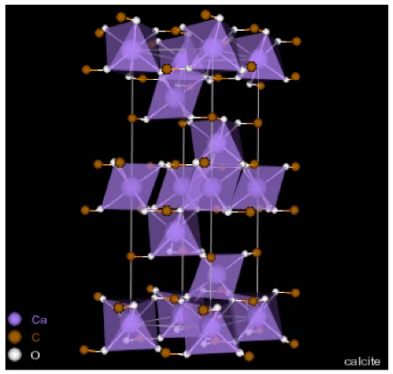
less than and/or comparable to interatomic positions

Ideal for diffracting conditions for atoms → crystal structure

Determining crystal structure & volume

- Determines *d-spacing & atomic positions*
- 3D crystal structure
- *Mineral ID!*
- Provides volume, hence density if chemistry is known (EMPA+SEM)
- Xtal Structure dictates behavior
  - Solid solution
    - $(Mg,Fe)_2SiO_4$ olivine
  - Vibrational modes
    - Raman, IR spectra
  - Ion-exchange
    - Zeolites
- Structural transitions

calcite



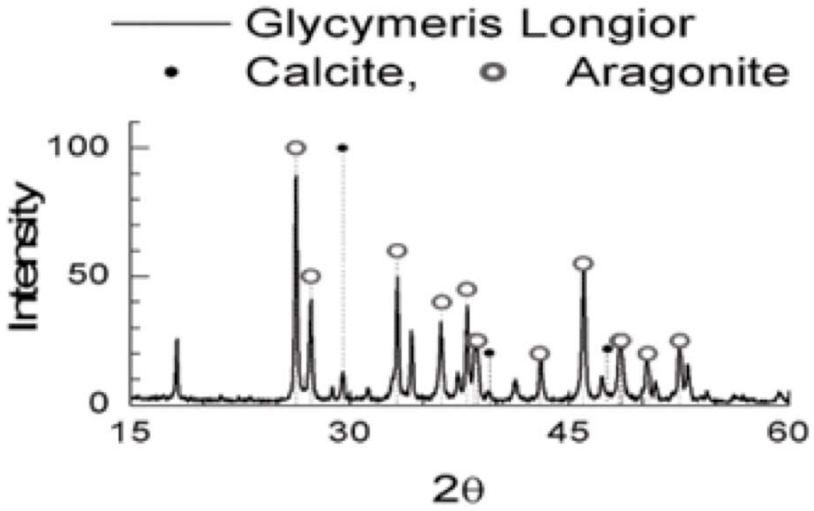


FIG. 1: XRD spectra of fossil shells, species Glycymeris Longior. Scattered points show data for Aragonite (open circles) and Calcite.

Specific information from x-ray diffraction

- Intensity of the diffracted photons, I, contains all static information of a crystal:
  - scattering factor, f
    - Atomic number, scattering angle, atomic thermal motion (Debye-Waller factor)
  - Structure factor, F
    - Summations of the scattering factors
- Atomic spacing
  - Atomic positions
    - From relative intensities from the same material
  - Structural information (space group): mineral ID
  - Lattice parameters
  - Volume
  - Density (if chemistry is known)

$$I = k\left[\sum_j f_j e^{i2\pi\left(hx_j + ky_j + lz_j\right)}\right]^2 = kF_{hkl}^2$$

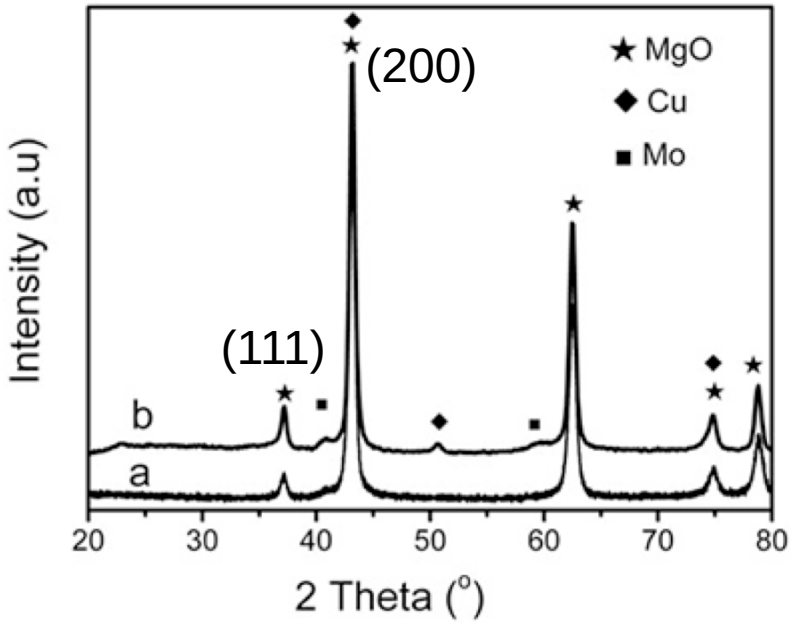
Other useful information from the spectrum:

- Phase proportions
  - Using relative intensities of the different phases present
- Strain analysis
  - Using peak widths
- Volume change with controlled thermodynamic constraints (*P-T*)
- Identify polymorphs (olivine and high-pressure phases, like wadsleyite)
- Structural Phase transitions
  - Identify polymorphs with certainty
  - In-situ monitoring of phase transitions
    - Determine the pressure (depth) at a fixed temperature, of a phase transition, for example.

Determining volume

- Cubic symmetry (NaCl):
  $d^2 = a^2(h^2+k^2+l^2)$
  $n\lambda = 2d\sin\theta$

- Important to fit all the peaks using weighted fits
  - Increased resolution at higher angles
- e.g., Celref: Fits peak positions, assuming space group & atomic positions
- If chemistry is known, one can accurately determine the density,
  - ρ = mass/volume
  - Watch unit conversions



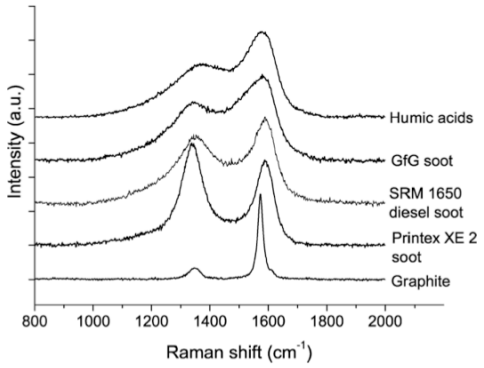
Origin of peak widths

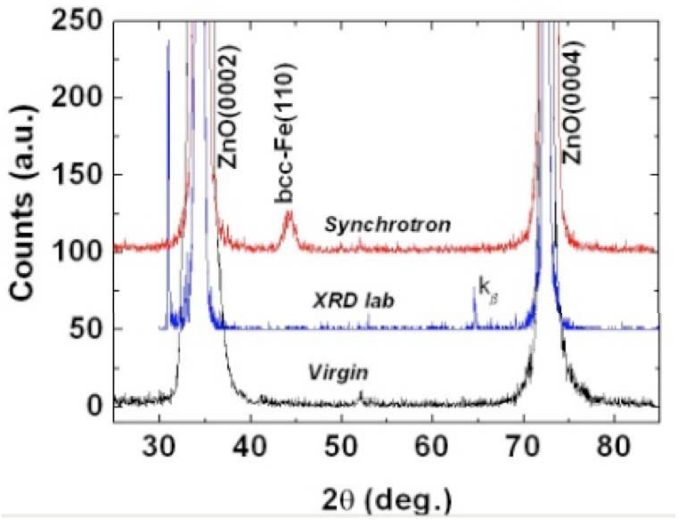
Instrument

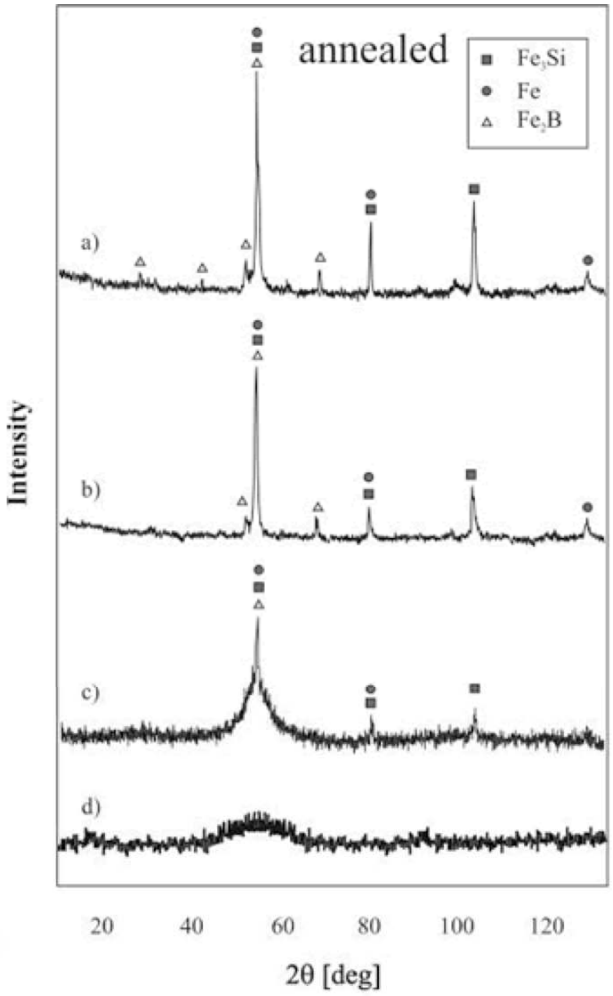
- Source wavelength
- Detector resolution

Sample

- Adsorption:
  - OH, organics
- Disorder
  - Mg-Fe, Ca-Na
- Strain
  - Tempered steel
- Grain size
  - If grain size is ~λ, get broadening
- Temperature
  - Debye-waller factor
  - Thermal ellipsoids
  - Exists at 300 K

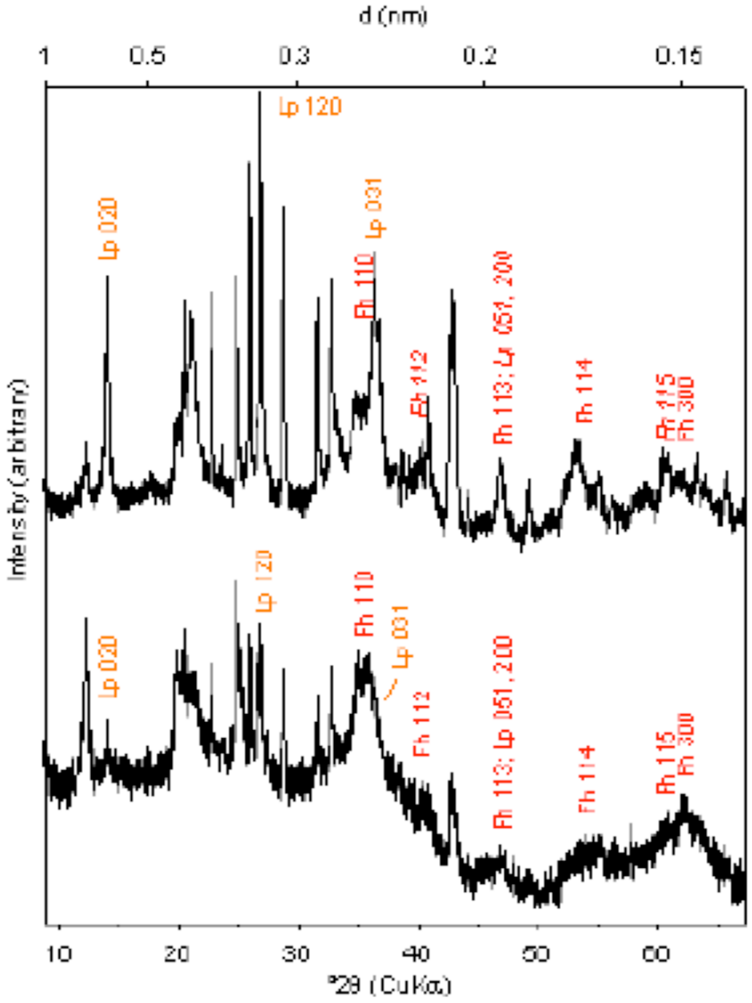






Mixed phases: determining proportion

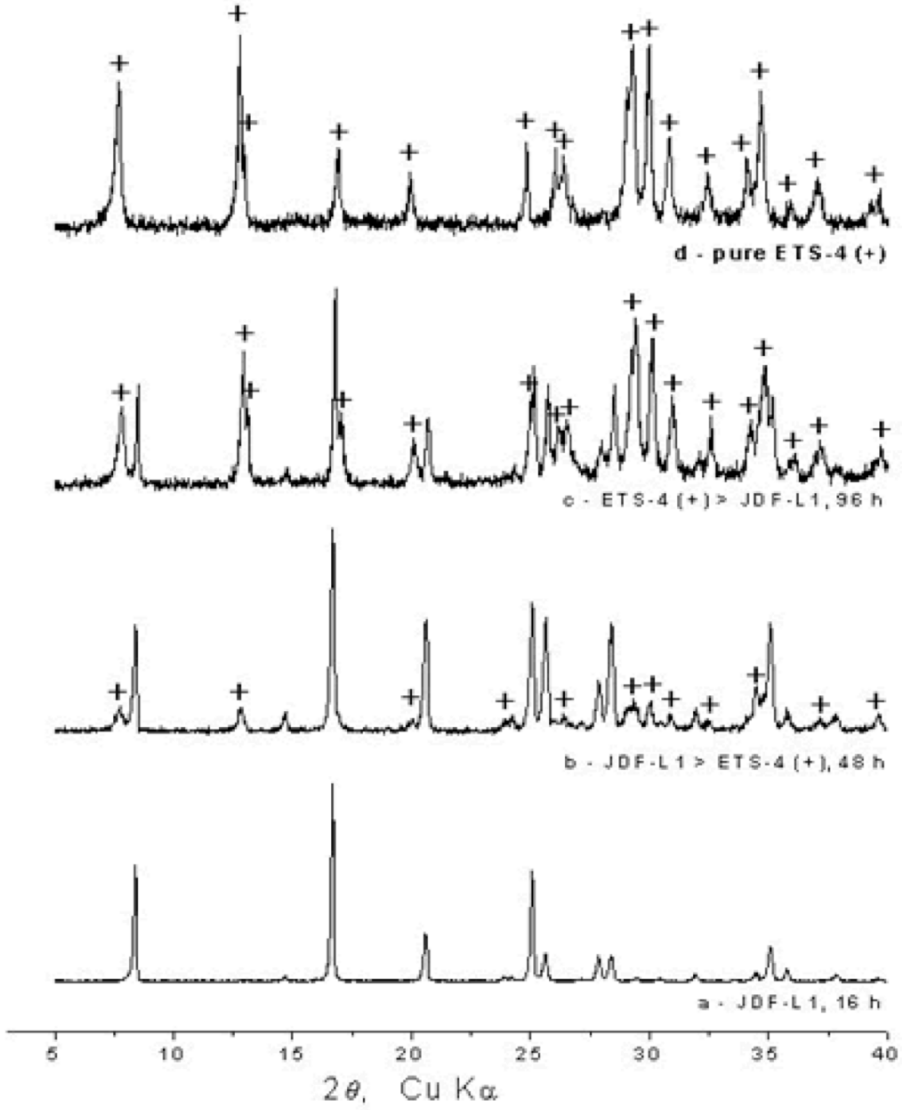
- Environmental sciences
- Quantity and type of clay is important
- Acid mine drainage areas
- Requires an analysis of relative intensities
  - Watch out for preferred orientation



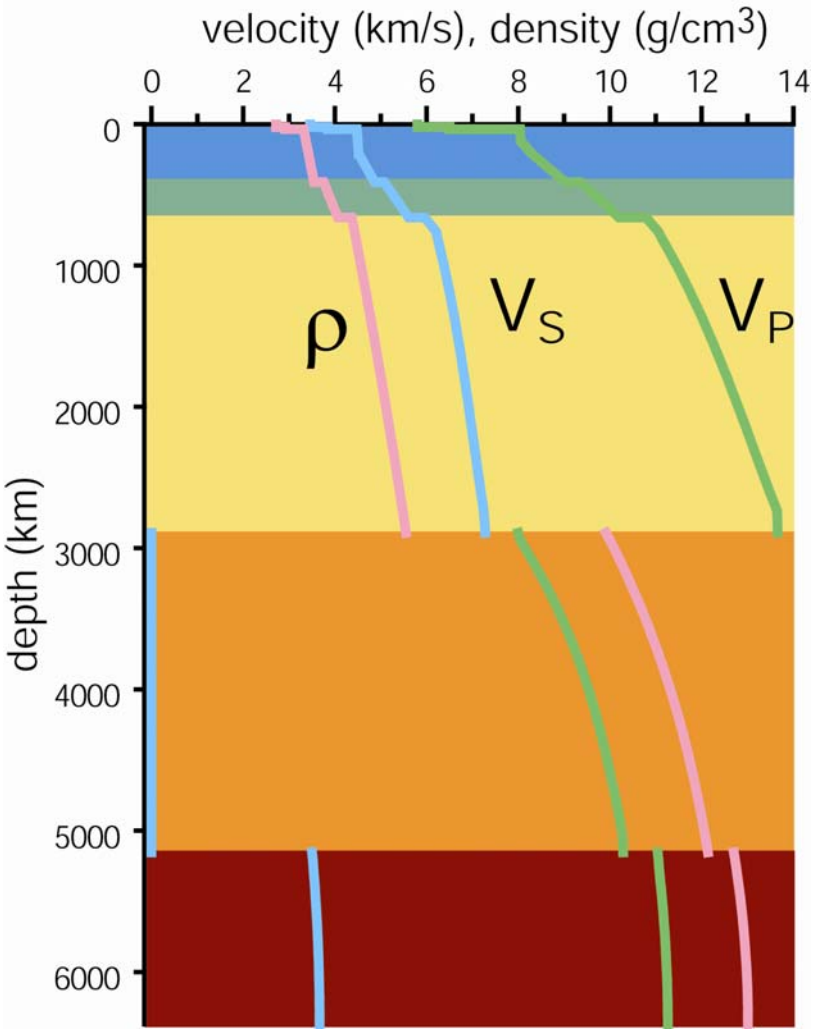
Two iron oxide coatings on lignite from Sokolov showing different relative proportions of kaolinite (not marked), ferrihydrite and lepidocrocite.

Determining phase transitions

- See evolution of diffraction peaks as a function of temperature, time, pressure, hydration, etc.
- Example: hydrothermal studies on titanosilicates: $Na_4Ti_2Si_8O_{22}$.$4H_2O$ to $Na_9Si_{12}Ti_5O_{38}$ (OH).$12H_2O$



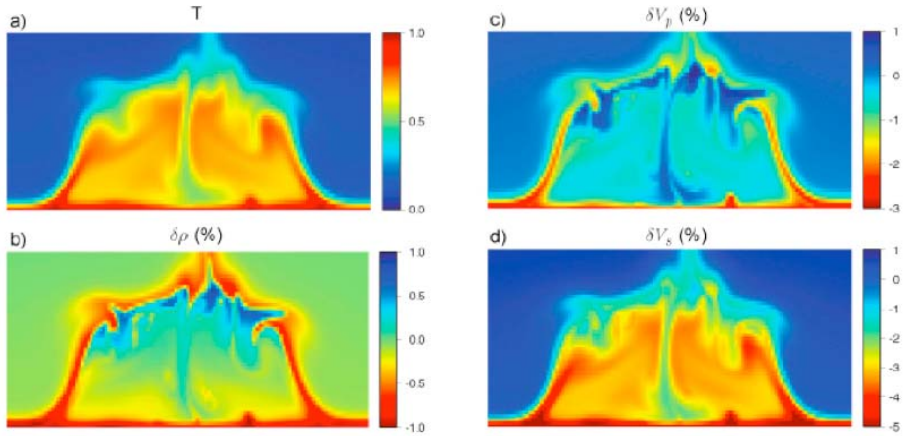
Determining the crystal structure and density of minerals in the interior of Earth



(Dziewonski & Anderson 1981)

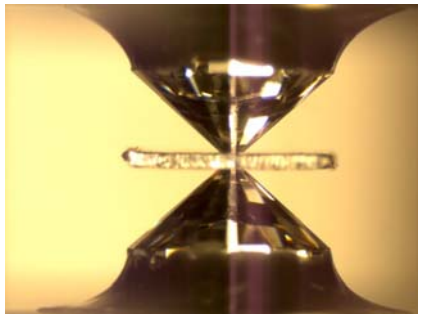
Preliminary Reference Earth Model (PREM)

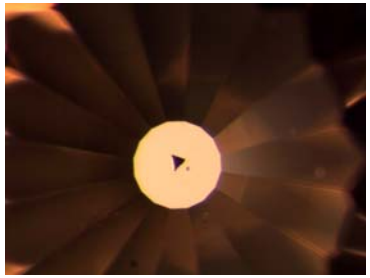
Measure candidate minerals At high-PT conditions:
Vp and Vs
Density (XRD + chemical info)



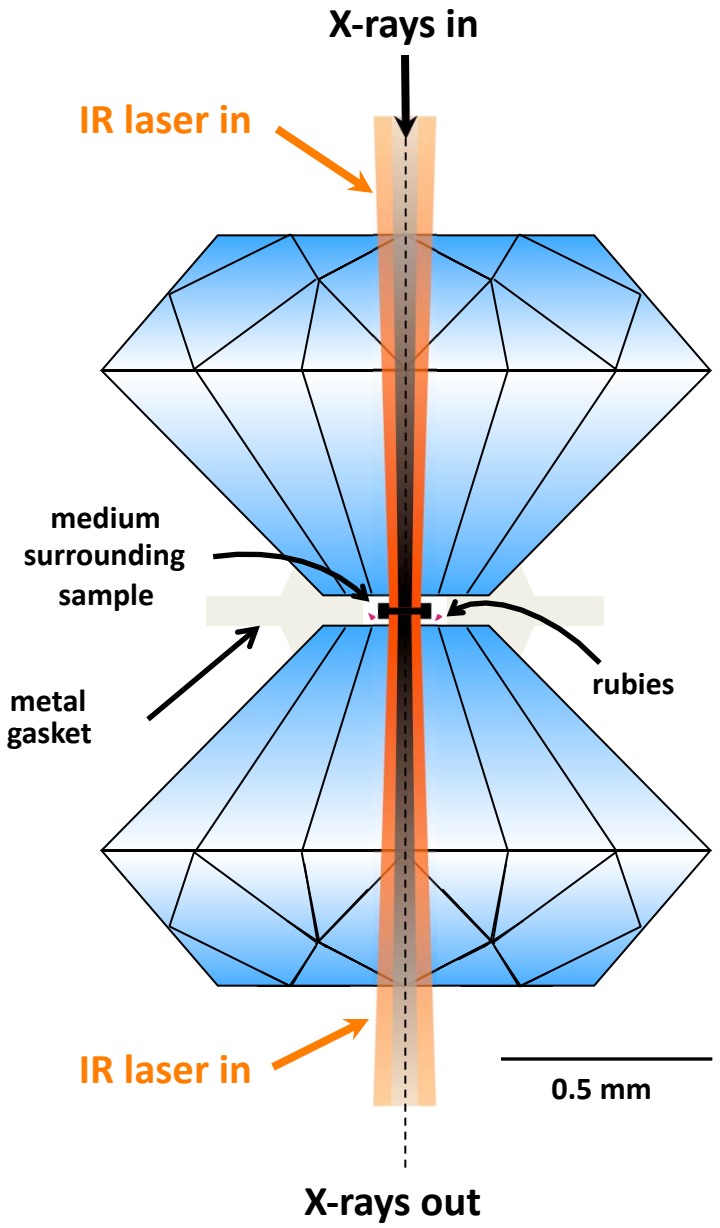
(Tan & Gurnis 2005)

The diamond-anvil cell





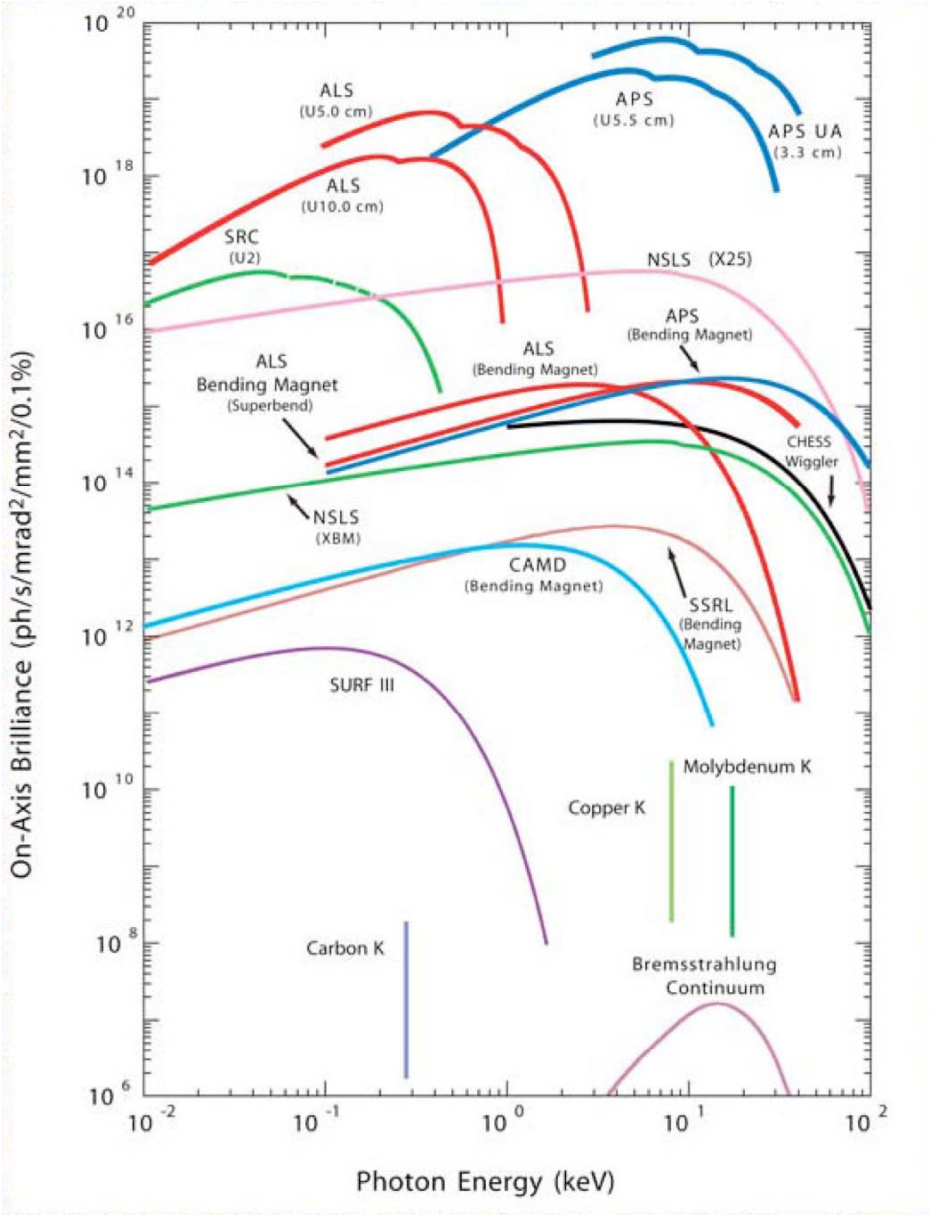
Diamond-anvil-cell laboratory,
Caltech



Synchrotron x-radiation

Advanced Photon Source (APS)
Argonne National Laboratory, IL

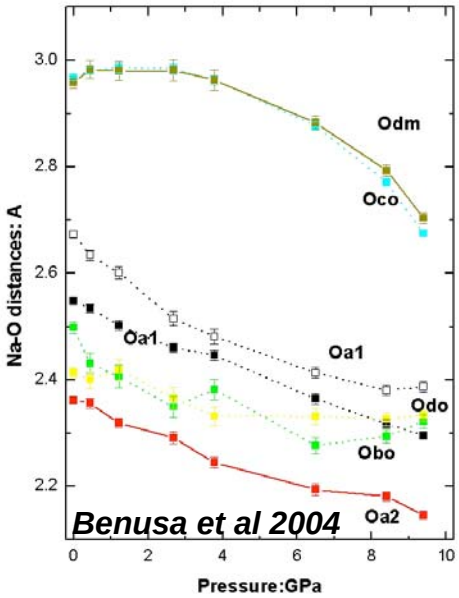
Storage ring: electromagnets

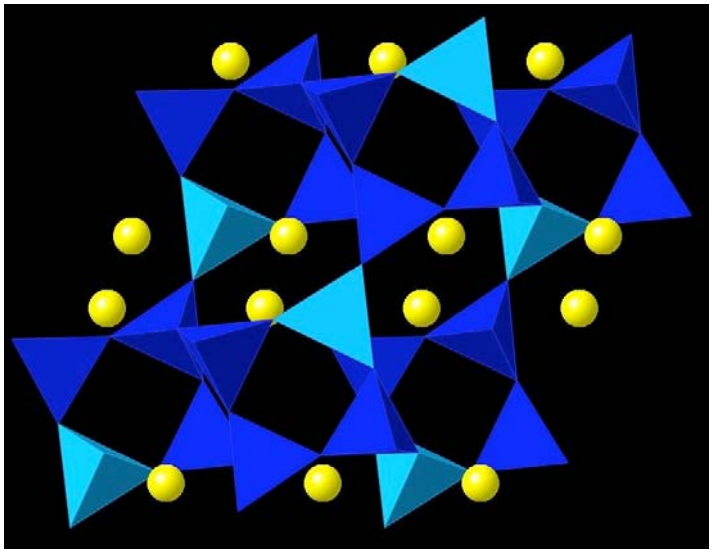


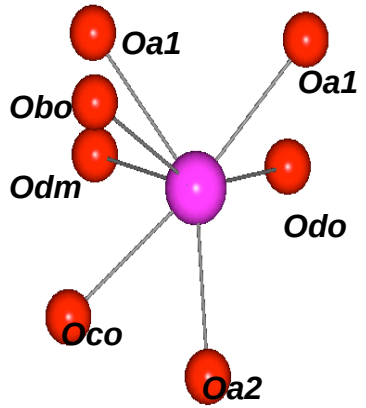
Crystal structures at high-pressures

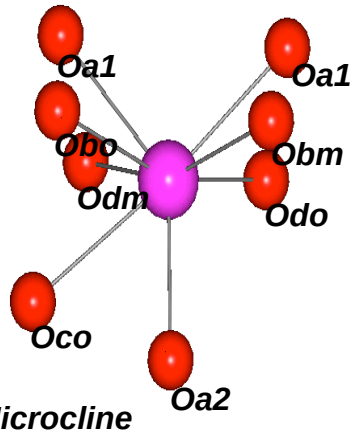
As framework minerals compress, the polyhedra compress and tilt, and the extra-framework cavity changes shape

- **Single crystal microcline, $KAlSi_3O_8$**
- **Cation partitioning**
- **Retention & Diffusion of non-bonded species**
  - ***Ar, K, Xe***
- **Elastic and hence, thermodynamic properties**







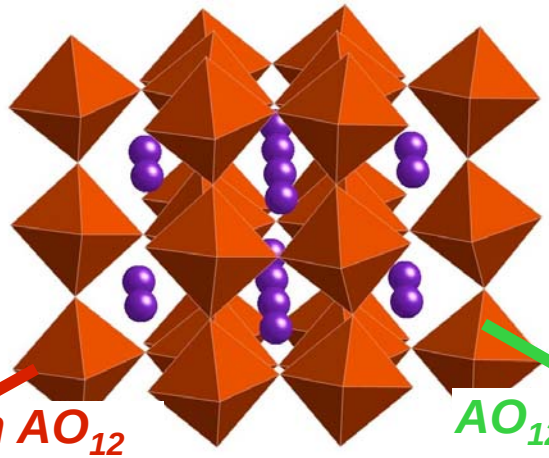


Microcline

Allan & Angel (1997) EJM

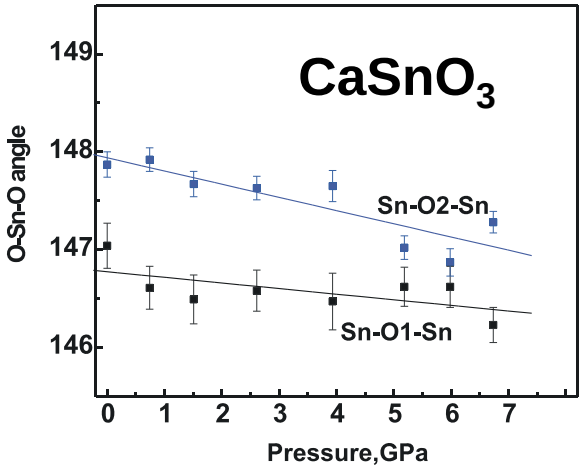
More structures: ABO_3 perovskites

As BO_6 rotate, the A-O bonds are compressed

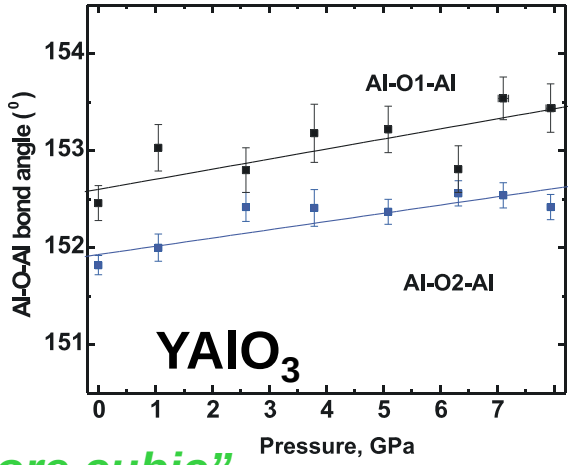


BO_6 stiffer than AO_{12}

AO_{12} stiffer than BO_6



"Less cubic"

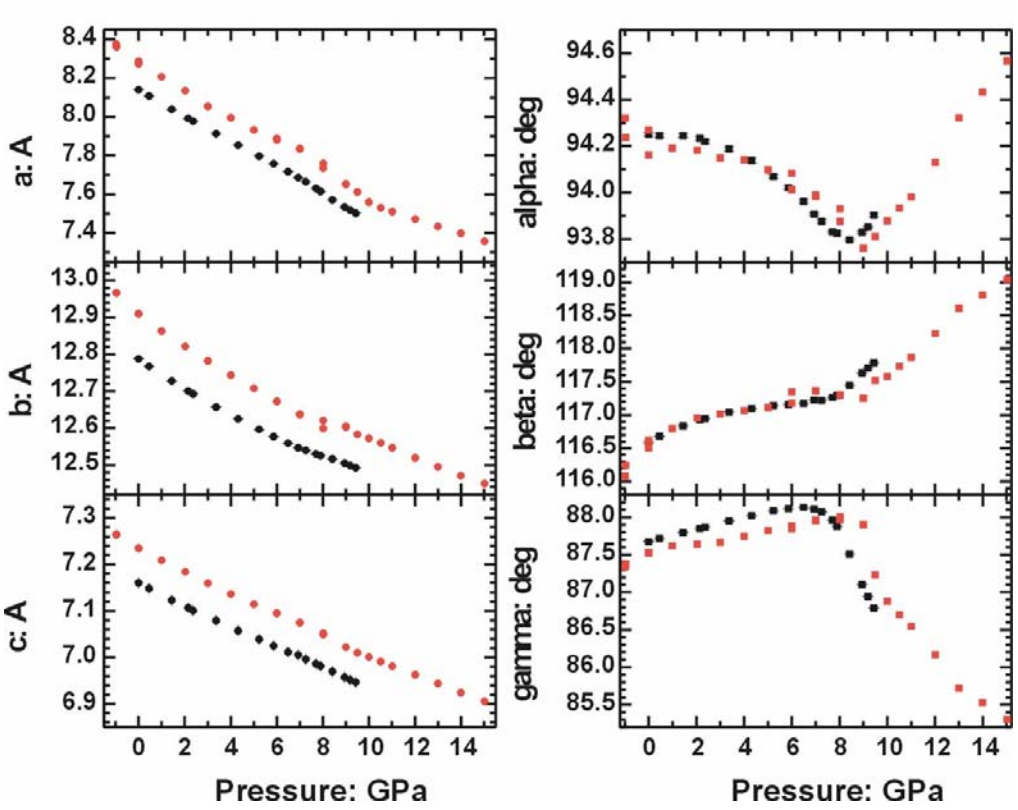


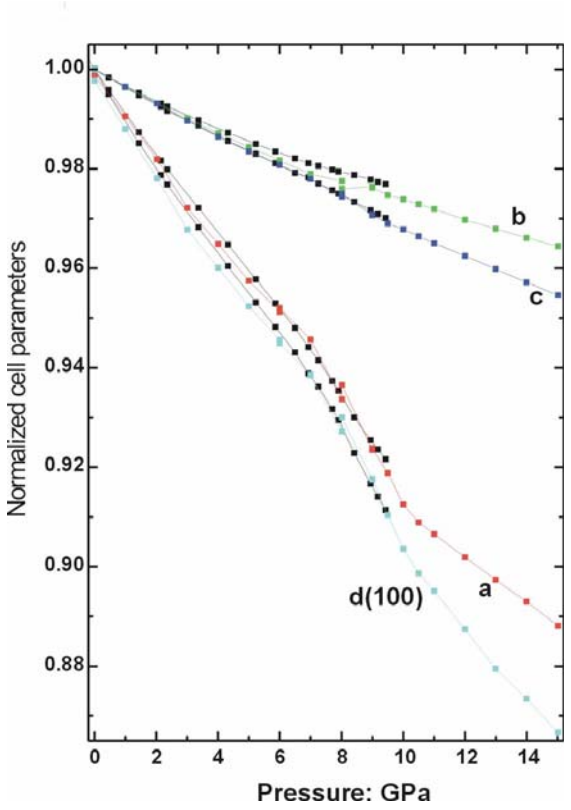
"More cubic"

(Zhao et al. 2005)

Albite ($NaAlSi_3O_8$) response to pressure

- **Unit cell parameters provide more information**
  - **Experiments went up to 10 GPa, supplemented with density functional theory (DFT) calculations**
  - **60% of albite compression is along (100)**
  - **Cell angles show softening**



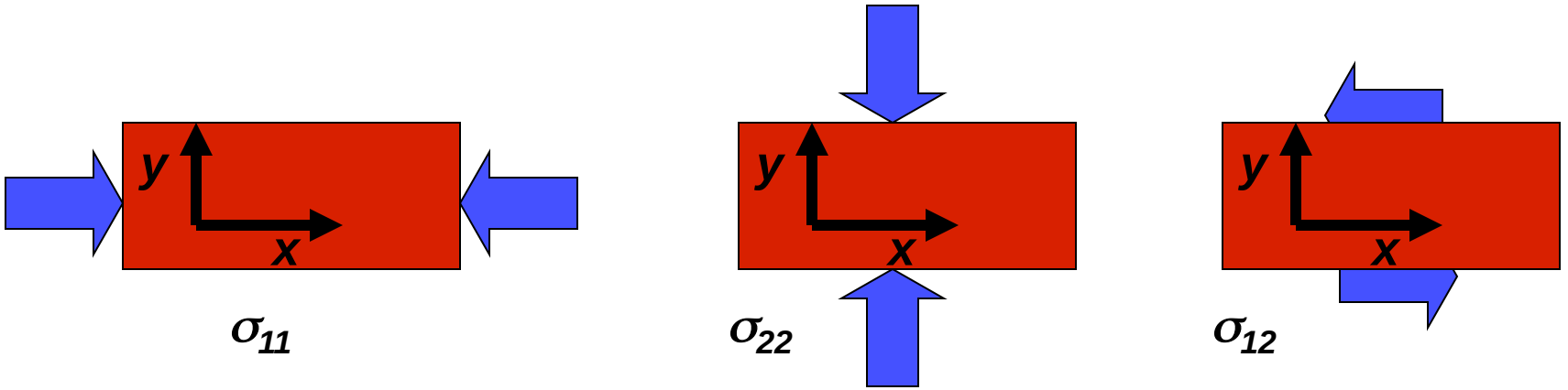


Elastic tensor

- **Elastic Compliance Tensor (s_{ijkl}):**
  - **4th rank tensor defining a physical quantity relating stress to the resulting strain within the linear elastic regime.**

Generalized Hooke's Law:

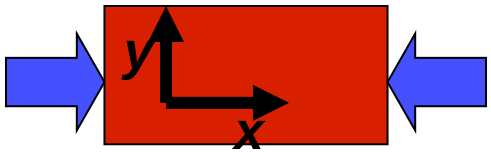
$$\varepsilon_{ij} = s_{ijkl}\,\sigma_{kl}$$



σ_{11} σ_{22} σ_{12}

Compliance = softness Modulus = stiffness

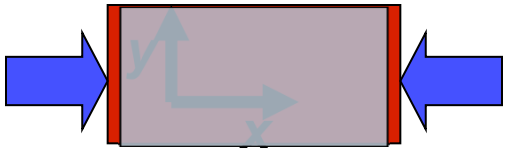
Strain and compliance tensors



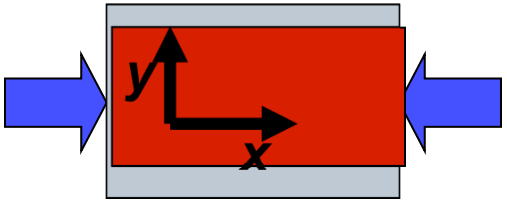
σ_{11}

Generalized Hooke's Law:

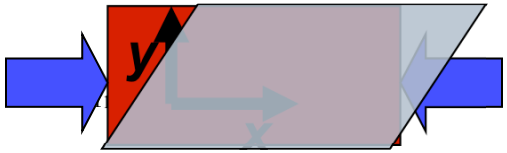
$\varepsilon_{ij} = s_{ijkl}\,\sigma_{kl}$



$\varepsilon_{11} = s_{1111}\sigma_{11}$



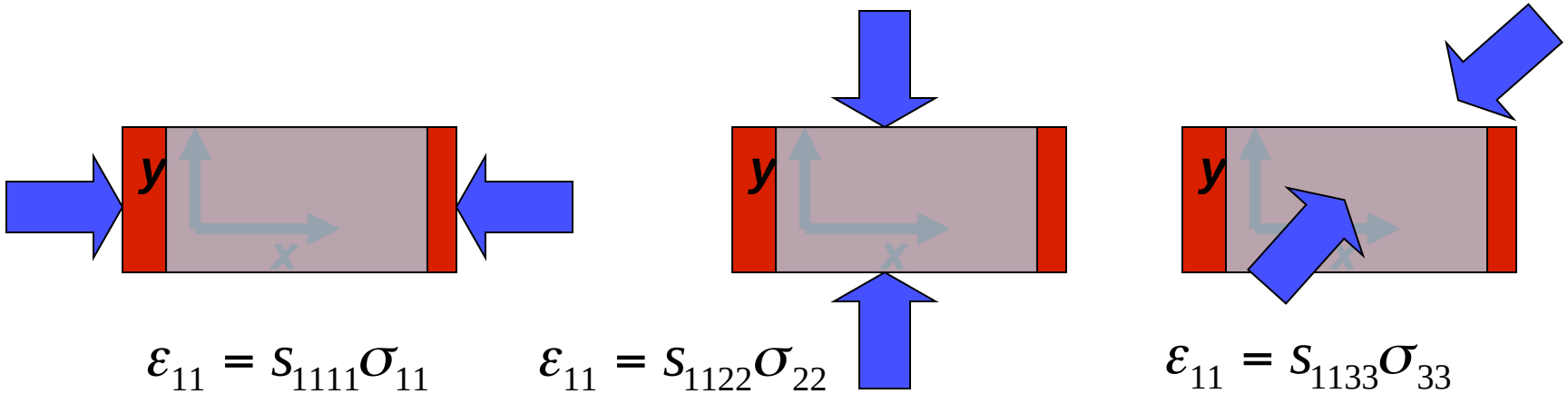
$\varepsilon_{22} = s_{2211}\sigma_{11}$



$\varepsilon_{12} = s_{1211}\sigma_{11}$

- **Potentially 81 components of s_{ijkl}**
- **Stress and strain must be symmetric**
  - **$\sigma_{ij} = \sigma_{ji}$ and $\varepsilon_{ij} = \varepsilon_{ji}$**
  - **S_{ijkl} must be symmetric in itself**
  - **….21 independent components of s_{ijkl}**
  - **Less if symmetry higher than triclinic**

Hydrostatic experiments



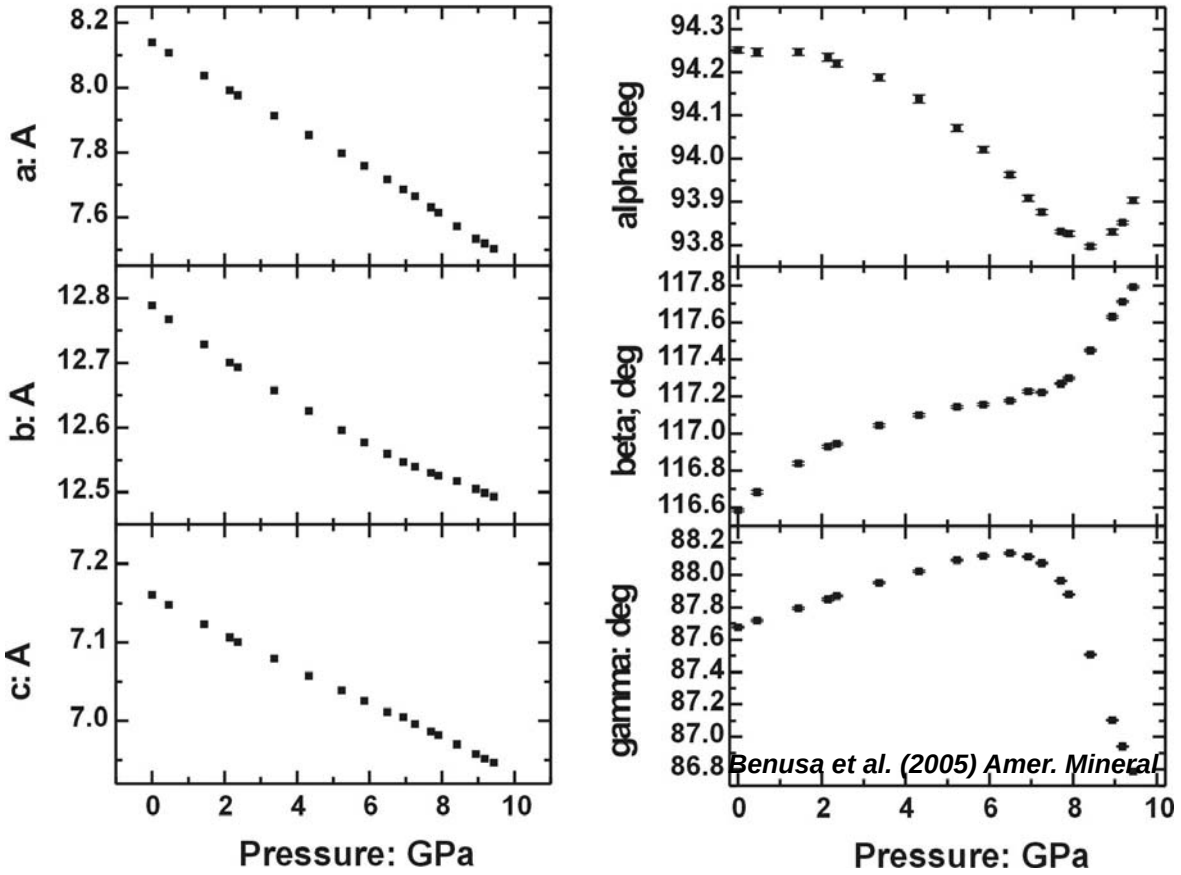
$\varepsilon_{11} = S_{1111}\sigma_{11}$ $\varepsilon_{11} = S_{1122}\sigma_{22}$ $\varepsilon_{11} = S_{1133}\sigma_{33}$

- **No shear stress**
  - $\sigma_{ij} = 0$
  - $\sigma_{11} = \sigma_{22} = \sigma_{33} = -P$

$$\varepsilon_{11} = S_{1111}\sigma_{11} + S_{1122}\sigma_{22} + S_{1133}\sigma_{33}$$
$$= -\left(S_{1111} + S_{1122} + S_{1133}\right)P$$
$$-\varepsilon_{11}/P = \left(S_{1111} + S_{1122} + S_{1133}\right)$$

- **Changes in cell parameters are strains**
  - Six components for triclinic crystals

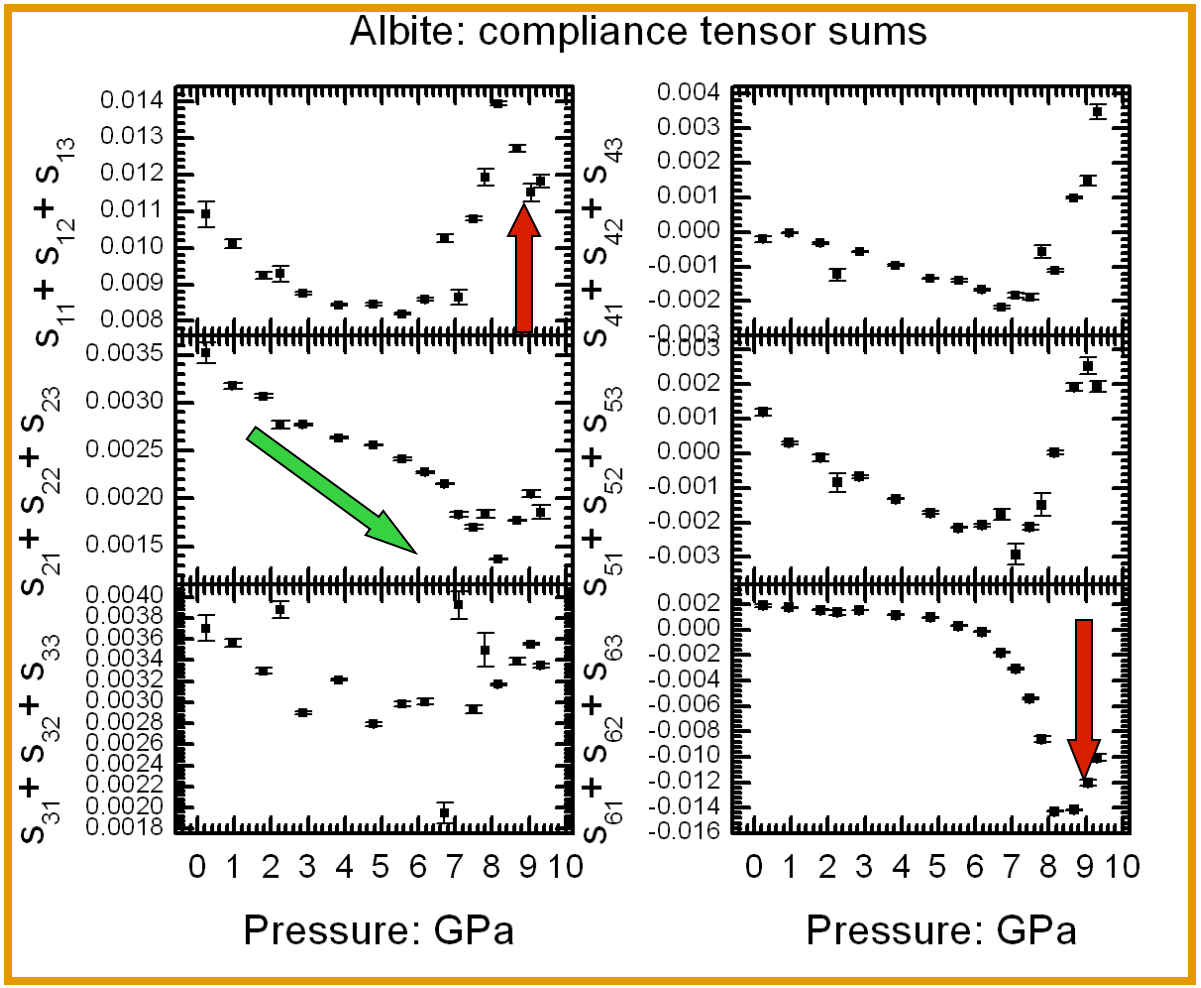
Obtaining compressional moduli



Benusa et al. (2005) Amer. Mineral.

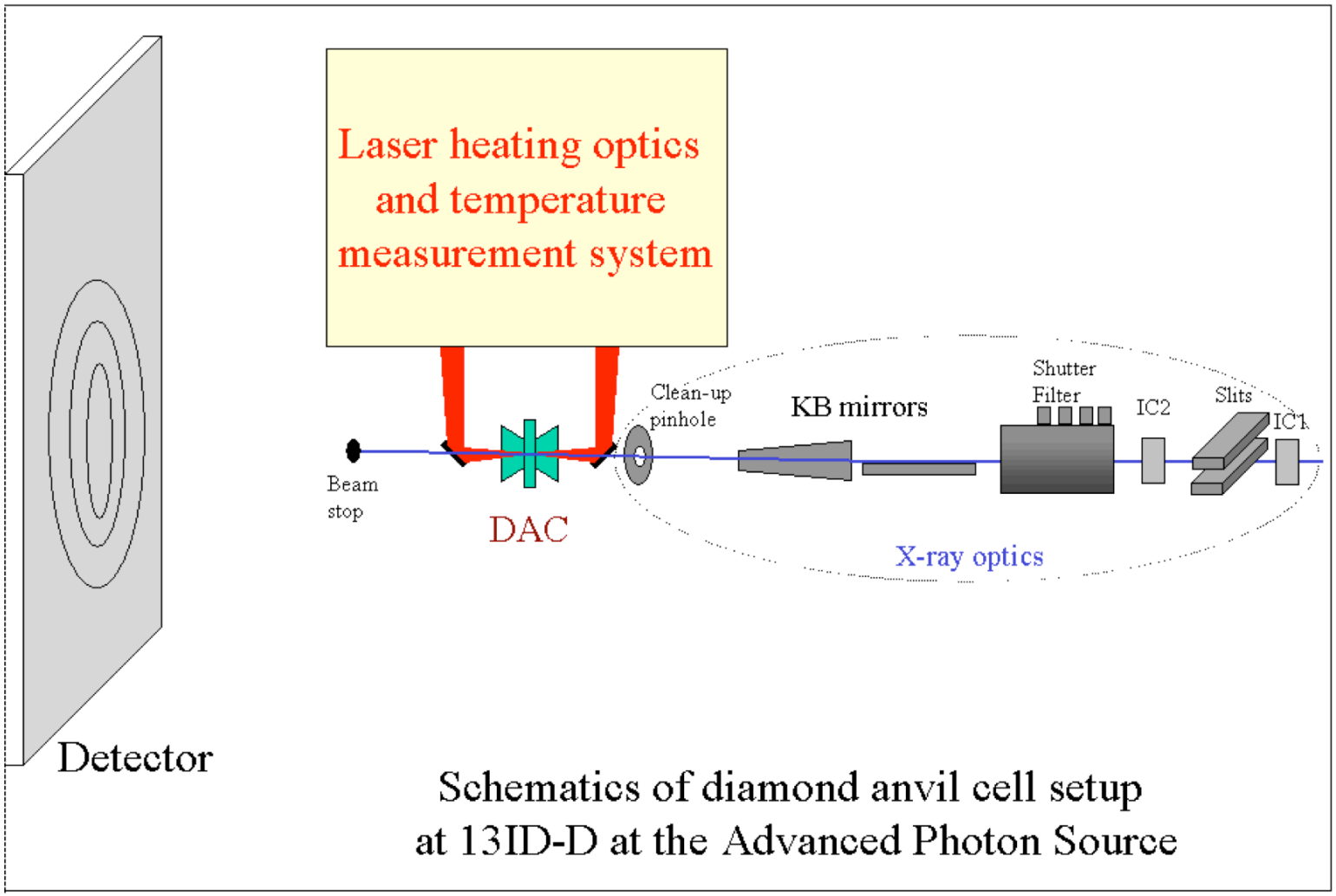
- **Triclinic cell parameters**

Obtaining compressional moduli



- **Triclinic cell parameters**
- **Calculate incremental strain tensor**
- **Calculate s_{1j} at pressure**
- **Fit to obtain s_{1j} at room pressure**

Synchrotron powder x-ray diffraction

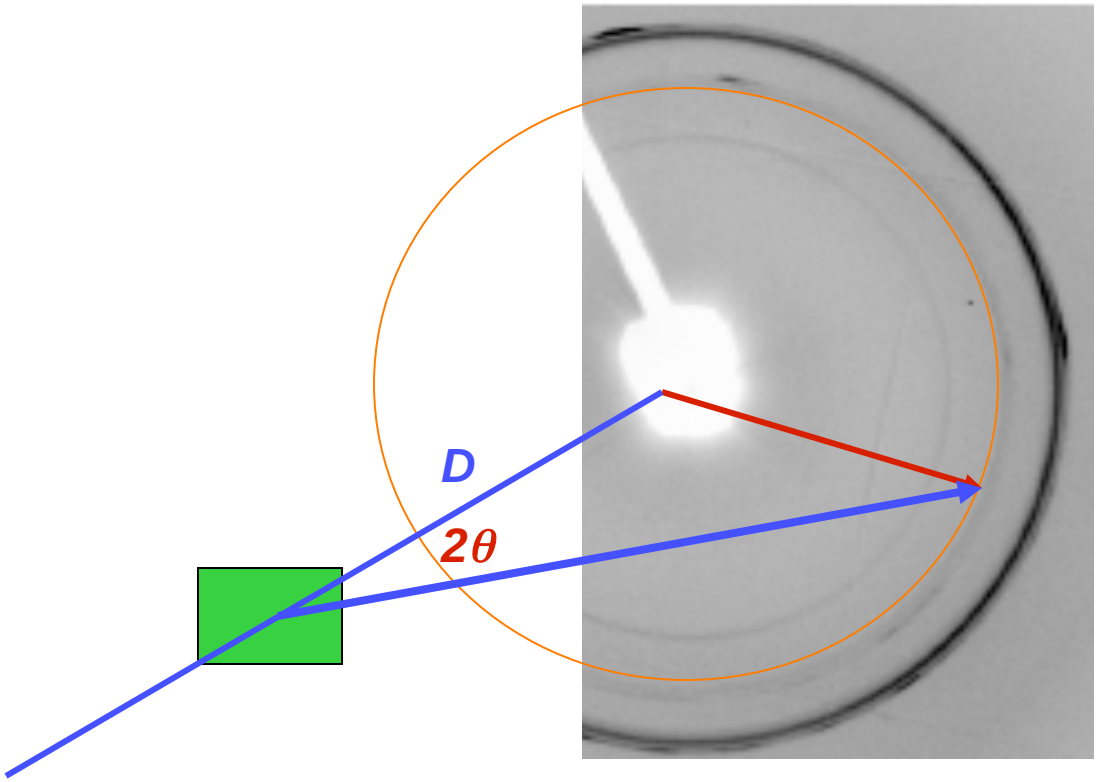


Schematics of diamond anvil cell setup
at 13ID-D at the Advanced Photon Source

$$\lambda = 0.04133nm = 30keV$$

Synchrotron powder x-ray diffraction

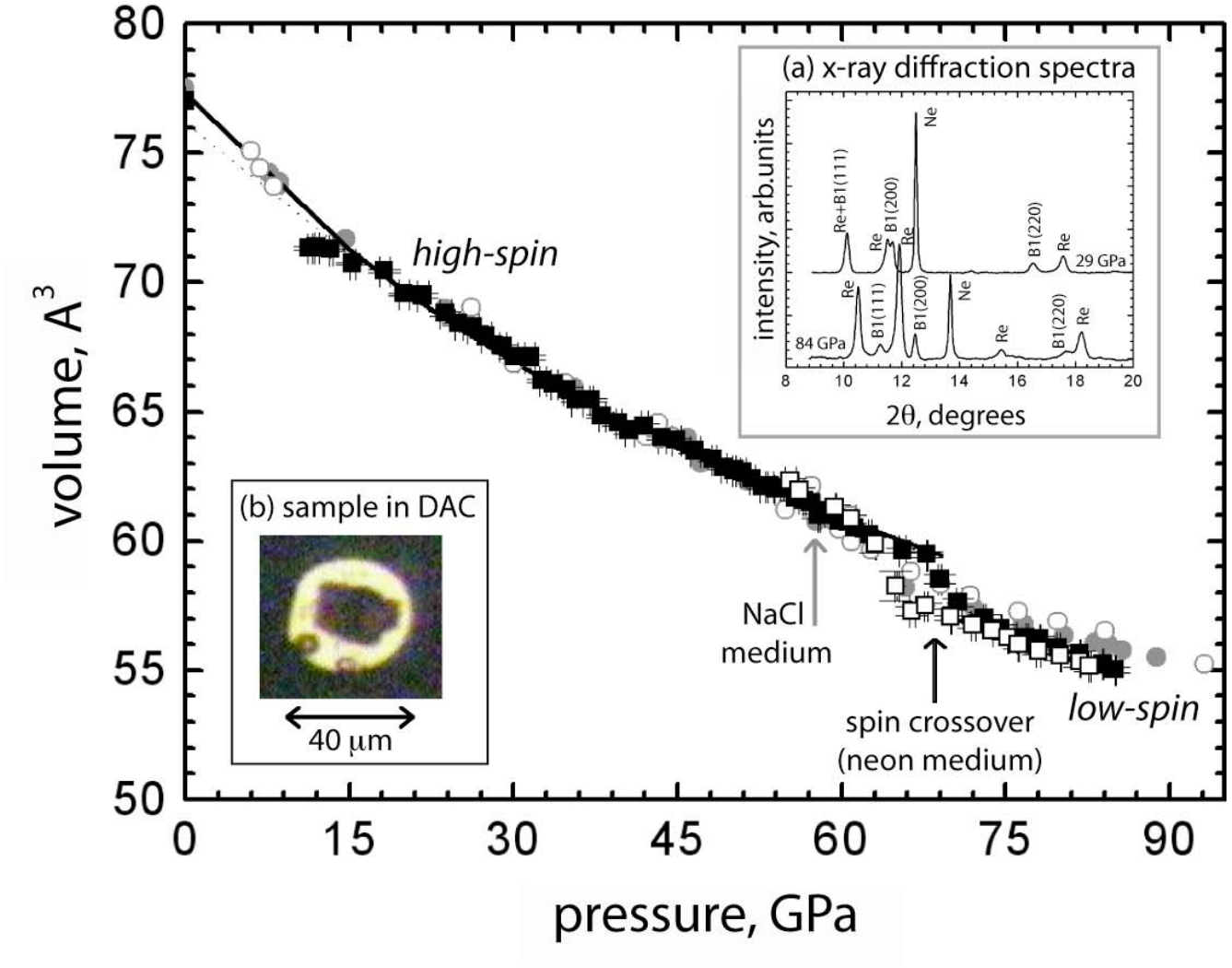
- **Determine d-spacings for (mostly) known structures as a function of pressure**



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

Volume (density) change of $(Mg_{0.61}Fe_{0.39})O$ through the spin crossover

Experiments conducted at The Advanced Light Source, Berkeley, CA



Zhuravlev, Jackson, Wolf, Wicks, Yan, Clark (2010) Phys. Chem. Min.

Other X-ray Diffraction Methods

- Small angle x-ray scattering
  - Structural deviations
  - Local scale
- Single-crystal x-ray diffraction
  - Can be done in-house or at the synchrotron
  - Solves for atomic positions
  - Solves structure
  - Structures of minerals
  - Protein crystallography

Our XRD experiments

339 Steele

- Sample preparation
  - Grind under alcohol using agate mortar & pestle
  - Grain size should be ~100 μm
  - Can influence quality of XRD spectrum
- Copper target
- Ni filter
- Cu Kα_1, λ = 1.54056 Å
- Cu Kα_2, λ = 1.54439 Å
- 8 keV
- Bragg's law:

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