Current and Planned Use of Micro-beams for Mineral-Water Interface Studies

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"Science with Microbeams"
Advanced Photon Source
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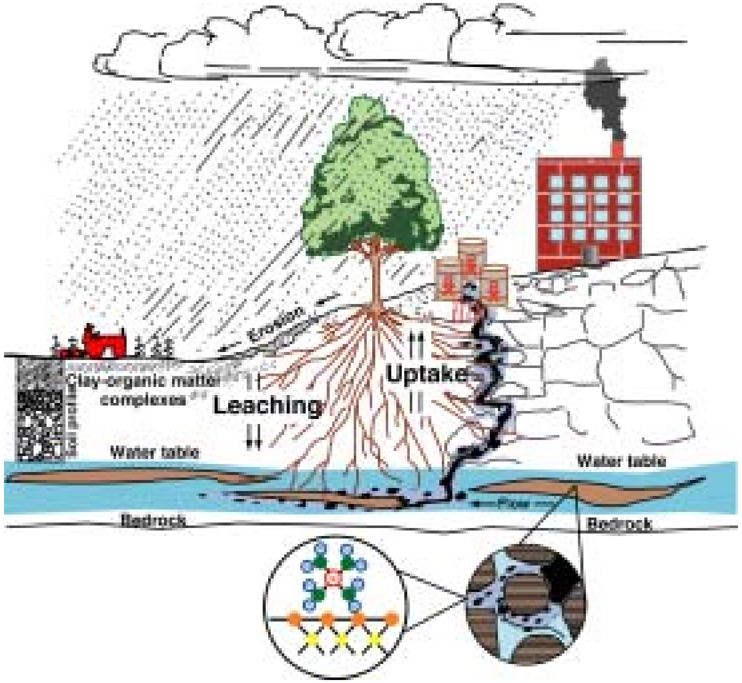
Outline:

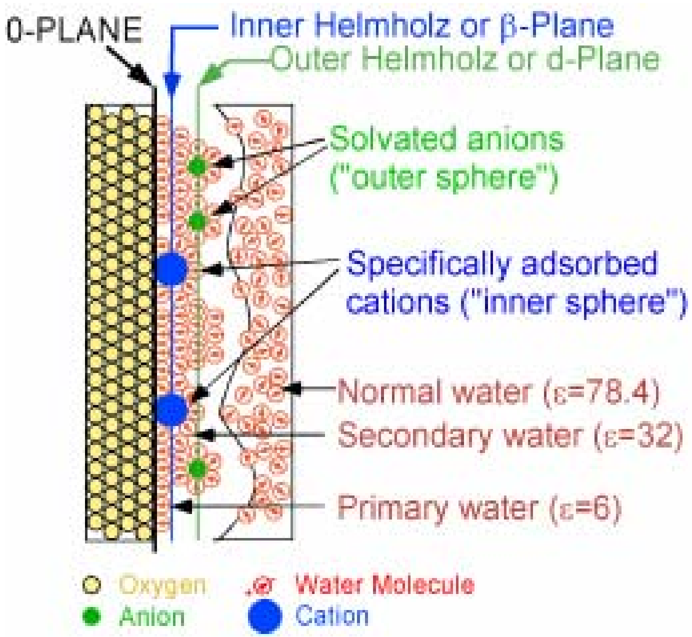
- Mineral-fluid interface geochemistry
- Extrinsic Heterogeneity
  - XSW imaging on imperfect crystals
  - Surface X-ray scattering with micro-beams
- Intrinsic Heterogeneity
  - Phase and elemental contrast
  - Surface x-ray microscopies
    - scanning probe
    - full field



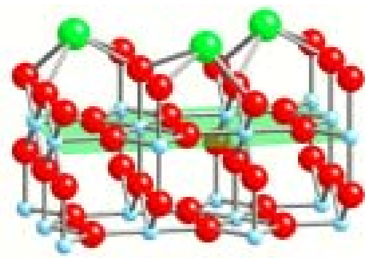
*Research sponsored by: U.S. Department of Energy, Office of Basic Energy Sciences
Division of Chemical Sciences, Geosciences, and Biosciences

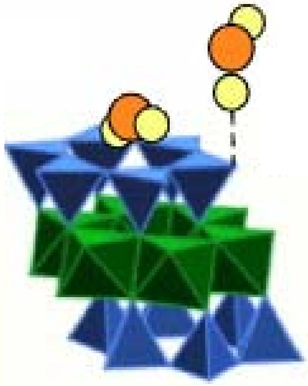
Fundamental Processes in Low-Temperature Geochemistry:

Electrical Double-Layer Structure



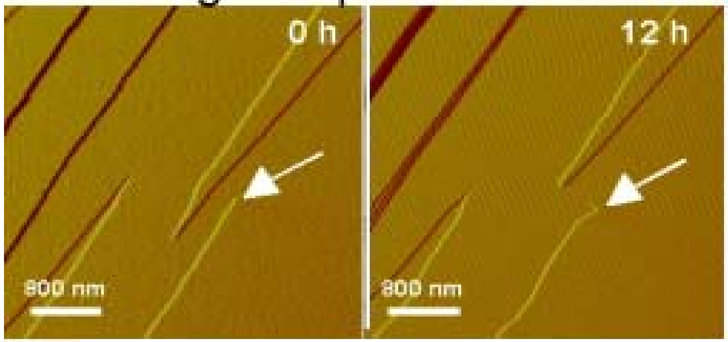
Interfacial Structure (mineral surface, water)





Mineral Reactivity (dissolution and growth)

Dissolving feldspar surface



Fundamental understanding derived mostly from highly homogeneous systems

- direct observations of mineral-fluid interfaces
- molecular-scale structure and processes

→ Heterogeneity is a key aspect of many natural systems and processes

Extrinsic Heterogeneity:

-Crystal mosaic, small angle grain boundaries...

Large, perfect single crystals:

Calcite ($CaCO_3$)

Large, imperfect single crystals:

Muscovite mica

Polycrystalline:

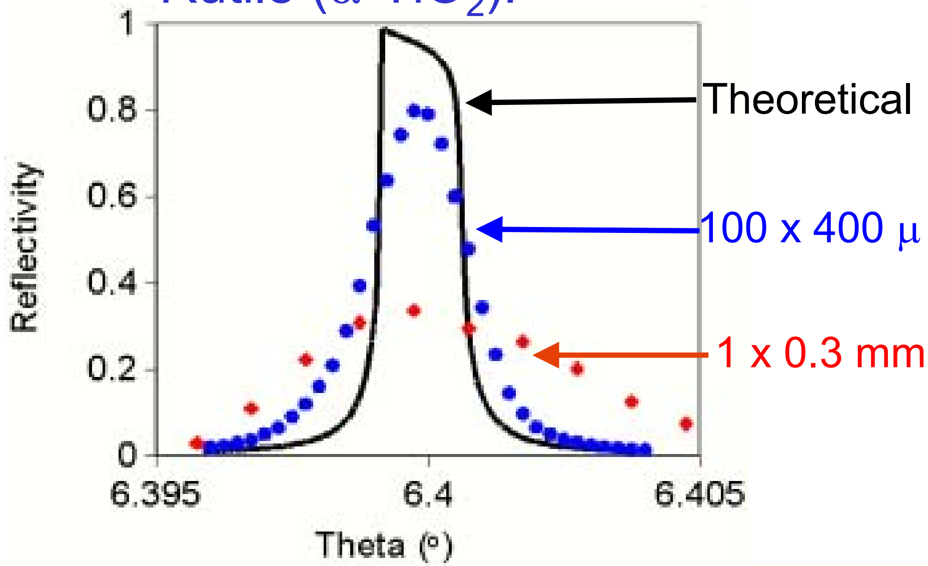
Weathered Feldspar

Relevant minerals:

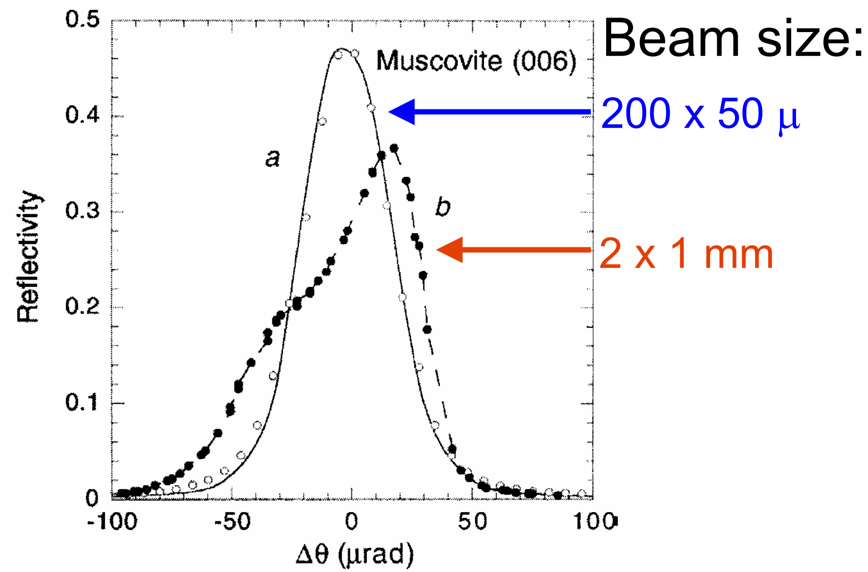
- variable quality (mineral to mineral, sample to sample)
- limits range of processes that can be studied
(e.g., with X-ray reflectivity, X-ray standing waves)

Bragg Diffraction from Imperfect Crystals

Rutile (α-TiO_2):



Muscovite mica:



Bedzyk and Cheng, *Rev. Mineral. Geochem.* **49**, 221-266 (2002)

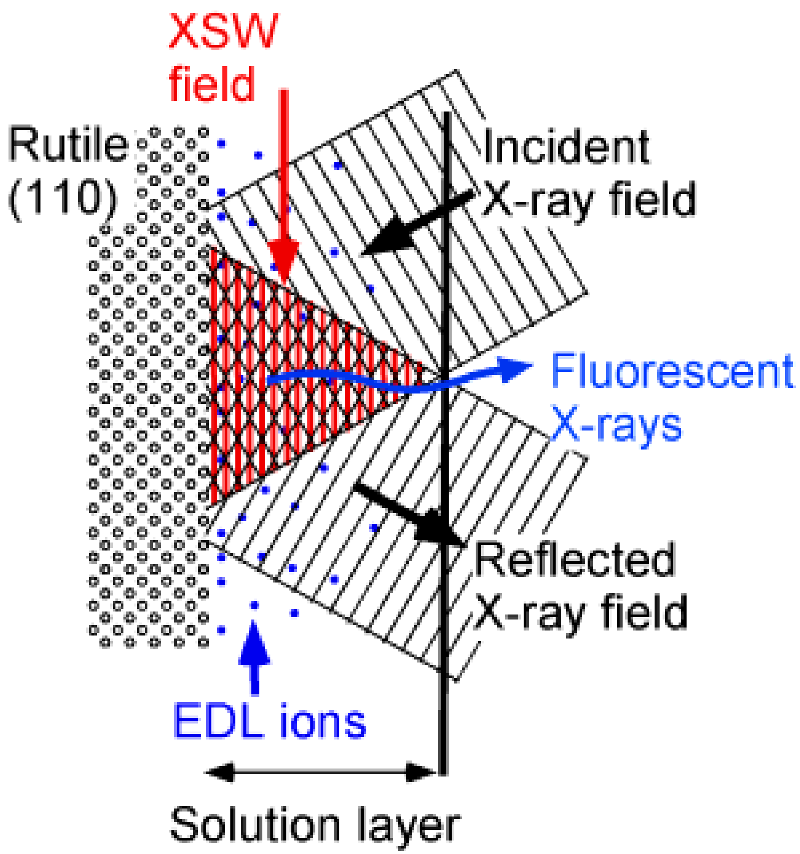
Crystal quality of most minerals not sufficient for XSW measurements

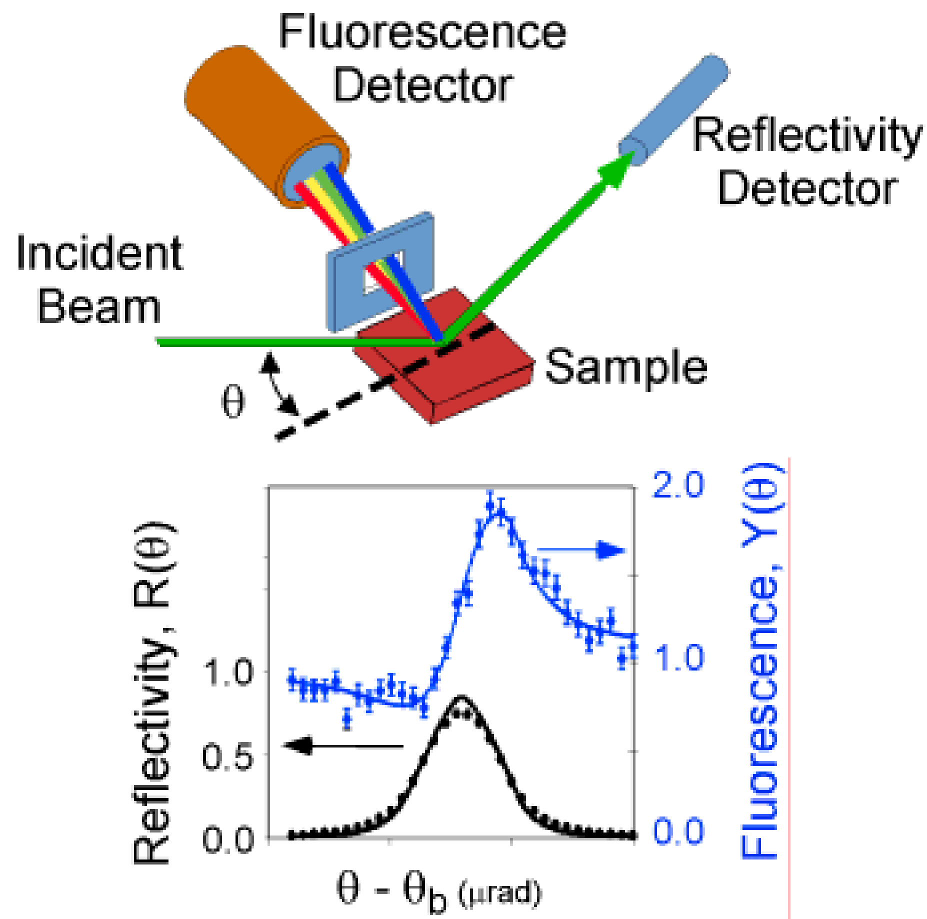
- intrinsic measurements need m-sized
- illuminate single crystal grains with μ-sized beams

XSW with imperfect samples requires high brilliance source:

- small beam cross section with high collimation

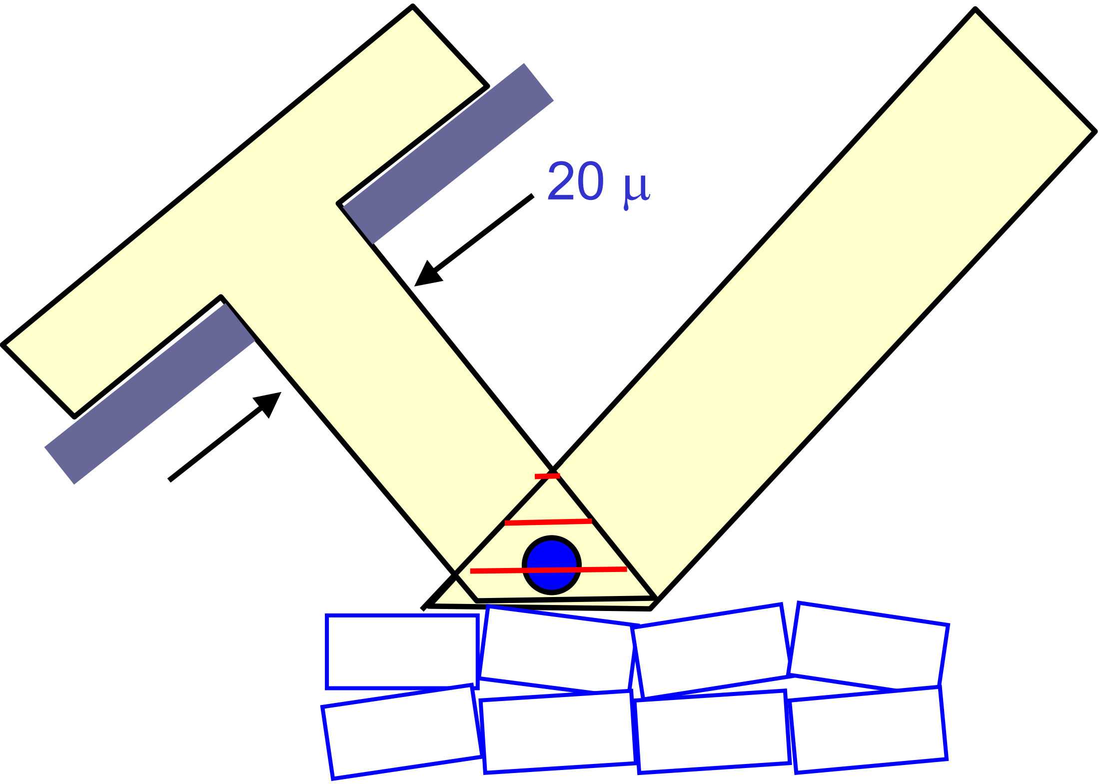
X-ray Standing Waves as a Probe of Ion Adsorption Sites

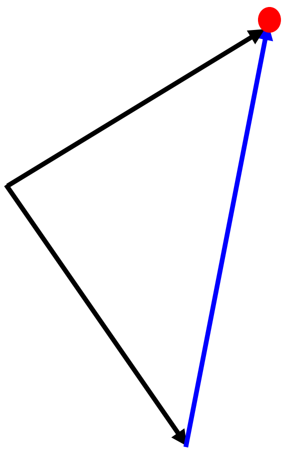




Fluorescent yield, Y, and bulk Bragg reflectivity, R, measured simultaneously

XSW with Perfect vs. Imperfect Crystals





XSW measurements of imperfect crystals requires high APS brilliance

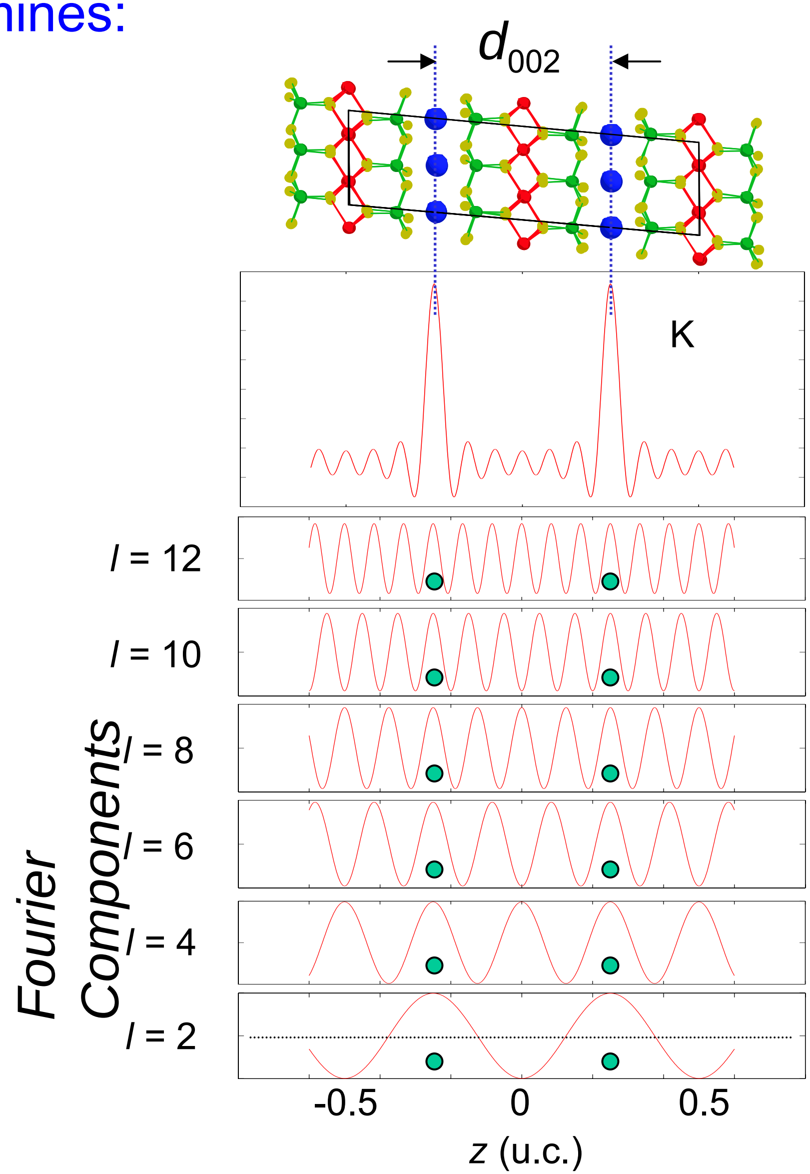
X-ray Standing Wave Imaging: The Basic Concept*

Each XSW measurement (at *H*) determines:

$$F_H = f_H \exp(i2\pi P_H) = \int \rho(r) \exp(iHr)\, dr$$

f_H = "coherent position" = amplitude
P_H = "coherent position" = phase

→ No loss of phase information!!



Density profile can be obtained by discrete Fourier summation by:

$$\rho(r) = \Sigma_H F_H \exp(iHr)$$

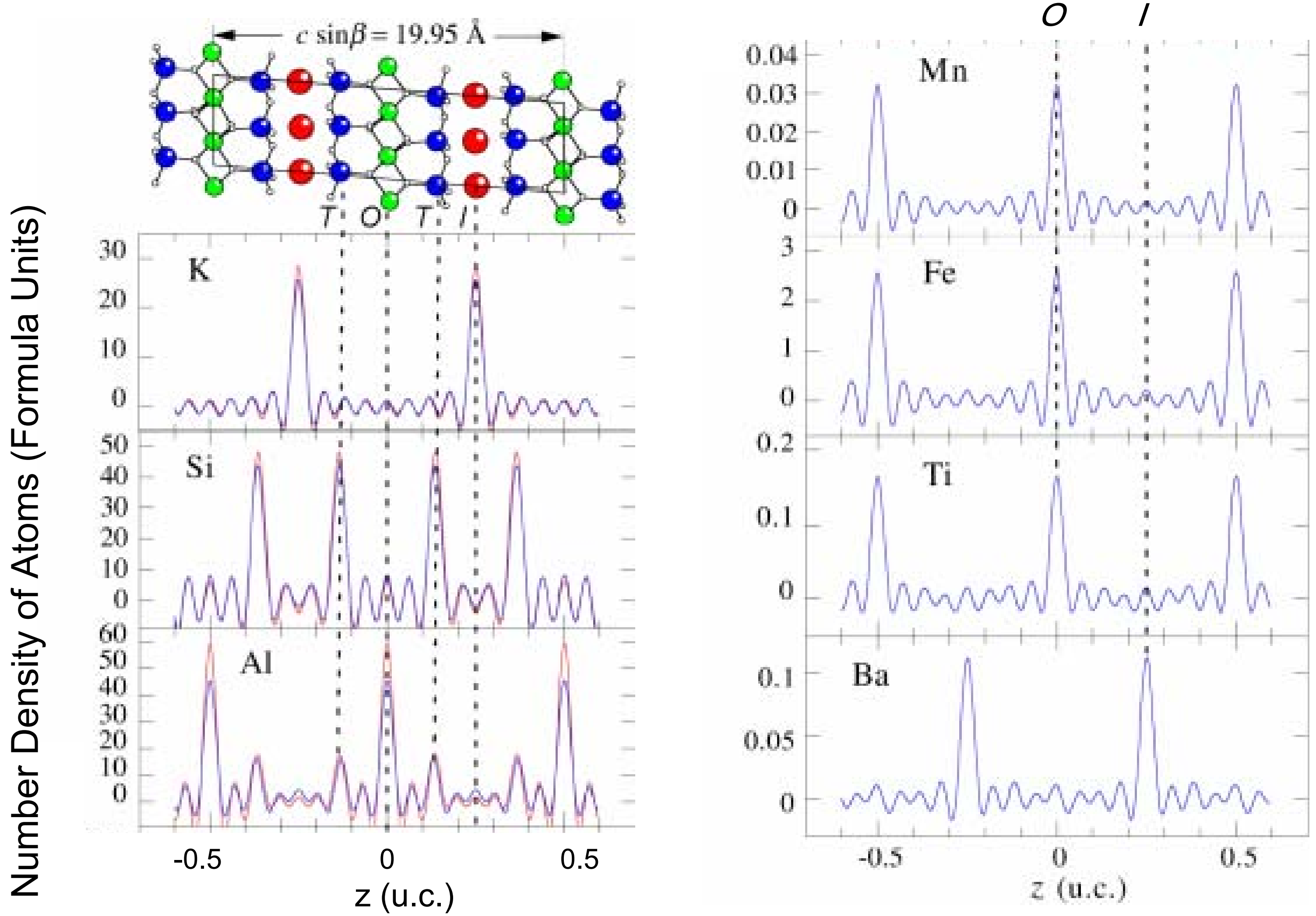
- No comparison to models
- No *a priori* assumptions

Directly measures elemental profiles for *each element*

*L. Cheng, et al., *Physical Review Letters*, **90**, 255503 (2003).

Real-Space Atom Distributions by Fourier Synthesis

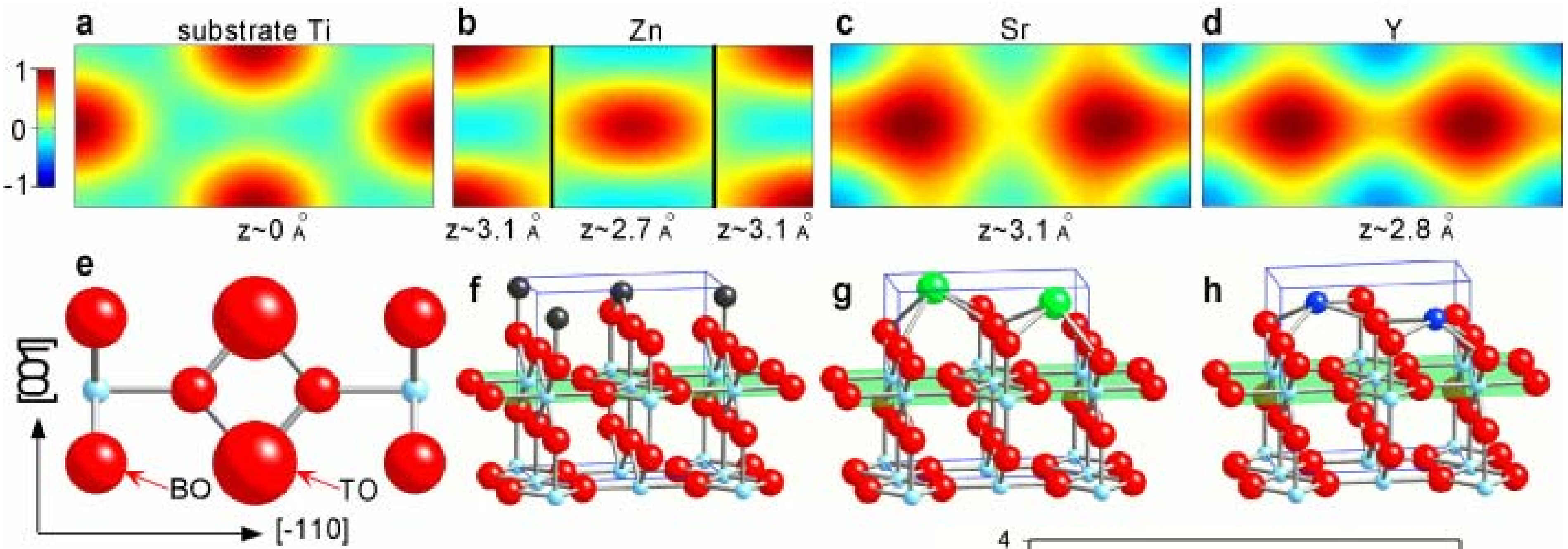
Muscovite: $K_2Al_4(Si_3,Al)_2O_{20}(OH)_4$



(1 u.c. = 19.95 Å)

Direct, real space imaging of elemental distributions with ~1 Å resolution

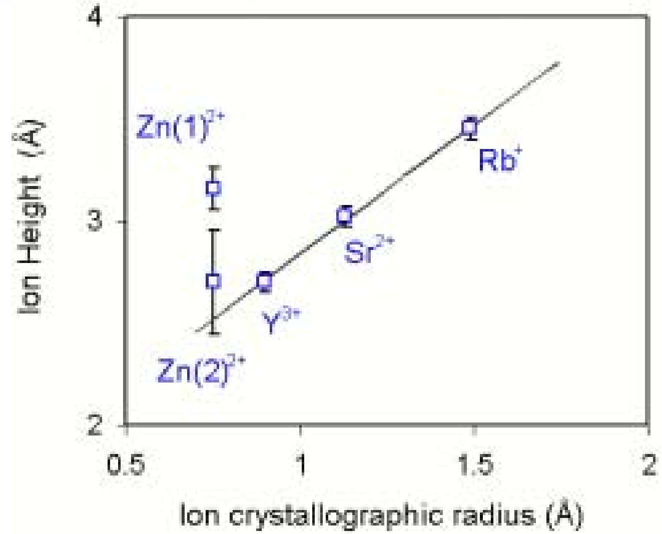
XSW Imaging Results: Three-Dimensional Imaging of Adsorbed Ion Sites on Rutile*



Sr^{2+}, Y^{3+} in 'tetradentate' site

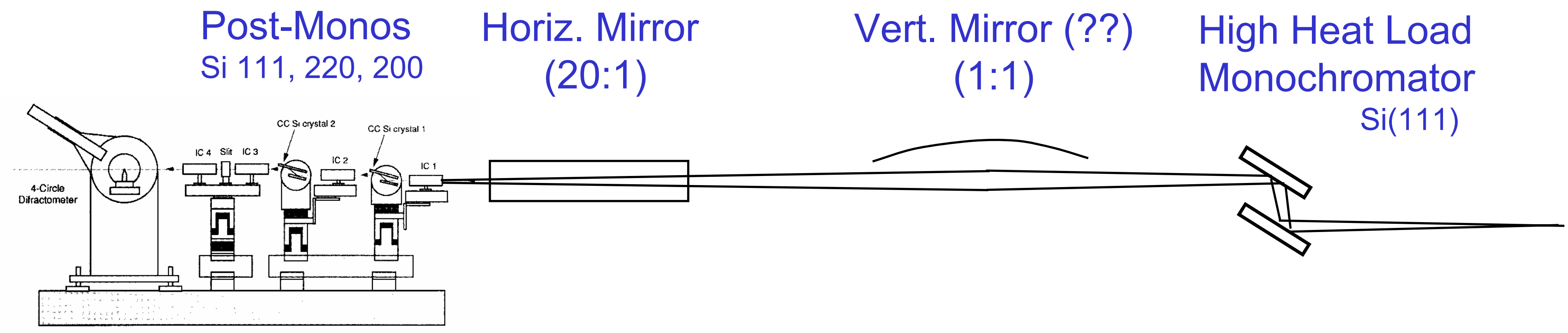
Zn^{2+} has two distinct adsorption sites:

- above BO
- bridging between two TOs



*Z. Zhang et al., Surf. Sci. Letters, in press (2004).

μ-XSW Imaging Concept

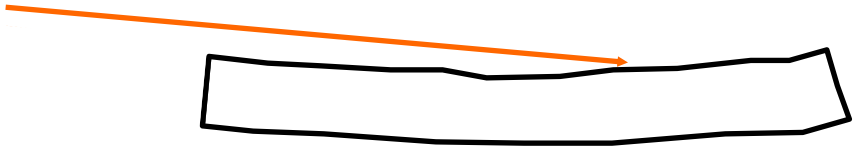


Couple μ-beam and XSW Imaging capabilities:

>10^3-fold gain of useful beam flux with focussing w/r to slitted beam

→ Model independent structures with: ~1 Å structural resolution and
~1-10 μ spatial resolution (and better?)

Surface X-ray Scattering with μ-beams



Extends X-ray scattering capability to small crystals:

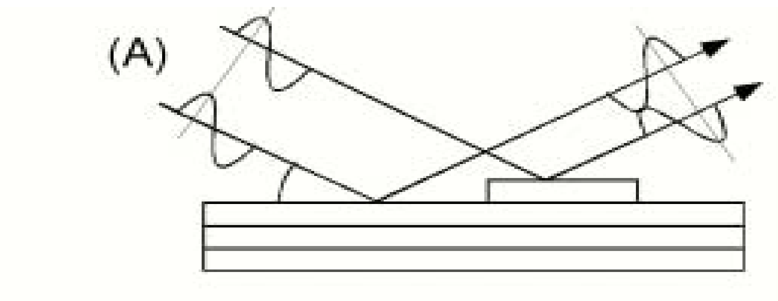
Surface scattering measurements on ~50 μ crystals?

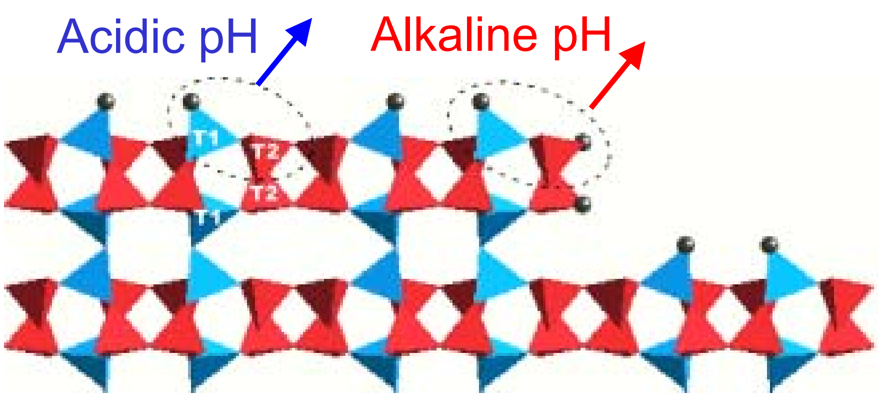
Dynamics: dissolution, etc..

Intrinsic Heterogeneity:

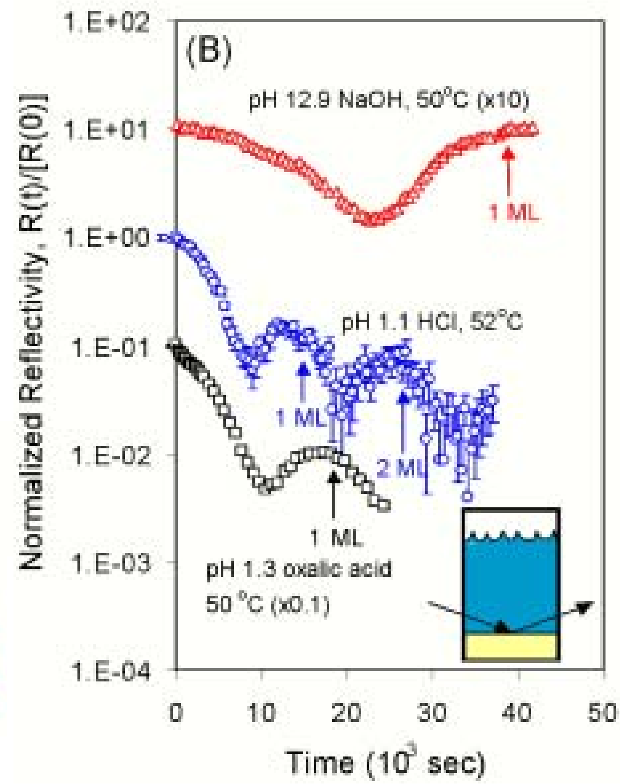
Mineral dissolution

Anti-Bragg condition:





Dissolution of orthoclase (001):

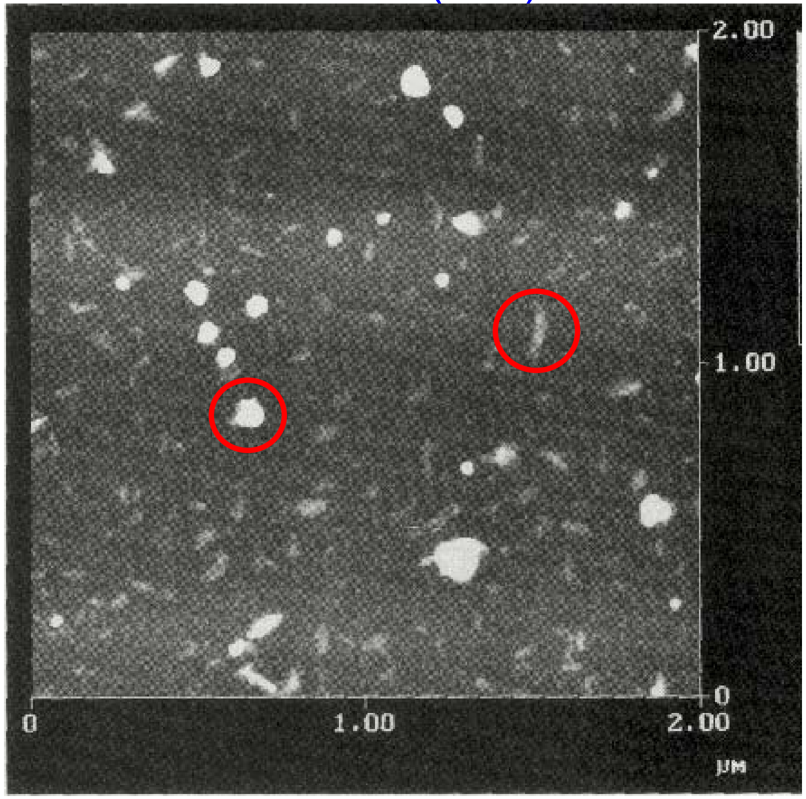


Reactive site specificity (step vs. terrace) controlled by pH

Intrinsic Heterogeneity:

Heterogeneous mineral nucleation

Gibbsite/muscovite (001)

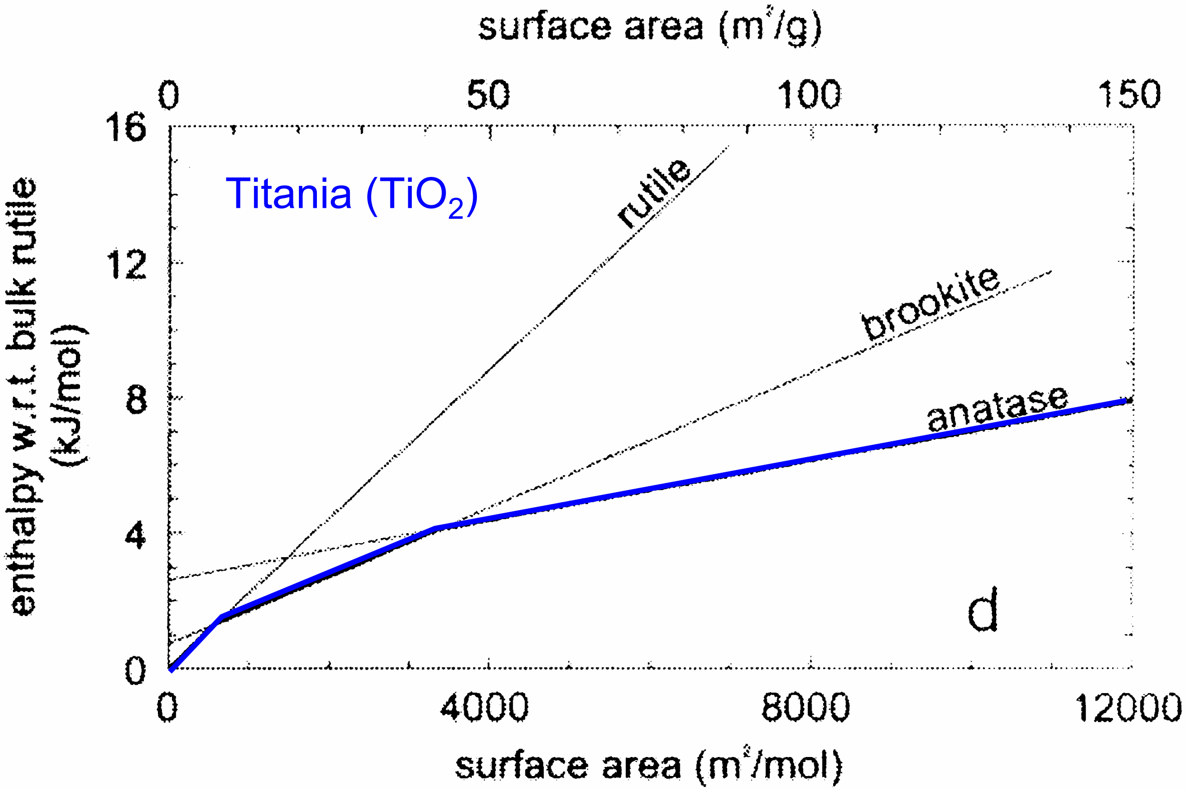


Bimodal distribution of particle size and shape

Nagy et al., GCA **63,** 2337 (1999)

Intrinsic Heterogeneity:

Phase stability vs. particle size



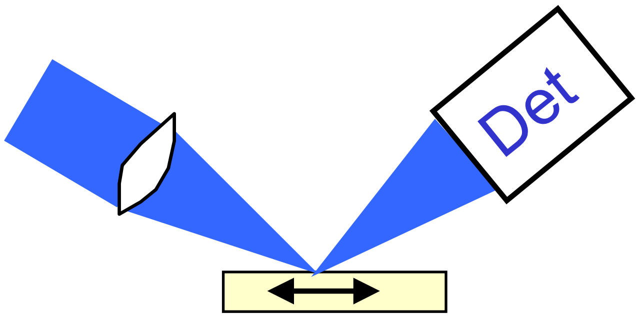
Ranade et al., PNAS **99,** 6476 (2002)

A *Surface* X-ray Microscope:

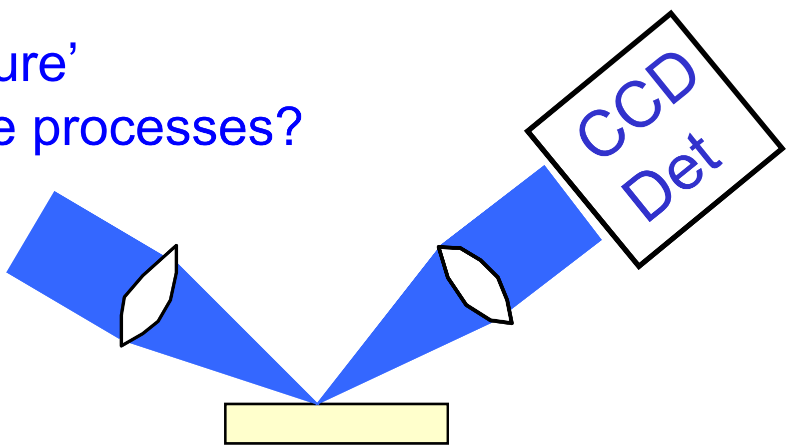
Spatially resolve heterogeneous interface structures

X-ray optics: ~100 nm spatial resolution
X-ray reflectivity: Phase contrast for Å-sensitivity to nano-structures
X-ray fluorescence: Elemental sensitivity (scanning probe mode)

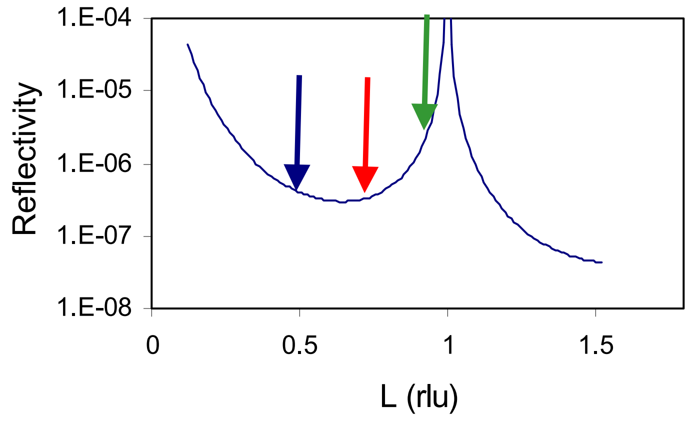
Scanning probe mode: better resolution
spatially resolve fluorescence

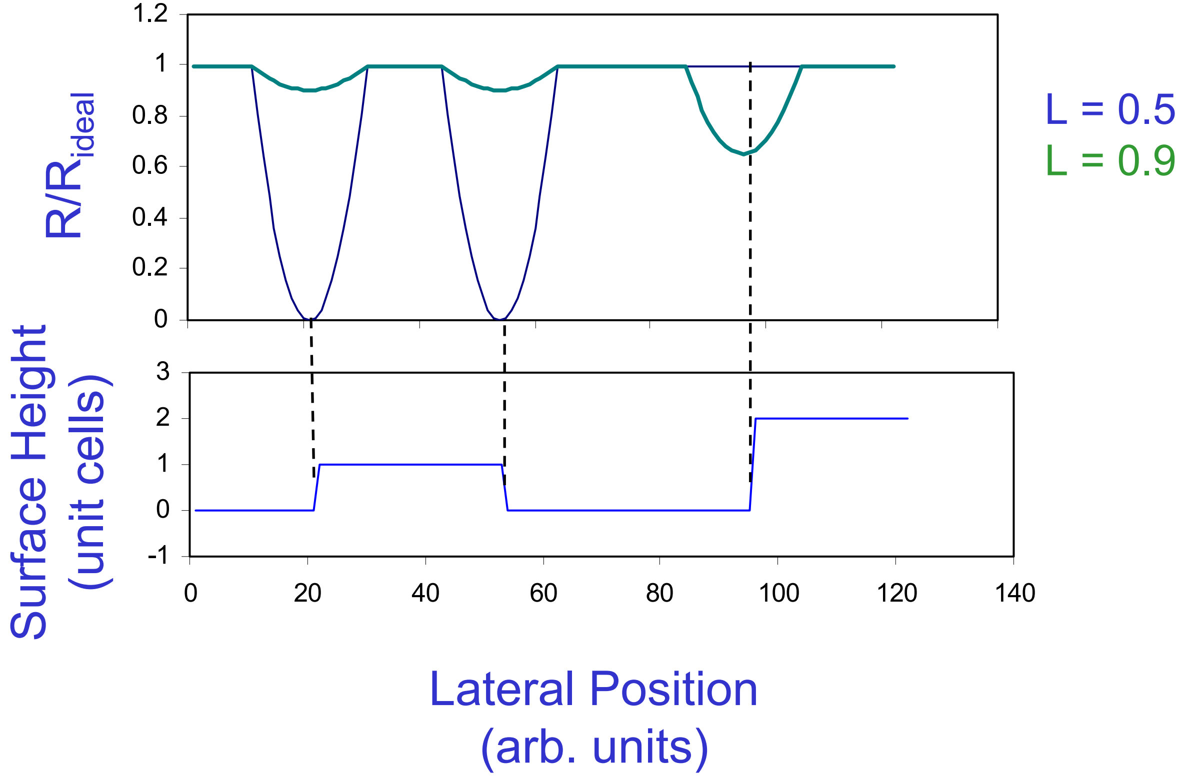


Full field imaging: 'big picture'
real-time processes?



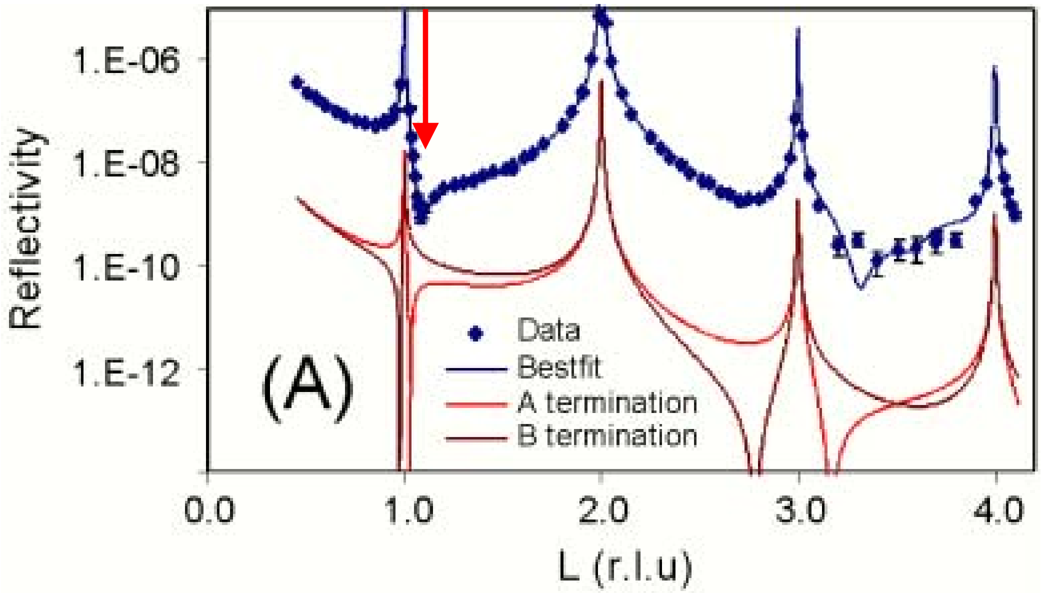
Phase Contrast from Elementary Steps:

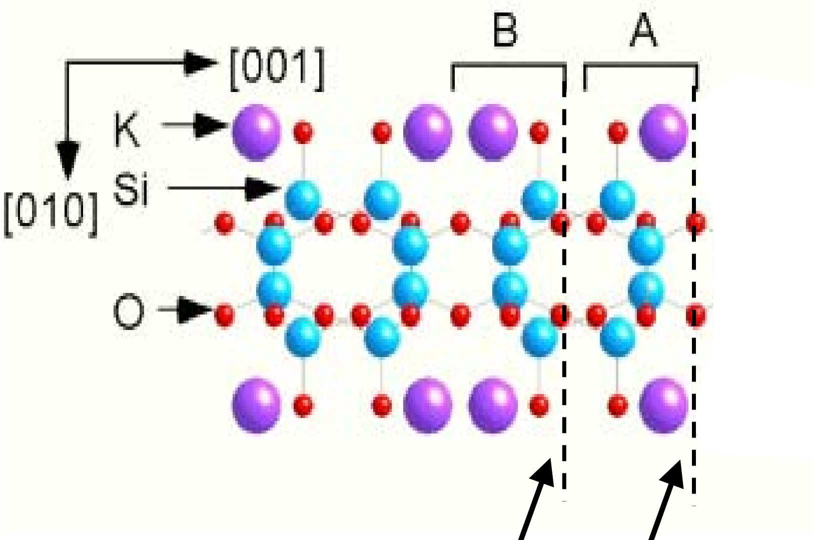




Phase Contrast from Crystal Termination:

Data and Model Calculations: Orthoclase (001)

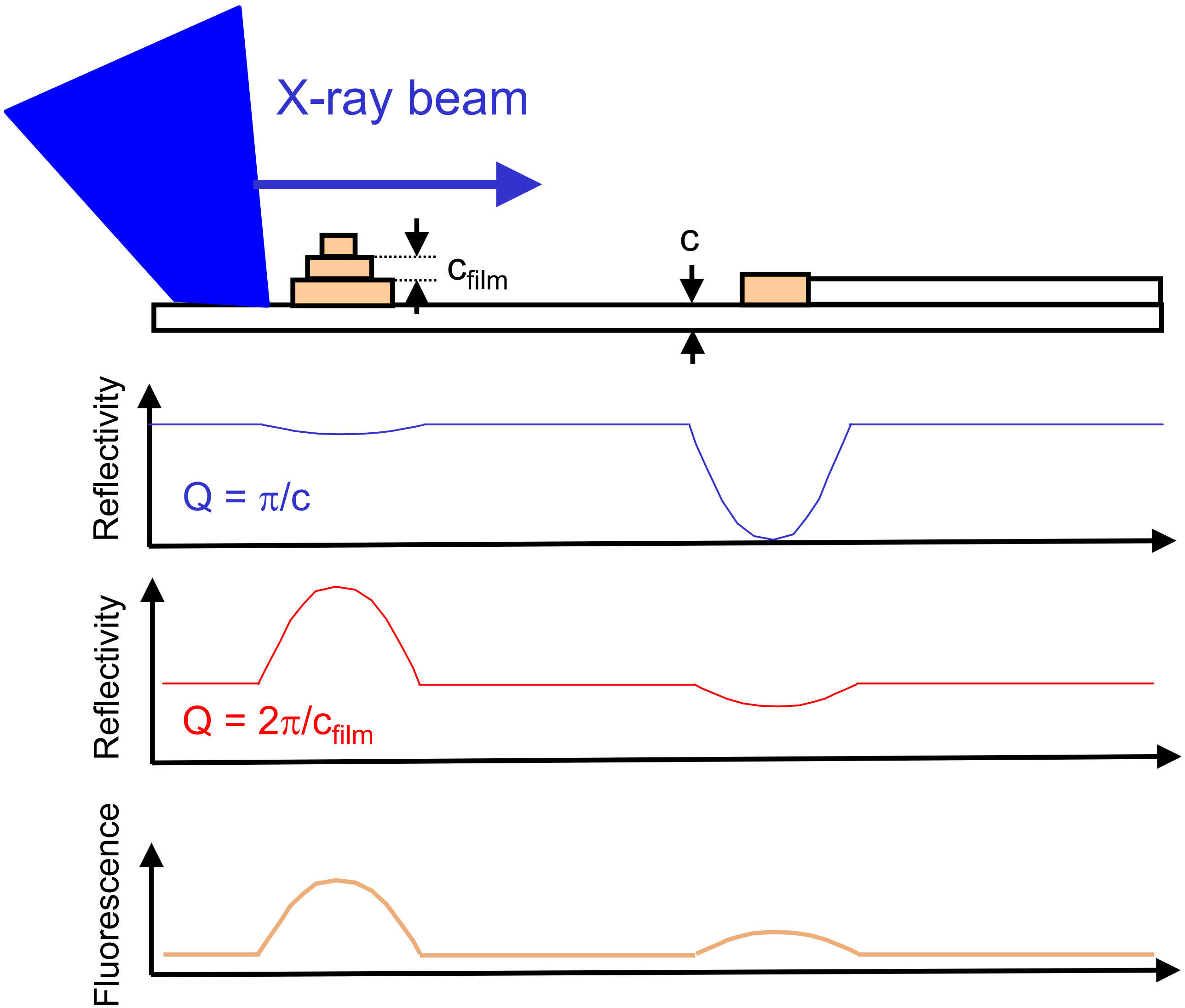


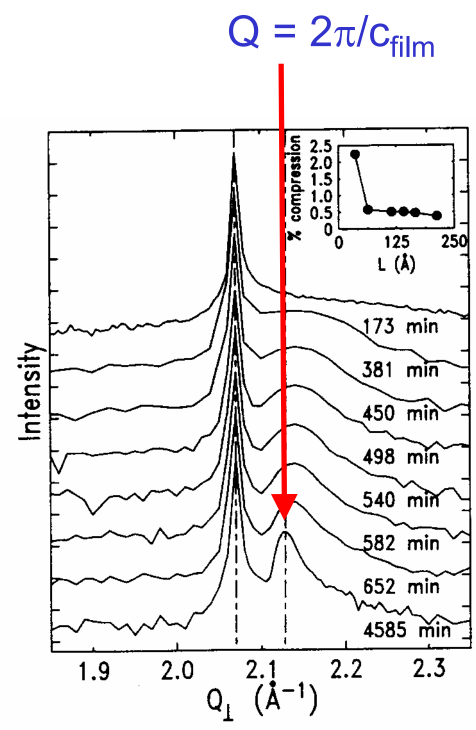


Surface terminations

*P. Fenter and Park, *Phys. Rev. B*, in review (2003)

Elemental and Structural Contrast (scanning mode):





Chiarello and Sturchio, GCA 58, 5633 (1994)

→ Correlate surface morphology, crystal phase, and elemental composition

Summary:

Micro-beams coupled with high resolution X-ray reflectivity and/or XSW :

- Yields new capabilities, broadly applicable to geochemistry, environmental, chemical, and materials sciences

~Å *structural* resolution with ~μ *spatial* resolution

- Transend "complexity gap" between homogeneous model systems and heterogeneous 'real' systems

- Can be done at planned facilities (e.g., Nano-CDT) or built as dedicated instrument (e.g., at BESSRC, Enviro-CAT...).

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