# Opportunities and Challenges with Interfacial X-ray Microscopy*

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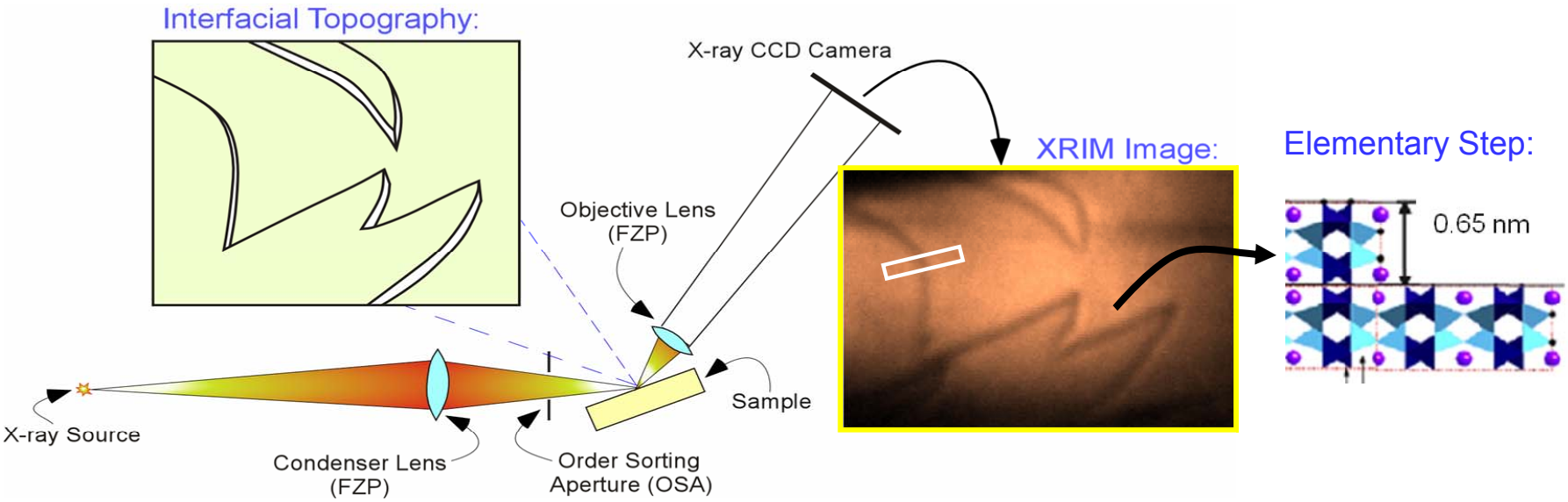
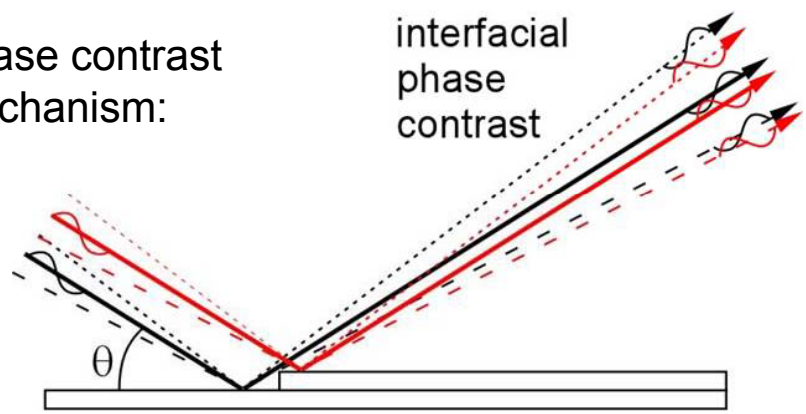
*Supported primarily by the Geoscience Research Program (DOE/BES)

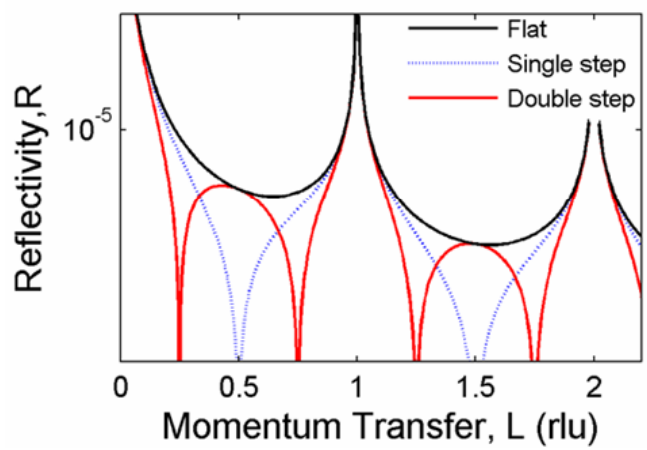
# *X-ray Reflection Interface Microscopy:*




Phase contrast mechanism:



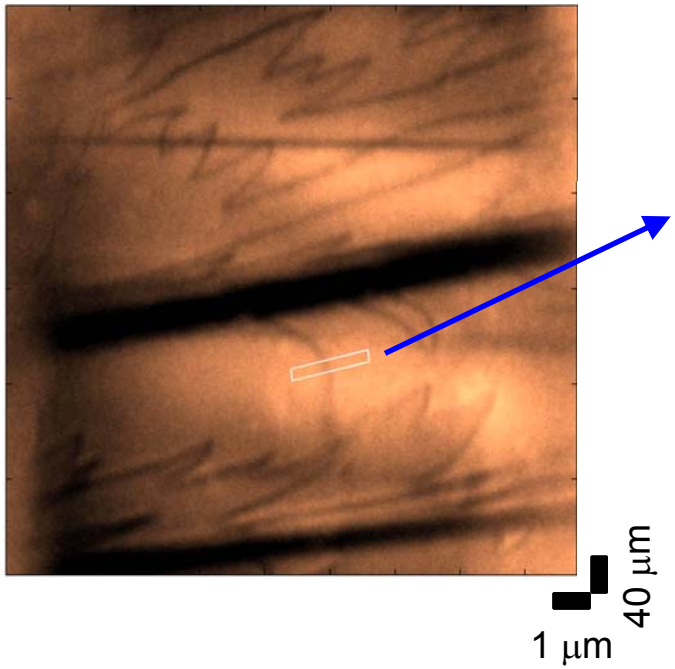

Intensity contrast at a step:




*Fenter et al., *Nature Physics* **2**(10) 700-704 (2006)

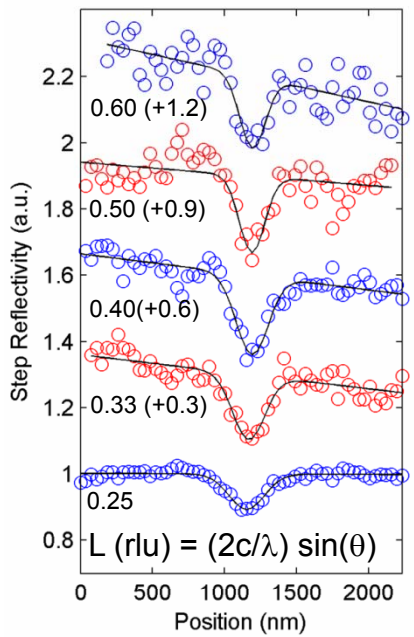
# *Step Identification by Intensity Contrast**

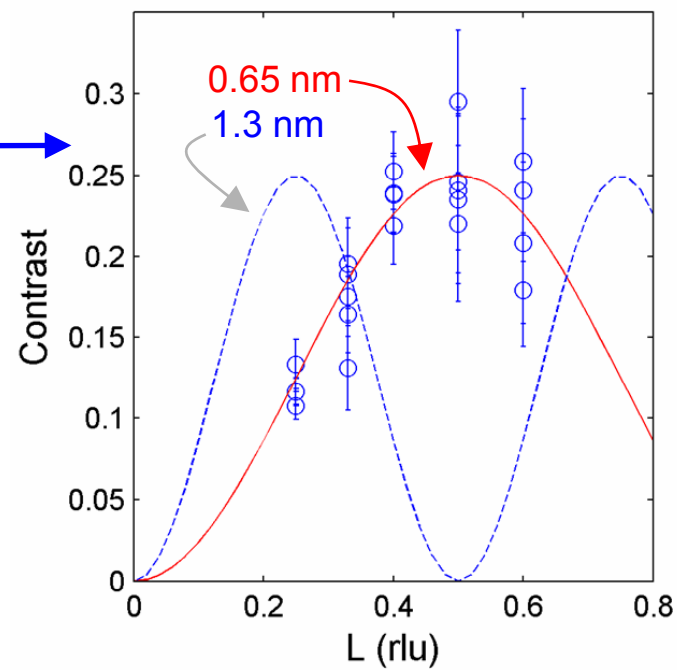
Step distributions on orthoclase (001)




Identification of step height:

Line scans vs. L

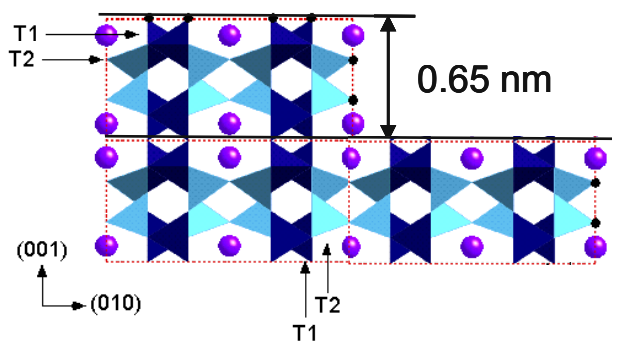



$$\text{Contrast} = \cos^2(Q_z Nc/2) - 1 = -\sin^2(NL\pi)$$

where Nc = step height

Elementary step structure:




Sub-nm vertical sensitivity:

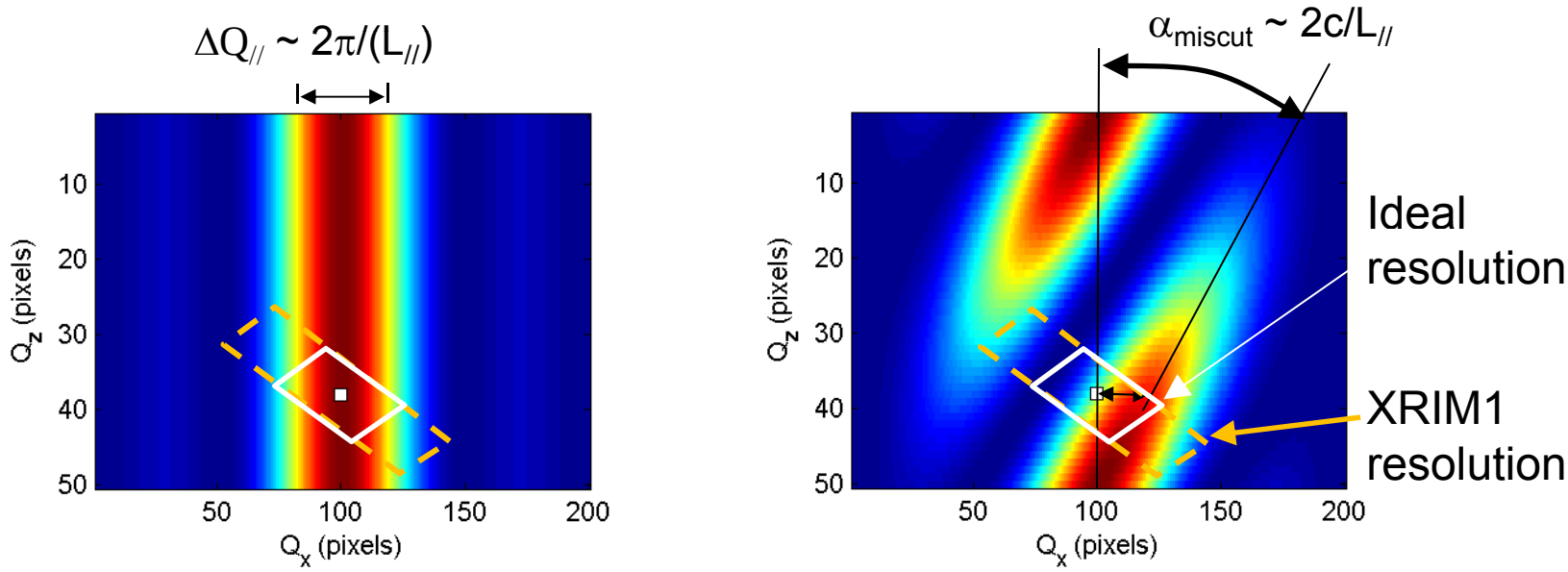
- derived through variation of phase contrast
- highlighted feature is a monomolecular step (0.65 nm high)

*Fenter et al., Nature Physics 2(10) 700-704 (2006)*

# *XRIM Control of Contrast: Step Contrast*

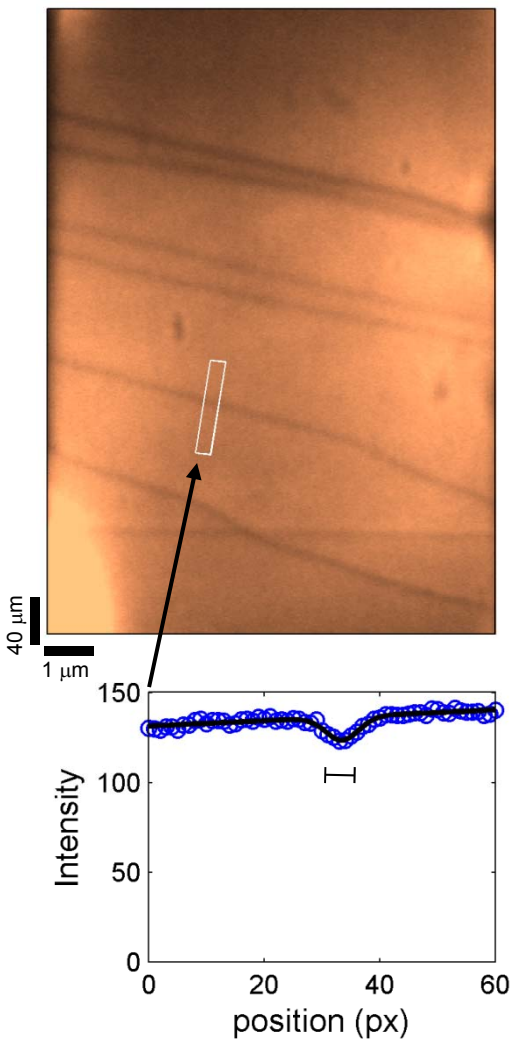
Surface Topography

Reciprocal Space Structure

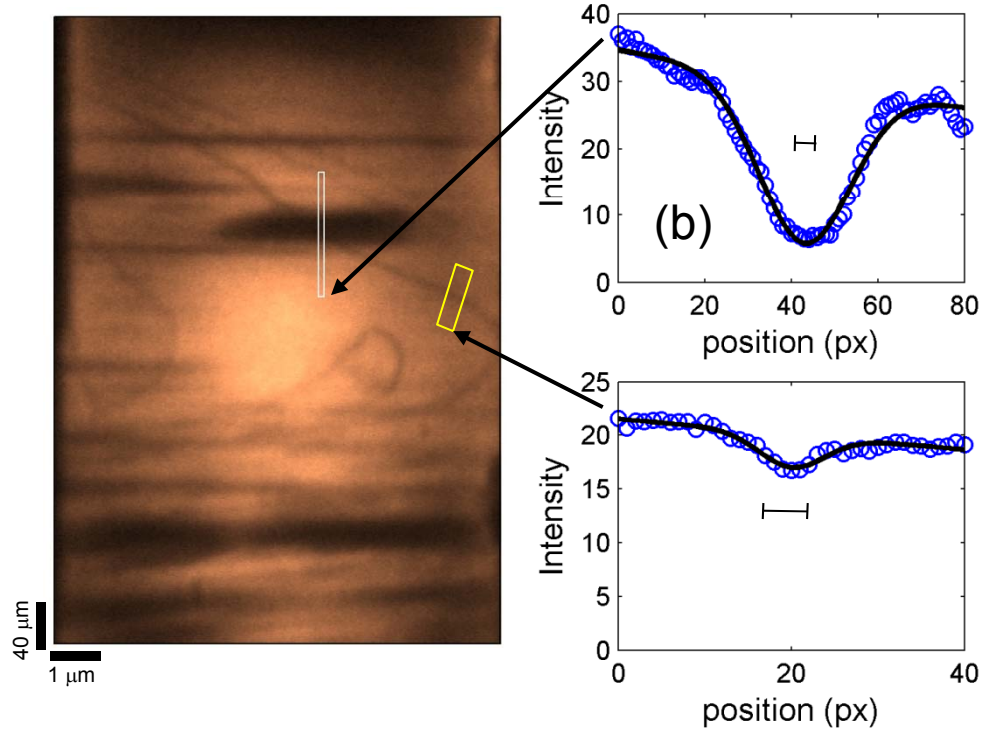


# *Applications: Observing Orthoclase Reactivity (ex-situ results)**

Reaction time: 0 min




15 min ([NaCl]=1 *m*, pOH 2, 84°C)




→Fraction of surface that is reacted is comparable to the rate observed in real-time in-situ measurements

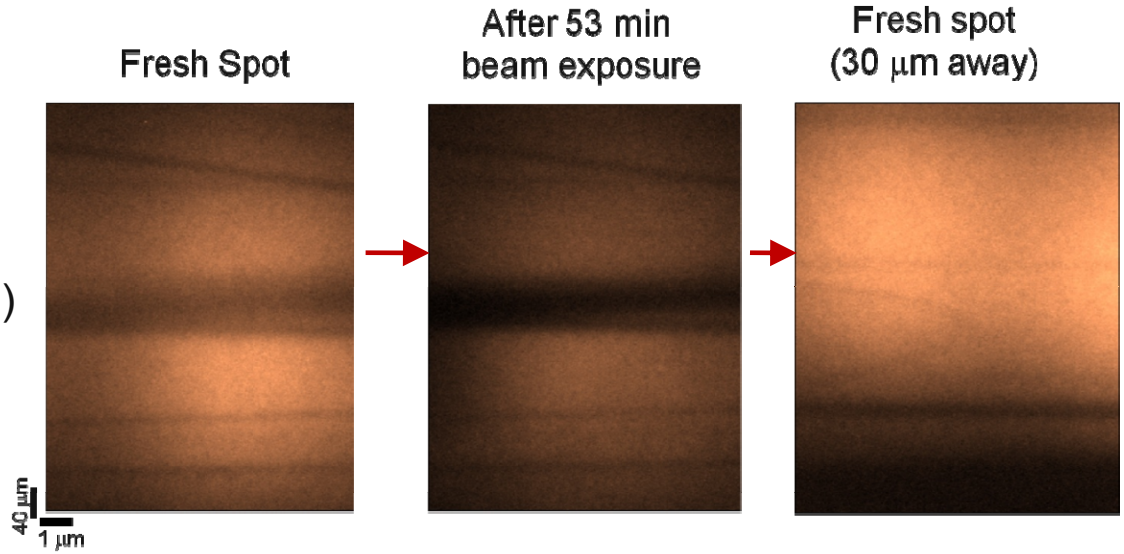
→ Reduction in reflectivity in reacted regions indicates multi-layer dissolution process

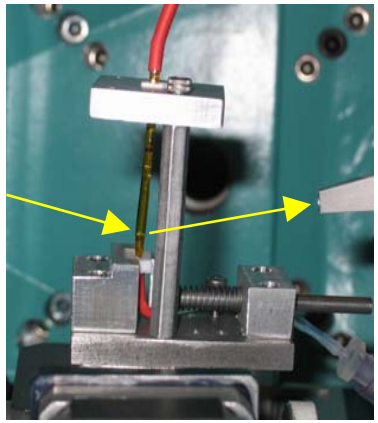
(Images obtained at L = 0.25 r.l.u.)

*P. Fenter et al., *Geochimica et Cosmochimica Acta* **74**, 3396-3411 (2010)

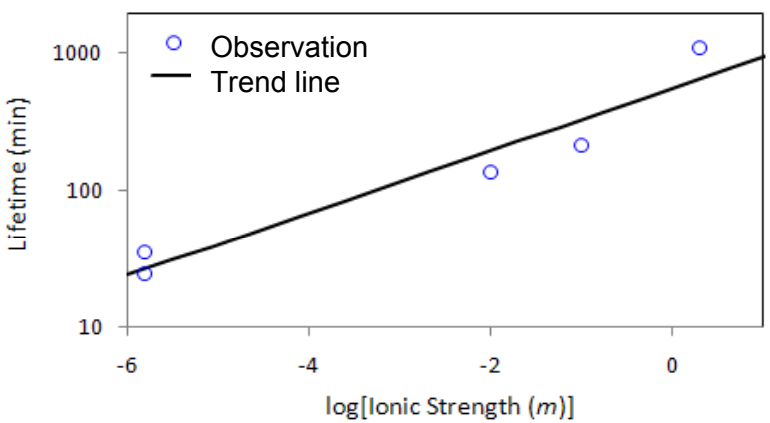
# *Applications: In-Situ Imaging of the Orthoclase-Water Interface*:*

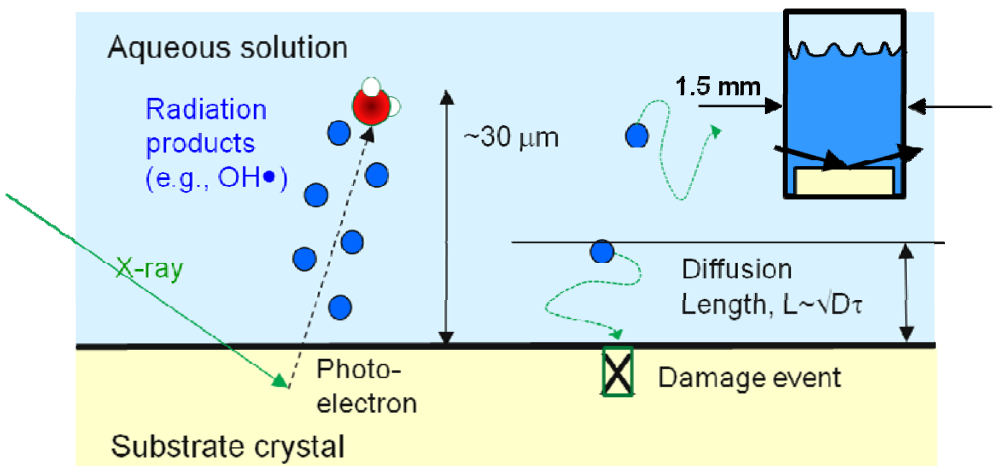
Orthoclase,
$KAlSi_3O_8(001)$
0.1 *m* NaOH



"Lifetime" of orthoclase-aqueous interface
(continuous exposure in the XRIM beam)

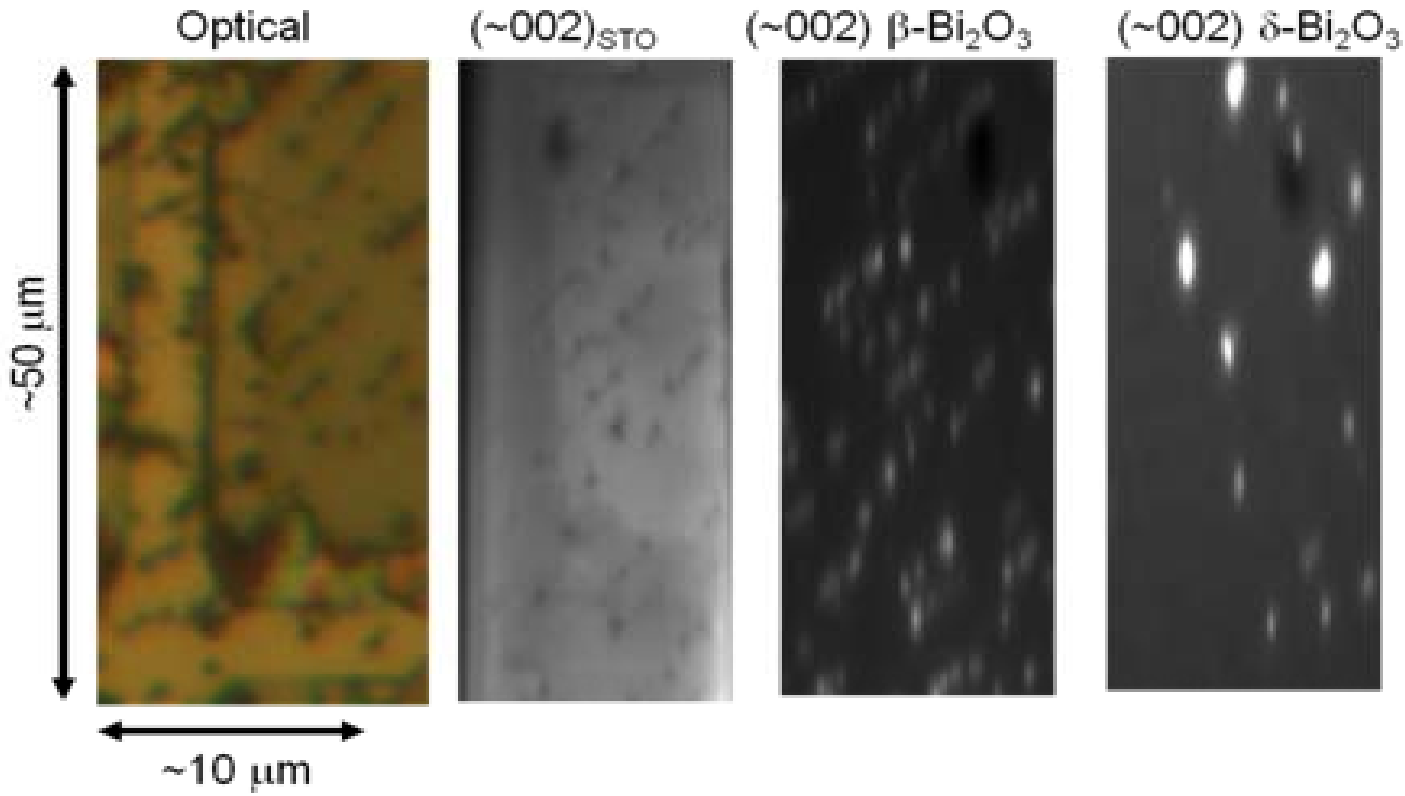



→ Damage is mediated by radicals formed within a diffusion length of the surface
→ High ionic strength reduces radical lifetime and decreases damage

*Fenter et al., *J. Applied Physics*, **110**, 102211(1-9) (2011).

## *Applications: Imaging $Bi_2O_3$ Polymorphs on $SrTiO_3$ (001)**




→Directly observes different lateral distributions of structurally-distinct but compositionally-identical phases ($\beta$-$Bi_2O_3$ and $\delta$-$Bi_2O_3$)

→Contrast from thin-film diffraction

→Similar capability will be used to understand nucleation of polymorphs from solution (e.g., calcite vs. aragonite)

**Proffit, Zhang, Zschack et al., unpublished results*

# *Opportunities with XRIM*

A new capability combining:

- exquisite structural sensitivity of interfacial X-ray scattering
  topography, thin films, etc.
- high spatial resolution of X-ray microscopy

A *non-invasive* structural tool (no probe tip):

- in-situ observations of interfacial structure/topography
- reactions in aggressive chemical conditions (extreme pH, corrosive gases)
- elevated temperature
- buried interfaces
- lateral elemental distributions (through RAXR)
  - ion adsorption
  - precipitation of nano-phases

- real-time studies of interfacial processing
  - growth, dissolution, etching…

## *Challenges with XRIM1*

Poor Time Resolution:

- intrinsically small interfacial reflectivity ($10^{-5}$)
- low efficiency of FZP optics (~5-10%)
- reduced contrast due to 2-fold mismatch of n.a. increases imaging time by 4x.

Beam Damage:

- High x-ray flux density at sample induces radiation chemistry (in water).

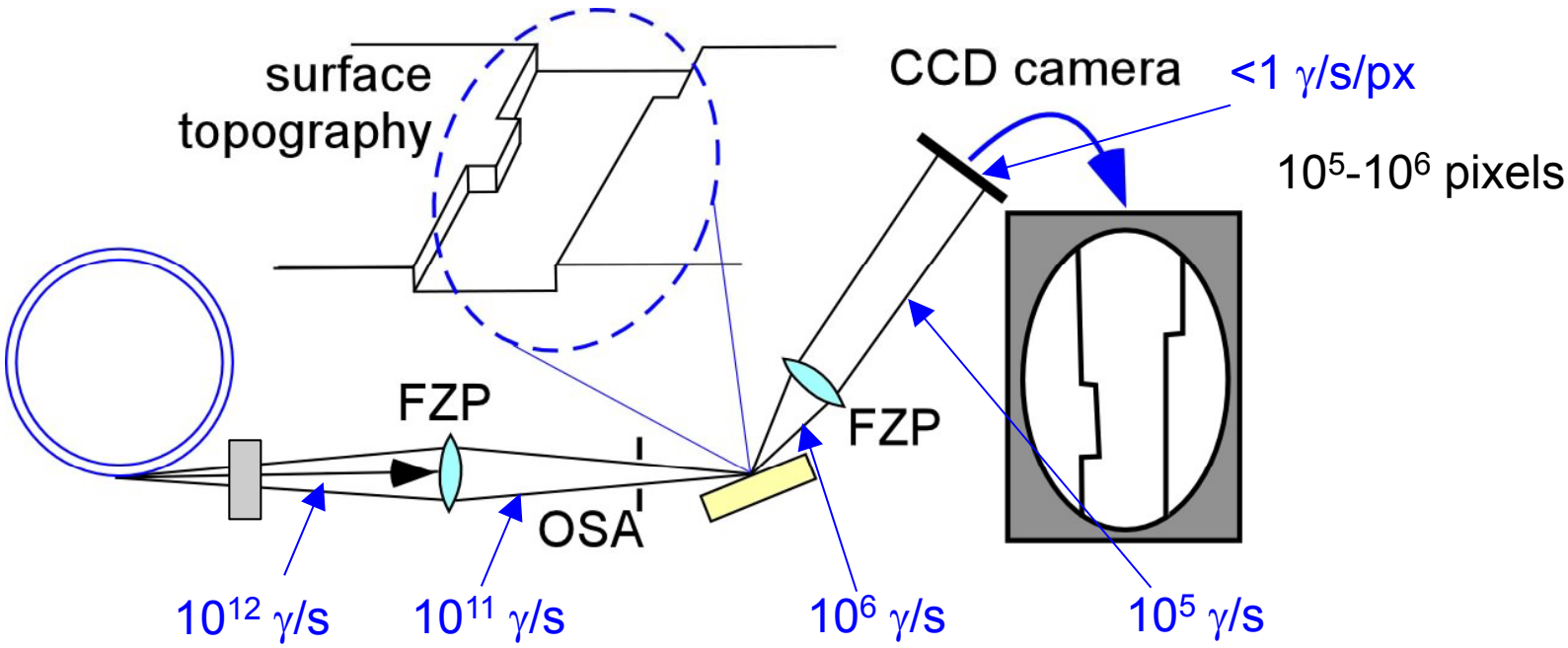
Spatial Resolution:

- Achieved resolution of 170 nm (compared to expected resolution of100 nm)

→Substantial improvements in capabilities are expected with an optics upgrade (now underway) for XRIM2, including:

- improved image acquisition time
- improved resolution
- improvement in image contrast

# *XRIM1: X-ray Flux Diagram*




APS undulator
Si(111) mono

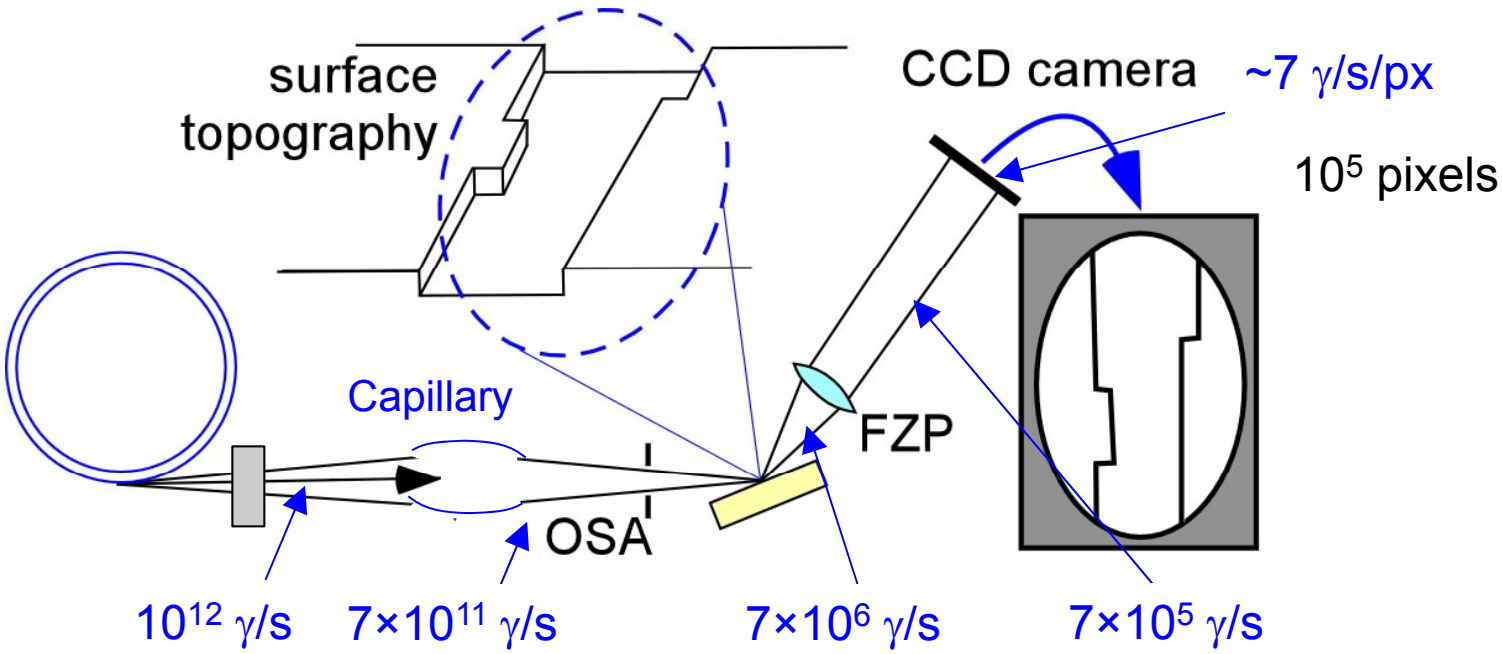
FZP efficiency
~10%

Interfacial
reflectivity
$R=10^{-5}$

FZP efficiency
~10%

→ XRIM is “photon starved” but feasible

# *XRIM2: Increasing the Useful X-ray Flux*




| | | | |
|---|---|---|---|
| APS undulator<br>Si(111) mono | Capillary<br>condenser<br>~70% | Interfacial<br>reflectivity<br>$R=10^{-5}$ | FZP efficiency<br>~10% |

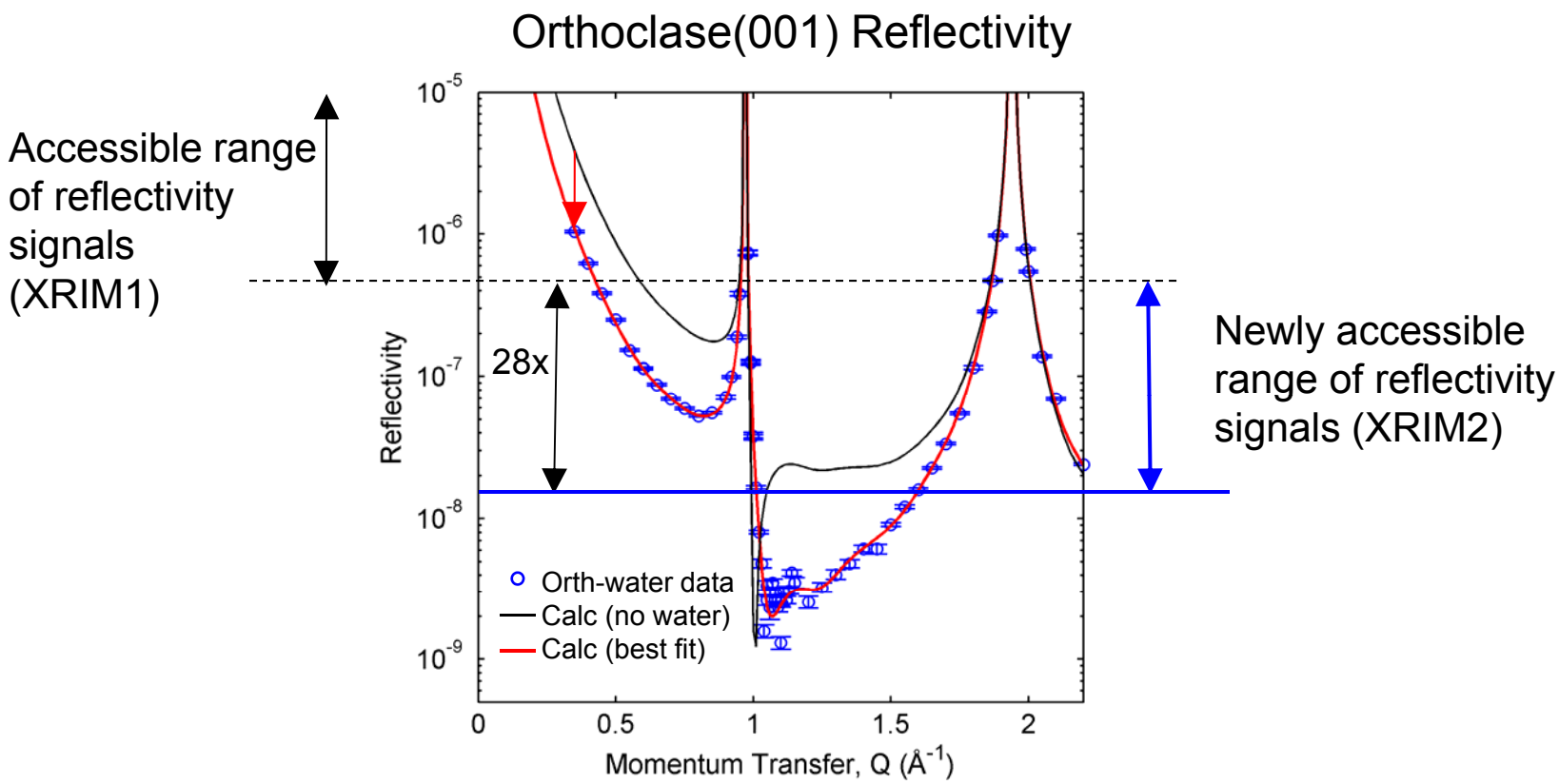
→Net improvement: 28-fold improvement of image acquisition rate

~7-fold improvement of useful X-ray flux on sample (~seconds instead of ~minutes)

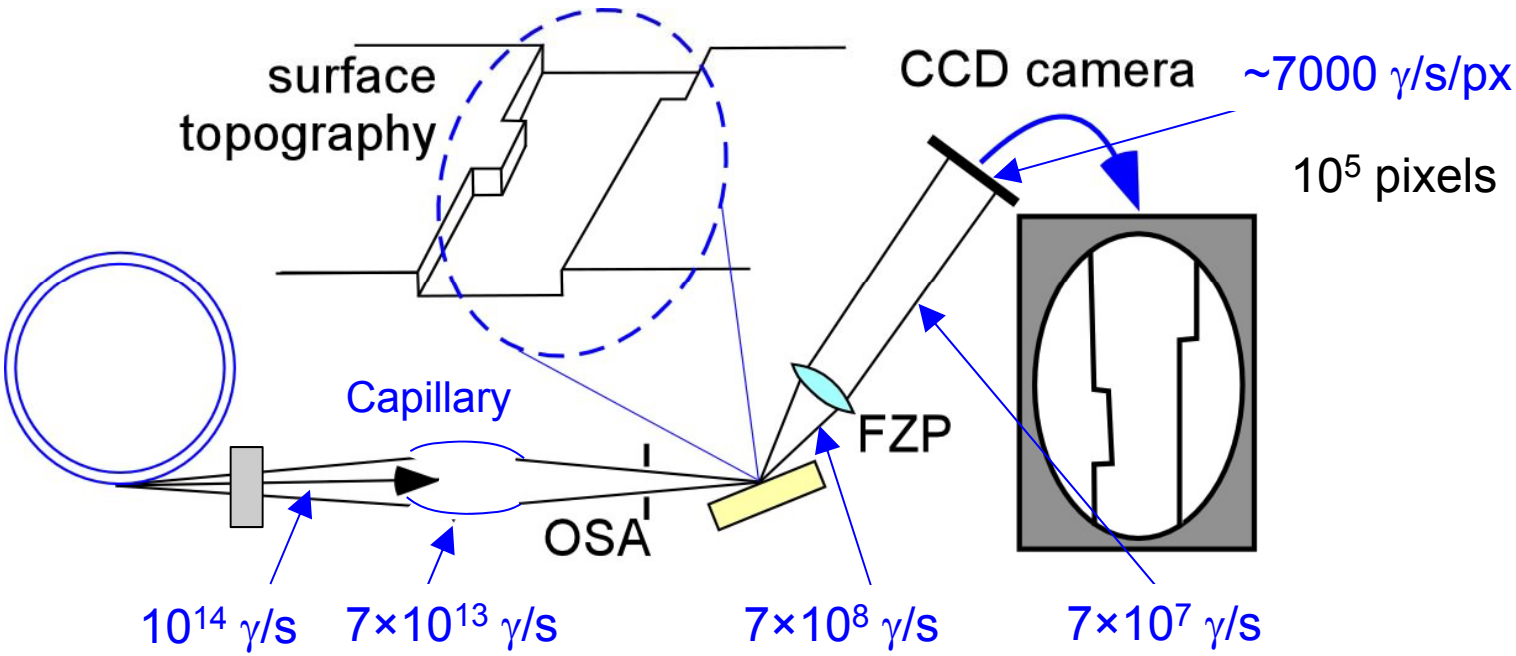
~4-fold reduction in image acquisition rate (i.e., reduced beam damage) due to matching NA of optics (i.e., improved contrast).

- 50 nm spatial resolution (from 170 nm)

# *XRIM2: Impact of More Flux:*



# *XRIM3: Increasing the Useful X-ray Flux*




| | | | |
|---|---|---|---|
| APS undulator<br>Multilayer mono | Capillary<br>~70% | Interfacial reflectivity<br>$R=10^{-5}$ | Blazed FZP efficiency<br>~50% |

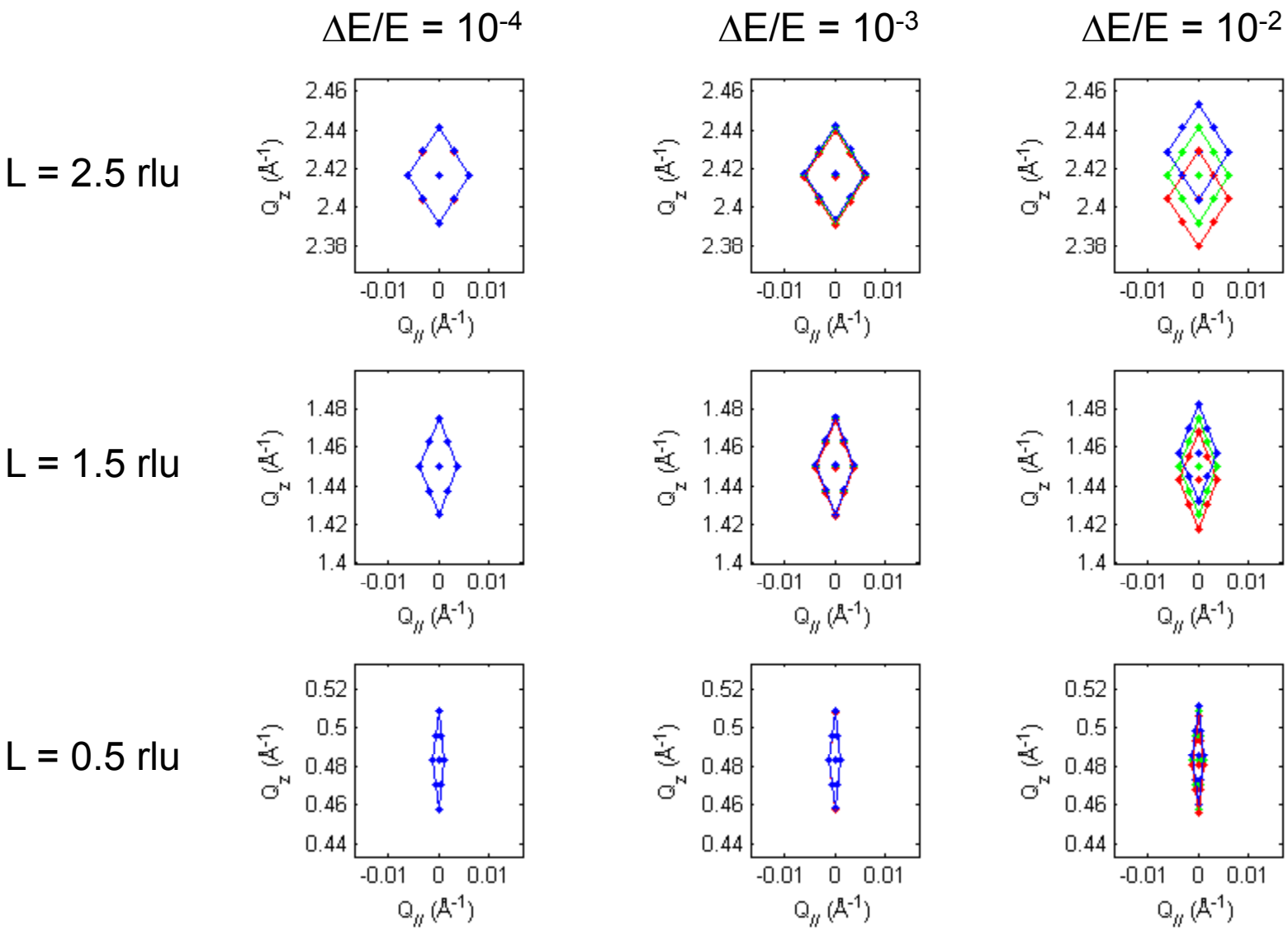
→Net improvements w/r to XRIM2:

~Additional 10 to100-fold improvement of useful X-ray flux on sample

~5-10-fold increase in objective lens efficiency (i.e., faster image acquisition rate and reduced beam damage)

→ 50-1000-fold faster imaging w/r to XRIM2; << 1 second per image

# *XRIM3: Monochromator Bandwidth vs. Reciprocal Space Resolution*




Effect of chromatic broadening minimal for $\Delta E/E = 10^{-3}$ for $Q < 3$ Å$^{-1}$

Beam width of $\Delta E/E = 10^{-2}$ is useful for $Q < 0.5$ Å$^{-1}$

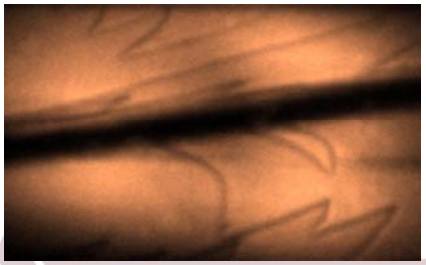
## *Outlook:*

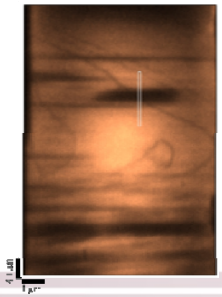
→Substantial improvements in time and spatial resolution are expected with future upgrades to XRIM design

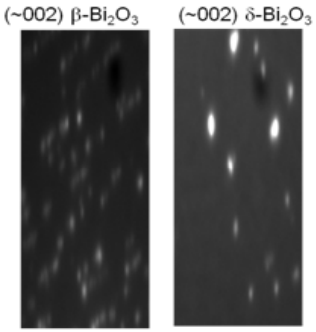
XRIM2: ~28-fold faster image acquisition time
>3-fold improvement in spatial resolution
~4-fold improvement in image contrast

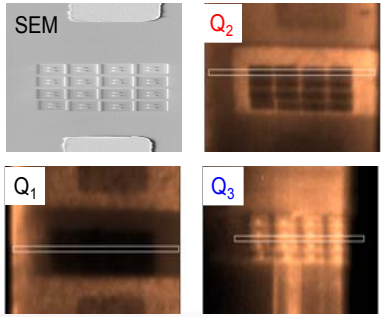
XRIM3: (improvements w/r to XRIM2):
~10 to100-fold improvement of useful X-ray flux on sample
~5-10-fold increase in objective lens efficiency (i.e., faster image acquisition rate and reduced beam damage)
→ << 1 second per image

XRIM4: Coherent XRIM/CDI system?
→These upgrades will enable in-situ, real-time observations of dynamic processes at interfaces, e.g., dissolution, growth, etc.







## *Contributors:*

Interfacial Processes Group (CSE/ANL):

Sang Soo Lee (Interfacial geochemistry; cation adsorption )
Tim Fister (Interfaces in lithium ion batteries)
Moritz Schmidt (Actinide-mineral interactions)
Numan Laanait (XRIM2 development; imaging interfacial processes)
Francesco Bellucci (Interfacial geochemistry/ ion adsorption)

Zhan Zhang and Paul Zschack, APS (XSW imaging, XRIM)
Hua Zhou, APS (Carbon-electrolyte interfaces)

External Collaborators

Neil C. Sturchio, University of Illinois at Chicago & ANL
Michael J. Bedzyk, Northwestern University (XSW)
Kathryn Nagy, UIC (ions & organics/muscovite)
Lynn Soderholm and Richard Wilson, (CSE/ANL) (Actinide-mineral interactions)
Steve Wang (APS/ANL), Michael Feser, Wenbing Yun, Xradia , (X-ray interfacial microscopy)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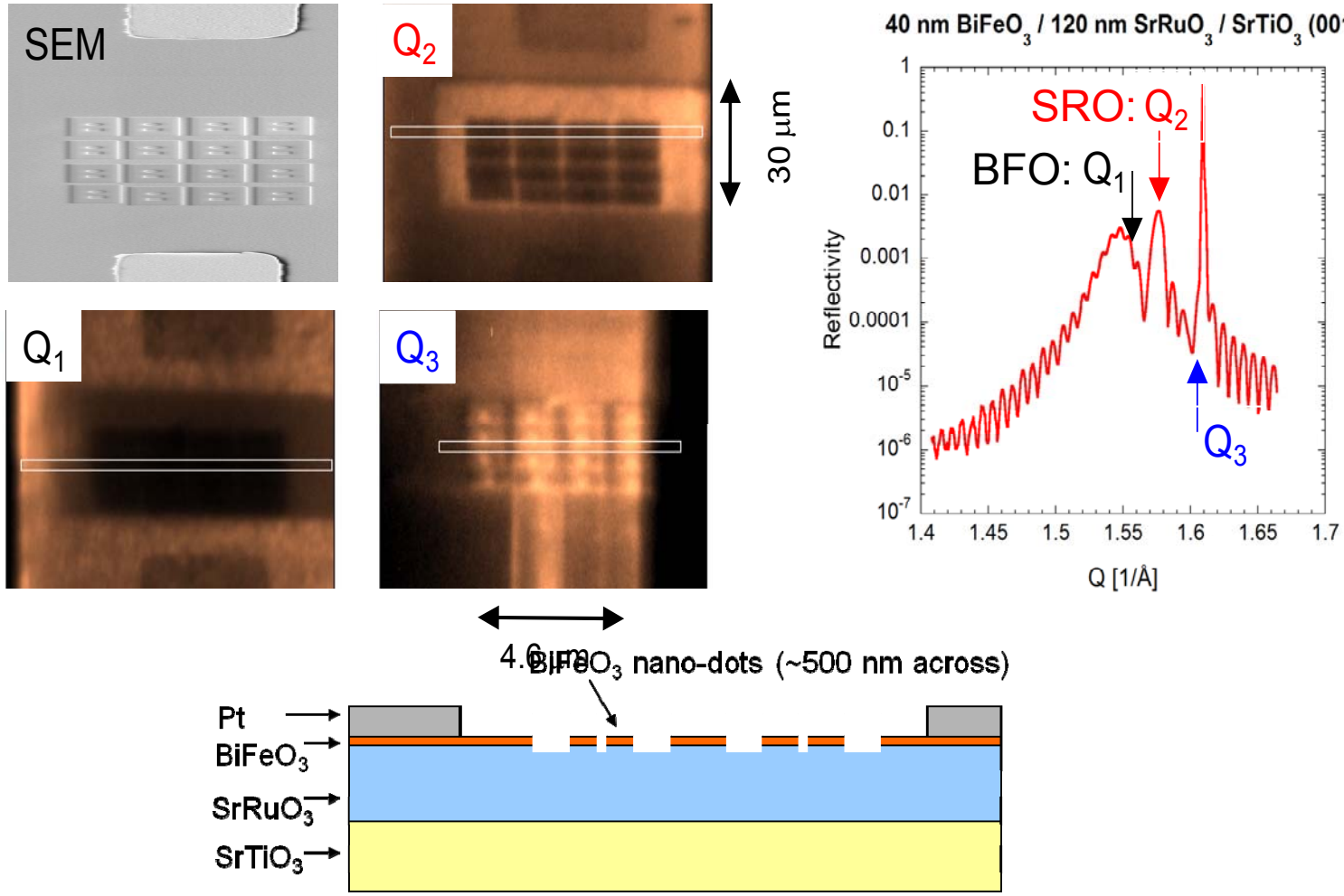
Center for Electrical Energy Storage (ANL/EFRC)
Fluid Interface Reactivity Structure and Transport (ORNL/EFRC)

Office of Biological and Environmental Research, U.S. Dept. of Energy (BER/DOE)

# Thank You!

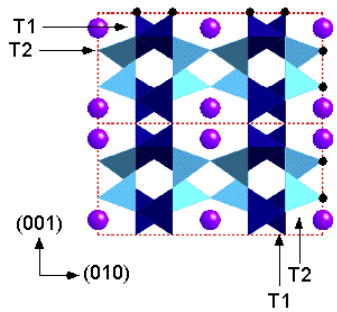
# *Imaging Laterally Structured Thin-Films: $BiFeO_3/SrRuO_3/SrTiO_3$ (001)**




- Use thin-film Bragg diffraction to spatially resolve nano-dot structure

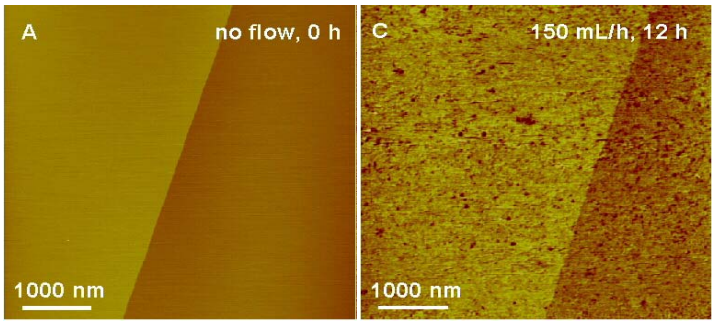
*J. Klug et al., unpublished results

# *Probing Interfacial Reactivity at the Orthoclase (001)-Electrolyte Interface*

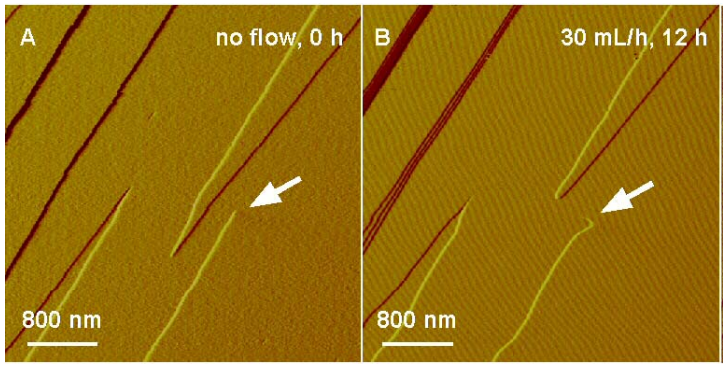



## Atomic Force Microscopy:

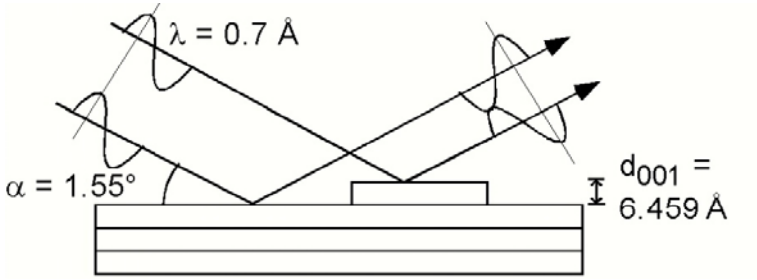
*Orthoclase, T=23°C,* pH = 1.1

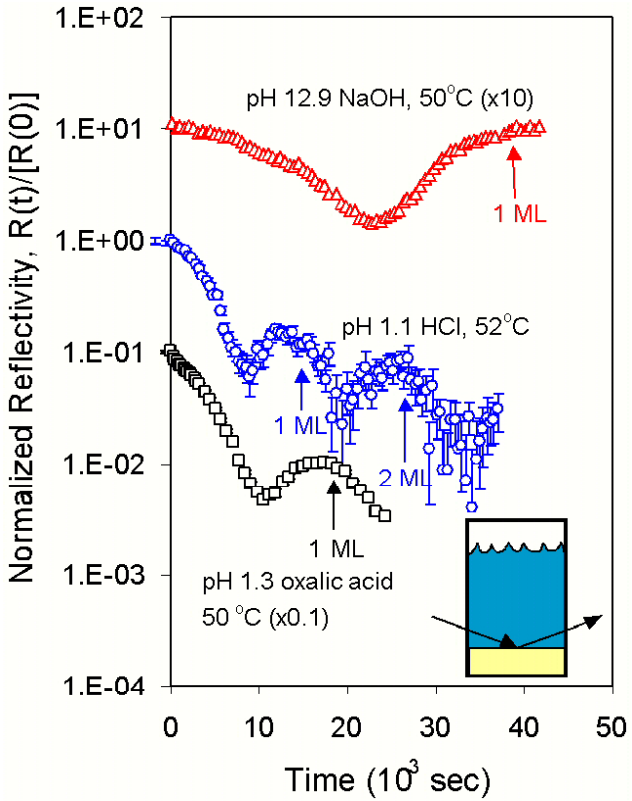



*Orthoclase, T=23°C,* pH = 12.9




## XR Observations of Orthoclase Dissolution

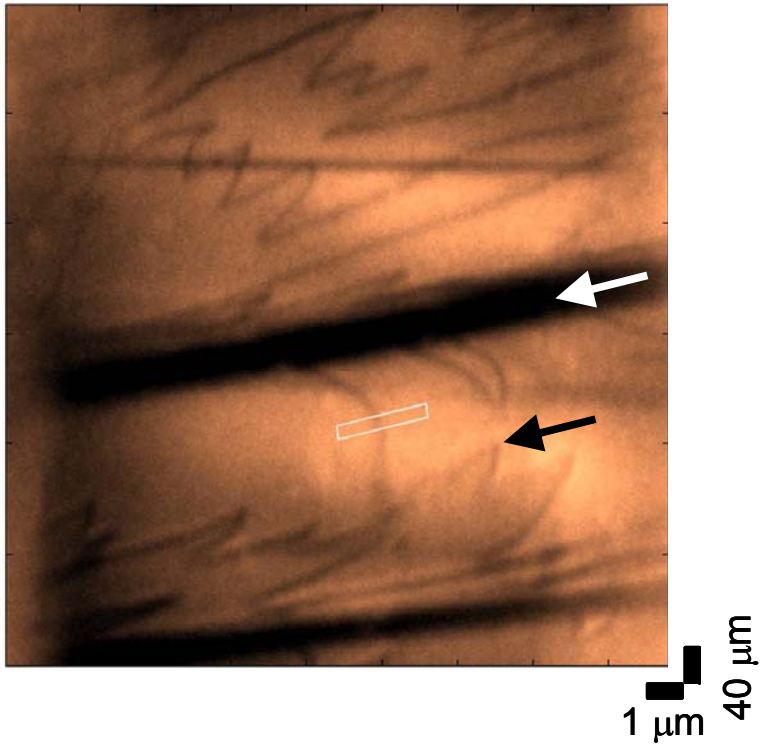


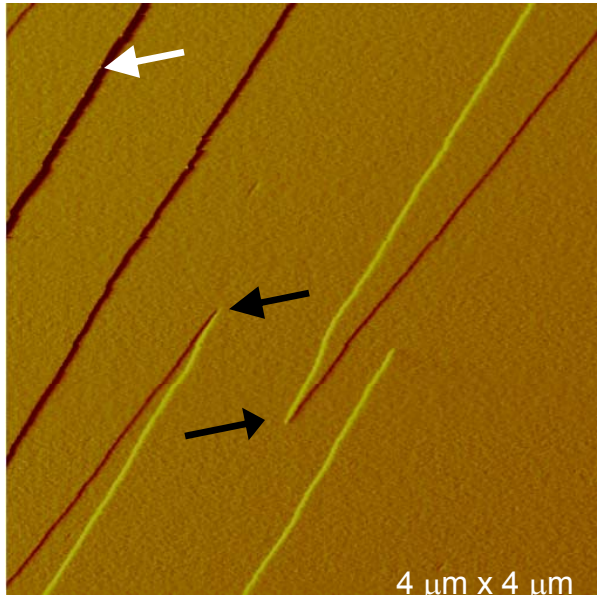

*H. Teng et al., *GCA* 65(20), 3459-3474 (2001)

# *Observation of Step Distributions with XRIM**

Step distributions on orthoclase (001)

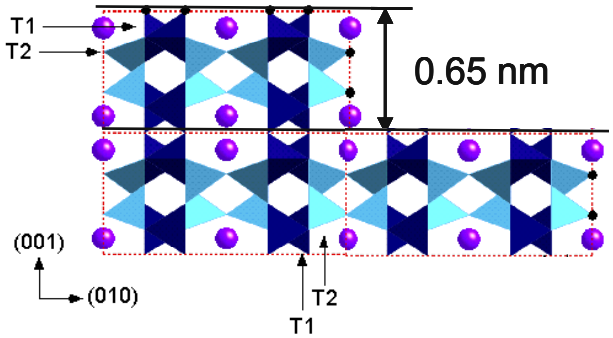



AFM of orthoclase, $KAlSi_3O_8$ (001)




Teng et al., GCA 65, 3459-3474 (2001)

Elementary step structure:




Imaging Conditions:

$\theta = 1.4°$

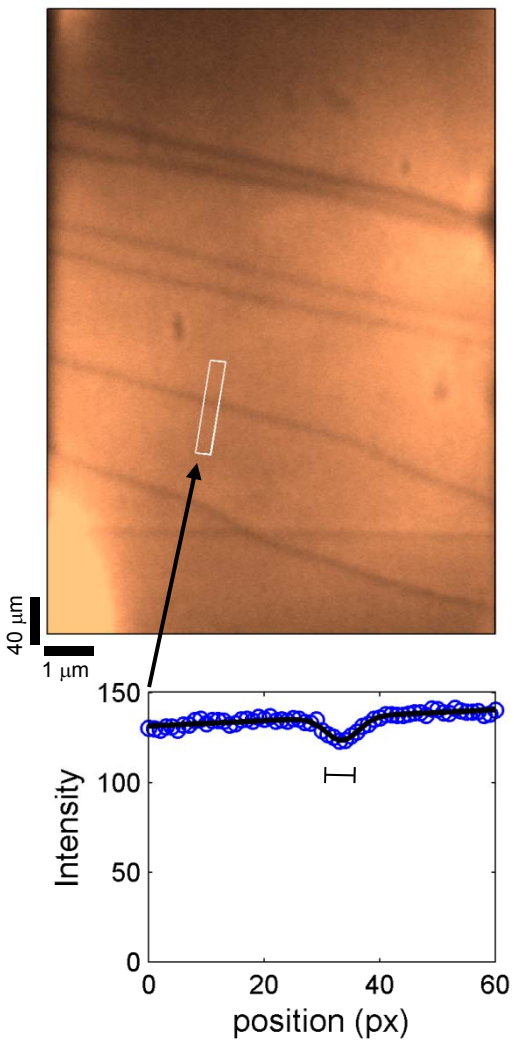
E = 10 keV

L = 0.25 rlu (Q = 0.24 $Å^{-1}$)

Sample in air

# *Observing Orthoclase Reactivity (ex-situ results)**

Reaction time: 0 min

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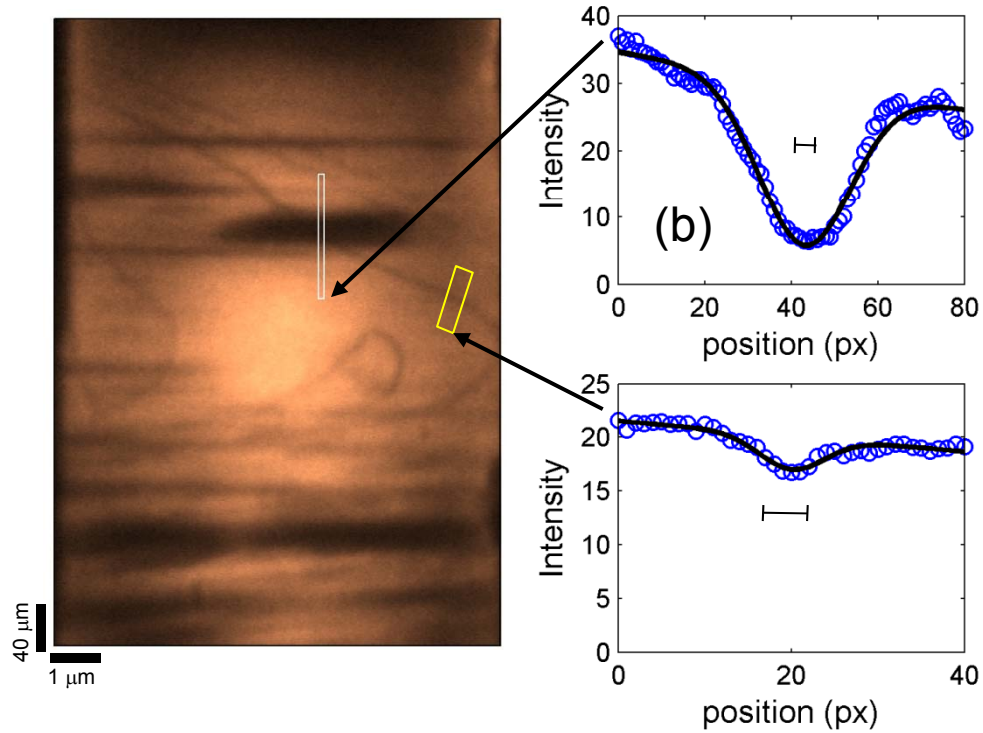


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(Images obtained at L = 0.25 r.l.u.)

*P. Fenter et al., *Geochimica et Cosmochimica Acta* **74**, 3396-3411 (2010)