Measuring Reactions at Solid Surfaces

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VIRGINIA TECH

Objective

- How do cements (or, more generally, any mineral) react?
- What is going on at the interface between the cement particle and water? More generally, what is going on at the *solid-fluid interface*?
- How does one take measurements or even “see” or “detect” these atomic-scale interactions?
    - Way too many available options!
    - Surface topography by physical probe (atomic force microscopy, contact profilometry)
    - Surface topography by optical probe (digital holographic microscopy, vertical scanning interferometry, confocal laser scanning microscopy)
    - Surface properties (nanoindentation, atomic force microscopy)
    - Chemical or elemental surface analysis (X-ray photoelectron spectroscopy, secondary ion mass spectrometry, Raman and infrared spectroscopic microscopy, fluorescence microscopy, energy dispersive X-ray spectroscopy, X-ray absorption spectroscopy, etc., etc.)
- ***Let’s just focus on some of these concepts***

Dissolution Kinetics of Cement Minerals

- At what rate do cement minerals dissolve before precipitating?
- Why do we even need to know this?
  - Next generation computational materials science models (*e.g.*, HydratiCA) require fundamental thermodynamic and kinetic properties (Bullard et al. 2011; Biernacki et al. 2013)
  - Rate laws and kinetics, such as the dissolution rate (or flux) as mol m^{-2} s^{-1}
  - Developing new chemical admixtures
- Historically, these fluxes were measured with powder suspensions in solution (*e.g.*, monitoring solution concentration)

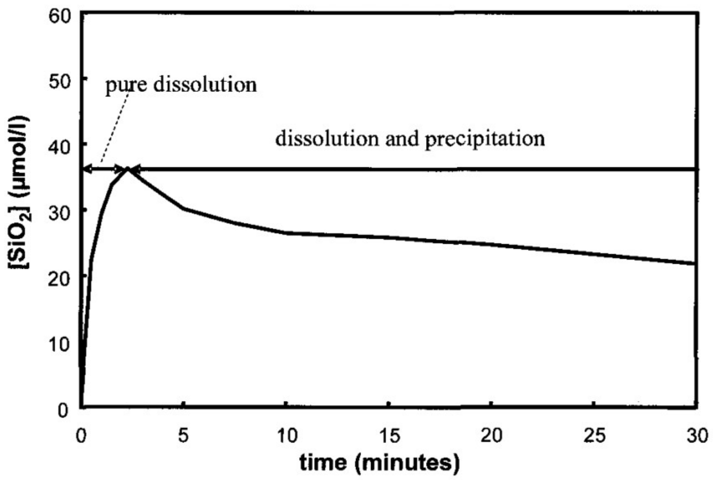


Fig. 1 - Variation of the silica concentration against time during Ca_3SiO_5 hydration in saturated lime solution.

Garrault et al. 2005

Dissolution: Powders vs. Surface Topography

- Issues with powder suspensions
  - Assumed surface area and particle geometry
  - Cannot (necessarily) truly guarantee that no additional phases are precipitating
  - Greater density of defects and kink sites
- <u>A different approach</u>: Monitor changes in surface topography
  - A concept from geochemists (*e.g.*, Luttge and Arvidson, 2010)
  - Examine micro- and nanoscale evolution of surface topography as a given surface reacts
  - The surface area and geometry is now known
  - We can actually see dissolution and precipitation occurring
  - Limited number of defect sites and kink sites to field-of-view

Measuring Micro- and Nanoscale Topography

Three primary methods that we'll discuss:

1. **Atomic Force Microscopy (AFM)**
   - Earliest technique used in the literature, with geochemical studies starting in the early 1990s
2. **Vertical Scanning Interferometry (VSI)**
   - More recent, being first utilized for geochemistry applications in the late 1990s and early 2000s
3. **Digital Holographic Microscopy (DHM)**
   - Relatively recent technology; NIST was the first to apply it to study mineral dissolution kinetics (2016/2017)

<u>So, which one is best?</u> Well that depends on what you're trying to measure, the time scale of reaction, the length scale of reaction, what the solid and liquid phases are, the resolution required, etc.

Atomic Force Microscopy

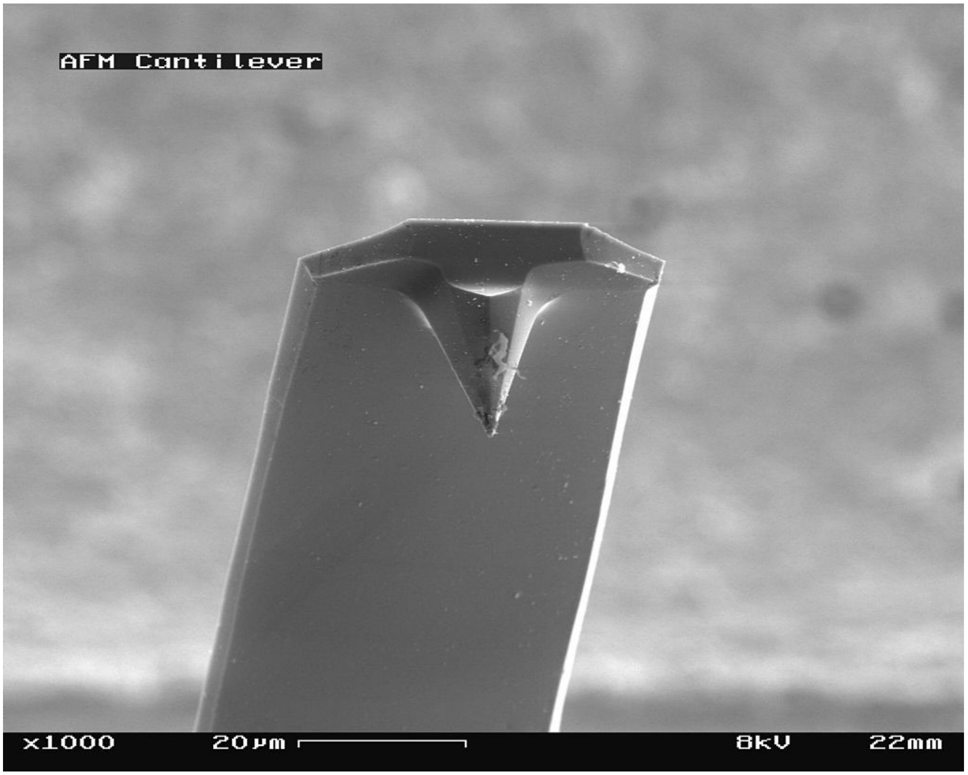
- Precursor to the AFM was the Scanning Tunneling Microscope (STM)
  - G. Binnig and H. Rohrer received the 1986 Nobel Prize in Physics for discovering and developing the STM
- The AFM was first developed by G. Binnig, C.F. Quate and C. Gerber in 1982 and was first commercially available in 1989
- AFM is primarily capable of:

1. High resolution topographic imaging (3D surface)
2. Force spectroscopy: measure force between probe and surface
3. Manipulation, such as by localized stimulation of cells

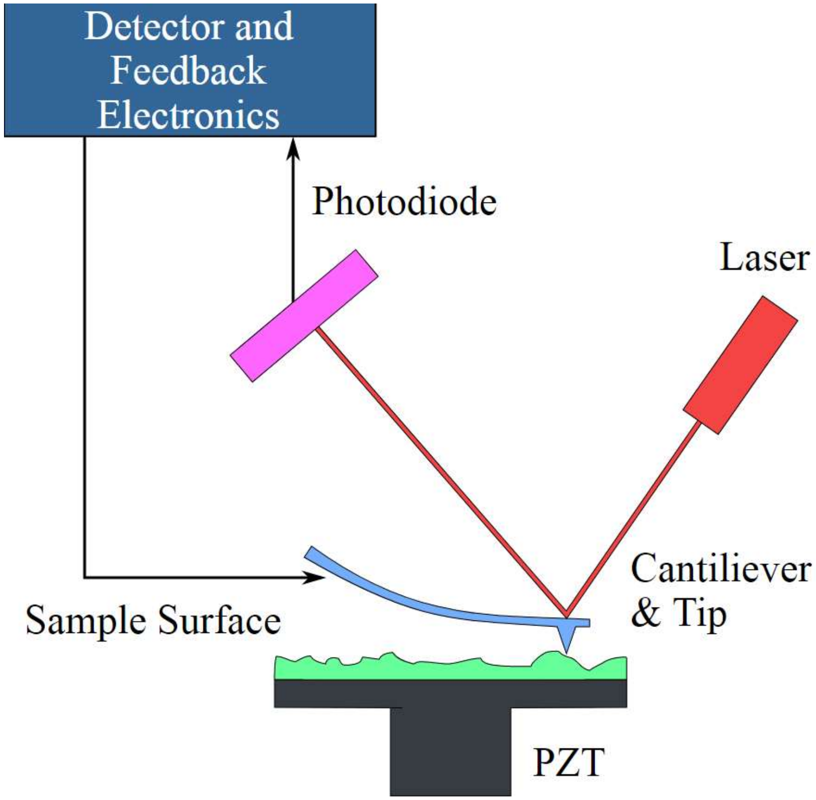
- AFM uses a physical probe (often Si or Si_3N_4) to scan a surface
  - For example, an image can be generated by rastering the probe in a tapping mode along the surface.
- The probe is actually a cantilever, which will deflect (by Hooke's Law) as forces are exerted on the probe
  - Forces: van der Waals, electrostatic, capillary, etc.

Atomic Force Microscopy

AFM tip is very sharp, ideally with a radius of a few nm or better, but can be up to 10s of nm



https://en.wikipedia.org/wiki/Atomic-force_microscopy



Some useful videos can be found at: http://virtual.itg.uiuc.edu/training/AFM_tutorial/

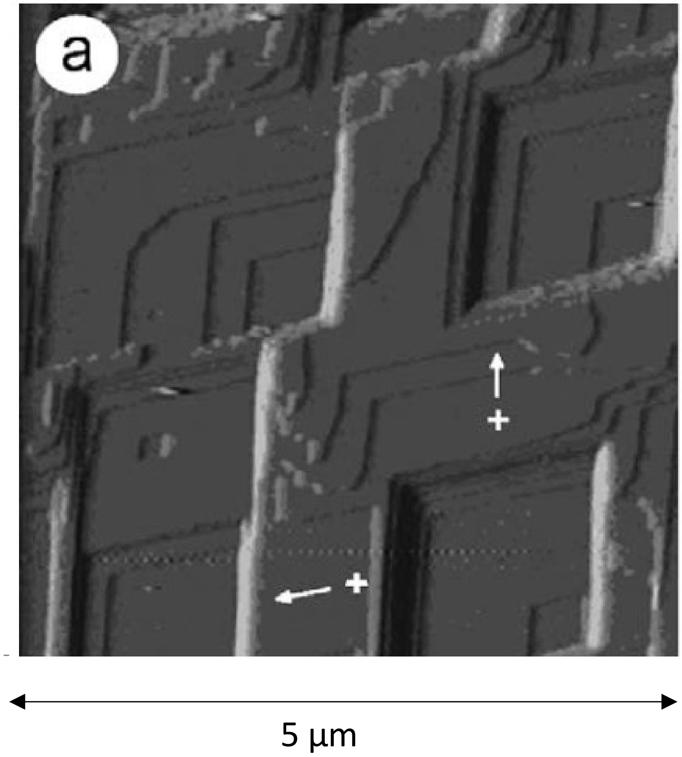
Atomic Force Microscopy

- Conventional AFM is performed *ex situ*
- However, *in situ* measurements can be made, such as with a fluid cell

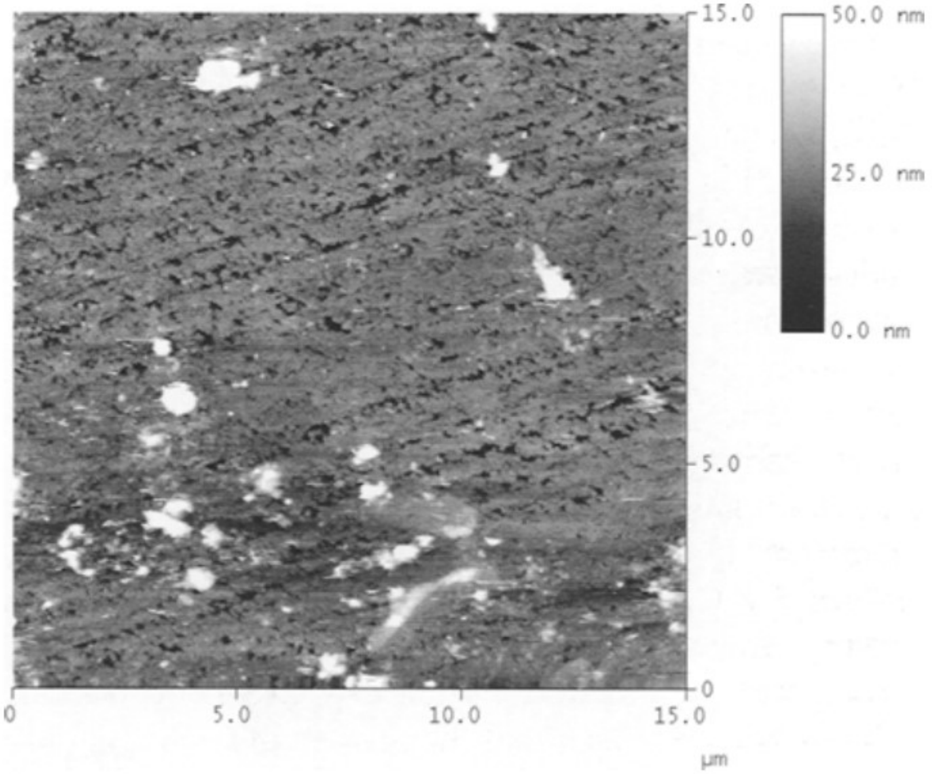
https://www.asylumresearch.com/Products/ClosedFluidCell/ClosedFluidCell.shtml

Examples of In Situ AFM

In situ observations of single crystal calcite ($CaCO_3$) after 2 min exposure to flowing 1 M NaCl solution. The surface exhibits rhombohedral etch pits. (Ruiz-Agudo et al. 2009)



In situ observations of polished alite after 7 hours of hydration. The surface shows signs of porosity and C-S-H. (Garrault et al. 2005)



Resolution in AFM

- AFM can generate very high resolution images
- Resolution is a function of the radius of the AFM tip
    - Sharper tip means better resolution
    - Ideal scenario resolutions can be sub-nm

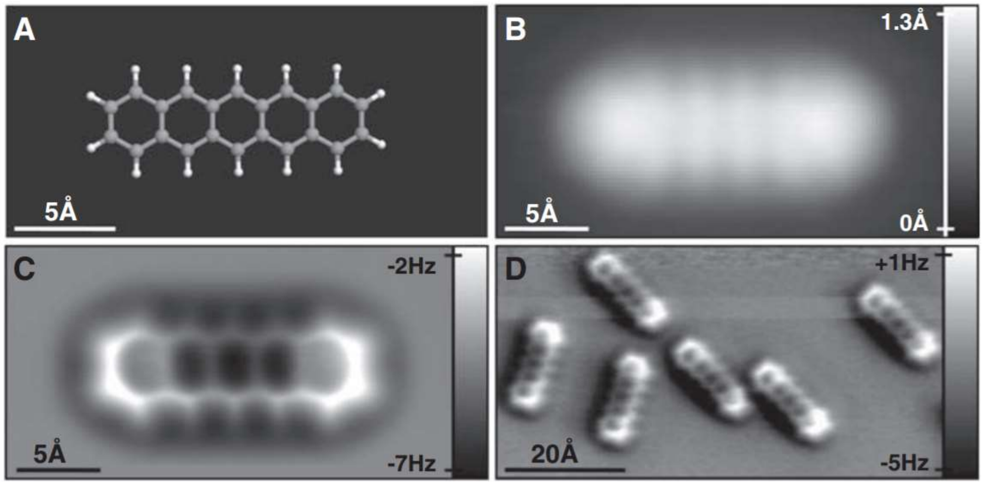


Fig. 1. STM and AFM imaging of pentacene on Cu(111). (**A**) Ball-and-stick model of the pentacene molecule. (**B**) Constant-current STM and (**C** and **D**) constant-height AFM images of pentacene acquired with a CO-modified tip. Imaging parameters are as follows: (B) set point $I = 110$ pA, $V = 170$ mV; (C) tip height $z = -0.1$ Å [with respect to the STM set point above Cu(111)], oscillation amplitude $A = 0.2$ Å; and (D) $z = 0.0$ Å, $A = 0.8$ Å. The asymmetry in the molecular imaging in (D) (showing a "shadow" only on the left side of the molecules) is probably caused by asymmetric adsorption geometry of the CO molecule at the tip apex.

AFM has been used to image single molecules!
(Gross et al. 2009)

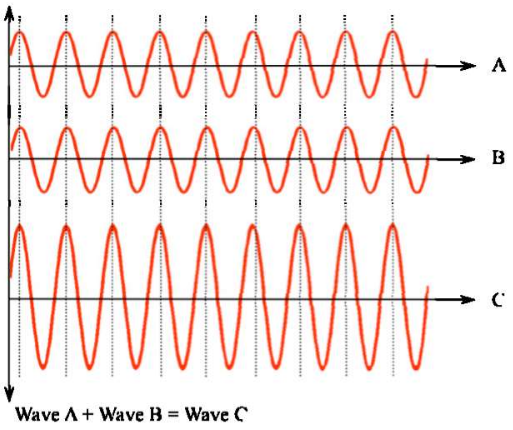
AFM – Advantages and Disadvantages

- **Advantages**
- Capability of very high resolution
- Can provide 3D surface topography
- No need for treatment or coating of surface
  - Does not require a conductive sample surface
- No need for vacuum
  - Ambient pressure or in liquid
- Measurements can be made *in situ* with fluid cell
- Can be combined with other instruments/techniques
  - Infrared and Raman spectroscopy, fluorescence microscopy, etc.

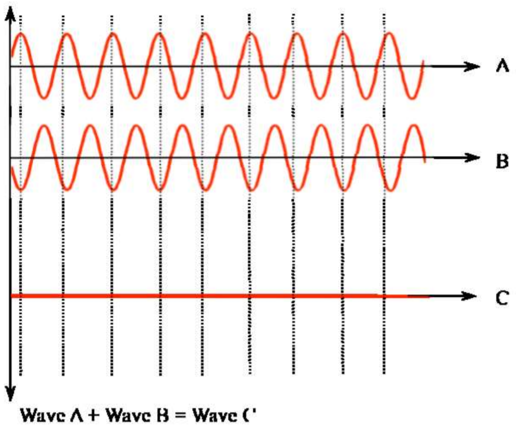
- **Disadvantages**
- Limited scanning area and height
  - ~100 to 150 μm with ~20 μm height
- Raster/scan speed
  - Can be slow, possible drifting
- Imaging artefacts, such as from a suboptimal tip conditions
- Effects of the probe on the hydrodynamics of the fluid cell (Peruffo et al. 2016)
- Cannot measure sudden, drastic changes in height
- Surface topographic image reflects the interaction between the probe and the sample surface and does not necessarily represent the true topography of the surface

Vertical Scanning Interferometry

- VSI uses an optical probe to examine a sample surface
- A broadband illumination source, such as white light, is used
- The technique combines vertical scanning and interferometry
- For the VSI, interferometry refers to the splitting of the light (via a beamsplitter) into a reference and an object beam. The interference is observed as these two beams are recombined.
- Recall **Constructive** and **Deconstructive** interference:



Constructive: Phase Offset = 0°



Deconstructive: Phase Offset = 180°

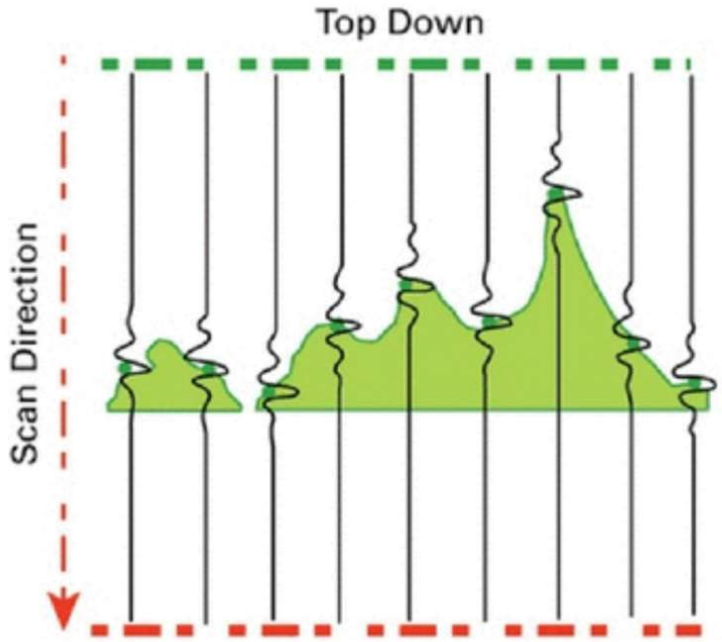
Petzing et al. 2010

Vertical Scanning Interferometry

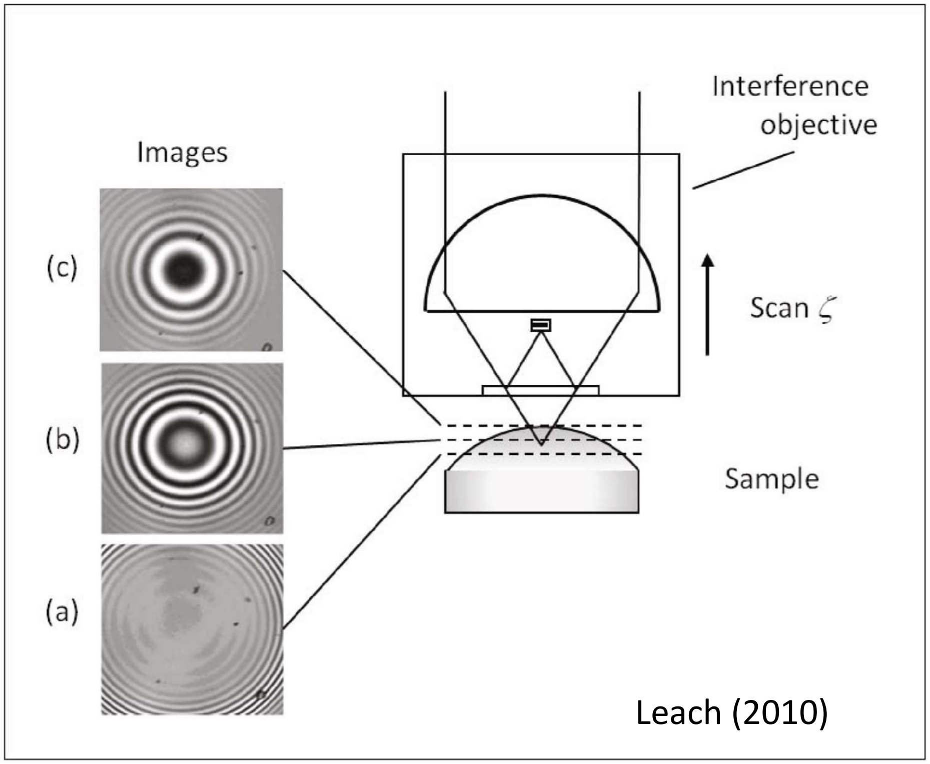
- VSI has multiple other names: vertical scanning white light interferometry, white light scanning interferometry, white light interferometry, coherence scanning interferometry
- Objective is moved (think: scanning) vertically (5-80 µm/s), collecting frames as fast as the camera frame rate allows
  - Relative height for a given pixel corresponds to the objective position that yielded the largest (maximum) fringe contrast (which is the best focus)
  - White light sources yield a short coherence length, so the fringes only occur near positions of optimal focus

Vertical Scanning Interferometry

- Relative height for a given pixel corresponds to the objective position that yielded the largest (maximum) fringe contrast (which is the best focus)

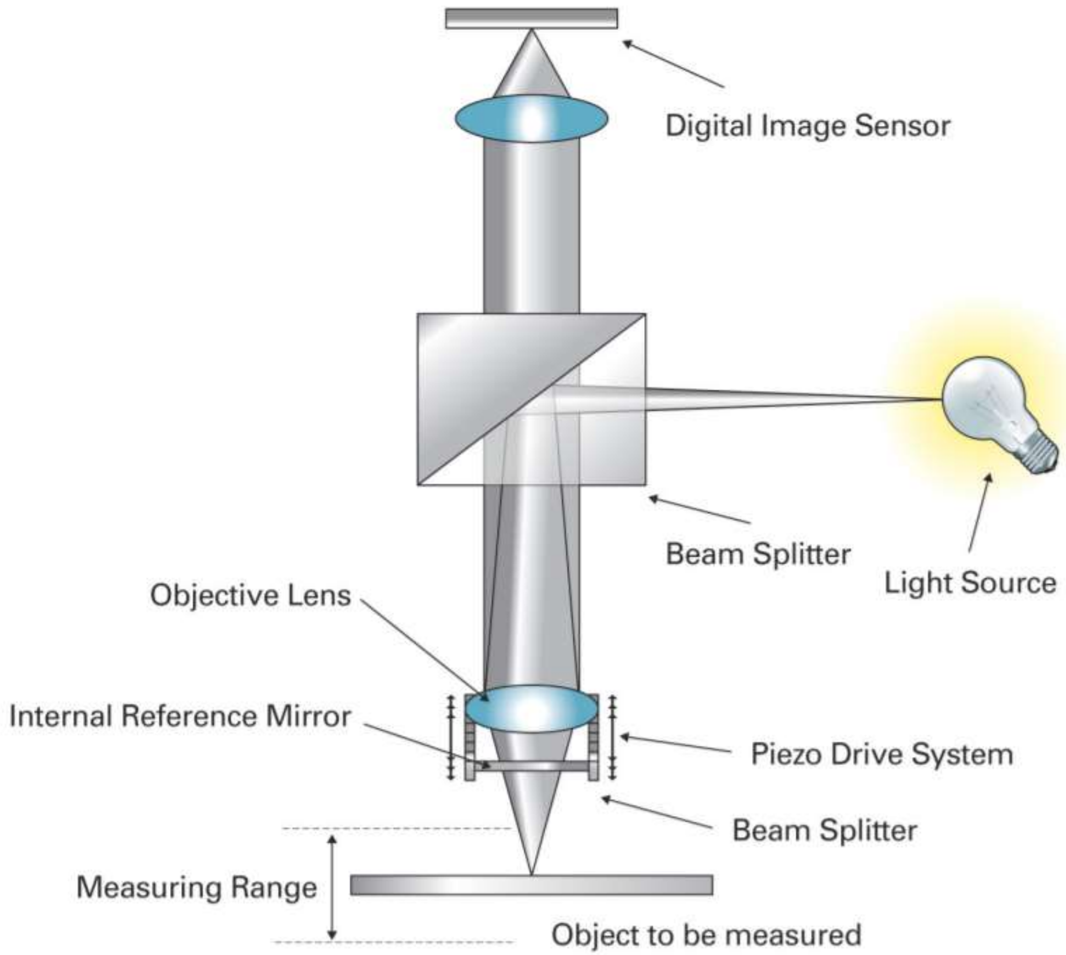


de Groot (2011)

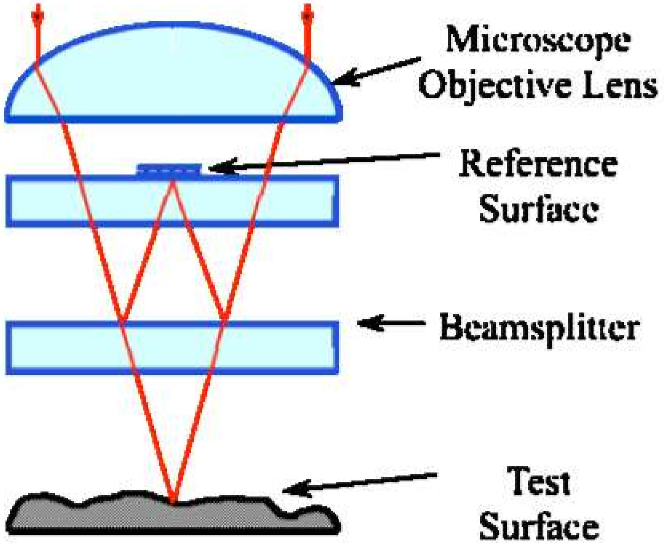


Leach (2010)

Vertical Scanning Interferometry



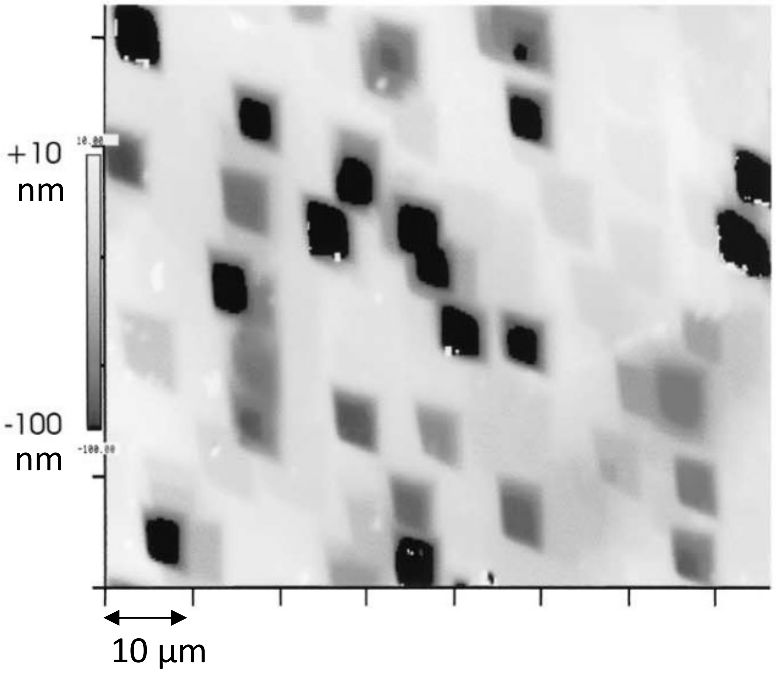
Mirau Objective

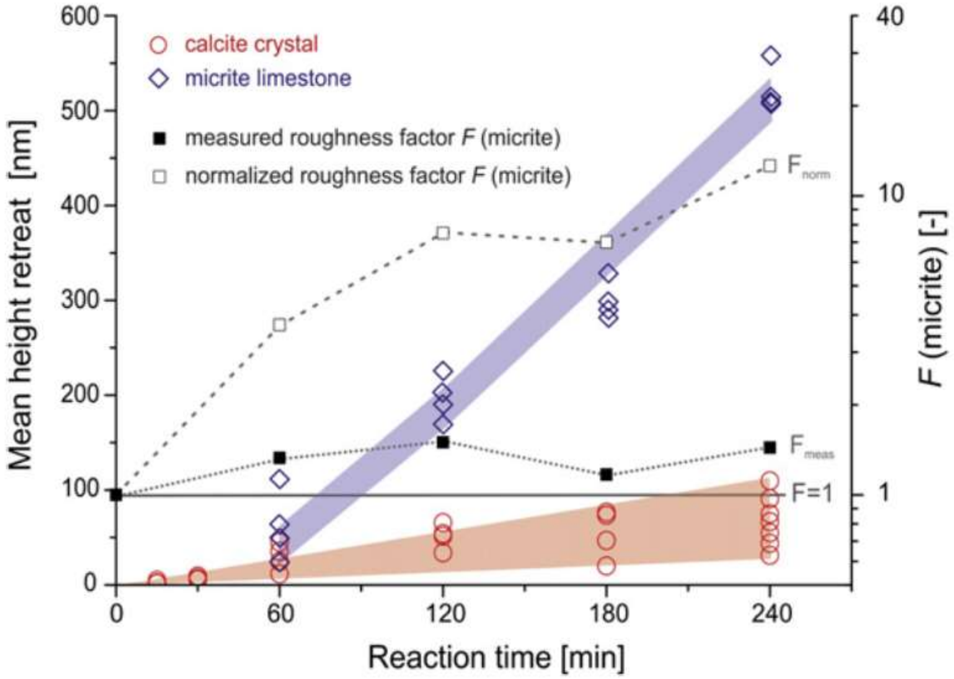


Petzing et al. 2010

VSI Studies of Calcite Dissolution

Ex situ VSI measurements of calcite dissolution

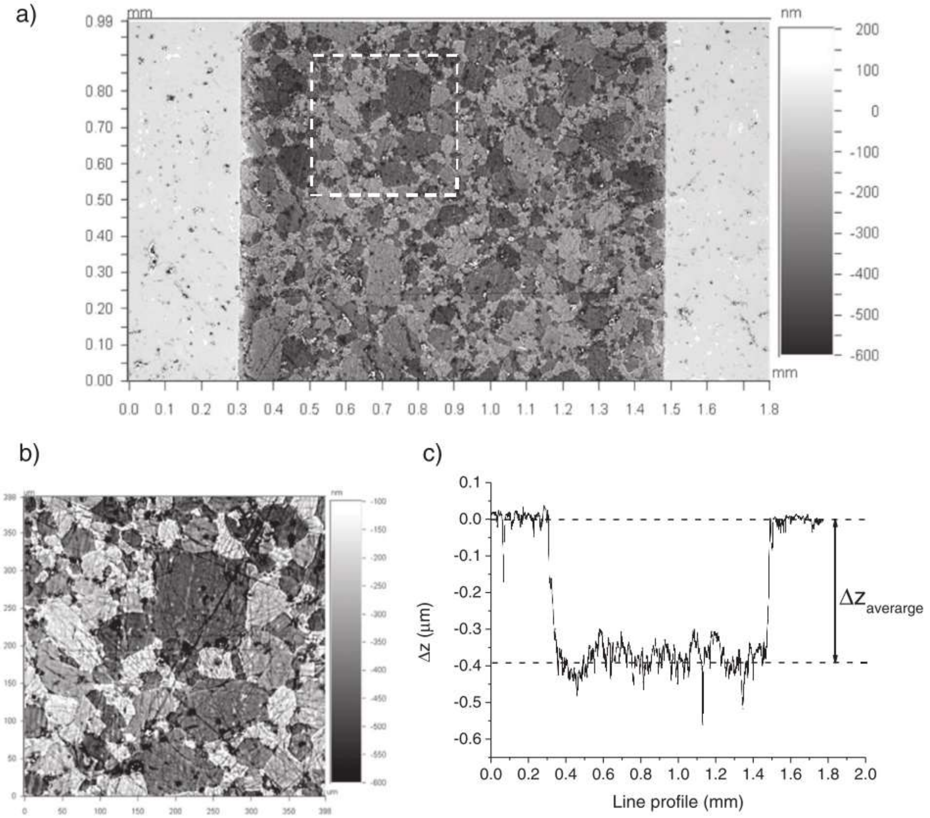




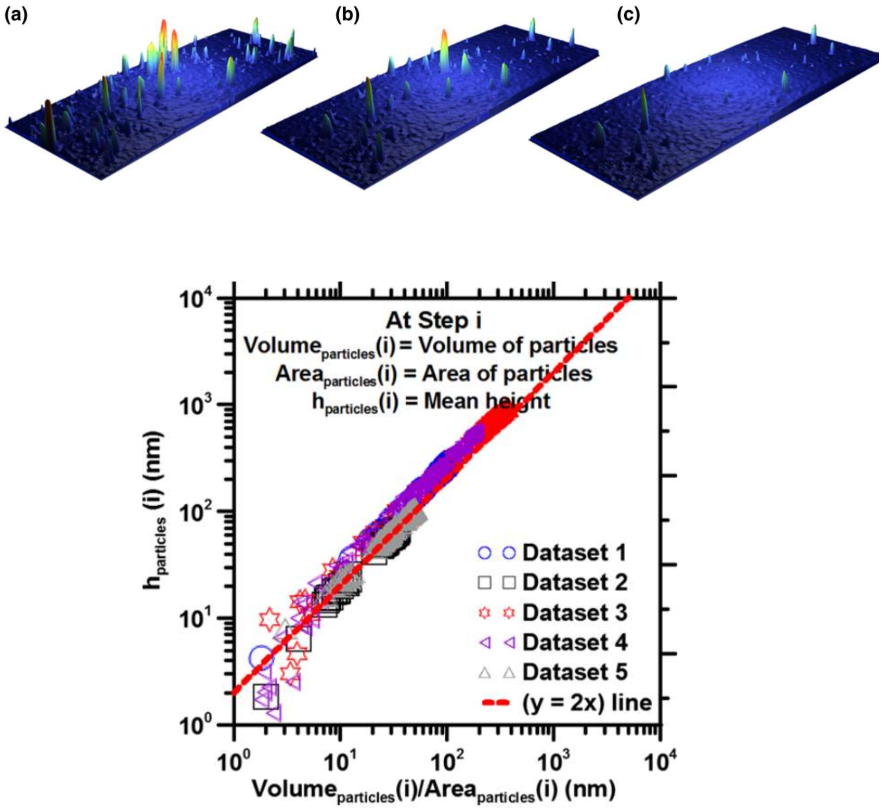
Arvidson et al. (2003); Fischer et al. (2012)

VSI Applied to Cement Dissolution

Ex situ VSI measurements of alite and cement dissolution

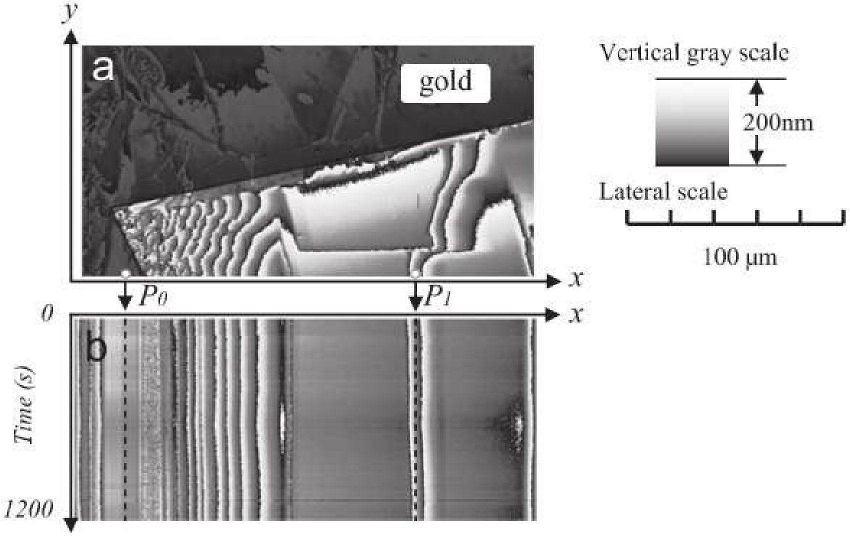


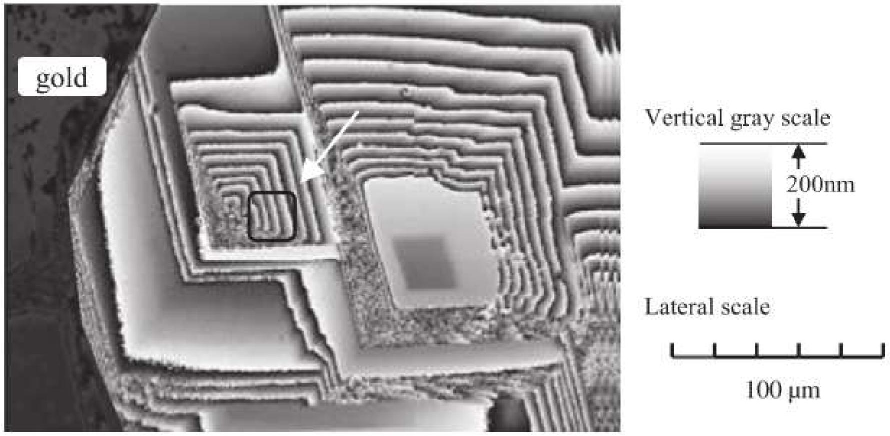
Alite, polished surface, channelized flow (Juilland and Gallucci 2015)

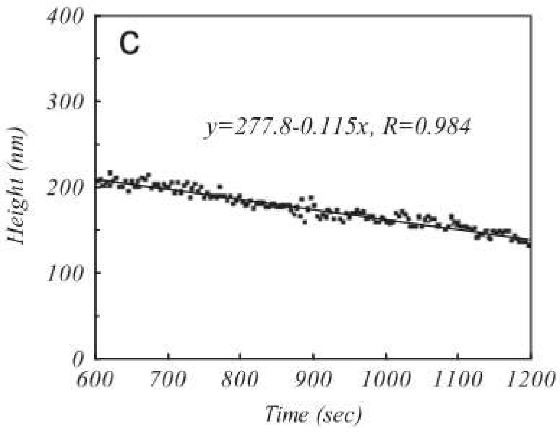


Cement powder, “rain drop” method (Kumar et al. 2013)

In situ VSI Studies of Calcite Dissolution







In situ PSI measurements of calcite dissolution. Instrument was modified from a commercially-available instrument. This setup did not use Mirau objective lenses.

Ueta et al. (2013)

VSI – Advantages and Disadvantages

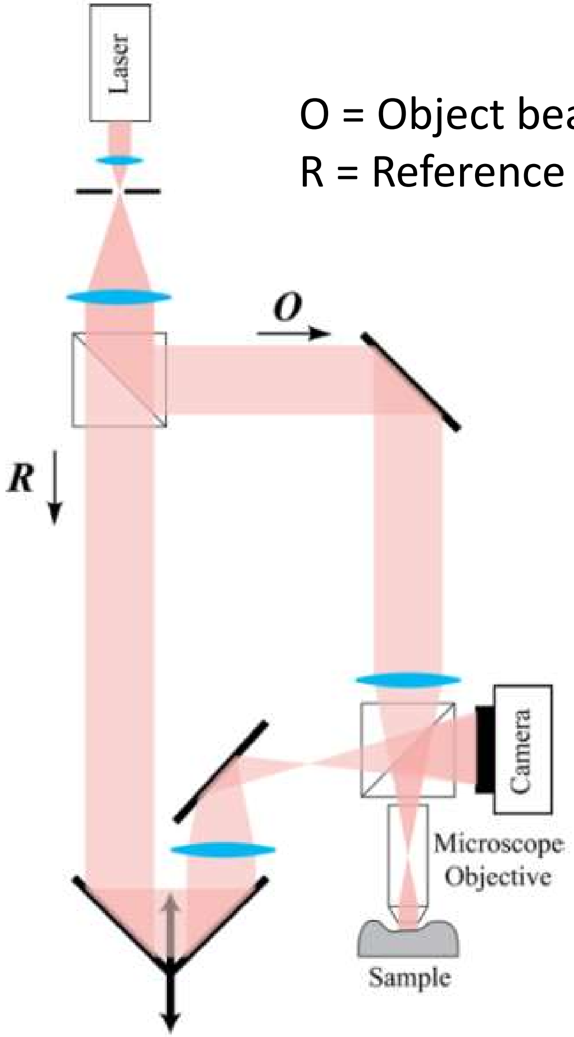
- **Advantages**
  - Can provide 3D surface topography, even of rough surfaces
  - Non-contact technique
  - Nanoscale measurements (1-5 nm vertical resolution)
  - Can use large field of view (10x to 100x)
  - Can measure up to 10mm height changes
  - Possibility of *in situ* measurements
    - Specialized equipment

- **Disadvantages**
  - Typically measurements are taken *ex situ* in air
  - Specialized Mirau objective lenses
  - Conducts vertical scanning, which may or may not be time-intensive (5-80 μm/s)
  - Typically needs an anti-vibration table
  - Lateral resolution is sub-μm

Digital Holographic Microscopy (DHM)

- “Home built” systems have been researched since late 1990s
- Commercially-available systems as of mid-2000s
- Originally developed for (and most subsequent research has focused on) *in situ* monitoring of biological systems
- Capable of monitoring real time, *in situ* topography changes
- Uses an optical probe with conventional microscope objective lenses
- Methodology and technique is based on interferometry
- Some interesting 4D videos:
  - Cells https://www.lynceetec.com/4d-cell-imaging/
  - MEMS https://www.lynceetec.com/mems-cantilevers/

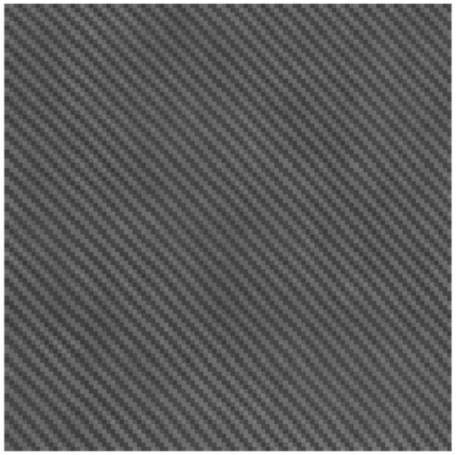
Inside the DHM



O = Object beam
R = Reference beam

https://www.lynceetec.com/

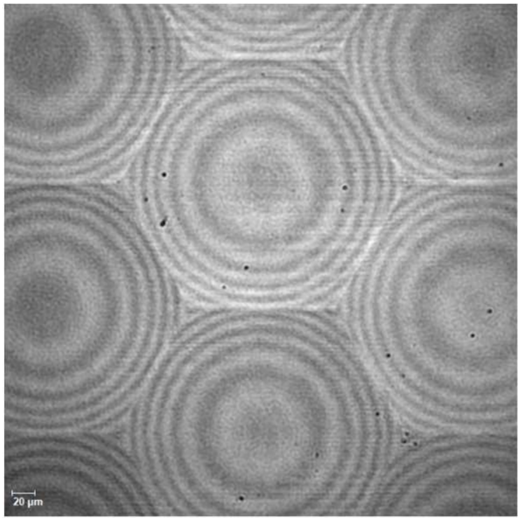
DHM – Hologram to Amplitude and Phase



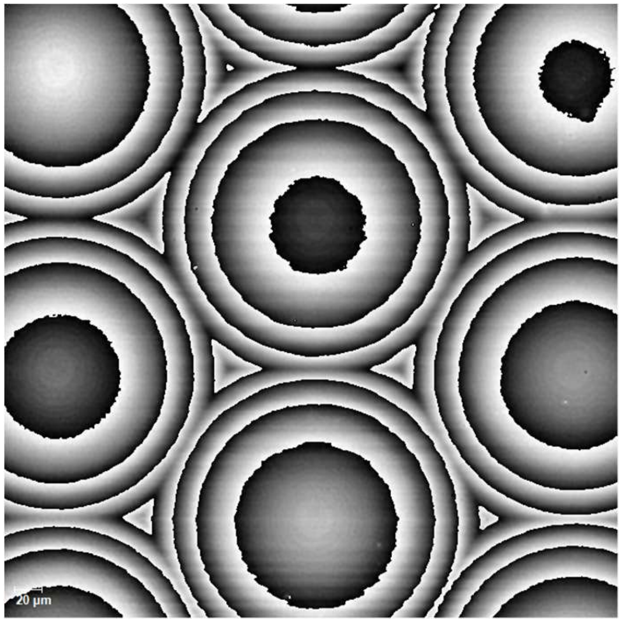
Hologram
(zoomed in)

Numerical
Reconstruction

Amplitude
Contrast

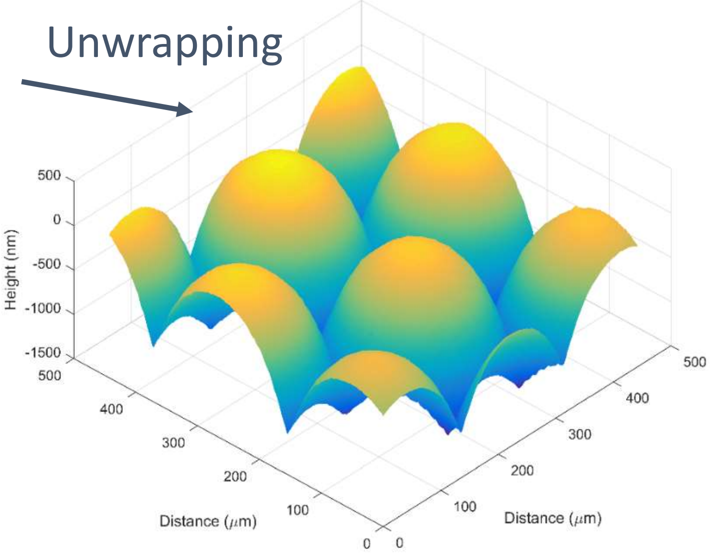


Phase
Contrast



White = 166.4 nm
Black = -166.4 nm

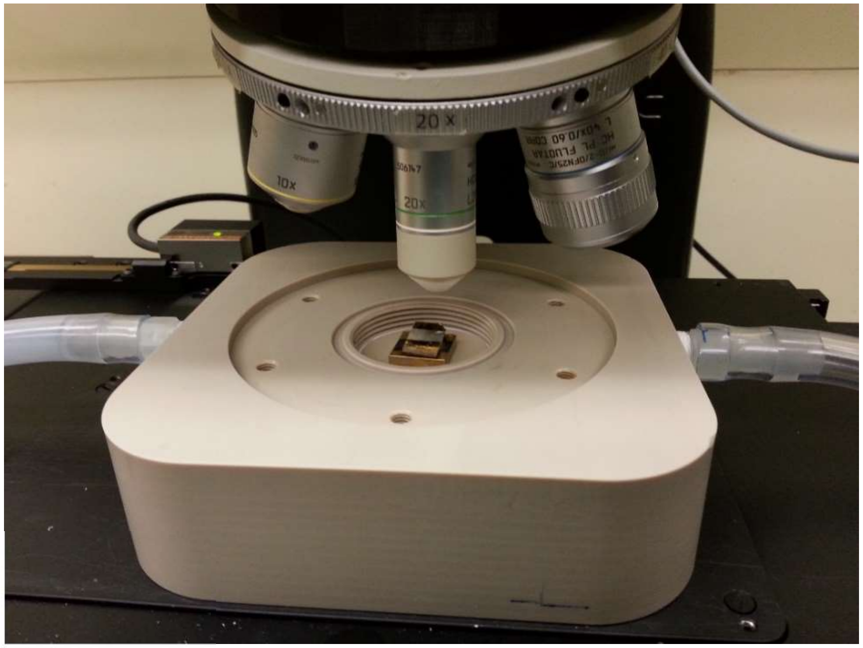
Unwrapping

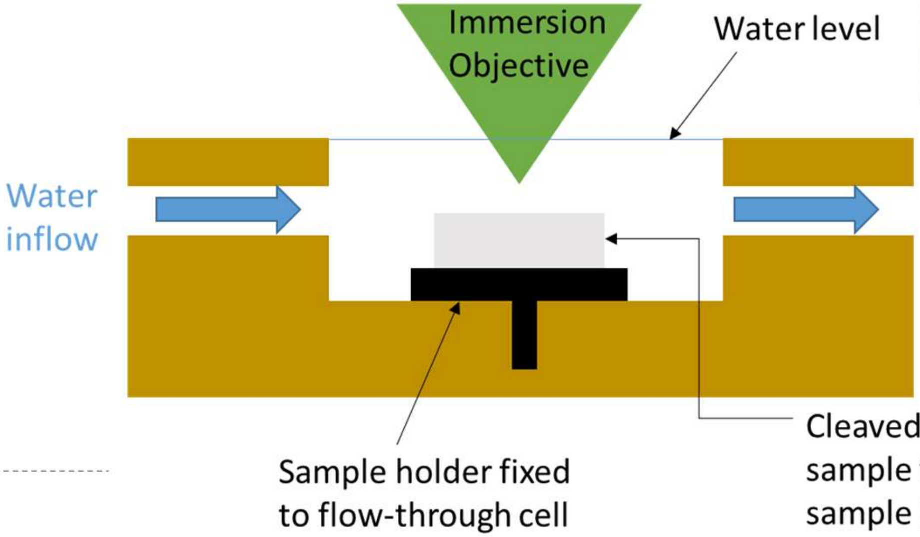


Microlenses
with 10x
objective in air

Brand (2017)

In Situ Experiment Configuration at NIST





Immersion Objective

Water level

Water inflow

Water outflow

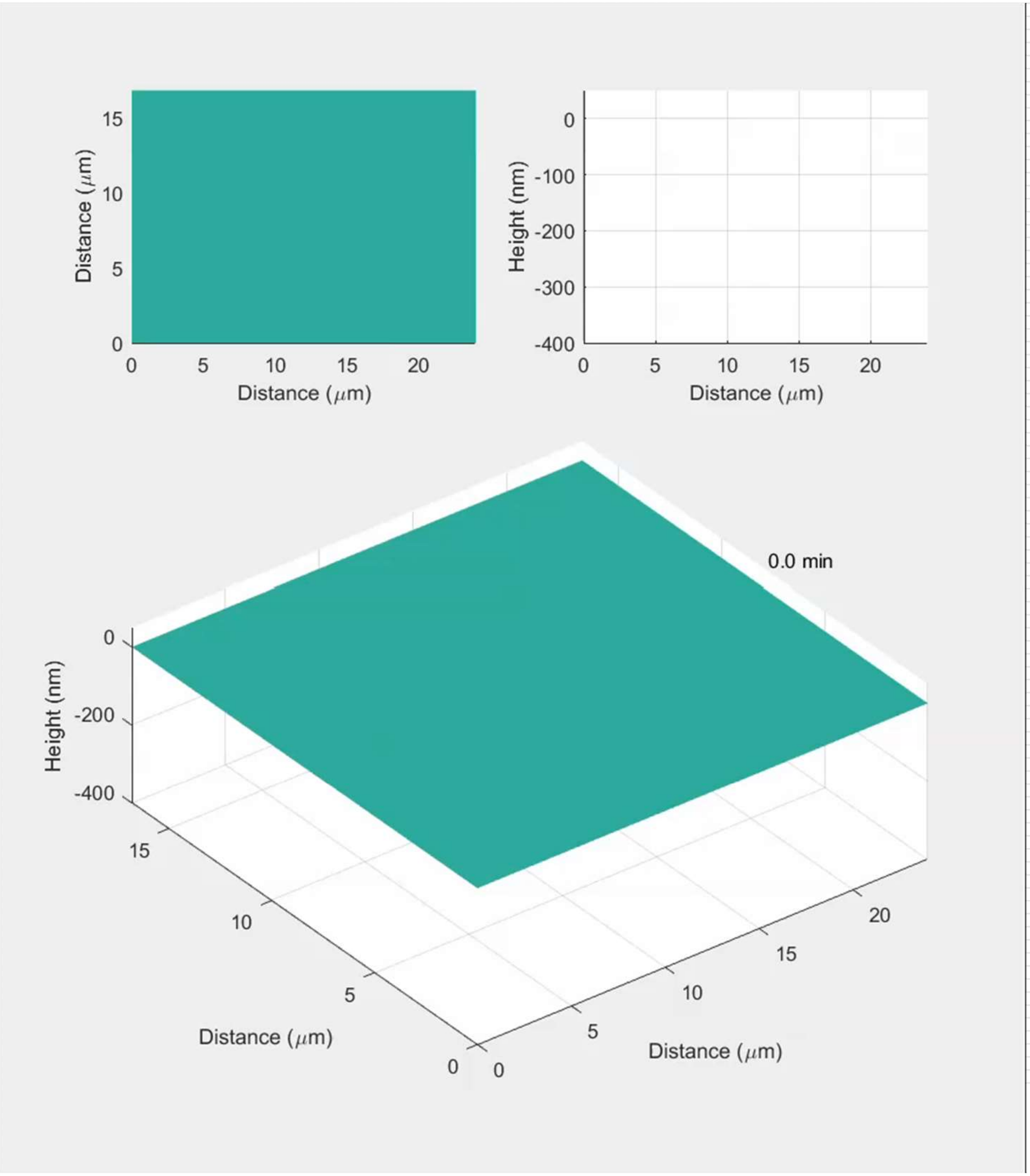
Sample holder fixed to flow-through cell

Cleaved calcite sample fixed to sample holder

Brand (2017); Brand et al. (2017); Feng et al. (2017); Brand and Bullard (2017)

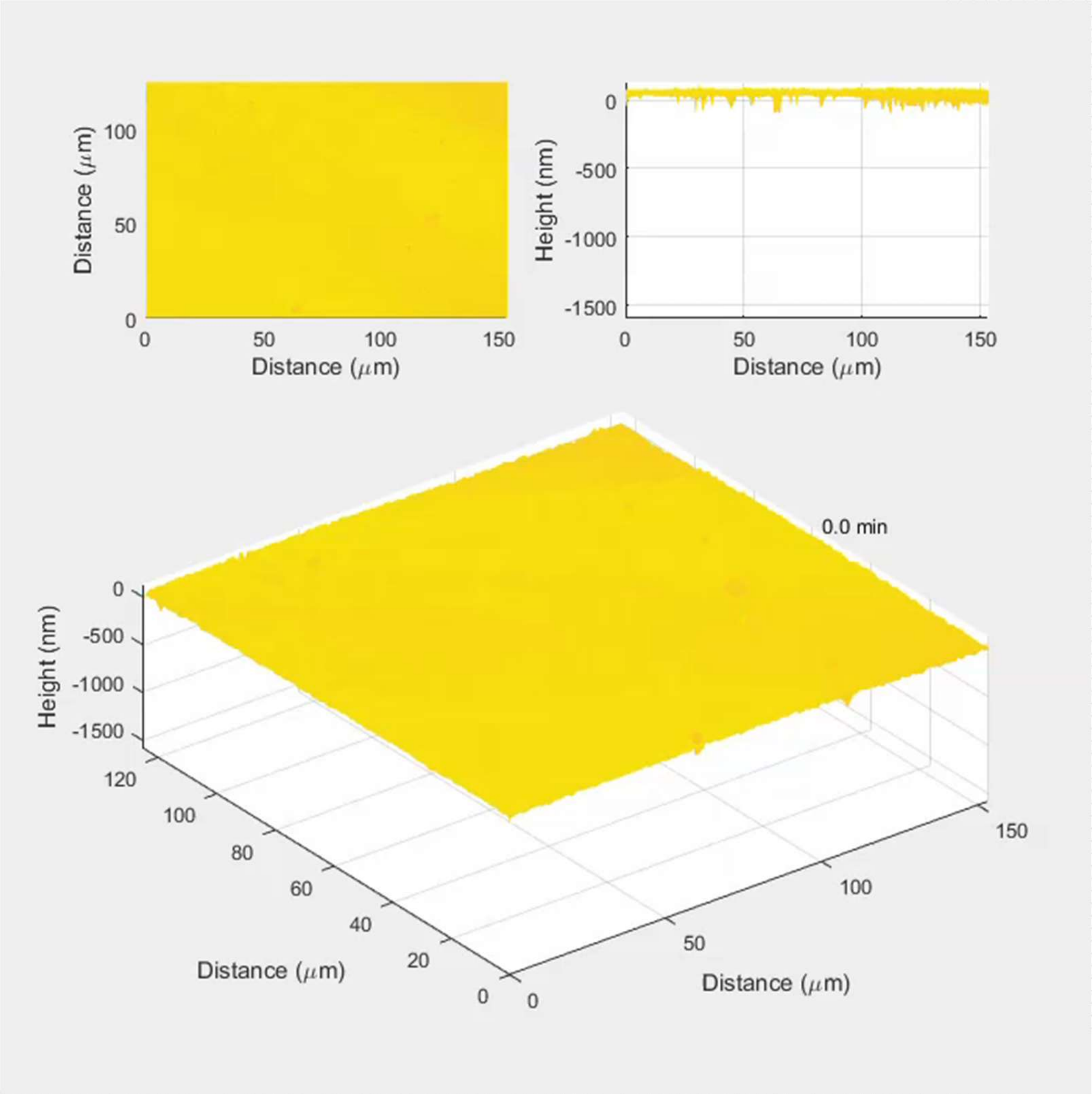
Calcite Etch Pit

- Zoomed-in view of rhombohedral etch pit formation in single-crystal calcite along the (104) plane
- 20x immersion objective lens
- Flowing deionized water
- Pixel size is 340 nm by 340 nm

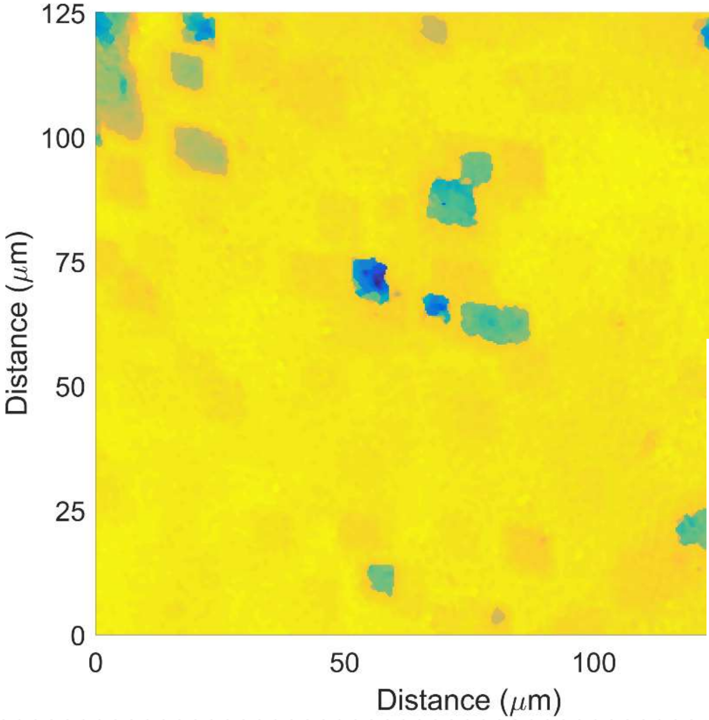


Calcite

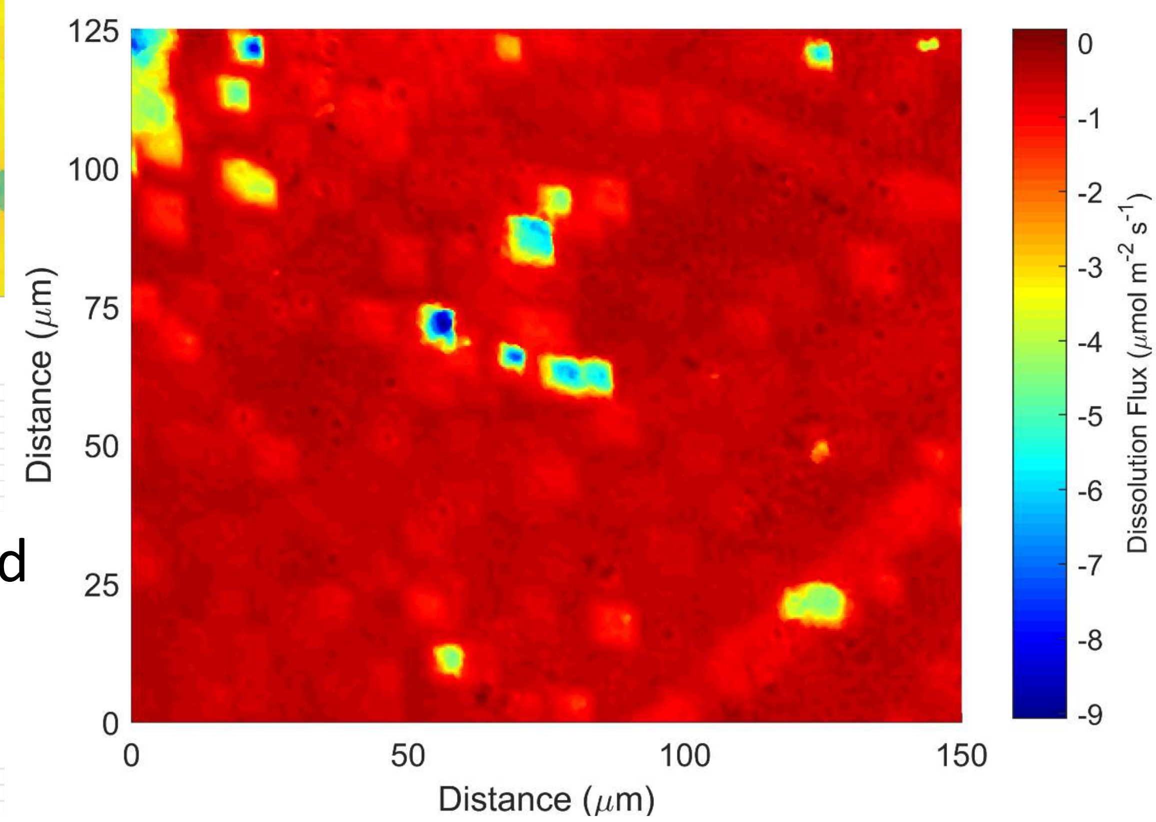
- Single-crystal calcite along the (104) plane
- 20x immersion objective lens
- Flowing deionized water
- Pixel size is 340 nm by 340 nm



Calcite Dissolution (Rate Map)

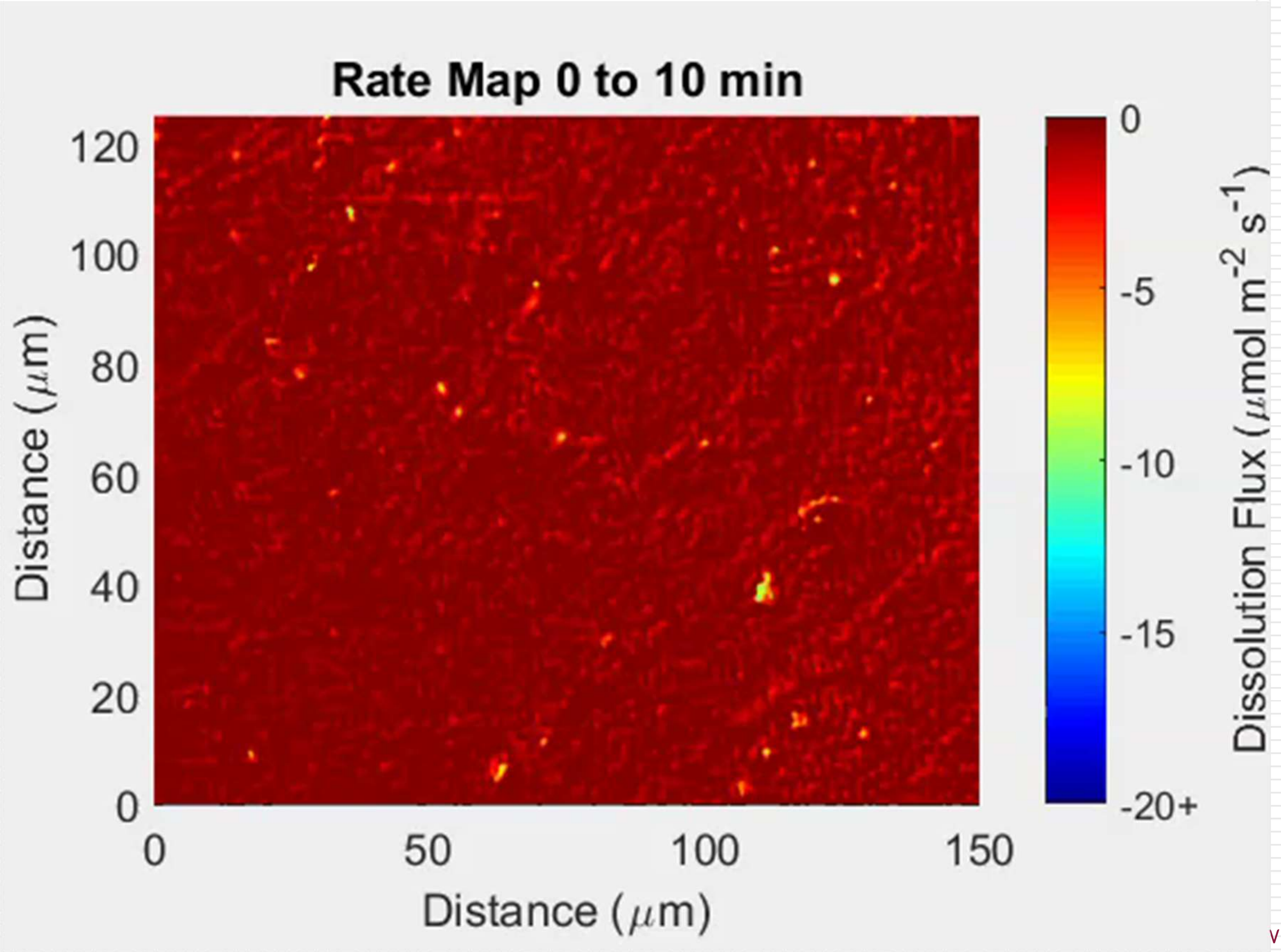


Surface topography at the end of the experiment (70 min)

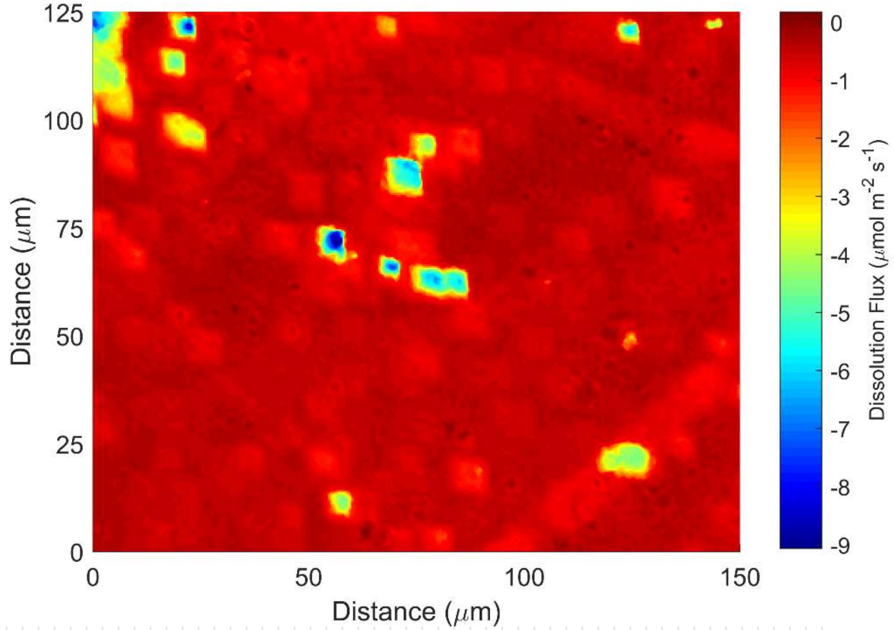


“Rate map” at the end of the experiment (from 0 to 70 min)

Calcite: Time Dependent Rate Map Movie

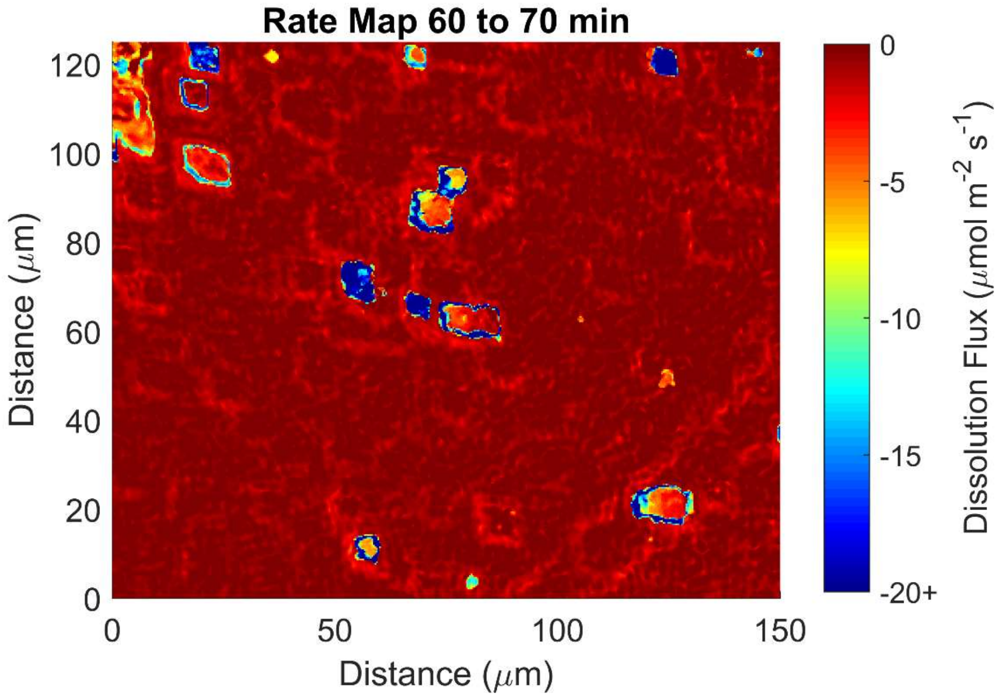


Calcite: Time Dependent Rate Maps



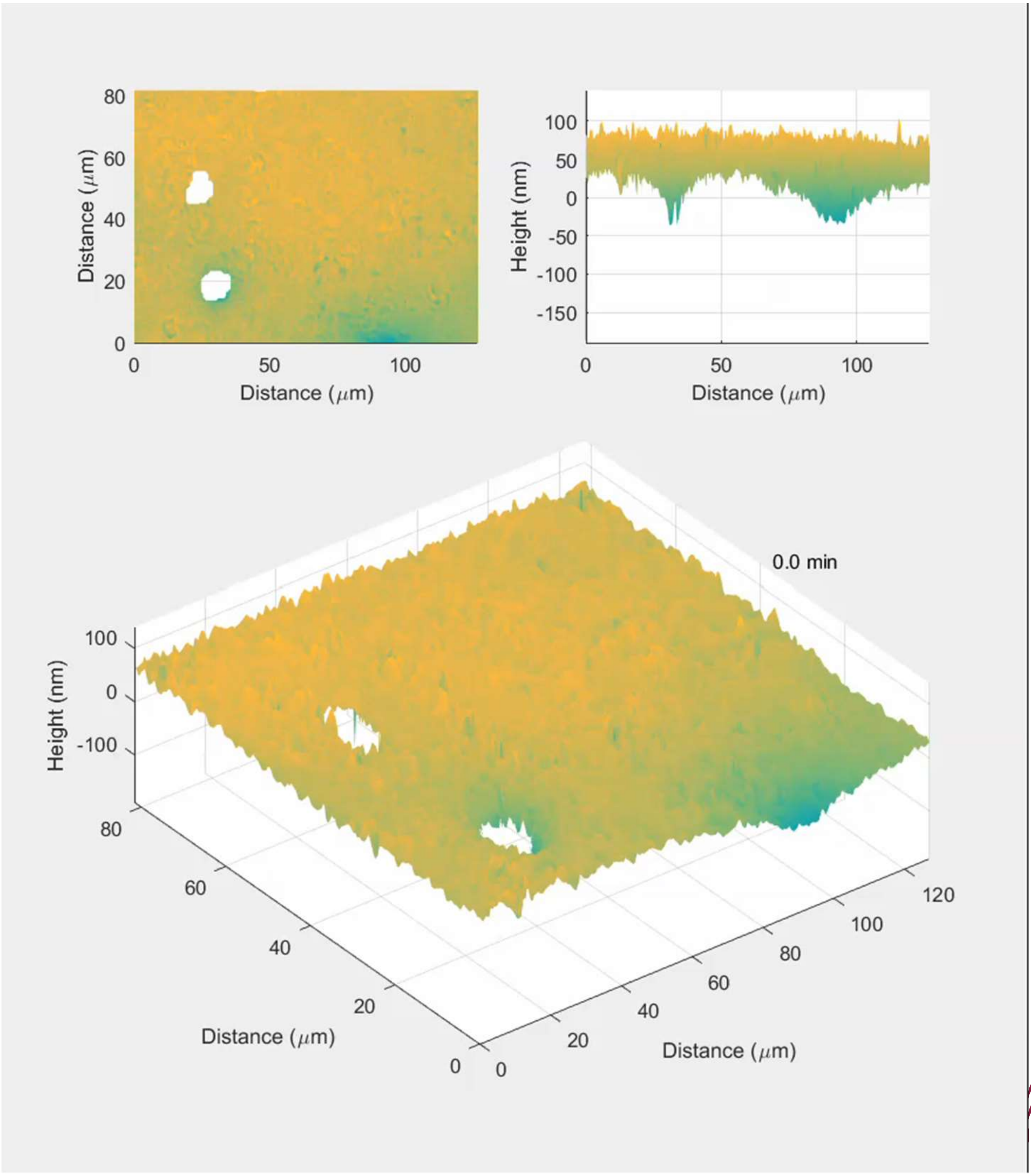
"Rate map" at the end of the experiment (from 0 to 70 min)

"Rate map" from 60 to 70 min



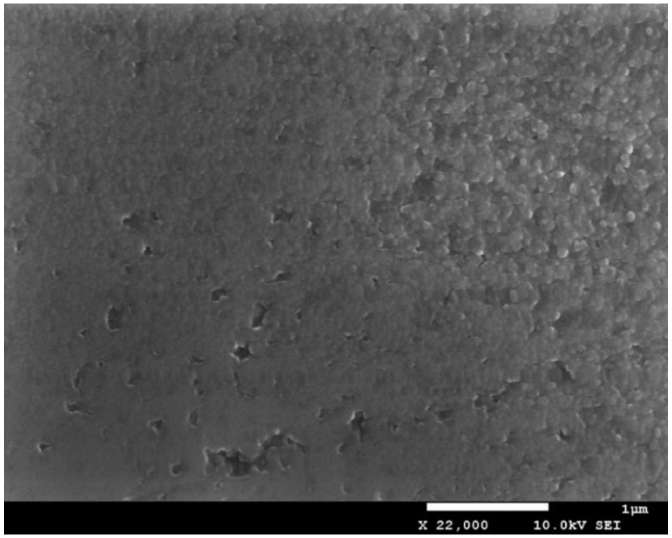
C_3A

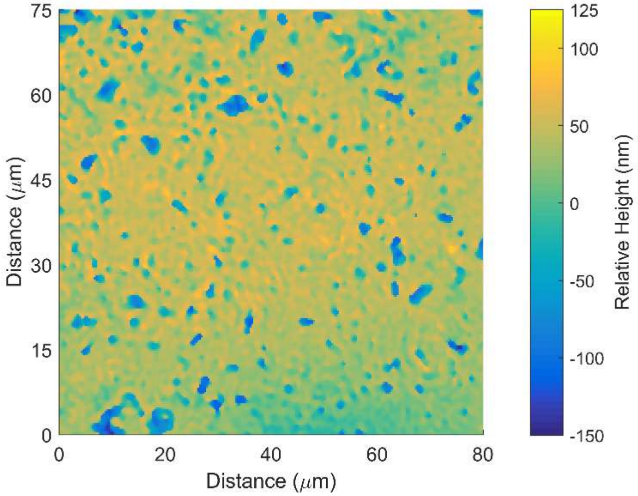
- Flowing solution of 60% ethanol and 40% water
- Formation of etch pits
- Note spatial variability in etch pit distribution
- Note white areas are pores that were removed

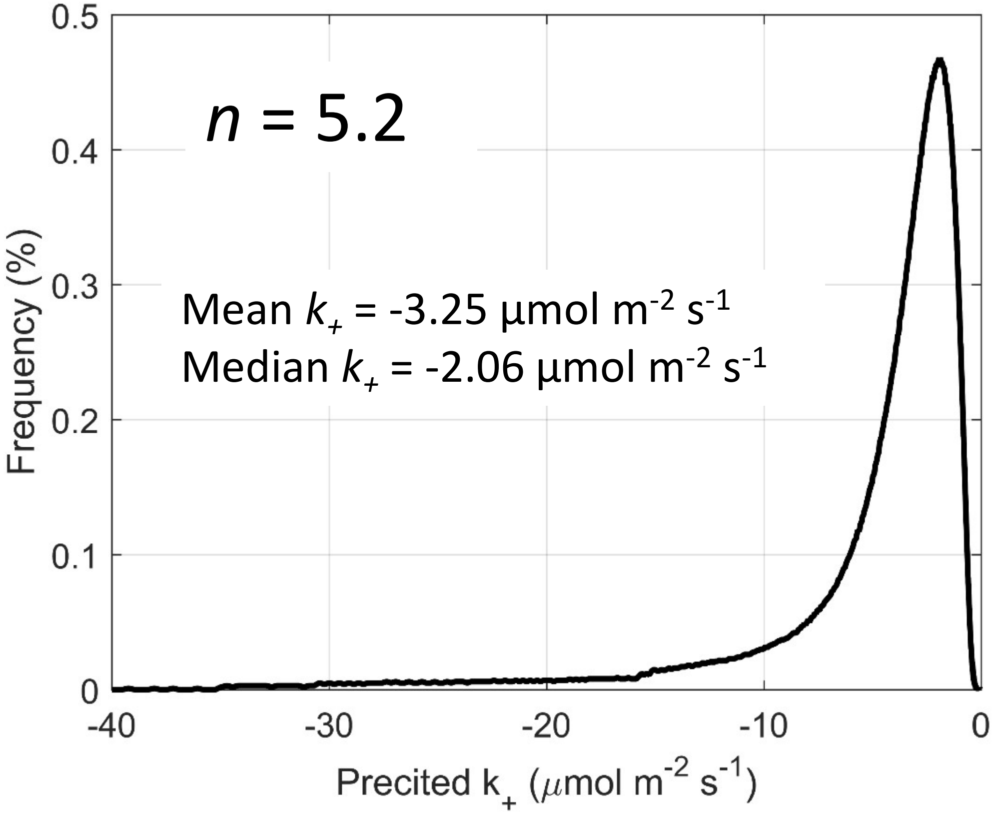


C_3A Dissolution by DHM

$$R = k_+ \left(a_{H_2O}\right)^n$$







n = 5.2

Mean k_+ = -3.25 μmol m^{-2} s^{-1}
Median k_+ = -2.06 μmol m^{-2} s^{-1}

Brand and Bullard (2017)

DHM – Advantages and Disadvantages

- **Advantages**
- Can provide 3D surface topography
- Non-contact technique
- Nanoscale measurements (sub-nm vertical resolution)
- Very rapid data collection
  - Depends on CCD camera
- Can use large field of view (2.5x to 100x)
- Possibility of *in situ* measurements
- Can use conventional microscope objective lenses

- **Disadvantages**
- Not widely available and can be expensive
- Height measurements can be limited by the objective lens's depth of focus
- Rough surfaces can be difficult to measure
- Depending on the sensitivity of the measurements, an anti-vibration table may be needed
- Lateral resolution is sub-μm

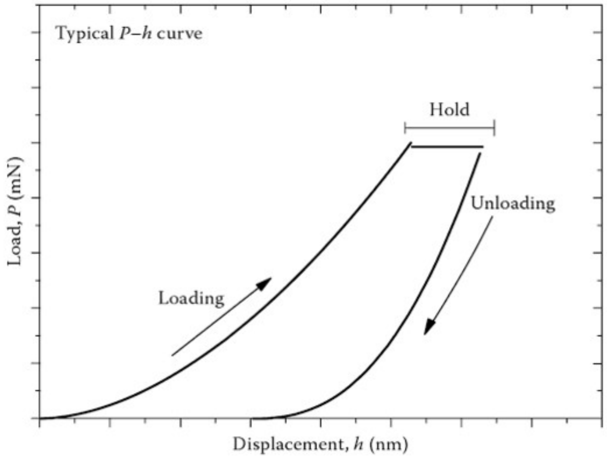
Surface Measurements

- AFM, VSI, and DHM
  - In summary: Select technique based on desired measurement, sensitivity, time, etc.

- What about other measurements of the surface?
  - Mechanical properties of the surface
    - Nanoindentation
    - Force spectroscopy with atomic force microscopy
  - Chemical properties of the surface
    - Various spectroscopic, spectrometric, and scattering techniques
    - Consider depth of interrogation, vacuum vs. ambient conditions, resolution requirements, what needs to be measured, etc.

Nanoindentation

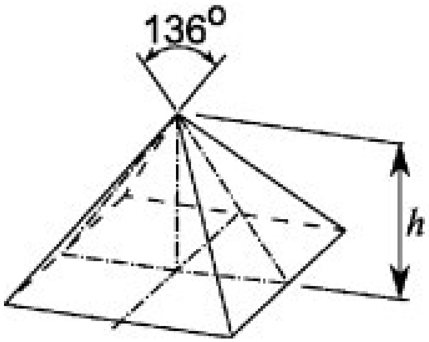
- A technique to measure elastic and mechanical properties of a material by sampling a very small volume
- A small force is applied (as low as a few µN up to 100s mN) to a sample surface, causing nm scale deformation
- Indenter is very rigid (*e.g.*, diamond, tungsten carbide, sapphire)
- In the experiment, the load or indenter displacement is controlled, resulting in a load-displacement curve from which the elastic modulus and hardness of the material can be estimated



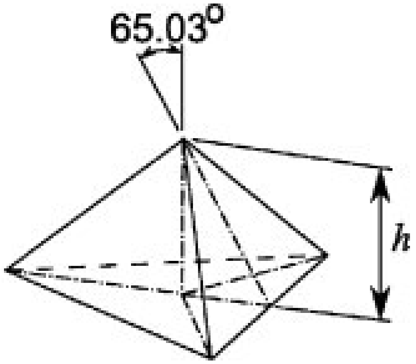
Logothetidis (2010)

Nanoindentation Tips

- Nanoindenter tips need to be sharp (ideally: tip radius < 50 nm)
- Need to account for contact area as a function of tip geometry
- Multiple tip geometries available
  - Berkovich: three-sided pyramid
  - Vickers: four-sided pyramid
  - Knoop: four-sided pyramid with rhombic faces
  - Spherical, Cube corner, Conical, Flat, Wedge, etc.



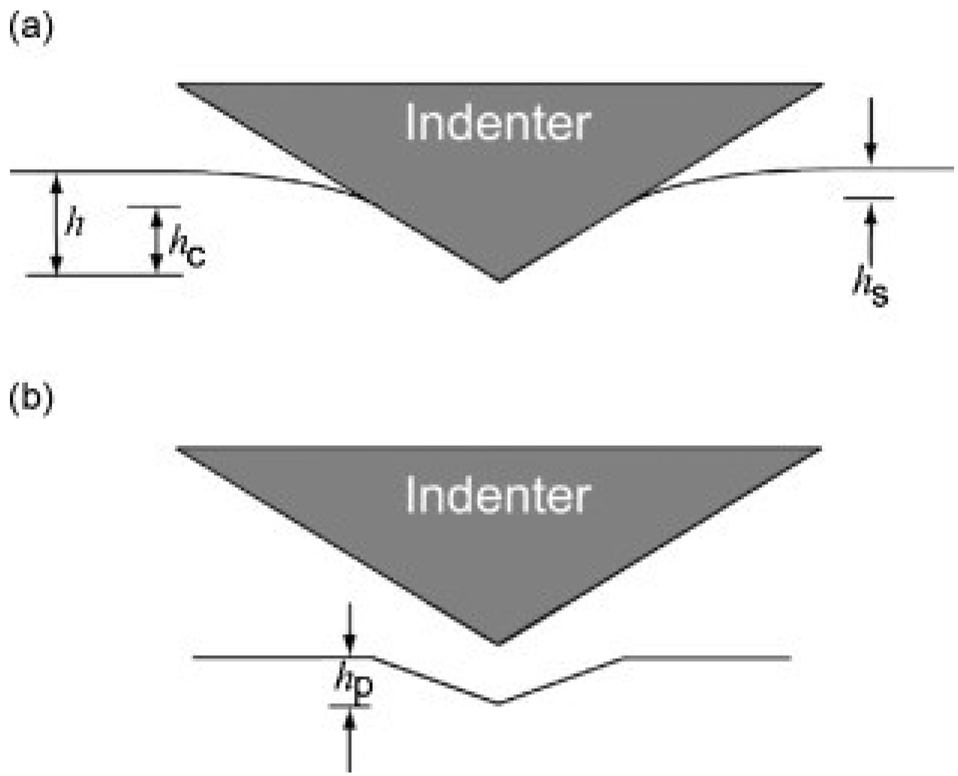
Vickers



Berkovitch

Lucca et al. (2010)

Nanoindenter Contact



h = total indentation depth while force is applied

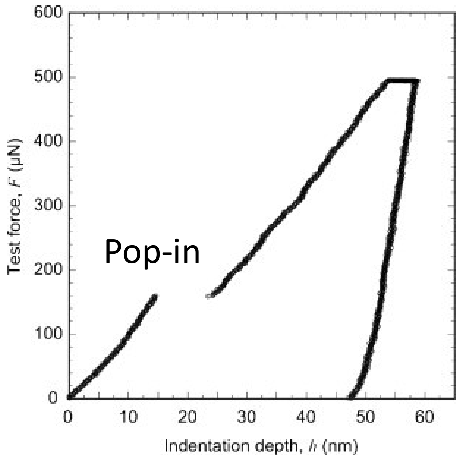
h_c = depth of indenter contact with sample

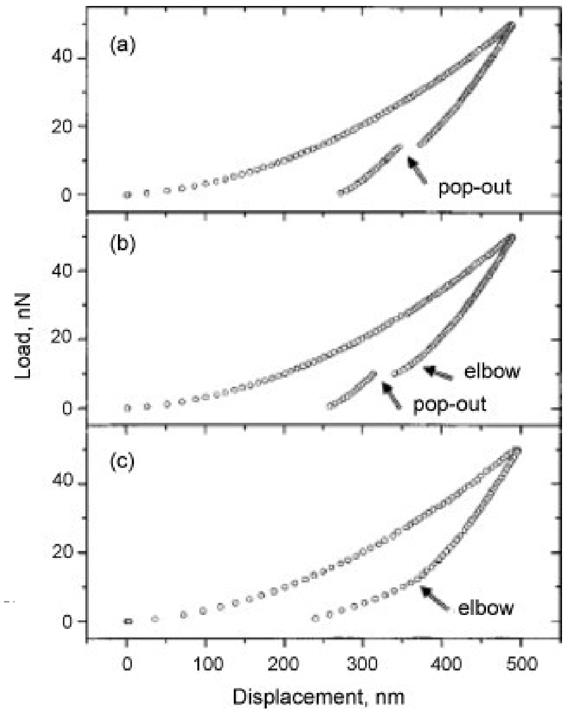
h_s = depth that indenter and sample are not in contact

h_p = permanent depth of indentation after load is removed

Lucca et al. (2010)

Nanoindentation Complications



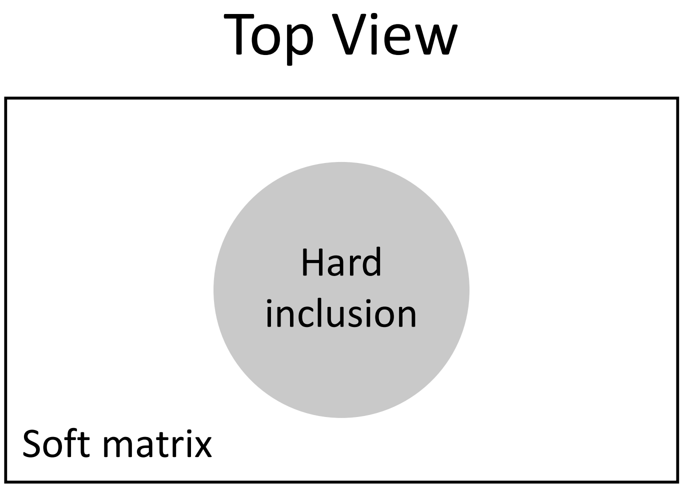


- Creep effects
- Plasticity
- Pop-in, pop-out, and elbows
  - Can be from: dislocations, onset of plasticity, oxide surface layer, etc.
- Indentation size effect (strain gradient plasticity)
- Effects of tip geometry
- Complicated results for heterogeneous composites

Lucca et al. (2010)

Nanoindentation Complications

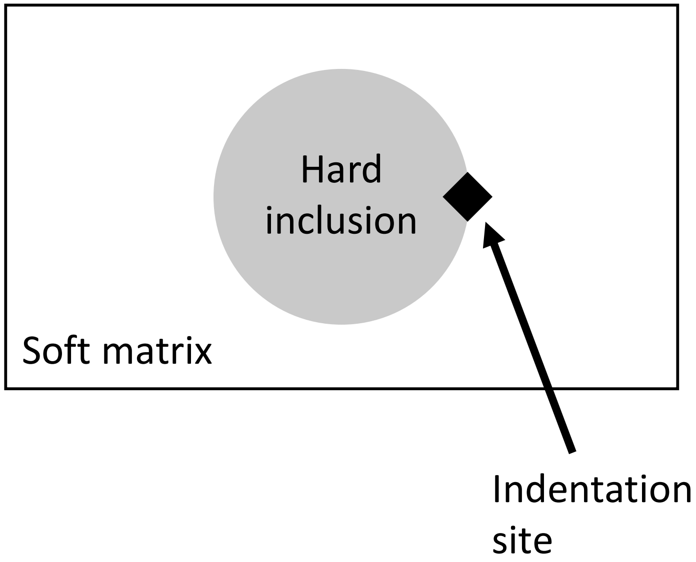
- Complicated results for heterogeneous composites



Nanoindentation Complications

- Complicated results for heterogeneous composites

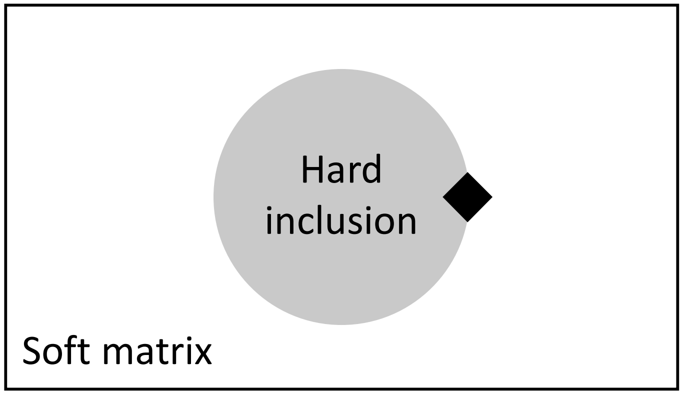
Top View

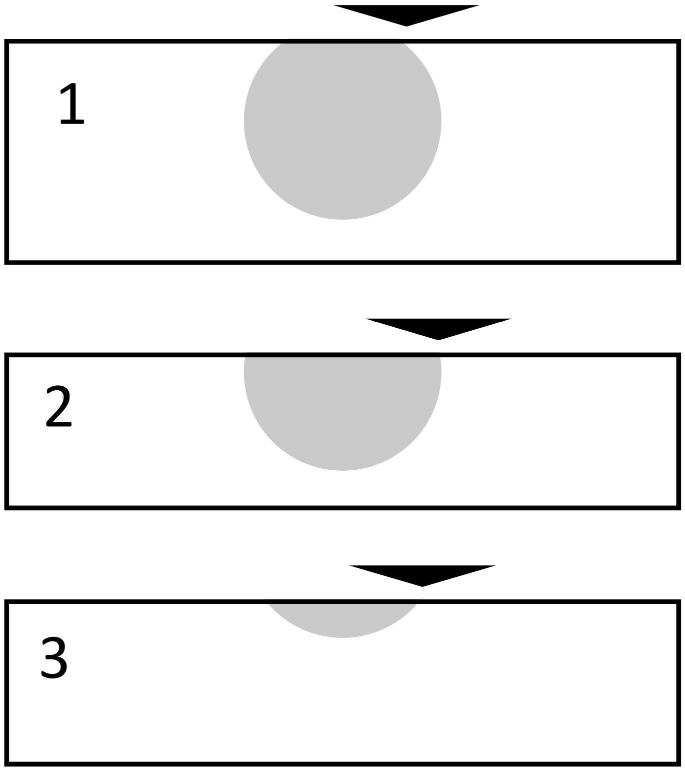


Nanoindentation Complications

- Complicated results for heterogeneous composites

Top View

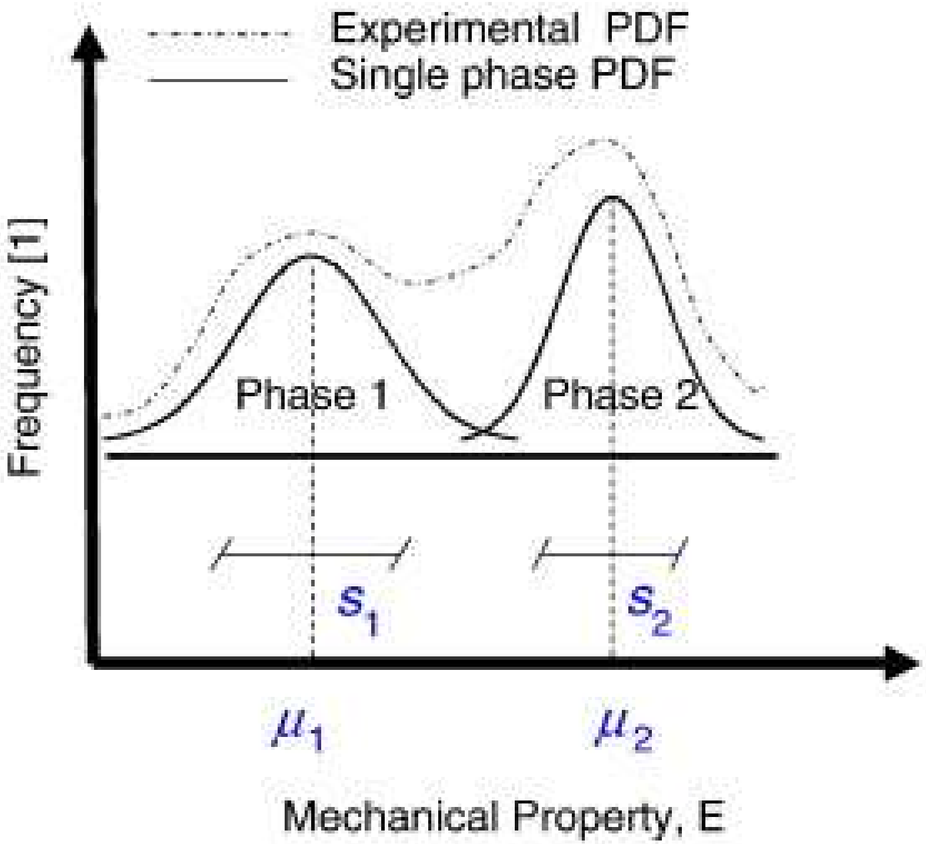


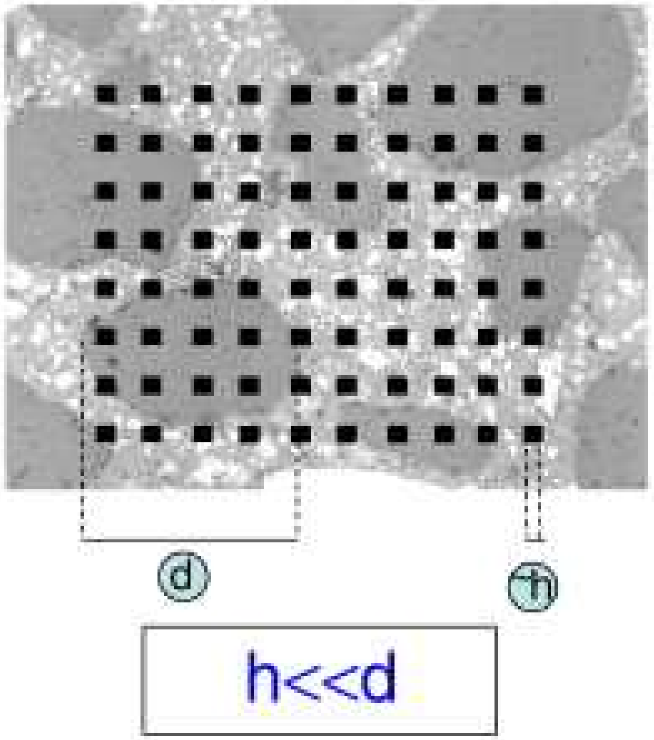


How would the results change for Cases 1, 2, or 3?

Nanoindentation Results for Concrete

- Statistical techniques were used to deconvolute material properties over a large data set

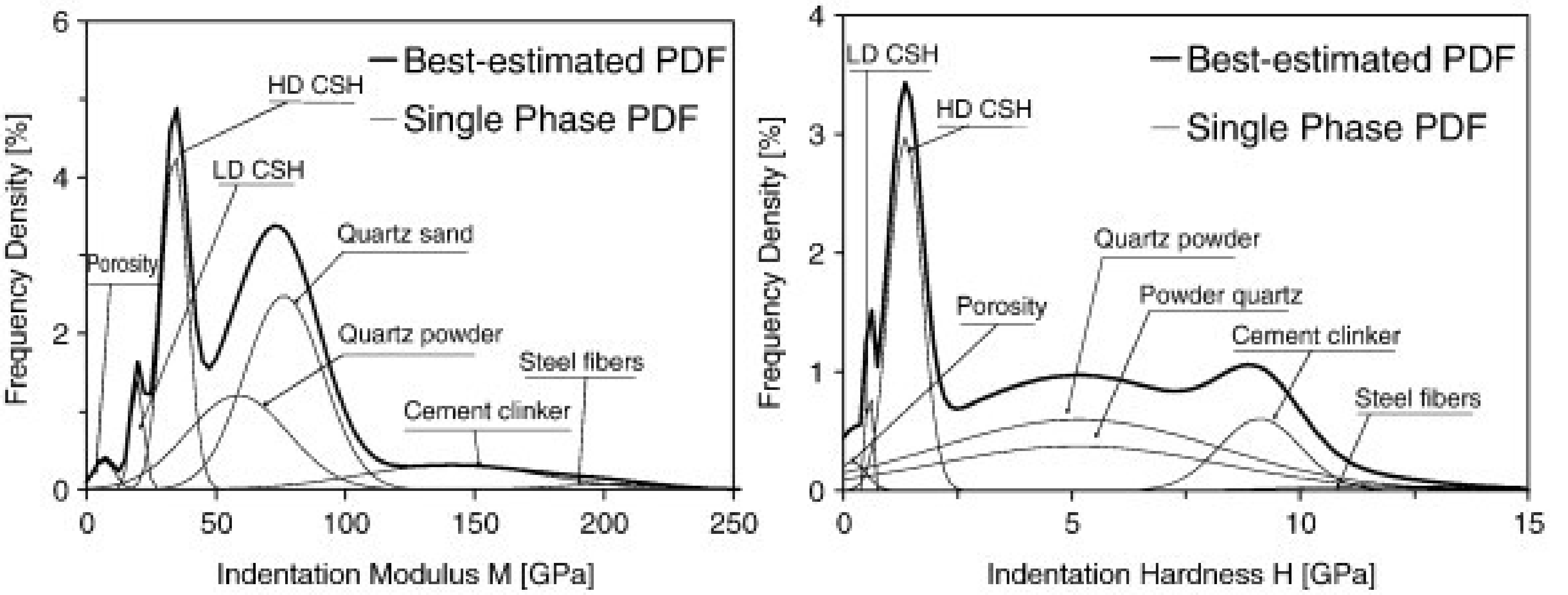




Sorelli et al. (2008)

Nanoindentation Results for Concrete

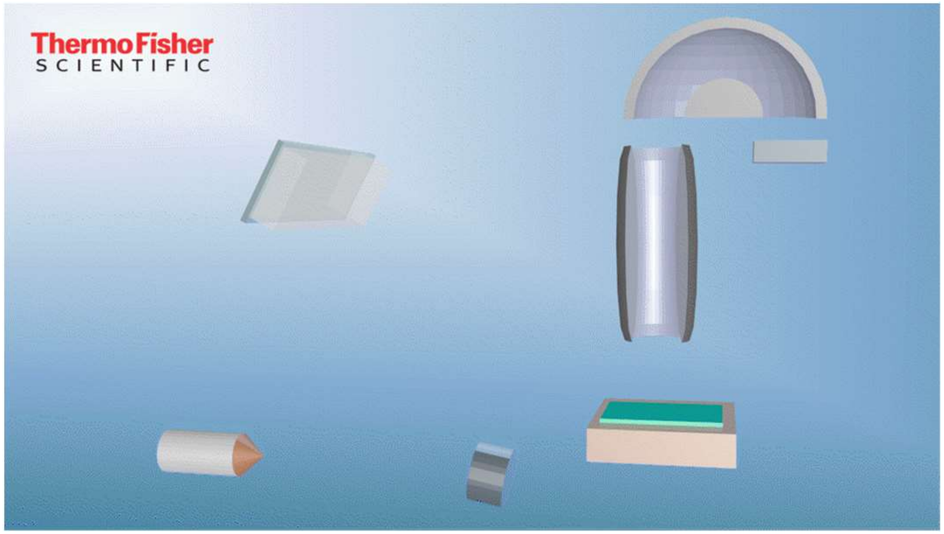
- Statistical techniques were used to deconvolute material properties over a large data set



Sorelli et al. (2008)

X-Ray Photoelectron Spectroscopy (XPS)

- A quantitative *surface chemistry* technique
  - Determine chemical composition within the top ~10 nm of the surface
  - Other measurements are possible too, such as chemical state of the element (*e.g.*, differentiate Fe^{2+} and Fe^{3+})
- Under high vacuum conditions, a monochromatic beam of X-rays is incident on the sample surface, and the kinetic energy and number of electrons that emit from the top 1-10 nm of the surface are detected

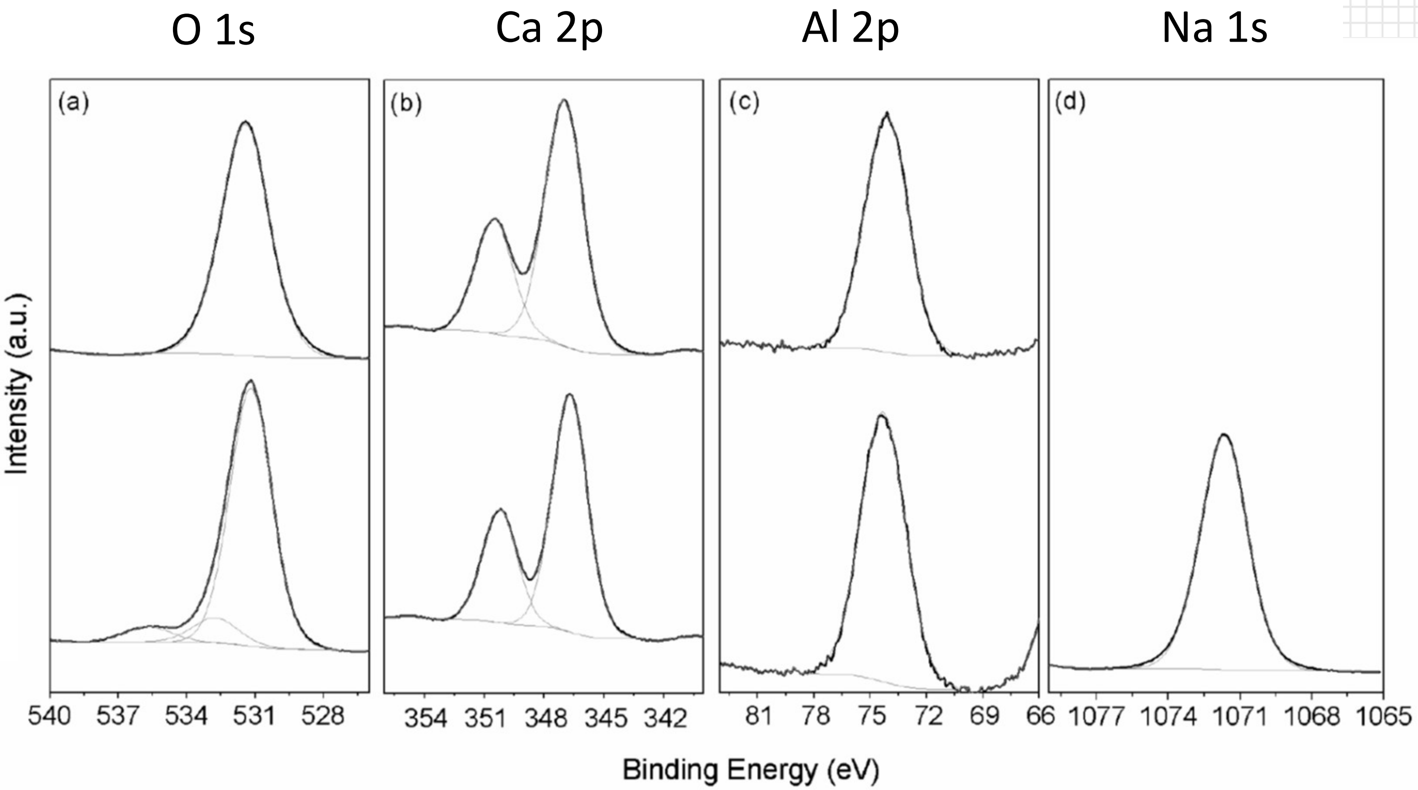


https://xpssimplified.com/whatisxps.php

XPS of C_3A

Cubic C_3A

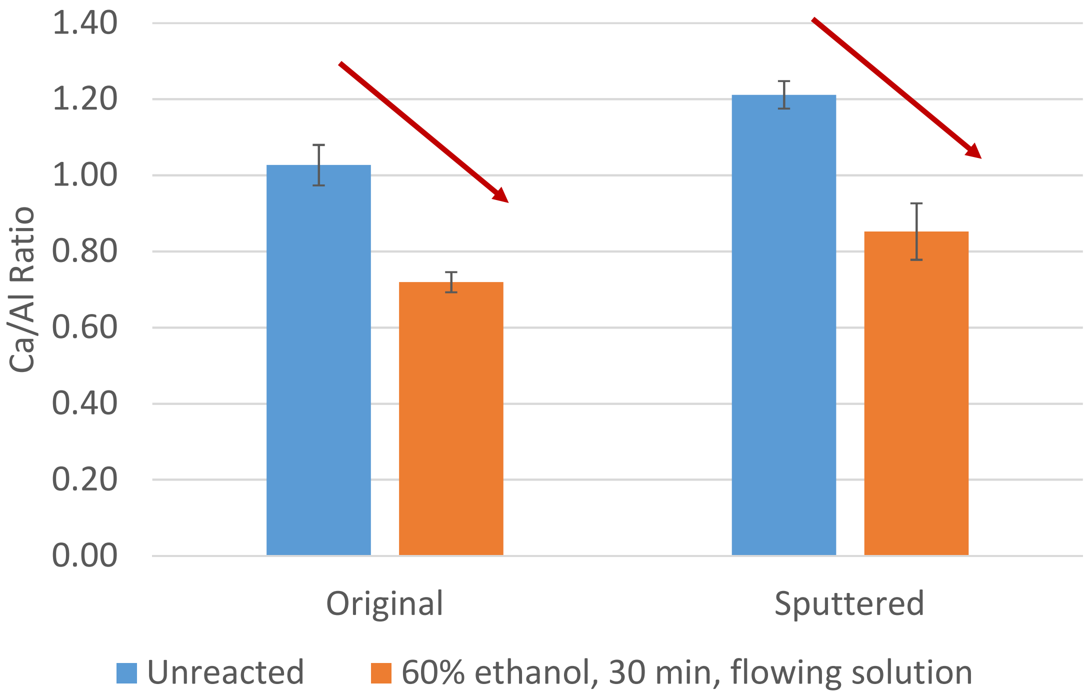
Orthorhombic C_3A



Rheinheimer et al. (2016)

XPS and C_3A Dissolution

- Incongruent (Nonstoichiometric) Dissolution *vs.* Interfacial Dissolution-Reprecipitation Mechanism



Brand et al., in preparation

So, What Have We Learned?

- If you need to measure some sort of surface property, there are probably a handful of available techniques.

- How do you know what technique is the best?
  - Research and weigh the technique’s limitations vs. your requirements (*e.g.*, resolution, accuracy, environmental condition)
  - Consider cost and availability
  - *Find someone who knows more than you and ask*

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