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Best Microscopy Practices for Characterization of Electron Beam-Sensitive Materials

Capabilities within NU*ANCE*

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NU*ANCE* Center, Northwestern University

November 14th, 2019

NUANCE
Northwestern University Atomic and
Nanoscale Characterization Experimental Center

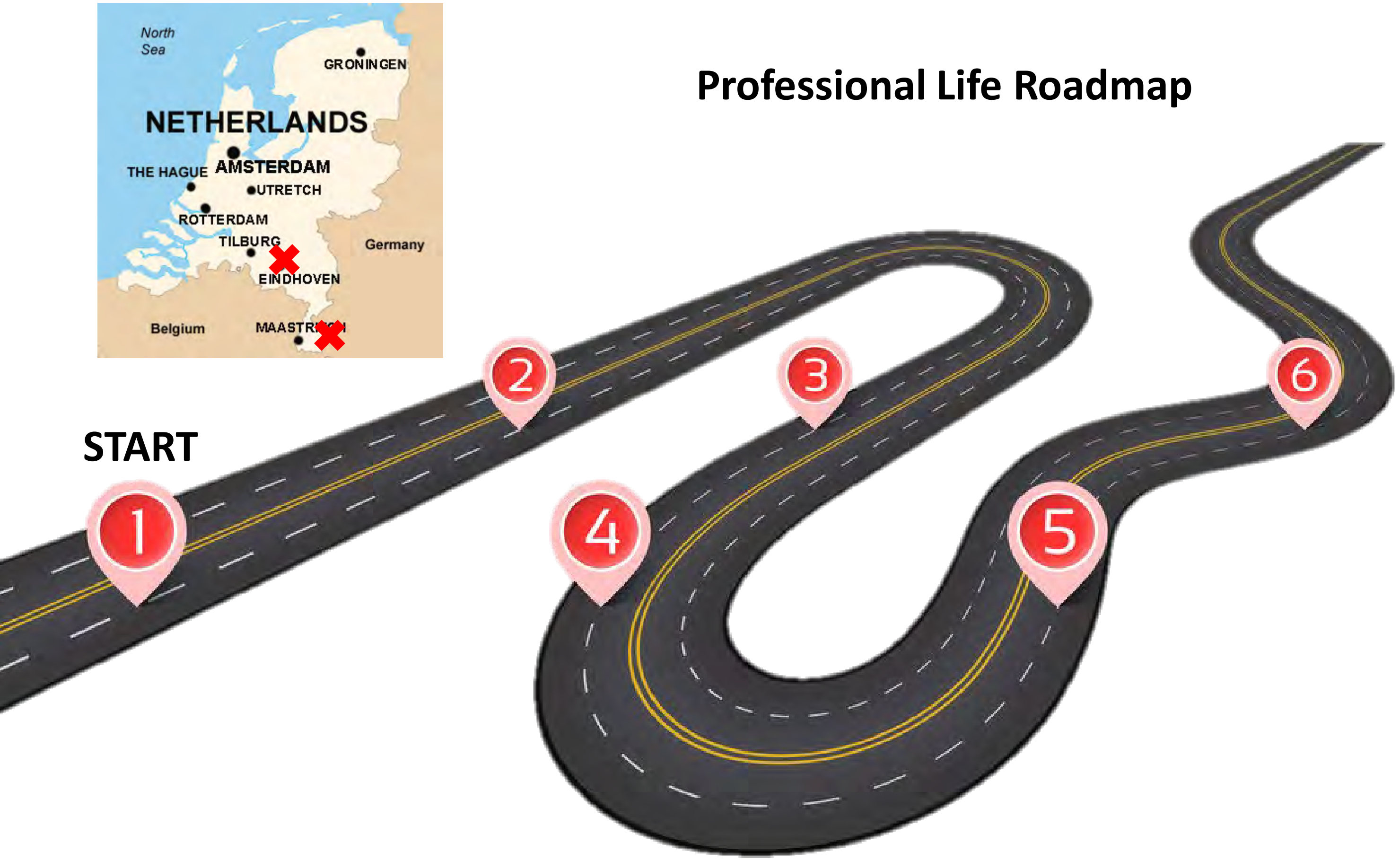
SHyNE
Soft and Hybrid Nanotechnology
Experimental Resource

Northwestern
EXPLORING INNER SPACE

Contents

- Introduction: Professional background
- Radiation Damage in (S)TEM: Theory
- Radiation Damage in (S)TEM: How to control?
- Practical examples

Introduction: Professional Background

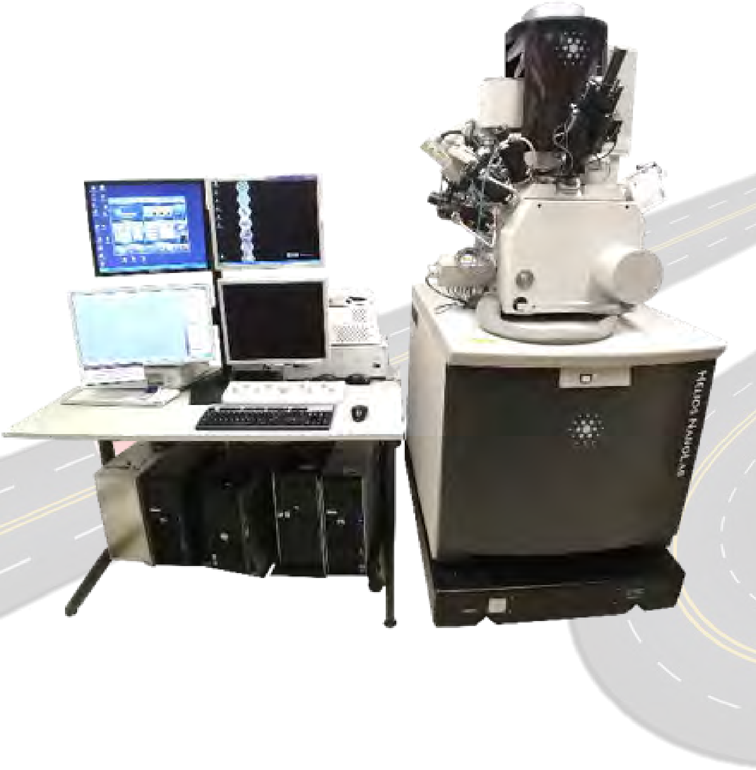


Professional Life Roadmap

1. Born in Kerkrade, The Netherlands
2. BSc. in <u>Chemical Engineering</u>, **2008**
   Eindhoven, The Netherlands
3. MSc. in <u>Chemical Engineering</u>, **2011**
   Eindhoven, The Netherlands
4. PhD in Molecular Systems and Materials Chemistry, **2016**
   Eindhoven, The Netherlands
5. Postdoc in the Joester Group (MSE, NU) work on characterization of <u>natural hard/soft materials</u>

Introduction: Professional Background

FEI Helios Nanolab SEM / FIB



JEOL ARM300F GrandARM TEM

1. Born in Kerkrade, The Netherlands
2. BSc. in Chemical Engineering, **2008**
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3. MSc. in Chemical Engineering, **2011**
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4. PhD in Molecular Systems and Materials Chemistry, **2016**
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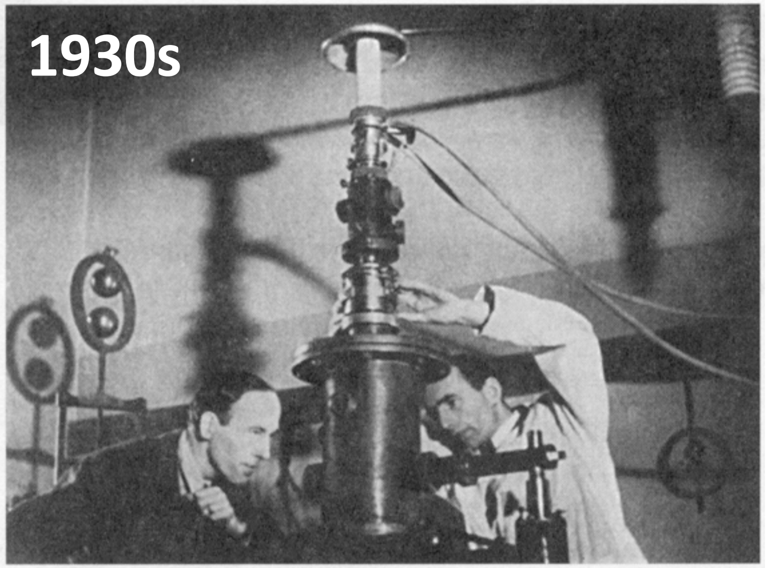
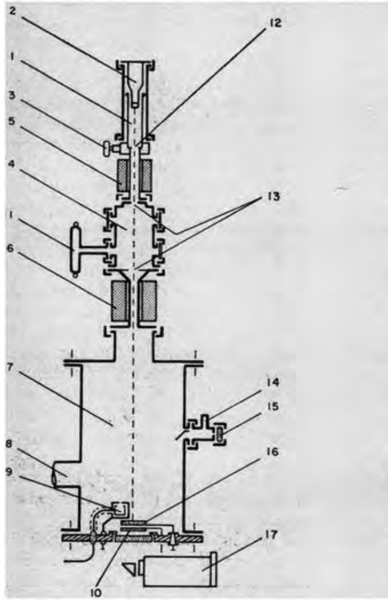
5. Postdoc in the Joester Group (MSE, NU)
   work on characterization of natural hard/soft materials
6. **Research Associate / Manager Helios FIB/SEM and ARM300F GrandARM TEM**

TEM: Then and Now..

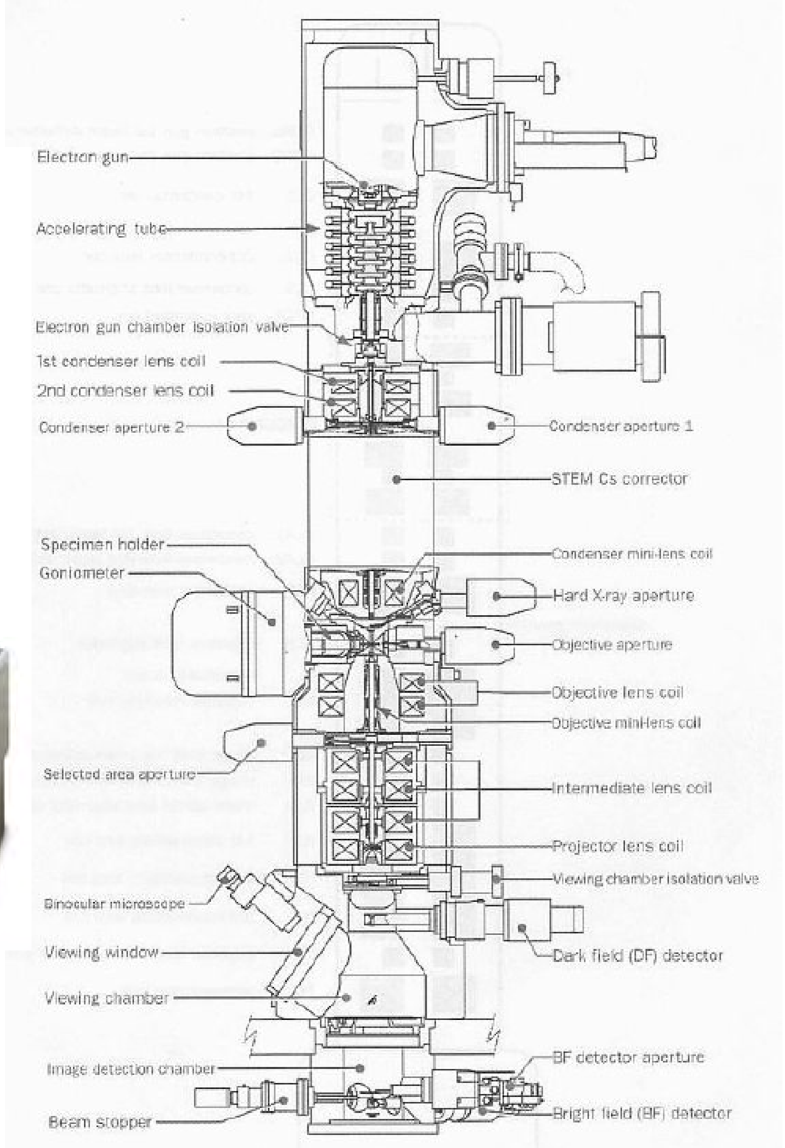




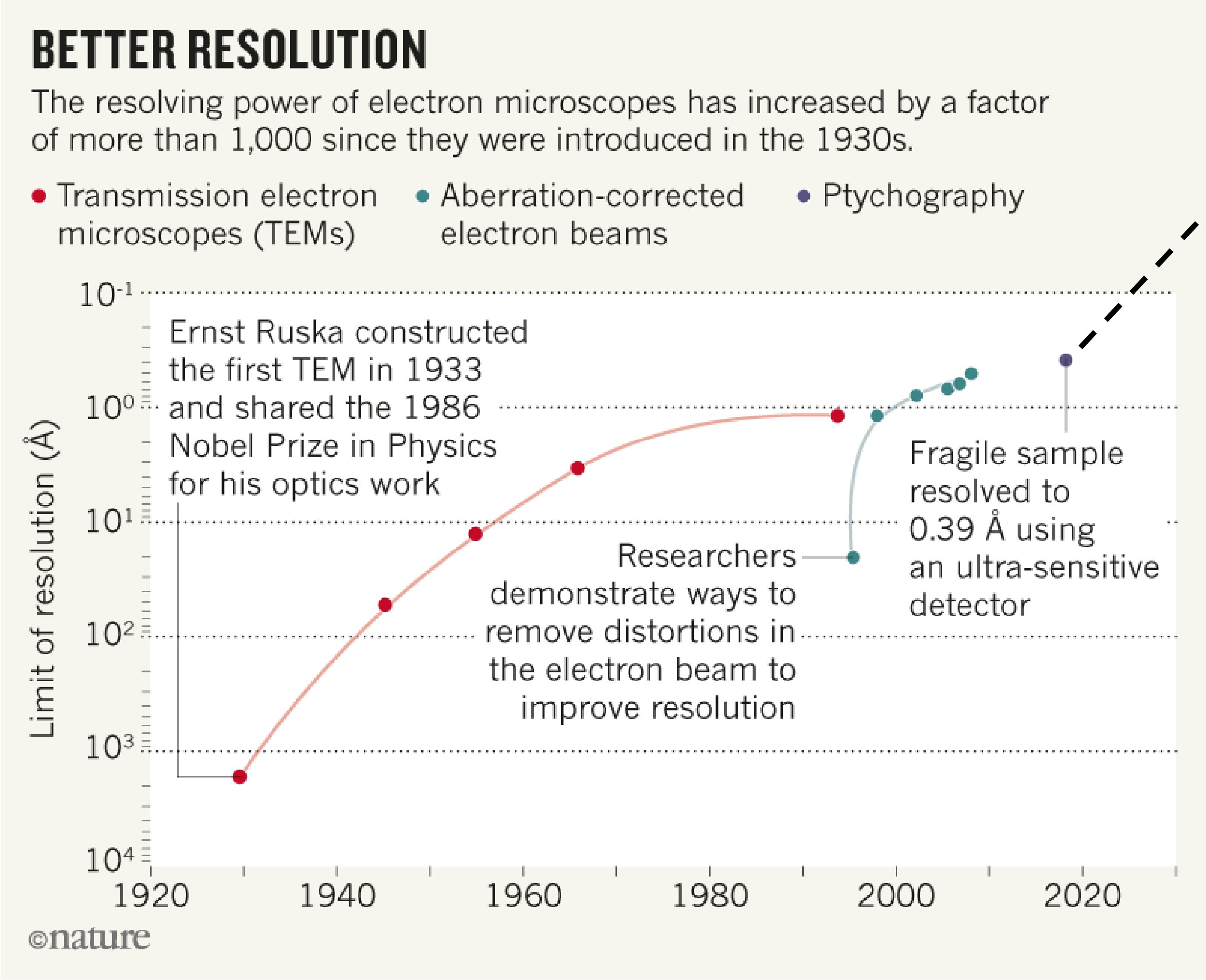
1. GAS DISCHARGE TUBE
2. CATHODE
3. AIR-INLET NEEDLE VALVE
4. CHAMBER FOR ELECTROSTATIC LENS (IF USED)
5. OBJECTIVE MAGNETIC LENS
6. PROJECTION LENS
7. HIGH VACUUM CHAMBER
8. VACUUM PUMP OUTLET
9. FARADAY CAGE FOR BEAM CURRENT MEASUREMENTS
10. FLUORESCENT SCREEN OR GLASS PLATE
11. GAS DISCHARGE TUBE FOR VACUUM TESTING
12. ANODE APERTURE
13. LIMITING APERTURES
14. OUTLET FOR VACUUM GAUGE
15. OBSERVATION WINDOW
16. REMOVABLE FLUORESCENT SCREEN FOR OBSERVATION
17. CAMERA

2019

JEOL ARM200CF TEM



Improvement in Resolution



BETTER RESOLUTION

The resolving power of electron microscopes has increased by a factor of more than 1,000 since they were introduced in the 1930s.

Ernst Ruska constructed the first TEM in 1933 and shared the 1986 Nobel Prize in Physics for his optics work

Researchers demonstrate ways to remove distortions in the electron beam to improve resolution

Fragile sample resolved to 0.39 Å using an ultra-sensitive detector

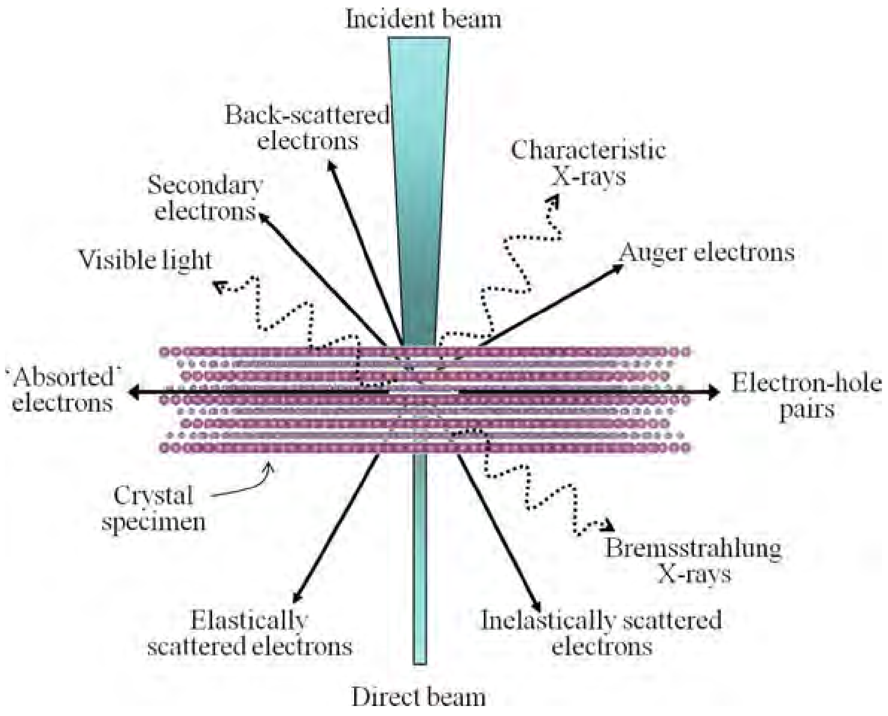
Electron dose on sample

~ 10^6 e^- $Å^{-2}$!!

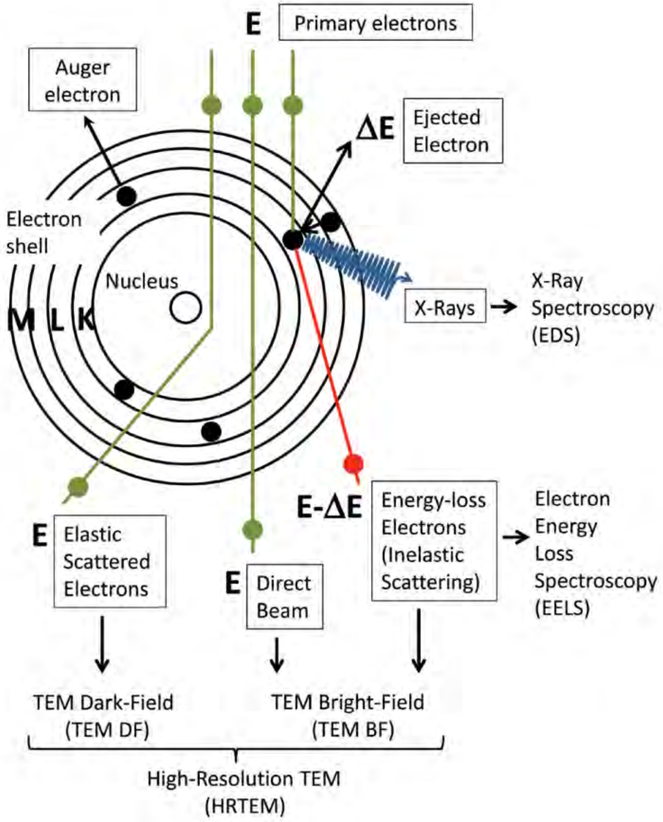
Specimen damage is the fundamental limit to all forms of microscopy capable of atomic resolution imaging

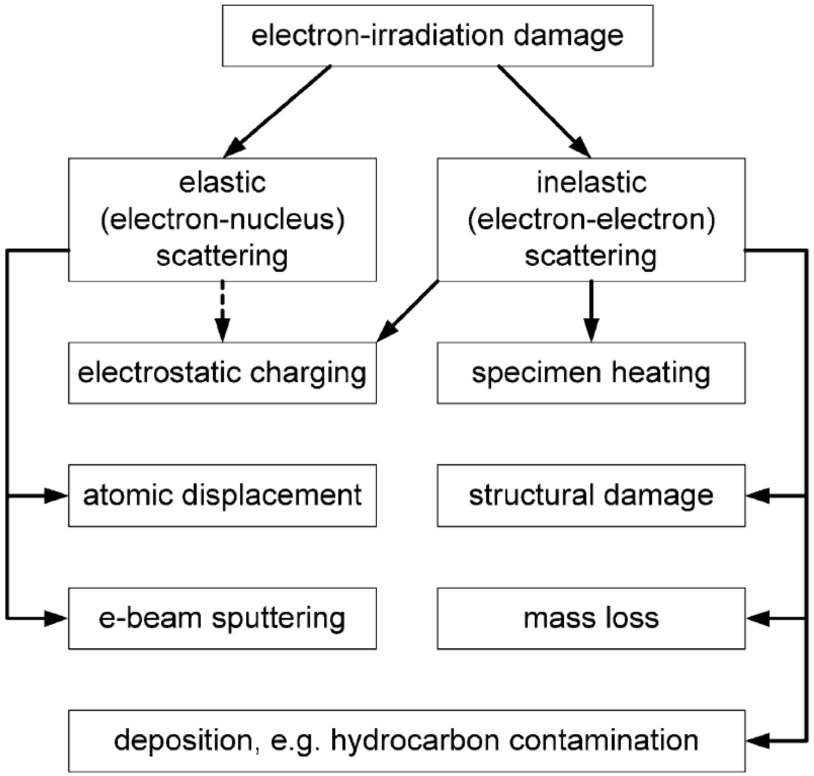
Radiation Damage in the TEM

Beam-sample Interactions



Elastic and inelastic scattering – induced damage




electron-irradiation damage

elastic (electron-nucleus) scattering

inelastic (electron-electron) scattering

electrostatic charging

specimen heating

atomic displacement

structural damage

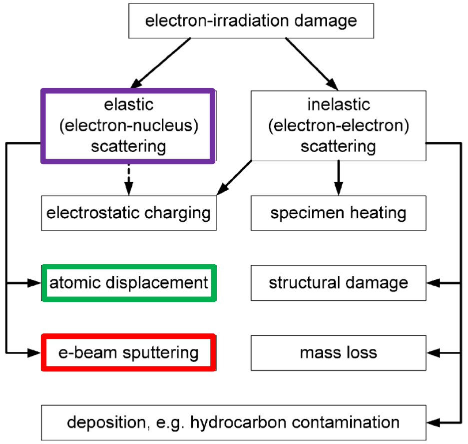
e-beam sputtering

mass loss

deposition, e.g. hydrocarbon contamination

Elastic Scattering – Induced Damage

“Knock-on damage”



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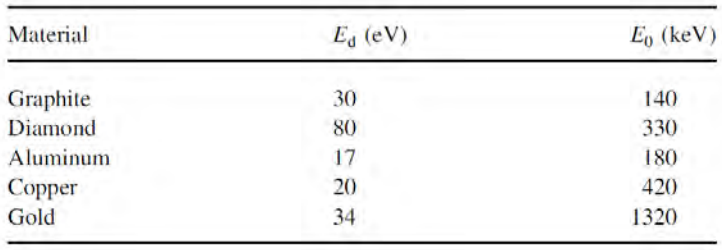
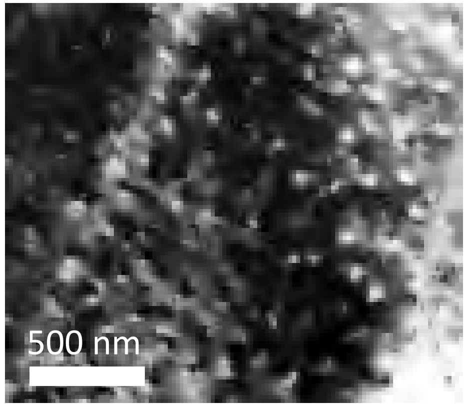
Atom displacement energy E_d

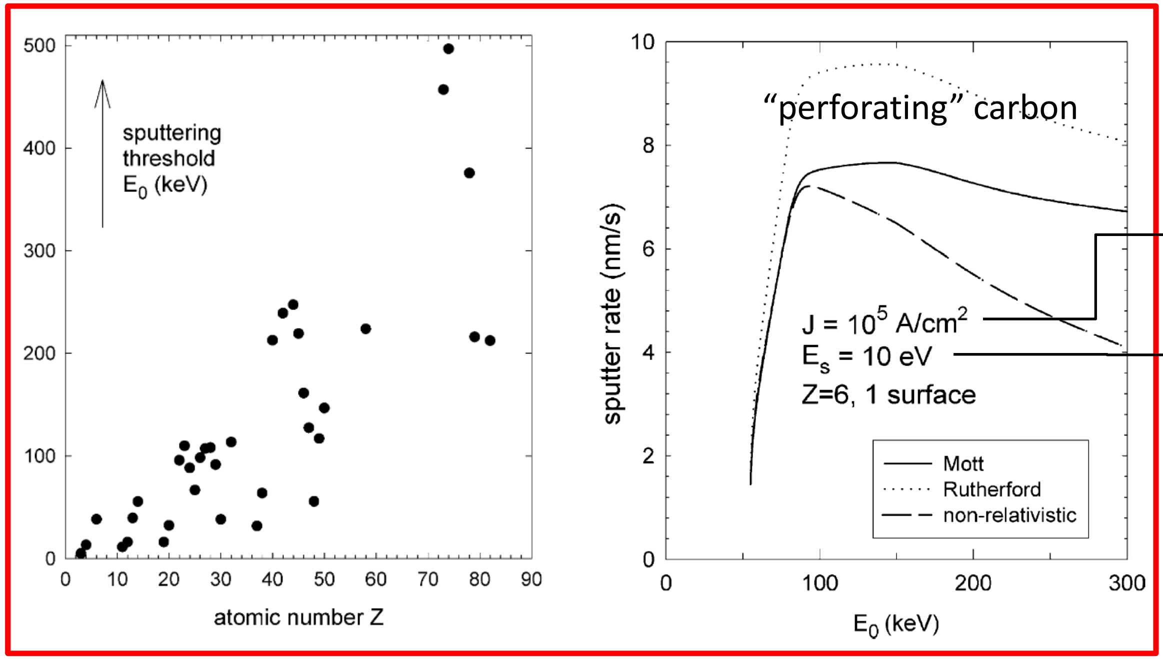


Material	E_d (eV)	E_0 (keV)
Graphite	30	140
Diamond	80	330
Aluminum	17	180
Copper	20	420
Gold	34	1320

→ property of specimen material



BF-TEM image of graphite crystal
(600 °C; 200 keV electrons)

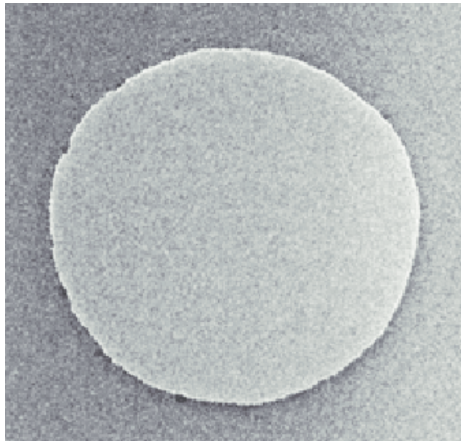


→ Current density 6.24×10^7 e$^-$Å^{-2}s^{-1}

→ sublimation energy per atom

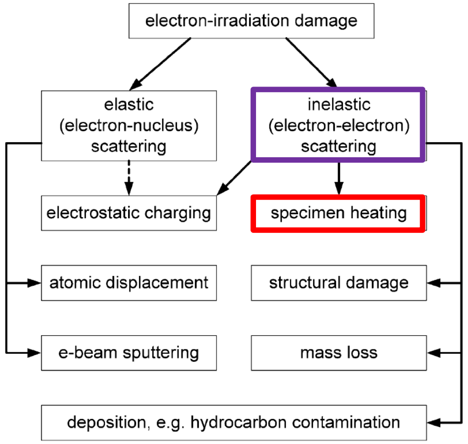
General rule of thumb for most elemental solids

- Above 200 kV → bulk displacement
- Below 200 kV → surface sputtering



Hole drilling above **incident electron energy**

Inelastic Scattering – Induced Damage


electron-irradiation damage

elastic (electron-nucleus) scattering

inelastic (electron-electron) scattering

electrostatic charging

specimen heating

atomic displacement

structural damage

e-beam sputtering

mass loss

deposition, e.g. hydrocarbon contamination

Two dominant factors determine **sample heating**

1) Total energy absorbed by the specimen from the electron beam
2) The quality of the thermal contact between the specimen and the specimen support

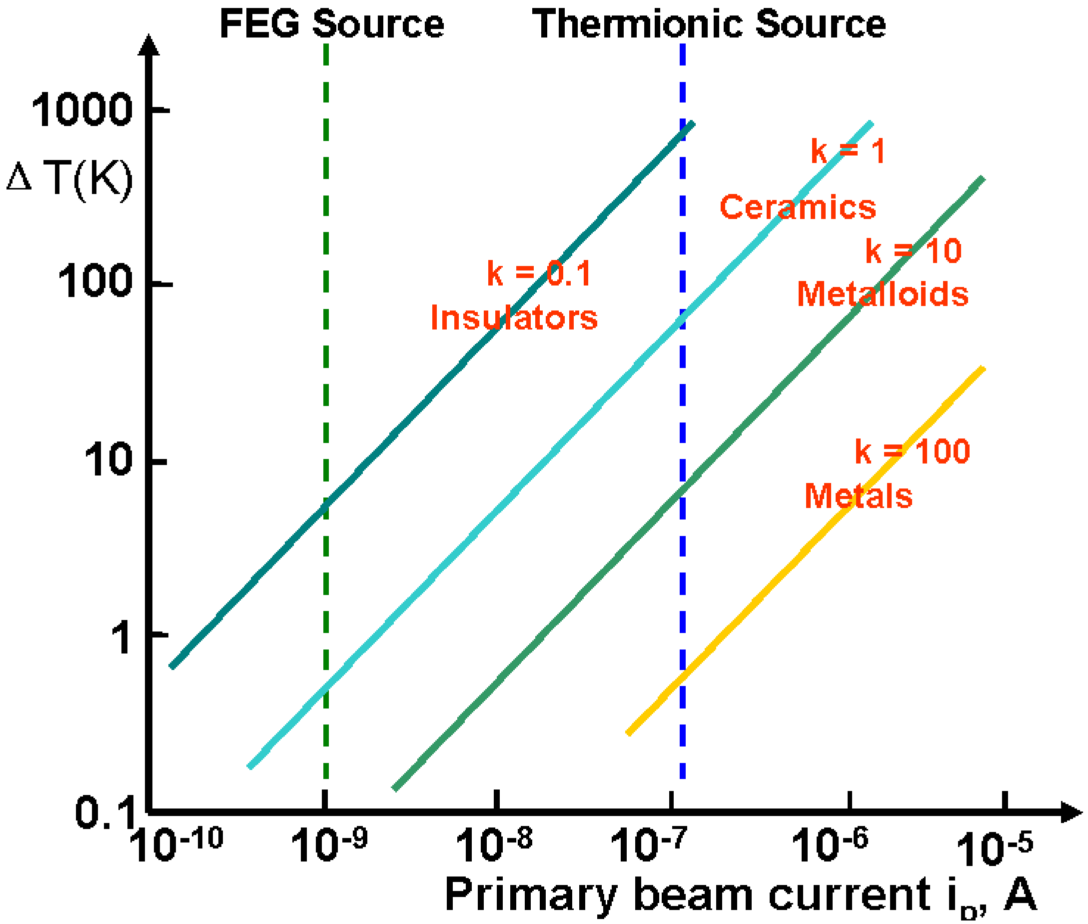
Temperature rise in specimen assuming heat is conducted away

$$\Delta T \approx \langle E \rangle (2R_0/d)/(4\pi\kappa\lambda_i)$$

<E> mean energy loss (in eV) per inelastic-scattering event

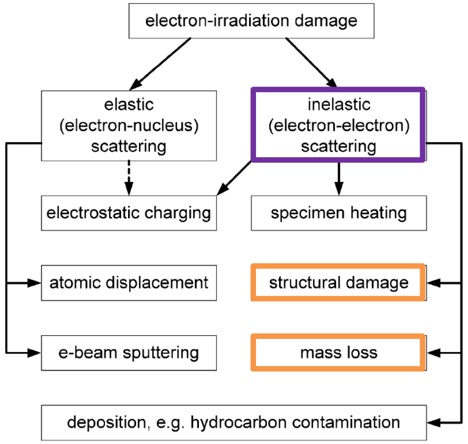
λ inelastic mean free path of the transmitted electrons

κ thermal conductivity of the specimen ($W{\cdot}m^{-1}K^{-1}$)



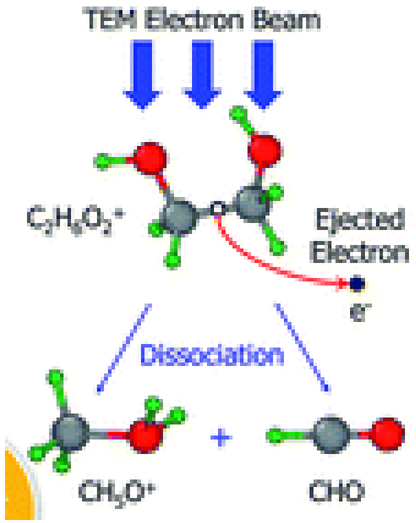
Inelastic Scattering – Induced Damage

“Radiolysis” or ionization damage

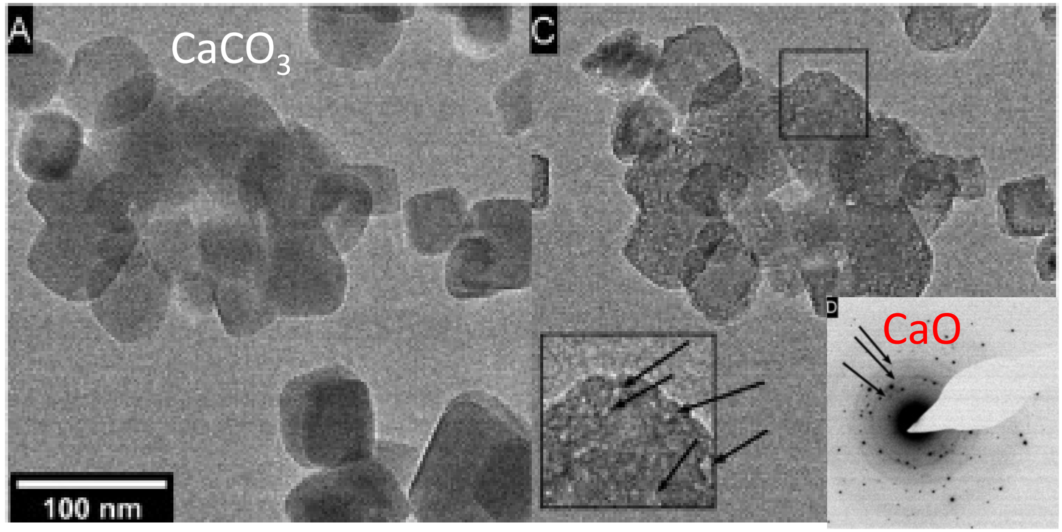

electron-irradiation damage
elastic (electron-nucleus) scattering
inelastic (electron-electron) scattering
electrostatic charging
specimen heating
atomic displacement
structural damage
e-beam sputtering
mass loss
deposition, e.g. hydrocarbon contamination

Energy loss *E* suffered by a primary electron may be transferred to a single atomic electron, damage α energy deposited per unit volume of specimen

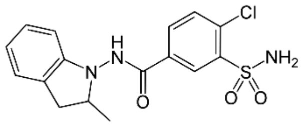
Inorganic materials → onset of radiolysis at threshold current density (e^{-}Å^{-2}s^{-1})
Organic materials → onset of radiolysis at critical dose (e^{-}Å^{-2})



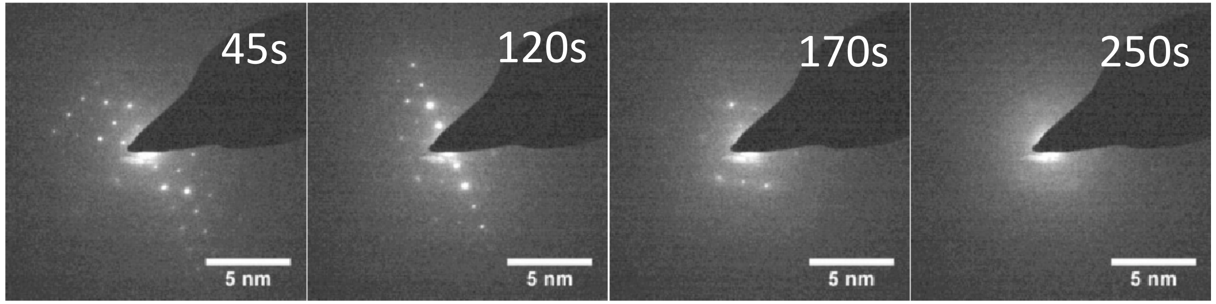
Mass loss → increase in transmitted intensity in the image



R. Hooley *et al., Micron*, **120** (2019)



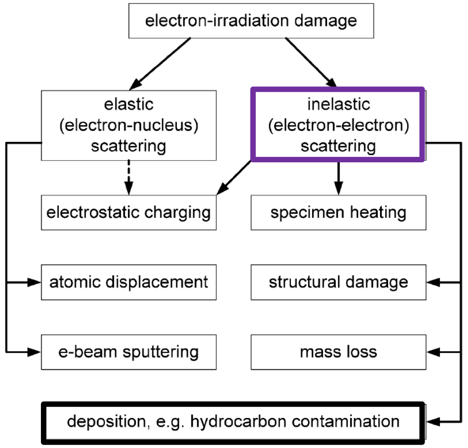
Indapamide; dose rate 3.59 × 10^{2} e^{-}Å^{-2}s^{-1}



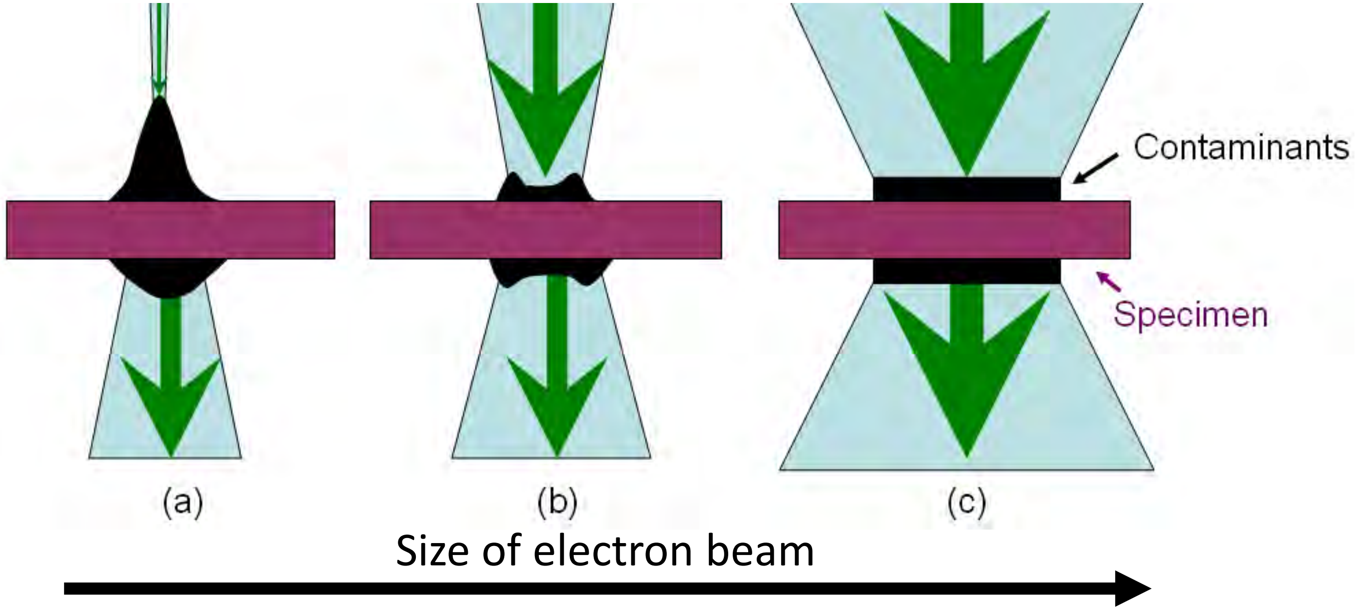
M. S’ari *et al. Journal of Physics*, **644** (2015)

Bond breakage (and SE generation) takes place on sub-fs time scale; mass loss (atom motion over large distances) e.g. seconds

Inelastic Scattering – Induced Damage



Hydrocarbon molecules on the surface of a TEM specimen are polymerized by the incoming (or outgoing) electrons



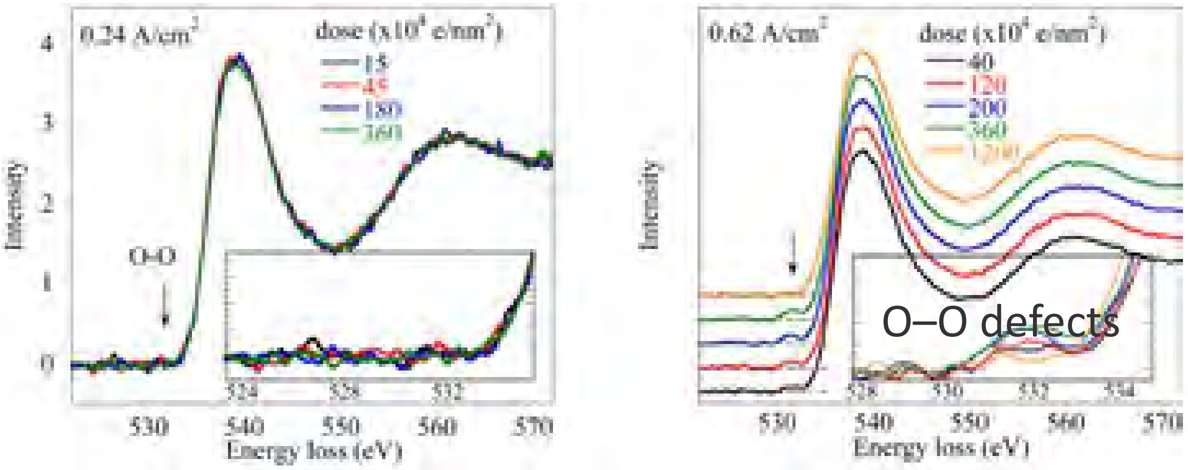
- The vacuum level of the microscope
- The size of incident electron beam
- The electron probe current density
- The sticking coefficient for hydrocarbons on the specimen
- The existing contamination within the microscope vacuum system
- The history of the specimen such as specimen preparation, handling of the specimen or specimen holder, back-streaming of oil from a diffusion-pumped ion milling system, chemicals used during electrolytic thinning, cleaning, and exposure to hydrocarbon vapors, etc.

Quantitative Measurement of Radiation Damage

Characteristic dose $\boldsymbol{D}_{\mathbf{ec}}$ and damage cross section ($\boldsymbol{\sigma}_{\mathbf{d}} = 1/D_{ec}$) for beam-sensitive materials determined by several techniques (100 kV; RT)

Method	Material	$D_{ec} = D_c/e$ (e/Å^2)	σ_D (Mb) = 100/D_{ec}
Fading of spots in electron diffraction patterns	Bacteriorhodopsin[s]	0.5	200
	Amino acid (glycine)[a]	1.6	64
	Polyethylene	6.0	16
	Coronene[e]	70	1.5
	Phthalocyanine (Pc)	120	0.83
	Cu-phthalocyanine	1600	0.06
	Chlorinated Cu-Pc	12000	0.008
	ZSM-5 zeolite[d]	300	0.33
	Calcite (200 kV)[g]	39,000	0.0026
TEM image	NaCl (Frenkel pairs)[b]	51,000	0.0020
	KCl (Frenkel pairs)[b]	2,400	0.041
EELS fine structure	Di-glycine[a]	20	5
	Cu-phthalocyanine[a]	300	0.3
	Coronene[e]	600	0.16
	Polycrystalline C_{60}	2.6×10^6	4×10^{-4}
	Nitrocellulose	1.2	80
	Nitrocellulose	3.7	27
	Polyvinyl formal	20	5
	PMMA	40	2.5
	Polycabonate	300	0.33
	PMMA	300	0.33
	NaCl ($< 10^{-4}$ A/cm^2)[c]	110	0.89
	Glycine	7.5	13
	Di-glycine	4	27
	Amorphous Al_2O_3[h]	1.6×10^6	6×10^{-5}
	H-removal (E_d = 0.1 eV)		5×10^{-4}
	H-removal (E_d = 4.4 eV)		1×10^{-4}
	C-removal (E_d = 5 eV)		1.5×10^{-4}
	C-removal (E_d = 10 eV)		5×10^{-5}

CaF_2-Al_2O_3-SiO_2 glass



O–O defects

N. Jiang, *Rep. Prog. Phys.* **79** (2016)

Radiation Damage in Various Classes of Materials

- Radiation sensitivity of different specimen materials varies widely
- Conductive materials → Mostly knock-on damage
- Semiconductors / insulators / organic specimens → Predominantly radiolysis (& heating/charging for the latter)
  - Organic materials → energy loss to valance electrons (20-30 eV), most of which goes into SE production → most damage for organic materials comes from **secondary electrons**
- Liquid-cell TEM → All experiments are affected by radiolysis
  - Radiolysis (of water) products (e.g. dissolved hydrogen/oxygen gas concentrations)

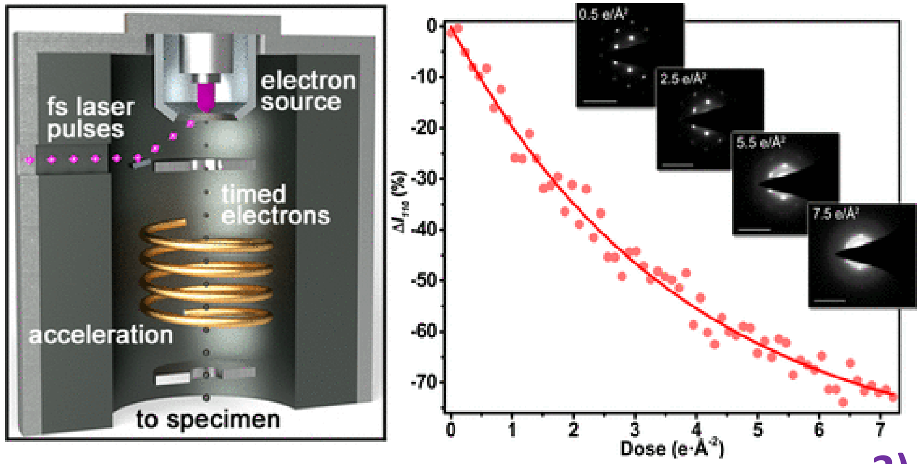
$$H_2O \xrightarrow{\text{Ionizing Radiation}} e^-_{aq}, HO\cdot, H\cdot, HO_2\cdot, H_3O^+, OH^-, H_2O_2, H_2$$

  - Changes in pH solution and ionic strength
  - Sample charging

Radiation Damage Control

1) Electron beam modifications to minimize dose

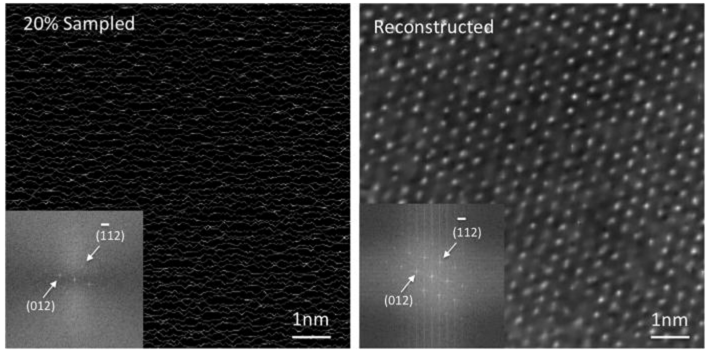
Laser-driven generation of ultra small electron packets



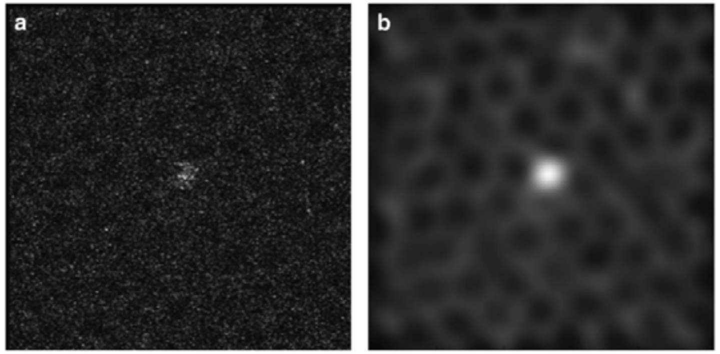
E. VandenBussche *et al.*, *Nano Lett.* **19** (2019)

2) Maximizing the Signal

Compressed (sparse) sampling / inpainting



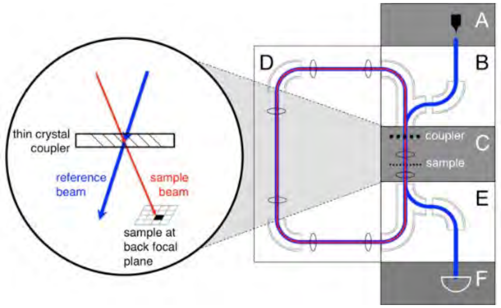
L. Stevens *et al.*, *Appl. Phys. Lett.* **109** (2016)



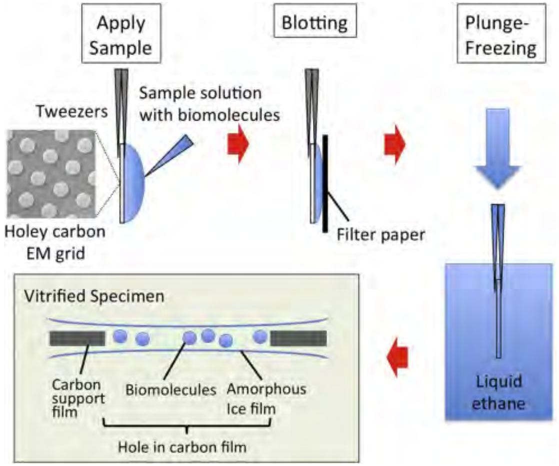
X. Li *et al.*, *Microscopy and Microanalysis* **24** (2018)

3) Sample preparation/protection

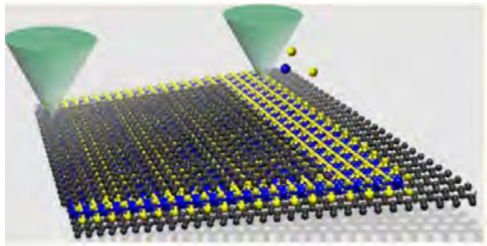
Quantum electron microscope



Cooling the Sample

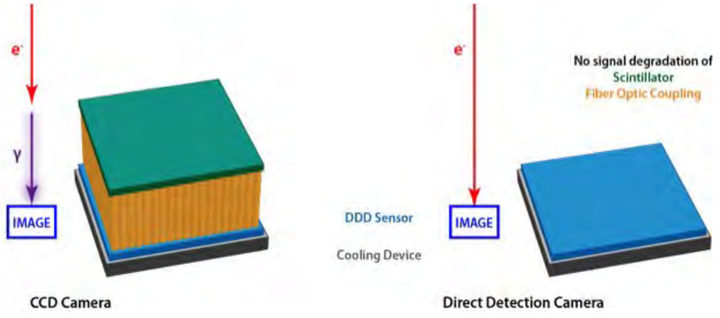


Encapsulation MoS_2 in graphene

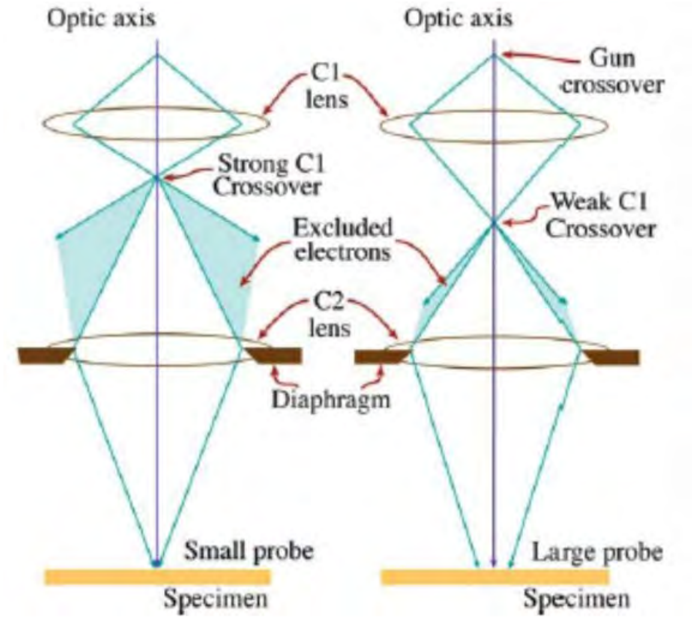


R. Zan *et al.*, *ACS Nano* **7** (2013)

Direct electron detectors



1) Minimizing Dose: Experimental Considerations to Modify Electron Beam

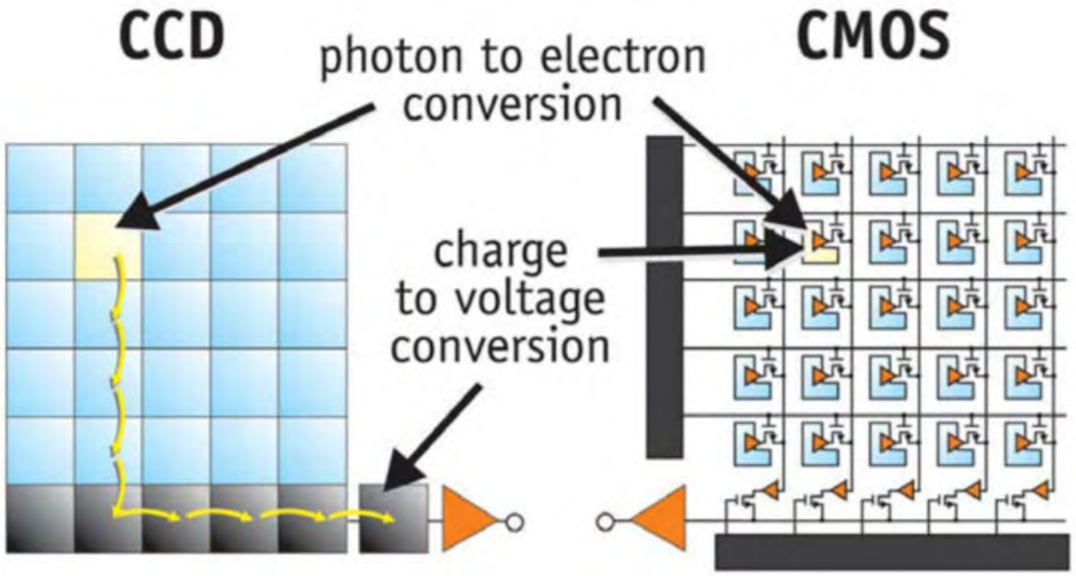


Low intensity beam (high spot number)

High intensity beam (low spot number)

	TEM	STEM
Lowering beam current	✓	✓
Increase spot size number (1-5)	✓	✗
Increase spot size number (1C-10C)	✗	✓
Reduce exposure time	✓	✗
Decrease condenser aperture size	✓	✓
Reduce beam dwell time	✗	✓
Decrease magnification	✓	✓
Focus/stigmate in a different area, then move over to acquisition area	✓	✓

2) High Speed Direct Electron Detectors on ARM200/300



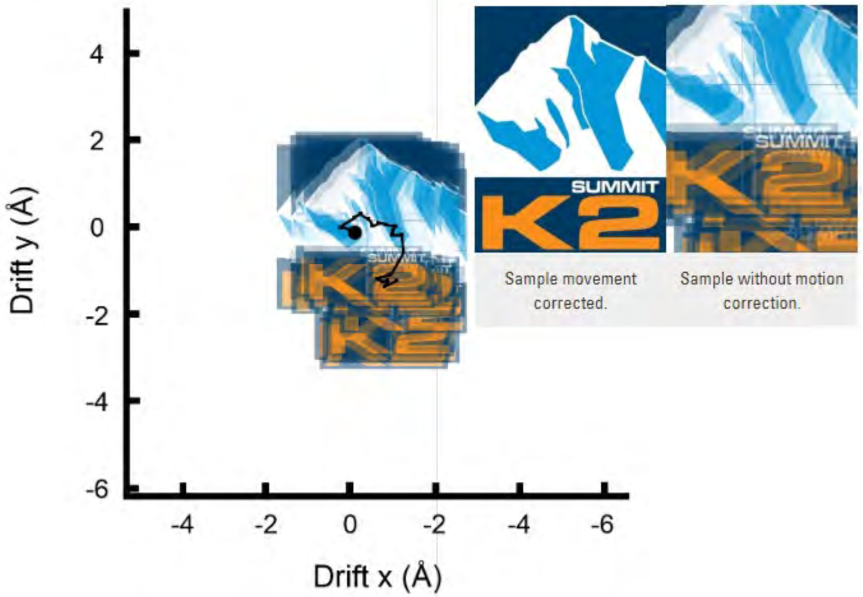
K2-IS

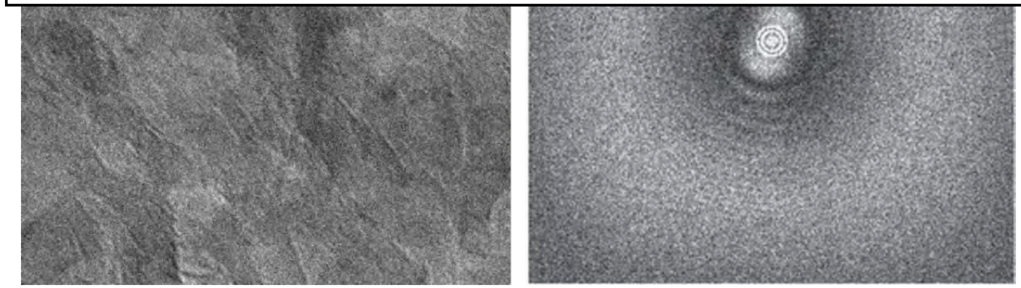
- Electron counting camera
- **400 full frames per second**
- K2 direct detection sensor
- Highest contrast for thin specimens
- Dose fractionation mode for beam sensitive materials
- Quantum GIF + K2 leverages the counting capabilities of the K2 camera
- Highest detective quantum efficiency (DQE) available for spectroscopy and spectrum imaging applications

K3-IS

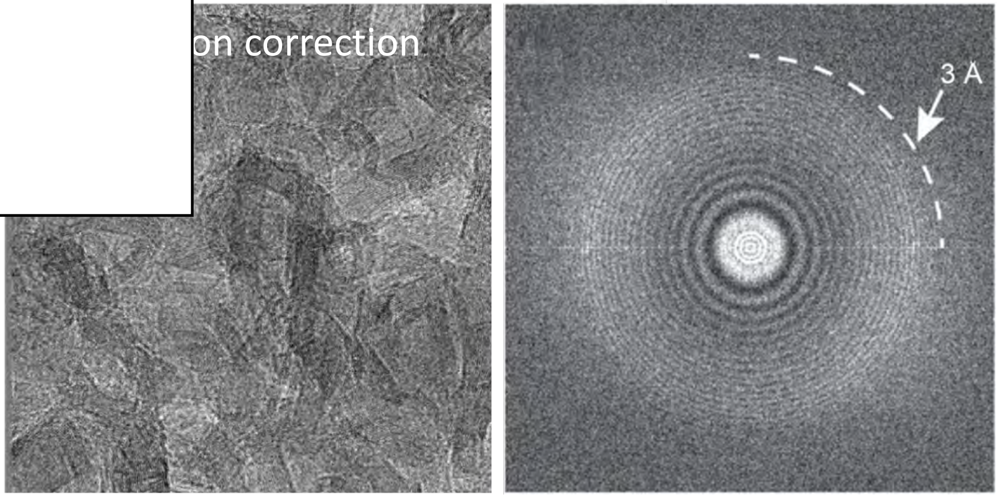
- The world’s first counting, high-speed, large format cameras for *in*-situ microscopy
- 24 megapixels (5,760 x 4,092) field of view
- **1,500 full frames per second**
- Synchronize frames for 4D STEM applications via STEMx

IS Camera’s – Dose Fractionation and Motion Correction

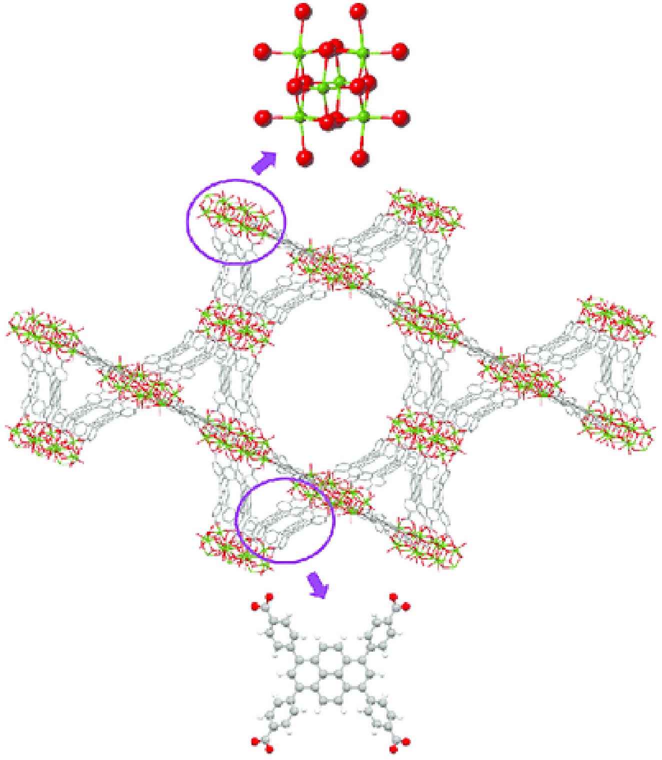




Source: gatan.com

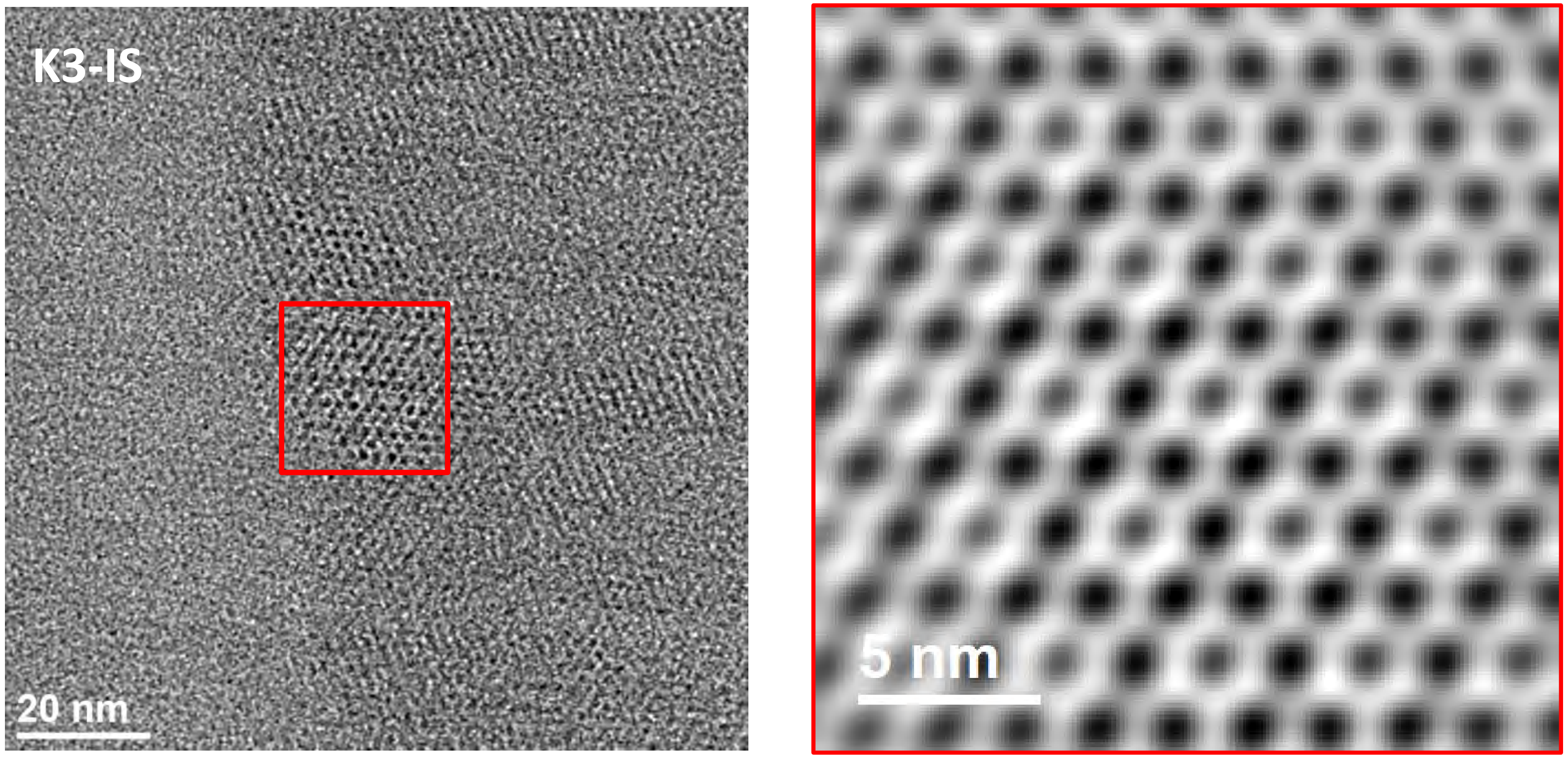


IS Camera's – Dose Fractionation and Motion Correction



NU1000 MOF structure

Direct Visualization of MOF structures



Left: 55 frames – total dose 8 $e^{-}Å^{-2}$
Right: Fourier filtered image from the marked area showing the pore structure

Image courtesy: Roberto dos Reis (in Collaboration with Omar Farha group (NU))

IS Camera's – Dose Fractionation and Motion Correction

Direct Visualization of KTiOF

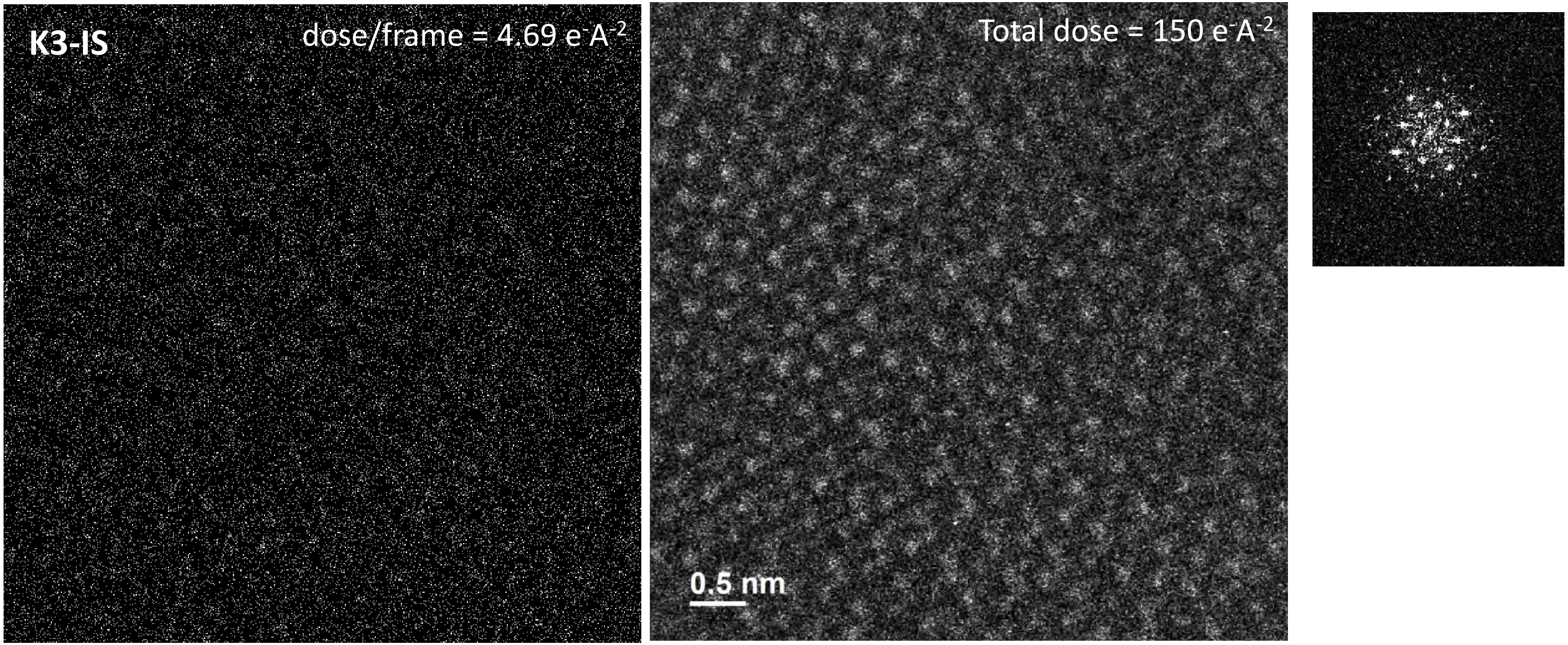


Image courtesy: Roberto dos Reis (in Collaboration with Chi Zhang; VPD and Poeppelmeier group (NU))

Radiation Damage Control against Specific Types of Radiation Damage

- **Radiolysis** → cool sample to liquid nitrogen temperature
  (Characteristic dose D_{ec} increases with E_0 & increases with decreasing **T**)

- **Knock-on damage** → reduce the TEM accelerating voltage below a threshold value
  (Characteristic dose D_{ec} decreases with increasing E_0 & varies little with **T**)

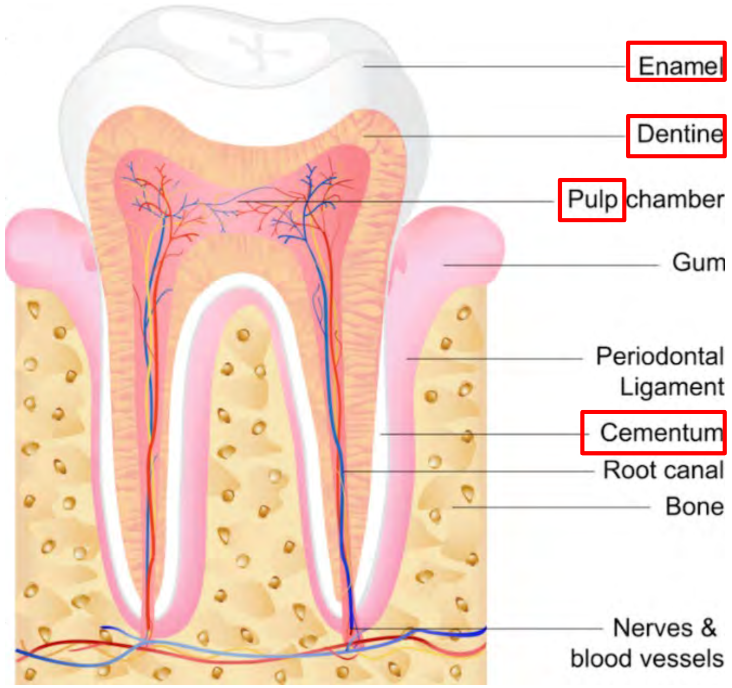
- **Charging** or **Heating** → Reduce the incident beam current, decrease E_0

Preventing Types of Beam Damage – Hydrocarbon Contamination

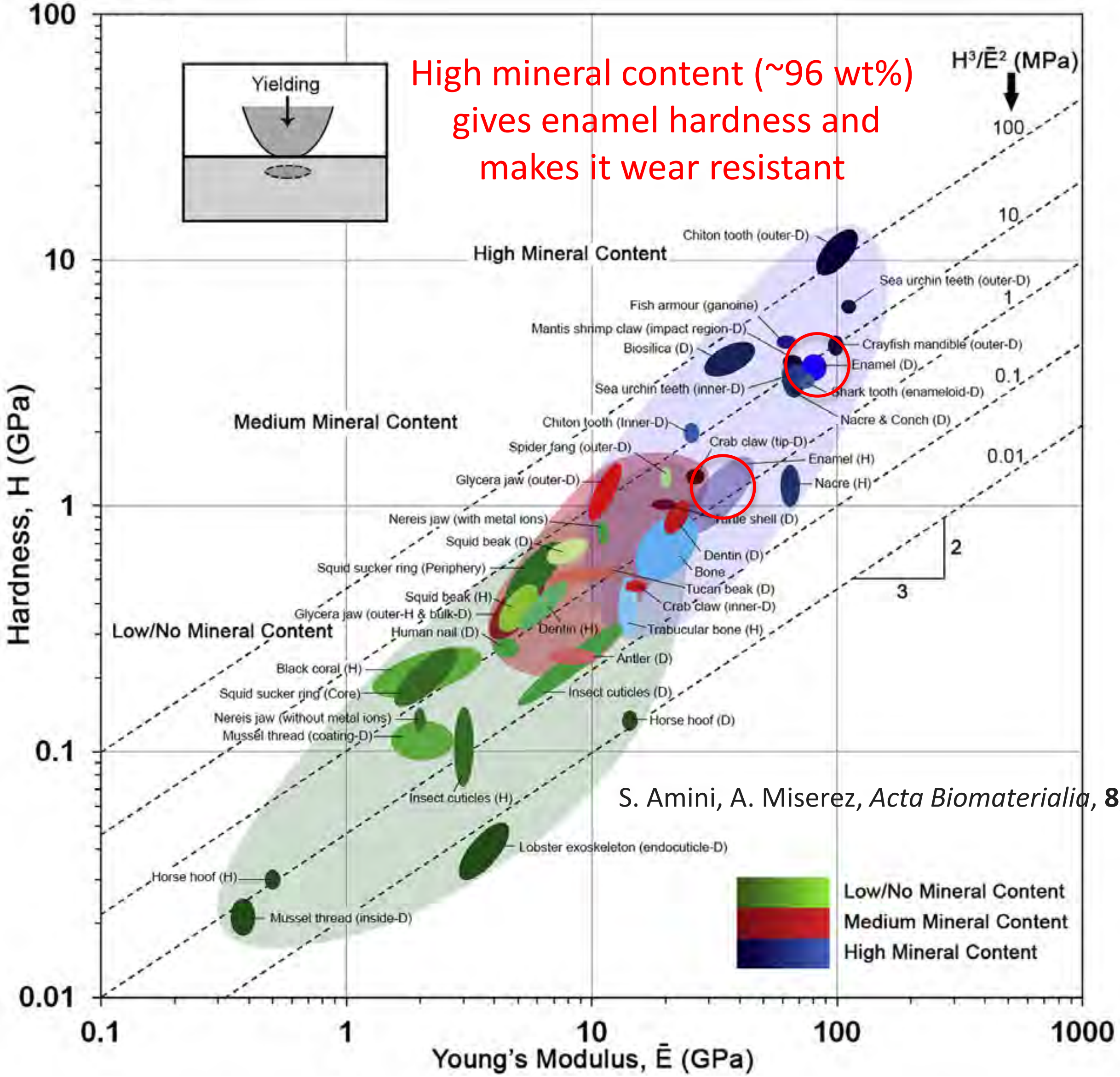
- **Heat specimen** with an electric lamp in air to desorb hydrocarbons from its surfaces (UV lamp for heat-sensitive samples)
- **Plasma clean** the surface (sputter away the surface layer using energetic ions)
- **“Beam shower”**: Flood the surrounding area with electrons, by defocusing the illumination and removing the condenser aperture in TEM (scanning low mag in STEM) to fix surface hydrocarbons and prevent them diffusing to a focused probe
- **Heat the surface** to 300°C **in the TEM** to desorb hydrocarbons
- **Cool specimen** during observation to reduce mobility of hydrocarbons
- **Ar milling** the surface
- **Leaving the specimen in the microscope overnight** and then the contaminants can fully or partially be desorbed in the vacuum

Practical Examples

Biominerals – Tooth Enamel



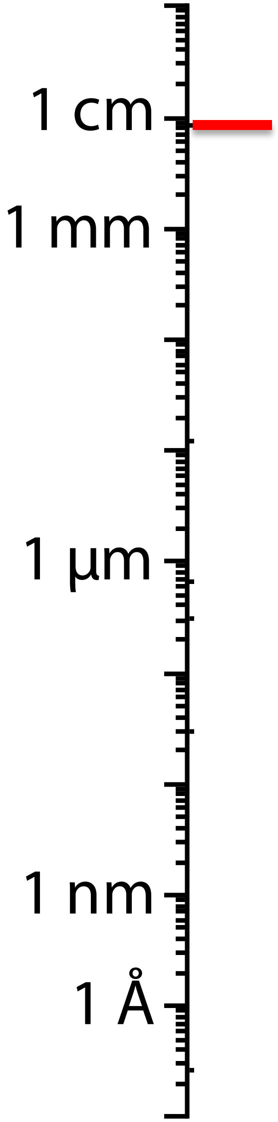
Mechanical abrasion

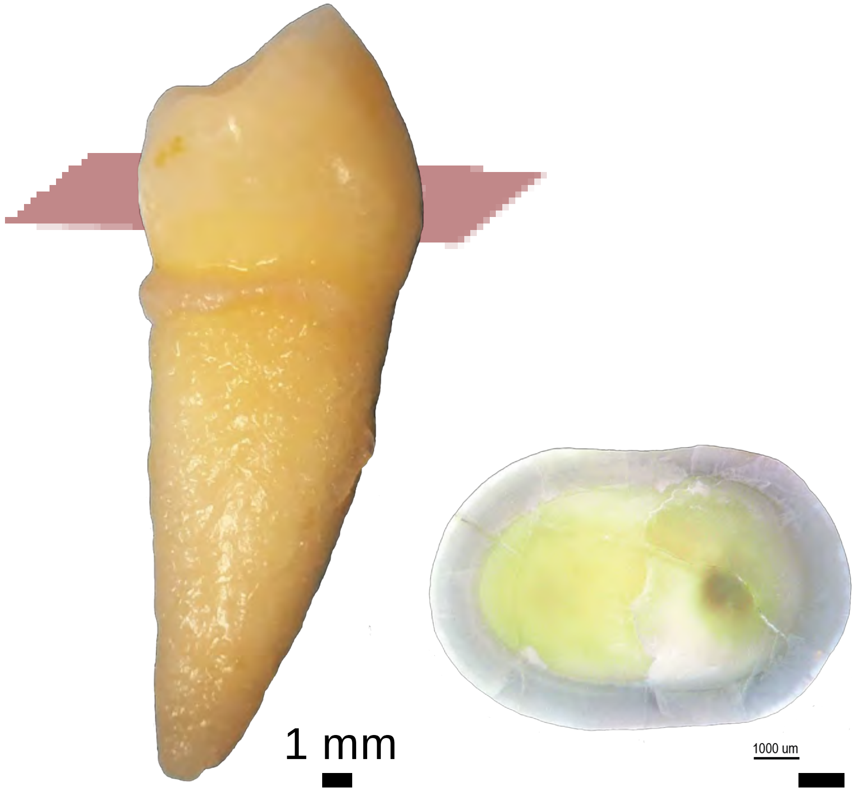


High mineral content (~96 wt%) gives enamel hardness and makes it wear resistant

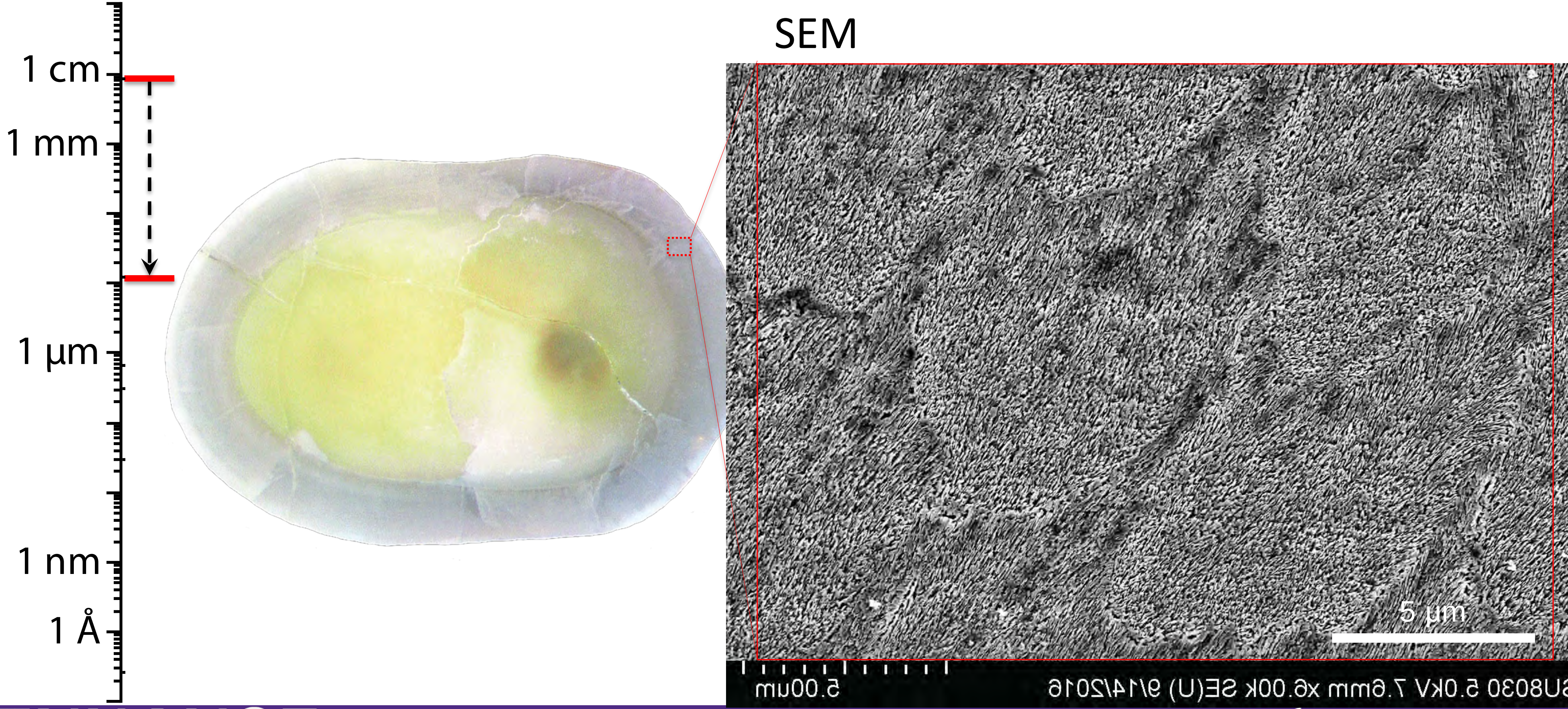
S. Amini, A. Miserez, *Acta Biomaterialia*, **8**, 7895 (2013)

Complex 3D Hierarchical Structure across Length Scales

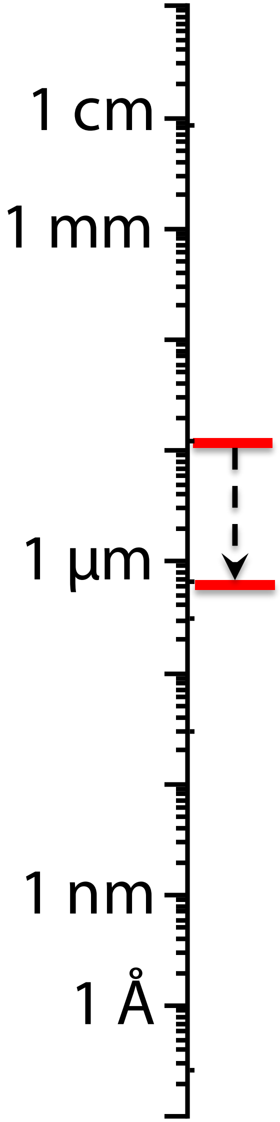


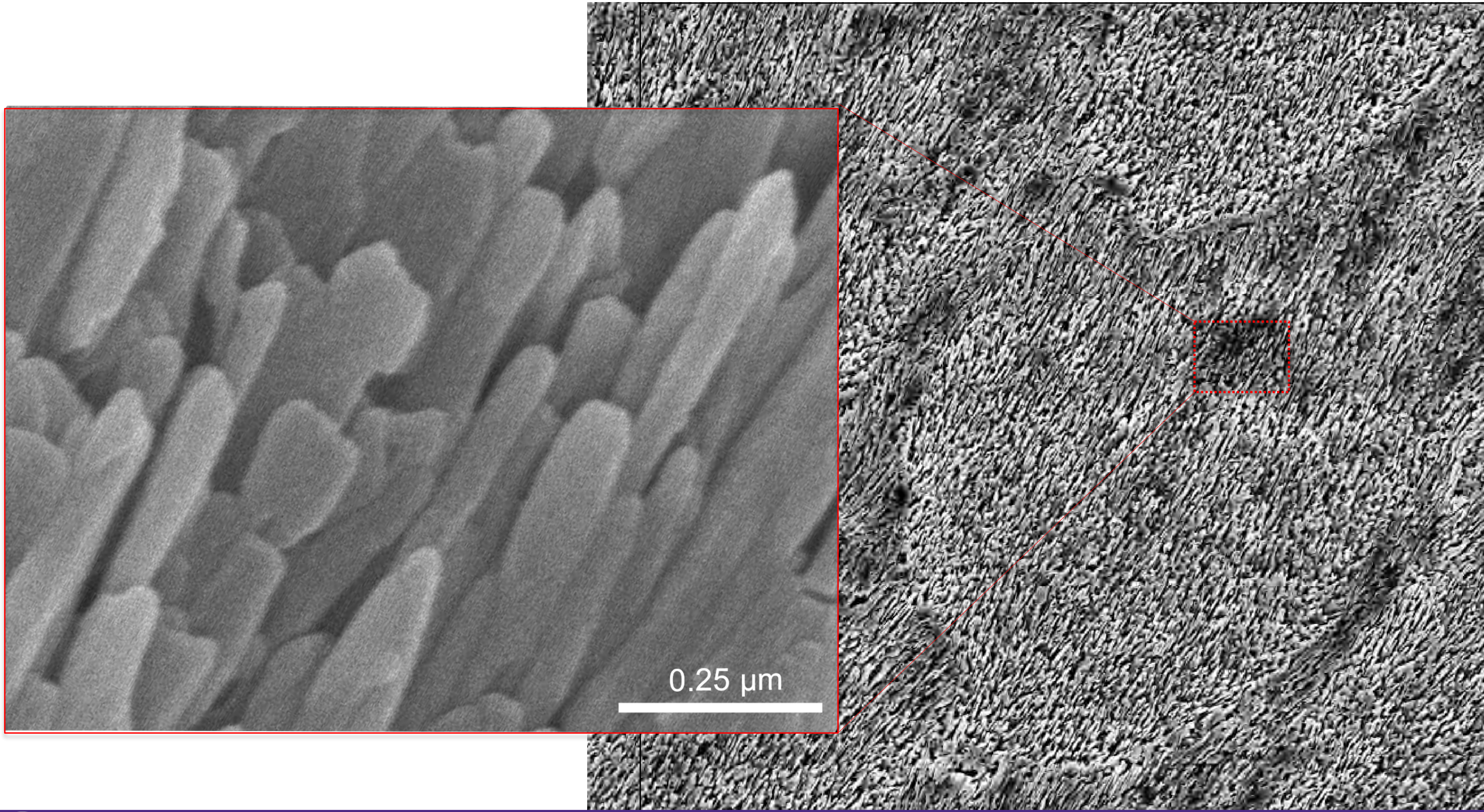


Complex 3D Hierarchical Structure across Length Scales

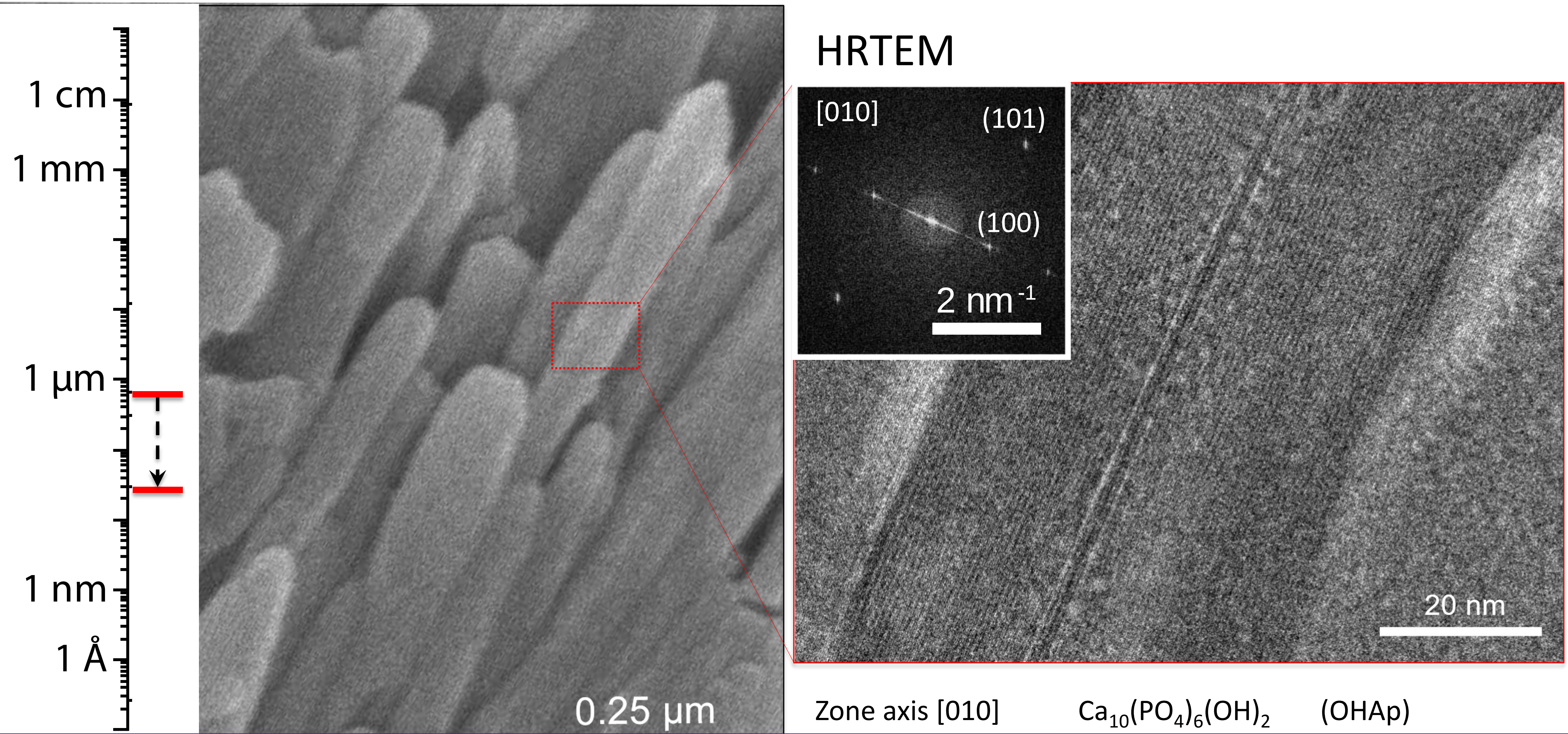


Complex 3D Hierarchical Structure across Length Scales



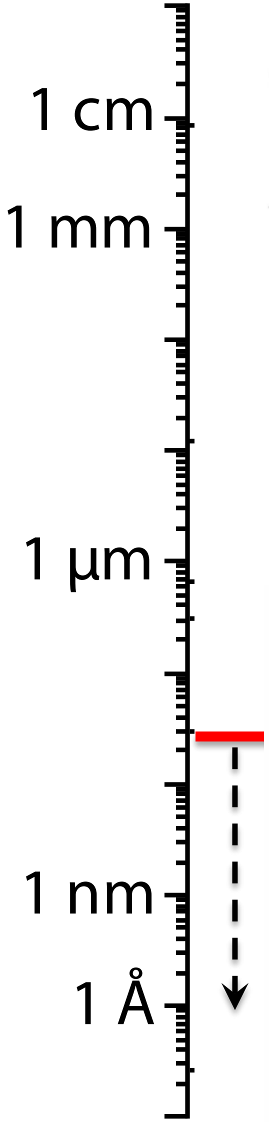


Complex 3D Hierarchical Structure across Length Scales

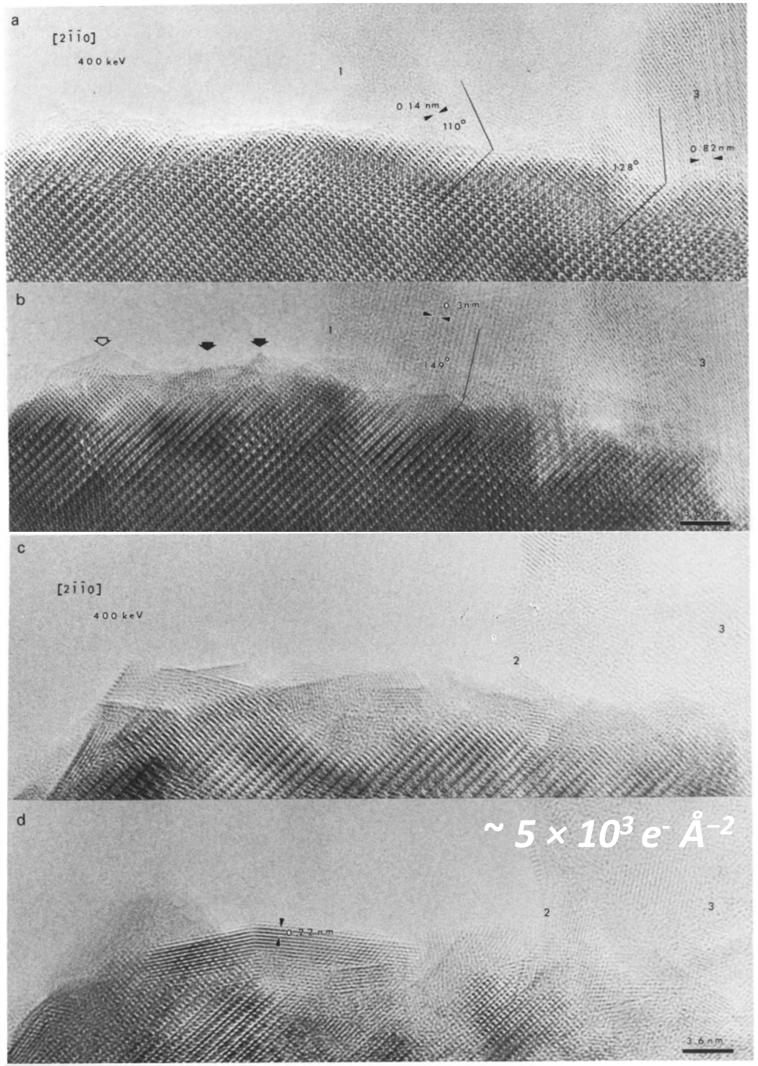


Zone axis [010] $Ca_{10}(PO_4)_6(OH)_2$ (OHAp)

Towards the Atomic Scale – Electron Beam Damage in Enamel & OHAp



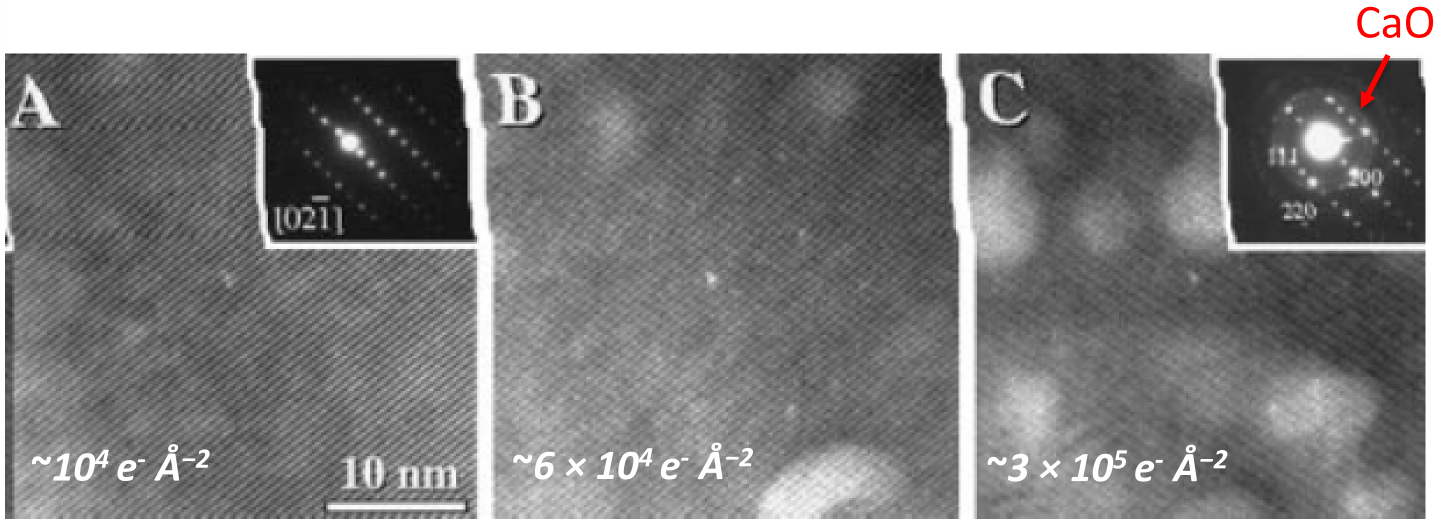
Enamel



OHAp

A. F. Marshall, K. R. Lawless, *J Dent Res* **60** 1731 (1981)

E.F. Brès *et al.*, *Ultramicroscopy* **35** 305 (1991)

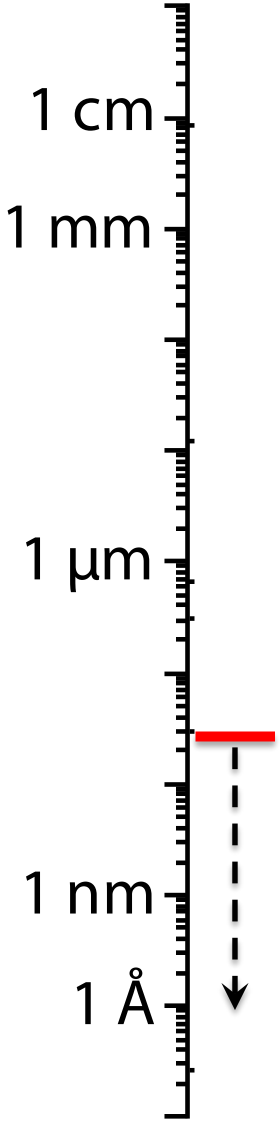


E.F. Brès *et al.*, *Eur Phys J Appl Phys* **67** 20401 (2014)

A. Meldrum *et al.*, *American Mineralogist*, **82**, 858 (1997)

-mass loss
-beam-induced diffusion
- recrystallization

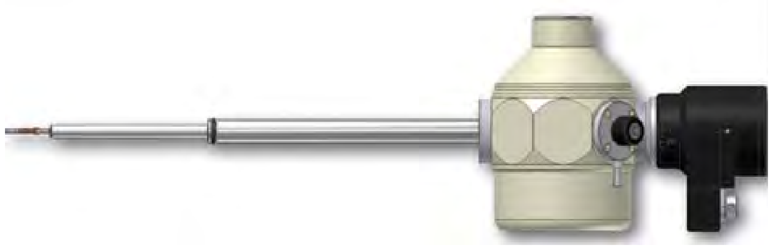
Necessary using lower dose (minimize radiolysis) to study OHAp/enamel samples at high resolution



Cs-corrected Cryo-STEM

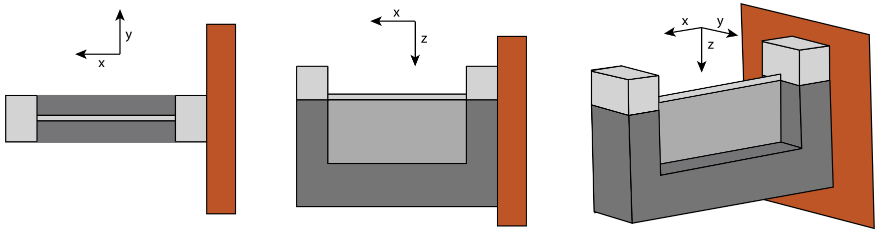
1) STEM at 300 kV; low beam current (2.0-8.5 pA) and short dwell times (1-2 µs) (<900 e$^-$ Å^{-2} per image at highest magnification)

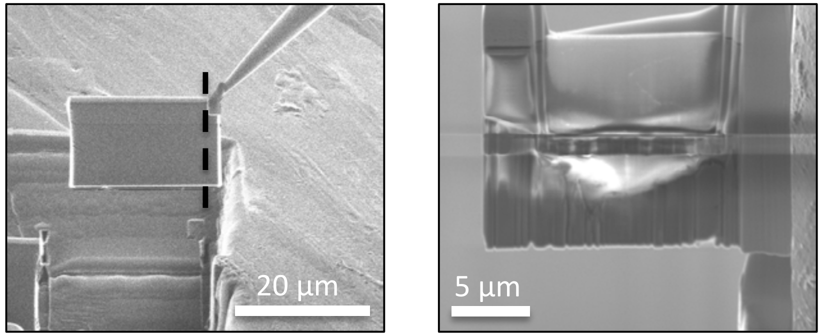
2) cooling the specimen down to **liquid N_2 temperature** reduces damage by inelastic scattering and specimen contamination

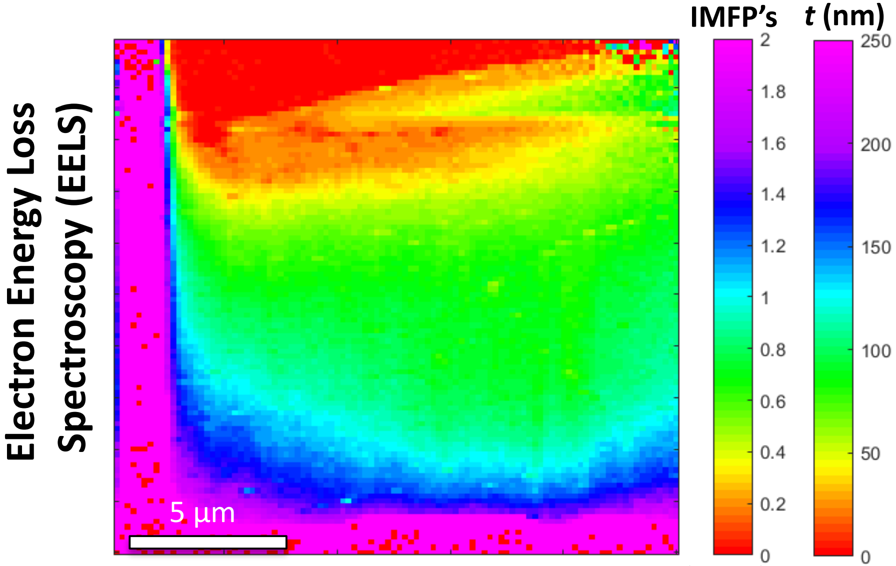


R.F. Egerton *et al. Micron* **35** 399 (2004)

3) Thin section (FIB-SEM)

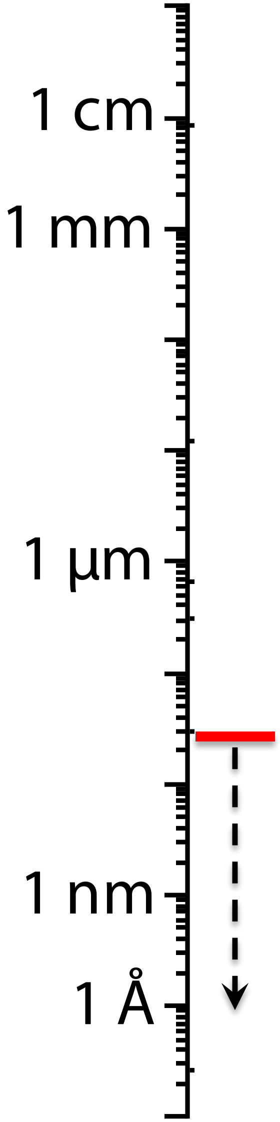






T. Malis *et al., J Electron Microsc Tech* **8** 193 (1988)

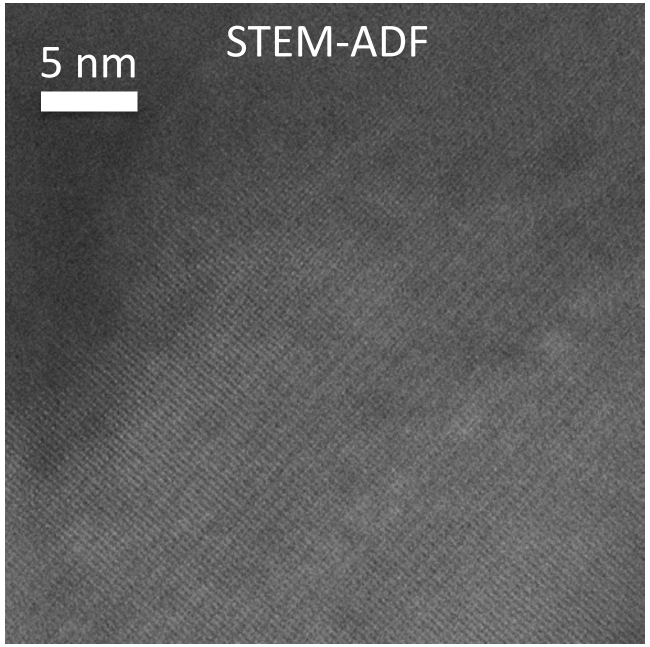
Image registration of low signal-to-noise (S/N) cryo-STEM data



Single image
Low S/N

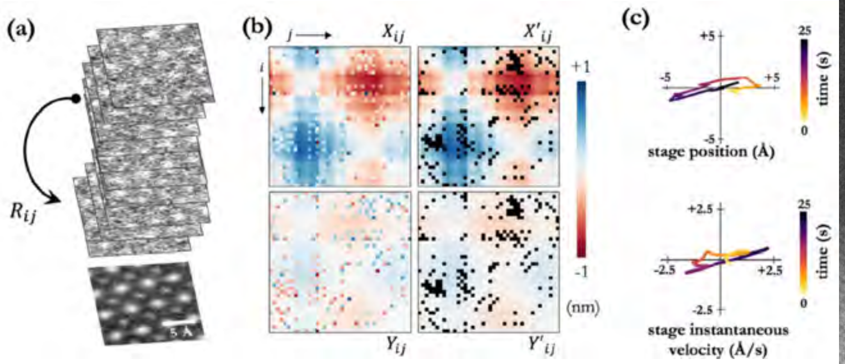
Cross correlation

Registered image
High S/N

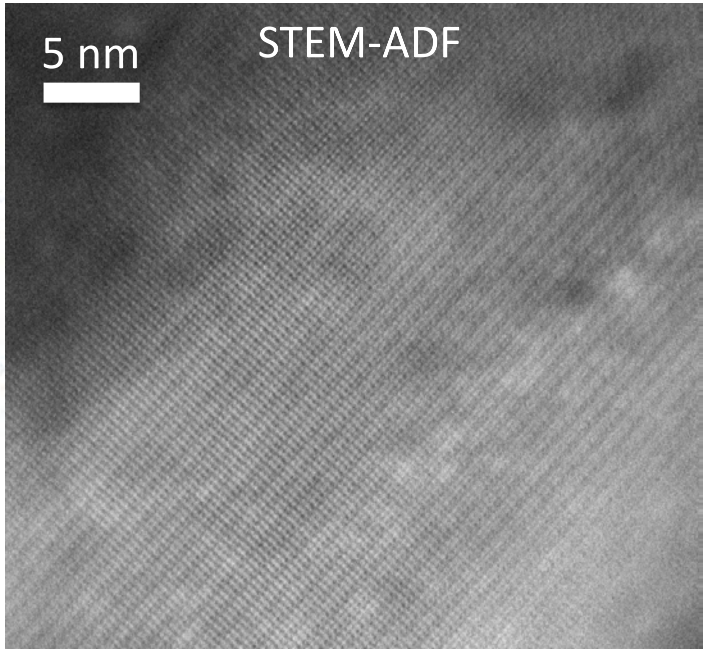


1 image

Optimized for low S/N cryo-STEM data



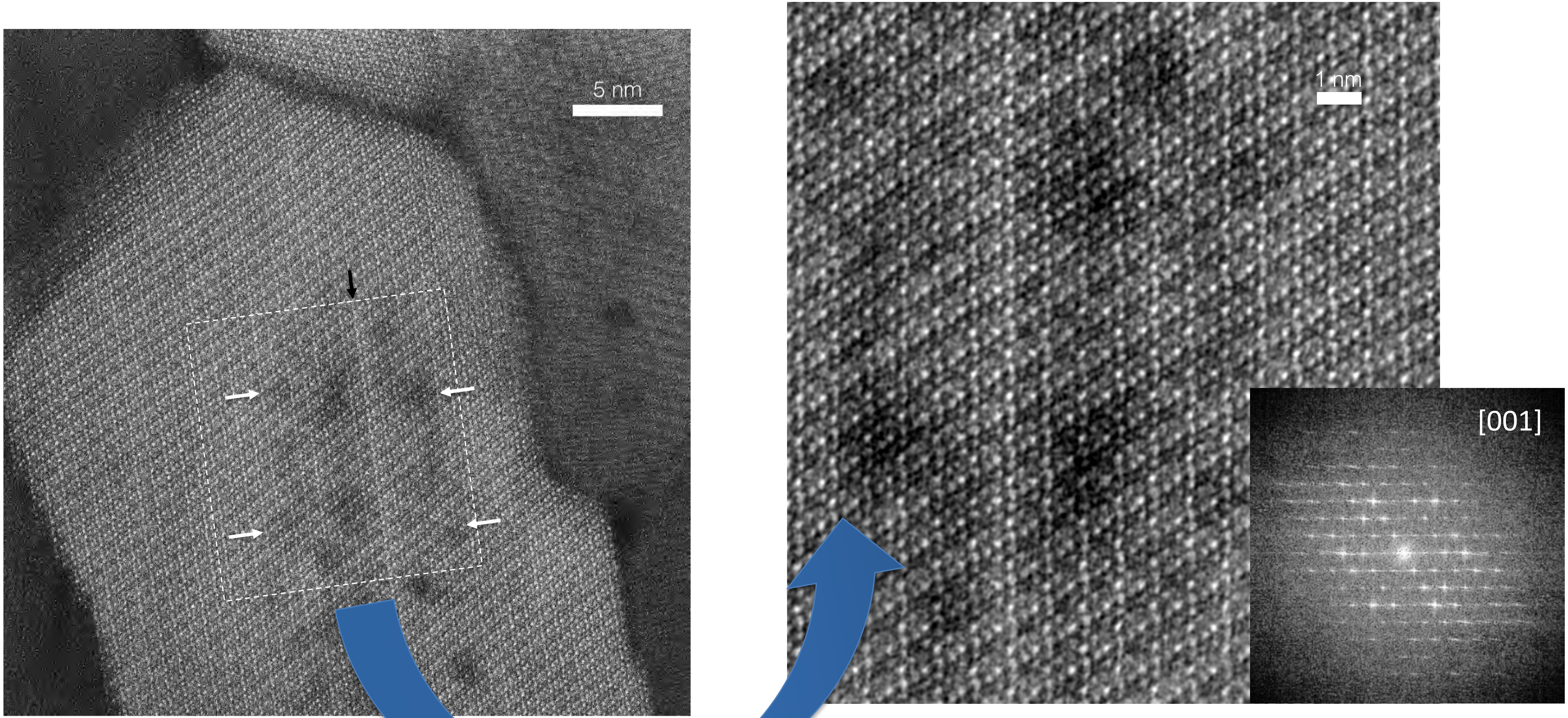
B.H. Savitzky *et al. Ultramicroscopy* **191** 56 (2018)



9 images **total dose 7.8×10^3 e$^-$Å^{-2}**

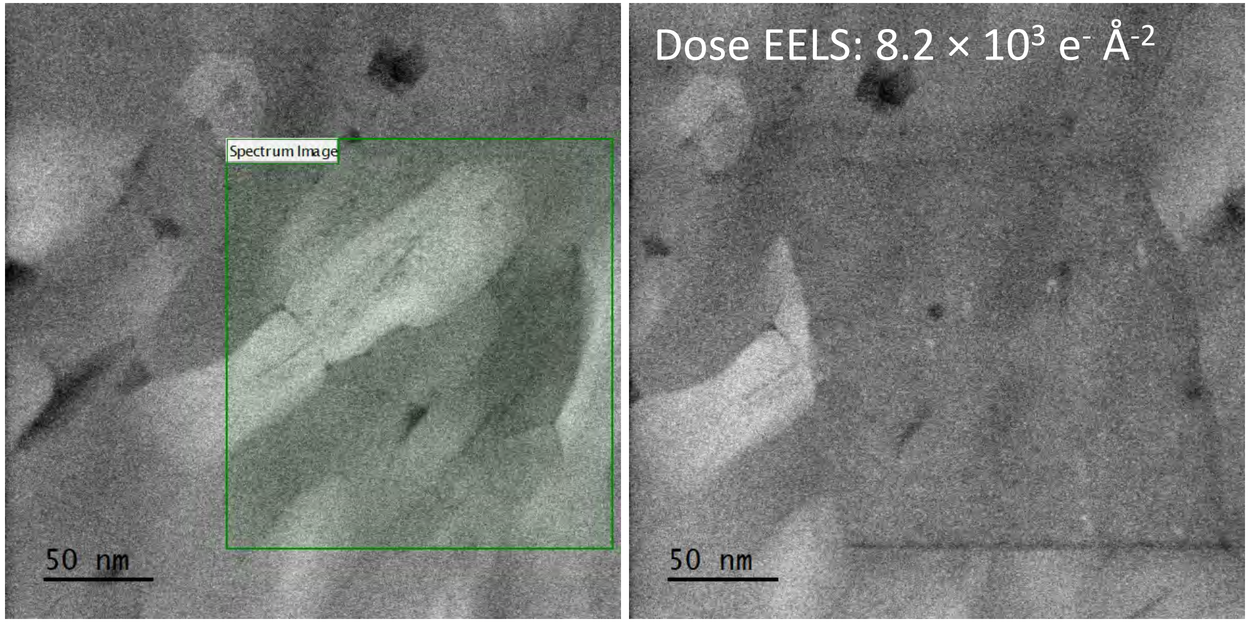
High S/N registered images are achieved at 300 kV and with the sample cooled to near liquid N_2 temperature

Atomic Resolution cryoSTEM-ADF image of Enamel Crystallite

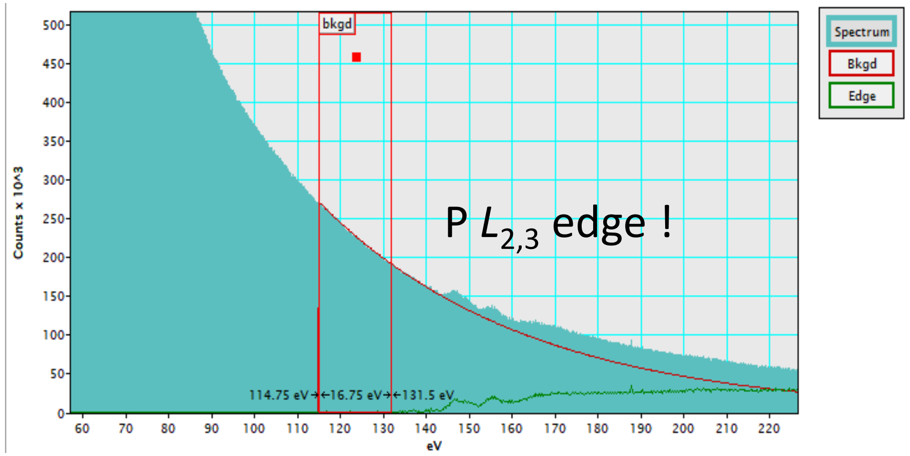


EELS of Enamel Crystallites: Ultrascan CCD vs Gatan K2 DED

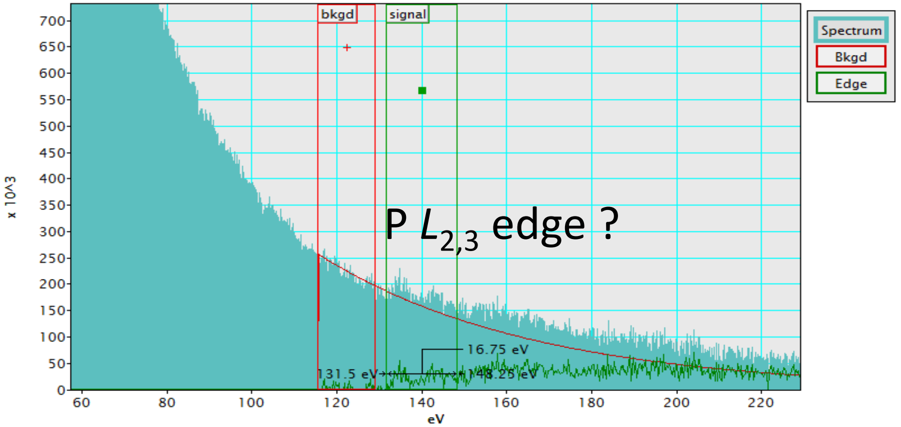
UltraScan® (US) 1000 CCD camera



Dose EELS: 8.2×10^3 $e^- Å^{-2}$

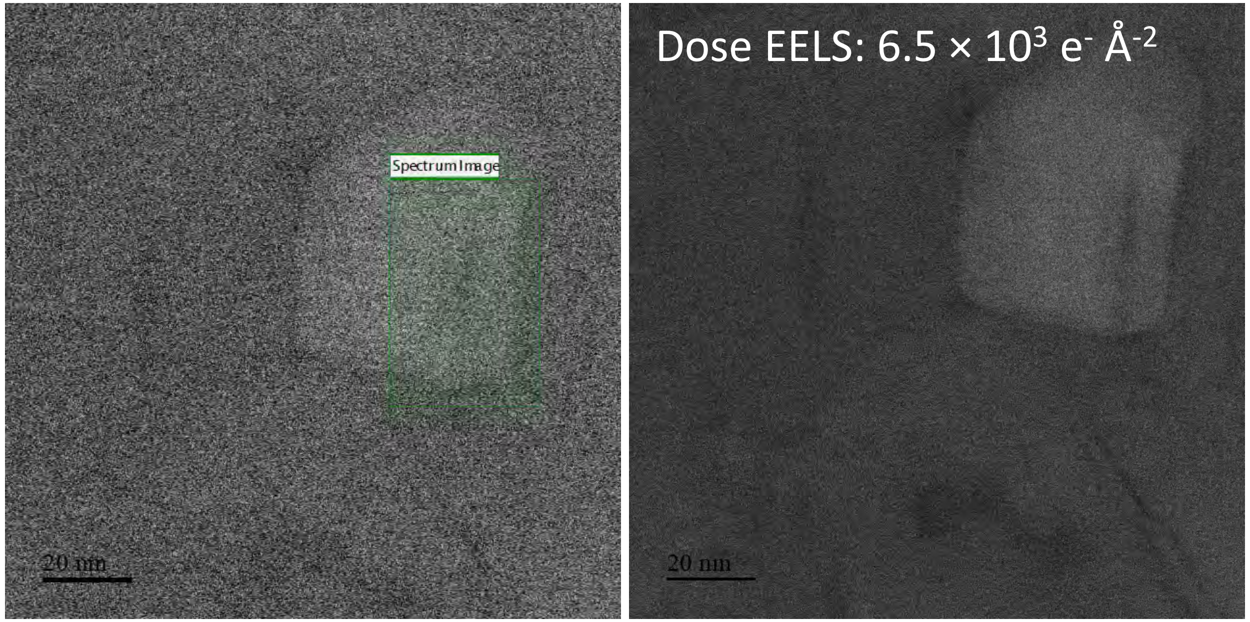


P $L_{2,3}$ edge !



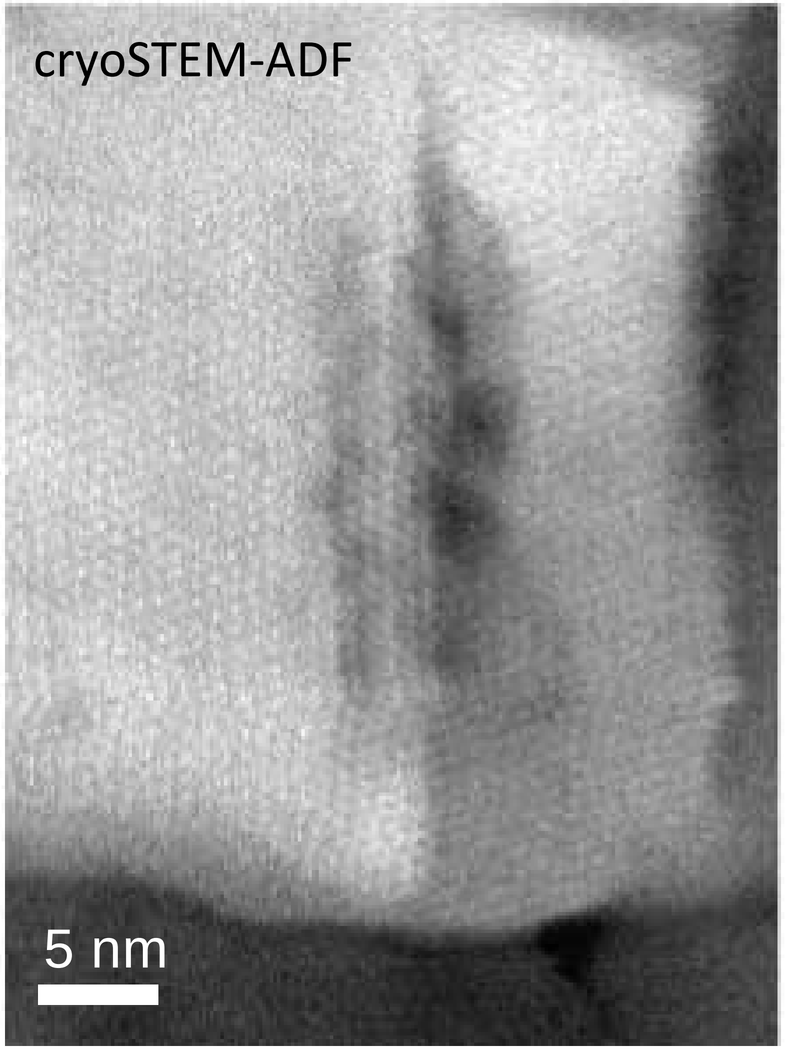
P $L_{2,3}$ edge ?

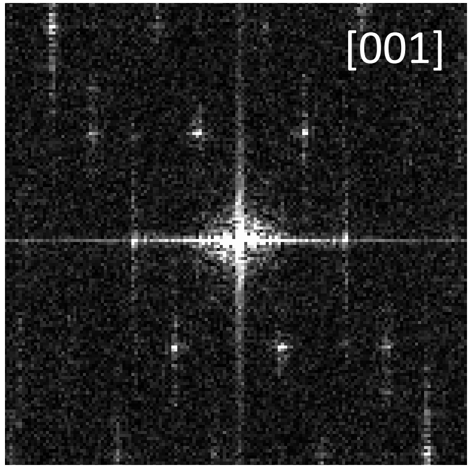
Gatan K2

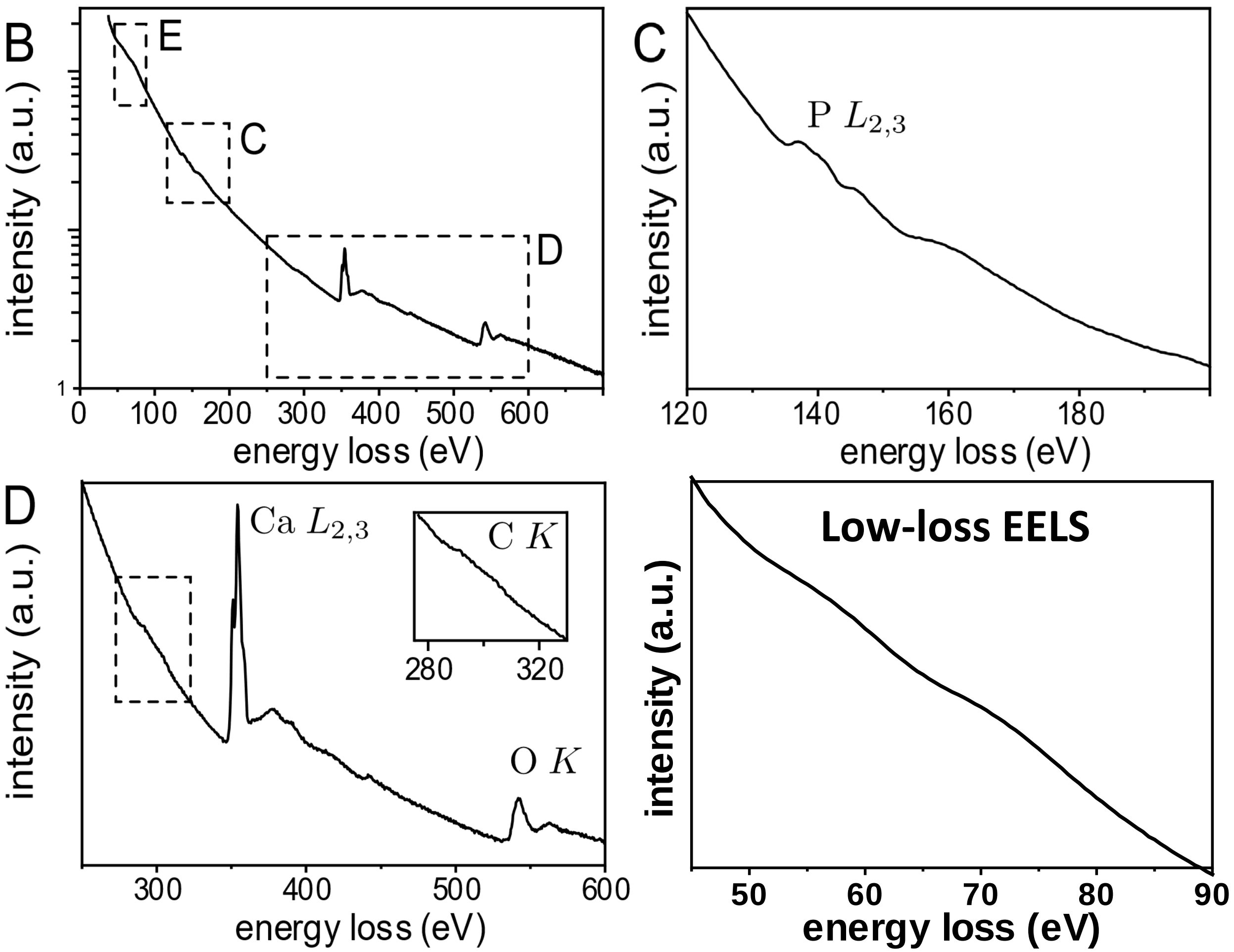


Dose EELS: 6.5×10^3 $e^- Å^{-2}$

EELS of Enamel Crystallites - Gatan K2 DED

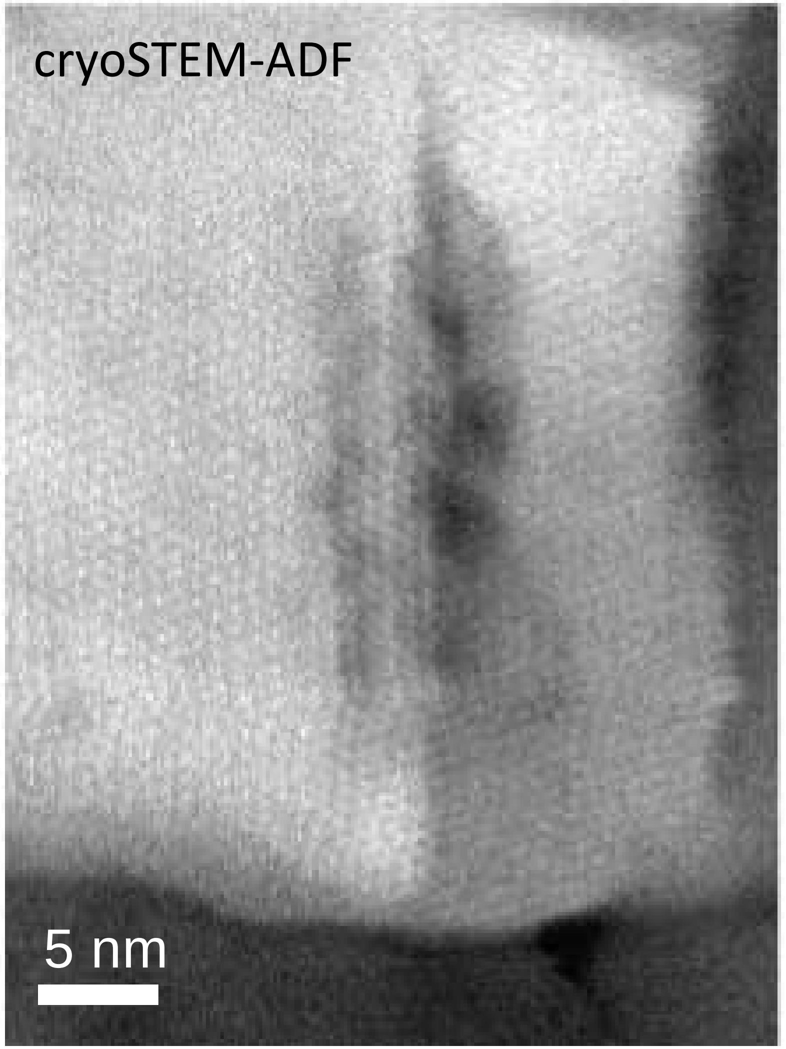


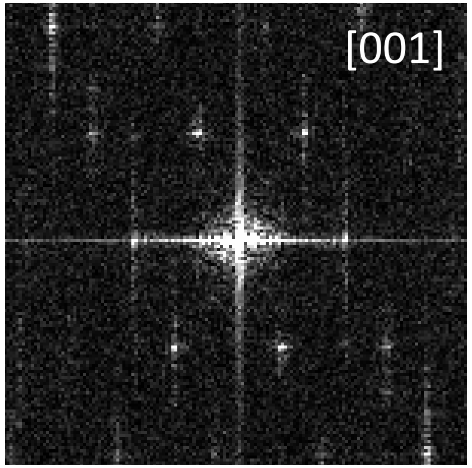


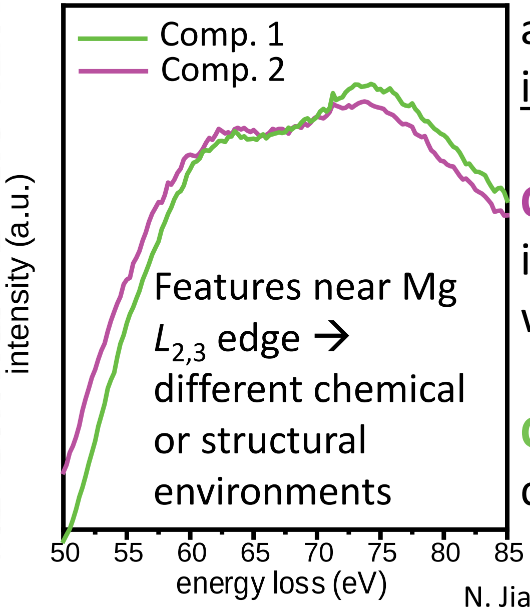


K.A. DeRocher†, P.J.M. Smeets†, B.H. Goodge, M.J. Zachman, P.V. Balachandran, L. Stegbauer, M.J. Cohen, L.M. Gordon, J.M. Rondinelli, L.F. Kourkoutis, D. Joester*, *submitted*

Mg EELS Components Reveal a Core-Shell Structure within Crystallites







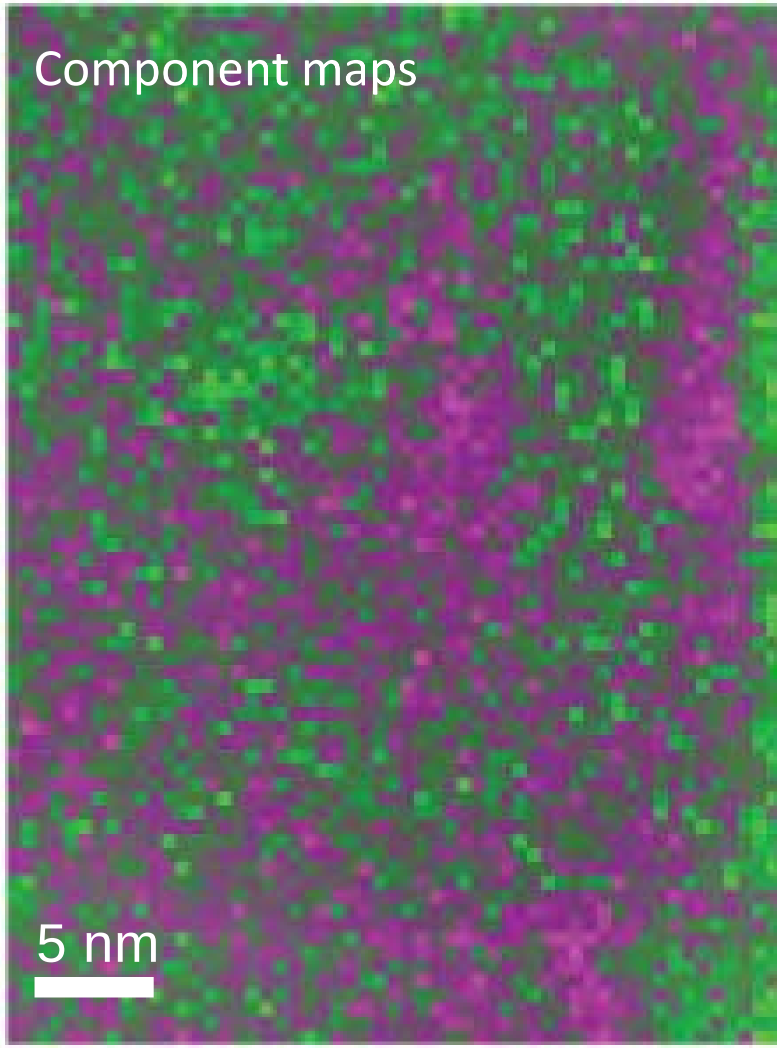
Features near Mg $L_{2,3}$ edge → different chemical or structural environments

EELS low-loss spectral analysis

Multivariate curve resolution (MCR) was used to decompose low loss spectra into component profiles and determine intensity maps

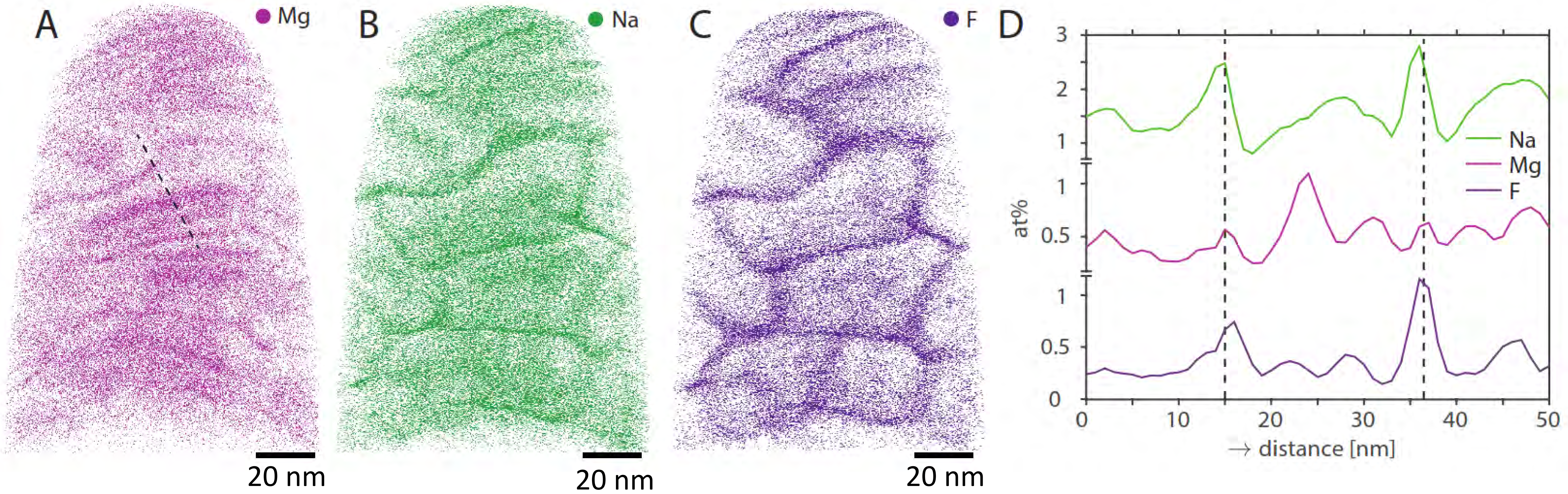
Comp. 2 primarily in intergranular regions; within crystallite core

Comp. 1 within crystallites



N. Jiang *et al.*, *Ultramicroscopy* (2008) **109**, 122

Laser-Assisted APT Shows Mg Gradients within Core



K.A. DeRocher[†], P.J.M. Smeets[†], B.H. Goodge, M.J. Zachman, P.V. Balachandran, L. Stegbauer, M.J. Cohen, L.M. Gordon, J.M. Rondinelli, L.F. Kourkoutis, D. Joester*, *submitted*

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- Dr. Xiaobing Hu
- NU*ANCE* staff

Cornell University

- Dr. Mick Thomas

KOURKOUTIS ELECTRON MICROSCOPY GROUP

- **Prof. Lena Kourkoutis**
- Berit Goodge
- Dr. Michael Zachman

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Platform for the Accelerated Realization, Analysis, & Discovery of Interface Materials
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- Dr. Don Werder

Joester group

- **Prof. Derk Joester**
- Karen DeRocher
- Michael J. Cohen
- Dr. Linus Stegbauer

Rondinelli group

- **Prof. James M. Rondinelli**
- Prasanna V. Balachandran

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R03 DE025303-01

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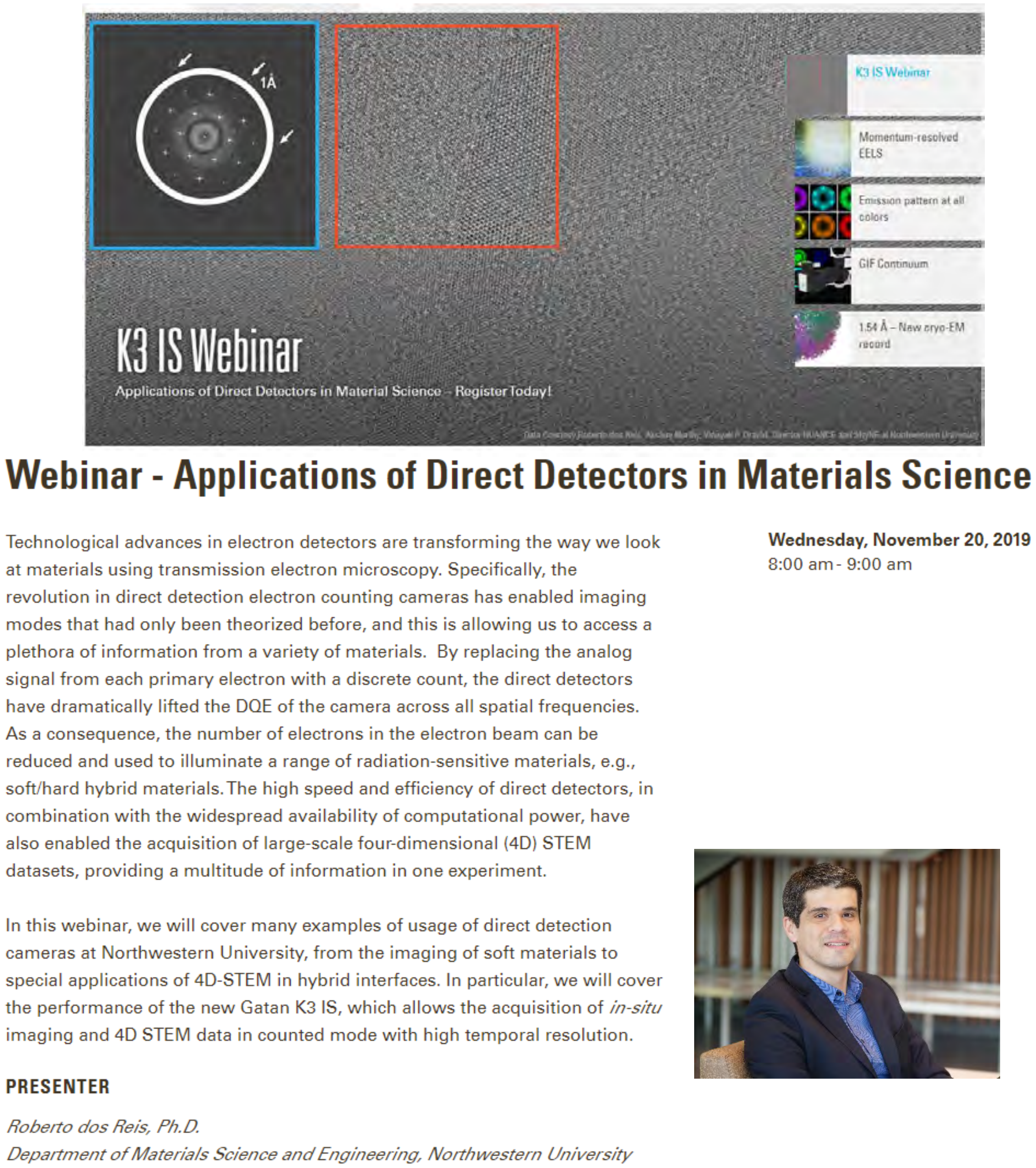
What Applications of Direct Detectors in Material Science

When Nov 20 2019 8:00 AM - 9:00 AM (PST)



Webinar - Applications of Direct Detectors in Materials Science

Wednesday, November 20, 2019
8:00 am - 9:00 am

Technological advances in electron detectors are transforming the way we look at materials using transmission electron microscopy. Specifically, the revolution in direct detection electron counting cameras has enabled imaging modes that had only been theorized before, and this is allowing us to access a plethora of information from a variety of materials. By replacing the analog signal from each primary electron with a discrete count, the direct detectors have dramatically lifted the DQE of the camera across all spatial frequencies. As a consequence, the number of electrons in the electron beam can be reduced and used to illuminate a range of radiation-sensitive materials, e.g., soft/hard hybrid materials. The high speed and efficiency of direct detectors, in combination with the widespread availability of computational power, have also enabled the acquisition of large-scale four-dimensional (4D) STEM datasets, providing a multitude of information in one experiment.

In this webinar, we will cover many examples of usage of direct detection cameras at Northwestern University, from the imaging of soft materials to special applications of 4D-STEM in hybrid interfaces. In particular, we will cover the performance of the new Gatan K3 IS, which allows the acquisition of *in-situ* imaging and 4D STEM data in counted mode with high temporal resolution.

PRESENTER

Roberto dos Reis, Ph.D.
Department of Materials Science and Engineering, Northwestern University


HYSTER
HYSTER 50
EXIT

Questions?

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