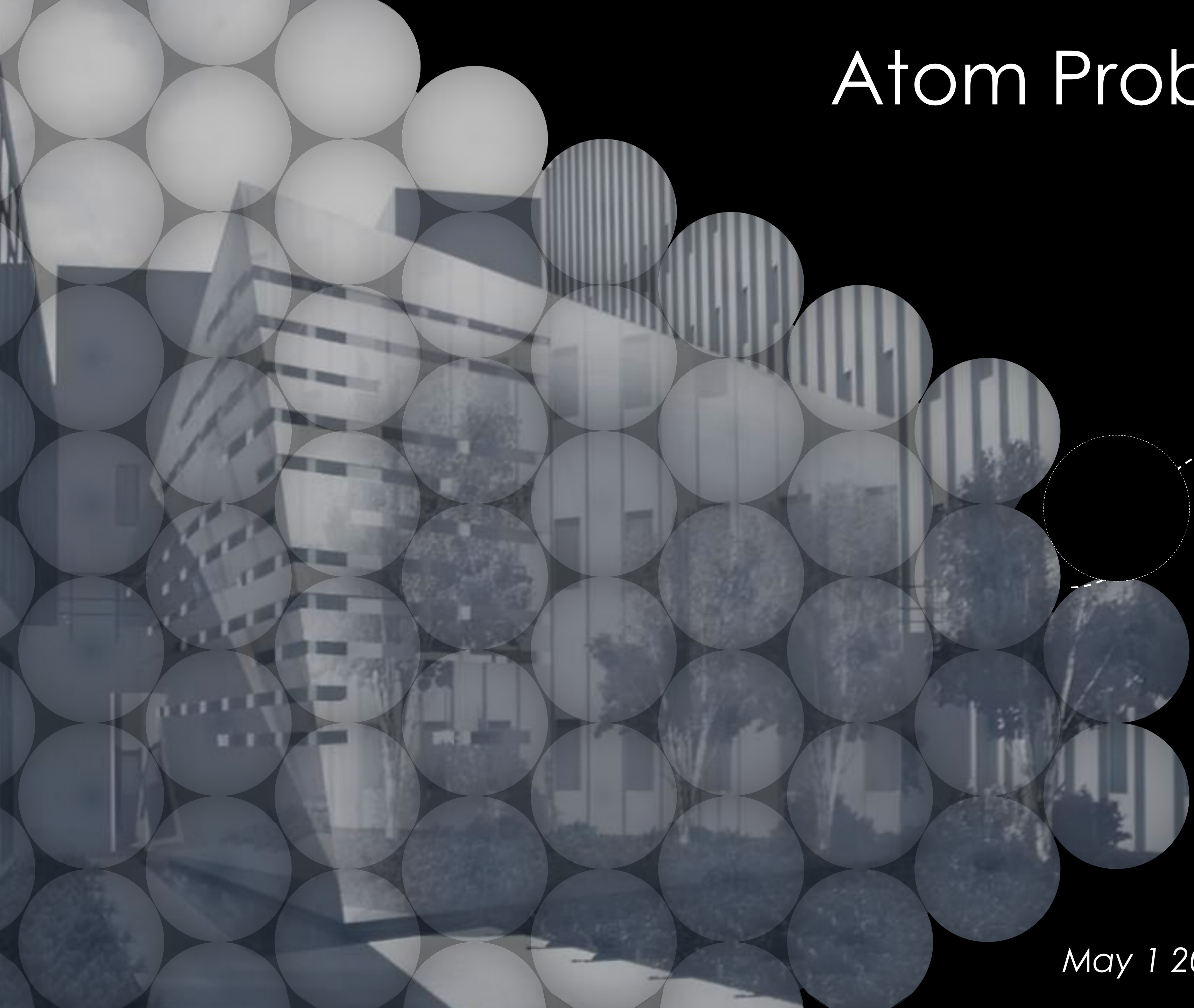


Atom Probe Tomography at the CCEM

Brian Langelier

Surface & Micro-Analysis Workshop

May 1 2019 – University of Western Ontario

I Introduction to APT

What is atom probe? How does it work?

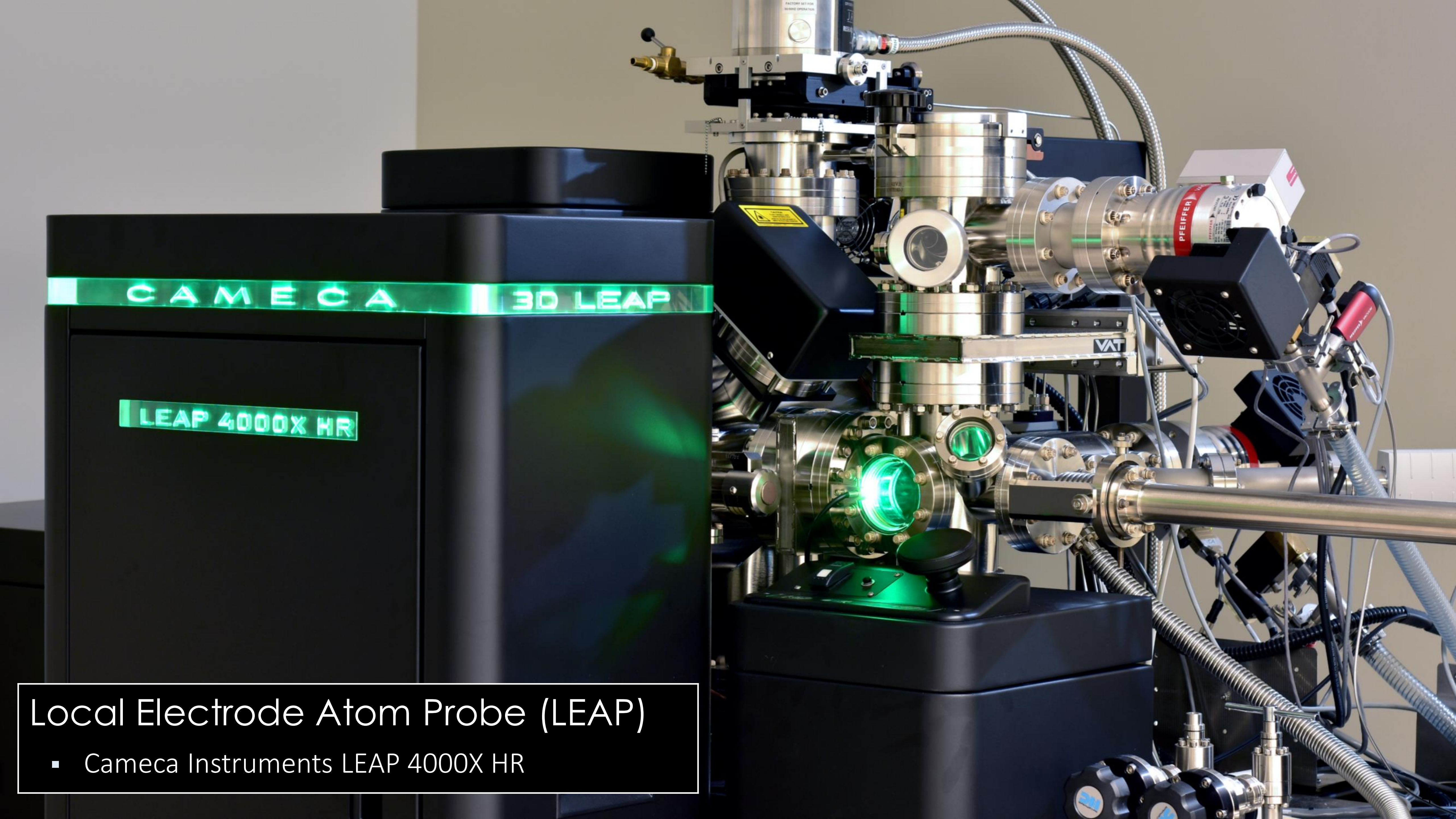
II Examples of APT Applications

Highlights of APT research from the CCEM

III Case Study: Internal Oxidation

APT analysis of sub-surface internal oxidation in Alloy 600

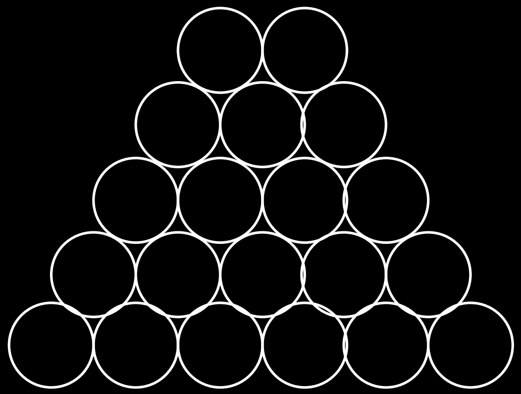
Introduction to APT



Local Electrode Atom Probe (LEAP)

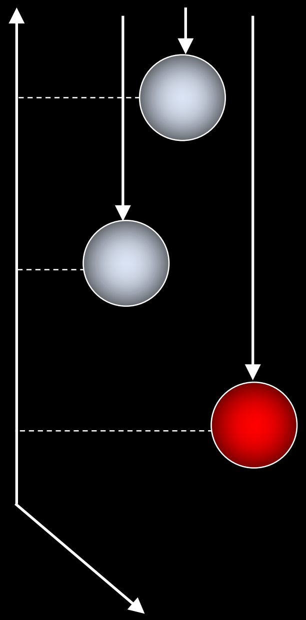
- Cameca Instruments LEAP 4000X HR

Materials Characterization by APT

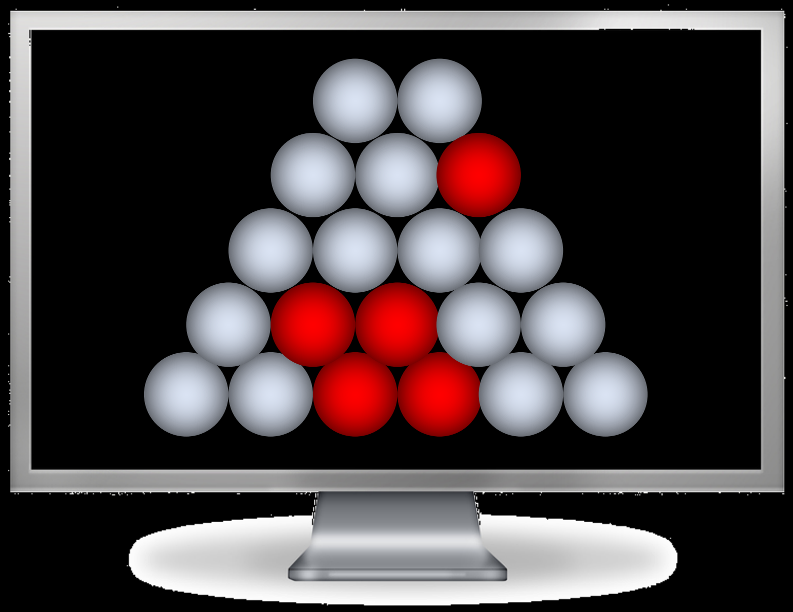


APT sample
(unknown atoms)

A sample is disassembled, atom-by-atom



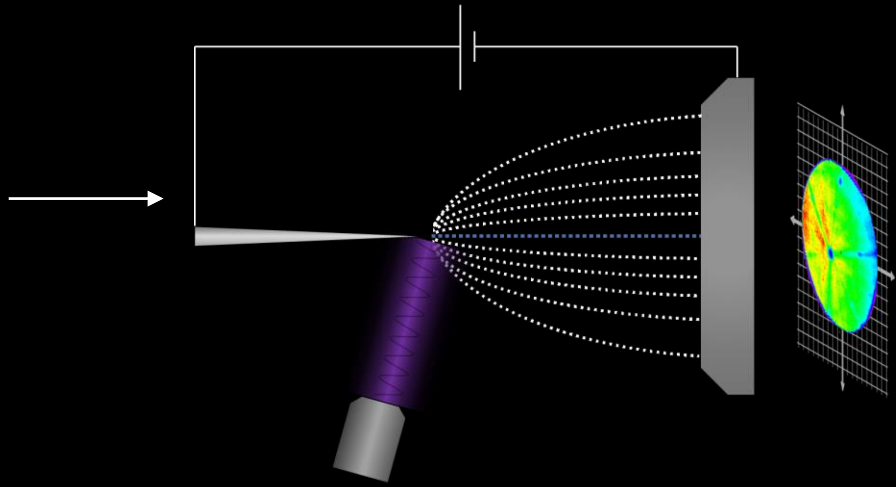
Atoms are measured and identified



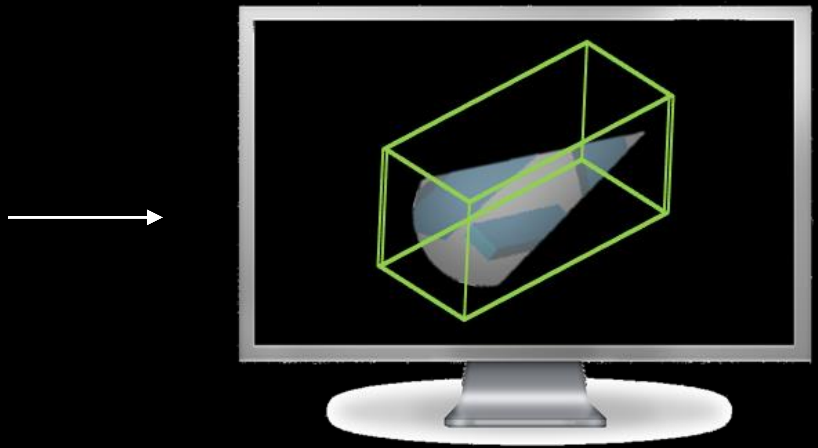
From these data, a 3D model of the original sample is reconstructed, atom-by-atom

An Atom Probe Experiment

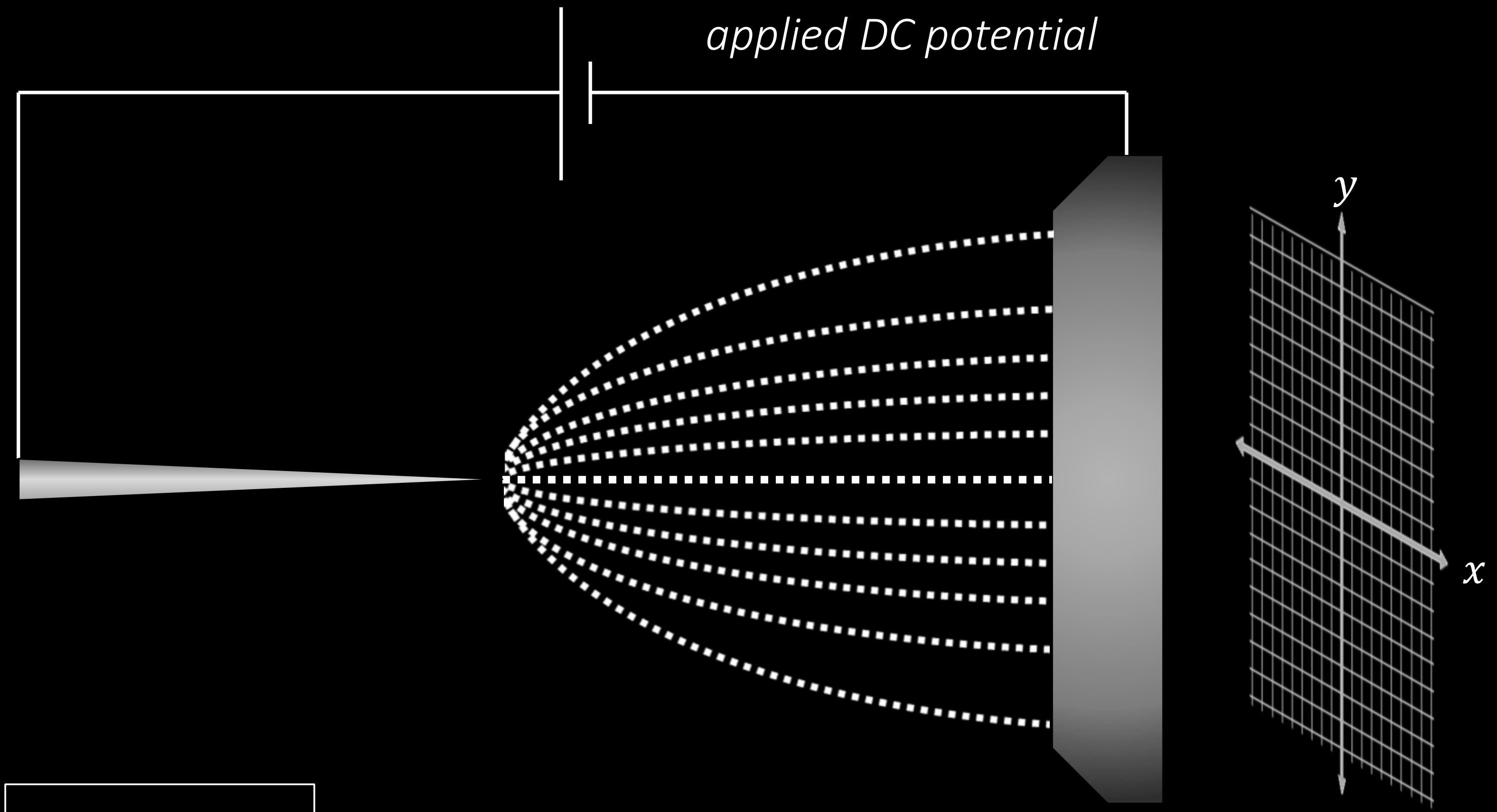
Acquisition



Reconstruction



Field Evaporation

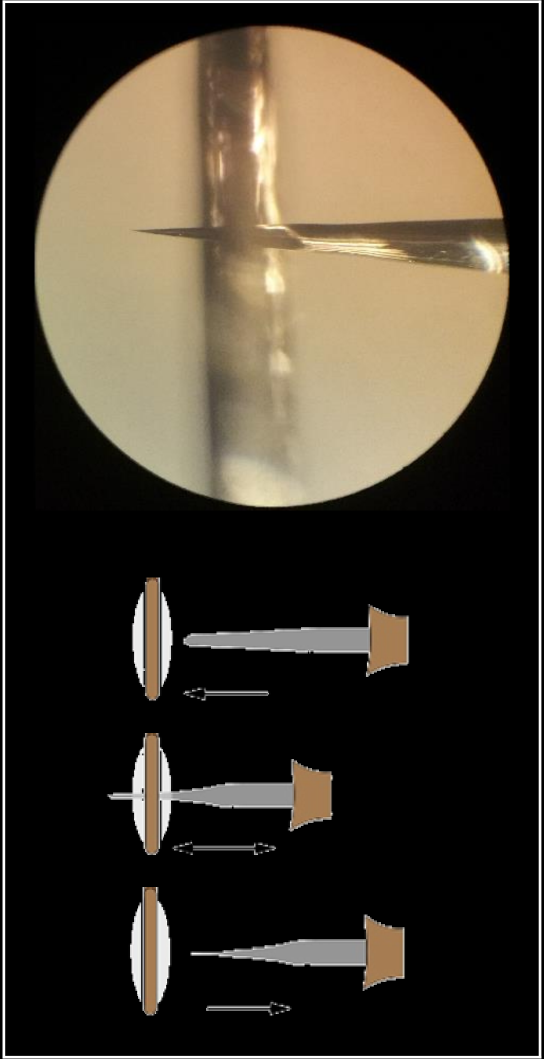


$$F = \frac{V}{k_f R}$$

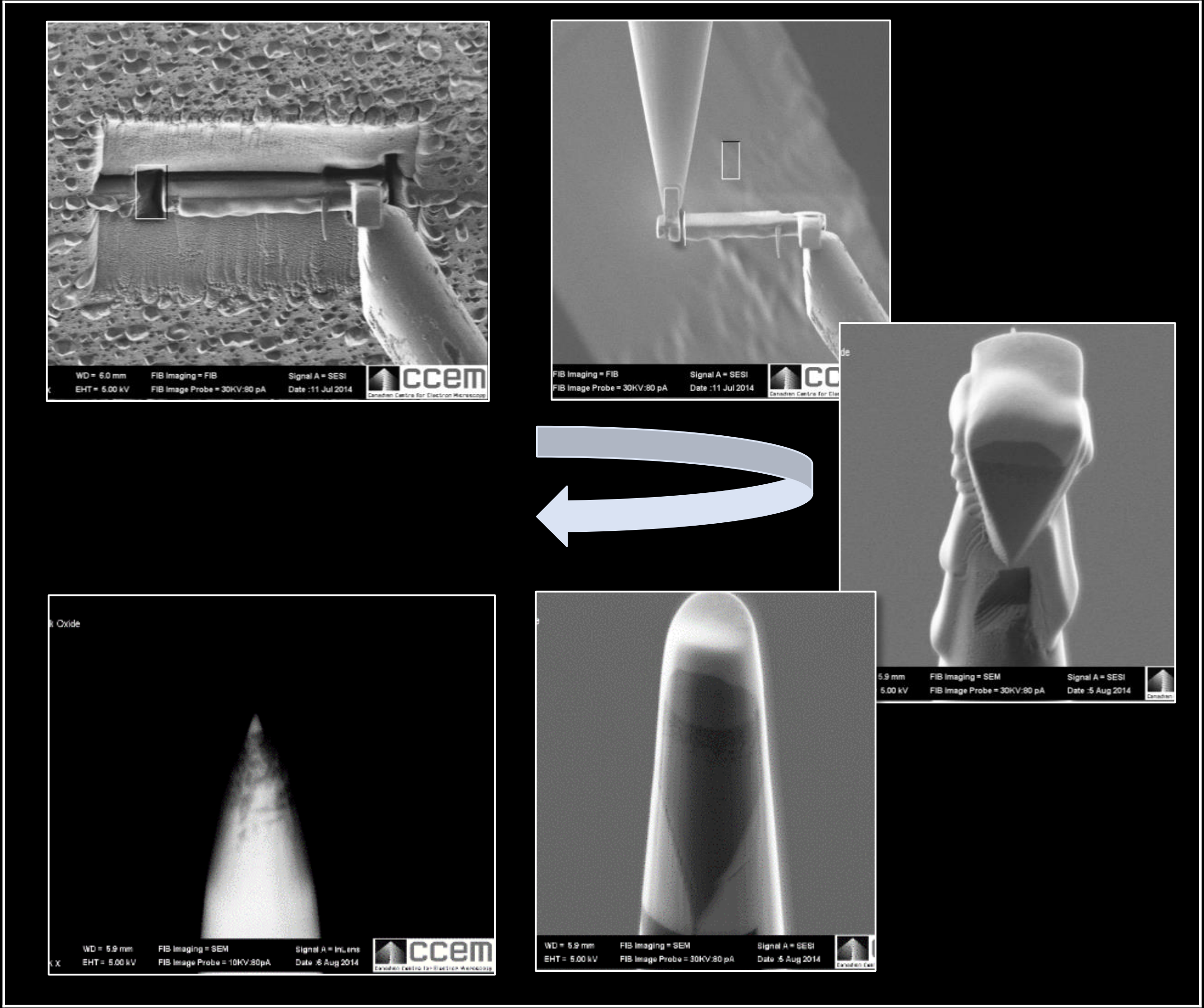
- Field depends on voltage (*V*) and sample radius (*R*)

Specimen Preparation

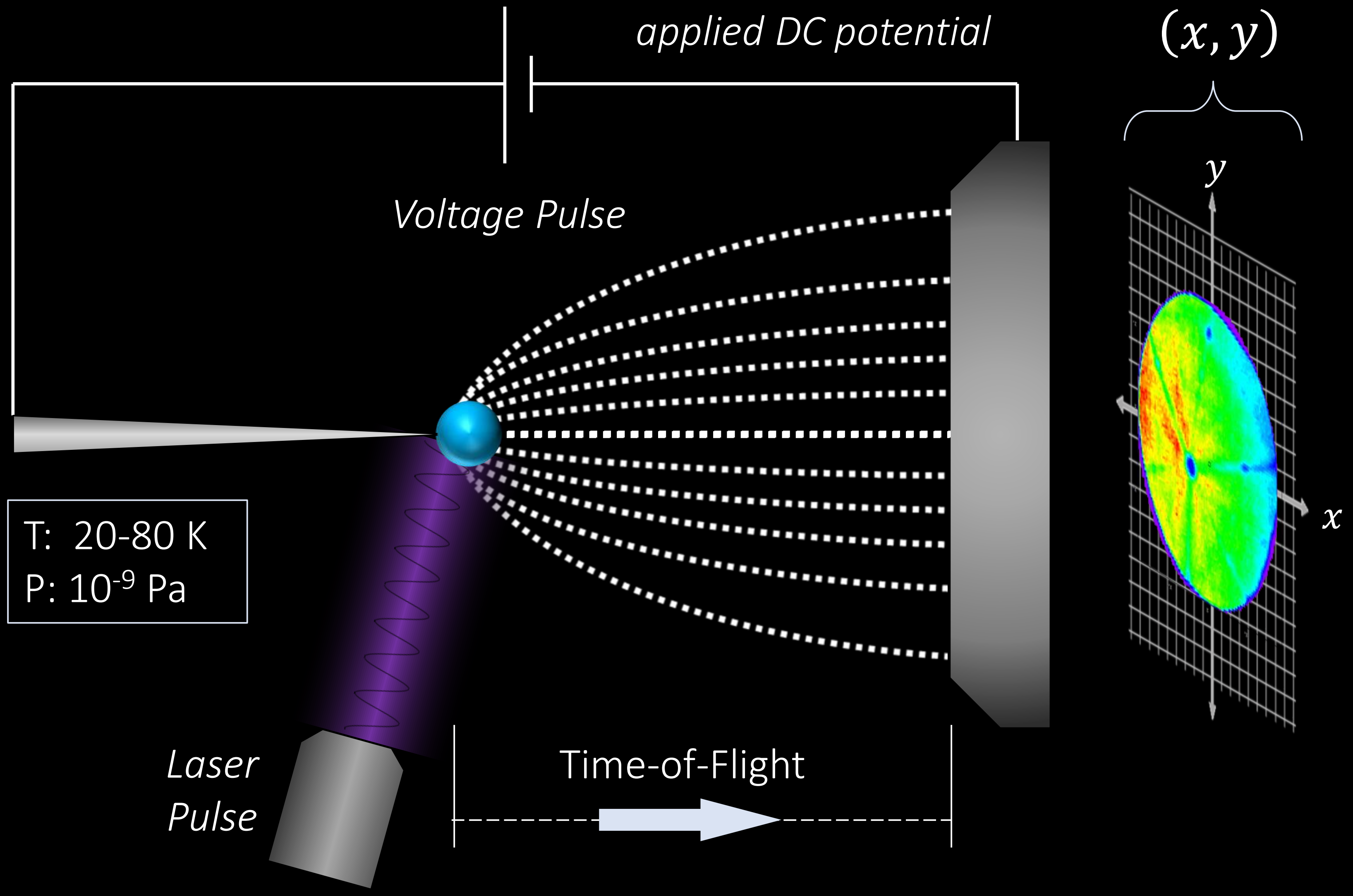
Electropolishing



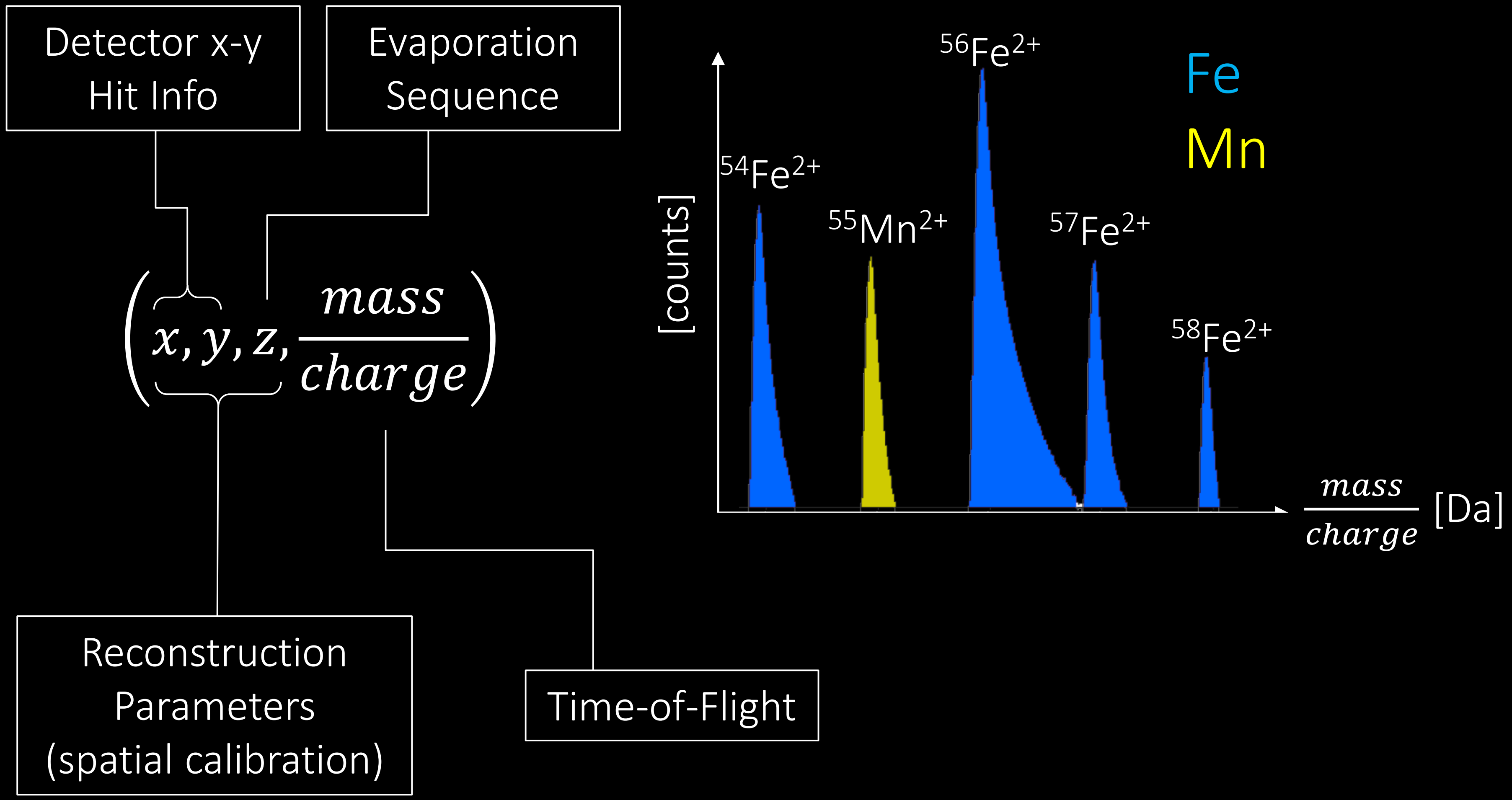
Focused Ion Beam (FIB)



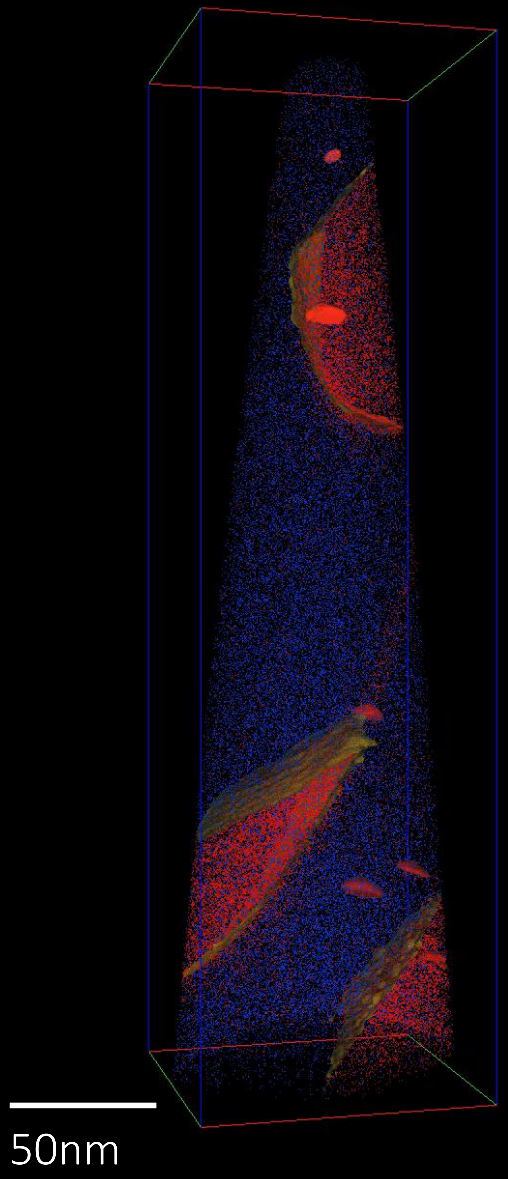
Data Acquisition



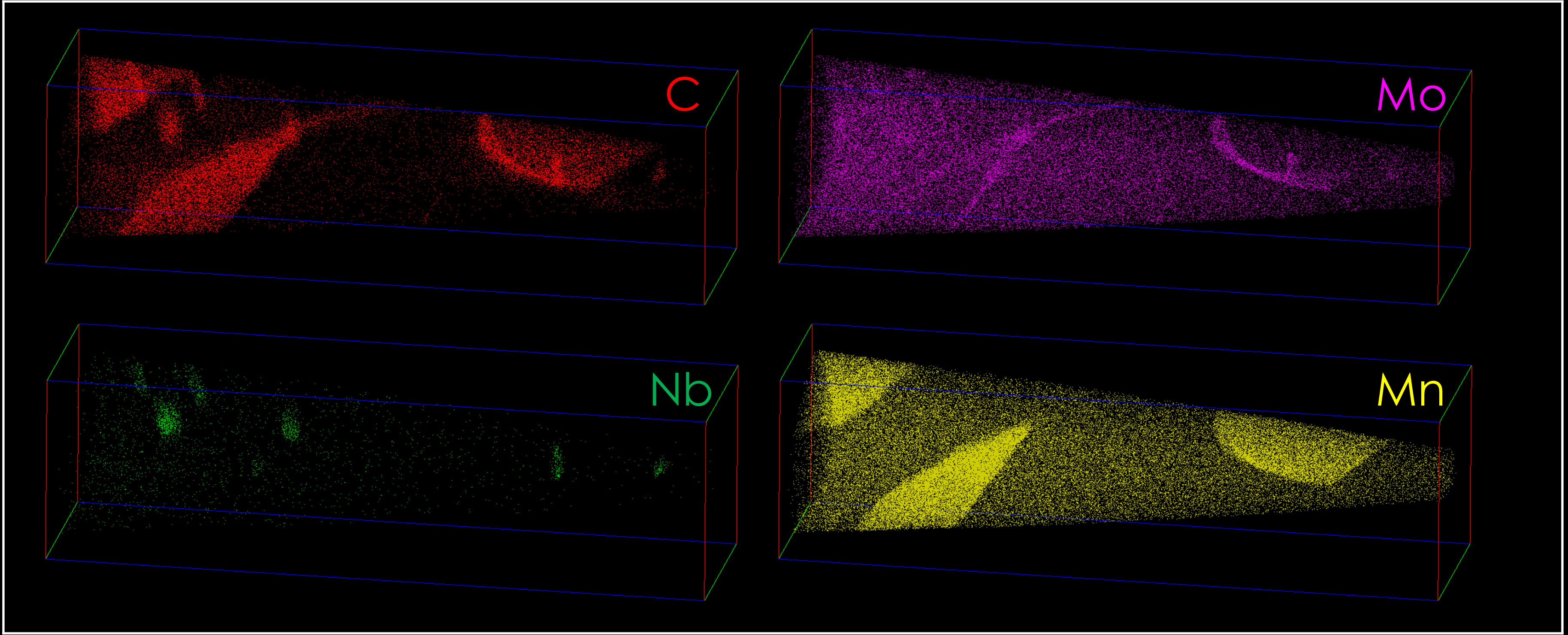
Data Reconstruction



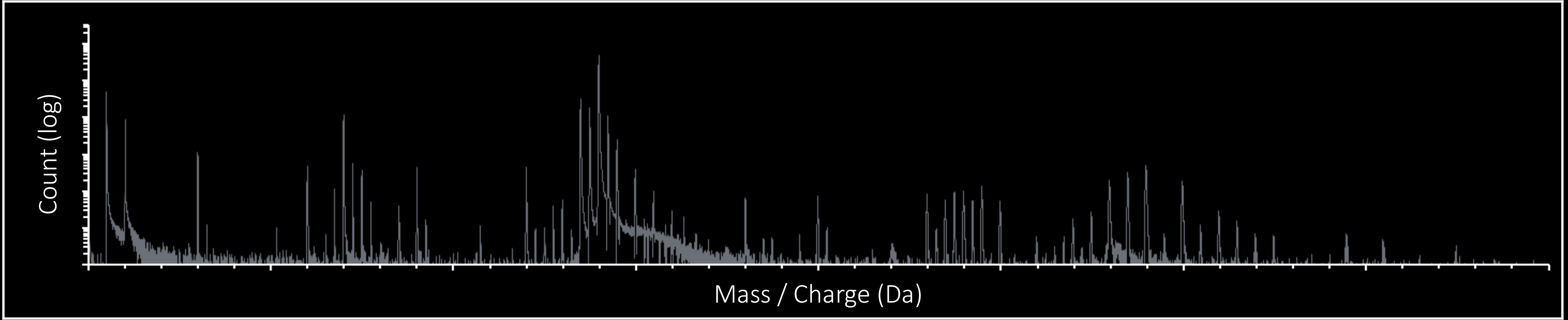
Reconstructed Data



3D Atom Maps



Spectrum



Capabilities

- Sub-nanometer spatial resolution
- Mass resolving power $\left(\frac{M}{\Delta M}\right)$ >1000 at FWHM
- Detectability limit approaching ppm level

  } *Sample/Material Dependant*
- Information provided in 3D
- Able to resolve individual isotopes
- Can analyze a wide variety of samples (laser-pulsing mode)

Limitations

- Detection efficiency <100% (but uniform across the spectrum)
- Peak overlaps in the mass spectrum
  - E.g. $^{14}N^{+}$ (14Da) and $^{28}Si^{2+}$ (14Da)
- Sample **fracture** can limit data yield

Examples of APT Applications

Metals & Alloys

- Steel transformation interfaces
- Carbide formation in pipeline steels
- Precipitation in Mg, Al alloys (6xxx, 7xxx)
- Nanoporous metals (Ag-Au)

Semiconductors

- Si devices (finFETs)
- GaN Nanorods
- RE:SiN
- Si:YAG

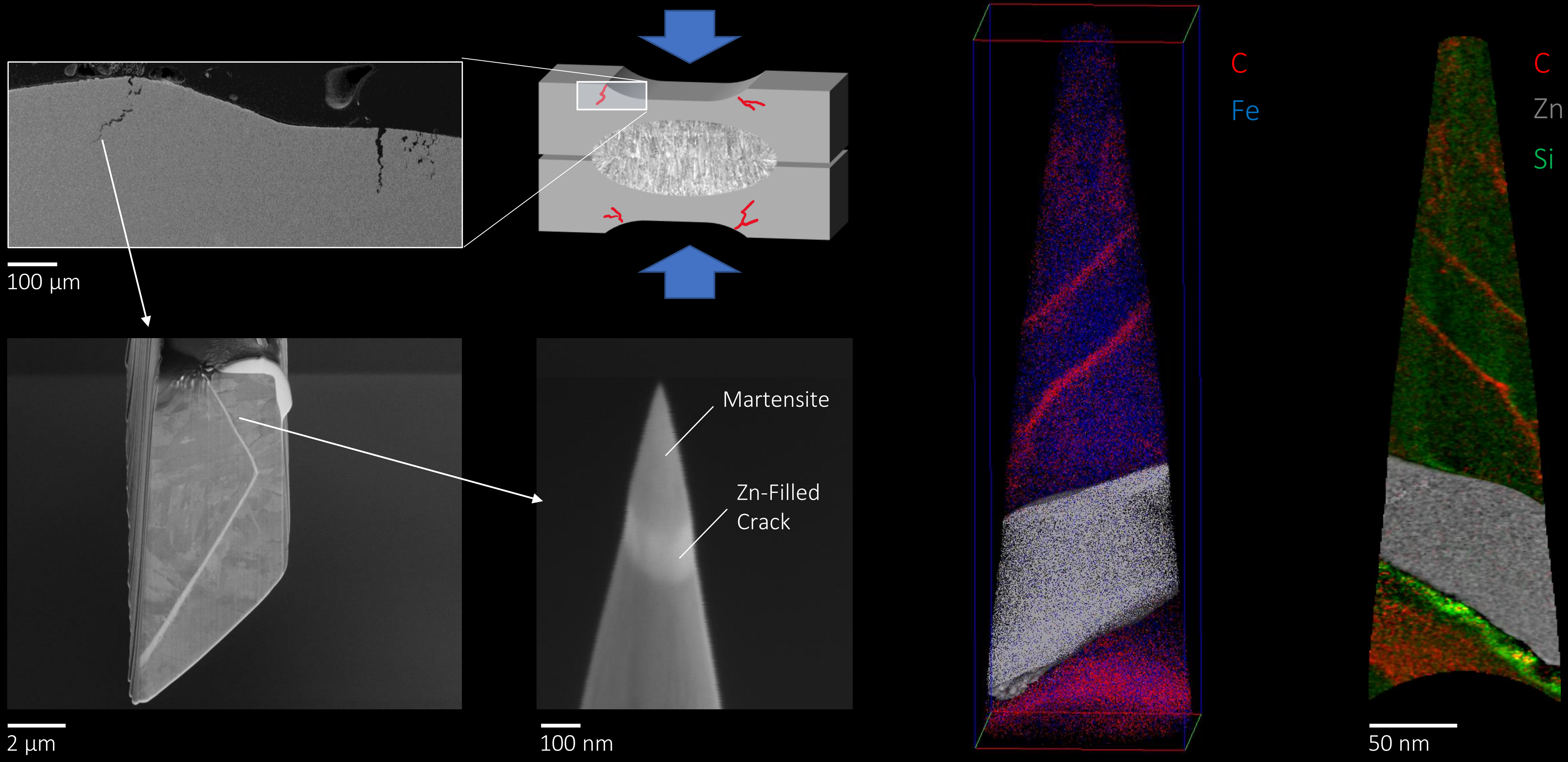
Oxidation & Corrosion

- Internal oxidation Ni Alloy 600
- Surface corrosion Mn/Sn – bearing steel
- Oxidation of galvanized steel
- Stress corrosion cracking Alloy 800

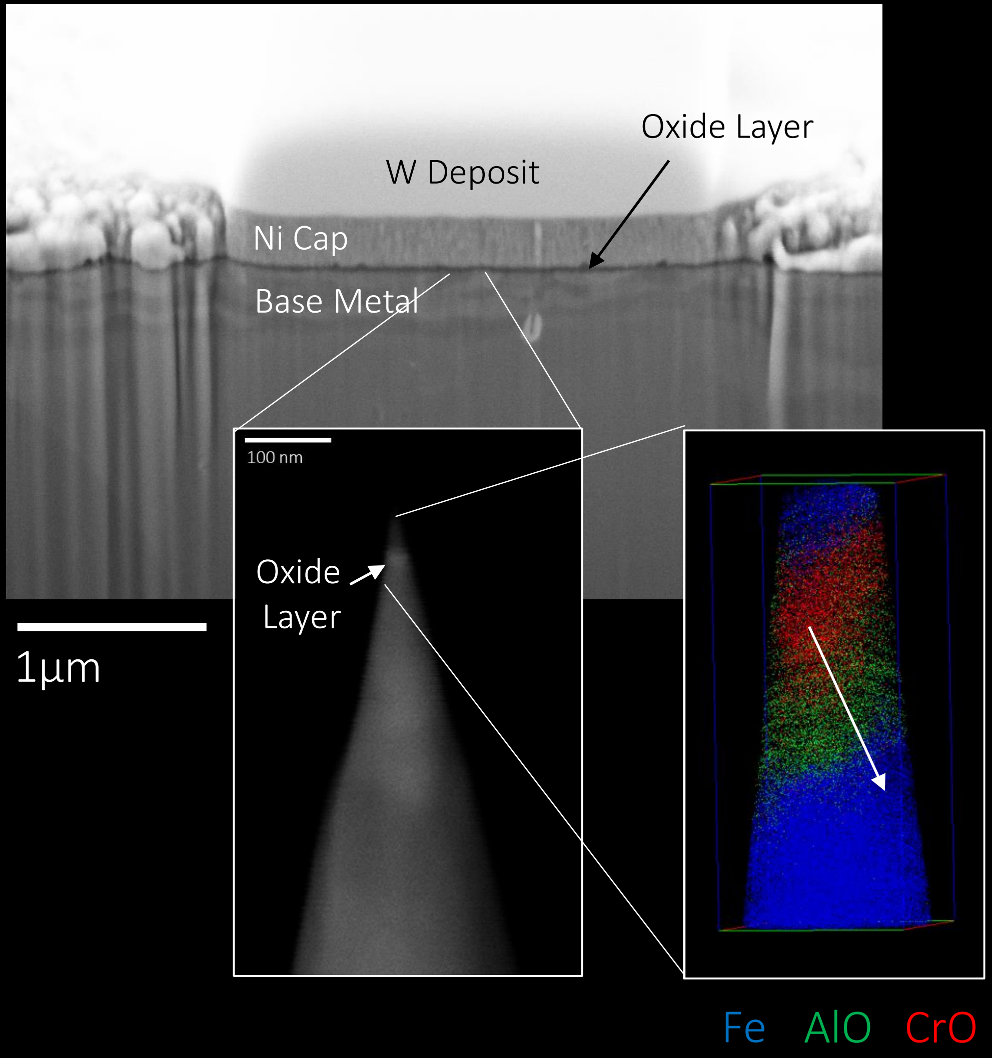
Biological, Mineral, & Ceramic

- Human bone, bone/Ti interface
- Lunar, Martian meteorites
- Zircon
- Cement

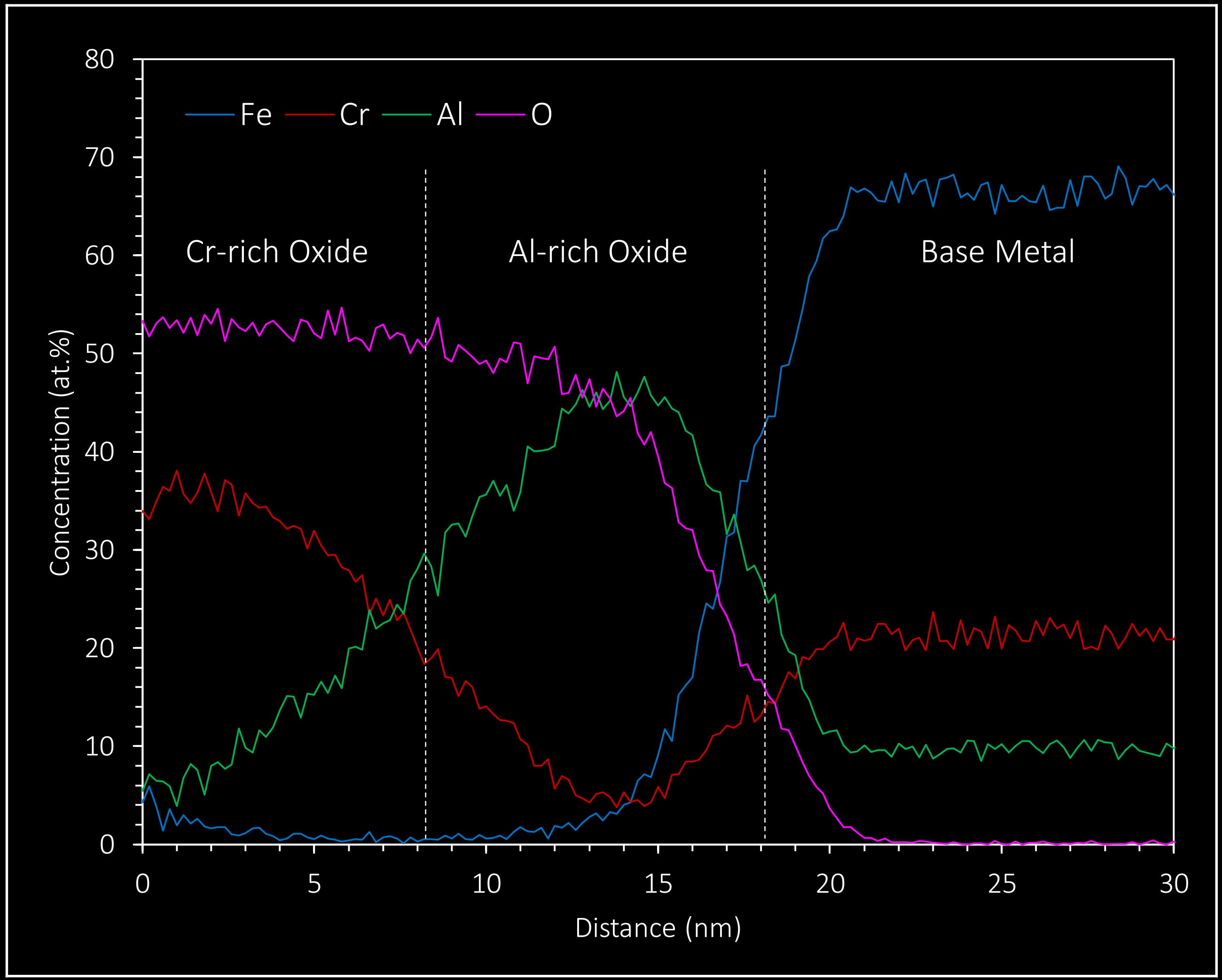
Liquid Metal Embrittlement



Surface Oxides in Nuclear Alloys

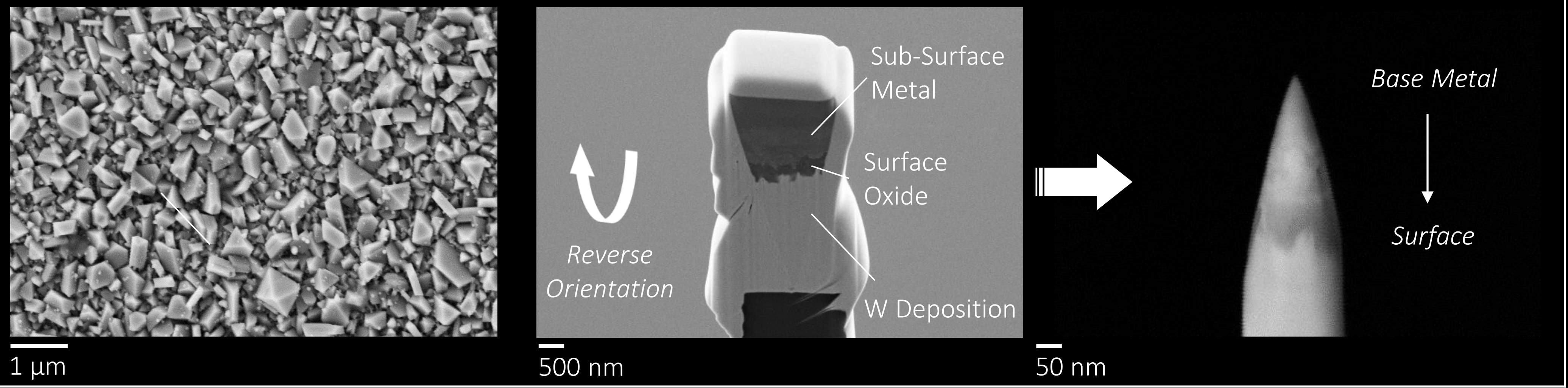


Surface Composition Profile: Fe-Cr-Al Alloy

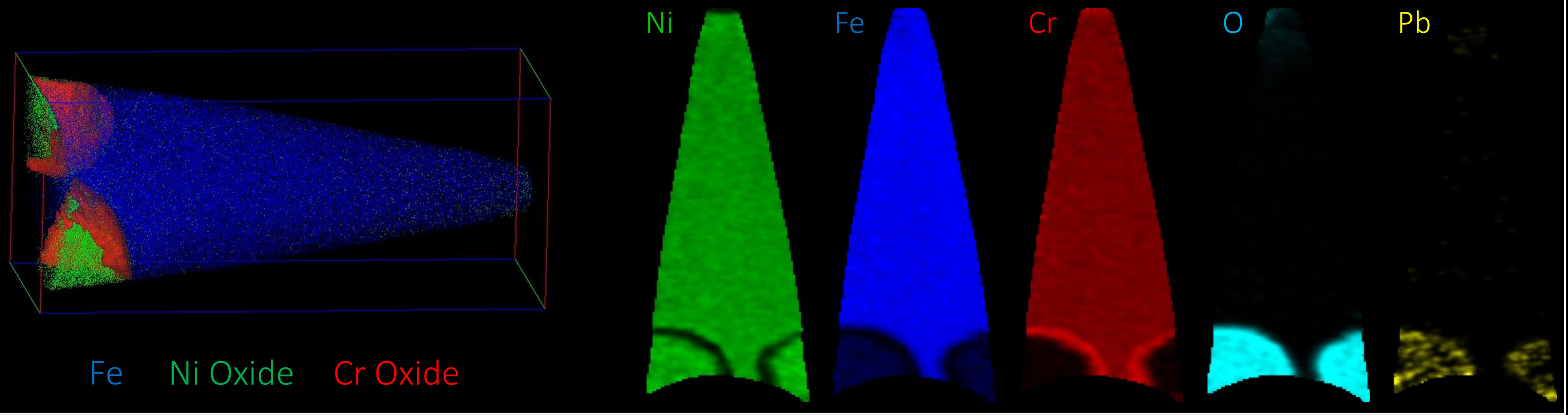


Surface Oxides in Nuclear Alloys

Sample Preparation

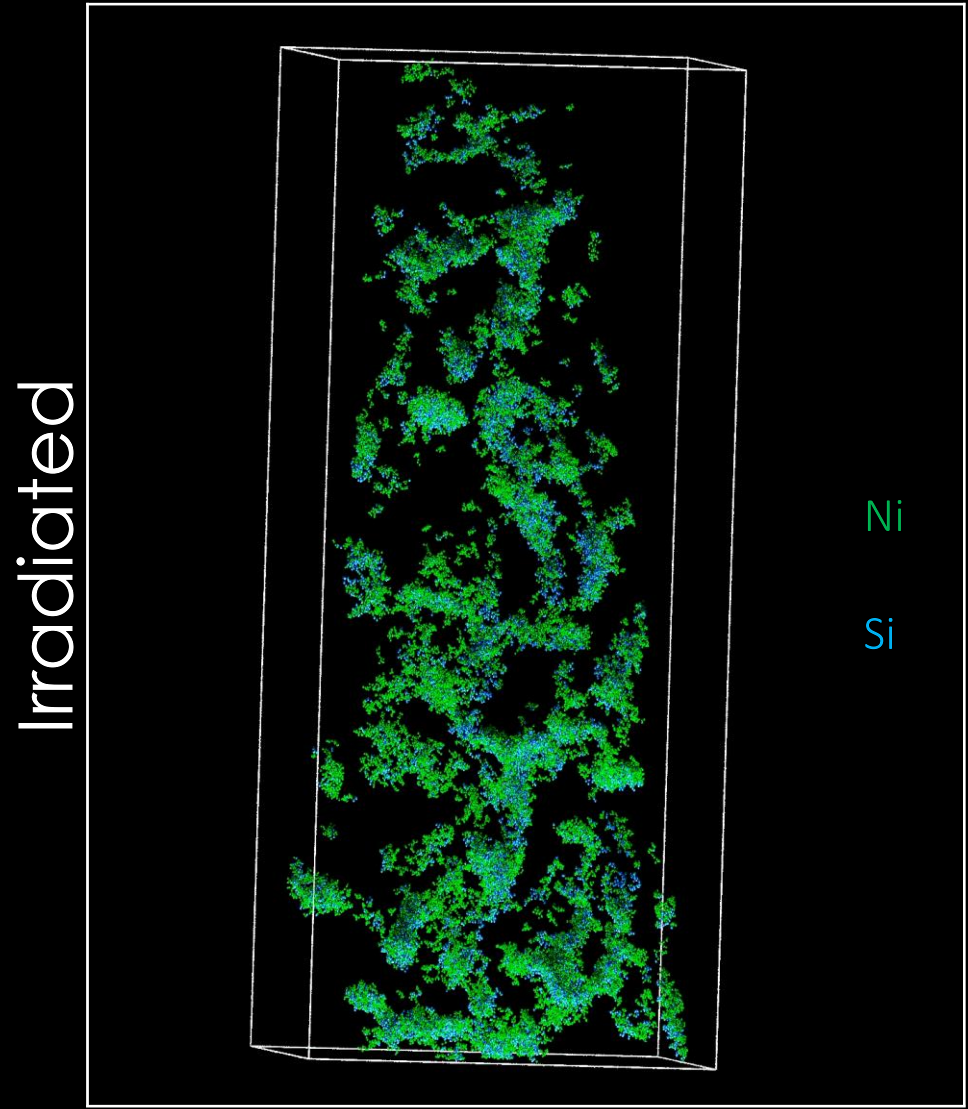


APT Results

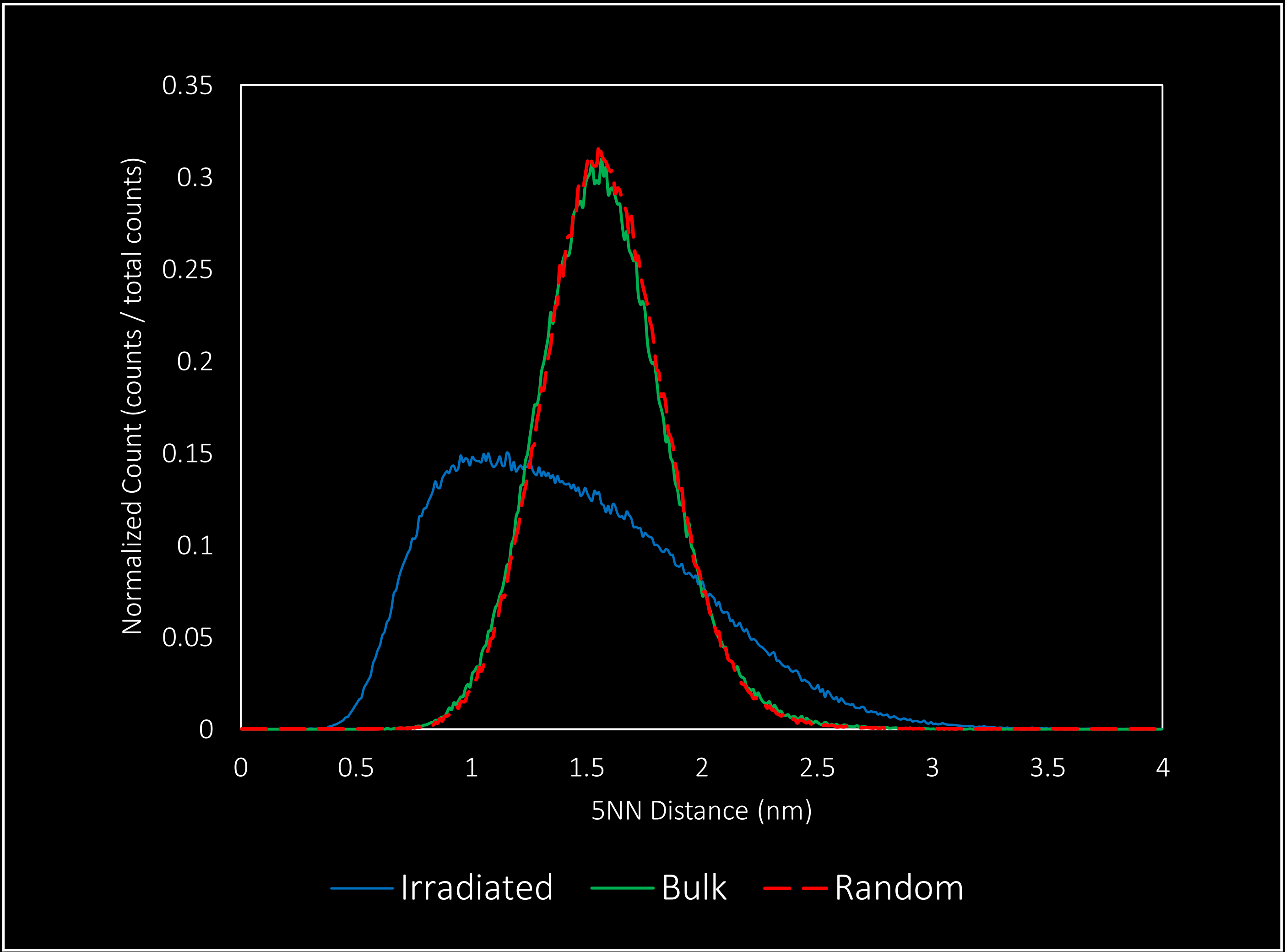


Damage in Irradiated Materials

Canadian Nuclear Laboratories
Laboratoires Nucléaires Canadiens



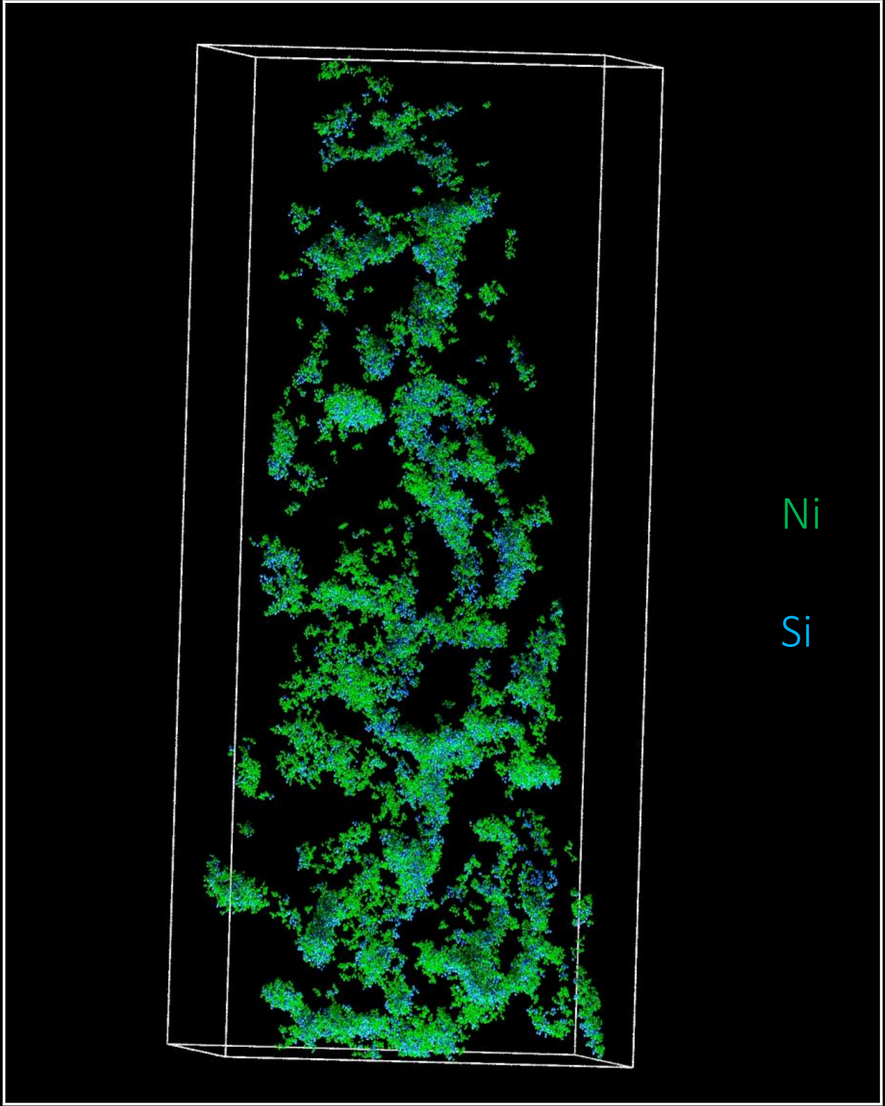
Si Nearest-Neighbour Distribution



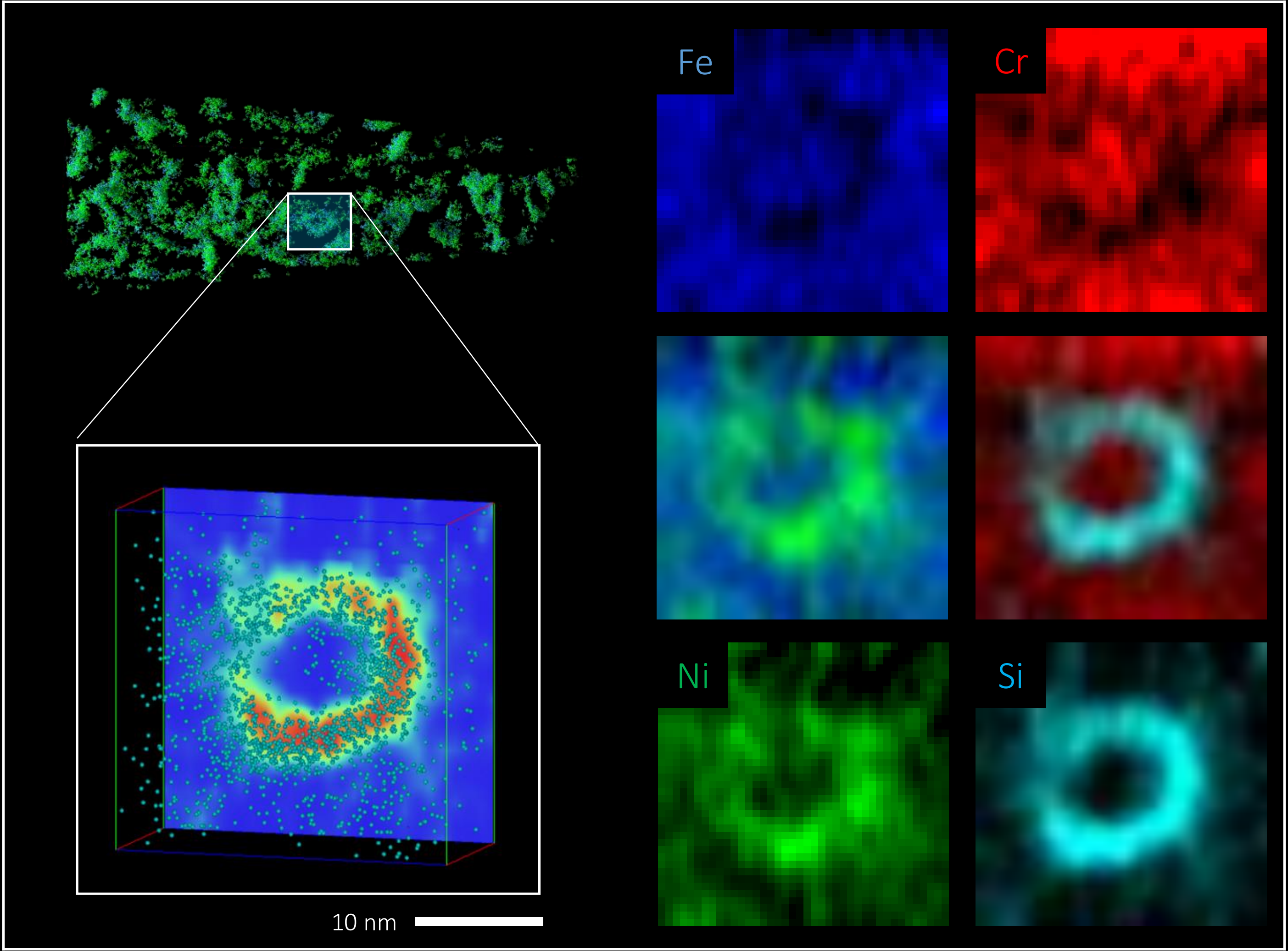
Collaboration: C. Judge, M. Mattucci, Canadian Nuclear Laboratories (manuscript in preparation)

Damage in Irradiated Materials

Irradiated

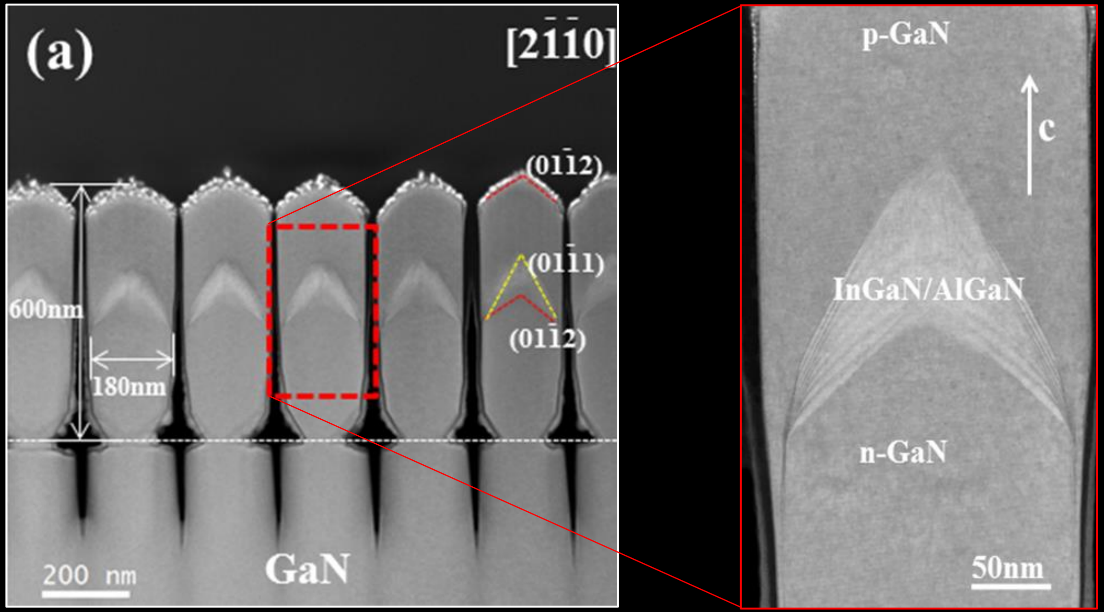


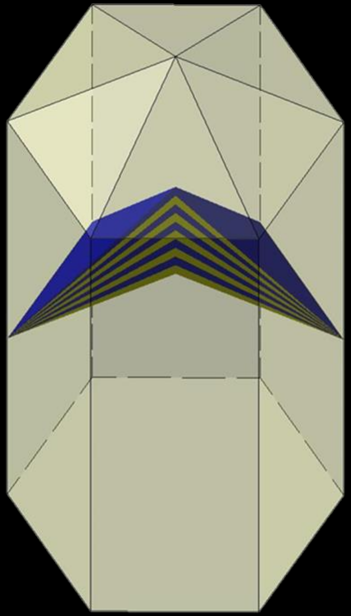
Dislocation Loops

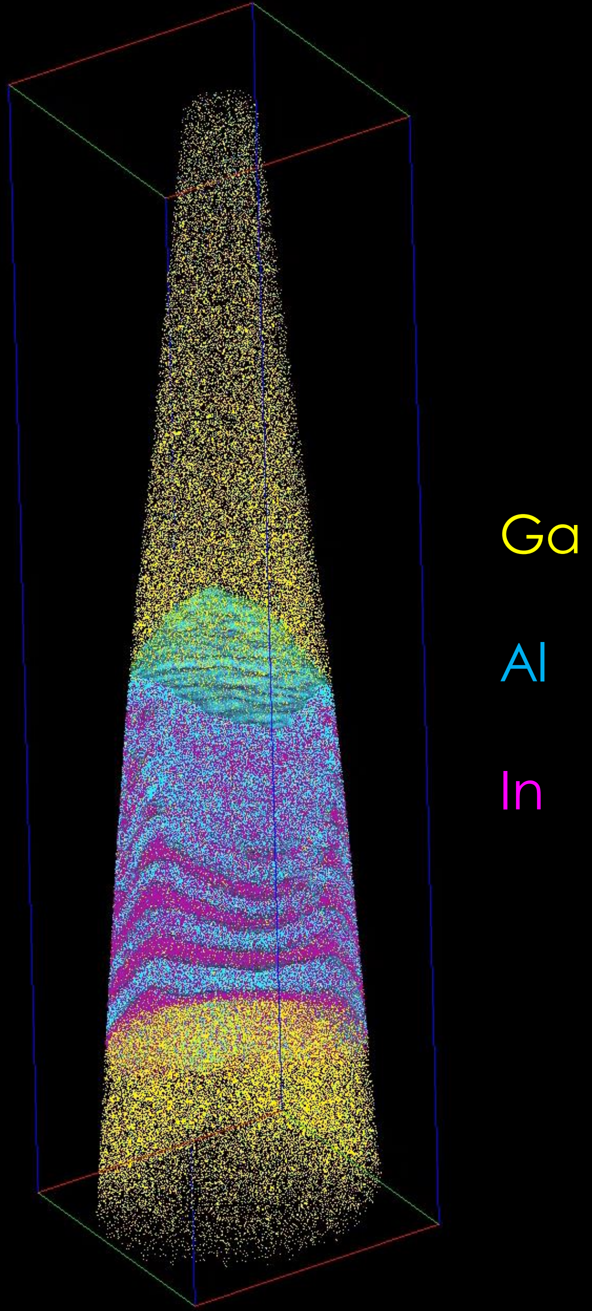


Collaboration: C. Judge, M. Mattucci, Canadian Nuclear Laboratories (manuscript in preparation)

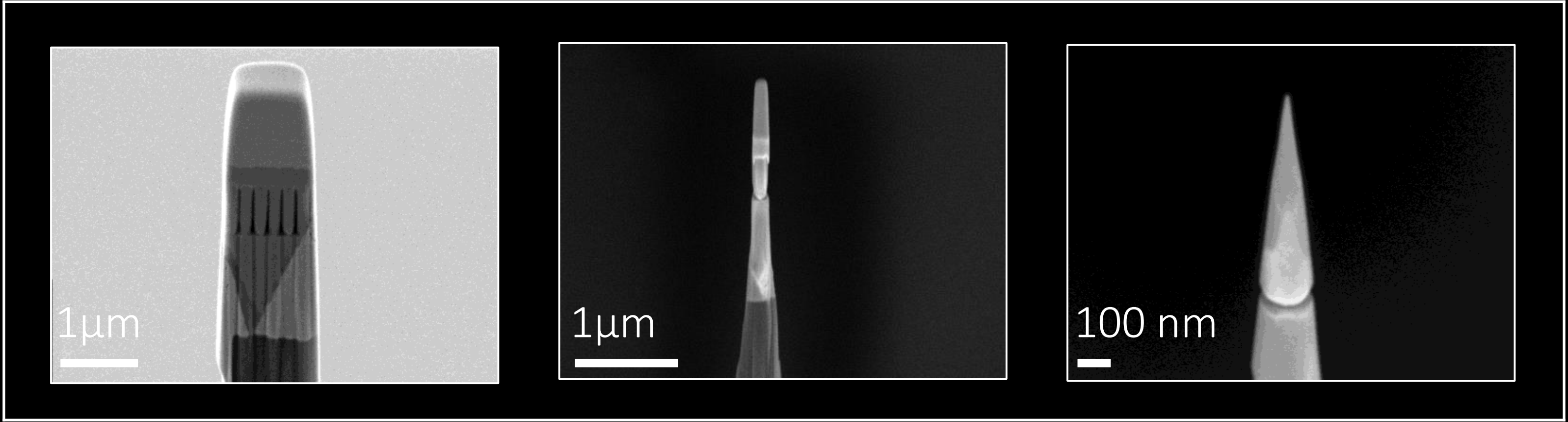
GaN Nanowires





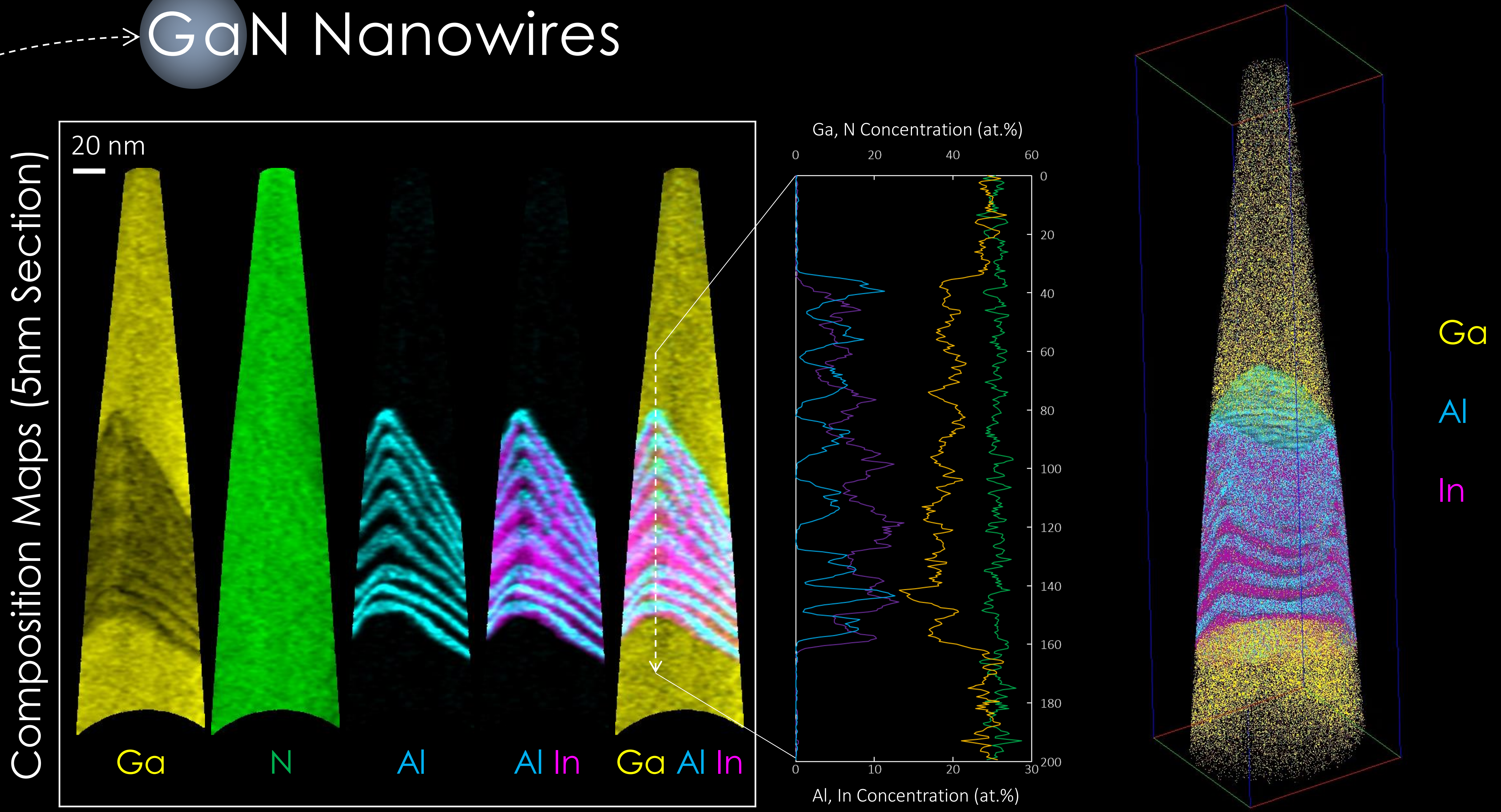


Sample Preparation



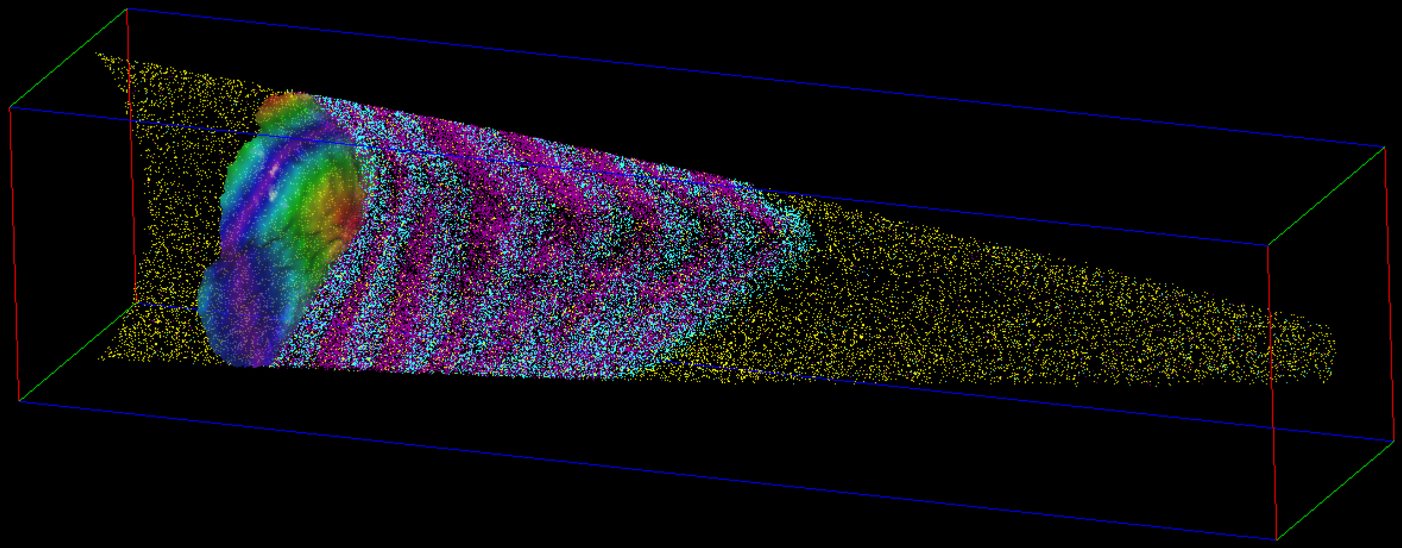
S. Cheng, B. Langelier, Y.-H. Ra, R.Rashid, Z. Mi, G. A. Botton, ***Nanoscale*** *(accepted manuscript)*

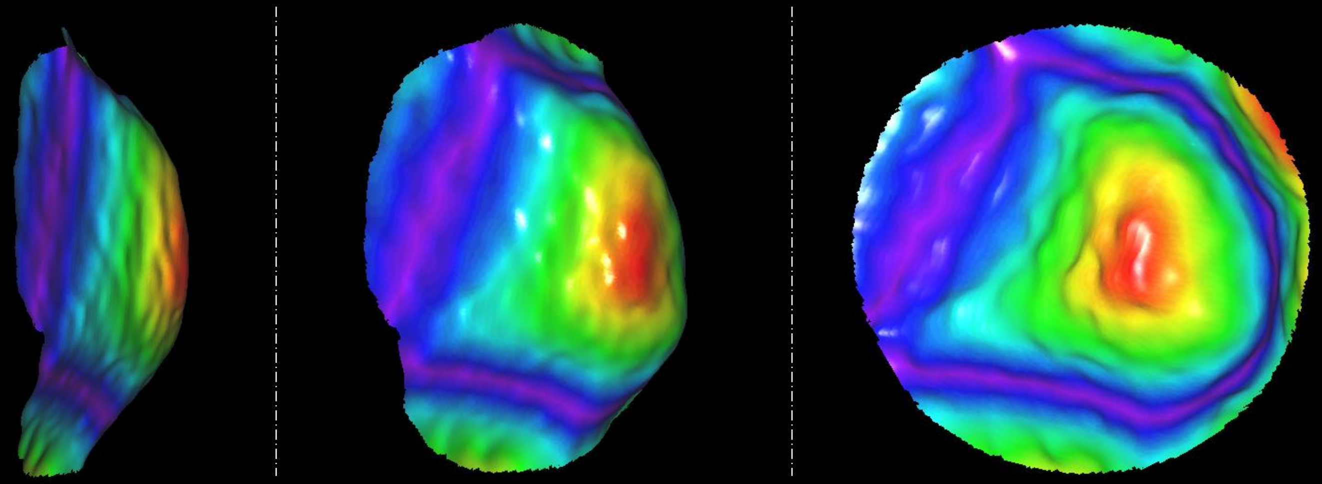
GaN Nanowires

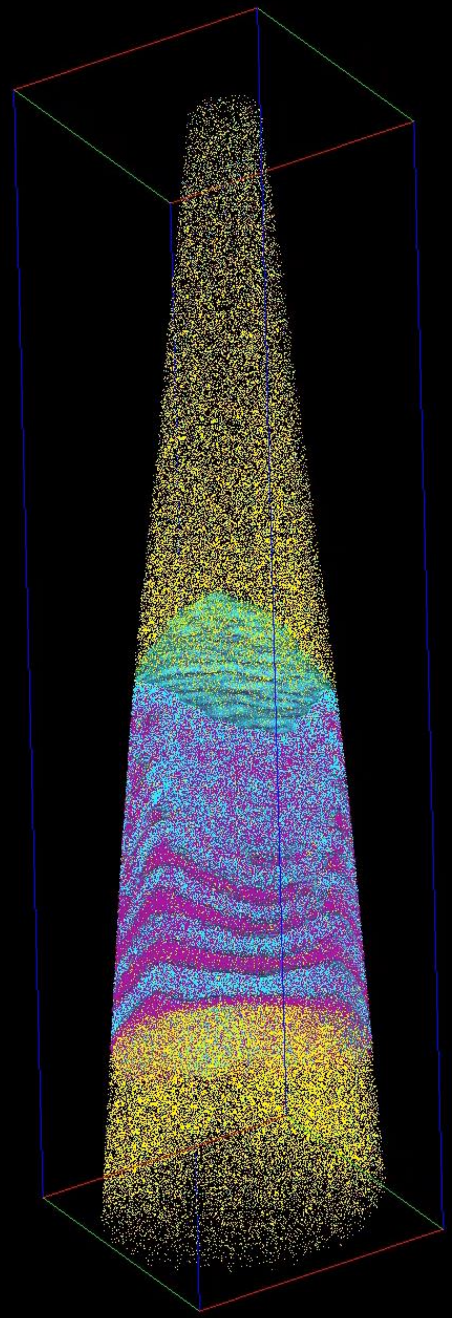


S. Cheng, B. Langelier, Y.-H. Ra, R.Rashid, Z. Mi, G. A. Botton, **Nanoscale** (accepted manuscript)

GaN Nanowires



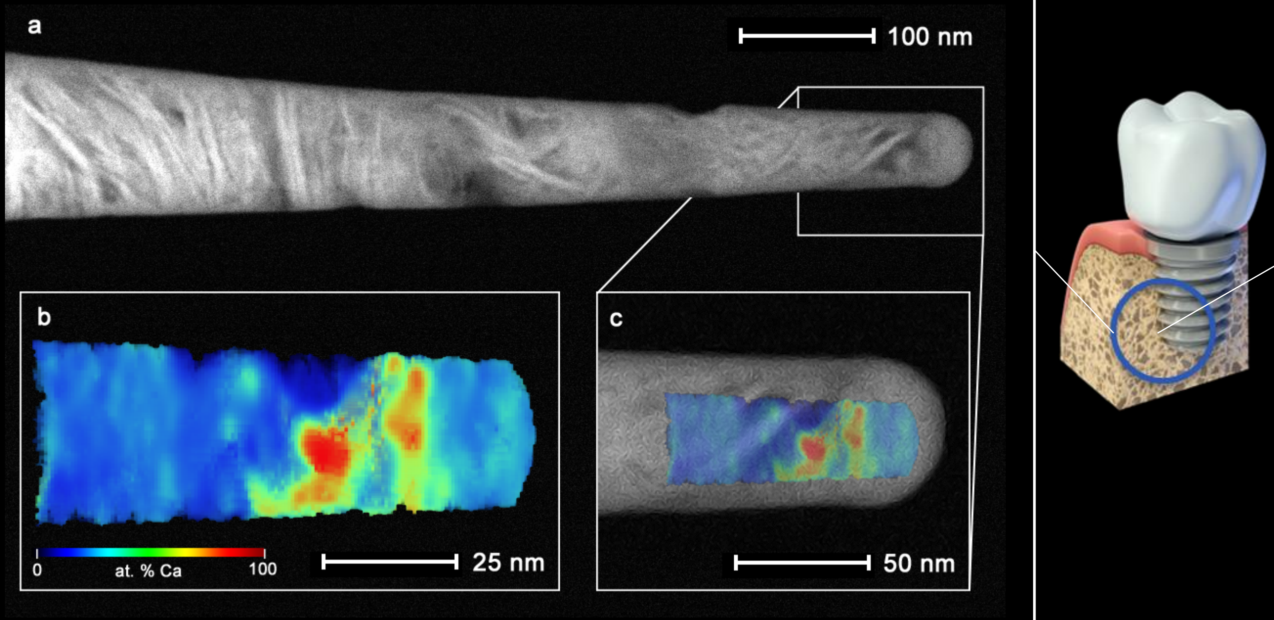




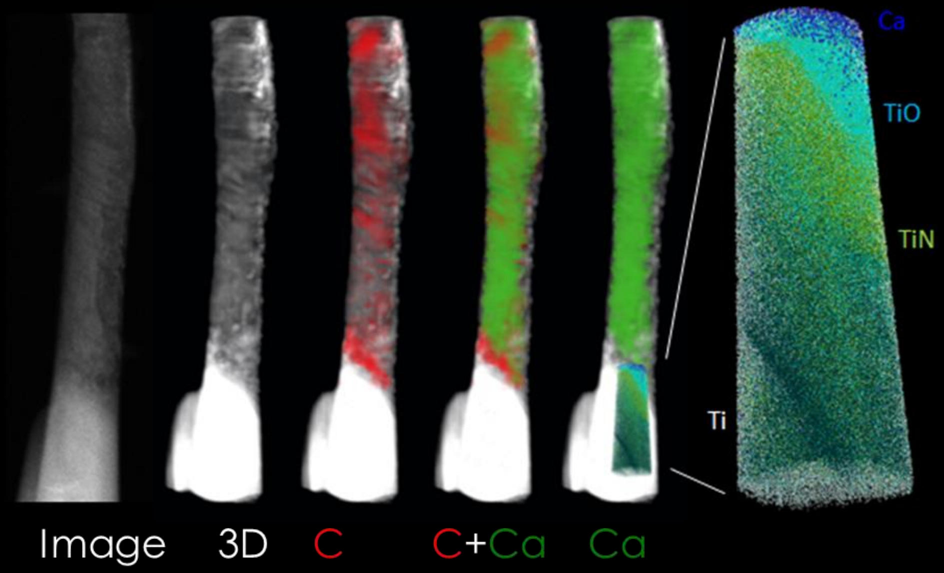
S. Cheng, B. Langelier, Y.-H. Ra, R.Rashid, Z. Mi, G. A. Botton, ***Nanoscale*** *(accepted manuscript)*

APT Analysis of Human Bone

Structure & Chemistry of Bone



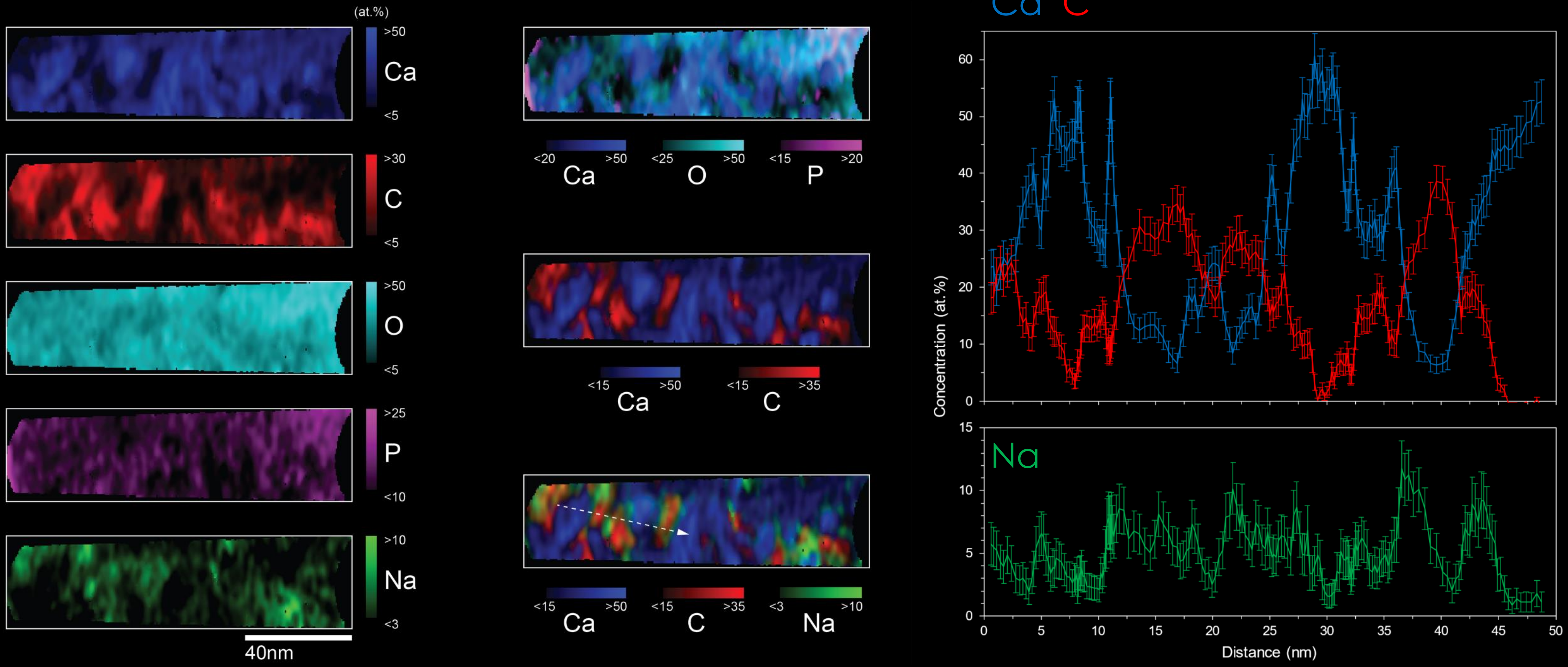
Osseointegration with Implants



B. Langelier, X. Wang, K. Grandfield, ***Scientific Reports*** *7 (2017)*

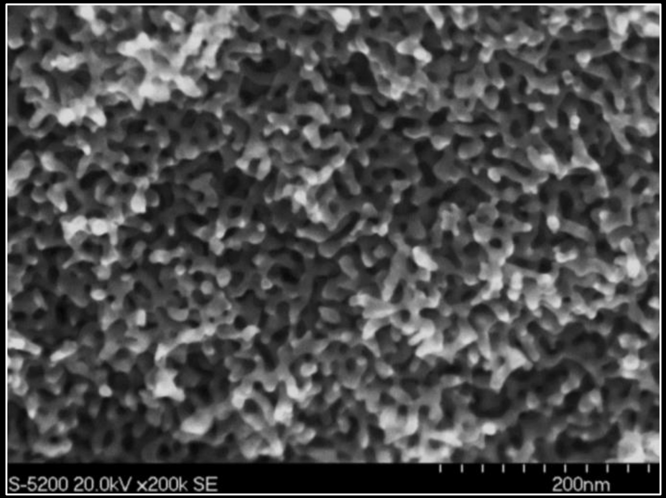
X. Wang, B. Langelier, F.A. Shah, A. Korinek, M. Bugnet, A.P. Hitchcock, A. Palmquist, K. Grandfield, ***Adv. Mater. Interfaces*** *(2018)*

APT Analysis of Human Bone



*B. Langelier, X. Wang, K. Grandfield, **Scientific Reports** 7 (2017)*

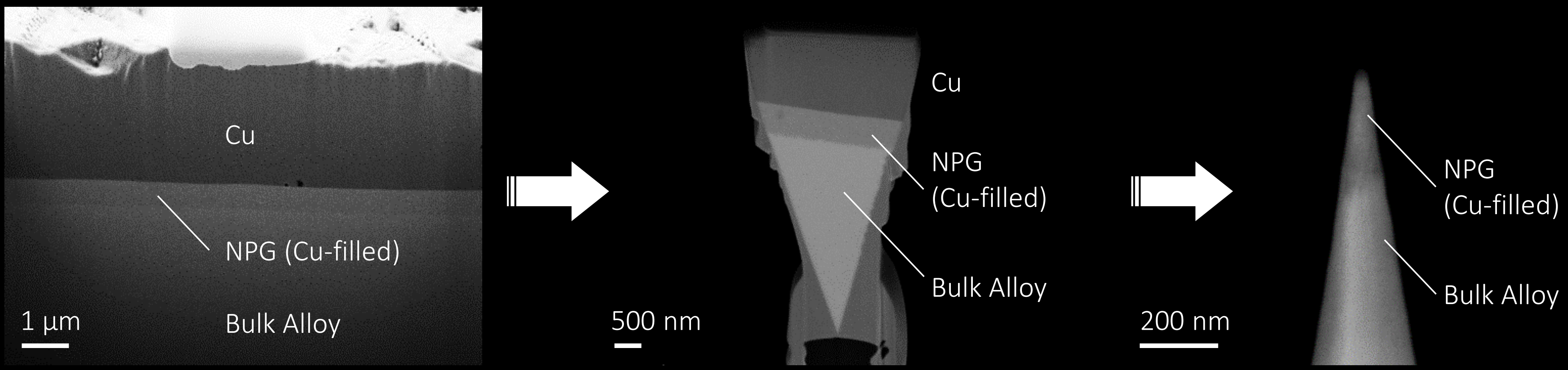
Nanoporous Gold



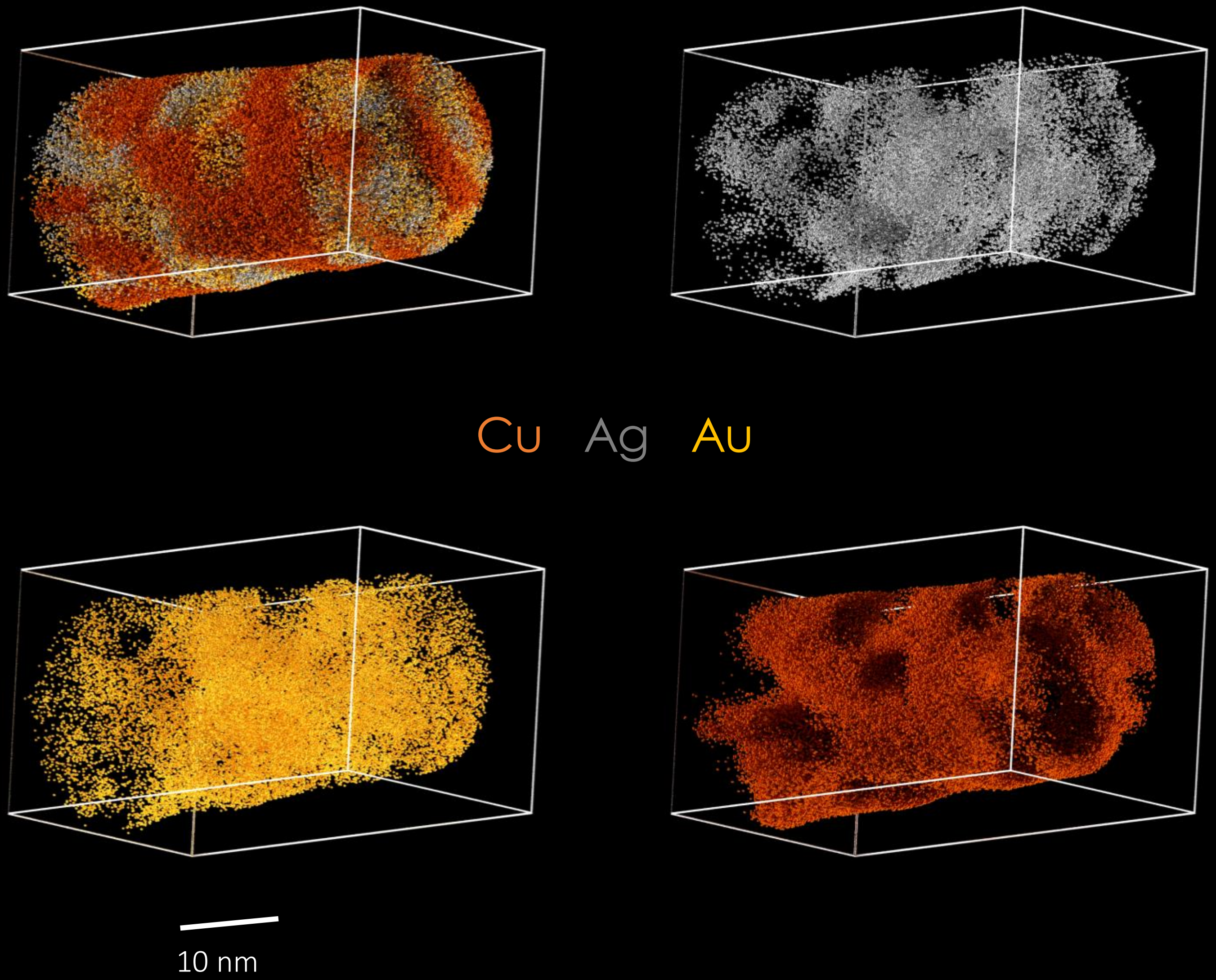
Dealloyed Binary alloy $Ag_{77}Au_{23}$

- Structure and chemistry of nanoporous gold (NPG) requires nanoscale 3D analysis, for which APT is ideal
- APT analysis cannot tolerate open pores without fracture
- Method of back-filling nanoporous structure with Cu developed to facilitate APT

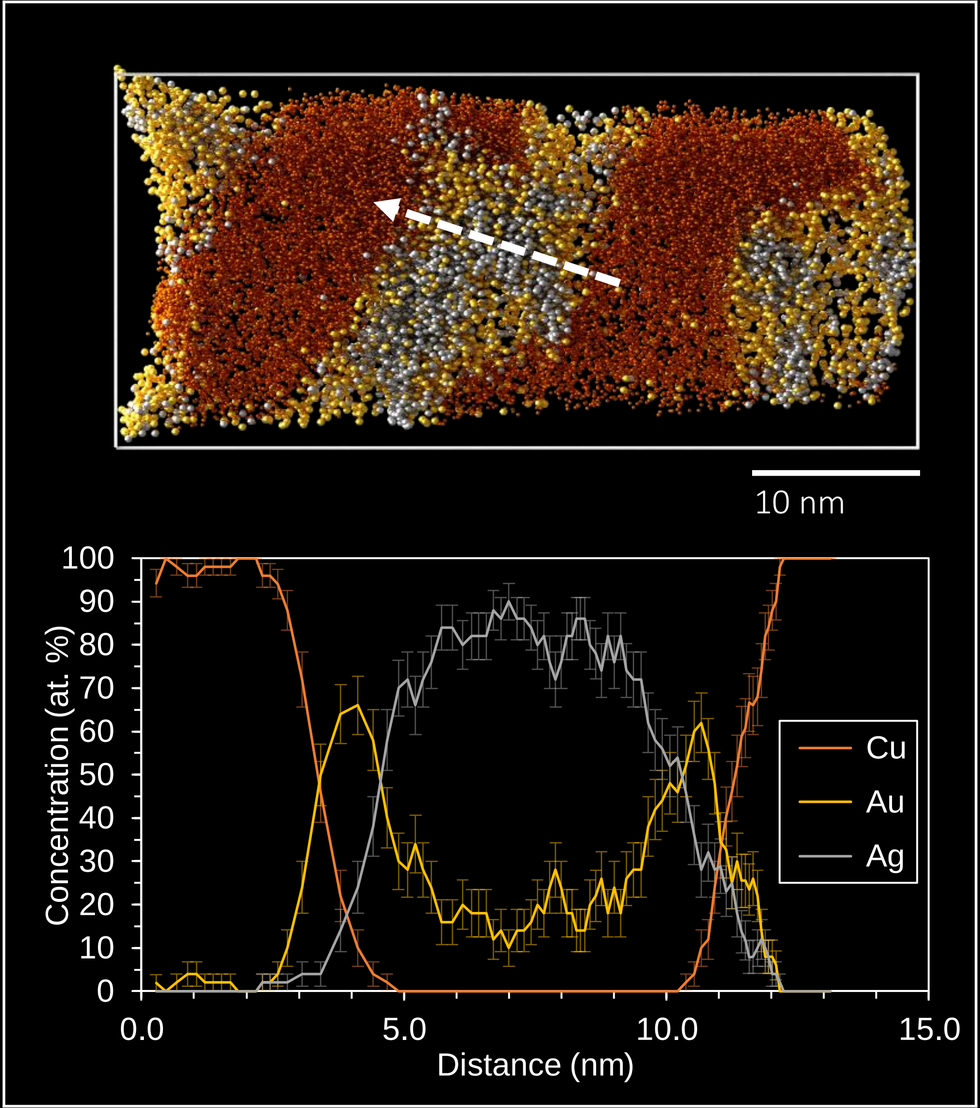
Sample Preparation



Nanoporous Gold



Composition Profiles



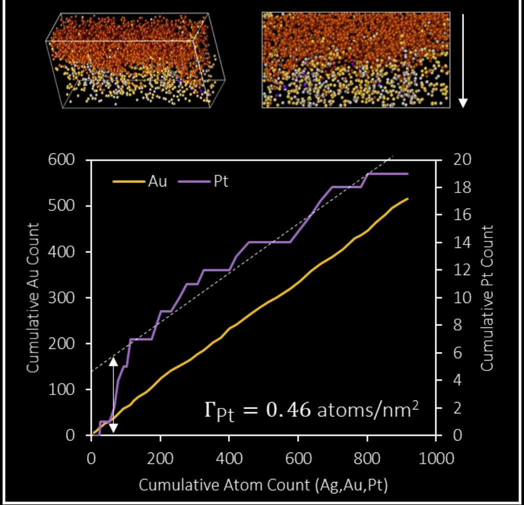
A.A. El-Zoka, B. Langelier, G.A. Botton, R.C. Newman, ***Materials Characterization*** *128 (2017)*

Nanoporous Gold

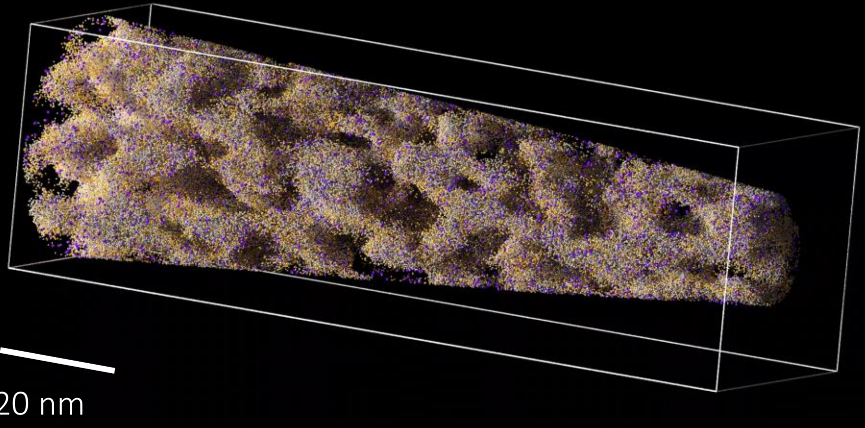
Pt Segregation

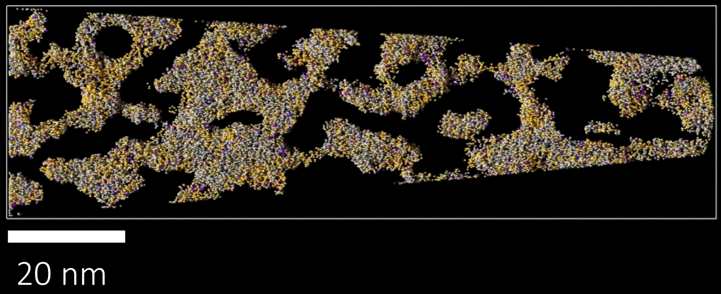
1% Pt

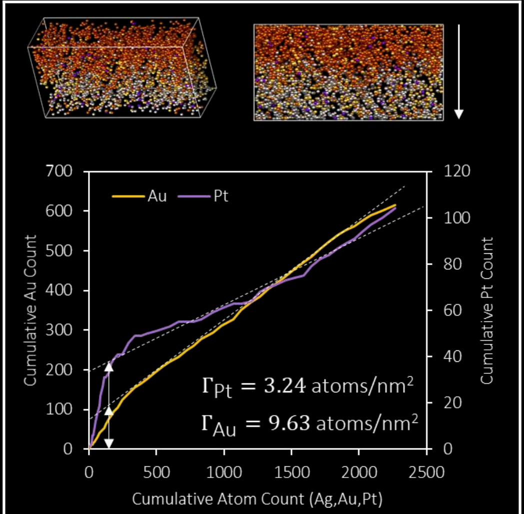
Ag Au Pt



3% Pt



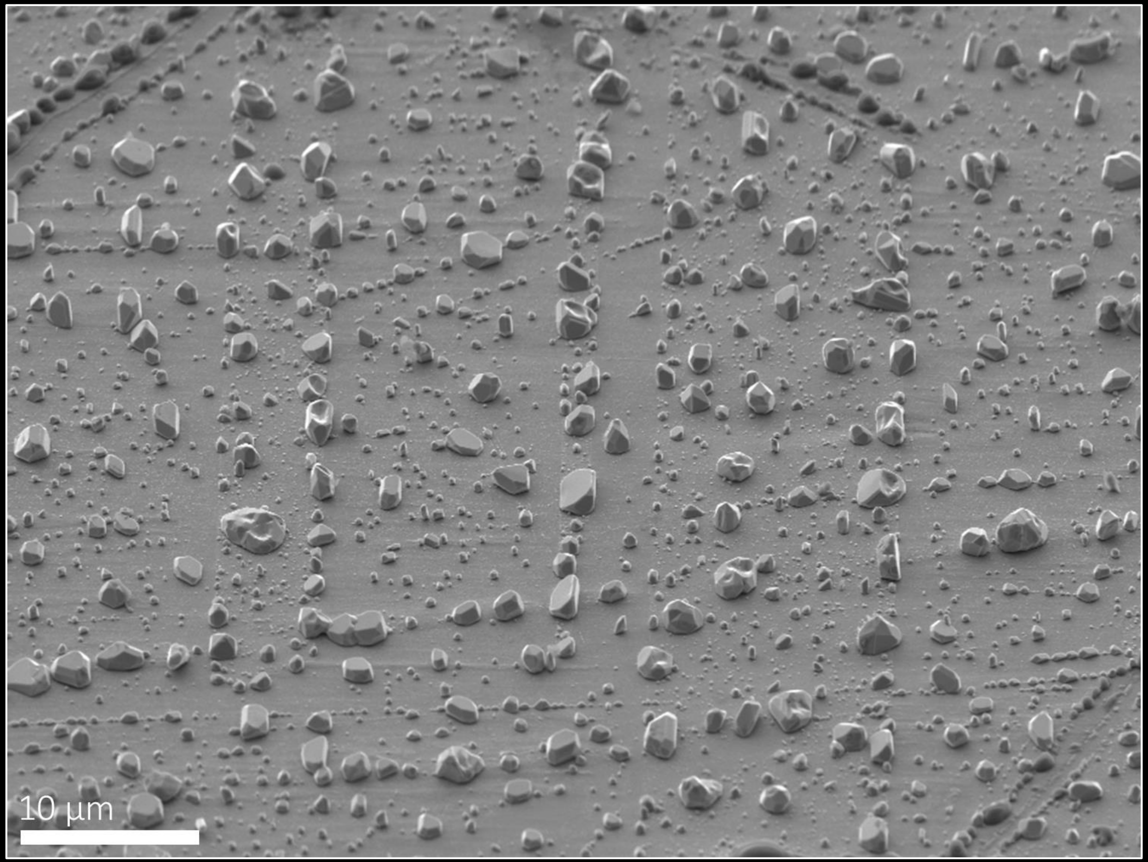




*A.A. El-Zoka, B. Langelier, A. Korinek, G.A. Botton, R.C. Newman, **Nanoscale** 10 (2018)*

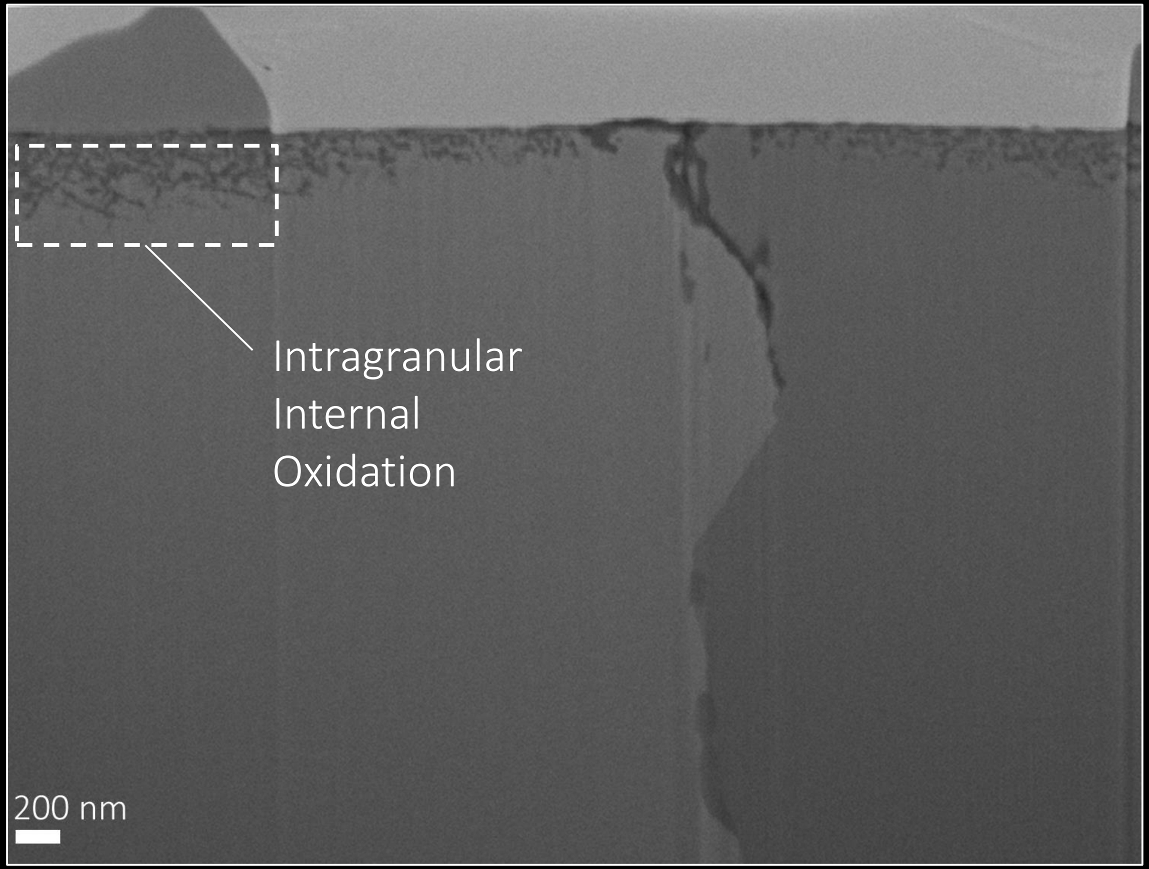
Case Study: Internal Oxidation

Internal Oxidation in Alloy 600



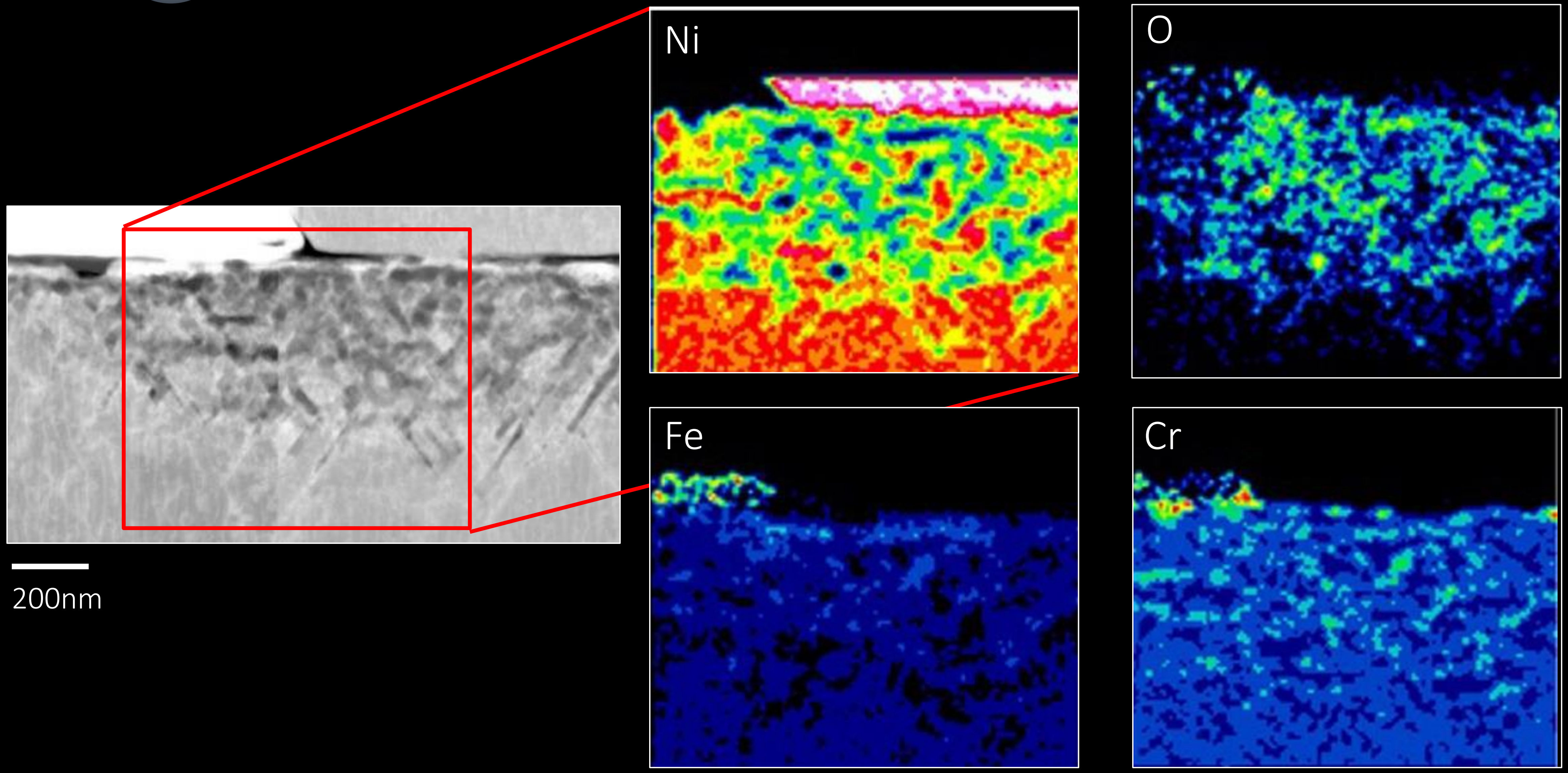
Steam exposure: 120h 480ºC

- Noble metal matrix: Ni
- Oxidation of reactive solutes: Cr and Fe



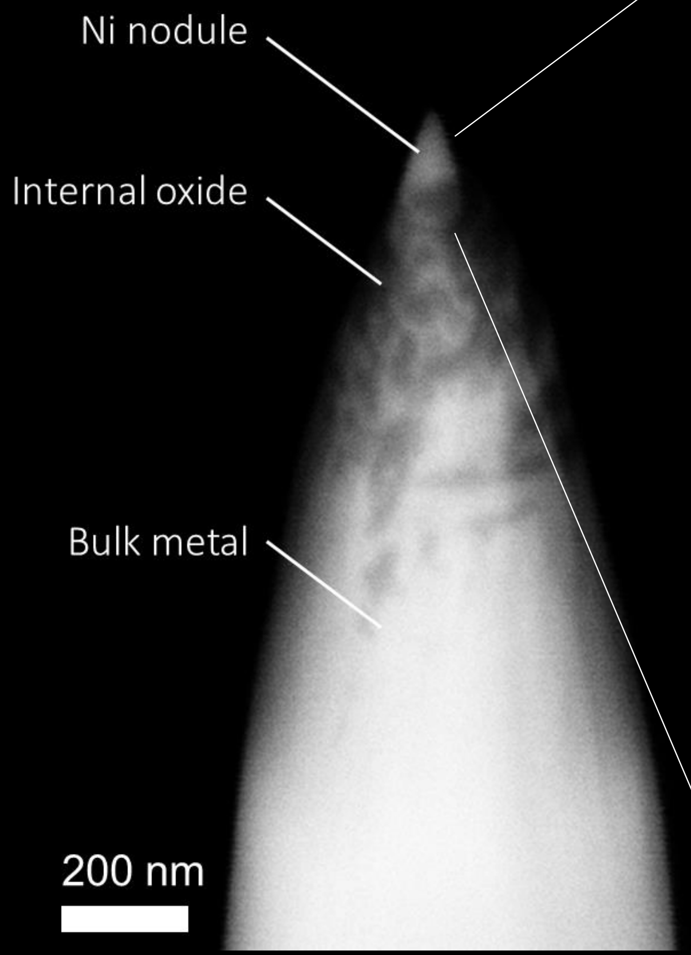
B. Langelier, S.Y. Persaud, R.C. Newman, G.A. Botton, ***Acta Materialia*** *109 (2016)*

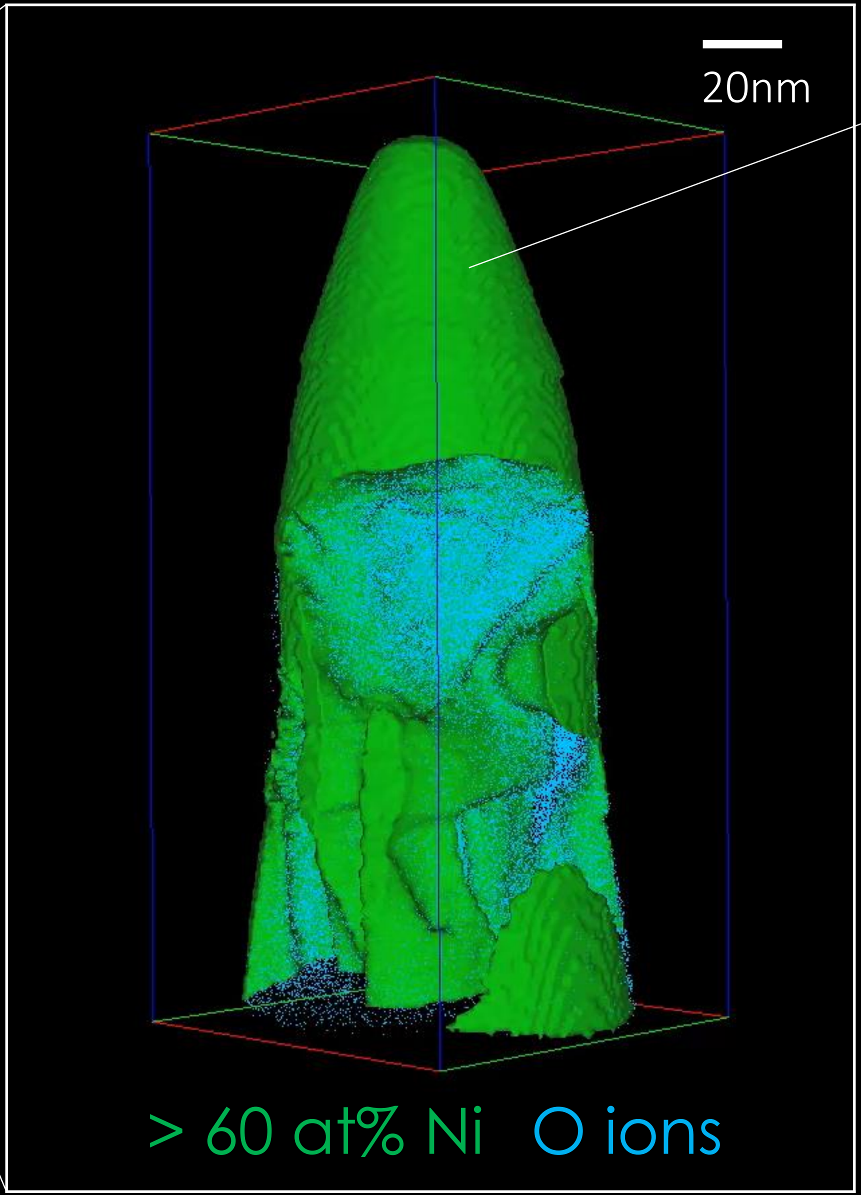
Internal Oxidation in Alloy 600



S.Y. Persaud, A. Korinek, J. Huang, G.A. Botton, R.C. Newman, **Corrosion Science** 86 (2014)

Nodule + Oxides APT

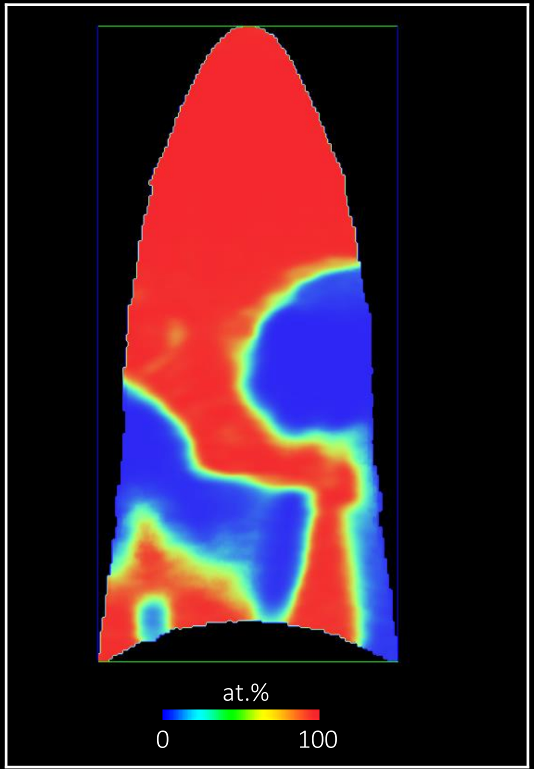




Metallic Nodule

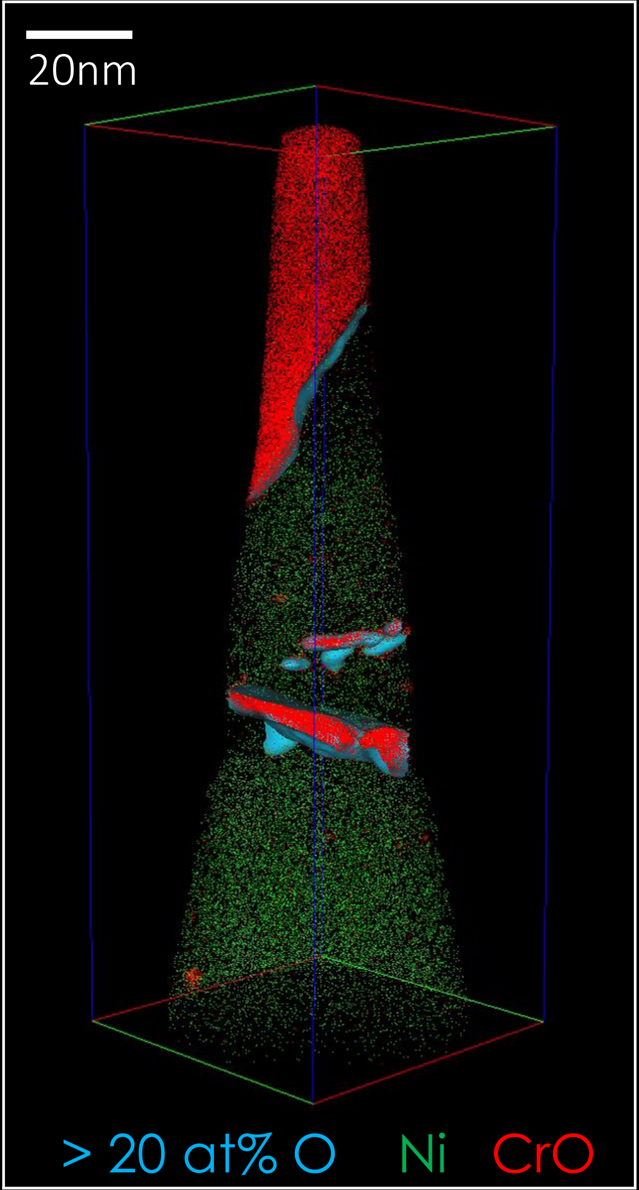
Element	(at %)
Ni	95.3
Cr	0.01
Fe	1.33

%Ni Map

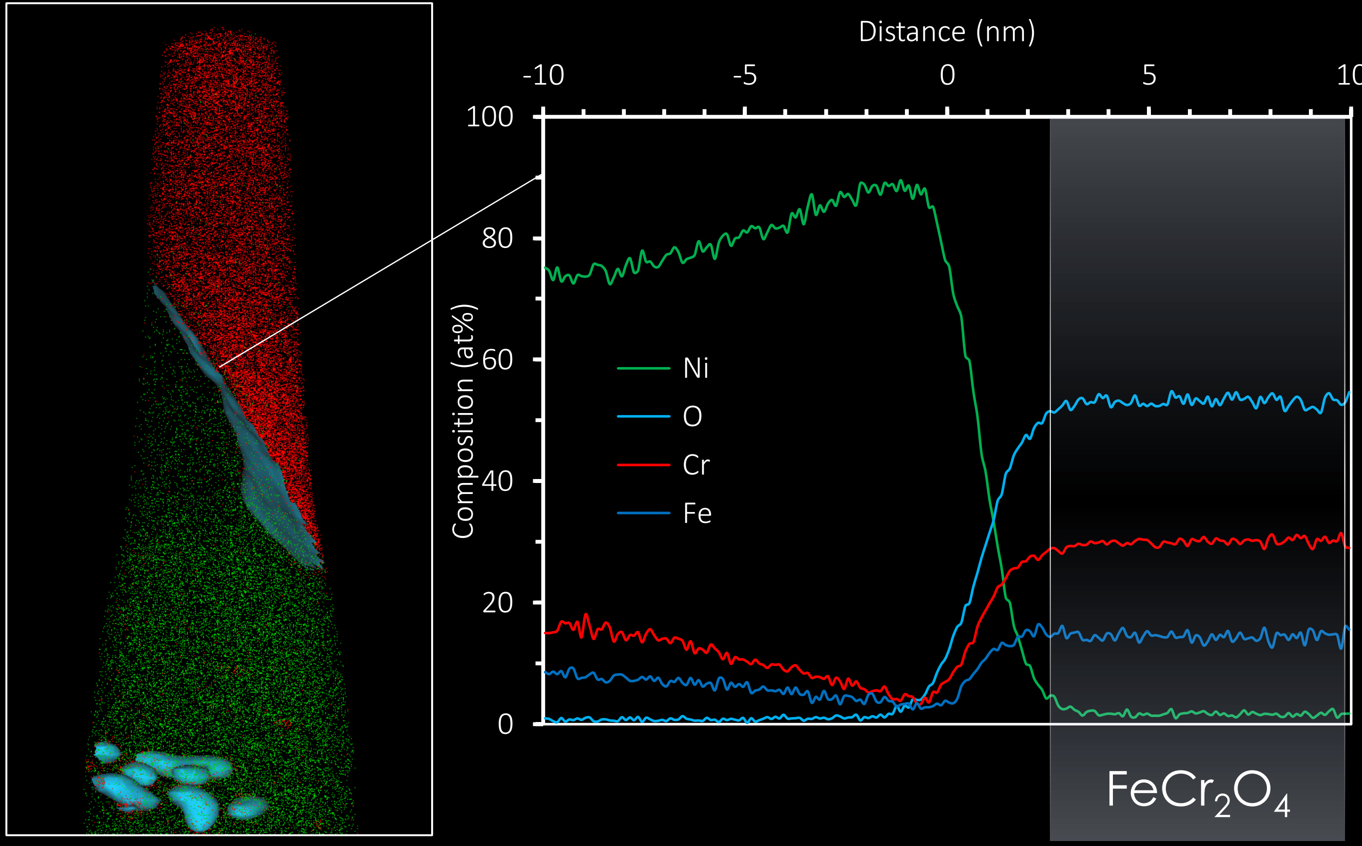


B. Langelier, S.Y. Persaud, R.C. Newman, G.A. Botton, ***Acta Materialia*** *109 (2016)*

Internal Oxides



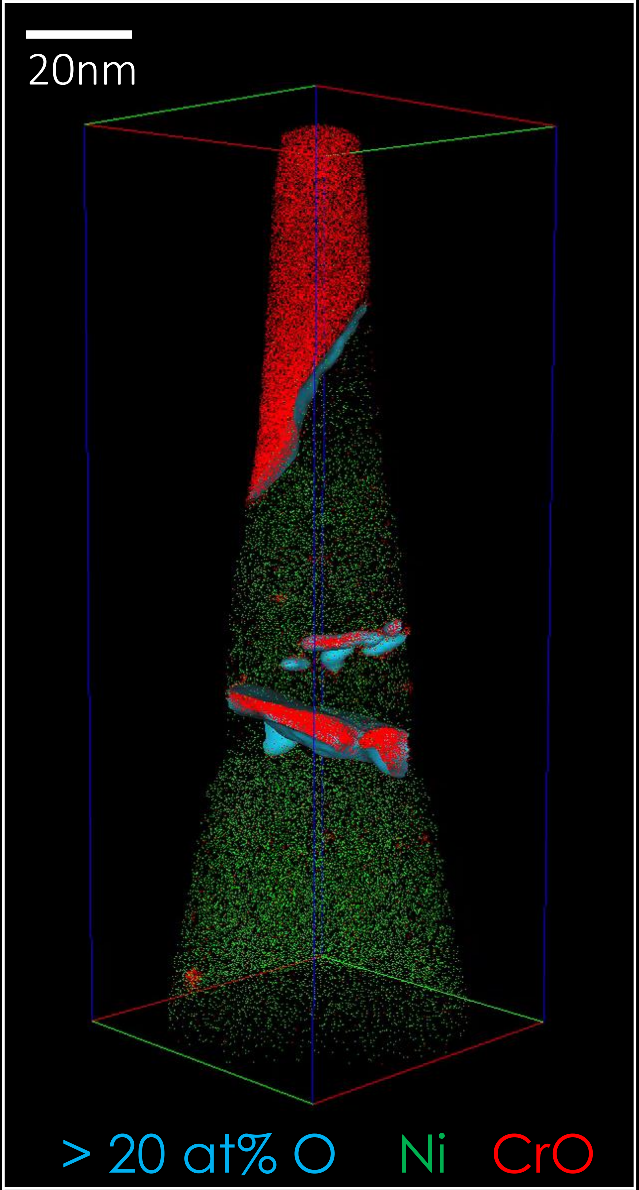
Composition Profile



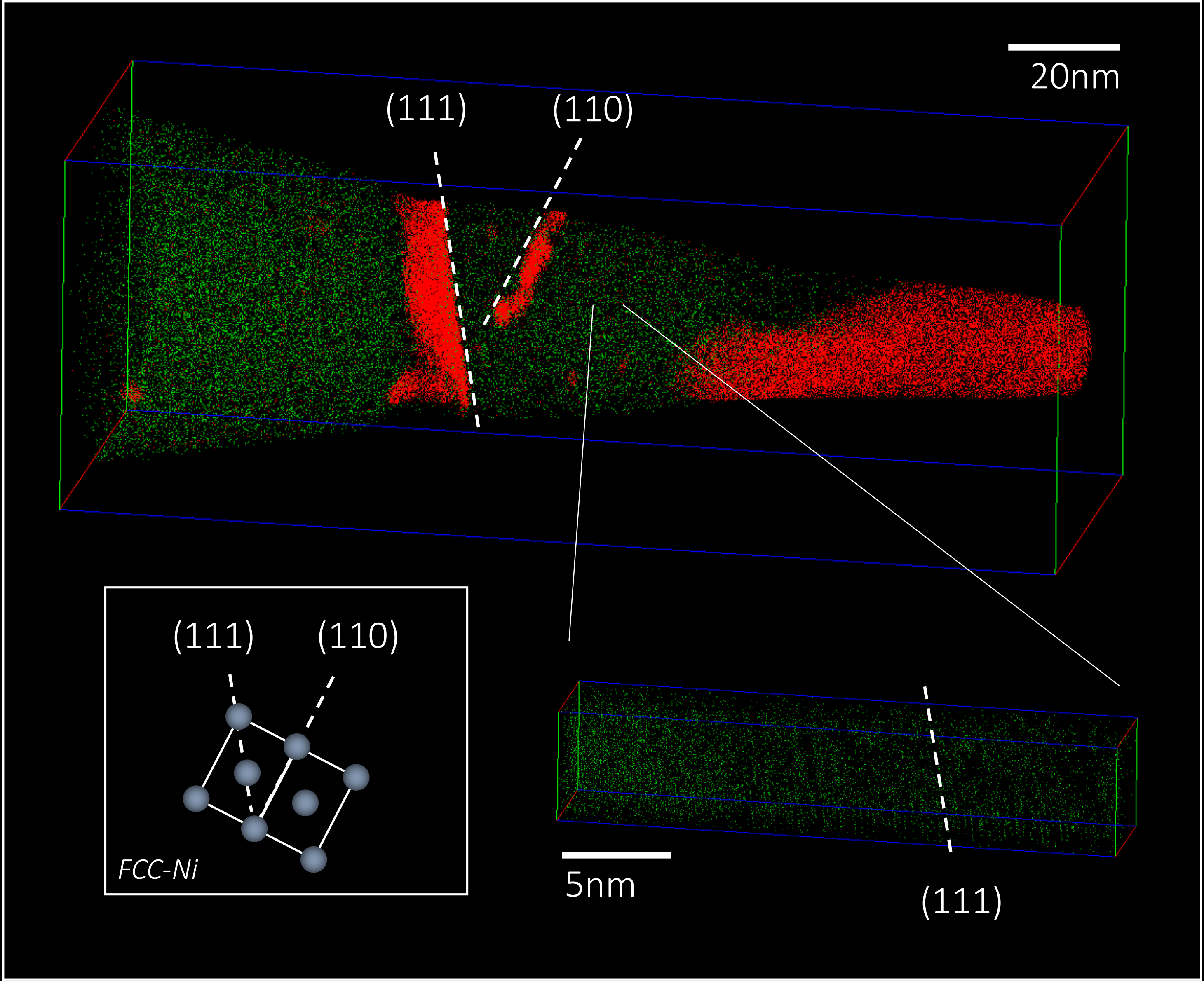
- Internal oxide network composition of $FeCr_2O_4$

B. Langelier, S.Y. Persaud, R.C. Newman, G.A. Botton, ***Acta Materialia*** *109 (2016)*

Internal Oxides

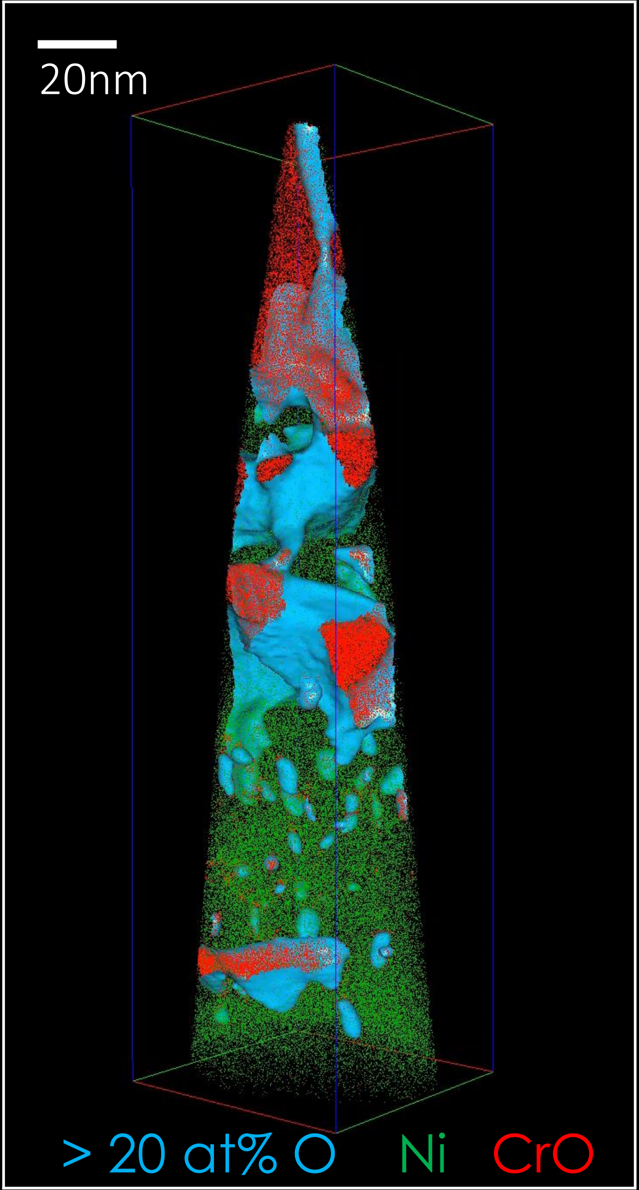


Internal Oxide Distribution

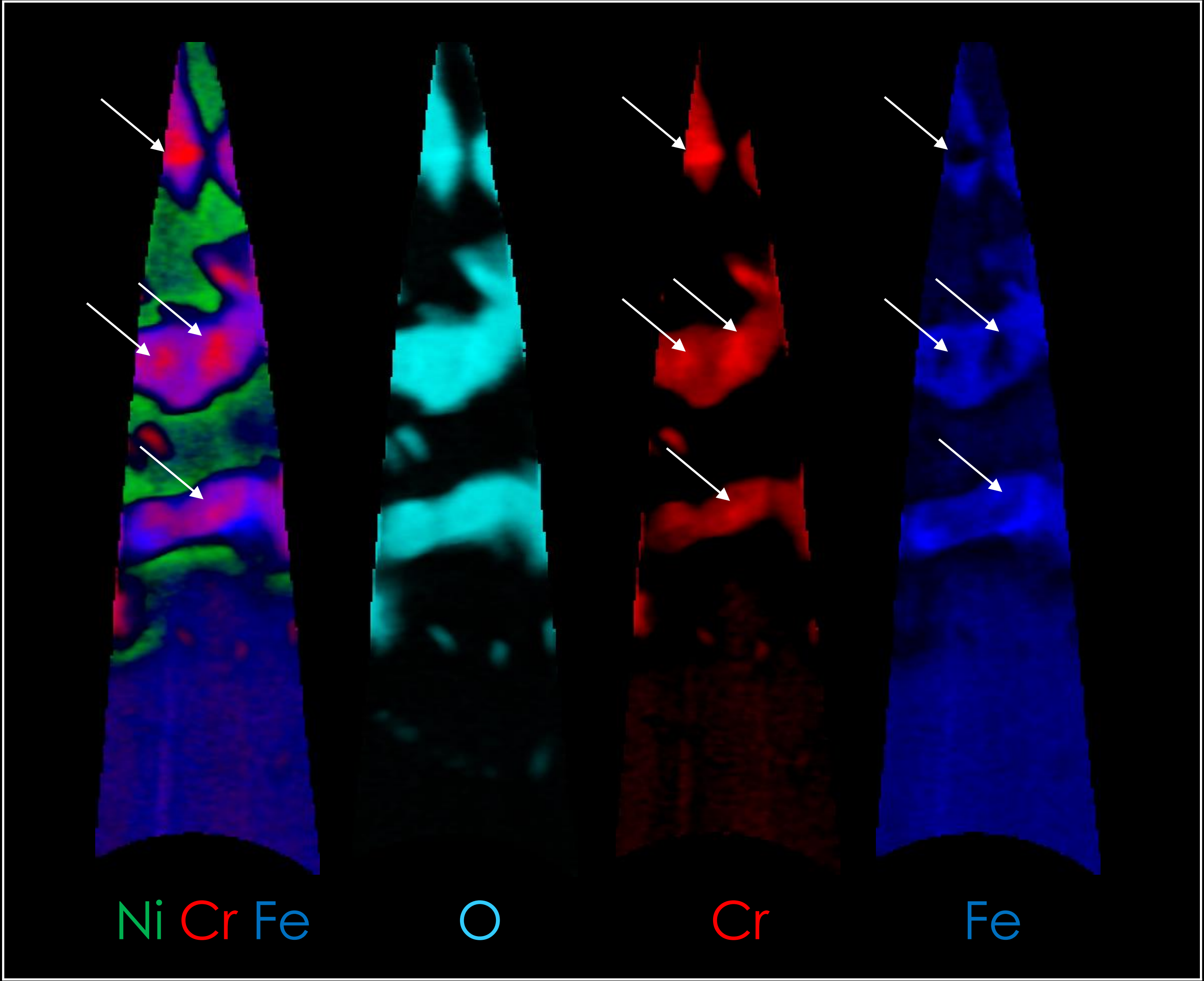


B. Langelier, S.Y. Persaud, R.C. Newman, G.A. Botton, ***Acta Materialia*** *109 (2016)*

Internal Oxides

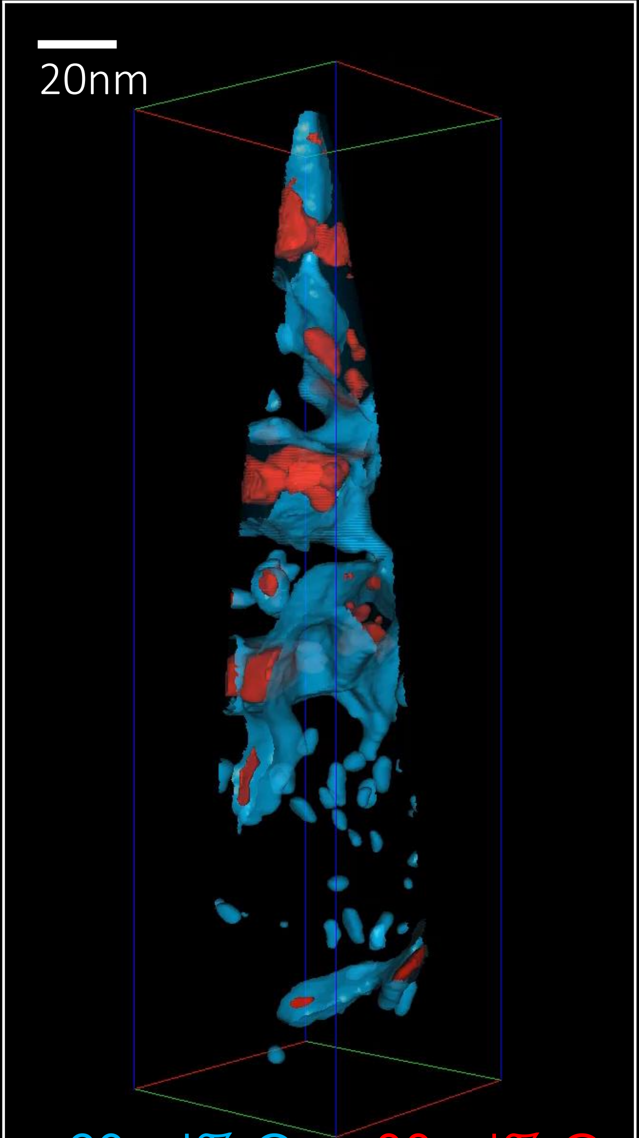


Composition Maps

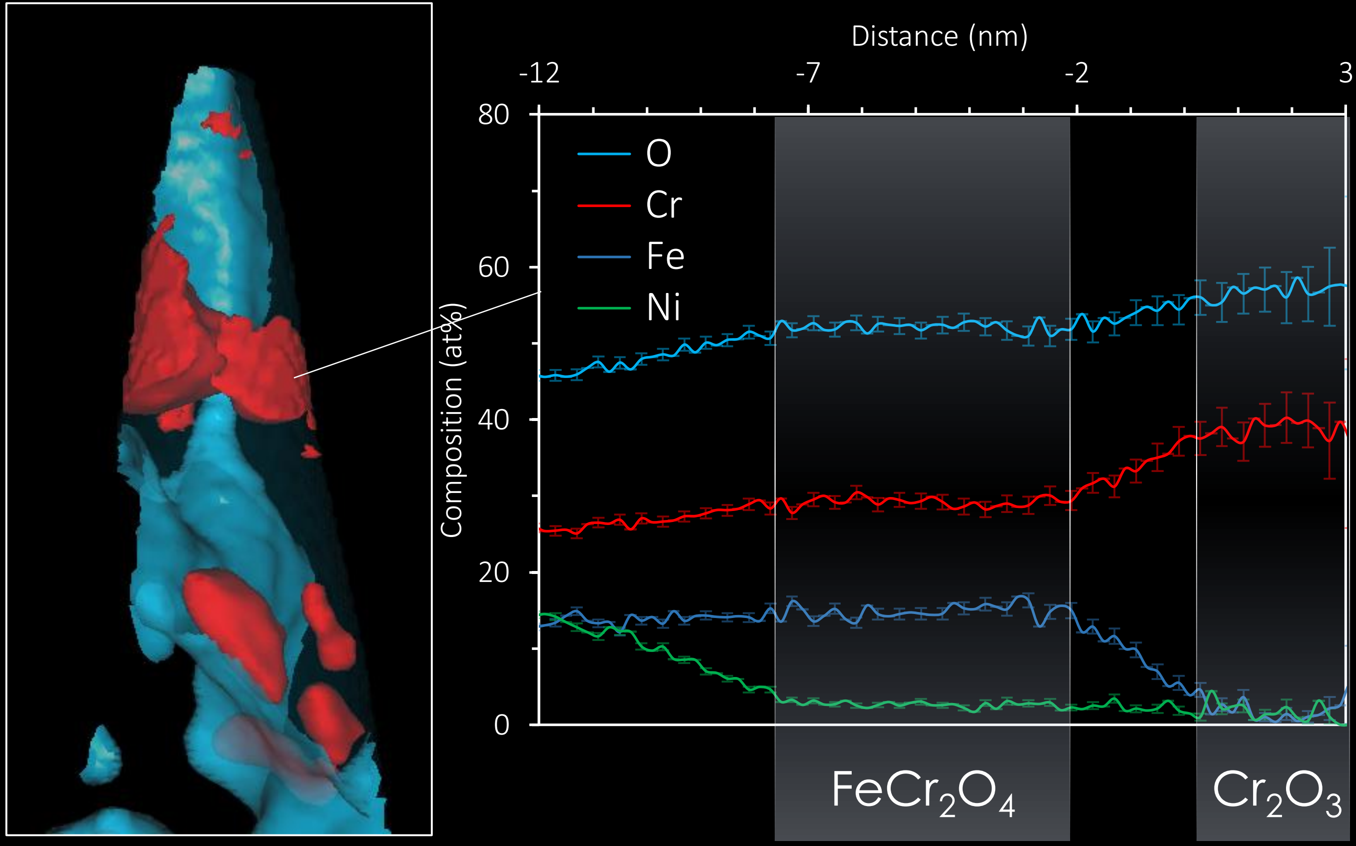


B. Langelier, S.Y. Persaud, R.C. Newman, G.A. Botton, ***Acta Materialia*** *109 (2016)*

Internal Oxides



Concentration Profile



- Cr-rich "cores" are found to be Cr_2O_3
- Transition to $FeCr_2O_4$ at greater sizes/distances

*B. Langelier, S.Y. Persaud, R.C. Newman, G.A. Botton, **Acta Materialia** 109 (2016)*

Thank you!

CCEM FACULTY & STAFF

- Gianluigi Botton
- Kathryn Grandfield
- Andreas Korinek
- Travis Casagrande

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- Roger Newman (Toronto)
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- Shahrzad Esmaeili (Waterloo)
- Hatem Zurob (McMaster)
- Colin Judge (Canadian Nuclear Labs.)
- Shaobo Cheng (McMaster)
- Xiaoyue Wang (McMaster)