Atom Probe Tomography

Thomas F. Kelly

Umbrella Winter School on Materials Characterization

December 12, 2018

Outline

Lecture 1

- Brief History
  - Early efforts
  - Modern Instrumentation
- APT Fundamentals
- Strengths and Limitations

What is Steam Instruments?

Lecture 2

- Materials Applications
  - Metals
  - Grain Boundary Analysis
  - Geological Materials
  - Nanoparticles
- Atomic-Scale Analytical Tomography

Review Article:
Atom Probe Tomography 2012
T.F. Kelly and D.J. Larson (Invited Review)
Annual Review of Materials Research 42 (2012)
pp. 10.1-10.31
eds. D. Clarke, M. Ruhle, D. N. Seidman
DOI: 10.1146/annurev-matsci-070511-155007

Acknowledgements

CAMECA LEAP Engineering Team

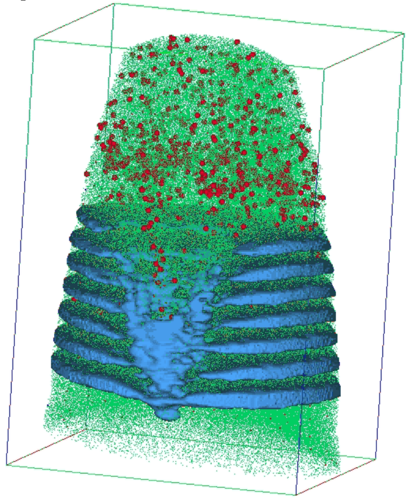
- D. Lenz, J. Bunton, T. Payne, E. Oltman, B. Geiser, E. Strennen, D. Rauls, D. Sund, G. Sobering, J. Shepard, J. Mandt, K. Rooney

CAMECA LEAP Applications and Scientific Marketing Team

- D.J. Larson, T. Prosa, D. Reinhard, I. Martin, H. Francois-Saint-Cyr, K. Rice, Y. Chen, S. Foldvari

CAMECA Management and Sales

- J. Olson, P. Clifton, R. Ulfig



Collaborators on Pending Programs

Project Tomo

- Rafal Dunin-Borkowski
  - Forschungszentrum Jülich
- Joachim Mayer
  - RWTH Aachen
  - Forschungszentrum Jülich
- Dierk Raabe
  - Max Planck Institute fur Eisenforschungs Düsseldorf
- Max Haider
  - CEOS

- Integration of LEAP and TEM

Project Laplace

- Dierk Raabe, Baptiste Gault,
- Gerhard Dehm, Christina Scheu
  - Max Planck Institute fur Eisenforschungs Düsseldorf

Phase I funded

- Integration of LEAP and STEM

Other Collaborators

ATOM Project

- Simon P. Ringer
  - University of Sydney
- Michael K. Miller
  - Oak Ridge National Laboratory
- Krishna Rajan
  - Iowa State University
- Ondrej Krivanek, Niklas Dellby
  - Nion Instruments

LEAP-STEM Imaging

- Brian Gorman, David Dierks
  - Colorado School of Mines
- Christoph Koch,
  Wouter van den Broek
  - Humboldt Universität – Berlin
- Hamish Fraser
  - The Ohio State University

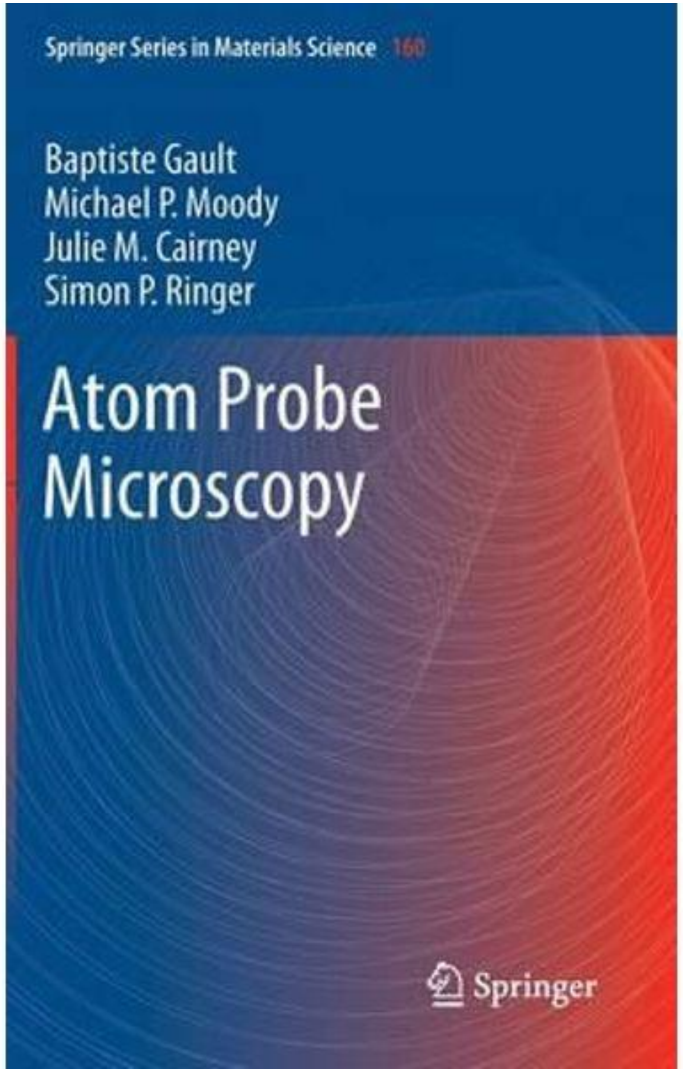
Superconducting Detector

- Robert McDermott
- Joseph Suttle
  - University of Wisconsin

Correlative Reconstruction

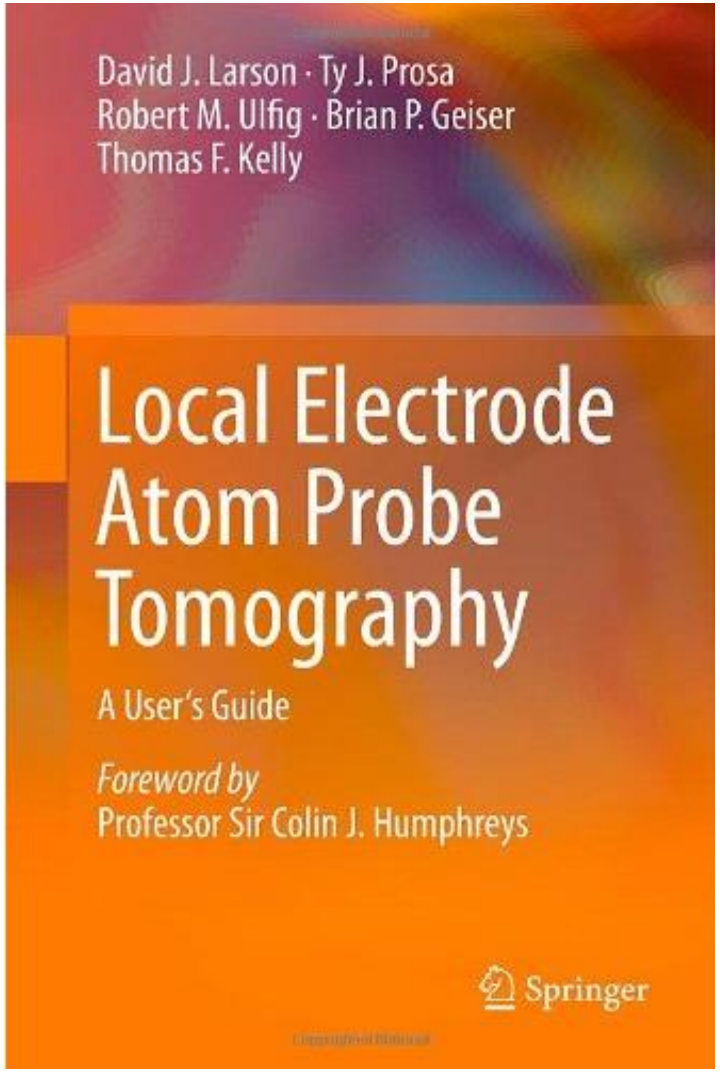
- Michael Moody
- Daniel Haley
- Charlie Fletcher
  - University of Oxford

Reference Texts – Gault et al.



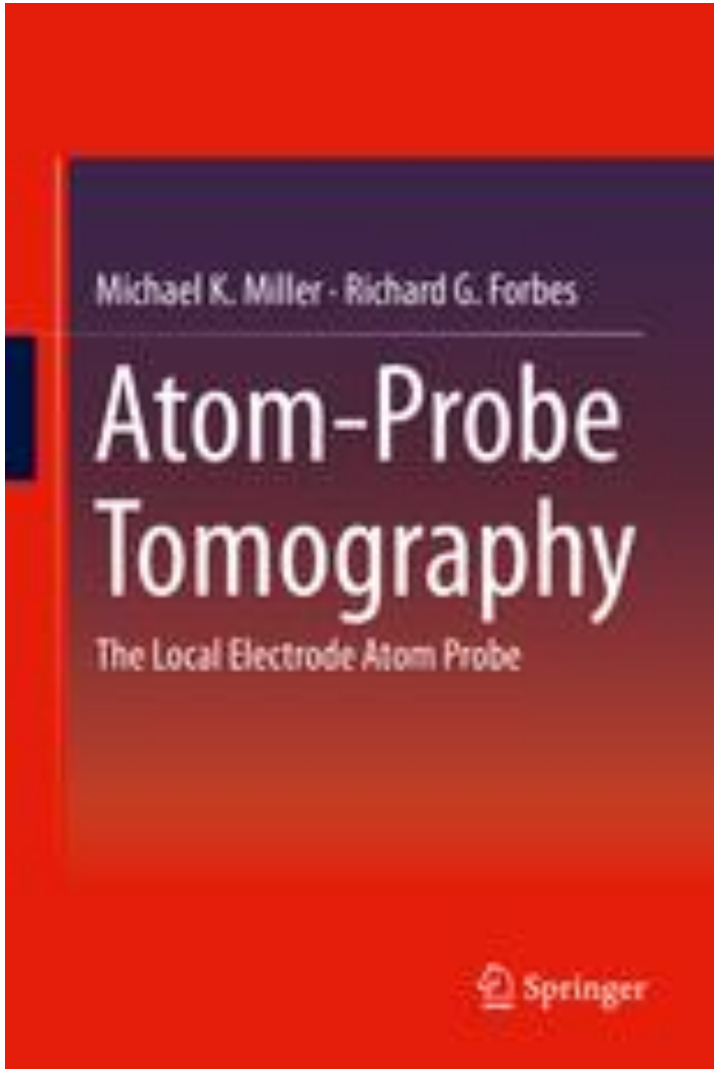
Treatment of all aspects of atom probe microscopy including underlying fundamentals and applications. (2012)

Reference Texts – Larson et al.



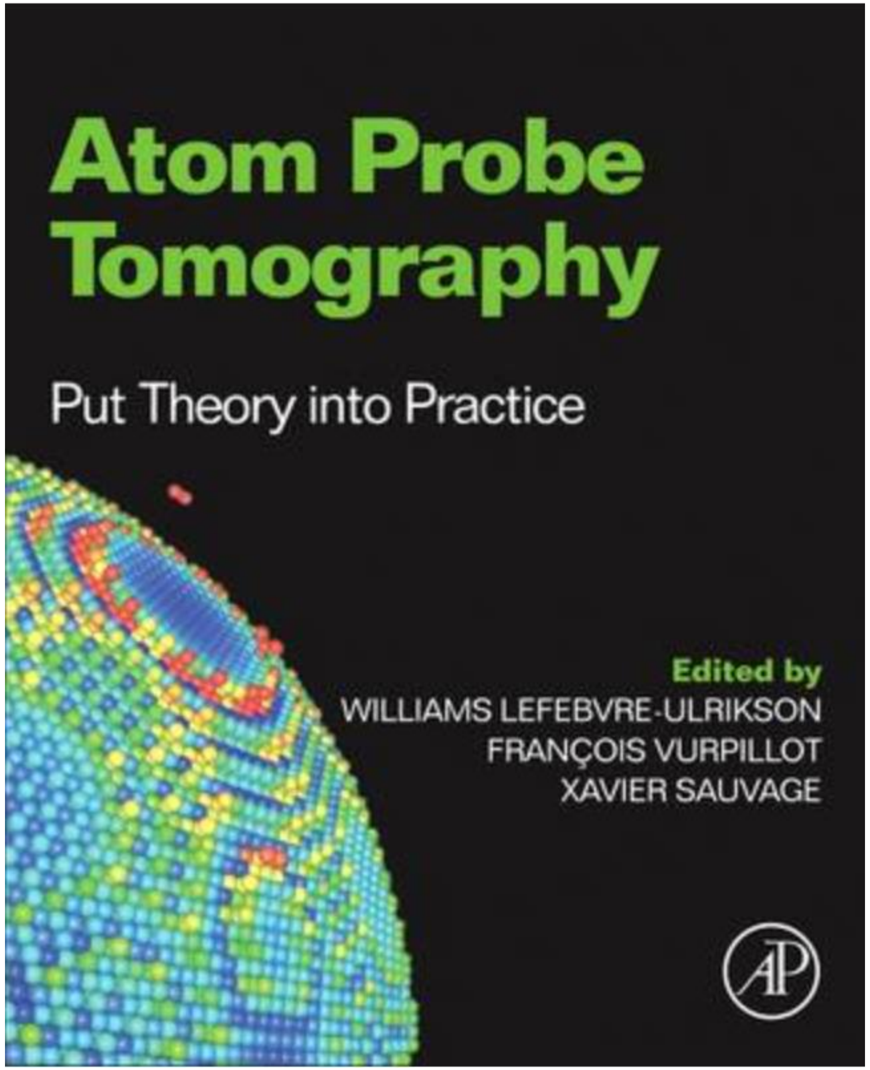
Thorough exposé of the use of a Local Electrode Atom Probe including applications and "How To" explanations for operation, reconstruction and data analysis. (2013)

Reference Texts – Miller and Forbes



In-depth treatment of atom probe tomography including underlying theory of field emission and field evaporation. (2014)

Reference Texts – Lefebvre et al.



Complete introduction to atom probe tomography developed from a course taught at the Université de Rouen (2016).

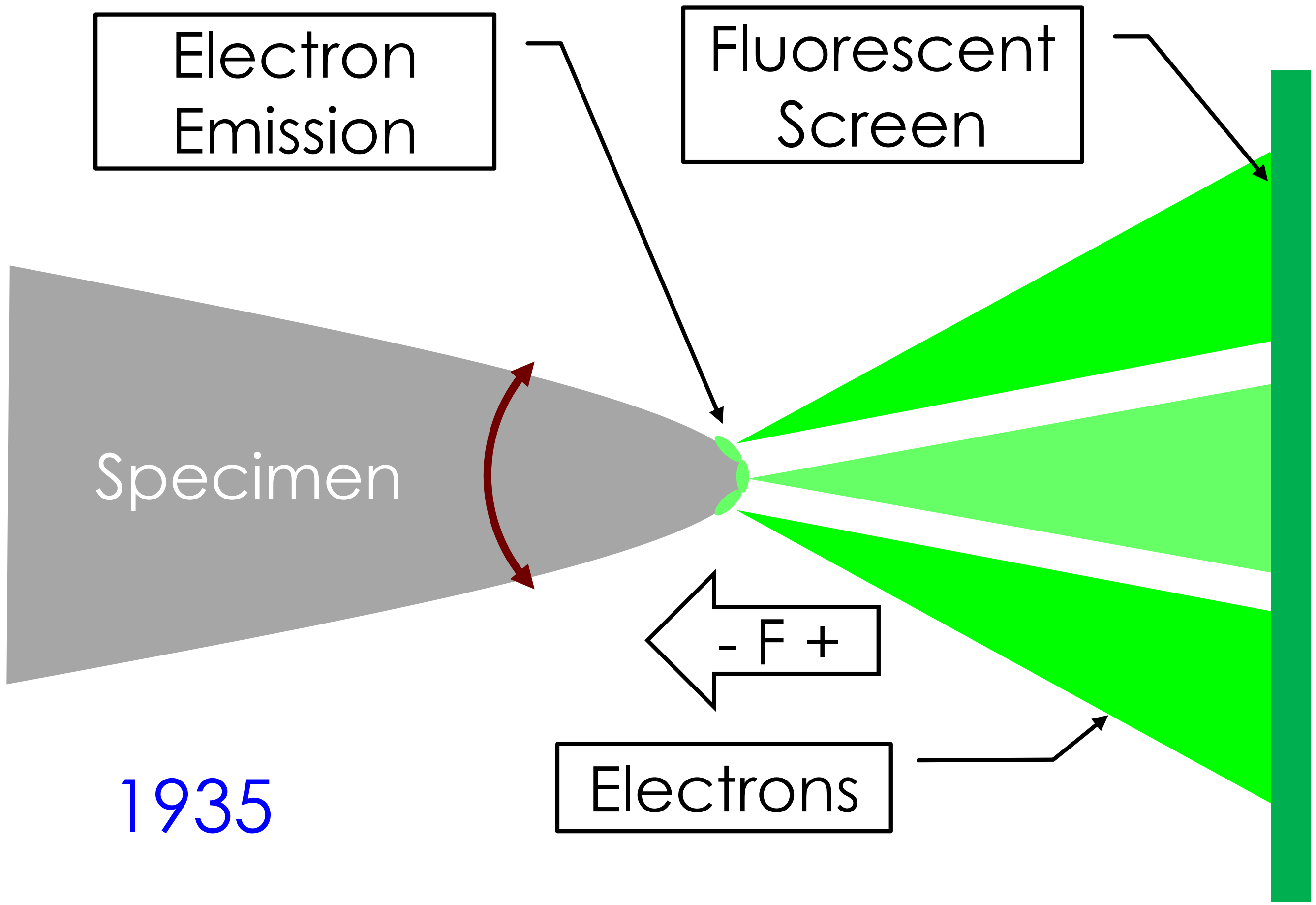
Brief History of Atom Probe

Erwin Wilhelm Müller

- 1911: Born June 13.
- 1936: Degree with Gustav Hertz.
- 1938: Invented the FEEM.
- 1941: Discovered field-desorption.
- 1951: Invented the FIM.
- 1952: Joined Penn State Faculty.
- 1956: First observation of atoms.
- 1966: Developed the Atom-Probe.
- 1975: Elected, National Acadamies of Science and Engineering.
- 1977: Received the National Medal of Science.
- 1977: Considered for the Nobel Prize in Physics.
- 1977: Died May 17.

Photograph of Professor Erwin W. Müller (1911-1977): Father of High Field Nanoscience

Field Electron Emission Microscopy



1935

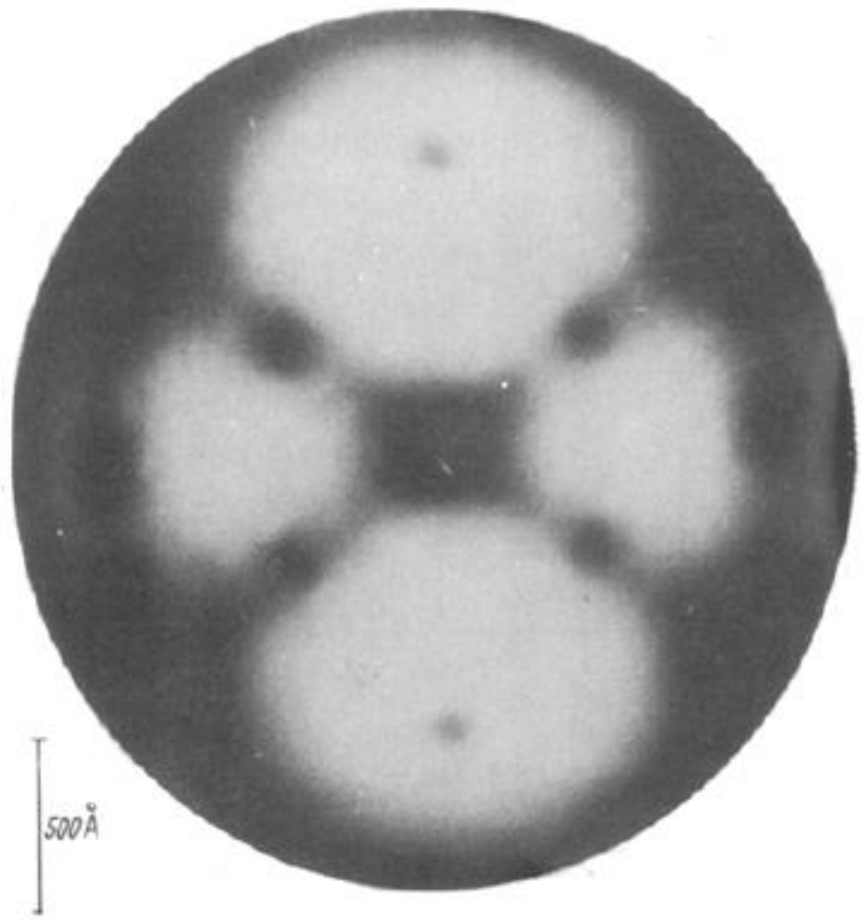
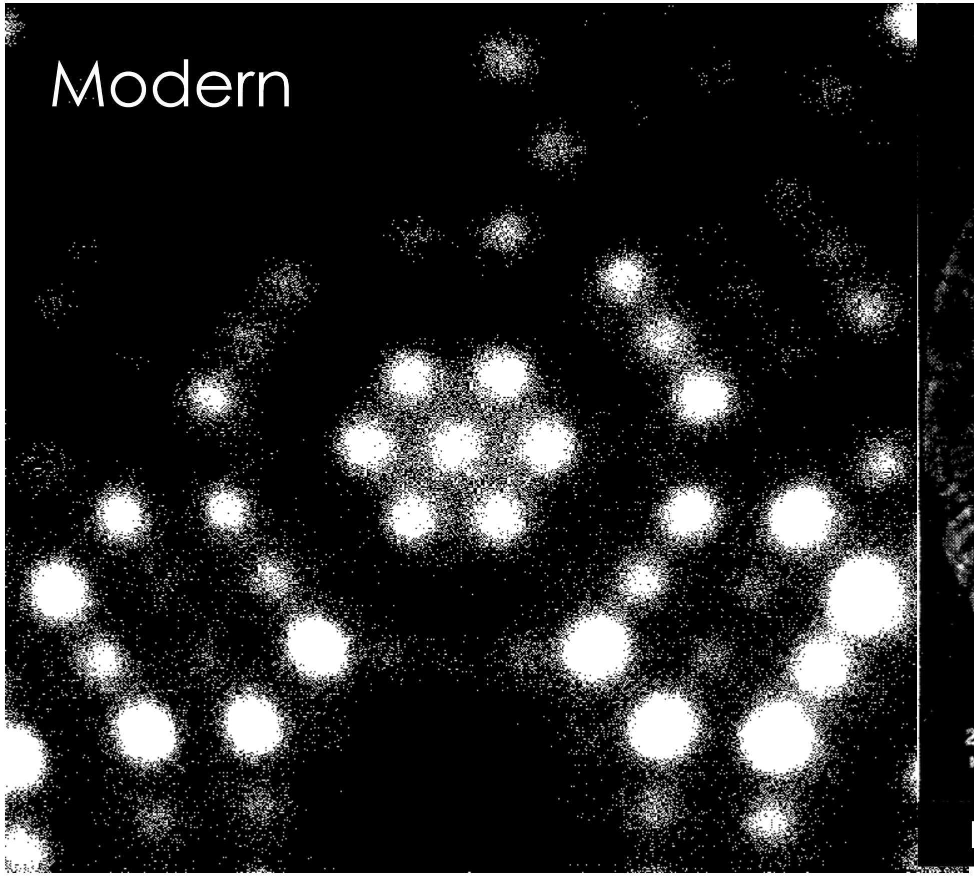
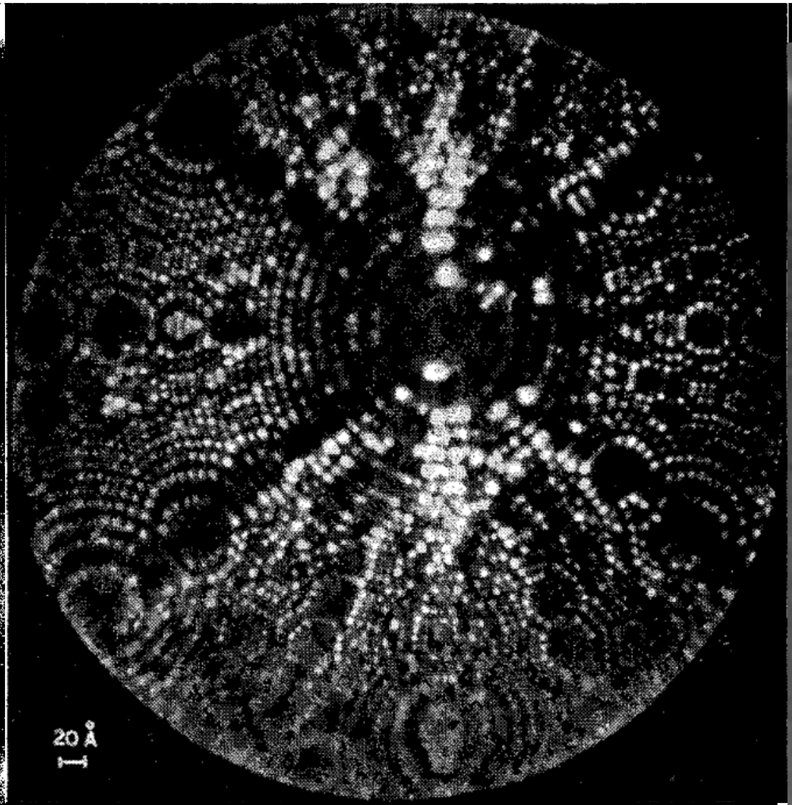


Fig. 5. Elektronenbild einer reinen Wolframkathode.

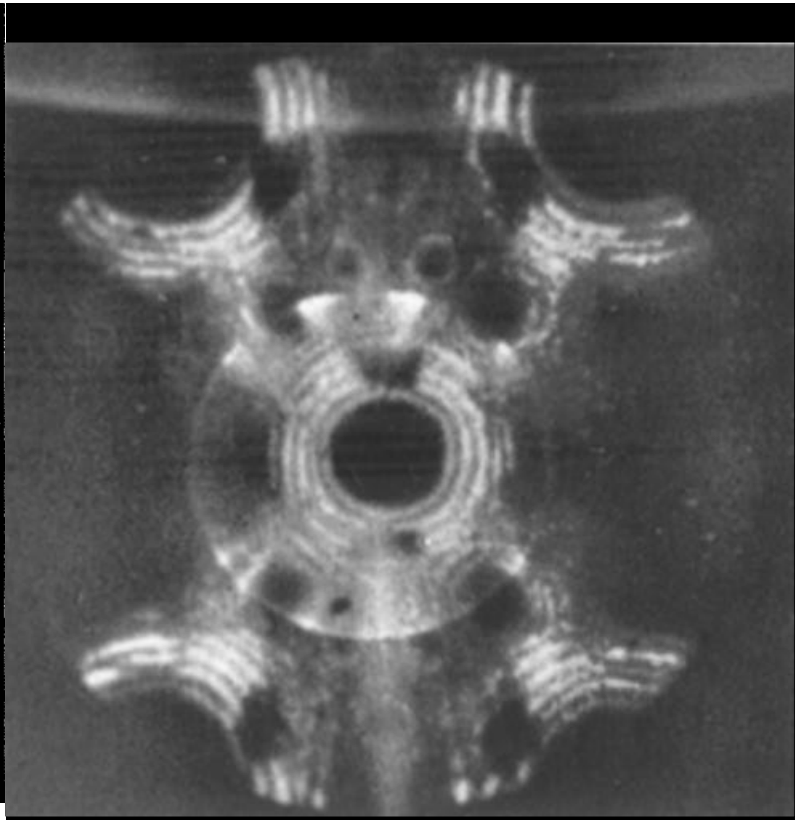
E. W. Müller, Z. Phys. 120 (1943) 270

Field Ion Microscopy





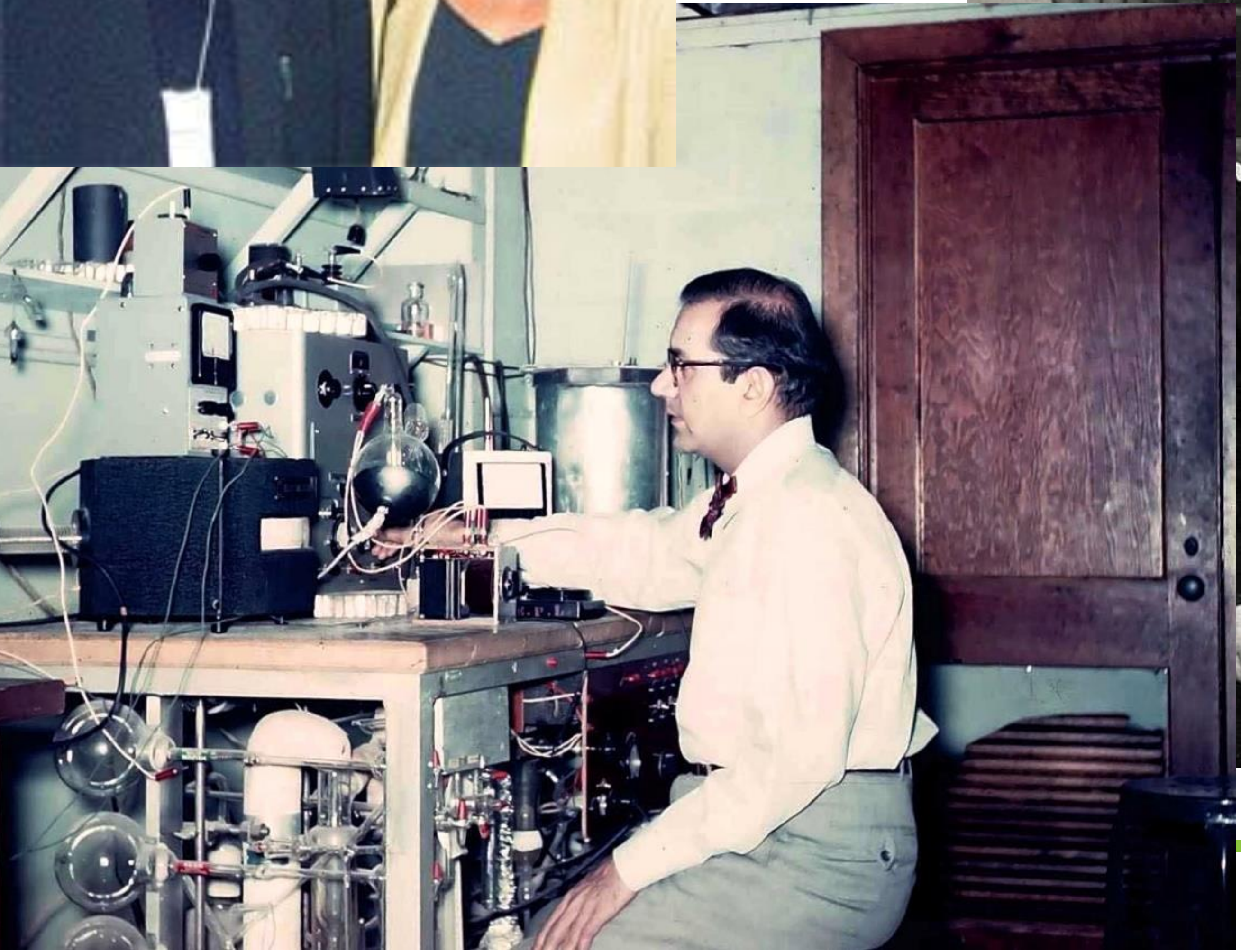
E. W. Müller, J Appl. Phys. 27 (1956) 474

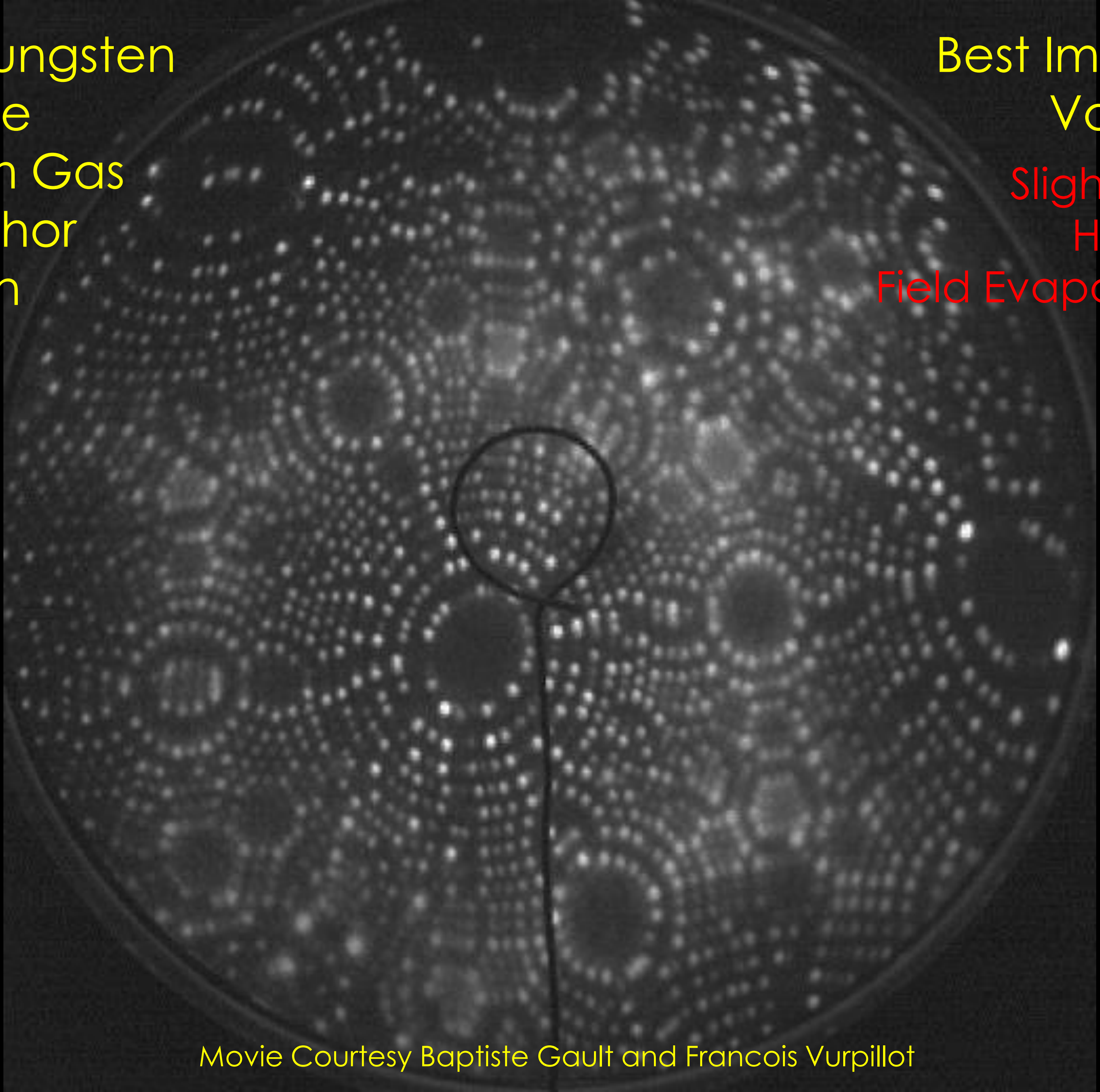


E. W. Müller, Z. Phys. 131 (1951) 136

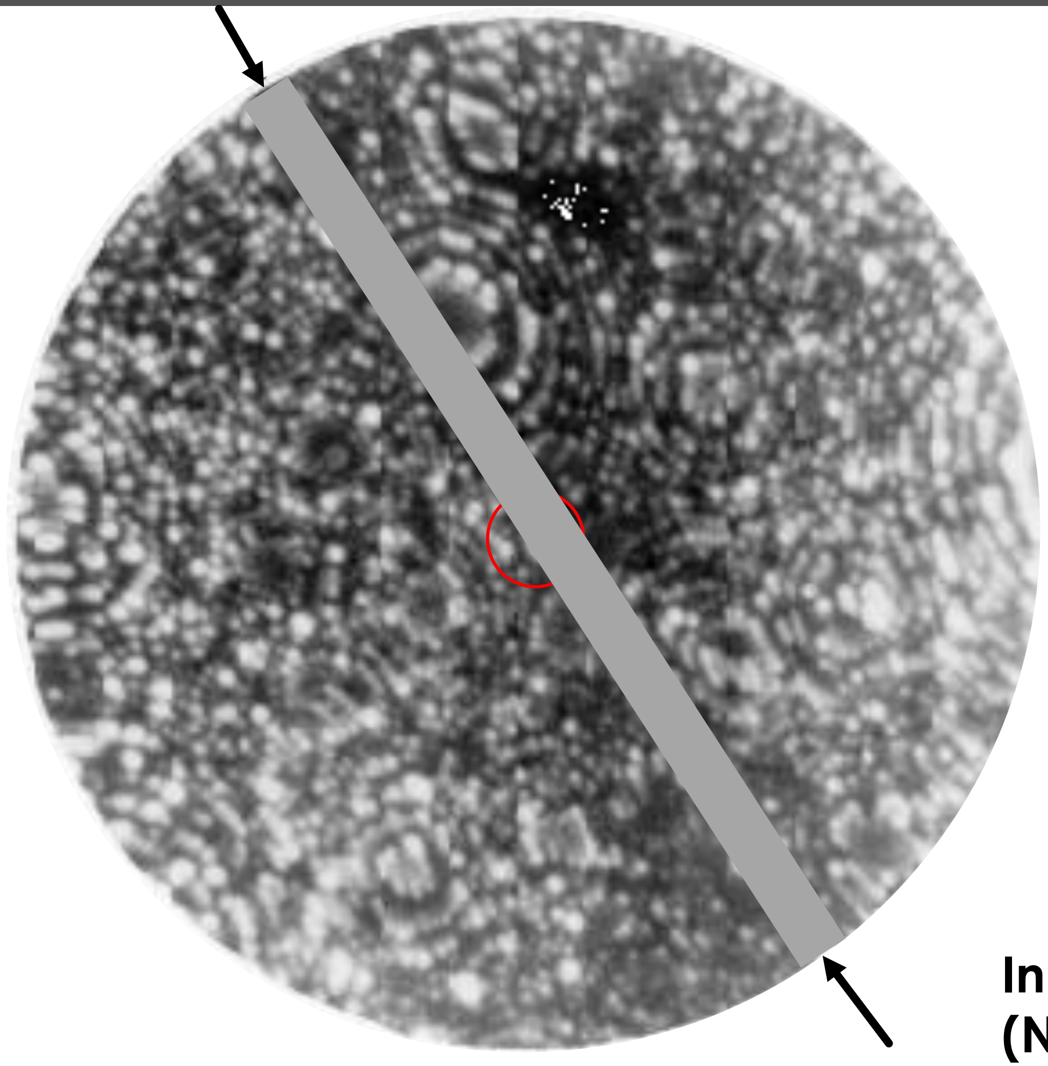
First FIM images of images ever of atoms (on ledges of tip surface): Summer 1951, Müller
First atomically resolved lattice on surface: October 11, 1955, Bahadur and Müller

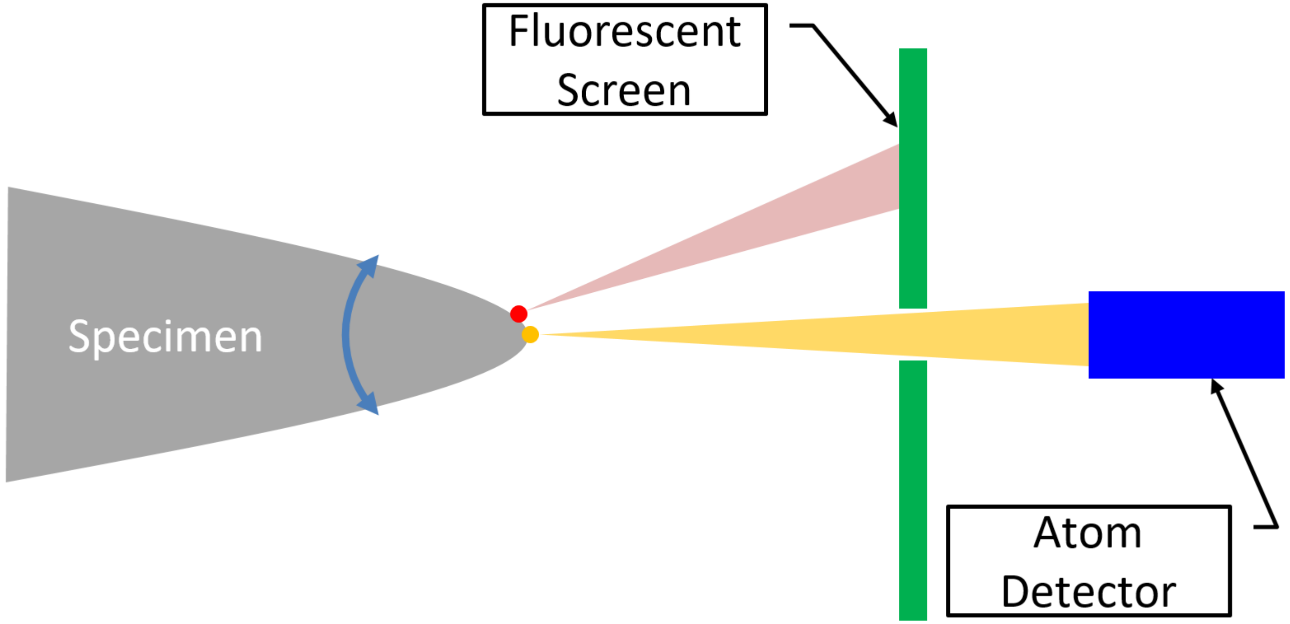
Kanwar Bahadur
The first human to see atoms




40 K Tungsten
Needle
Helium Gas
Phosphor
Screen
Best Imaging
Voltage
Slight Laser
Heating
Field Evaporation
Movie Courtesy Baptiste Gault and Francois Vurpillot

Compositional Contrast in FIM



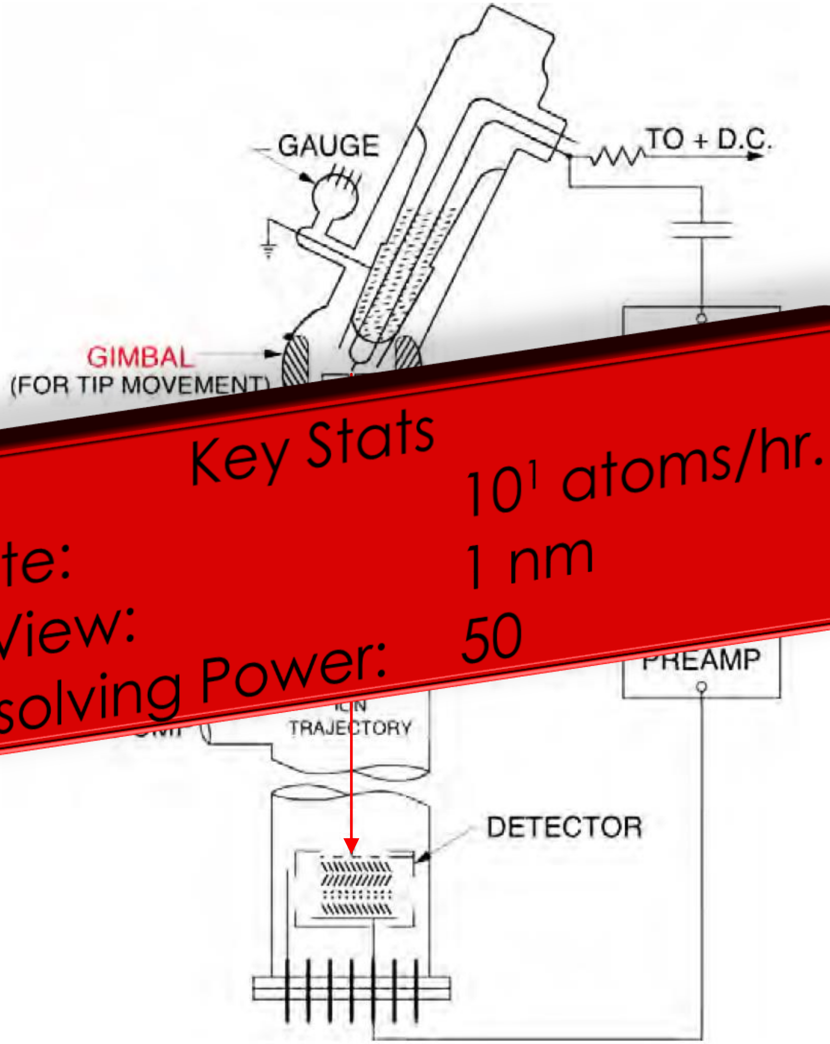


Atom-Probe Field Ion Microscope

In this field ion micrograph of boron-doped nickel aluminide (Ni_3Al), the bright dots are individual boron atoms that have segregated to a grain boundary (arrowed).

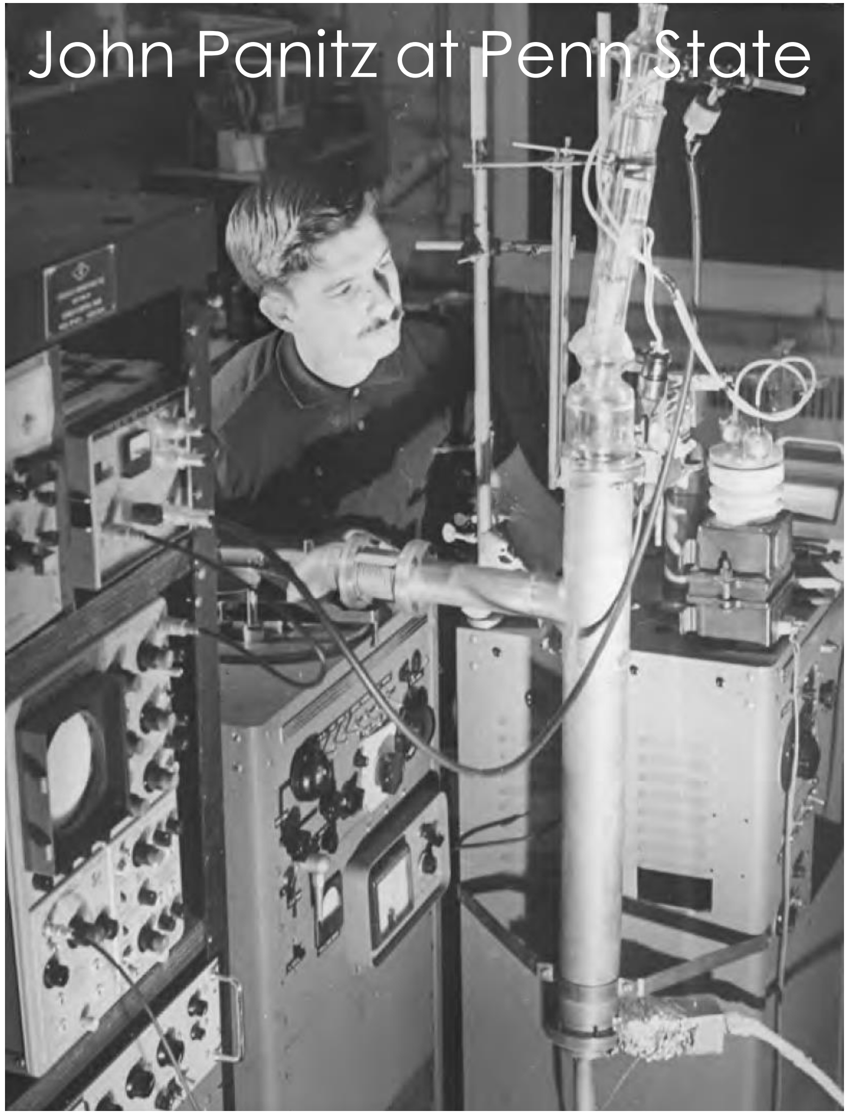
Original Atom-Probe Field Ion Microscope

1967

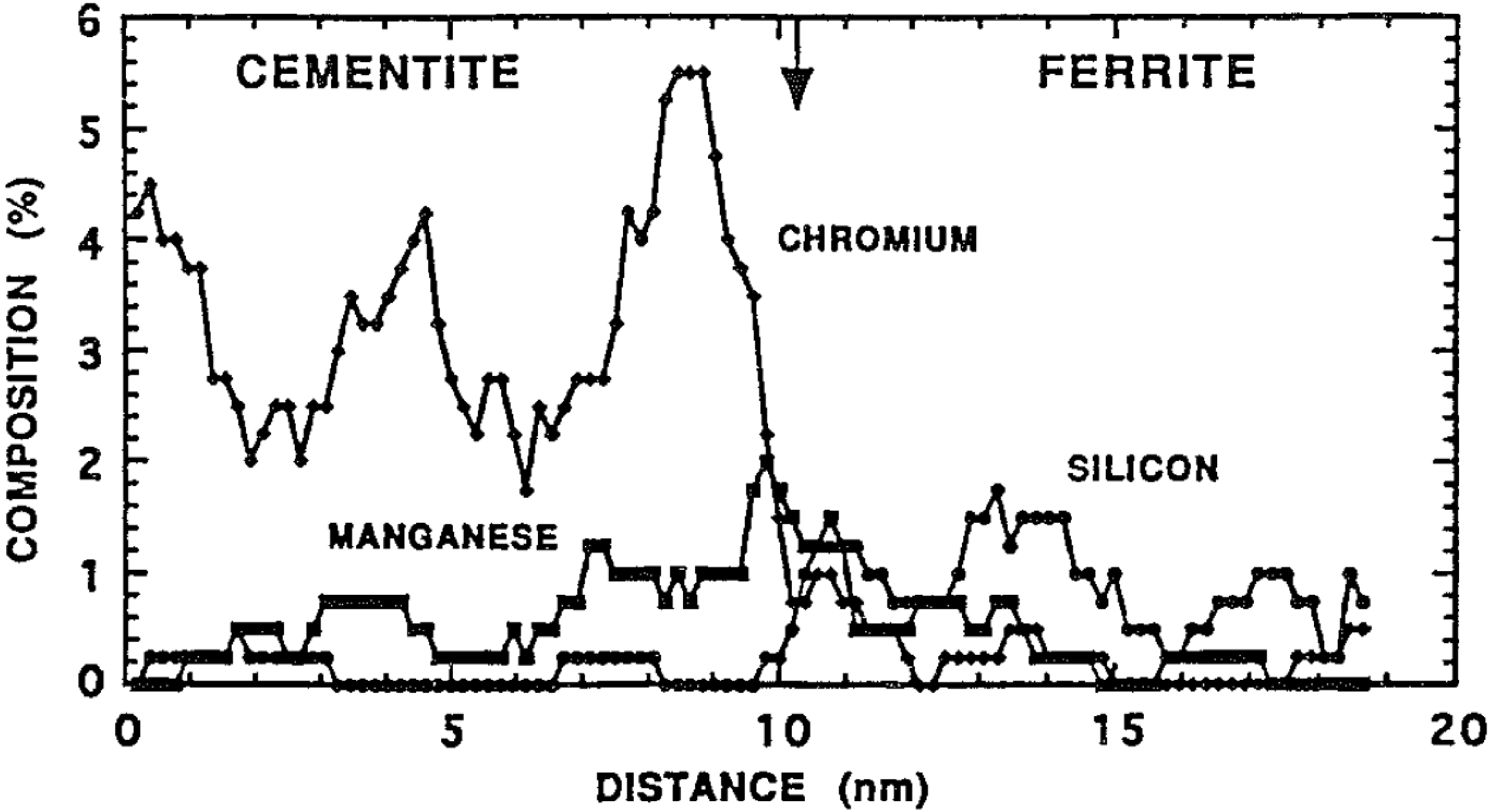


Key Stats

Data Rate:	10^1 atoms/hr.
Field of View:	1 nm
Mass Resolving Power:	50



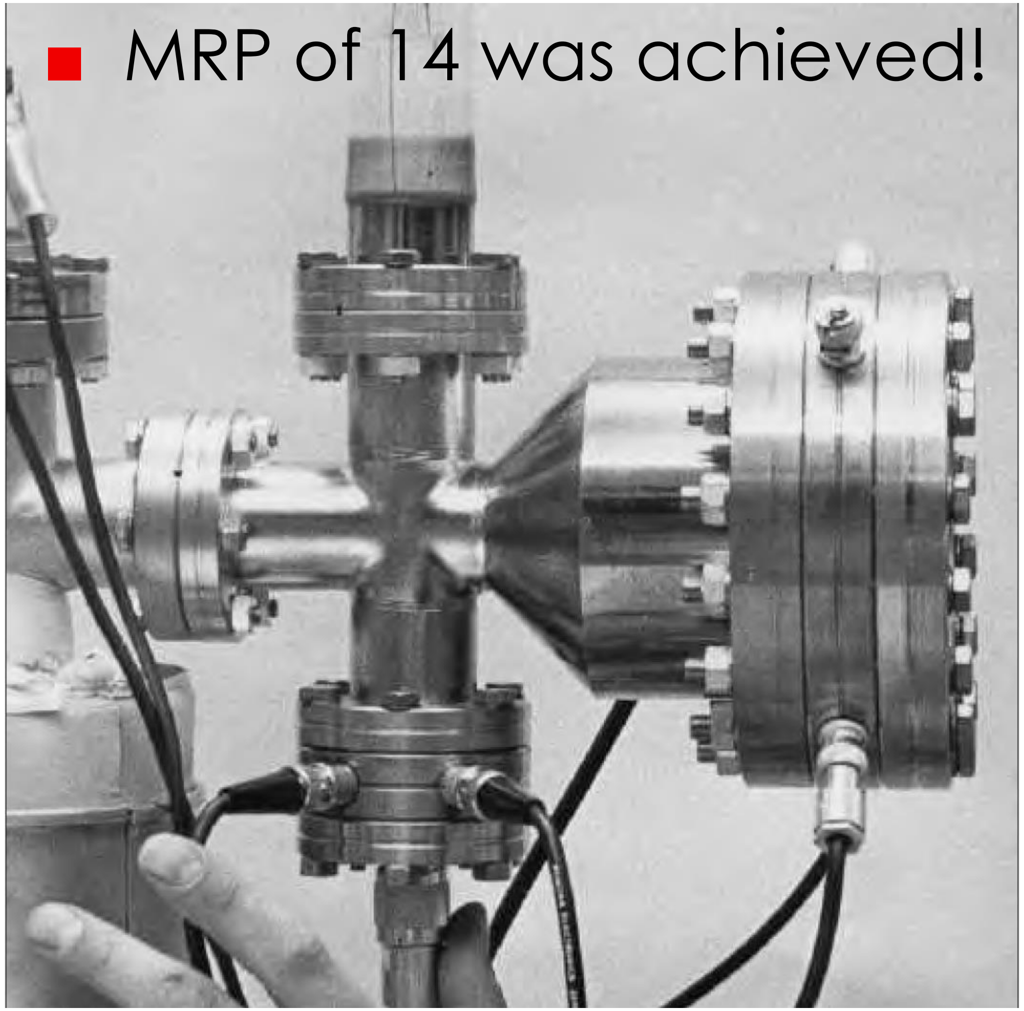
One-Dimensional Atom Probe Profile



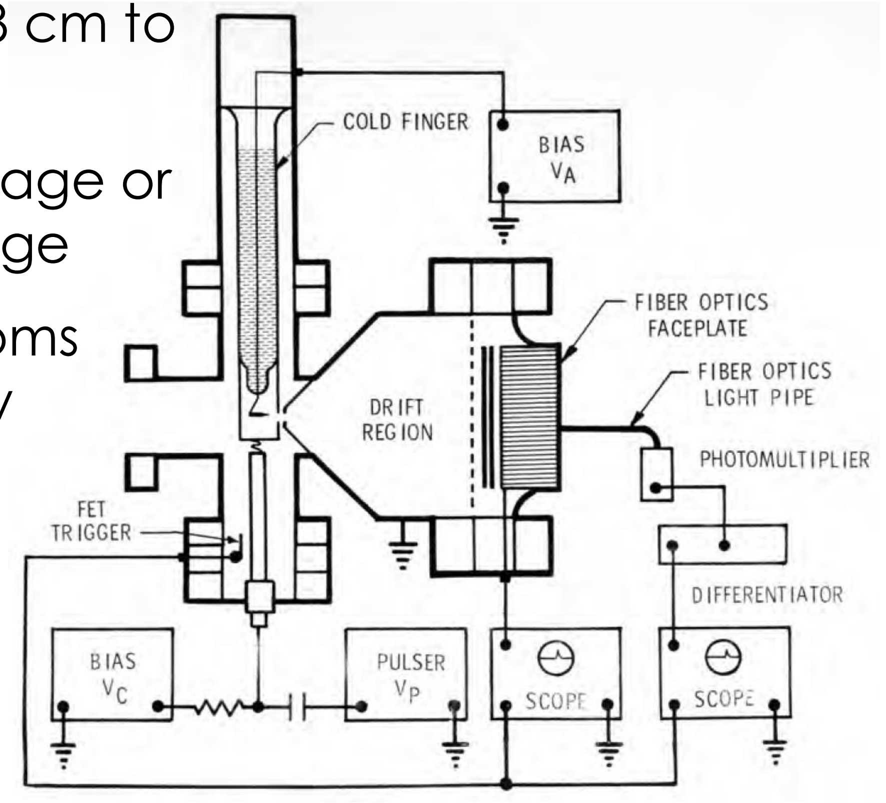
M. K. Miller and G. D. W. Smith, "Atom Probe Microanalysis of a Pearlitic Steel," *Met. Sci.*, vol. 11, no. 7, p. 249, 1977.

Imaging Atom Probe: the Progenitor of Atom Probe Tomography

- MRP of 14 was achieved!

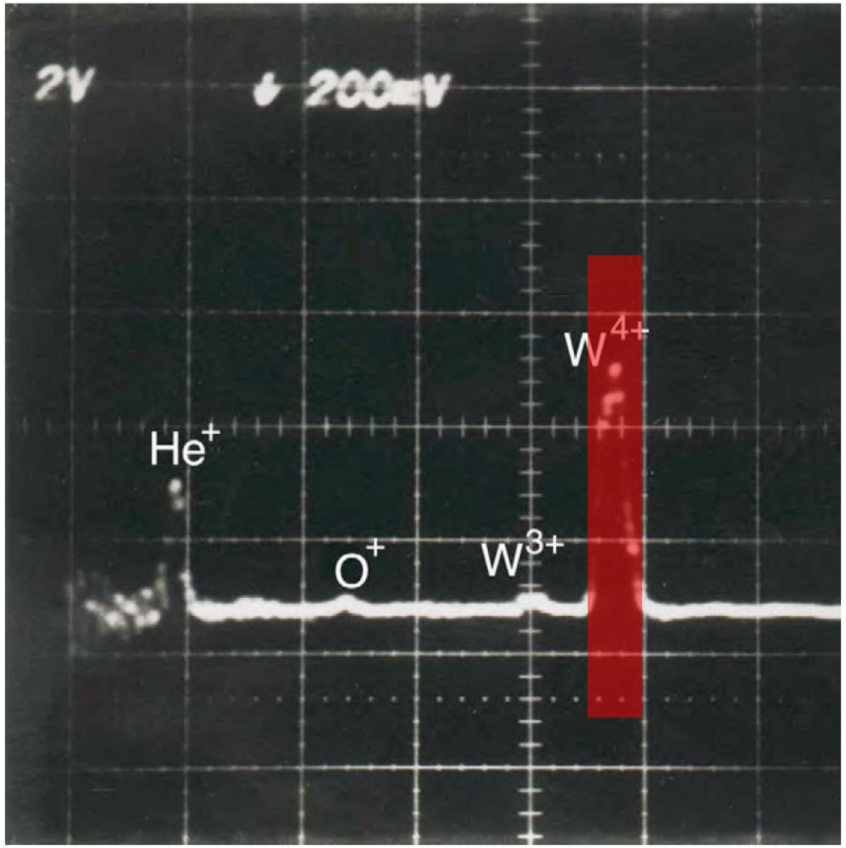


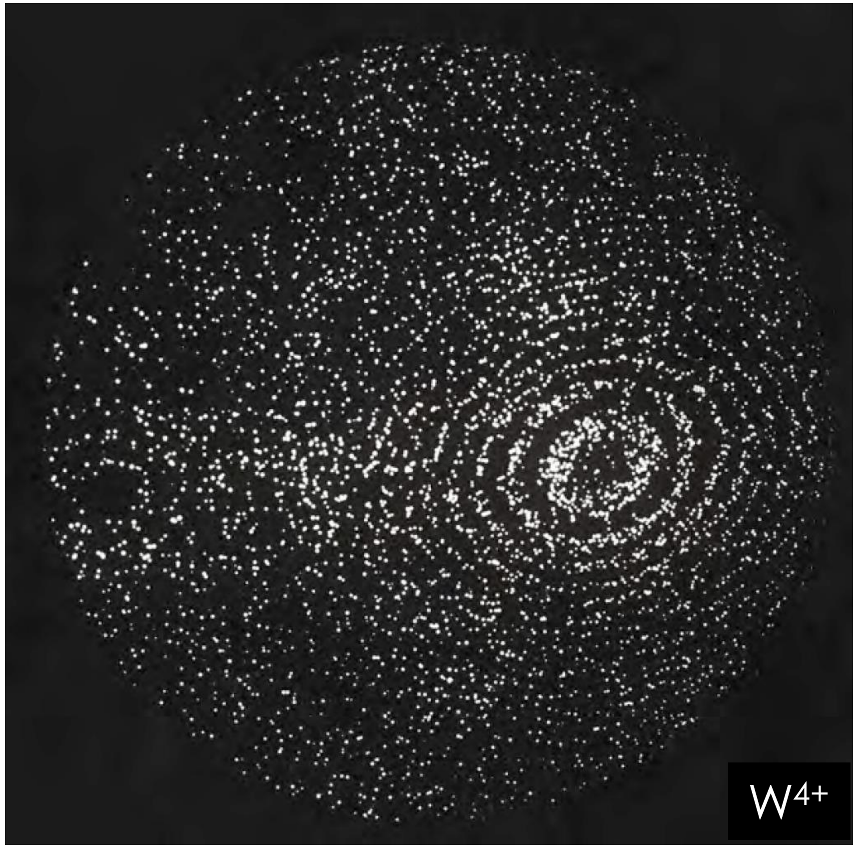
- Tip tilting not needed
- Flight distance 11.38 cm to center
- Observe field ion image or field desorption image
- Mass analyze all atoms within a field of view



J. A. Panitz, “The 10 cm Atom-Probe,” *Rev. Sci. Instrum.*, vol. 44 (1973) p. 249.

Field Desorption Images of Single Specie



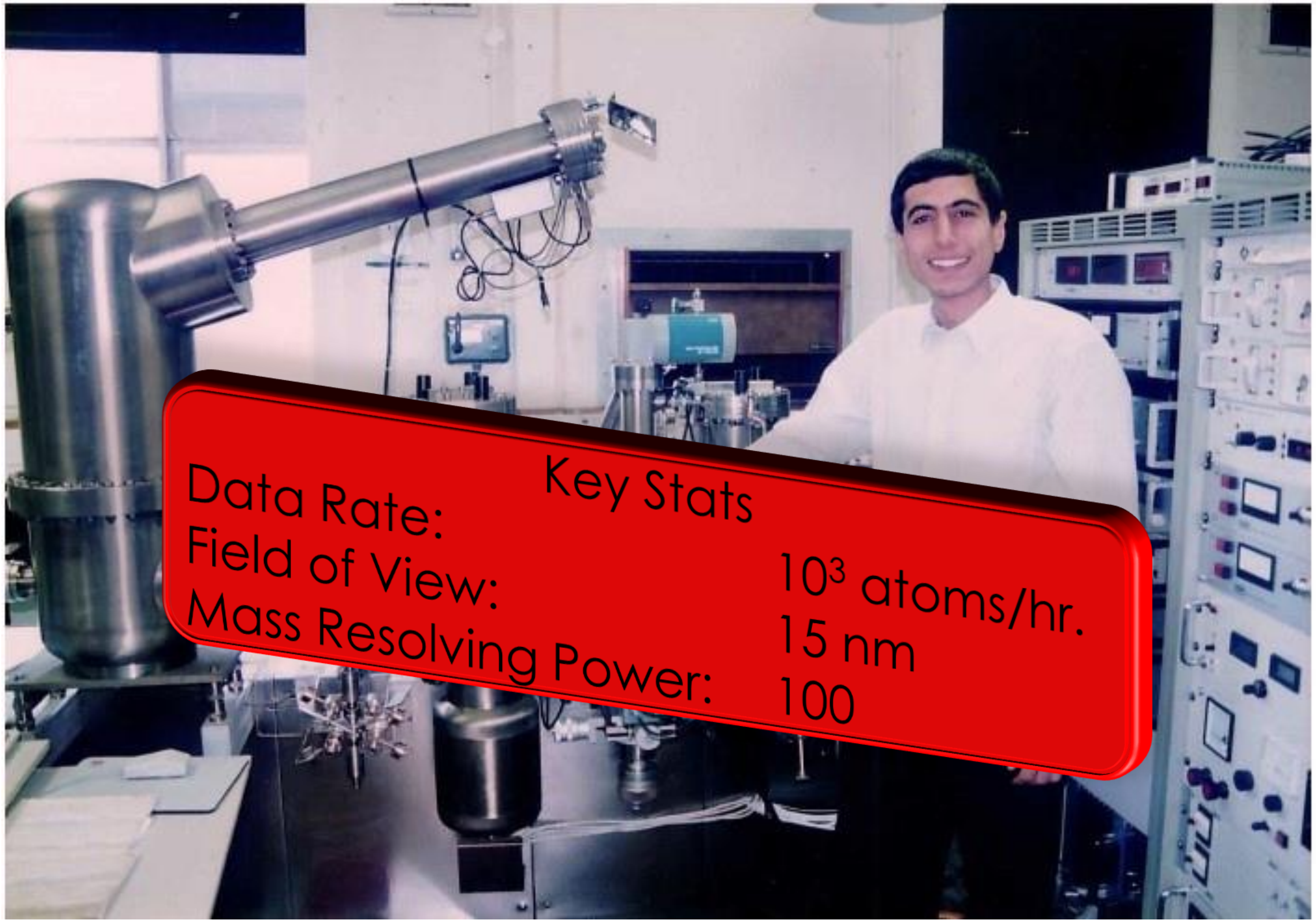


- Time gate on MCPs

J. A. Panitz, "The Crystallographic Distribution of field desorbed species," *J. Vac. Sci. Technol.*, vol. A11 (1974) p. 206.
J. A. Panitz, "Field desorption spectrometer," United States Patent 3,868,507 (1975).

The Position-Sensitive Atom Probe

1988

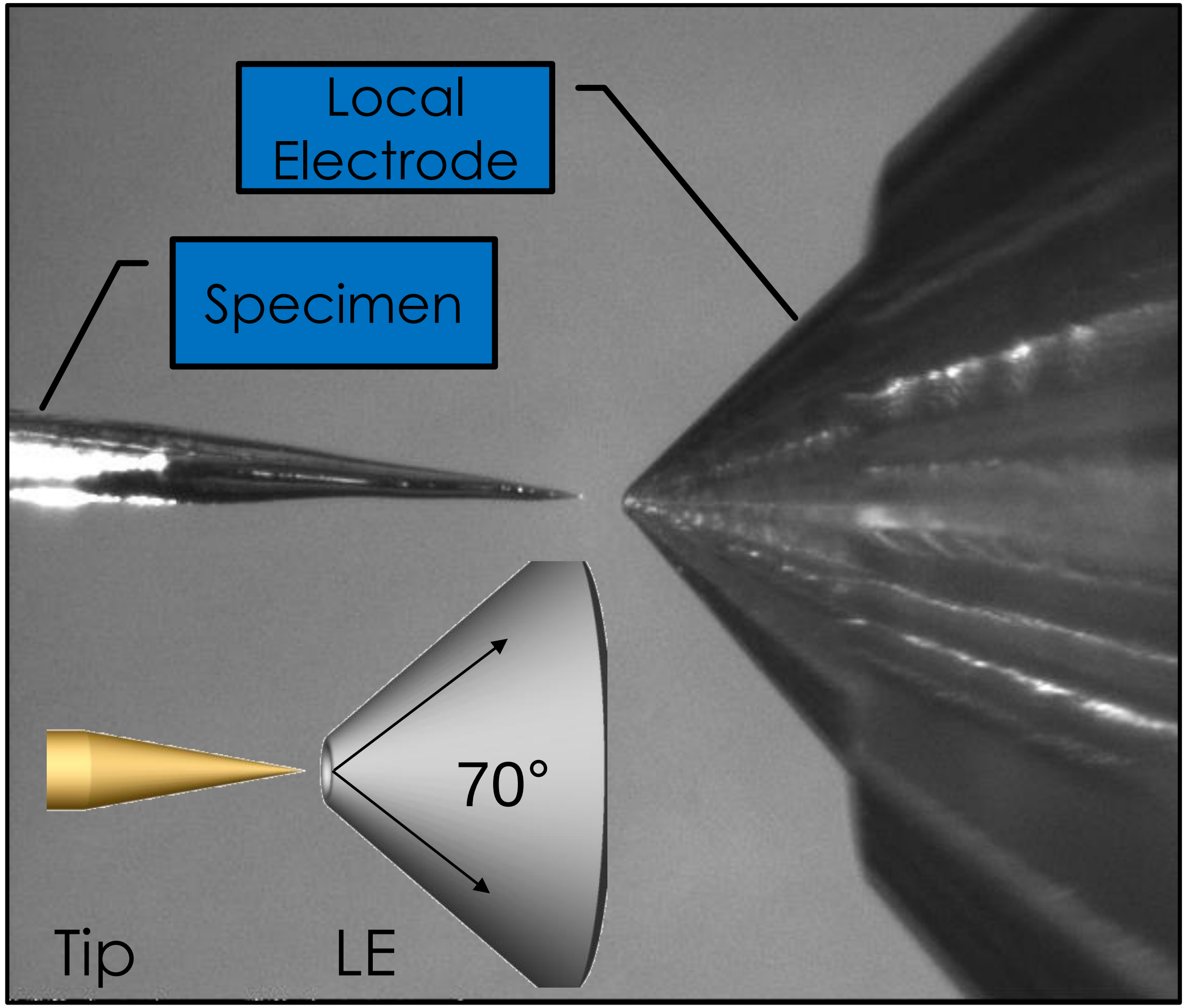


- First operational 3DAP
- Adapted a Wedge-and-Strip detector from astronomy
- 1988 Fall MRS presented by George Smith

A. Cerezo, T. J. Godfrey, and G. D. W. Smith, "Application of a position-sensitive detector to atom probe analysis," *Rev. Sci. Instrum.*, vol. 59(6) (1988) p. 862-866.

Local Electrode

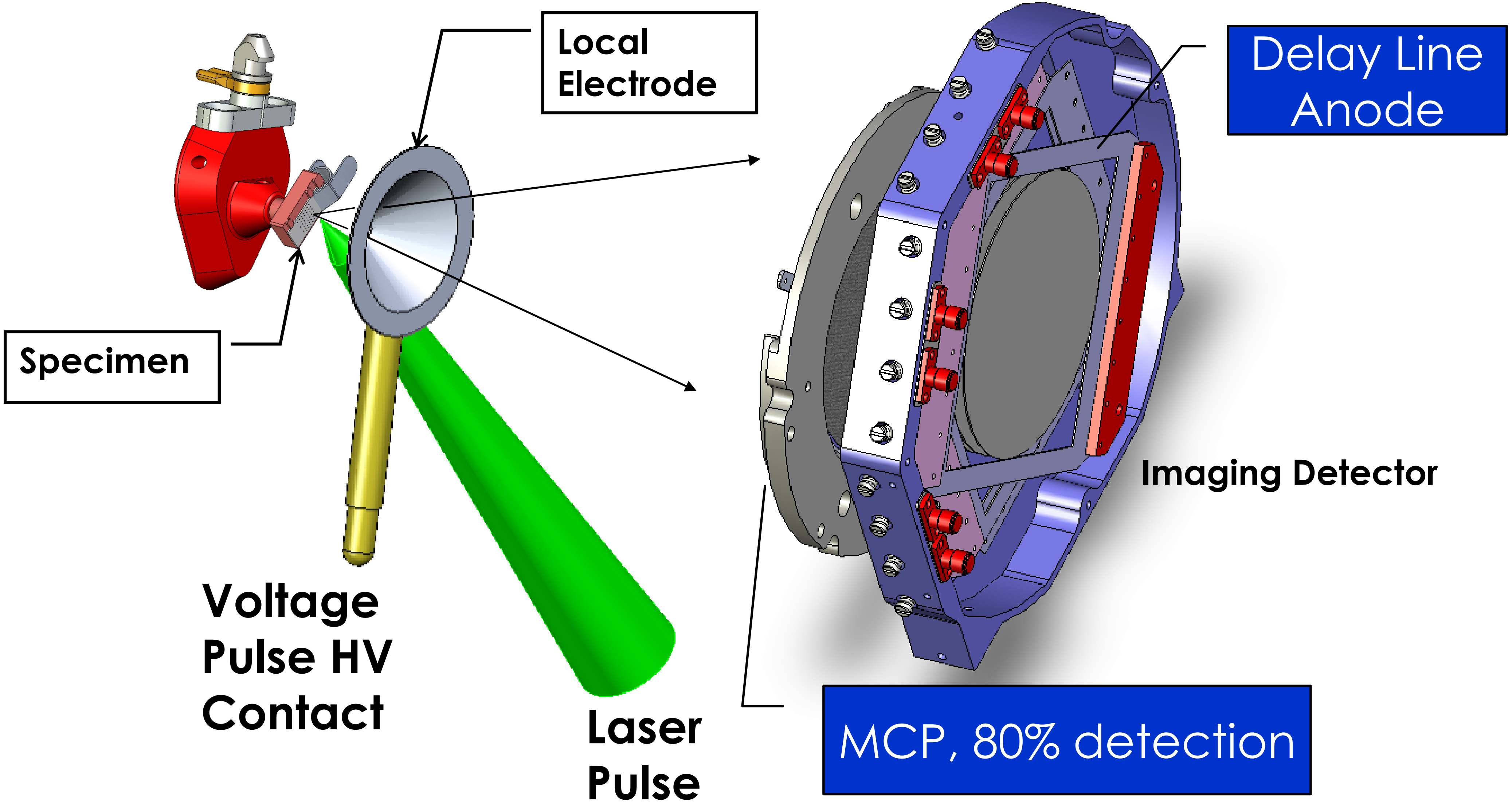
- Field enhancement of the local electrode design enables:
  - Analysis of blunter specimens
  - Large field of view (FOV)
  - Improved mass resolving power
  - Voltage pulsing rates up to 500 kHz



Inspired by Nishikawa work:
O. Nishikawa and M. Kimoto, "Toward a scanning atom probe – computer simulation of electric field," Appl. Surf. Sci., vol. 76/77 (1994) 424-430.

T. F. Kelly, P. P. Camus, D. J. Larson, L. M. Holzman, and S. S. Bajikar, "On the Many Advantages of Local Electrode Atom Probes," ***Ultramicroscopy*****, vol. 62 (1996) p. 29-42.**

Atom Probe Microscope



Commercial LEAP Progression

LEAP 3000

2003

- 10x FoV
- 10^3x speed increase

LEAP 3000X

Green Laser

2006

- First available laser mode
- FIB-based specimen preparation

LEAP 3000X Si/HR

Voltage Energy Compensation

2007

- Advanced energy-compensated design
- Innovative new Detector Technologies
- Greatly Expanded Application Range

LEAP 4000X Si/HR

Small Spot UV Laser

2010

- New, advanced laser platform
- Breakthrough performance for ceramics/ insulators & complex/ device structures
- Enables commercial APT adoption

Key Stats

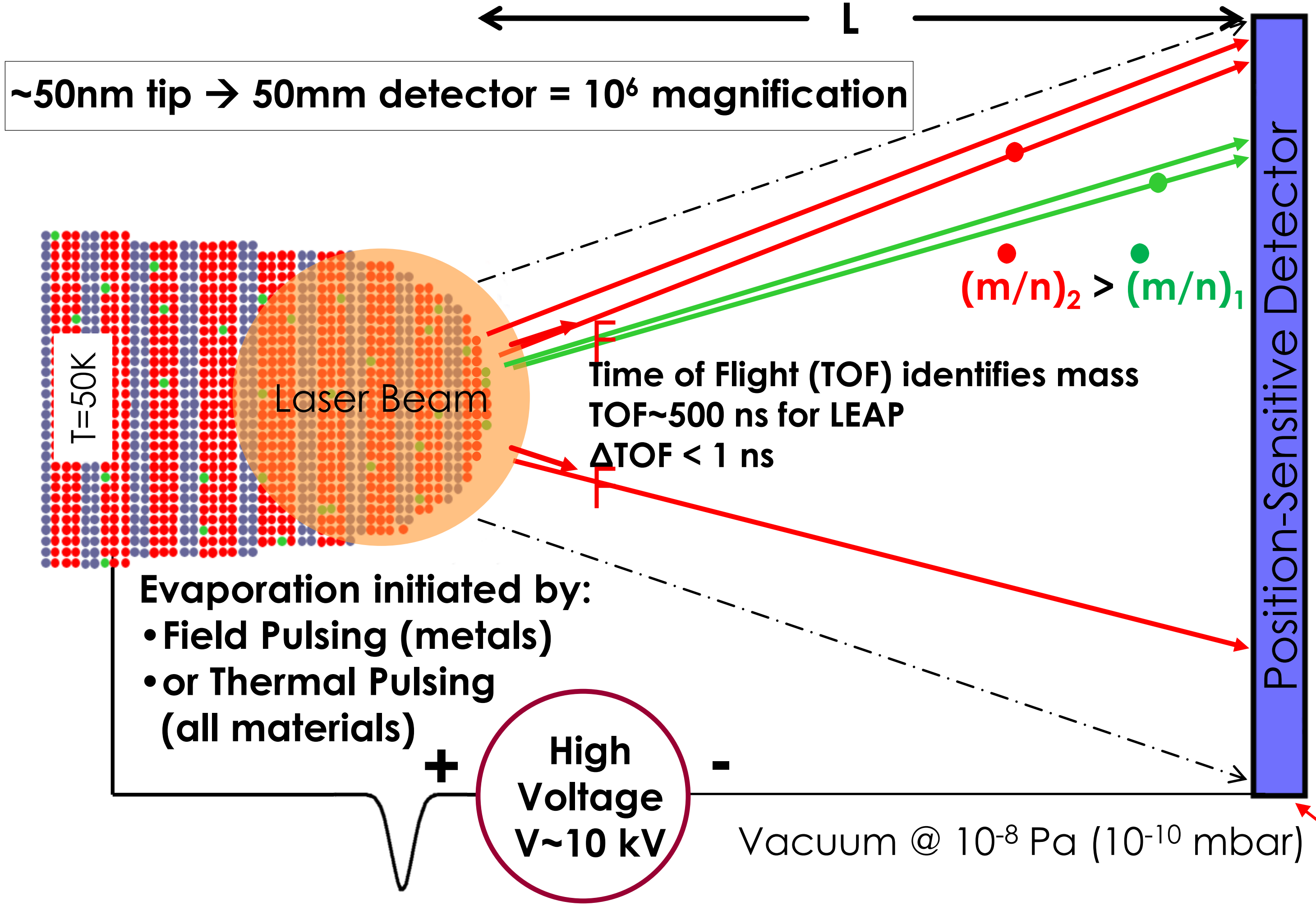
Data Rate:	10^8 atoms/hr.
Field of View:	200 nm
Mass Resolving Power:	1200

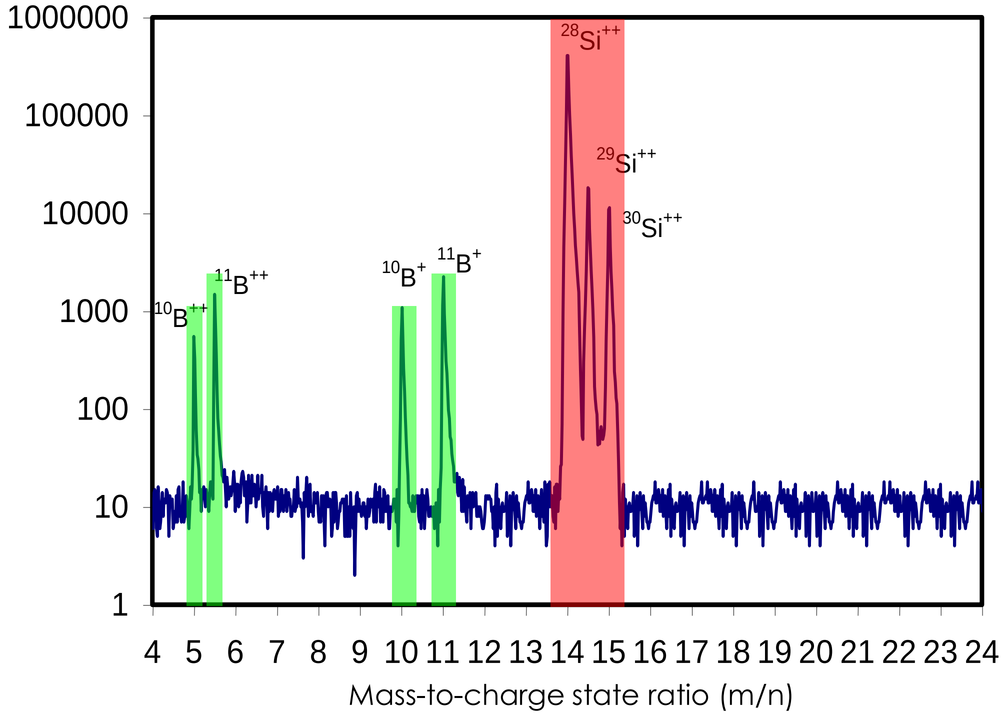
The LEAP 5000

APT Fundamentals

Description of Atom Probe Operation

Atom Probe = projection imaging with time-of-flight mass spectrometer





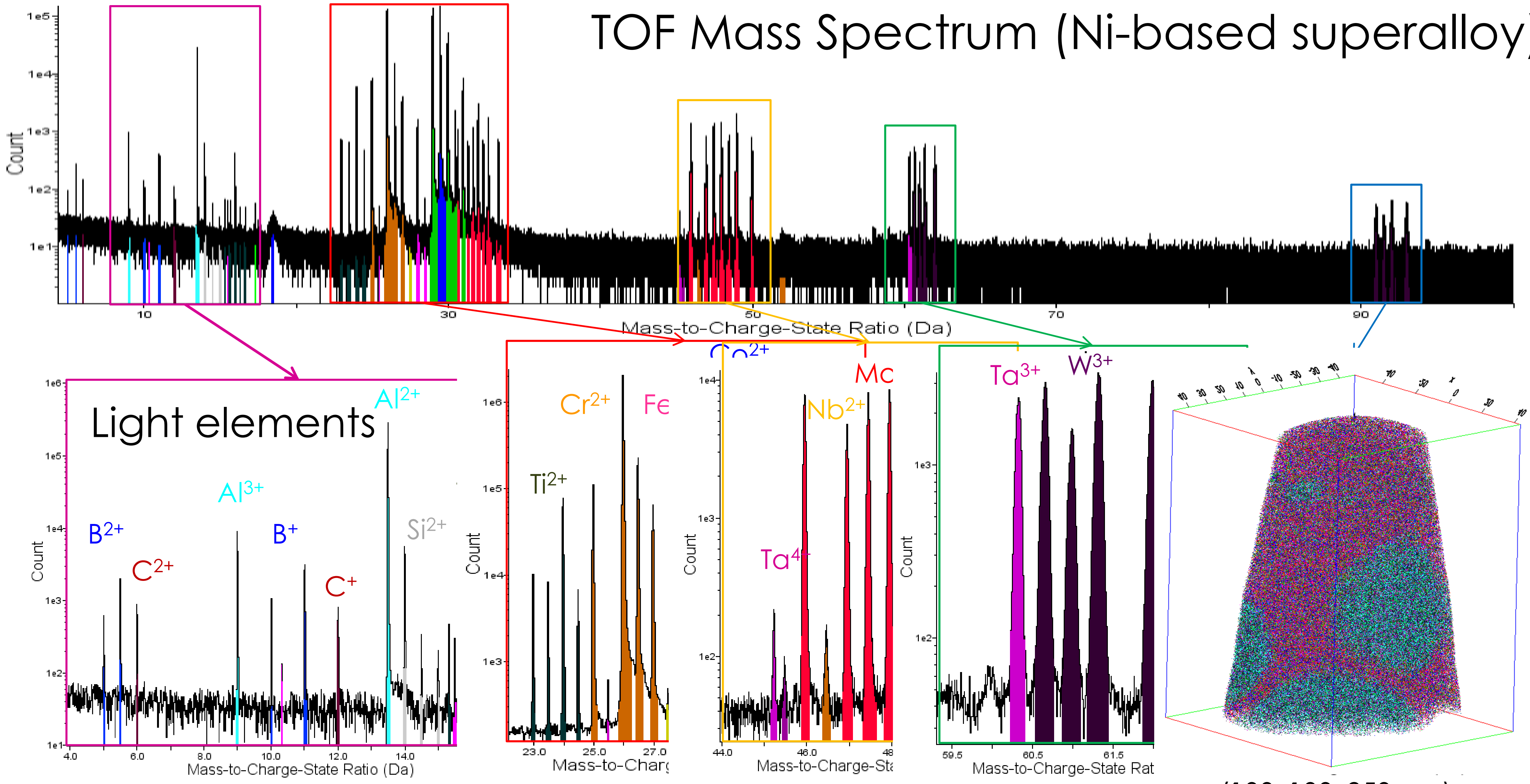
~80% Detection Efficiency

$neV = \frac{1}{2}mv^2$

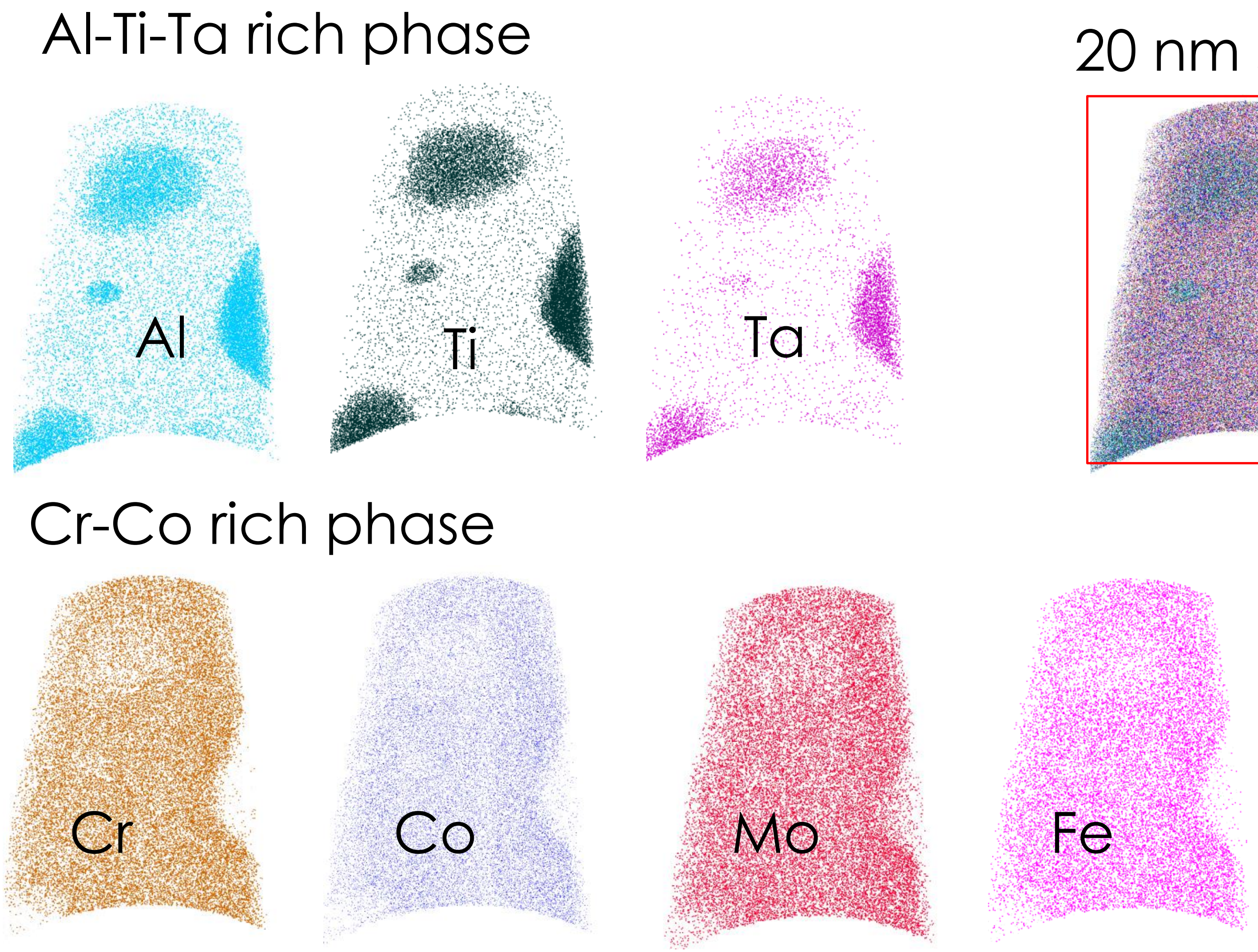
$v = L/t = \text{constant}$

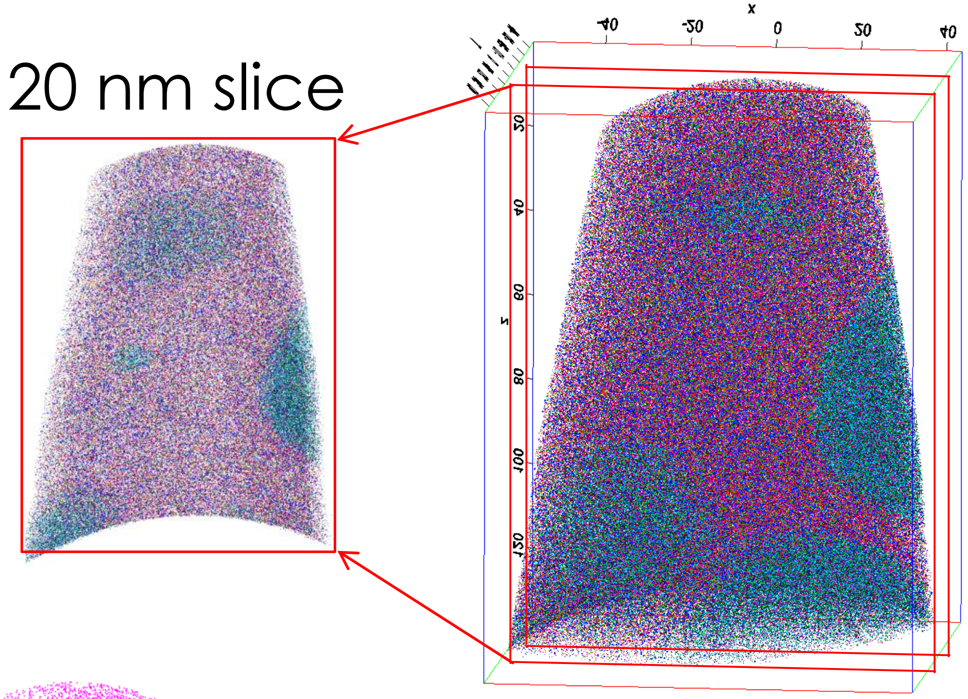
⇨ $m/n = 2eV\, t^2/L^2$

TOF Mass Spectrum (Ni-based superalloy)



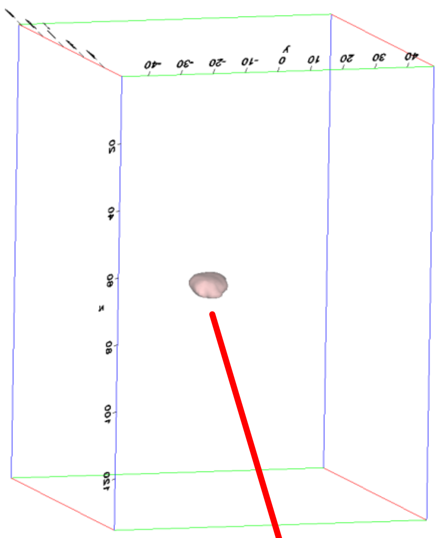
3D Compositional Mapping



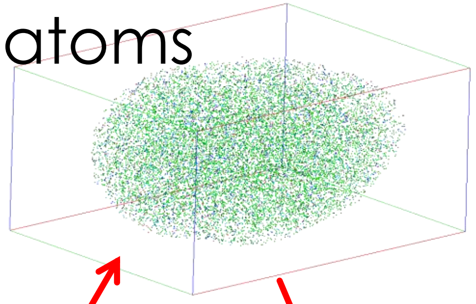


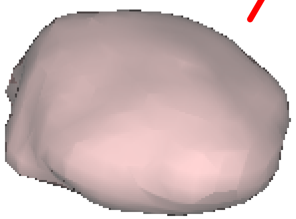
Local Compositional Analysis

Interface Visualization



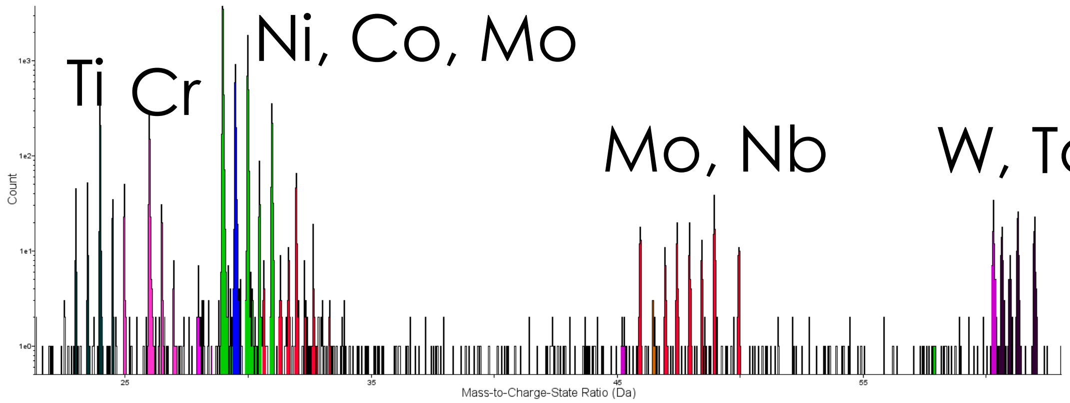
Precipitate atoms





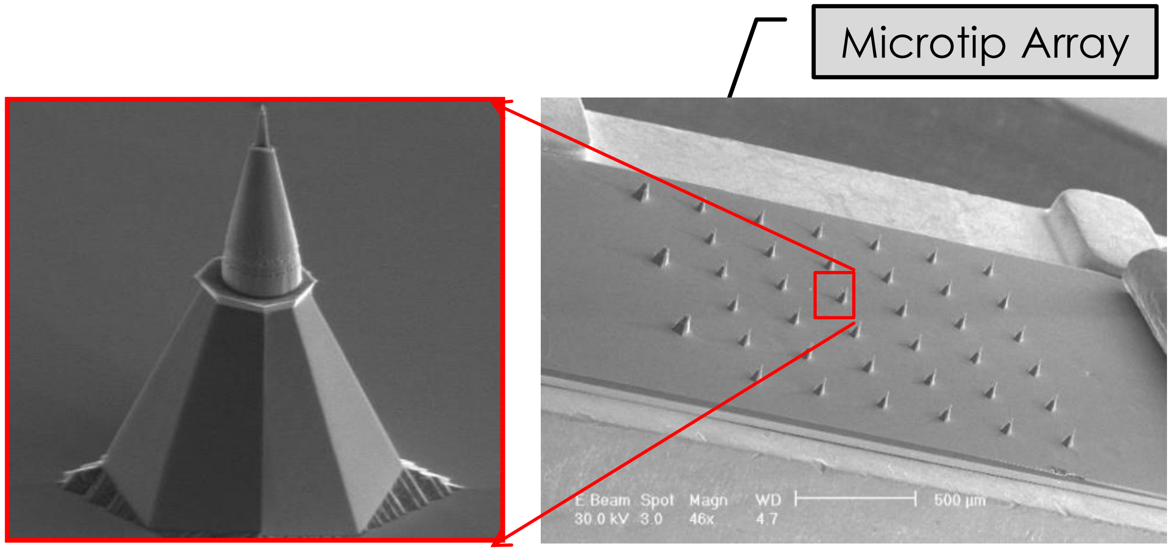
Selected volume analysis

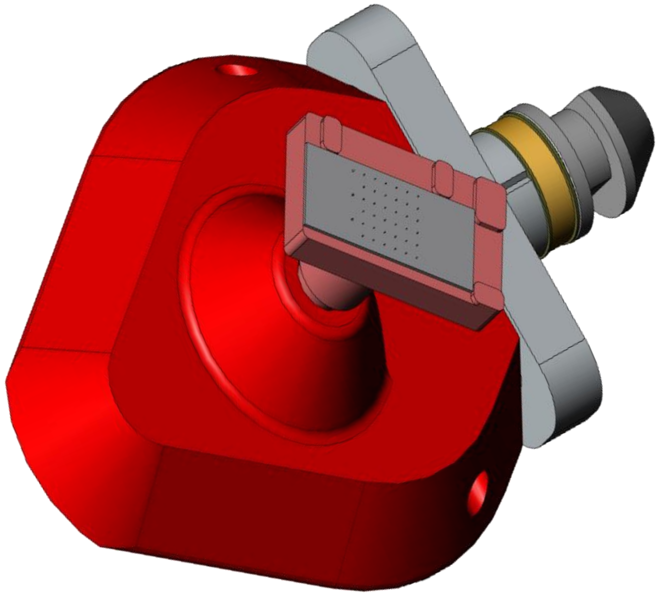
Selected Volume Mass

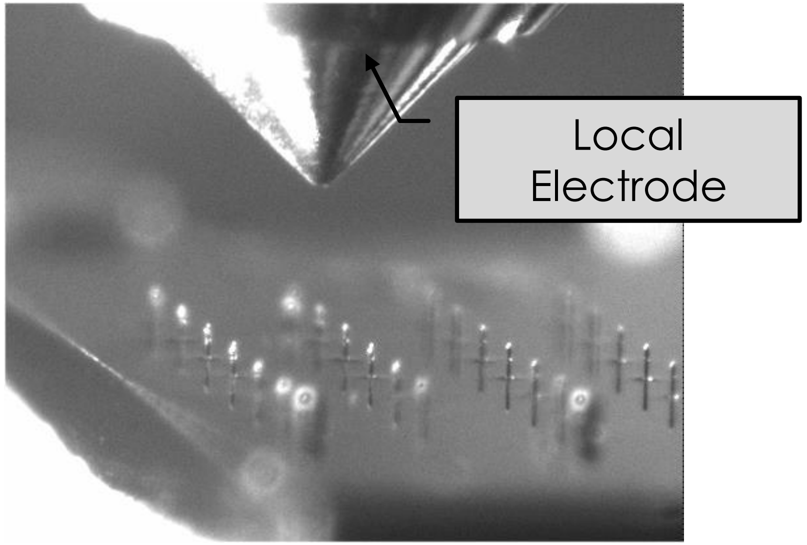


Composition of Particle		
Element	No ions	At %
Ni	11929	62.81%
Al	2777	14.62%
Co	1791	9.43%
Ti	880	4.63%
Cr	679	3.58%
Mo	541	2.85%
W	246	1.30%
Ta	86	0.45%
B	17	0.09%
Fe	16	0.08%
Nb	10	0.05%
Si	9	0.05%

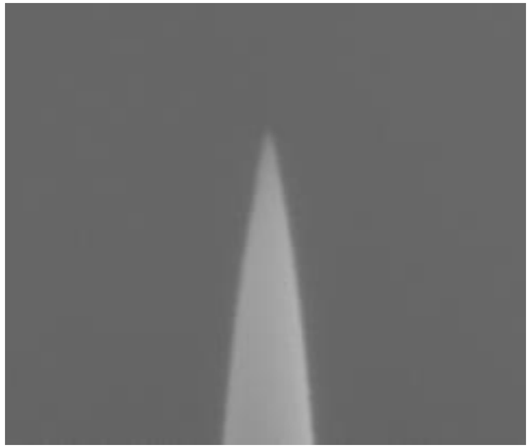
Microtips™ in the LEAP®



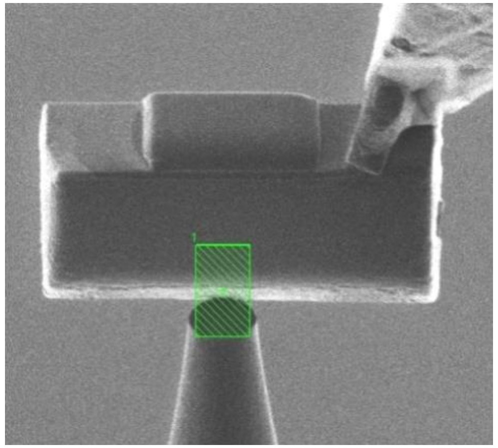


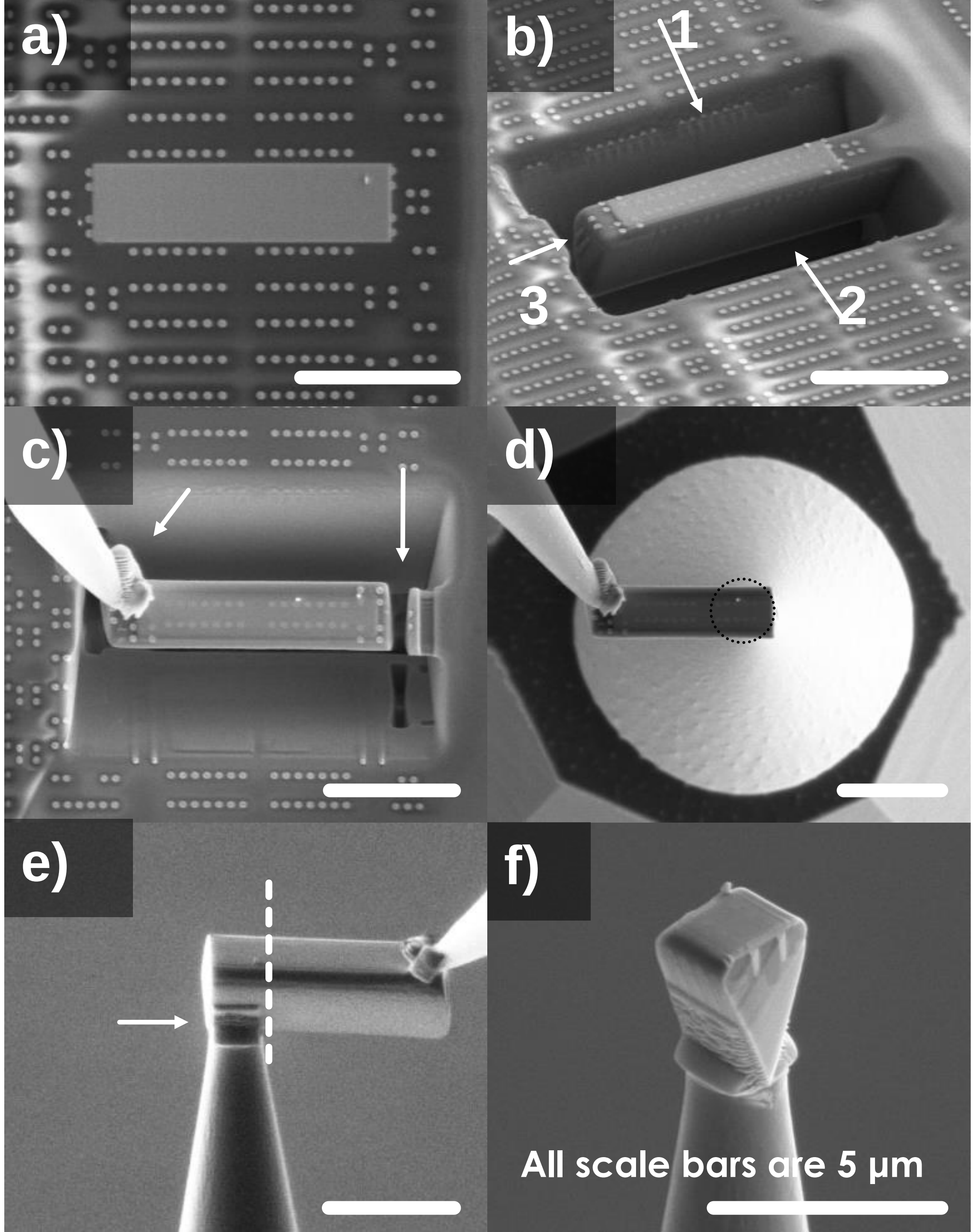


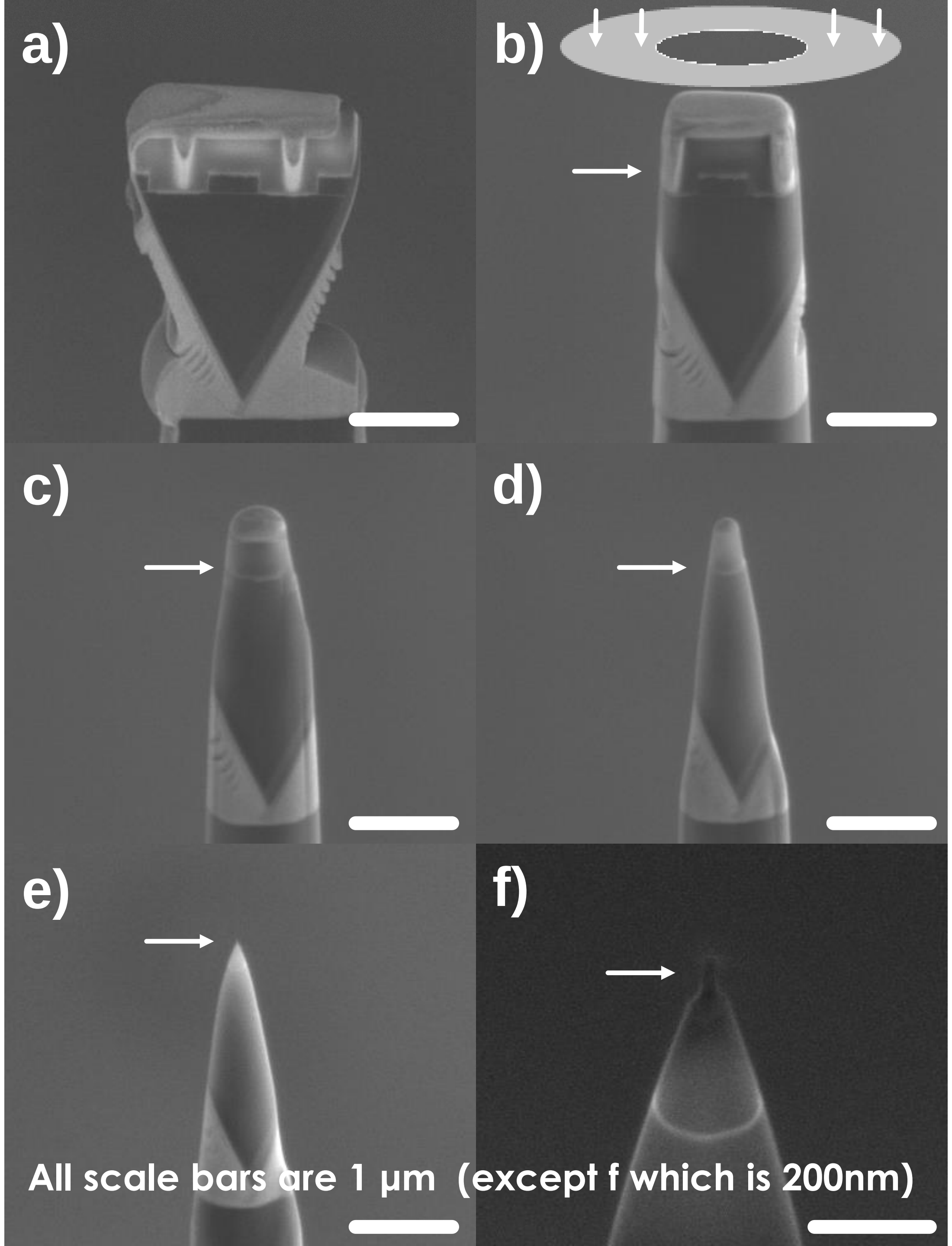
Sharp



Flat Top




a)
b)
1
2
3
c)
d)
e)
f)
All scale bars are 5 μm


a)
b)
c)
d)
e)
f)
All scale bars are 1 μm (except f which is 200nm)

STEAM INSTRUMENTS

Limitations and Strengths of APT

Limitations of APT as an Analytical Technique

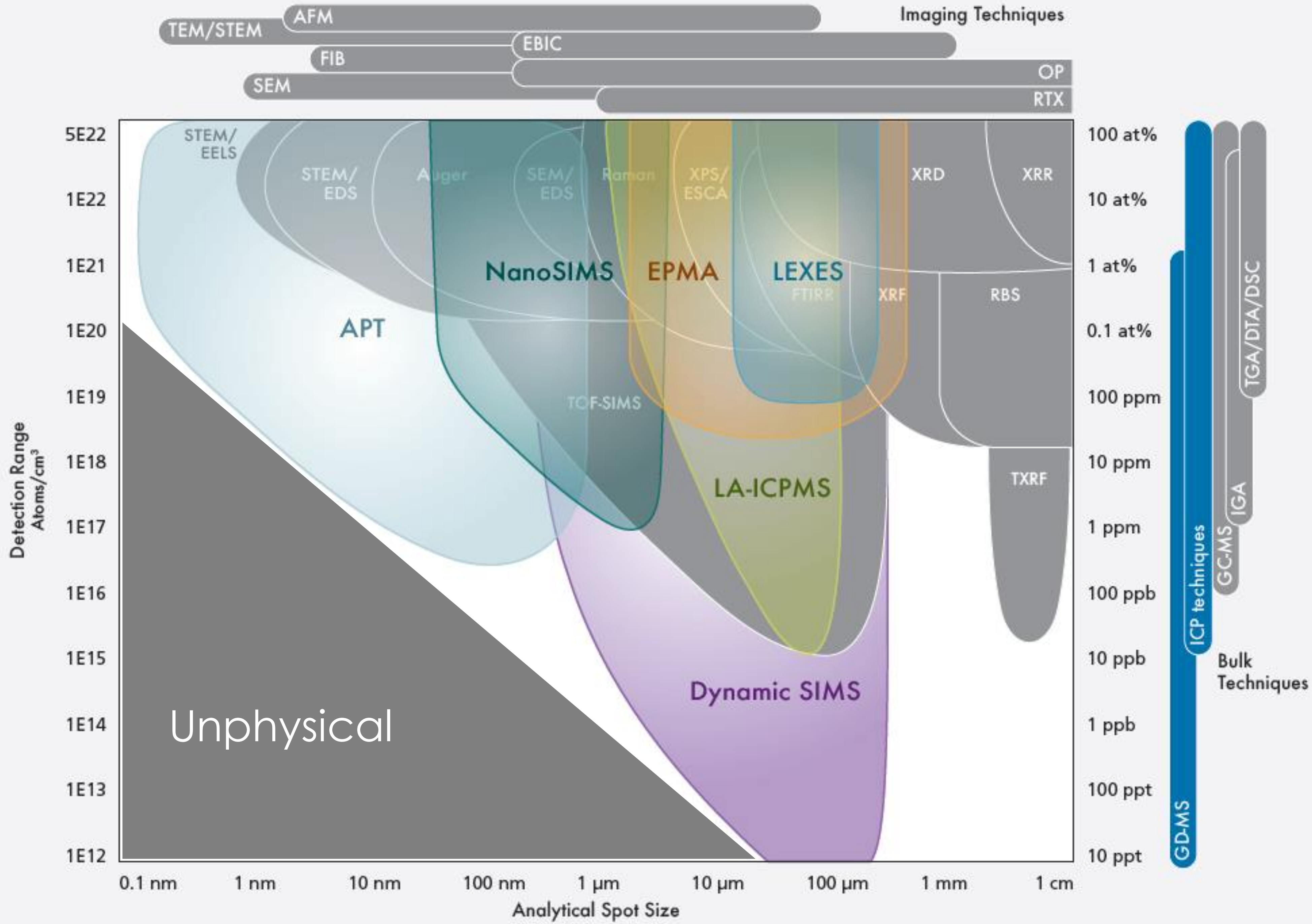
- Not Always Applicable
  - Not all materials will run well
  - Low Specimen Yield in Some Cases
- Projection aberrations limit spatial resolution in some locations
- Compositional Inaccuracies
  - Limits of species discrimination-mass interferences
  - Finite multihit resolution of detector
- Detection Efficiency High ~80% (but not 100%)
- Field of View <200 nm diameter
- Crystallographic information is limited
- No chemical information

Strengths of APT as an Analytical Technique

- Discrete 3-Dimensional Image (one atom at a time)
- All atoms detected with equal efficiency
- High analytical spatial resolution (0.2 nm locally)
- High analytical sensitivity (up to 1 appm)

Key Points

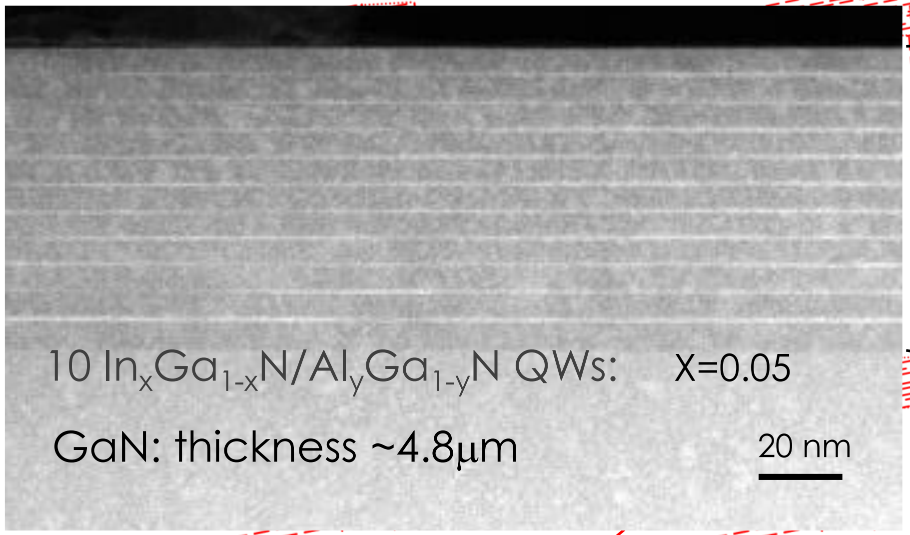
- Time to Knowledge is acceptable (~1 day)
- Specimen preparation is similar to TEM
- High detection efficiency (~80%)

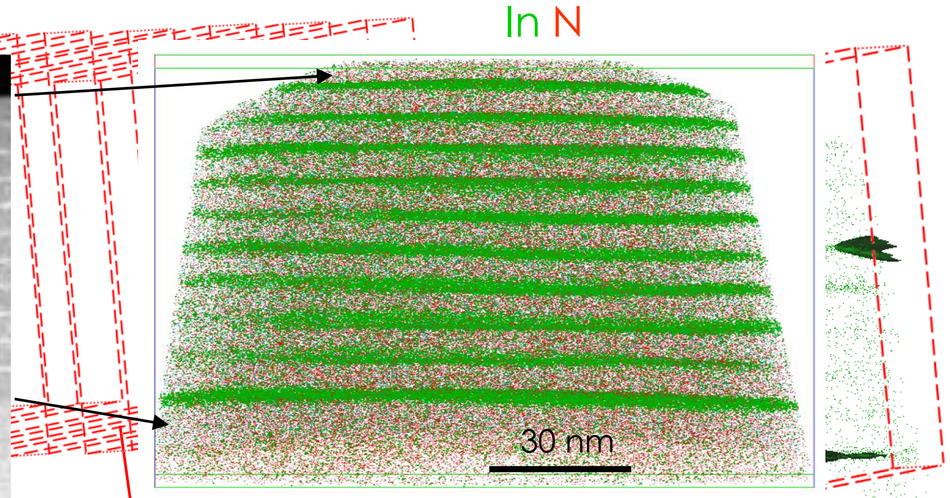

Imaging Techniques
AFM
TEM/STEM
EBIC
FIB
OP
SEM
RTX
STEM/
EELS
STEM/
EDS
Auger
SEM/
EDS
Raman
XPS/
ESCA
XRD
XRR
NanoSIMS
EPMA
LEXES
FTIRR
XRF
RBS
APT
TOF-SIMS
TXRF
LA-ICPMS
Dynamic SIMS
Unphysical
Detection Range
Atoms/cm³
5E22
1E22
1E21
1E20
1E19
1E18
1E17
1E16
1E15
1E14
1E13
1E12
100 at%
10 at%
1 at%
0.1 at%
100 ppm
10 ppm
1 ppm
100 ppb
10 ppb
1 ppb
100 ppt
10 ppt
0.1 nm
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
Analytical Spot Size
GD-MS
ICP techniques
GC-MS
IGA
TGA/DTA/DSC
Bulk
Techniques

Photonics

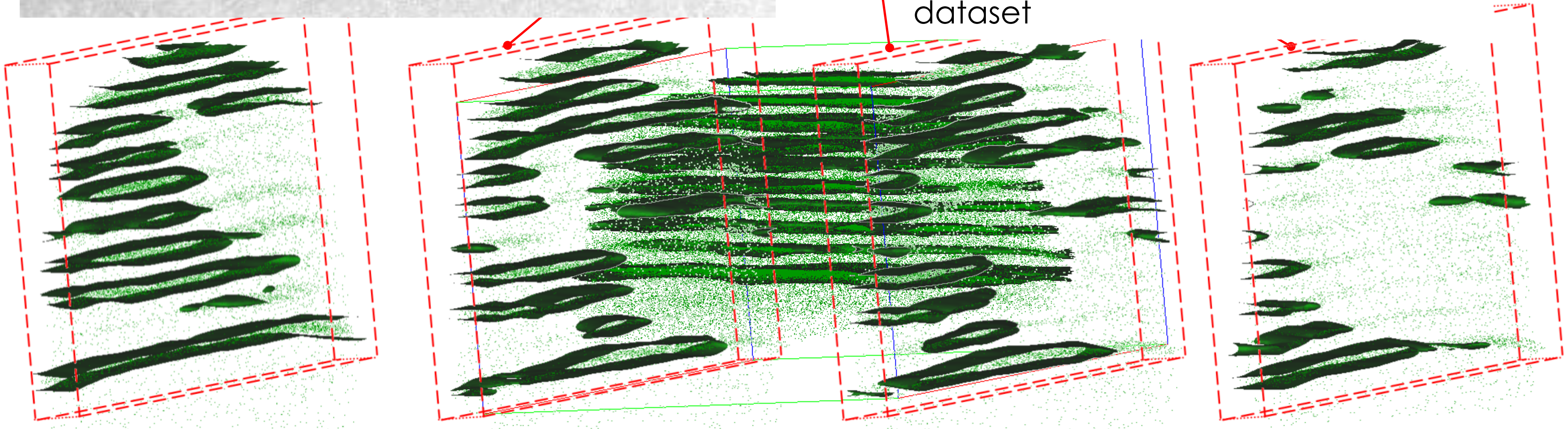
HAADF STEM

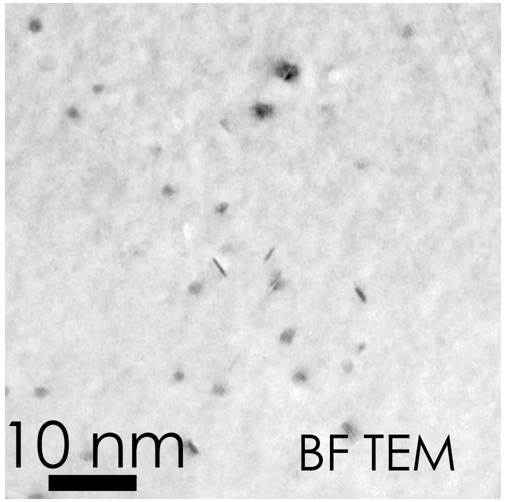
APT

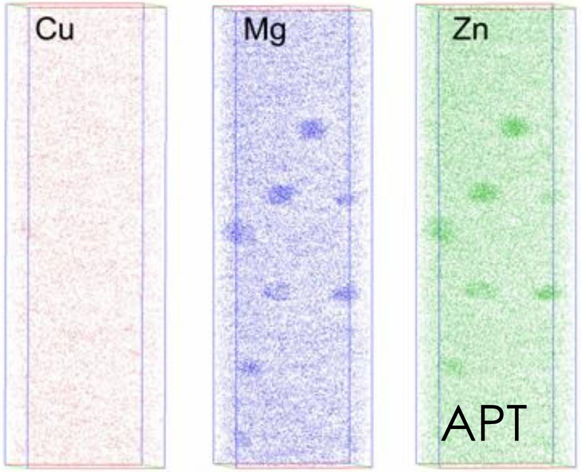




Entire structure captured within dataset







~30×30×100nm

Scientific 7xxx Al-Zn-Mg-Cu: Early stages of ageing at 150 °C

- H_{VHN} (as quench) = 58
  H_{VHN} (age 150°C) = 104
- TEM images show no difference
- TEM reveals precipitates

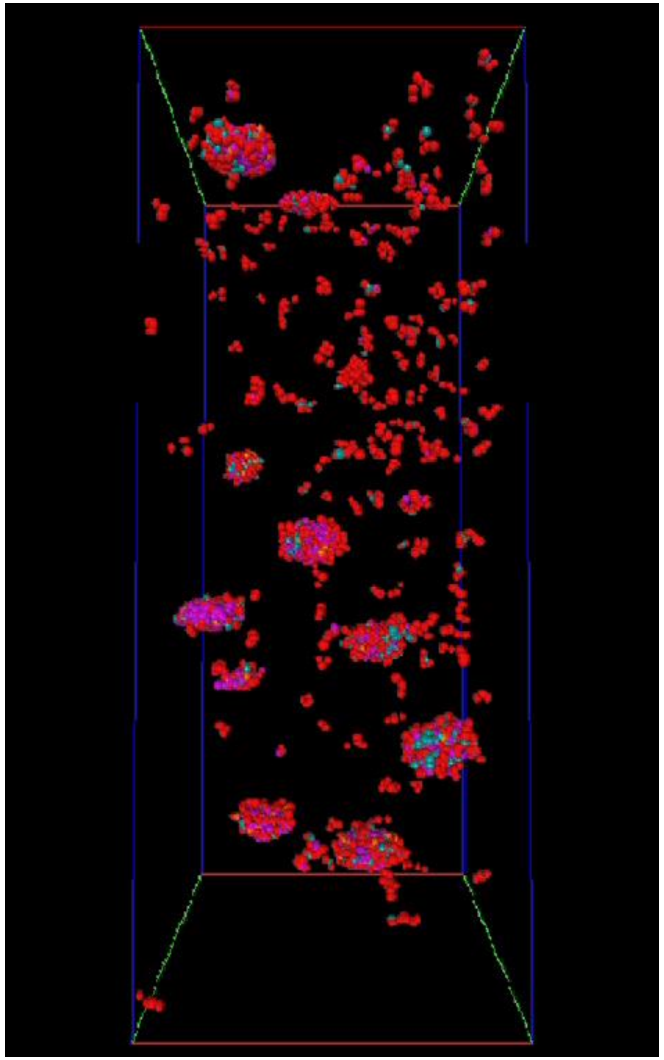
Cluster Strengthening Concept

- Atom probe reveals precipitates and clusters
- Clusters are responsible for strengthening

ammrf
Australian Microscopy & Microanalysis Research Facility

The University of Sydney

Ringer, Mater Sci For, 519-521, 25, 2006; Stephenson, Moody, Liddicoat & Ringer, *Microscopy & Microanalysis*, 13, 448 (2007)

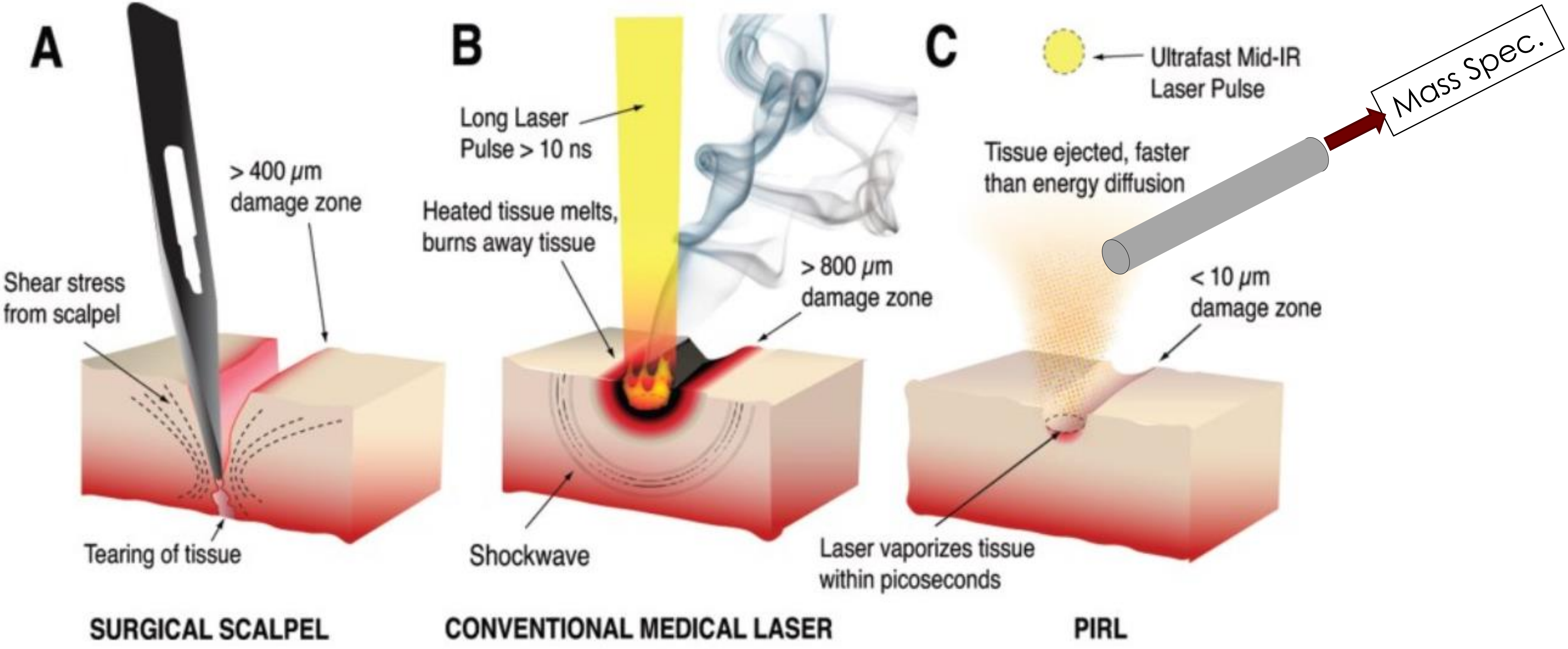


Brief Overview of Steam Instruments

Overview

- Picosecond InfraRed Laser-Desorption by Impulsive Vibrational Excitation (PIRL-DIVE) developed by:
  R.J. Dwayne Miller of Univ. of Toronto and Max Planck Hamburg
- The PIRL DIVE process can launch large biomolecules without fragmentation: it is gentle
- Build mass spectrometer to analyze whole biomolecules launched by DIVE

PIRL DIVE Compared



Thank you