Solid State Ionics 2024

An Introduction to Atom Probe Tomography

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Imperial Centre for Cryo Microscopy of Materials I(CM)²

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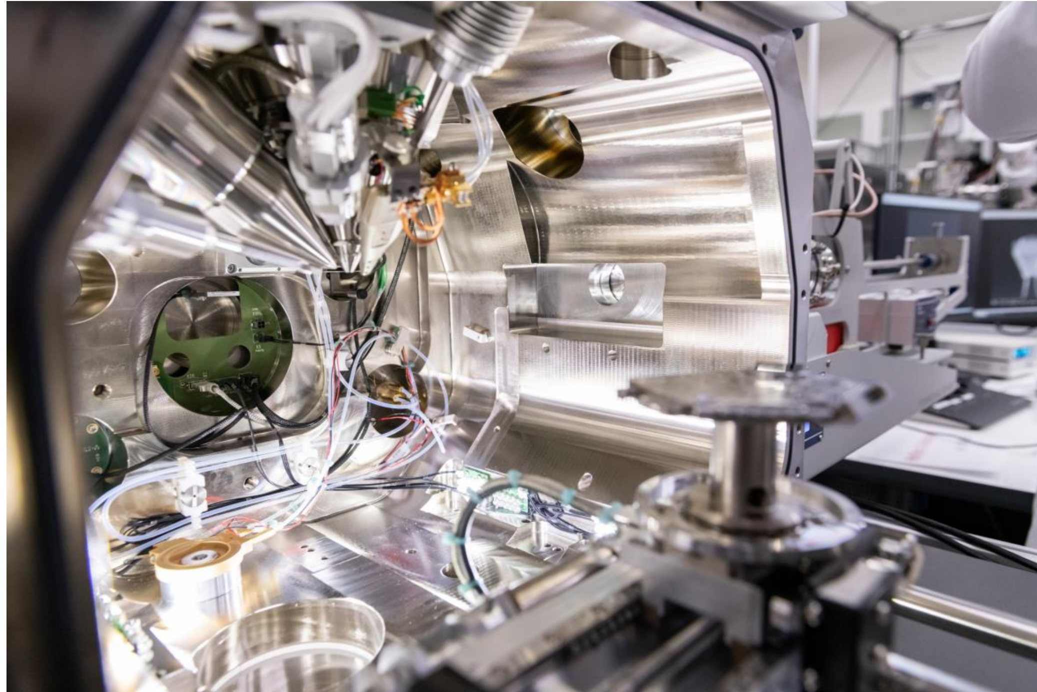

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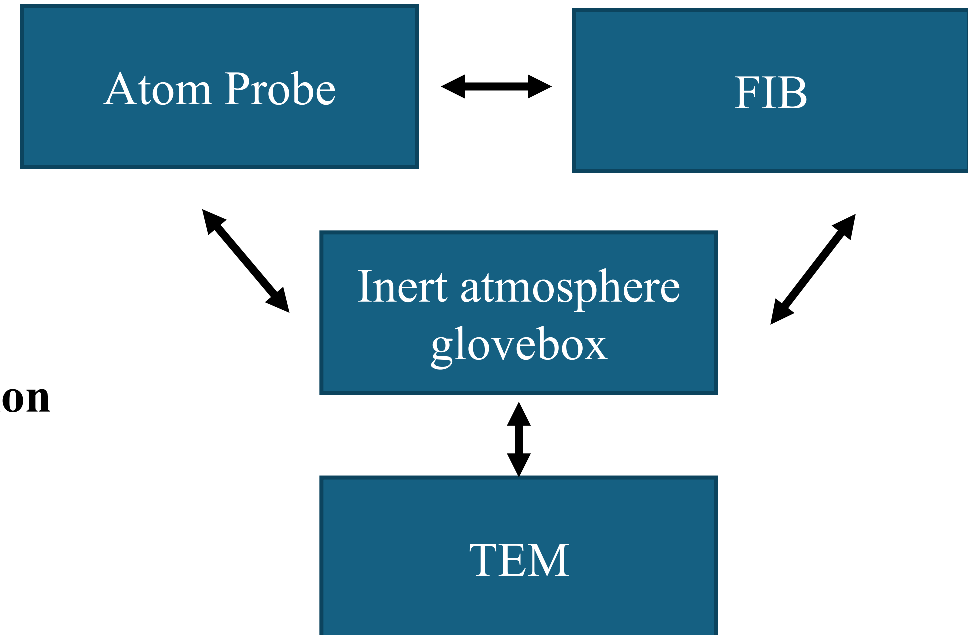
Imperial Centre for Cryo Microscopy of Materials – I(CM)^2

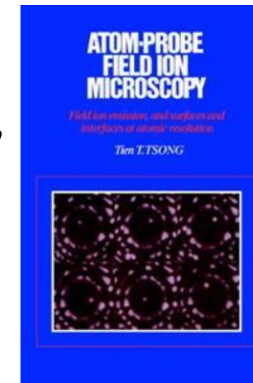
- Cryogenic sample preparation, cryo-vacuum sample transfer and cryo analysis has become of increasing interest to the electron microscopy and atom probe tomography (APT) community.
- Allows analysis of frozen liquids, frozen liquid/solid interfaces and light, mobile elements such as hydrogen and lithium.
- Integration of multiple high resolution cryo microscopy techniques allows nanoscale structural and compositional analysis of material systems across multiple length scales.
- Sample preparation and transfer between multiple instruments under cryo/vacuum conditions requires in-depth analysis of each stage of the process flow.

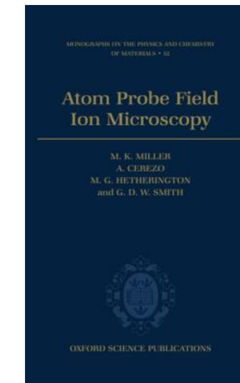


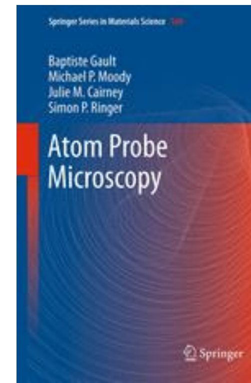
The I(CM)2 is a new facility for the development and application of cryo-microscopy to environmentally sensitive materials.

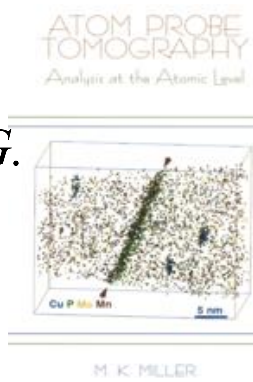
Useful literature for atom probe

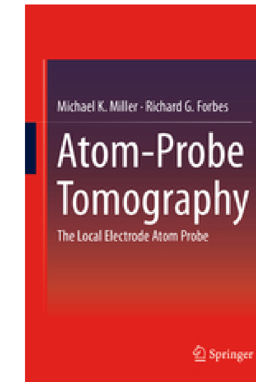
- *R. Gomer, Field Emission and Field Ion Microscopy, Harvard University Press, (1961)*
- *E. W. Mueller and T. T. Tsong, "Field Ion Microscopy - Principles and Applications", American Elsevier, New York, 1969.*
- *Miller M.K. Atom Probe Field Ion microscopy 1989*
- *T. T. Tsong, "Atom-Probe Field Ion Microscopy", Cambridge University Press, Cambridge, 1990.*
- *Atom Probe Field Ion Microscopy, M. K. Miller, A. Cerezo, the late M. G. Hetherington, and G. D. W. Smith, Monographs on the Physics and Chemistry of Materials 1996*
- *Miller M.K. Atom Probe Tomography 2000*
- *Gault B. et al. Atom Probe Microscopy 2012*
- *Larson, D.J., Prosa, T.J., Ulfig, R.M., Geiser, B.P., Kelly, Th.F.,2013, Local Electrode Atom Probe Tomography, A User's Guide, XVII*

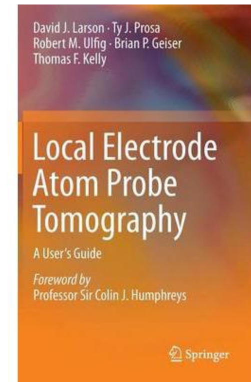








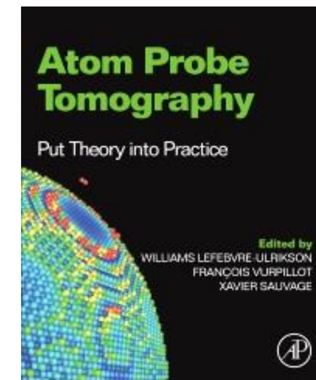




Atom probe tomography. *Nat Rev Methods Primers* **1,** 52 (2021).

https://doi.org/10.1038/s43586-021-00054-x

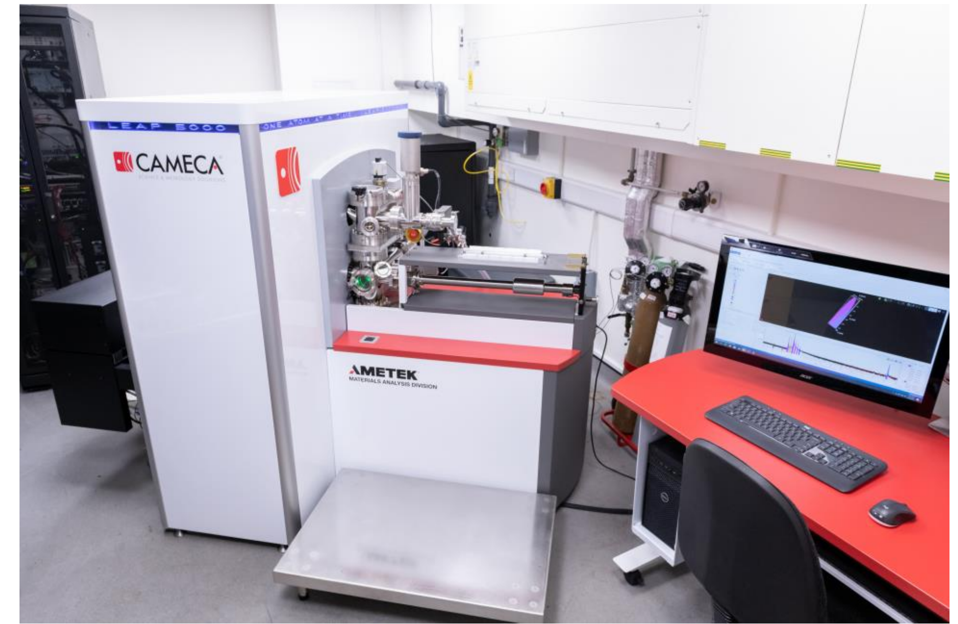
Baptiste Gault, Ann Chiaramonti, Oana Cojocaru-Mirédin, Patrick Stender, Renelle Dubosq, Christoph Freysoldt, Surendra Kumar Makineni, Tong Li, Michael Moody & Julie M. Cairney



Atom Probe Tomography

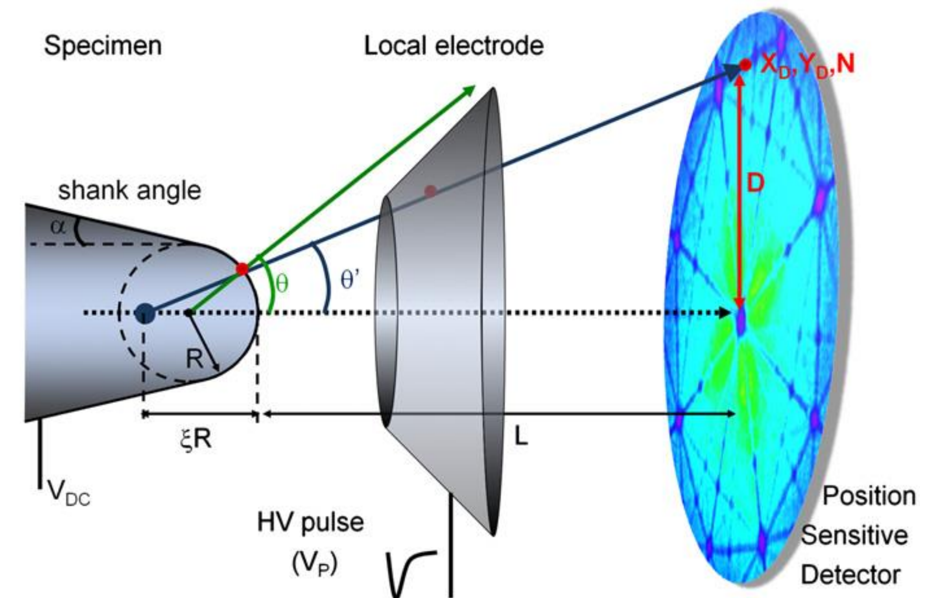
- Atom probe tomography is a high resolution microscopy technique that allows up to sub nm spatial resolution and ppm compositional information in a ~ 50 nm x 50 nm x 80 nm volume.

Cameca Local Electrode Atom Probe (LEAP) 5000 XR.



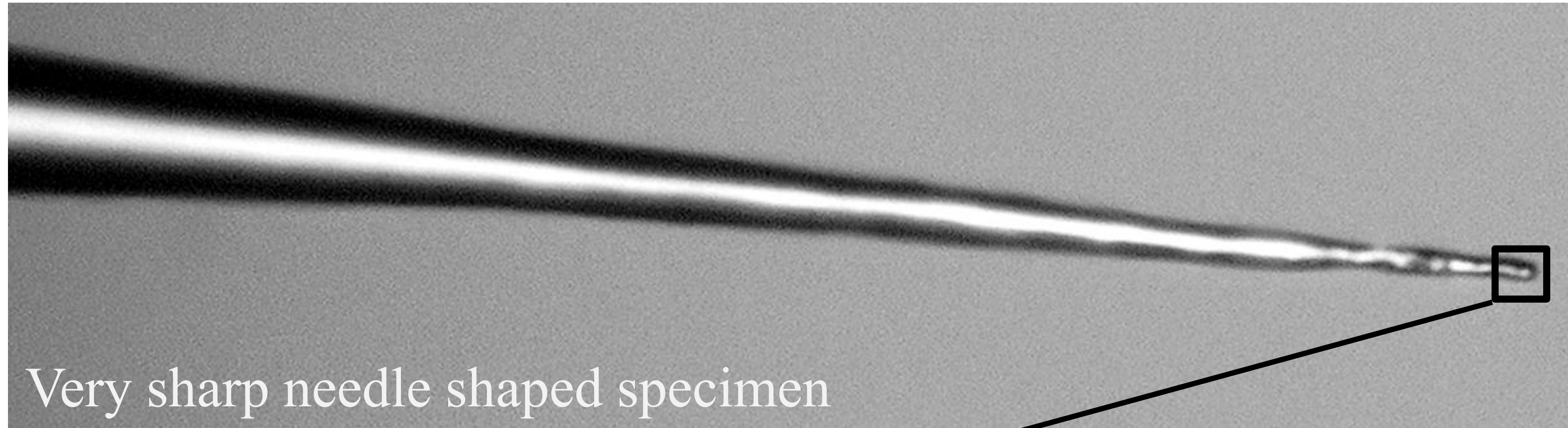
- Needle shaped specimens with an apex less than 100 nm are cooled to ~50 K in high vacuum (~1E-11 torr) and exposed to high electric fields (2-10 kV). The surface atoms are then evaporated by a voltage or laser pulse and accelerated towards a position sensitive detector.

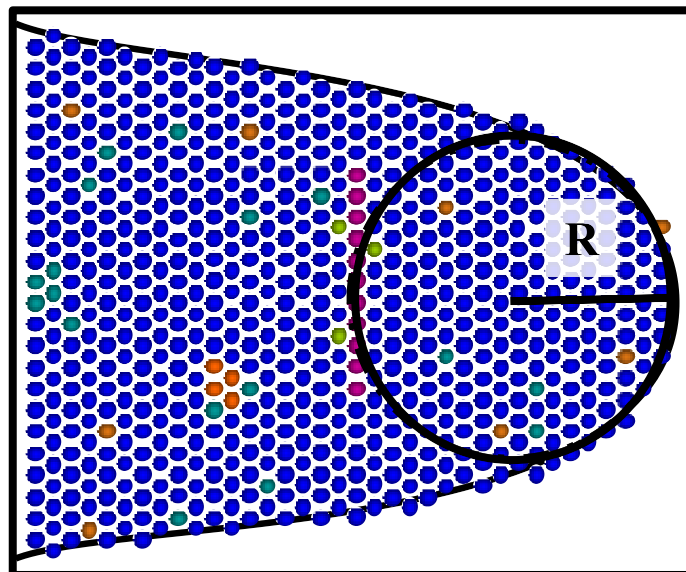
- The time of flight and the XY location of the detected ions is combined with order of arrival onto the detector and back projected to form a 3D reconstructed model of the original specimen.



Gault et al Ultramicroscopy 111(2011)1619–1624

Field ionization -applying electric fields to sharp tips



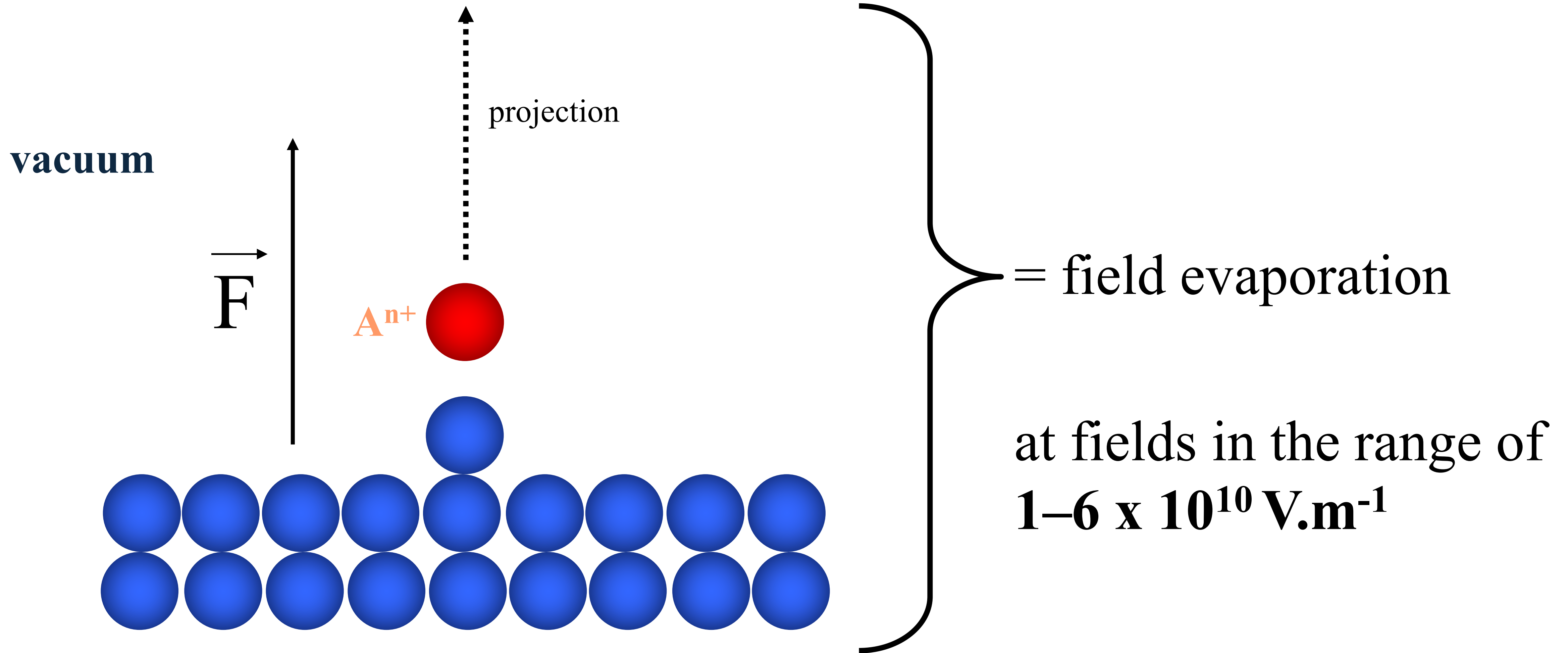


R<100 nm

Application of a DC Voltage (V) produces an intense electric field (F) since:

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

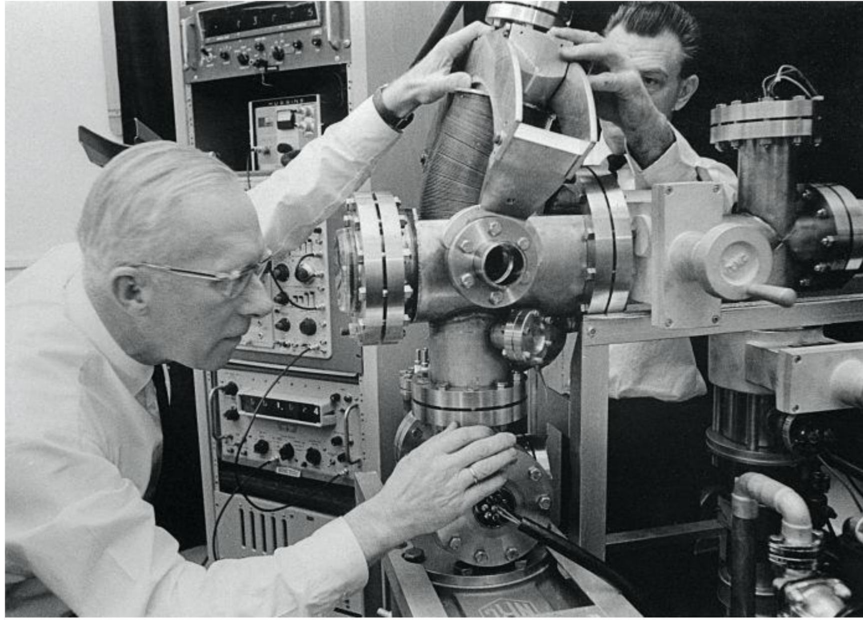
Intense electric field on surface atoms



= field evaporation

at fields in the range of **1–6 x 10^{10} V.m^{-1}**

Ion emission – Field ion microscopy

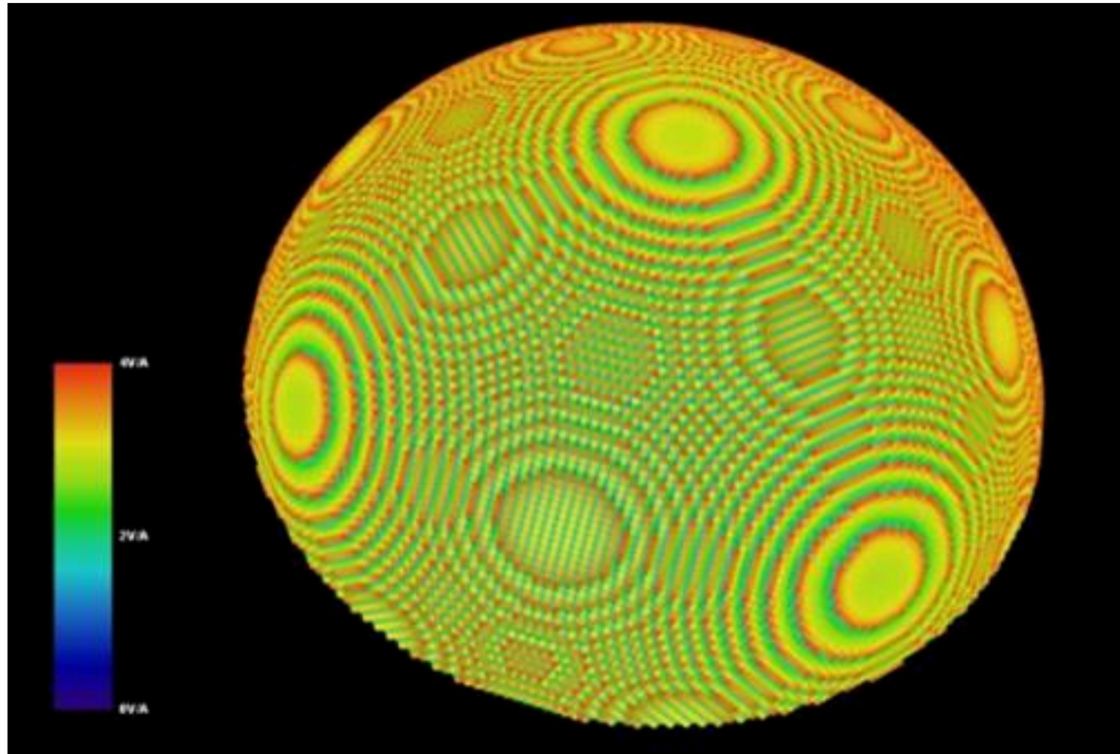


- Nanoscale needle-shaped specimen at low temp (10-150 K)
- Insert low pressure of rare gas (He,Ne,Ar)
- Add an image intensifier (Multi Channel Plate/phosphor screen)
- Apply a positive voltage to the tip

W, 60 K,
V=0 to 10 kV

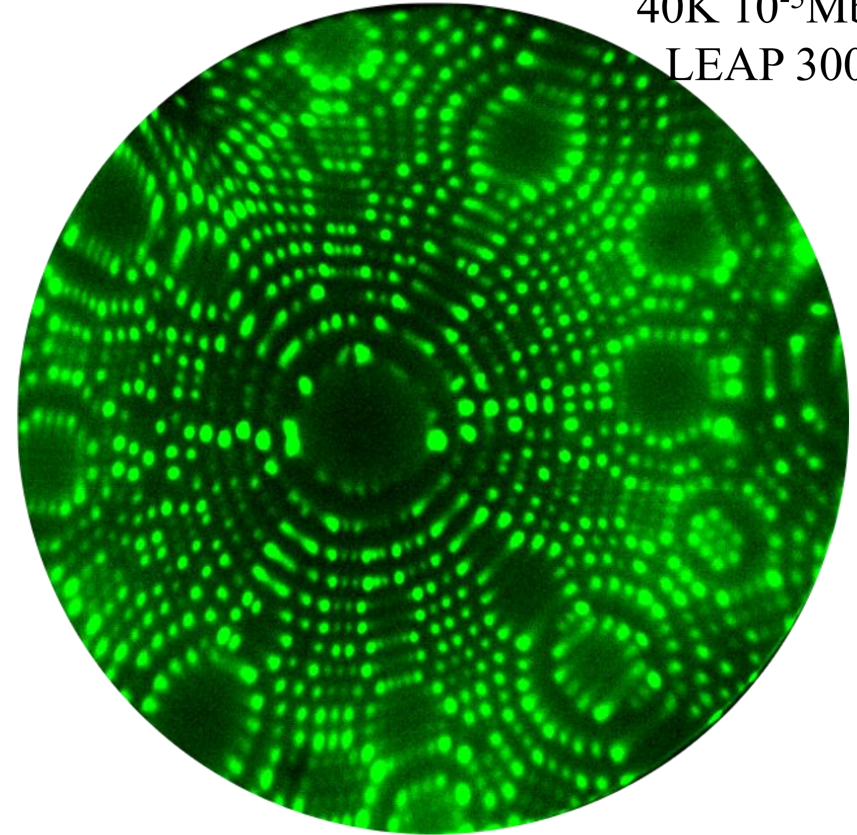
Courtesy of F. Vurpillot and co-workers

Microscopic electric field variations



- Imposing a needle shaped (hemispherical apex) geometry on a crystalline material leads to a terraced surface structure.
- Concentric rings linked to crystallographic pole orientations are visible, with highest field experienced by atoms at kink sites and edge sites.

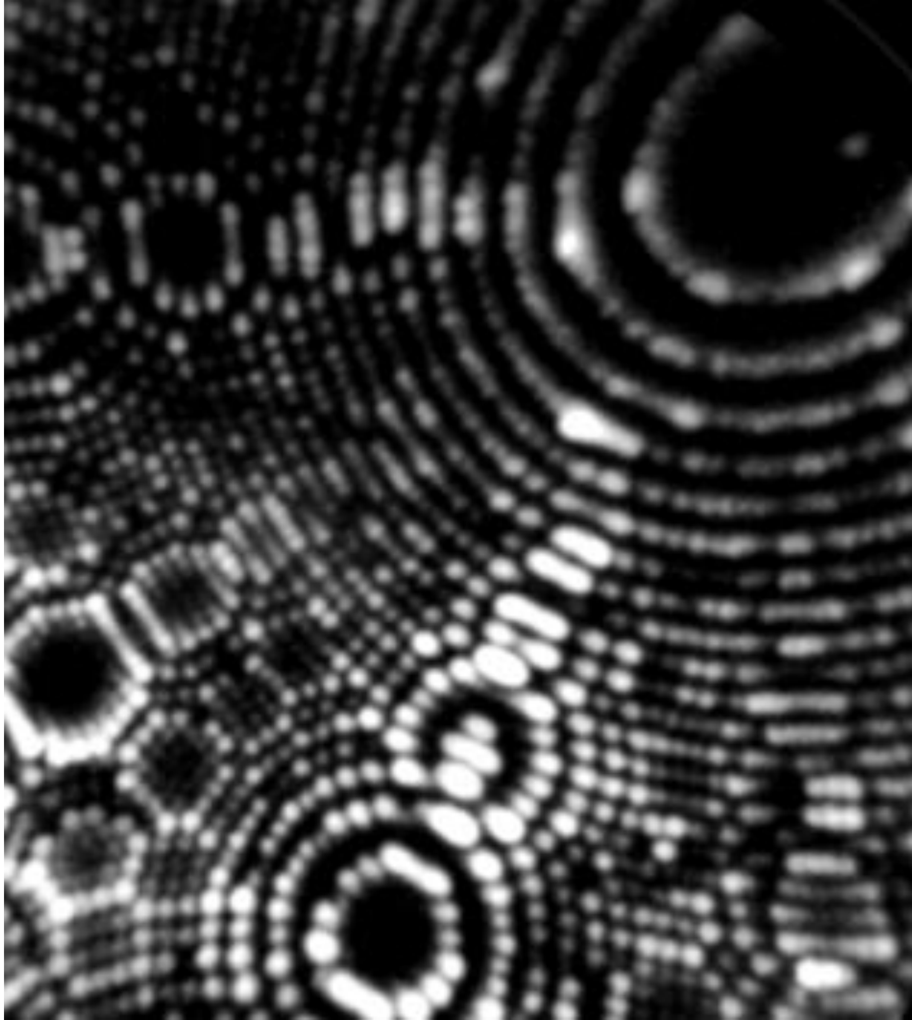
Tungsten, 8 kV
40K 10^{-5}Mbar He
LEAP 3000X Si



- Variation in surface field linked to the local topography can be observed through increased numbers of gas atoms desorbing from them via Field Ion Micrographs.

Courtesy of F. Vurpillot and co-workers

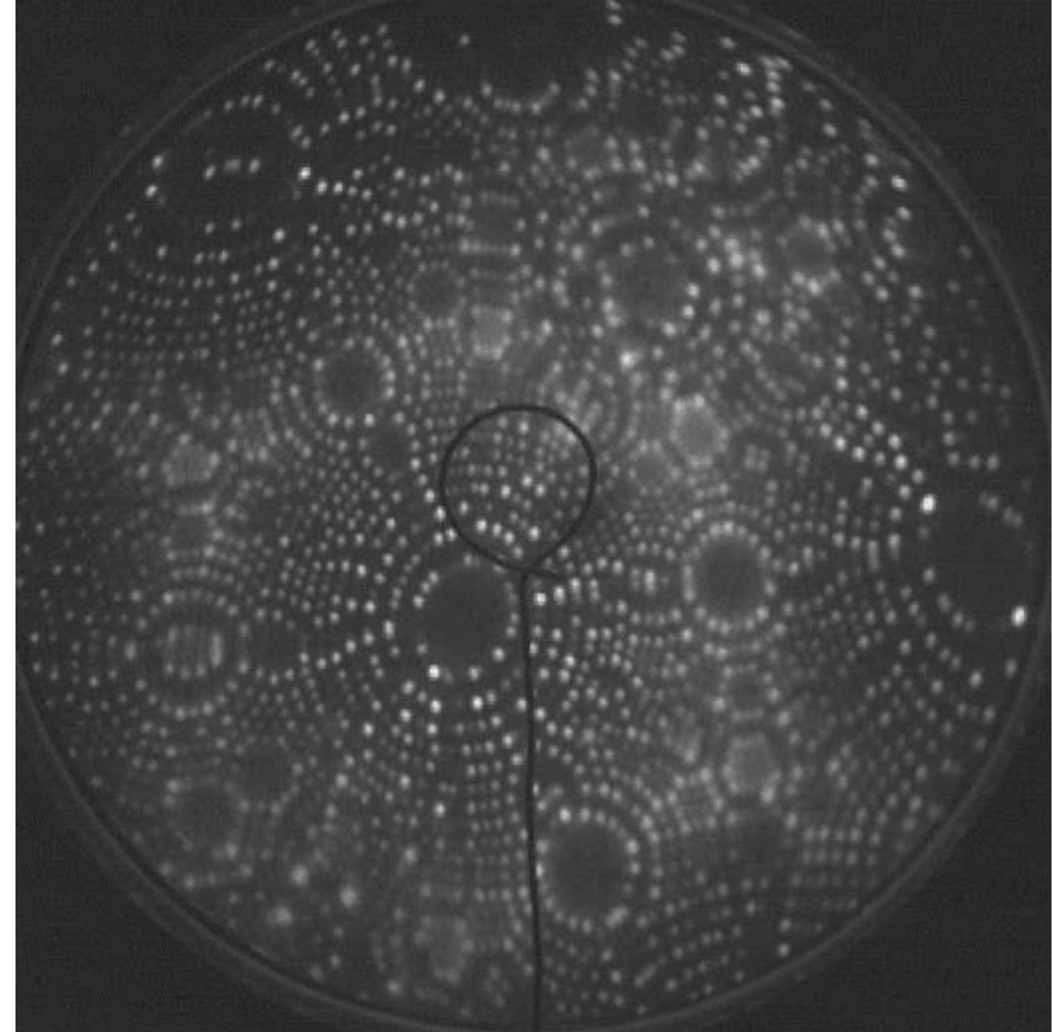
Increase standing voltage or pulse voltage



DC mode

Gold, 10 kV
20K 10^{-5}Mbar Ne

Evaporation rate ~ 10^5 at/s



Pulsed mode
tungsten, 8 kV
40K 10^{-5}Mbar He

Field ion Microscopy and Atom Probe

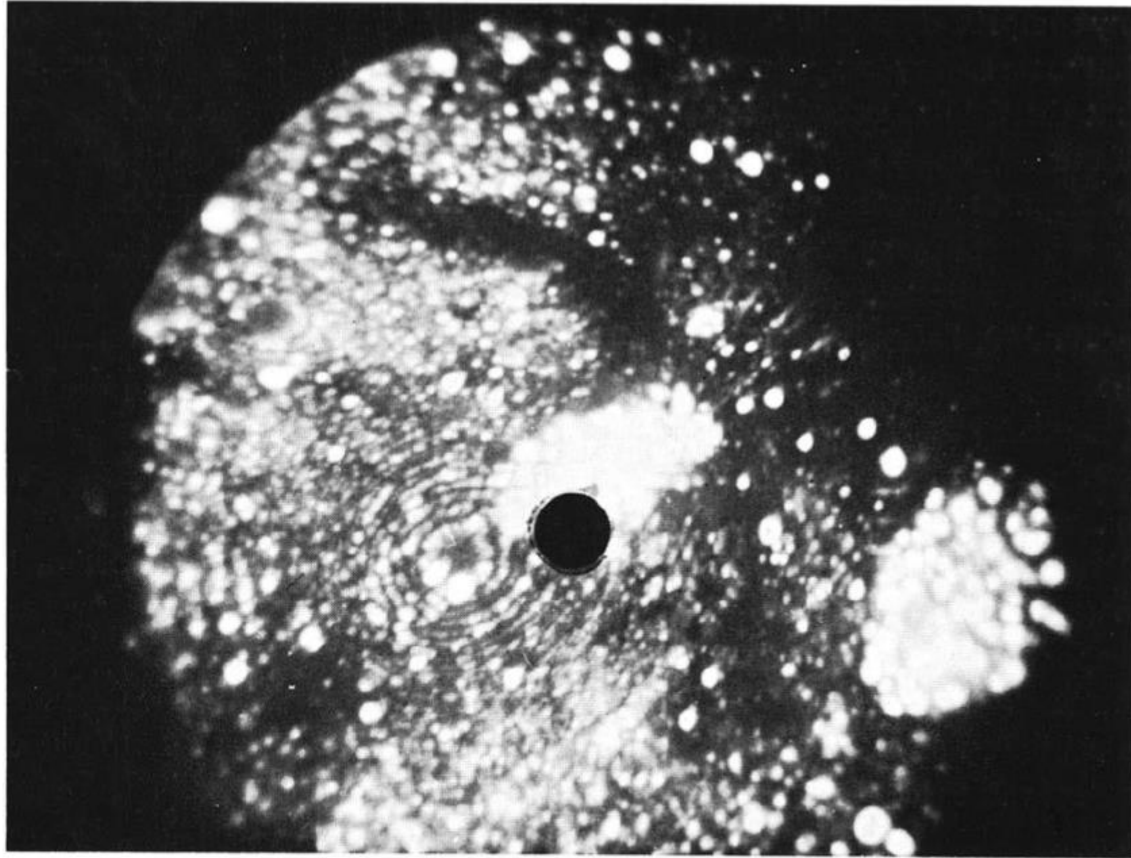
Pt surface imaged using field ion microscopy for catalysis research

- Professor Erwin Muller pioneered the Field Emission Microscope (later Field Ion Microscope) in the 1950s.

- Through preferential emission of adsorbed gas atoms onto protruding atoms on crystal terraces, allowed first imaging of atoms and still used today for high resolution surface analysis.

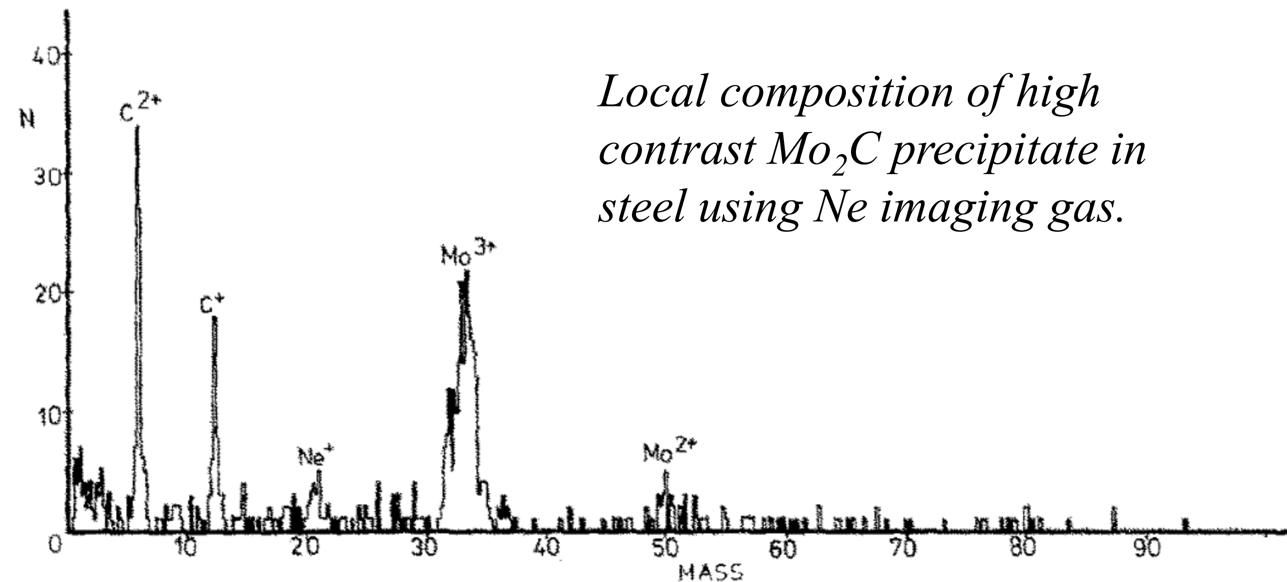
- Limited elemental analysis possible through contrast variation. How to improve this?

Field Ion Microscopy and Atom Probe



Turner *et al Surface Science*, vol. 35, pp. 336–344, 1973.

- Early atom probe used a FIM image to select a region of a few nm (black 'pinhole' in FIM image).
- The imaging gas was then removed, sample rotated towards a time of flight detector and high voltage pulsing applied.
- This allowed a 1D concentration profile measured from time of flight mass spectrometry from the selected region.
- Selective analysis of nanoscale features was now possible.

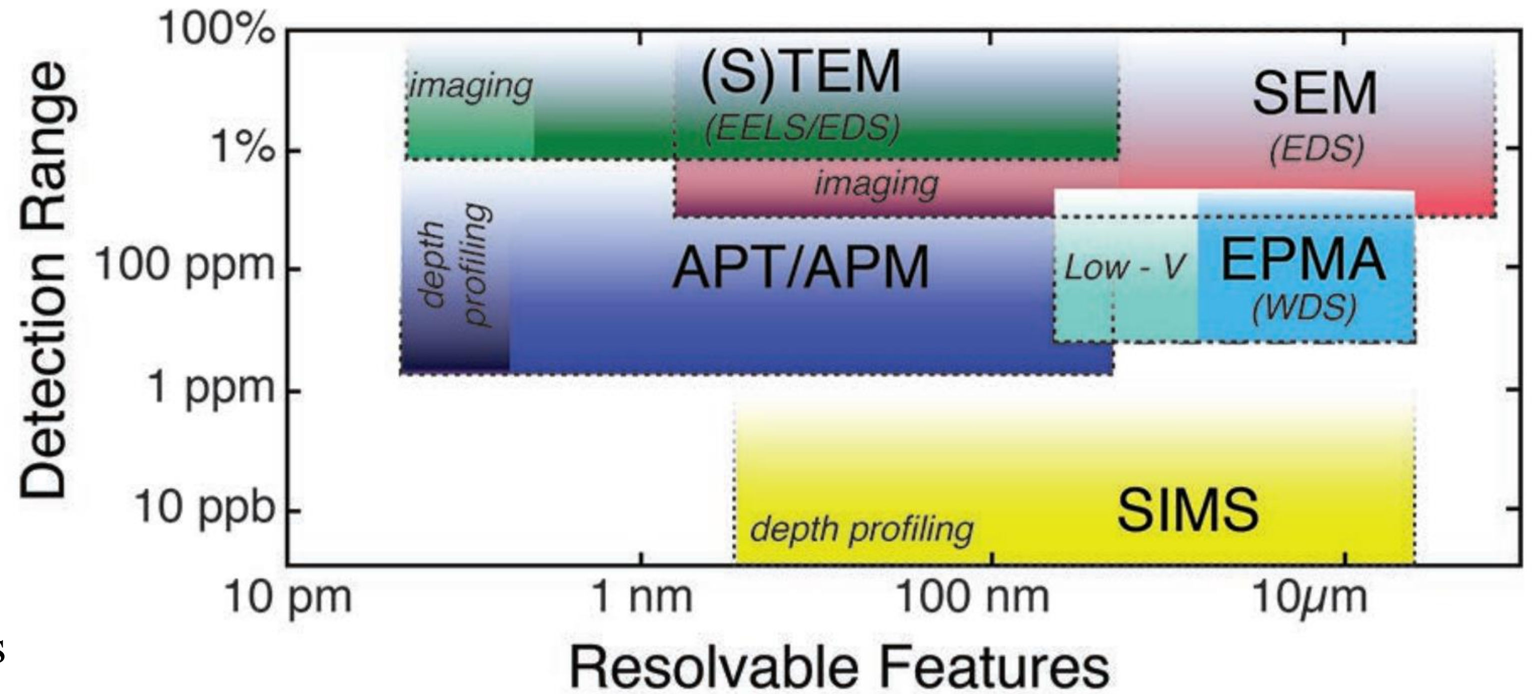


Local composition of high contrast Mo_2C precipitate in steel using Ne imaging gas.

Modern instruments have much increased fields of view.

What does APT give us?

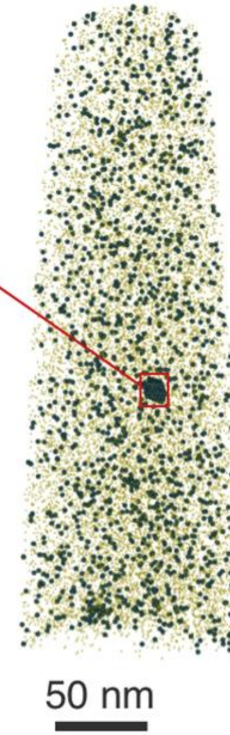
- Sub nm spatial resolution with high compositional sensitivity in nanoscale volumes.
- Reconstructions can show compositional variation within 3D nanoscale structures.
- All species are detected equally (with a few caveats…where are often material system specific).
- Detection efficiencies up to 80% of all ions incident on the detector.
- No requirements for calibrated standards as sample geometry plays a larger role but standardisation of analysis conditions and reconstructions is important.



Valley J W et al. 2015 American Mineralogist. ***100*** *1355–1377*

- Ideal for observing nanoscale features where localised compositional variation can be expected.
- Due to the nanoscale volumes analysed, APT data interpretation often requires larger scale analytical techniques to give context.

What does APT data look like?

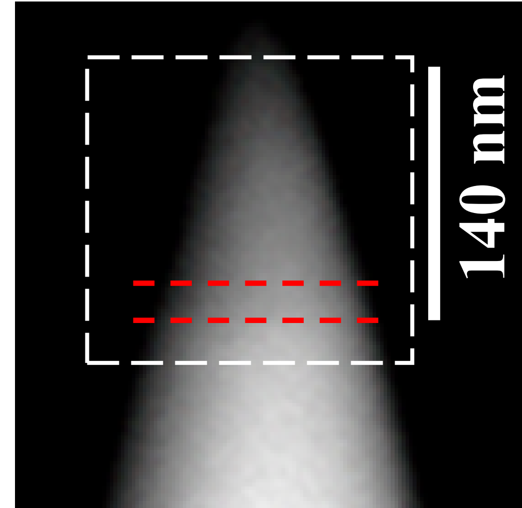


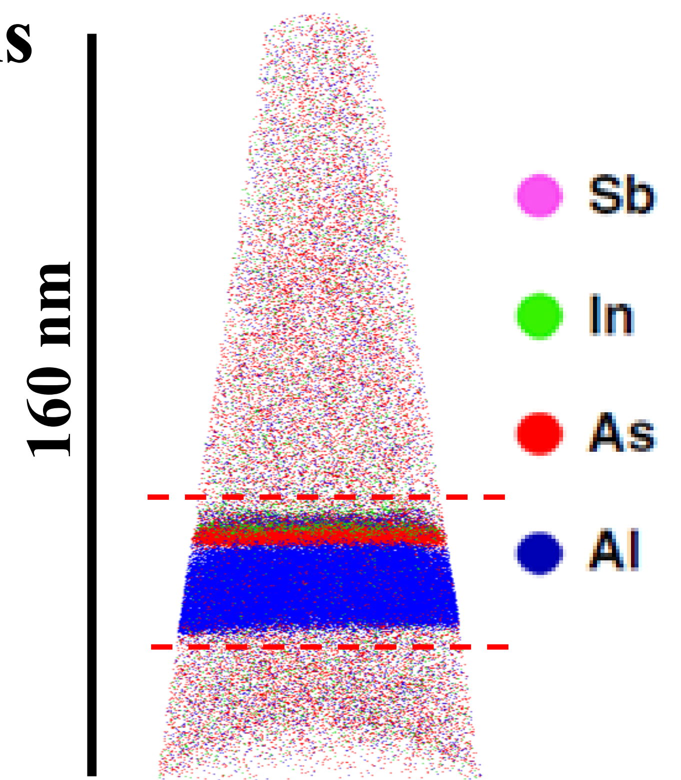
- Data is presented in a 3D point cloud where each point is a single ion with a defined mass-to-charge stage ratio.
- The size and size of the reconstructed volume is guided by ion-projection models and complementary techniques such as Transmission Electron Microscopy.
- As a 3D point cloud, this data can be analysed in a number of different ways. Isolated nanoscale regions can be extracted from the bulk dataset.
- Species are identified by their "isotopic fingerprint" and ranged between two mass-to-charge state ratio.
- Compositional variation visible in 3D, allowing analysis of nanoscale clusters or interfacial segregation in complex structures.

*Saxey D W et al. 2018 Scripta Materialia **148** 115–121*

General workflow summary for atom probe analysis

Three main stages of carrying out APT:



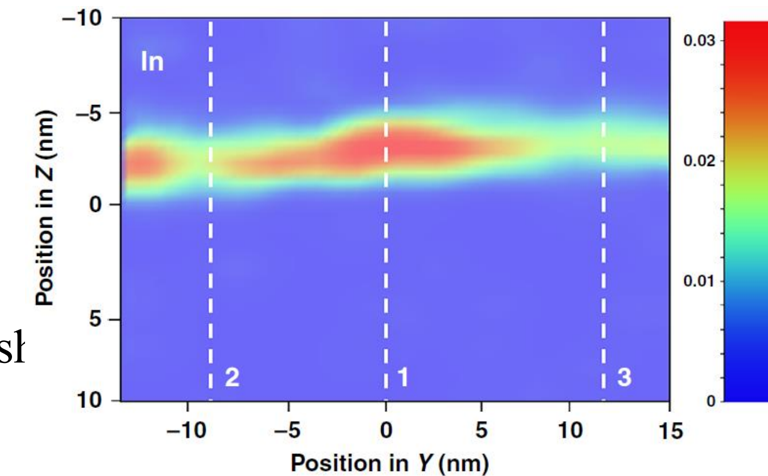


Sample preparation: Initial material selection to final tip fabrication.

How representative is my sample?
Does my APT sample have the region of interest within ~50-100 nm of the tip apex.

Analysis: Optimisation of analysis parameters for the data required. Obtaining suitable amounts of representative data

How does the method in which the sample is analysed affect the data?
How do I balance high quality data with sufficient amounts of data?



Reconstruction : Putting together 3D volume with reasonable physical parameters. Identification of ionic species in the mass spectra. Determining compositions (bulk and segregated), compositional profiles from selected interfaces, cluster searching, size and sh of features determination of errors and much more…..

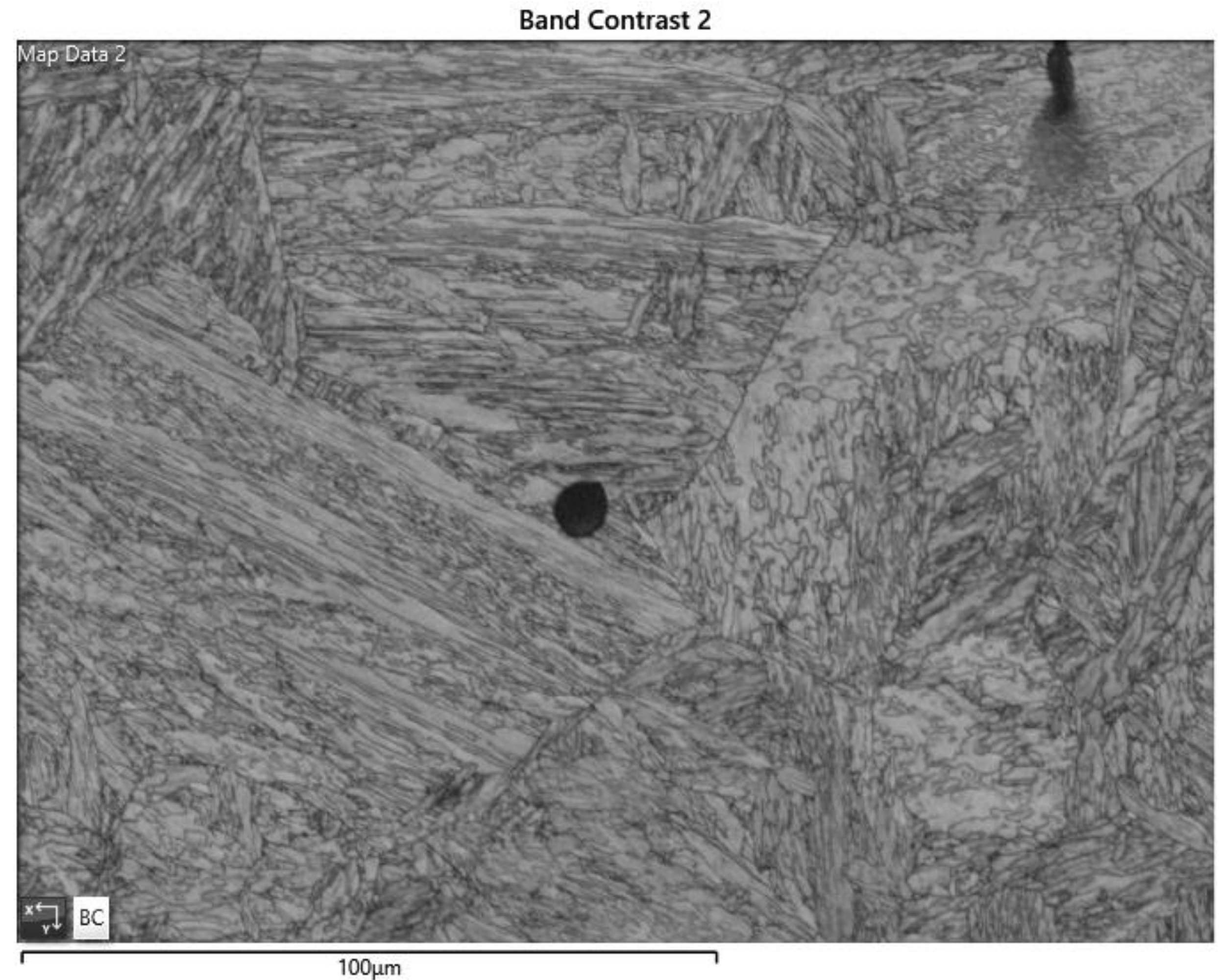
How does the method in which the data is reconstructed affect the interpretation?
Is the data spatially and compositionally representative of the original sample?

Gajjela, R.S.R., Hendriks, A.L., ***Douglas, J.O****. et al. Light Sci Appl 10,* ***125*** *(2021).*

Sample preparation: Initial material selection

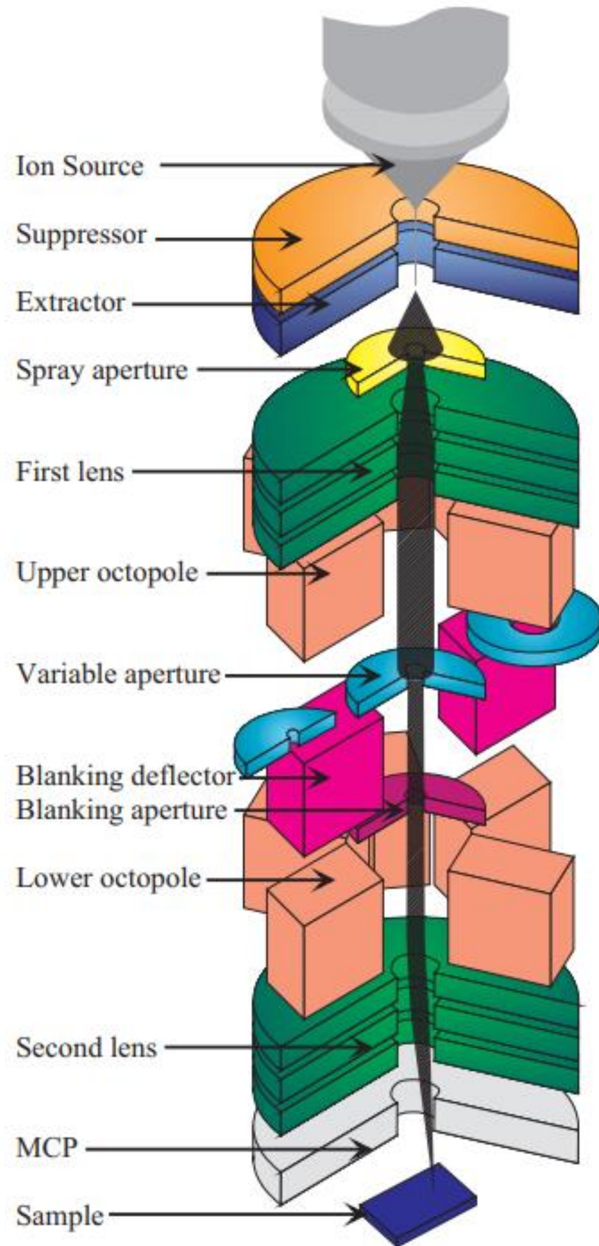
- Very few materials have a uniform composition over the nanoscale length scale that is analysed by atom probe.
- The length scales on which that are considered homogeneous also depend on the applications and so suppliers/fabricators may have different ideas on what is important.
- However, some materials can be considered "homogeneously inhomogeneous" in composition and/or structure.
- Atom probe analysis often needs to be part of a suite of techniques.
- Different length scales require different techniques and each complement the other.

- **NB – Your material may not be *precisely* what collaborators/ manufacturer state….**

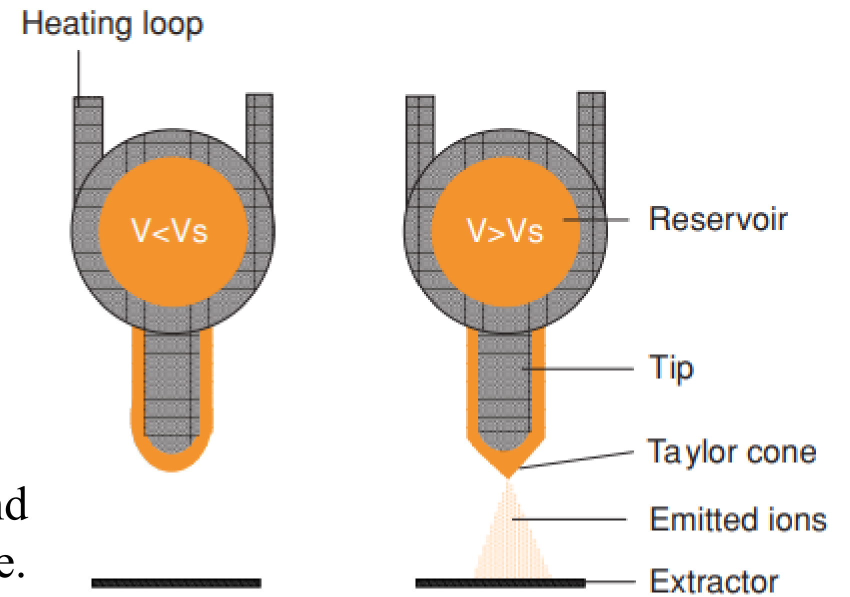


- Example of bainitic steel "homogeneously inhomogeneous" lath structure within larger scale prior austinite grains. Determination of which type of interface is which solely using APT data is challenging.

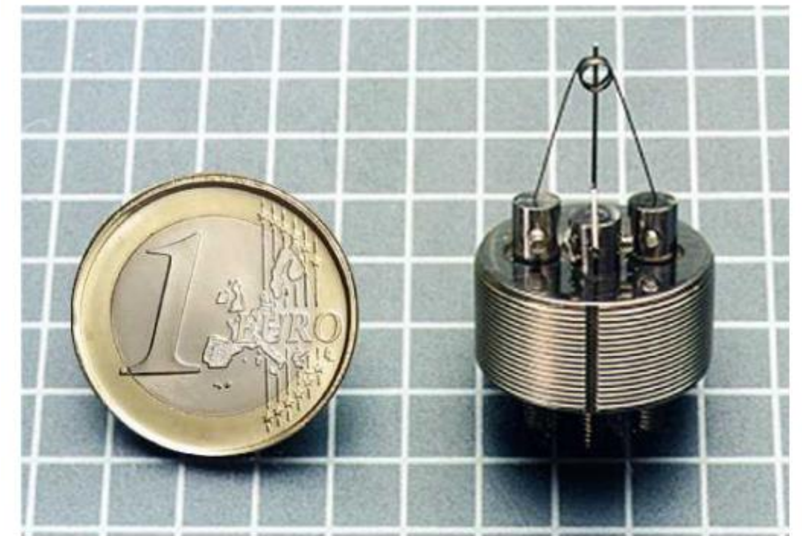
Focused Ion Beam



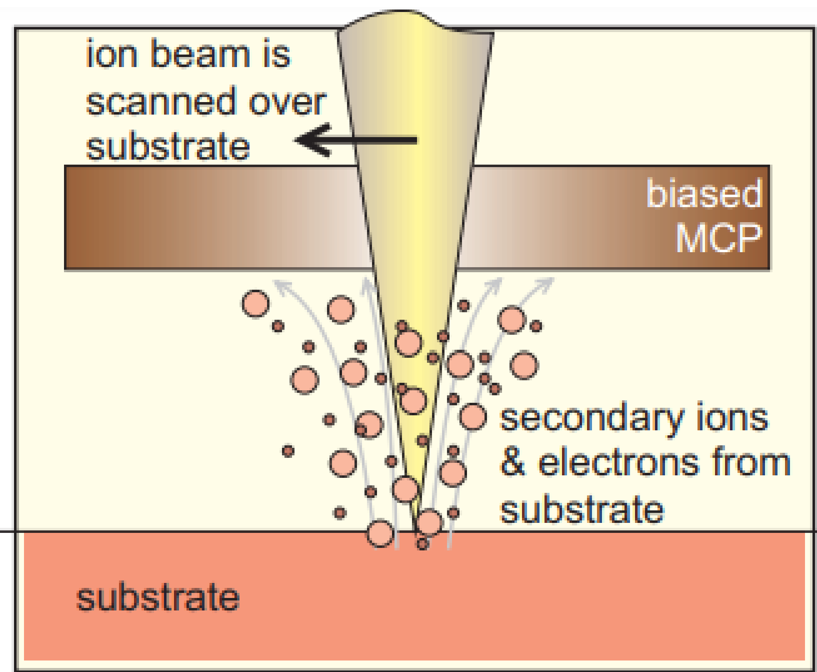
- Similar but not identical approach to Scanning Electron Microscope.
- Ion source depends on required ion species, most commonly liquid metals such as gallium.
- Gallium metal wets an emitter tip and can be extracted using a high voltage.
- Modern laboratory FIBs will have a voltage range from around 500 eV to 30 kV. These energies allow surface and sub-surface interactions for milling and imaging.
- Beam of gallium ions can then be focused and scanned over a sample.
- Other ion sources exist for different applications.



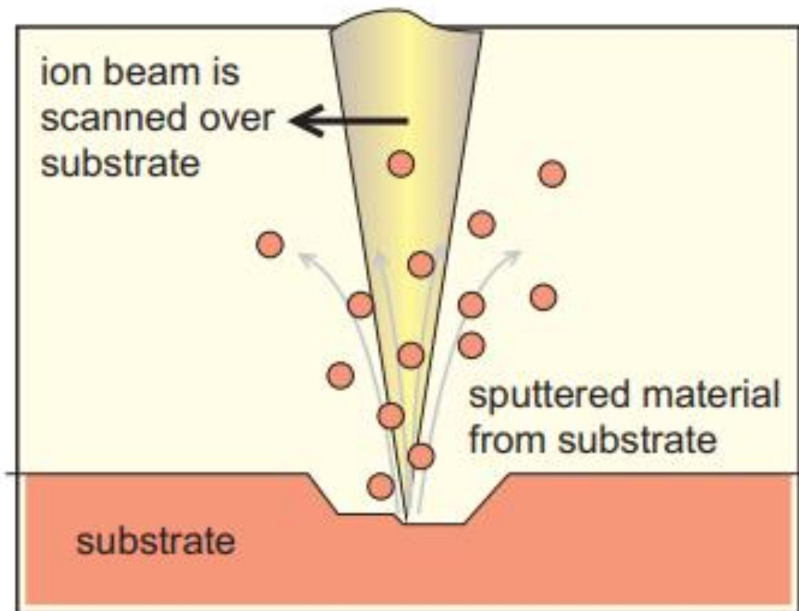
J. *Micromech. Microeng. 11 (2001) 287–300*



Ions – Imaging and sputtering



J. Micromech. Microeng. 11 (2001) 287–300

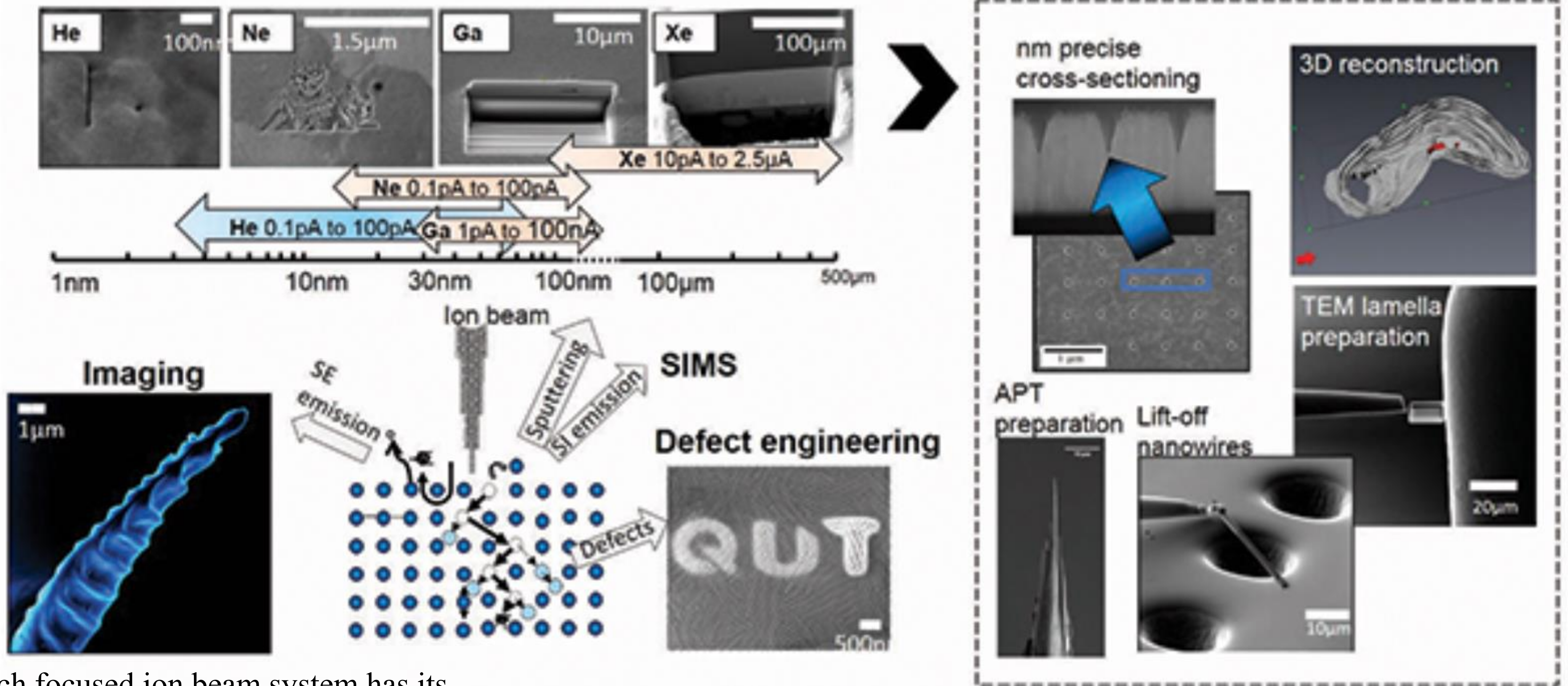


- The scanned ion beam will then interact with the surface and generate secondary electrons and secondary ions.
- These can be detected in similar ways to electrons but can carry different amounts of information as depending on the secondary ion and electron energies and intensity.

Bischoff, Lothar, and Jochen Teichert. "Focused ion beam sputtering of silicon and related materials." (1998).

- Due to their higher energy and mass compared to electrons, incident ions can sputter material from the substrate.
- This is the main feature of the Focused Ion Beam compared to the Scanning Electron Microscope.
- There is a great deal of scientific investigation and associated functionality that comes from this relatively simple idea of "the FIB can sputter material".

Variation in Focused Ion Beam systems : Ion Source



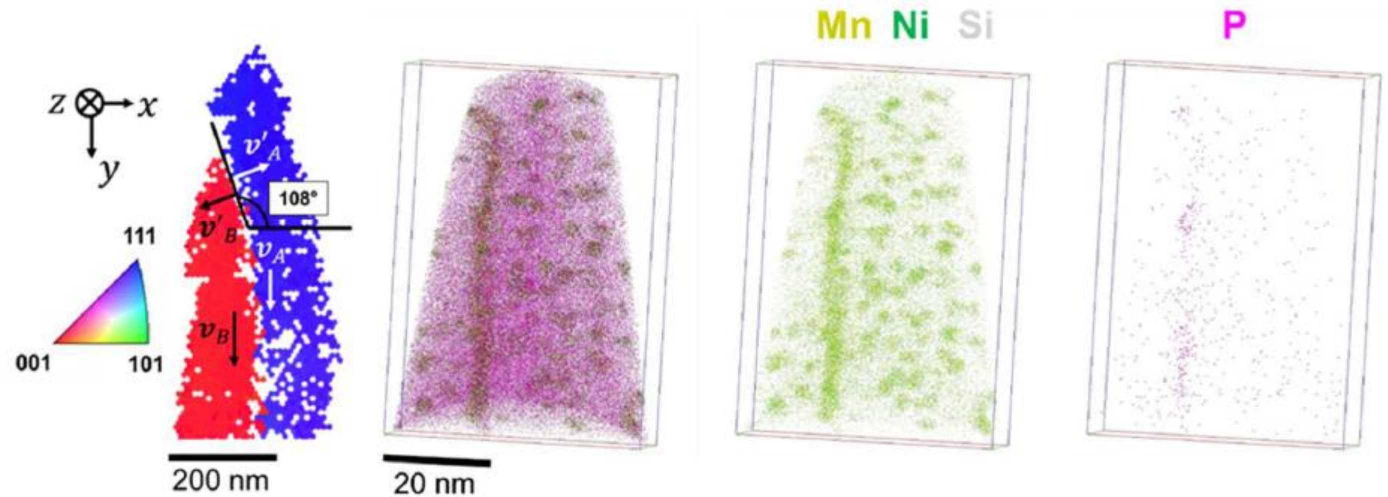
- Each focused ion beam system has its distinct area of application. There can be overlaps between them but there is not one ion type that will satisfy all requirements.

Electron and Ion Microscopy: 29 May 2020
Focused ion beams: An overview of the technology and its capabilities

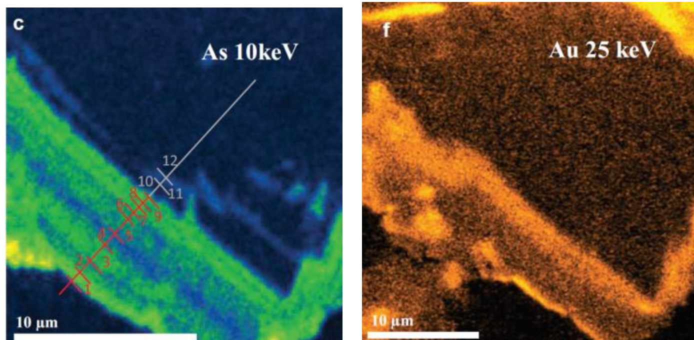
- Modern triple beam systems which combine SEM and two other milling systems such as a PFIB and a laser FIB are now becoming commercialized.

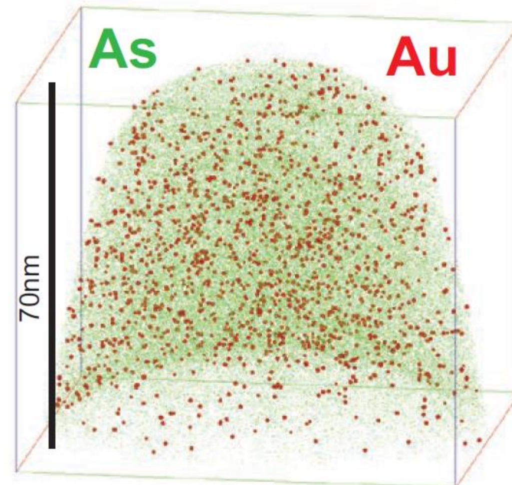
Sample preparation

- A major aspect of APT is ensuring that your sample contains a representative piece of material, with the feature of interest within the first 50 of a nanoscale tip
- This often requires complementary microscopy on multiple length scales to provide context and relevance of the atom probe data collected.



B.M. Jenkins et al . Applied Surface Science, Volume 528, 30 October 2020, 147011.





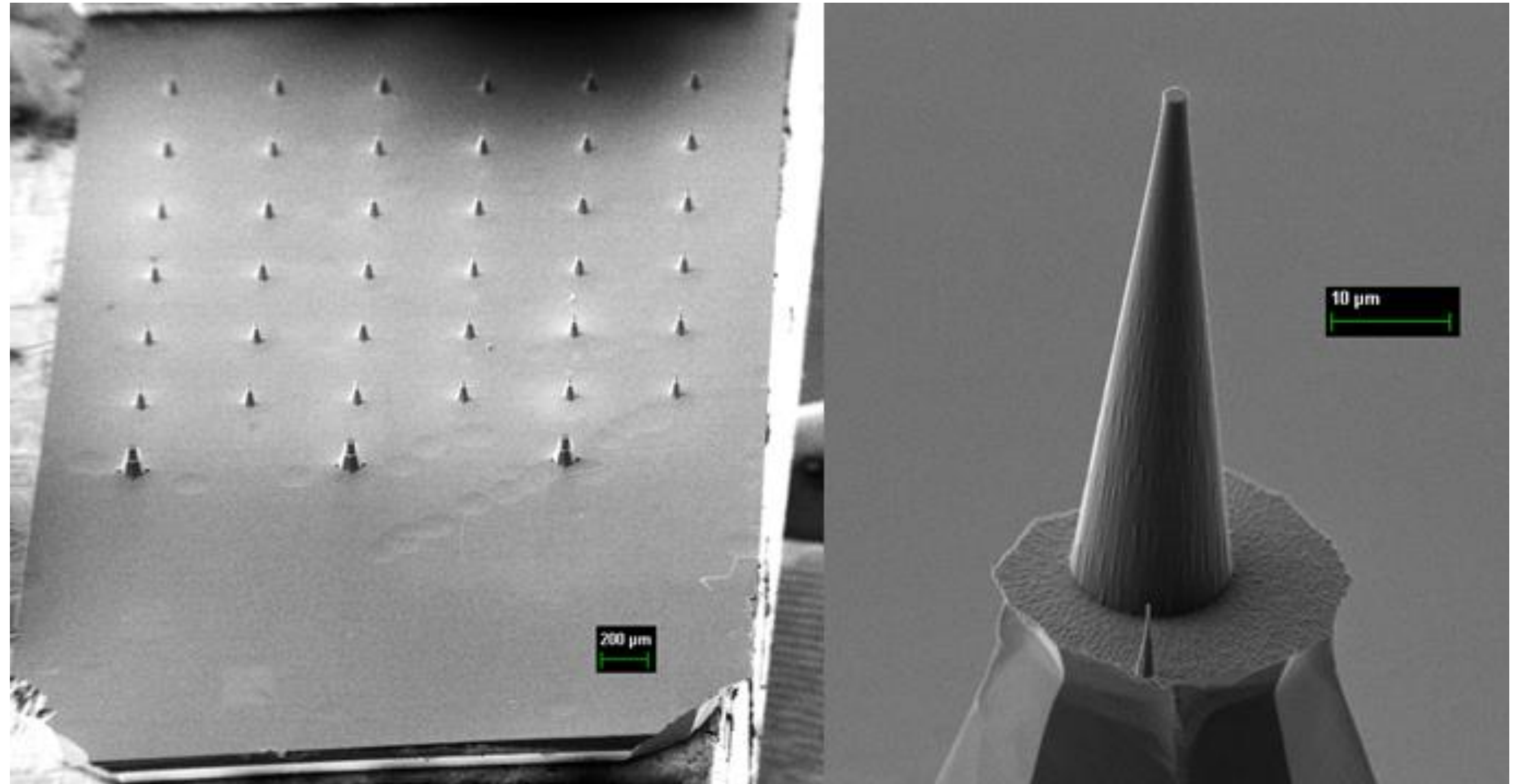
P. Gopon et al, Economic Geology (2019) 114 (6): pages 1123–1133.

- Optimised sample preparation is closely linked with useful and high quality atom probe data and each material system may require a different approach.

Sample Preparation -Focused Ion Beam

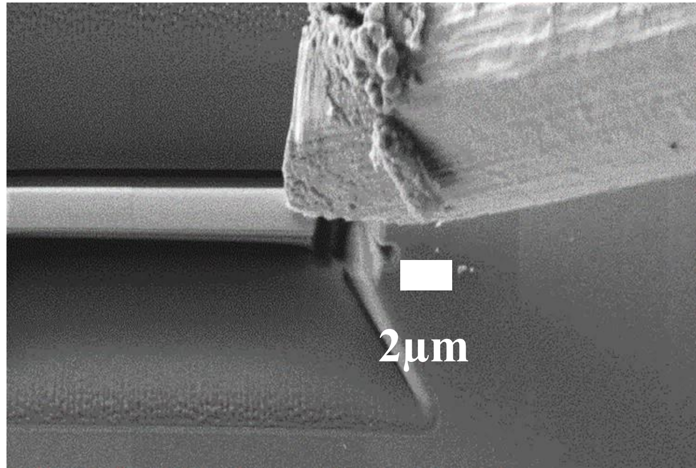
- Standard sample preparation tool for TEM and APT. High energy ions used to selectively mill regions of materials with nanoscale precision.
- Typical volume of lift out cantilever is **5 μm** x **5 μm** x **25** μm.
- Allows selection of specific sub-micron regions for analysis.

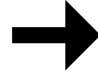
- **2 μm** x **2 μm** x **2 μm** wedges from the liftout bar are placed upon individual high aspect ratio support structures and sharpened to needle shapes.
- Commercially available arrays of posts suitable for mounting APT samples. Average yield of 6 - 8 samples per liftout, taking 6 – 8 hours per liftout.
- These times are for relatively simple, bulk liftouts. More challenging samples can take considerably more time!

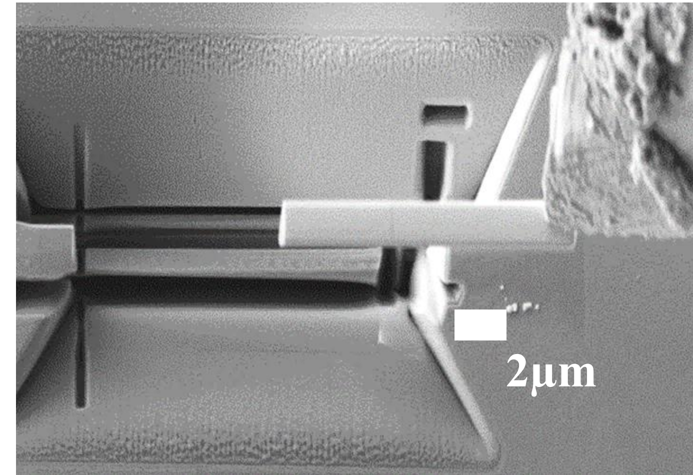


Douglas J O et al. 2016 Semiconductor Science and Technology, ***31*** *84004*

Focused Ion Beam (liftout and mounting)

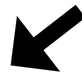


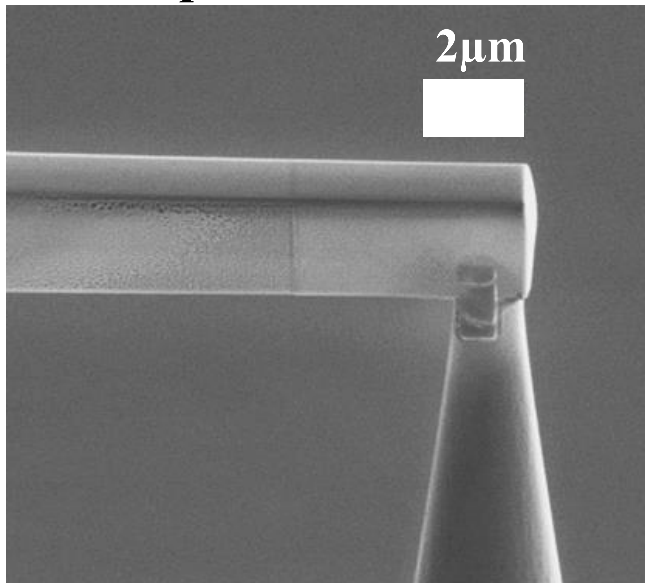


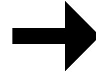


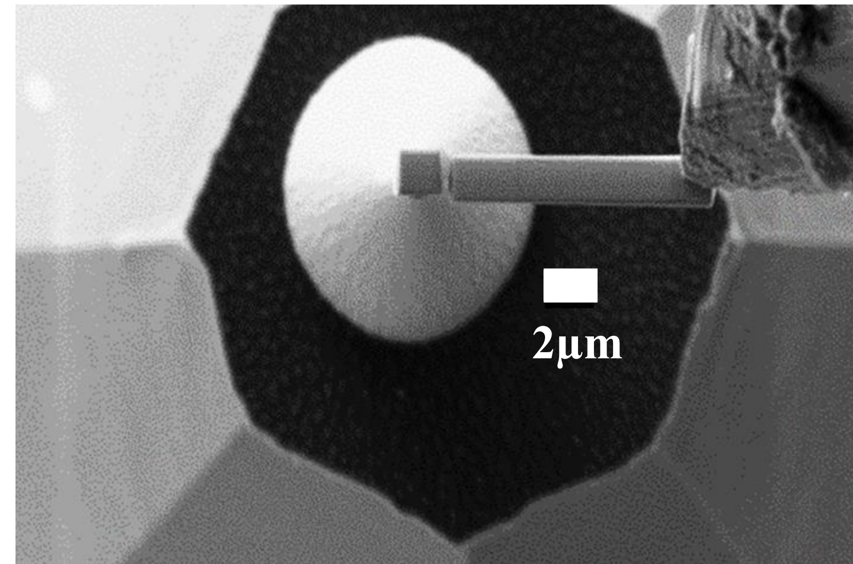
1: Attach in situ micro-manipulator to cantilever

2 : Lift out wedge from the specimen





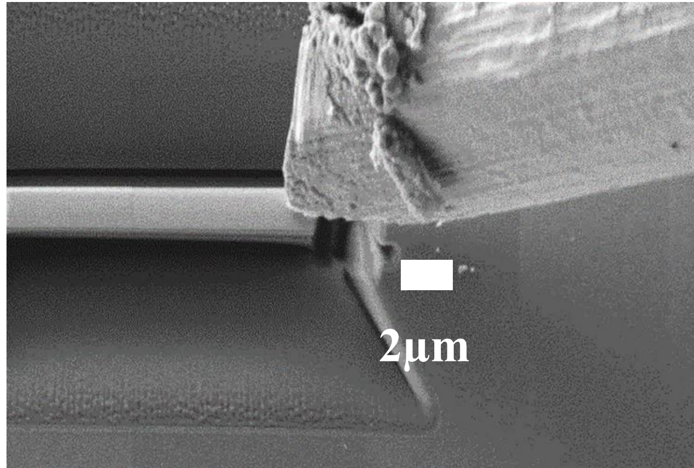




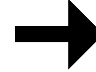
3: Attach wedge to micro post

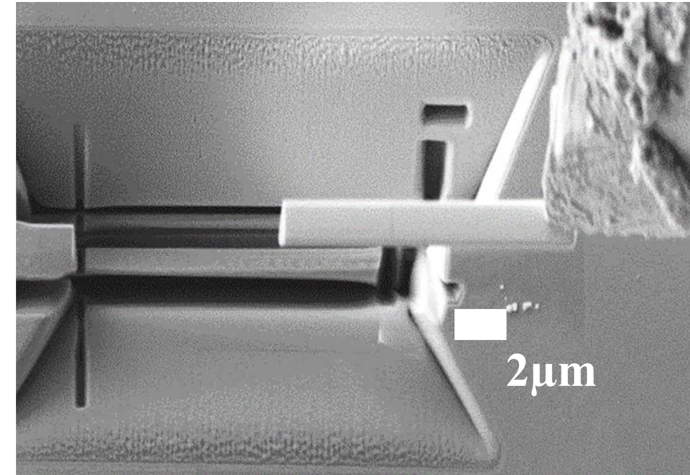
4: Cut non-attached remainder of wedge from micro post

Sample Preparation -Focused Ion Beam

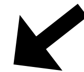


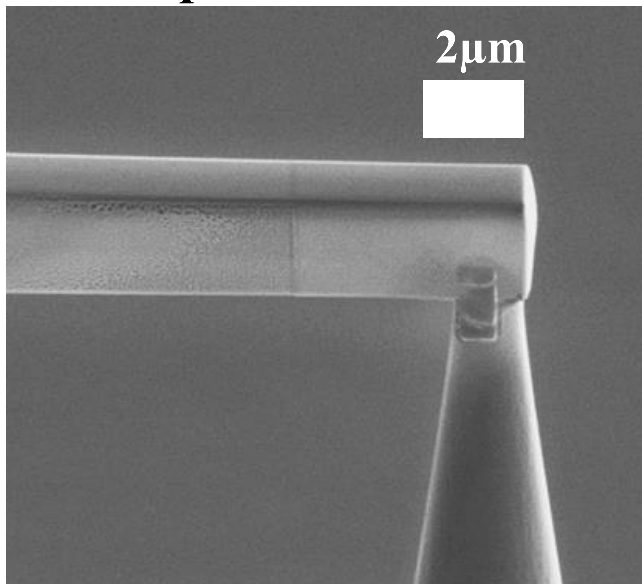
1: Attach in situ micro-manipulator to cantilever



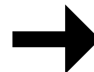


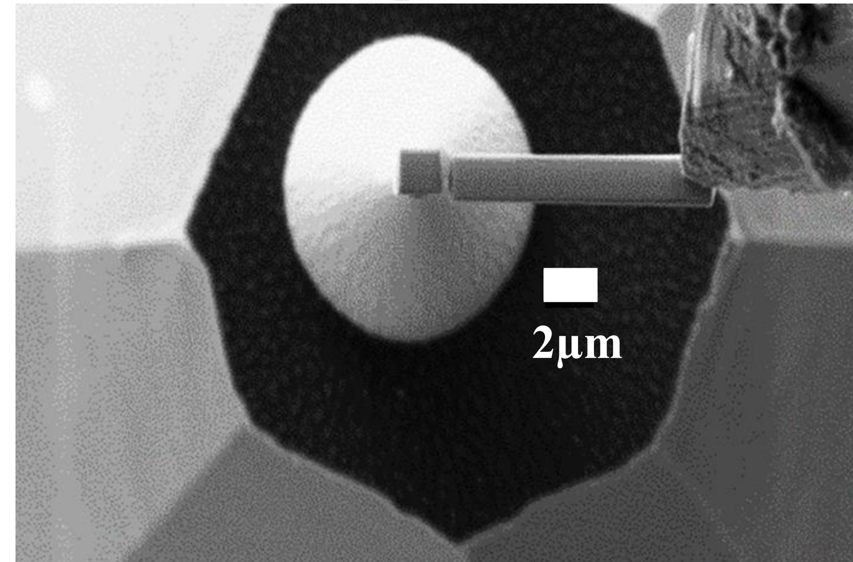
2 : Lift out wedge from the specimen





3: Attach wedge to micro post



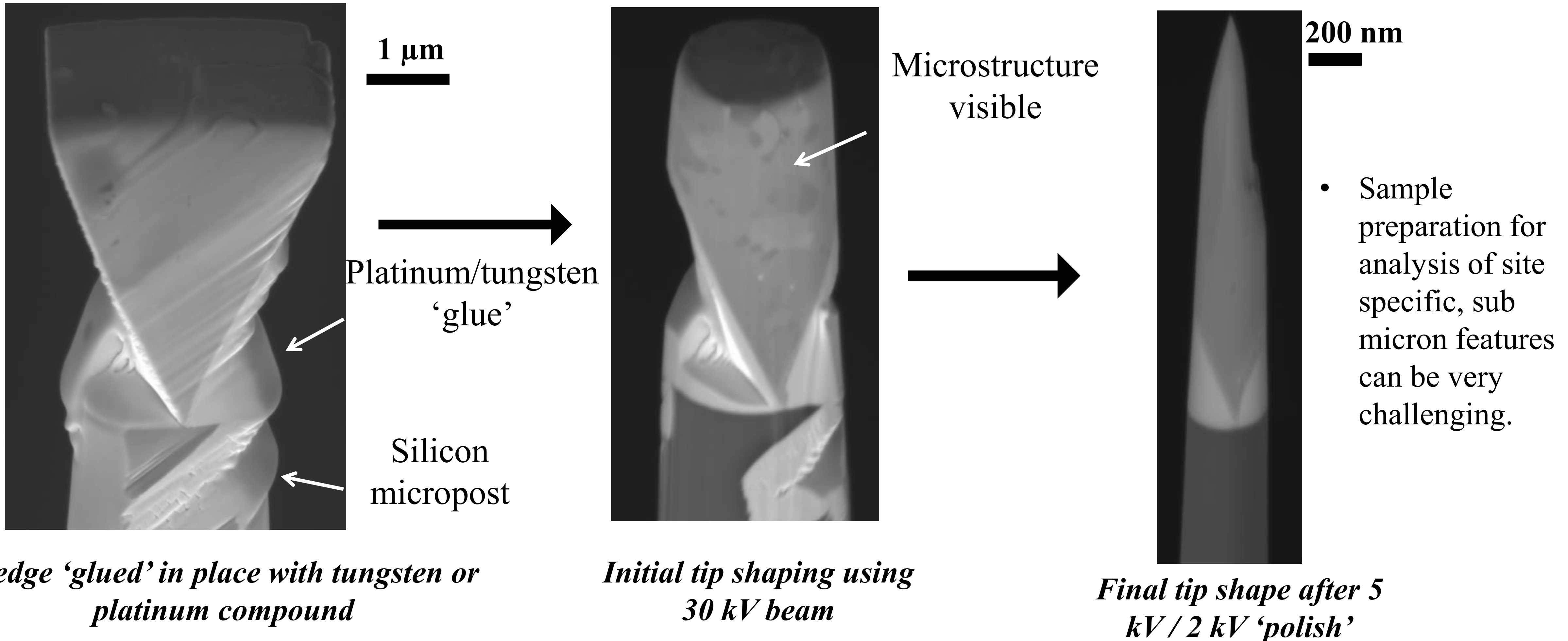


4: Cut non-attached remainder of wedge from micro post

Focused Ion Beam (FIB) sample preparation

- Representative micron scale pieces of material are selected for APT analysis by Focused Ion Beam and sharpened into needle shaped specimens.

- Successive annular milling stages with decreasing radii shapes the wedge into the required tip shape.

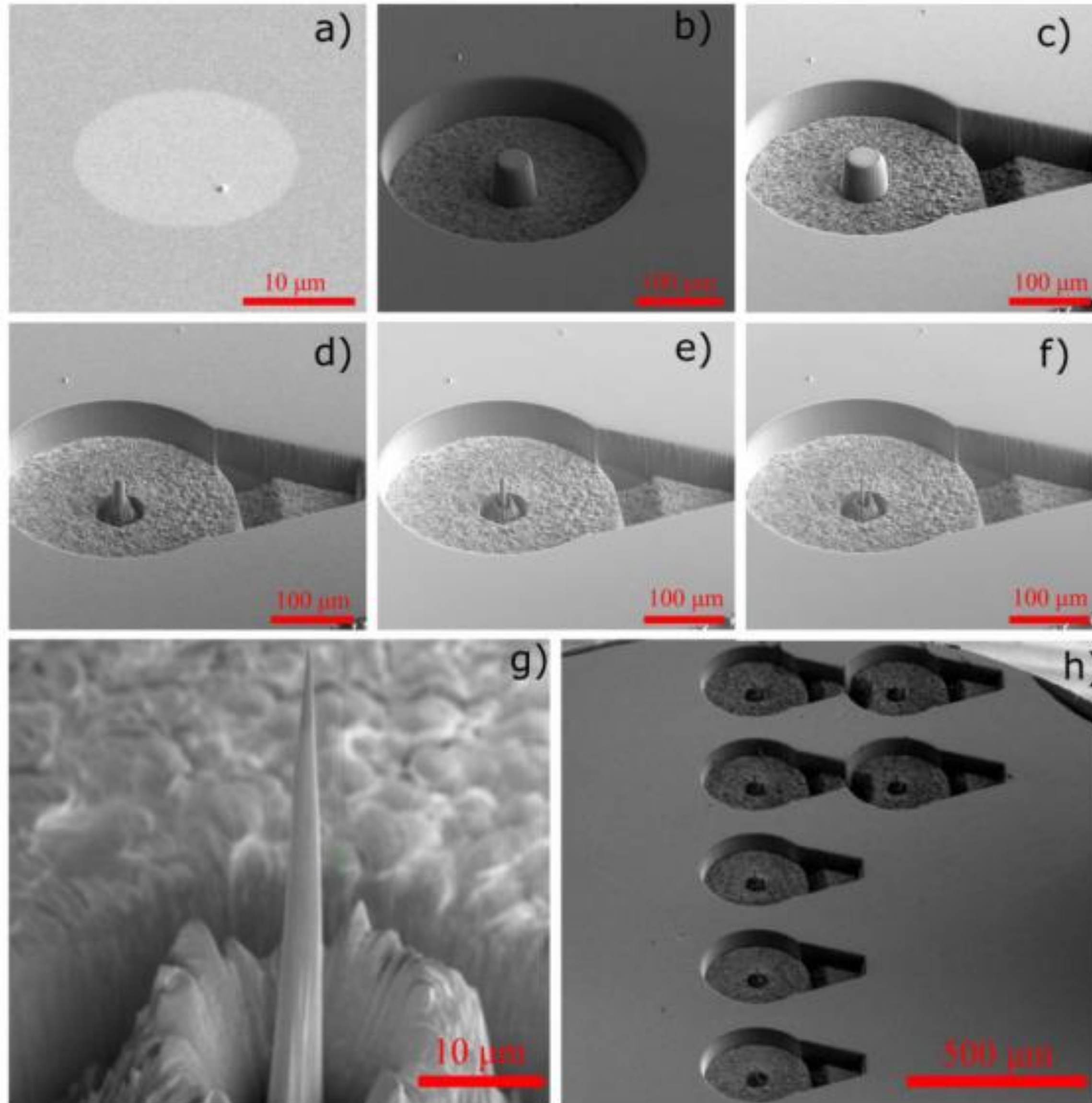


Wedge 'glued' in place with tungsten or platinum compound

Initial tip shaping using 30 kV beam

Final tip shape after 5 kV / 2 kV 'polish'

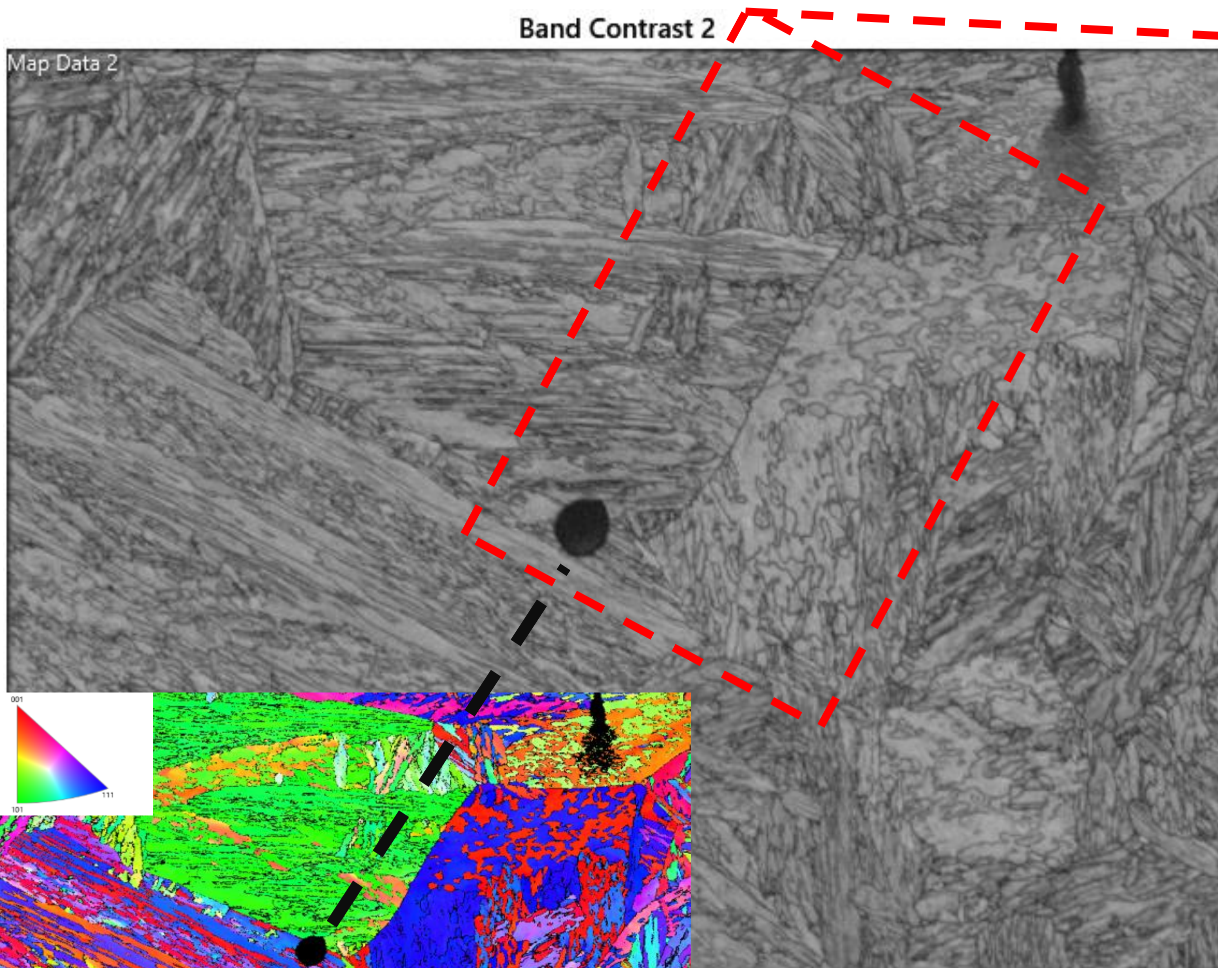
Plasma FIB – Satellite Dish method

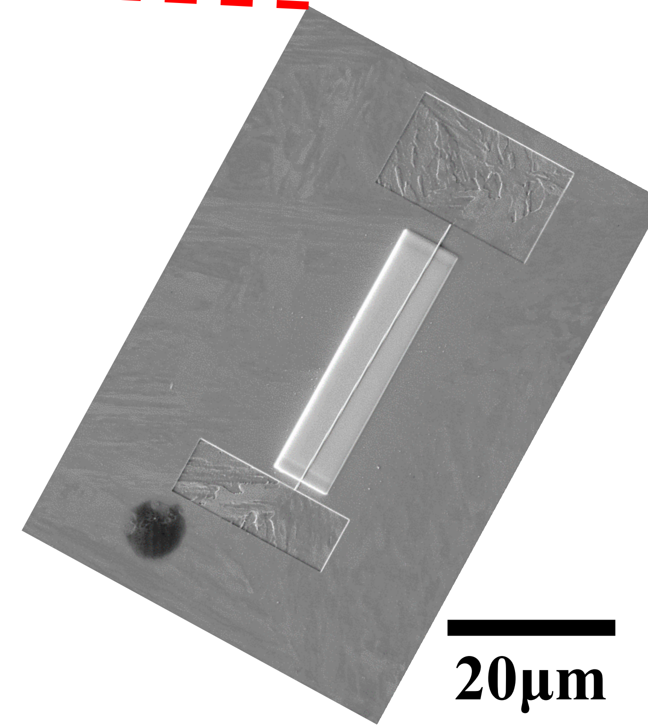


- High currents from modern plasma FIB instruments offer an alternative to liftout.
- Circular trenches or “satellite dishes” can be quickly milled to expose a central region.
- An isolated sharpened tip, with no “glue” section, can be made directly onto the surface of a flat surface.
- Multiple samples can be made on a single substrate.
- Issues with target specificity and when only small amounts of material are available.

Halpin et al, Ultramicroscopy, Volume 202, July 2019, Pages 121-127

Liftout from grain boundary as identified by EBSD

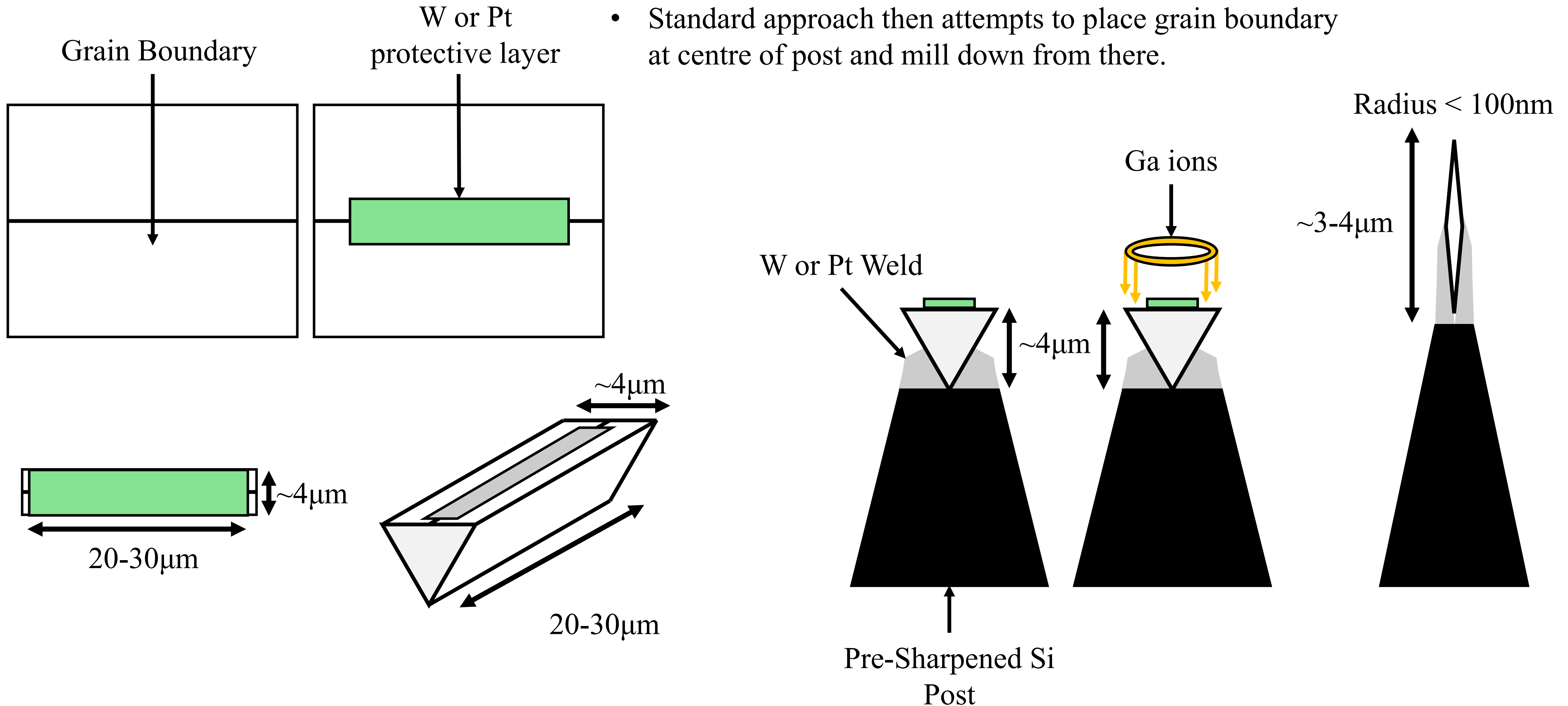




- Ebeam deposition of Pt over grain boundary to provide initial proection.
- Linear section of grain boundary delineated by thin Pt line.
- Standard protective layer then deposited.
- Either side of bar imaged using FIB to confirm grain boundary either side via ion channelling contrast.

FIB Lift-out of Grain Boundaries For APT

- Standard approach then attempts to place grain boundary at centre of post and mill down from there.



- In-situ techniques such as Transmission Kikuchi Diffraction (TKD) or Energy Dispersive Electron Spectroscopy (EDS) can be used

Analysis and data collection

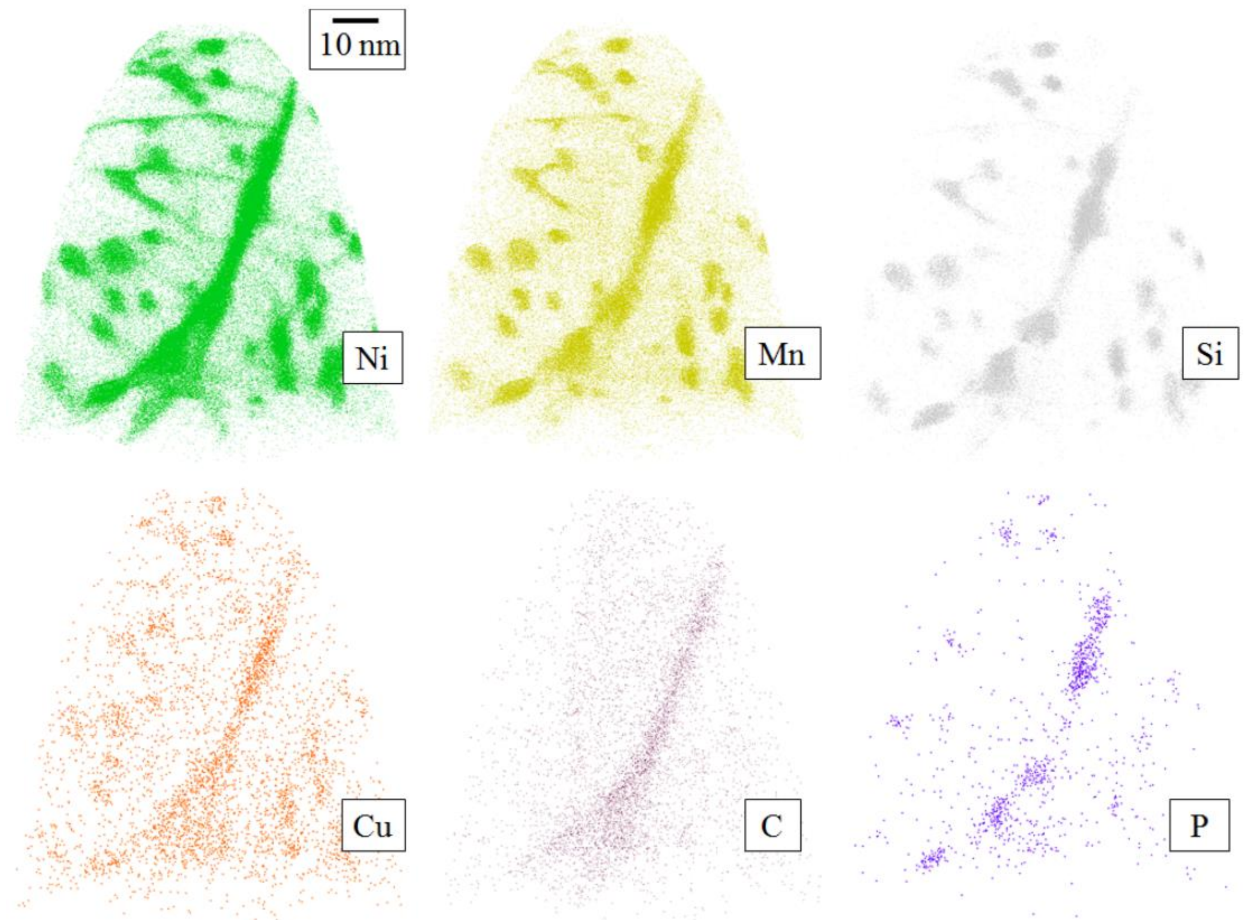
- Optimisation of analysis parameters for the data required.
- *How do I know if my data is high quality?*
- *What do we expect to see and why?*
- *How does the method in which the sample is analysed affect the data?*
- *How do I balance high quality data with sufficient amounts of data?*

- Is this a brand new material or is this something similar to a known material and a known scientific problem?

- What are some reasonable initial conditions that we can use with the aim of getting **some** data and then check that if it's **good** data?

- High temperature, high laser energy generally leads to larger datasets.
- Low temperature, low laser energy or voltage pulsing generally leads to high quality data but smaller datasets.

J. Zelenty – (DPhil thesis) Effects of nickel and manganese on the embrittlement of low-copper pressure vessel steels. University of Oxford, 2016. As reconstructed by J.Douglas.



- Steel Reactor Pressure Vessels in fission reactors undergo extended neutron irradiation at high temperatures for many decades. Nanoscale clustering of certain solutes increase material hardness and thus likelihood of fracture.

- Established "best practice" analysis parameters for this material system have been determined and allow comparison with historical data.

Reconstruction of atom probe data

The "Raw" data coming from the atom probe
consists of a sequence of hit records, for each event we have:

$X_{Detector}$, $Y_{Detector}$, dT_{Pulse}, $V_{Specimen}$, (Sequence #)

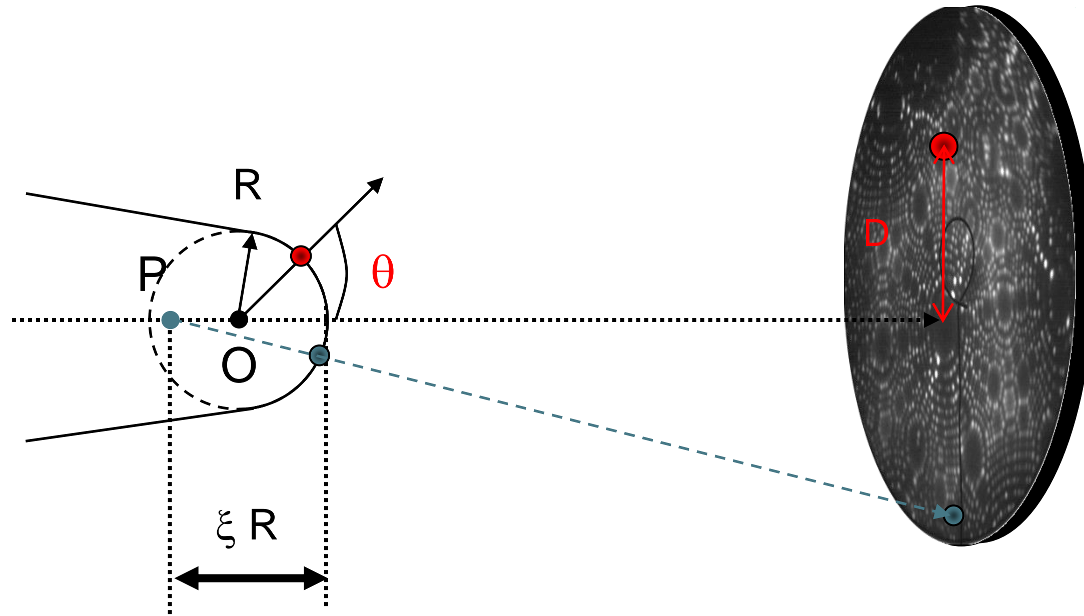
Reconstruction is the process that transforms this data into a 3D model of the specimen, typically a sequence of atomic positions:

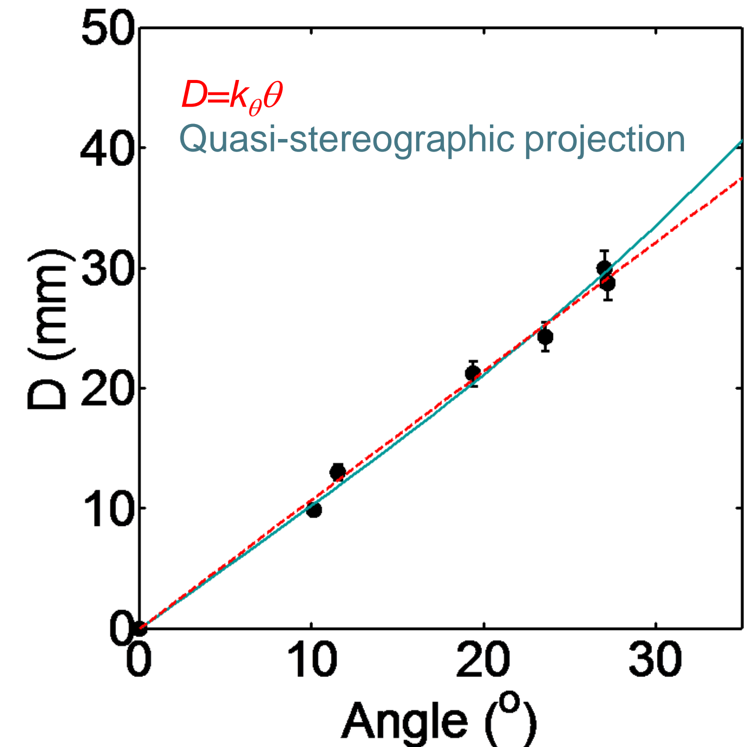
X_{Tip} , Y_{Tip} , Z_{Tip} , Mass , (Sequence #)

What do we need to know to build this three dimensional reconstruction?

Projection Laws

1. $D=k_{\theta}\theta$, D relative distance to the detector centre, θ angle relative to the tip axis

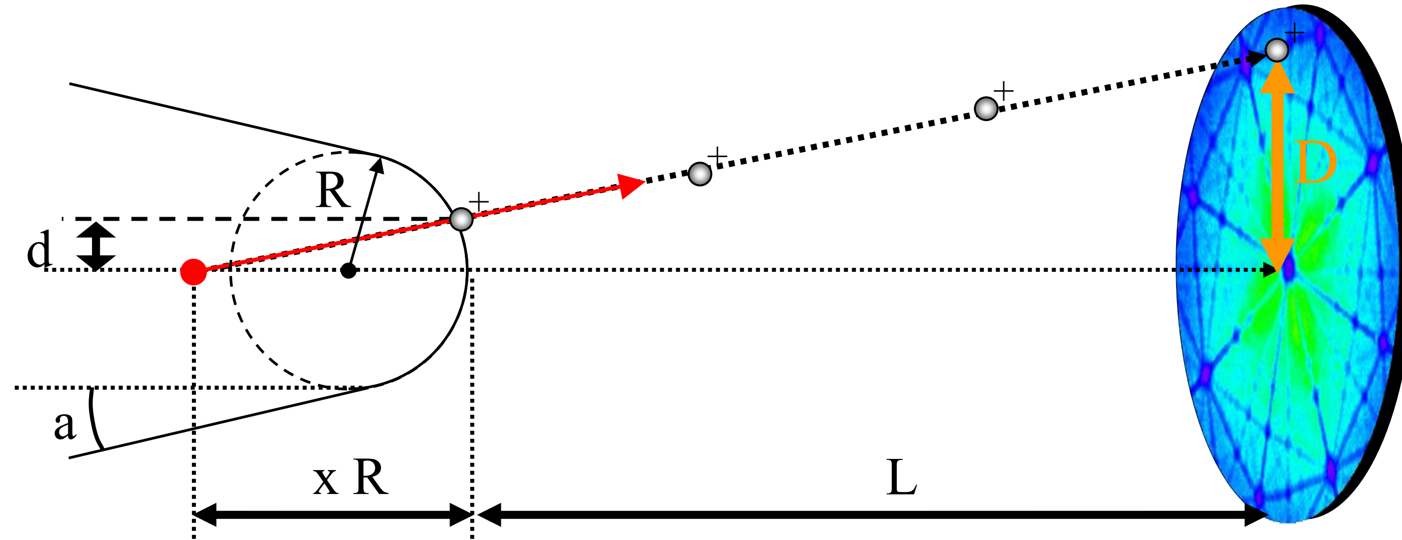




2. Quasi-stereographic projection, ion trajectories are all supposed to originate from a single point P located on the tip axis. The distance OP is generally referred to as m between and the distance between P and the apex is ξ R = (m+1)R with and ξ *is* called the *image compression factor*

Despite its limitations this is the projection used in most reconstruction software.

Magnification



$$M = \frac{D}{d} \approx \frac{L}{\xi R}$$

The magnification is proportional to the tip to screen distance.

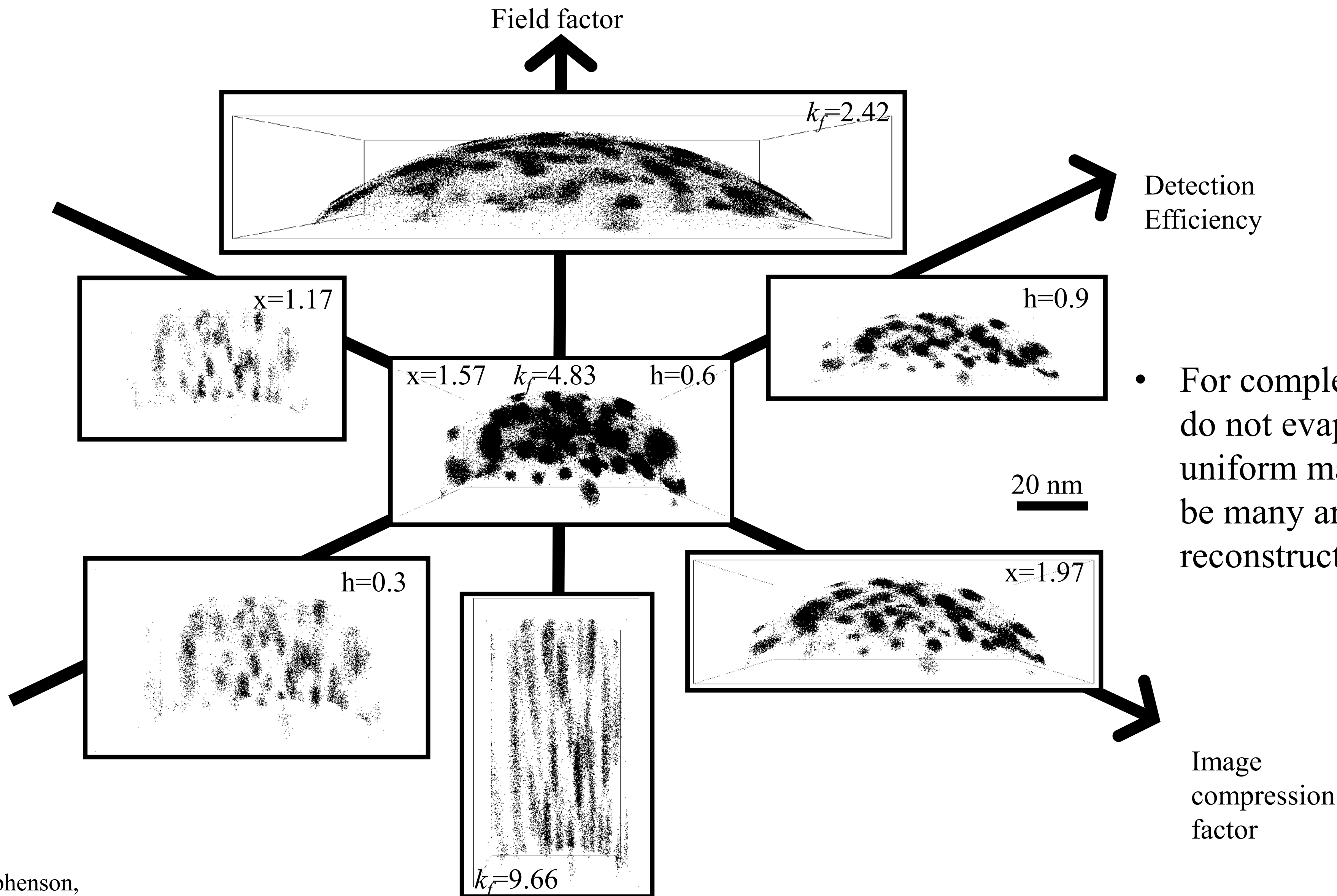
x should depend on the specimen geometry (a, R).

x lies between 1 (radial projection)

and 2 (stereographic projection)

Magnification of tip surface is on the order of a million times.

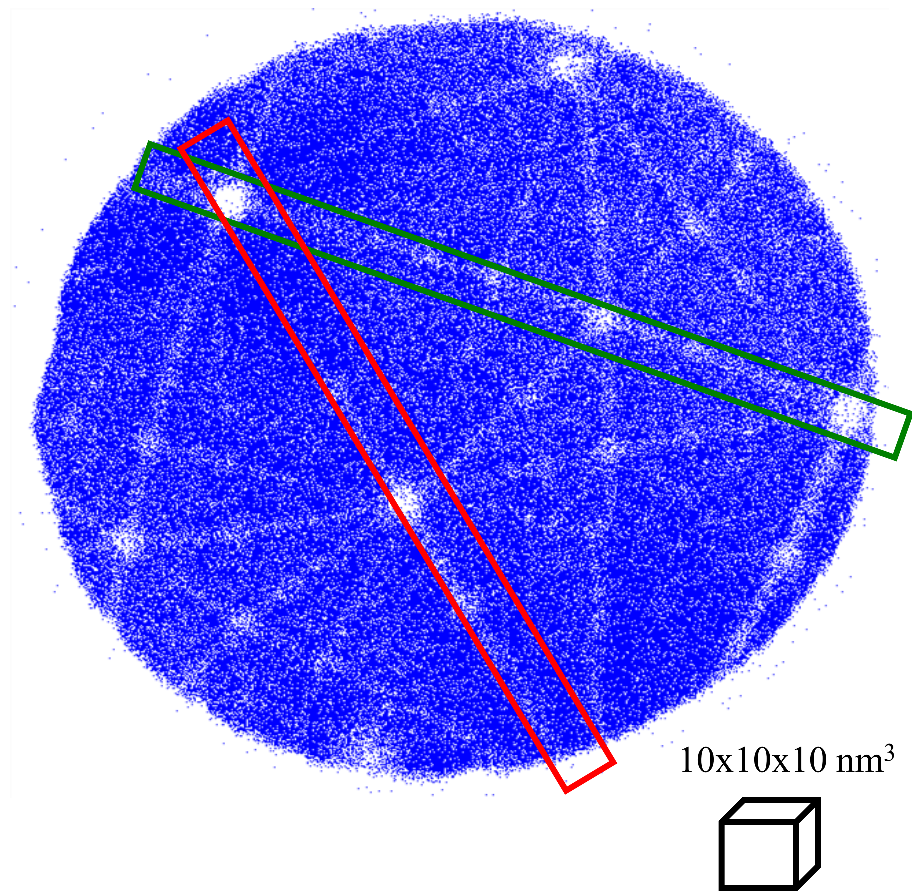
Change in reconstruction with various reconstruction parameters

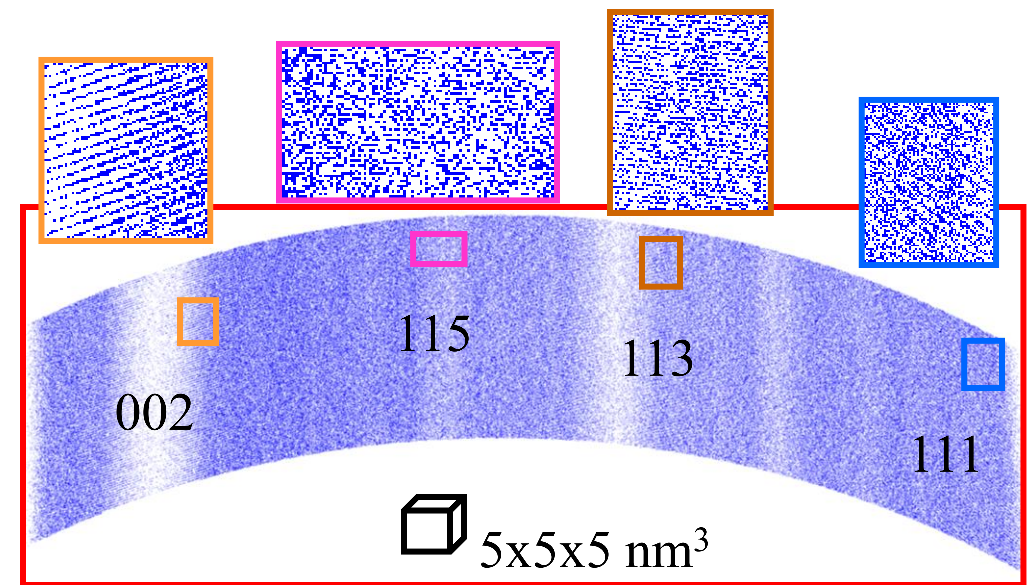


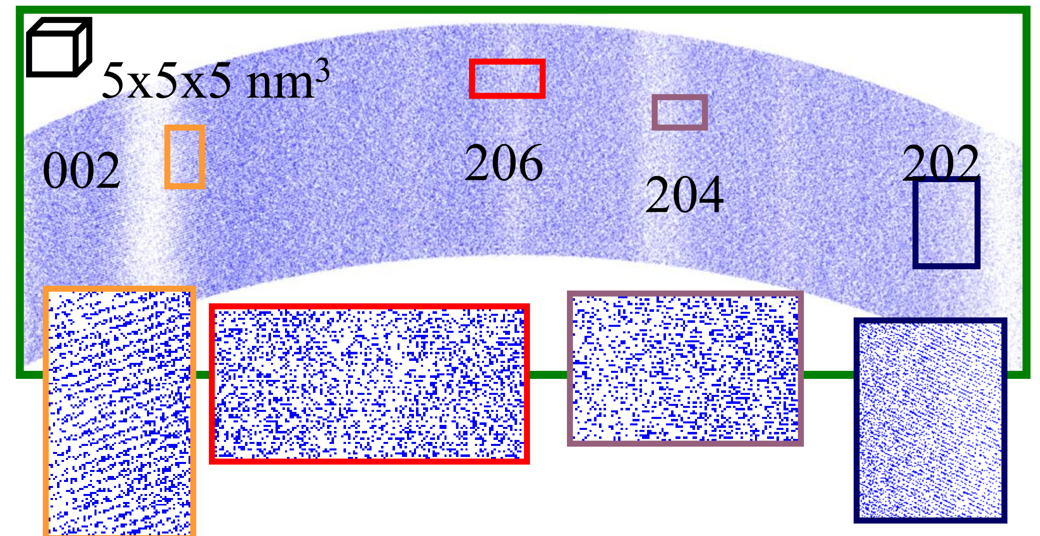
- For complex systems which do not evaporate in a uniform manner, there can be many artefacts in the reconstruction process.

AlCuAg alloy from L.T. Stephenson, University of Sydney

Reconstruction

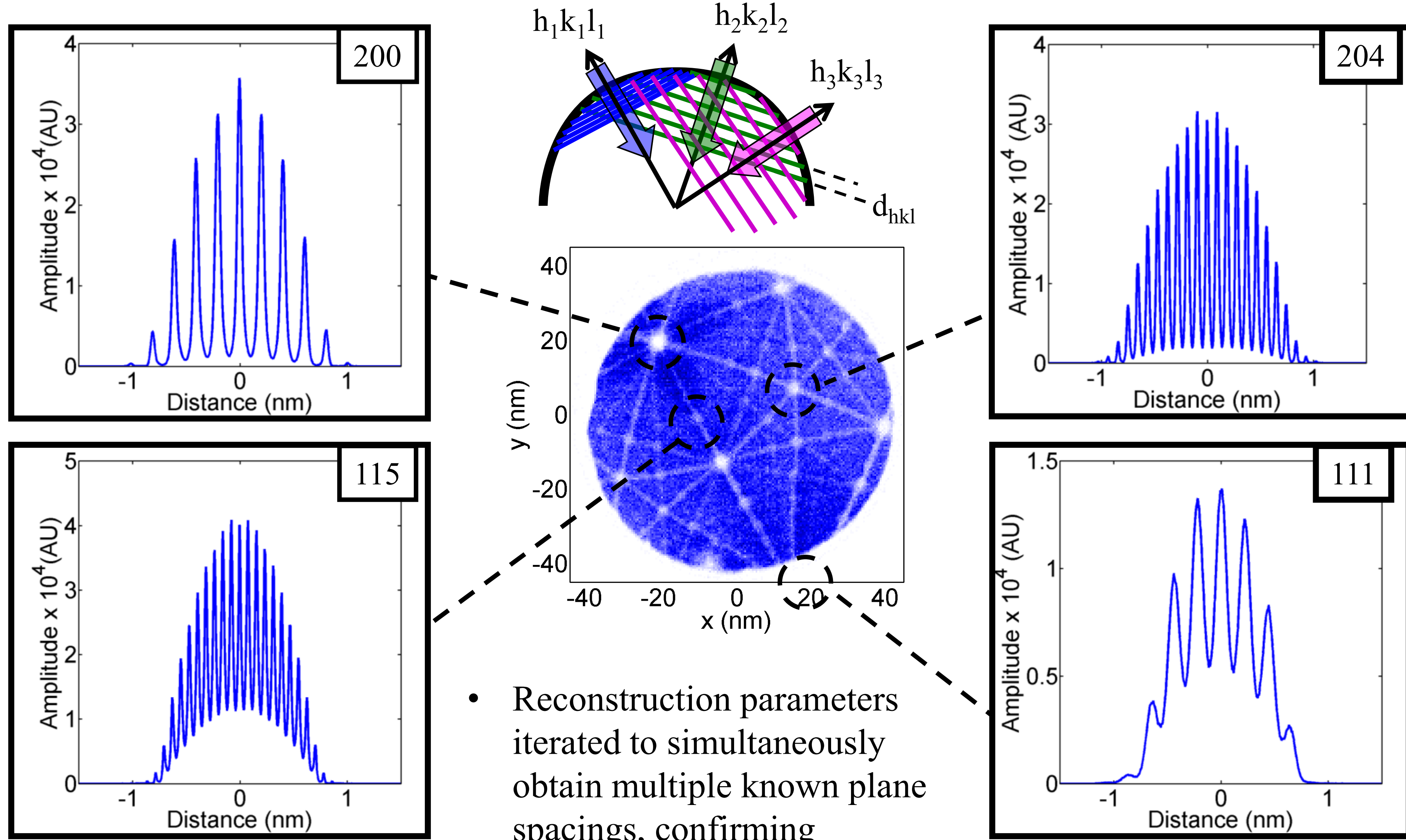






- Periodicity can be observed in various orientations in the reconstruction that match known crystal plane spacings.

Spatial Distribution Maps of pure aluminium

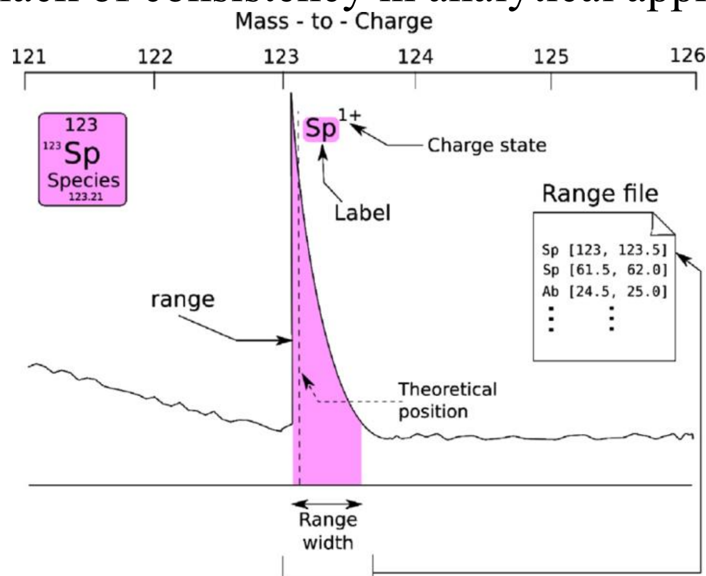


- Reconstruction parameters iterated to simultaneously obtain multiple known plane spacings, confirming physicality of reconstructed volume.

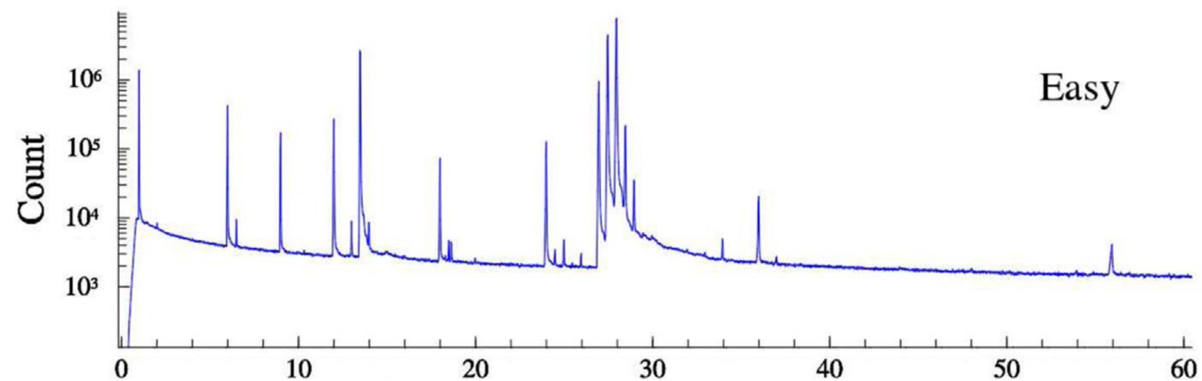
M.P. Moody, B.Gault, L.T Stephenson, D. Haley, S.P Ringer - Ultramicroscopy 109(7) 815-824 (2009).

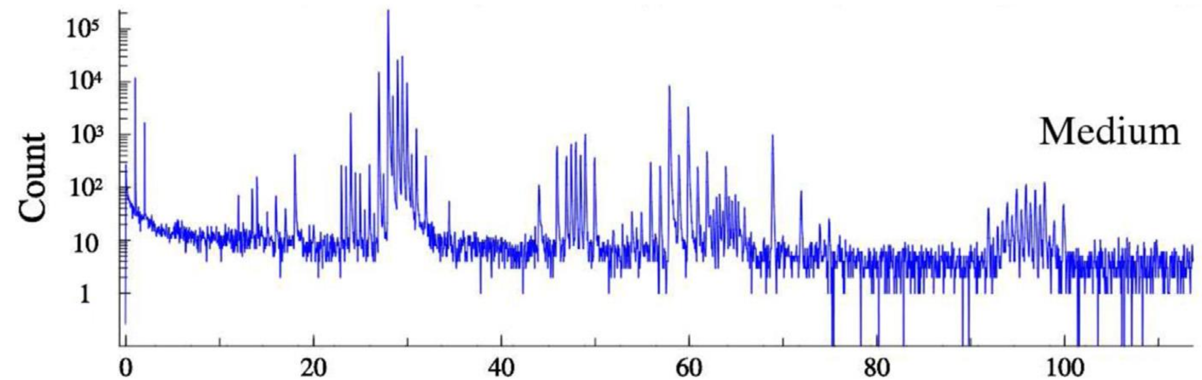
Consistency in Ranging

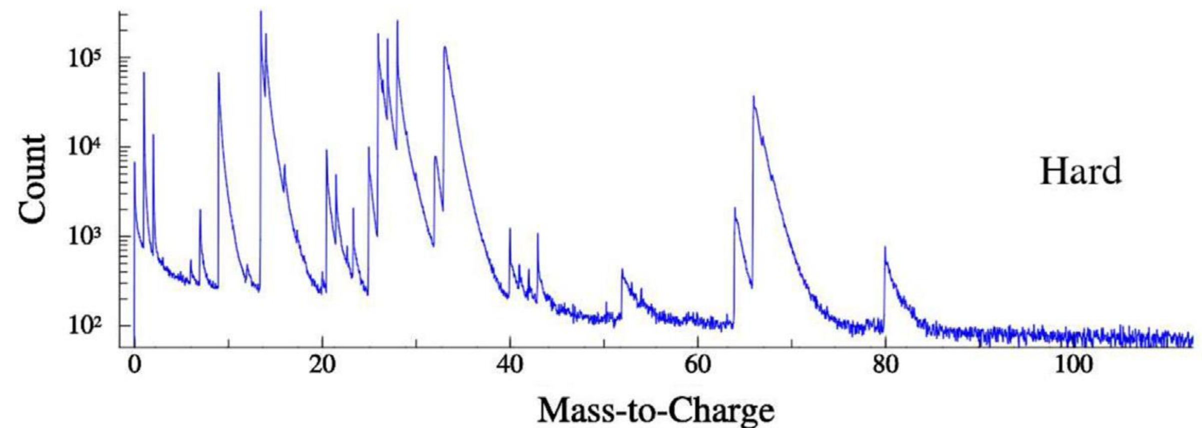
- All APT compositional information is based upon accurate and reproducible ranging of mass spectra peaks.
- Ranging of species is mostly still human driven although automatic systems do exist.
- No regulated way to range, multiple techniques have been used but each material system may require a different approach.
- Consistency is key if comparing similar datasets.
- Large variations in data interpretation between users have been observed, especially with complex mass spectra and lack of consistency in analytical approach.



- Complex mass spectra typically contain multiple overlapping species within difficult to define peak shapes.

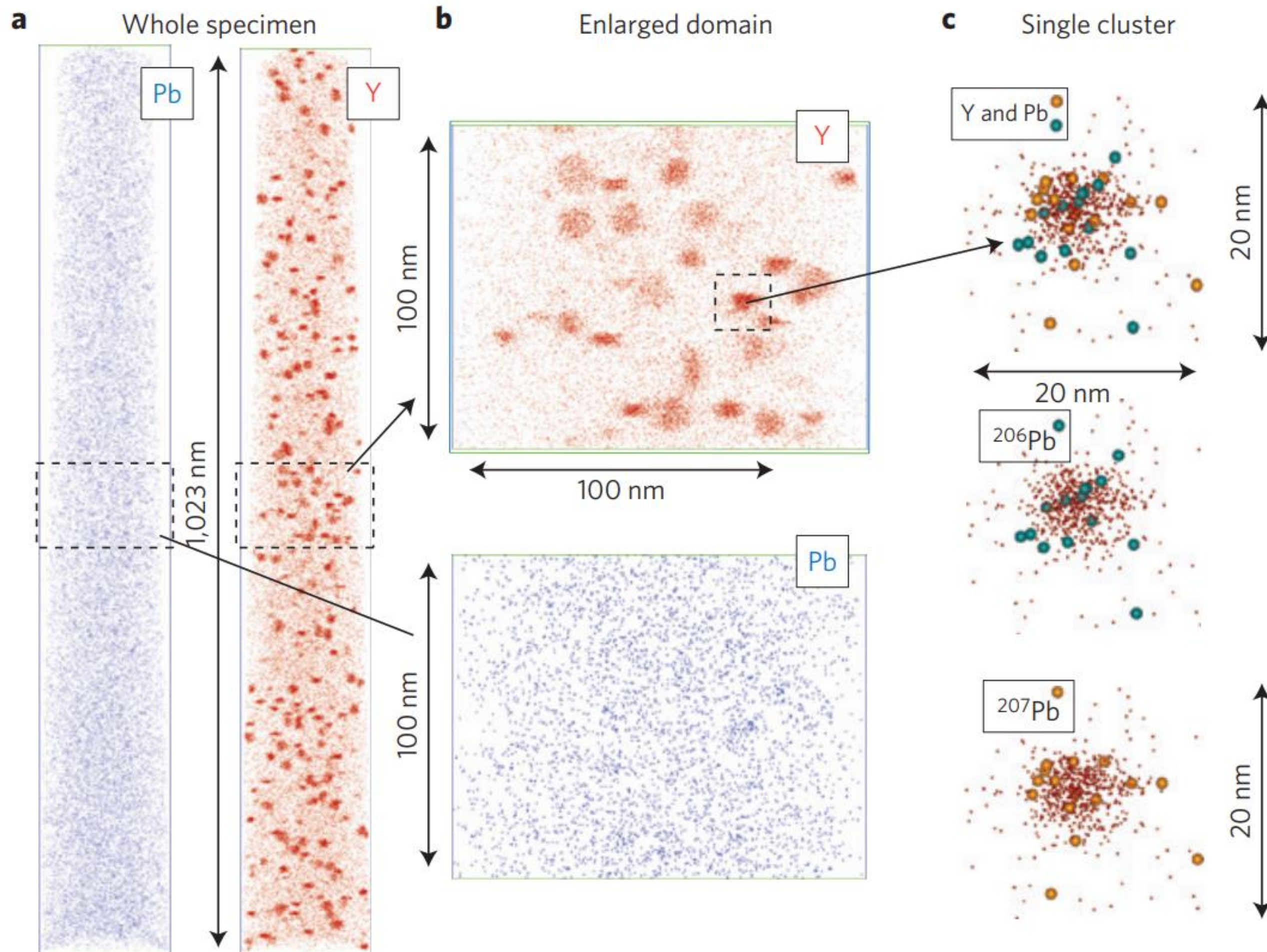






Haley et al, Ultramicroscopy, Volume 159, Part 2, December 2015, Pages 338-345

Clusters



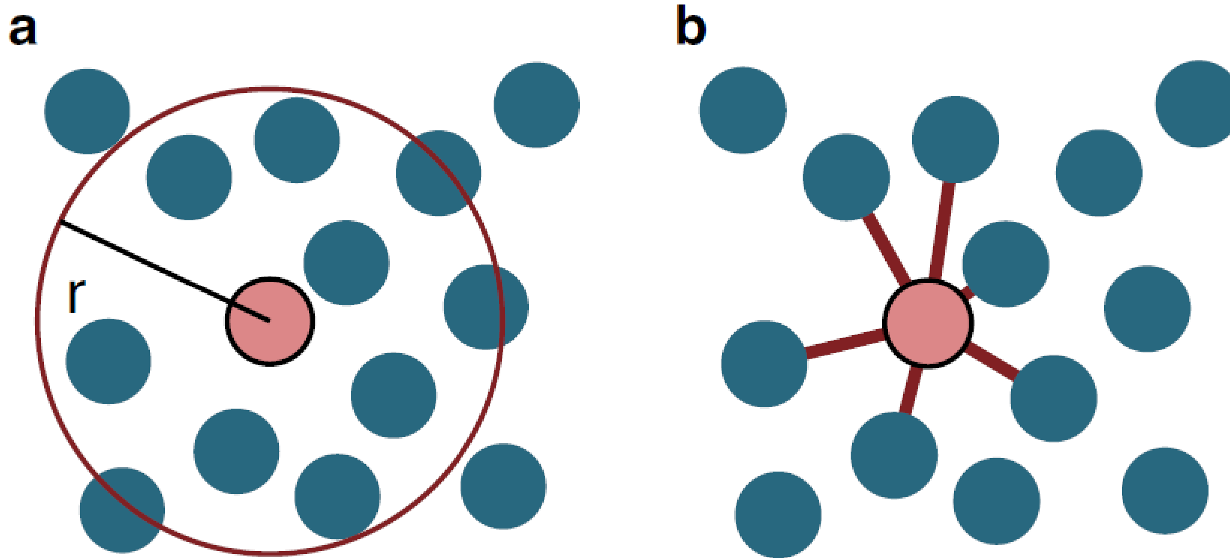
Valley J W et al. 2014 Nature Geoscience 7 219–223

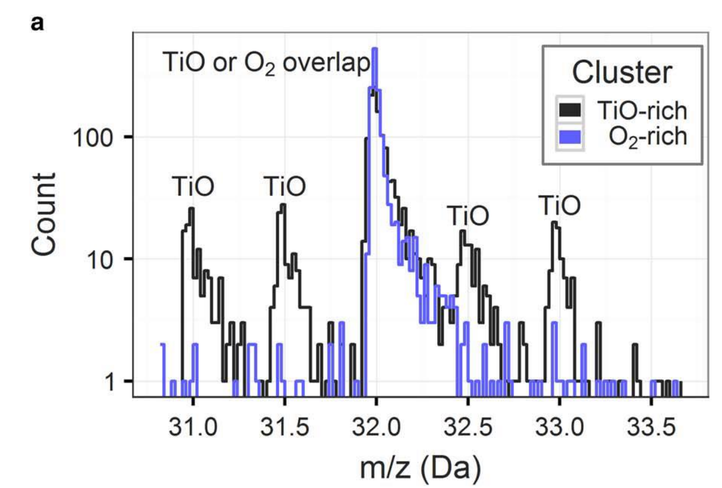
- What is a cluster?
- Specific ions are closer together than a random distribution would suggest.
- Number of different ways to identify and quantify clusters.
- We can use high concentration species that are co-segregated to low concentration species in order to know where to look.
- This allows us to only select specific sub-volumes in order to increase signal to noise of low concentration species.
- APT allows Pb dating within sub micron volumes of 4.4 billion year old zircon

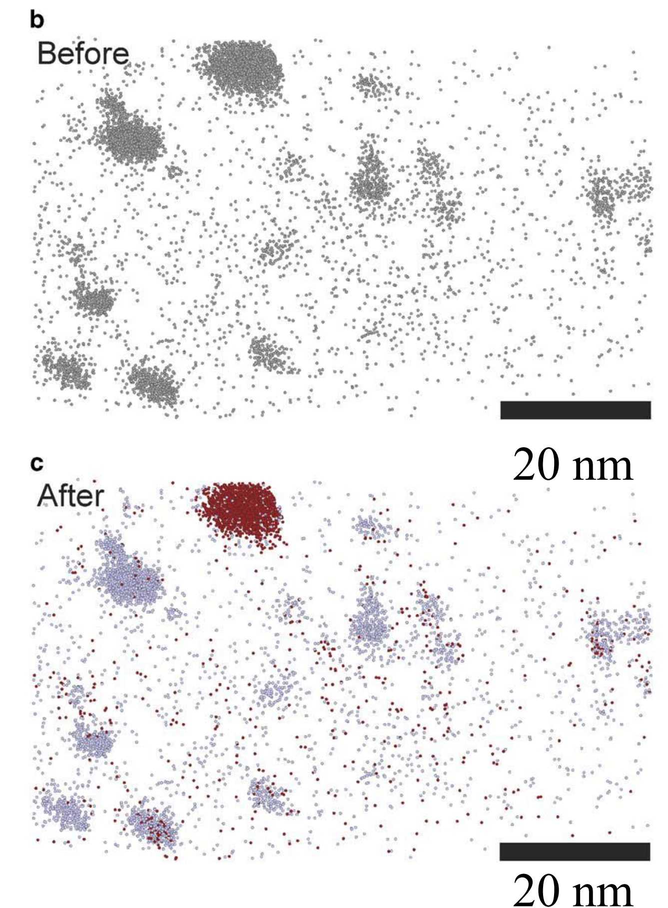
Analysing these sub-volumes (already within the nanoscale volume of an APT sample!) are an extremely powerful aspect of atom probe analysis. This combination of 3D spatial and compositional information can give information on nanostructures which cannot be obtained by other current techniques.

Local deconvolution

- What about overlaps in clusters or sub-volumes? Global deconvolution is not always suitable.
- We can assist this analysis somewhat by carrying out more in depth deconvolution on sub-volumes or clusters.
- Deconvolution can be carried out via the Maximum Likehood Method by sampling local environment around each ion.



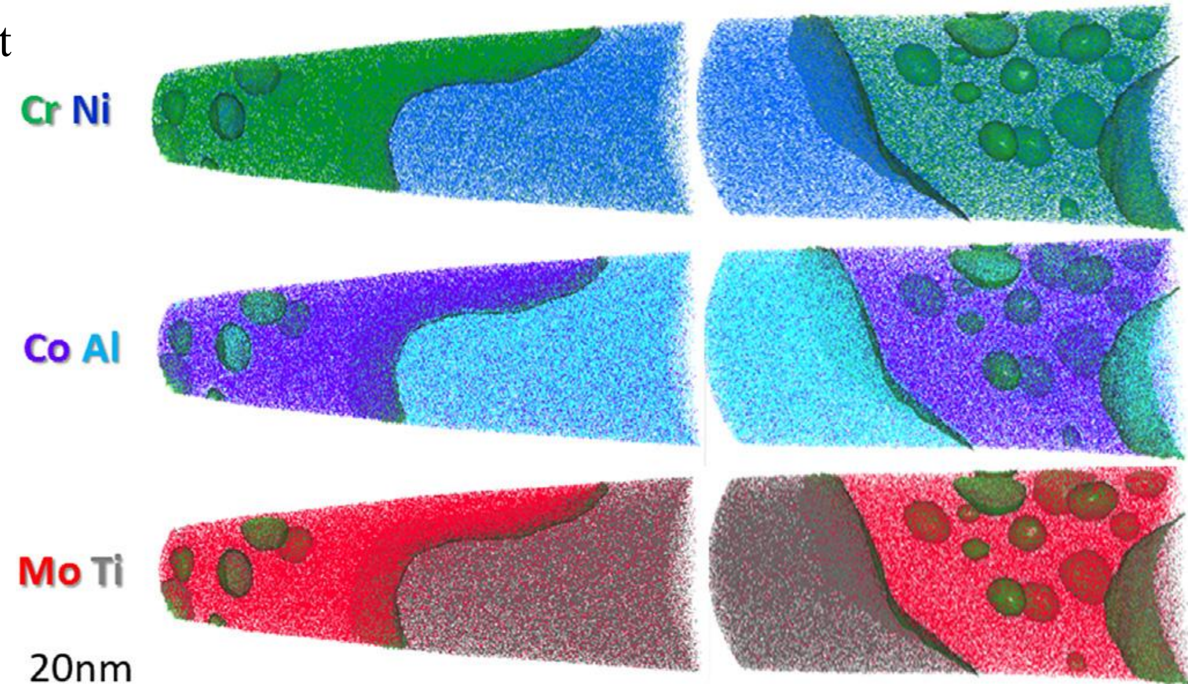


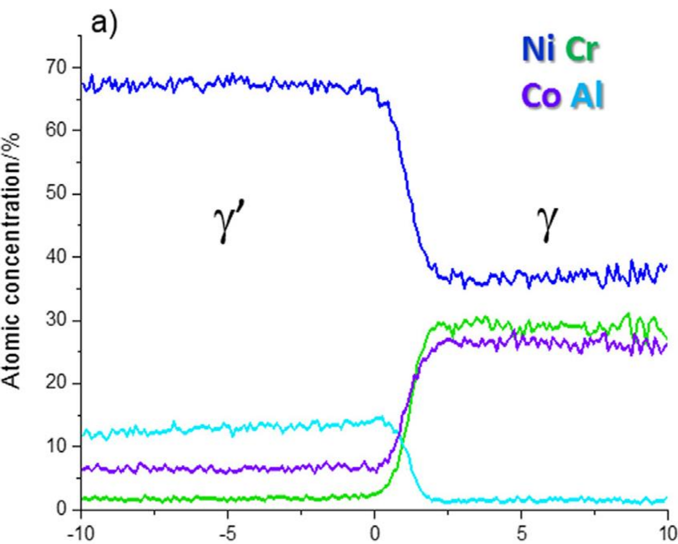


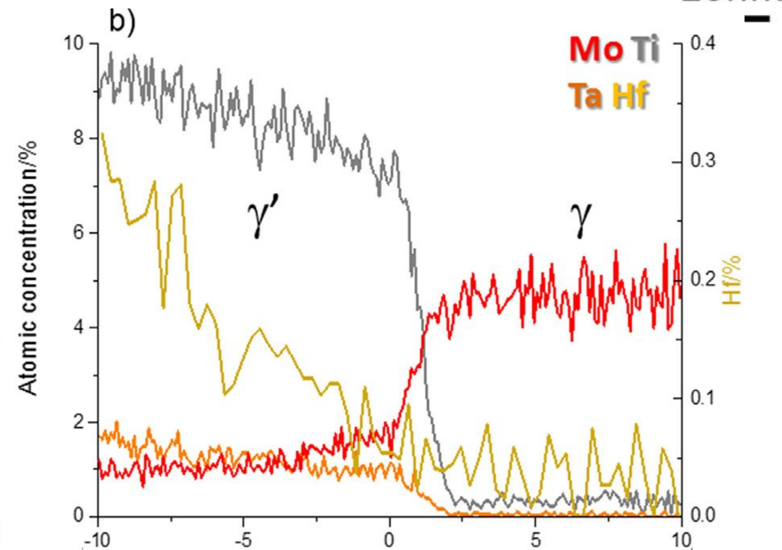
London A J et al. 2017 Microscopy and Microanalysis ***23*** *300–306*

Iso-surfaces

- Deliniating a surface between two regions is generally carried out using variation in composition or density.
- Specific species of interest are tallied in voxels, voxels are then joined together.
- Measured interfacial width can vary as a function of orientation within tip (due to variation in spatial resolution with direction).





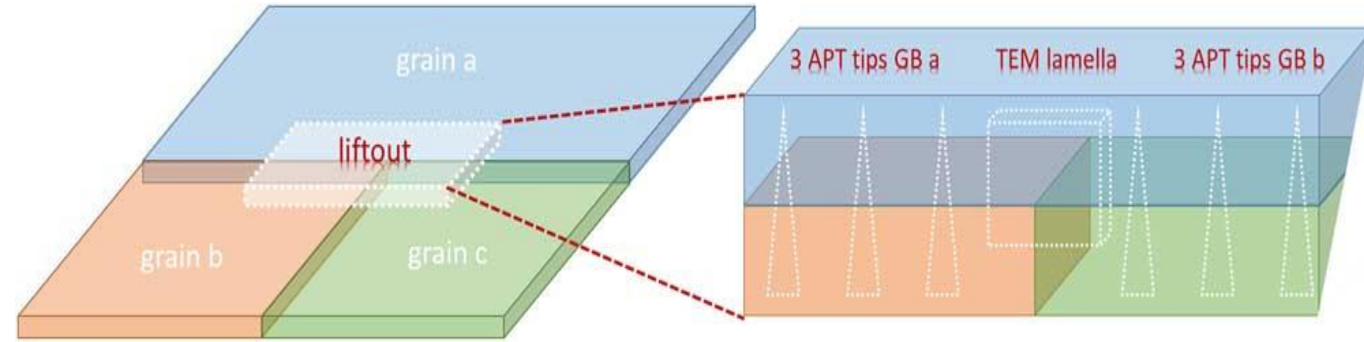


- From these surfaces (which can be summed when small), proximity histograms can be produced.
- Compositional profiles from curved interfaces can show presence of diffusion profiles of specific species.

Bagot et al Acta Materialia 125 (2017) 156-165

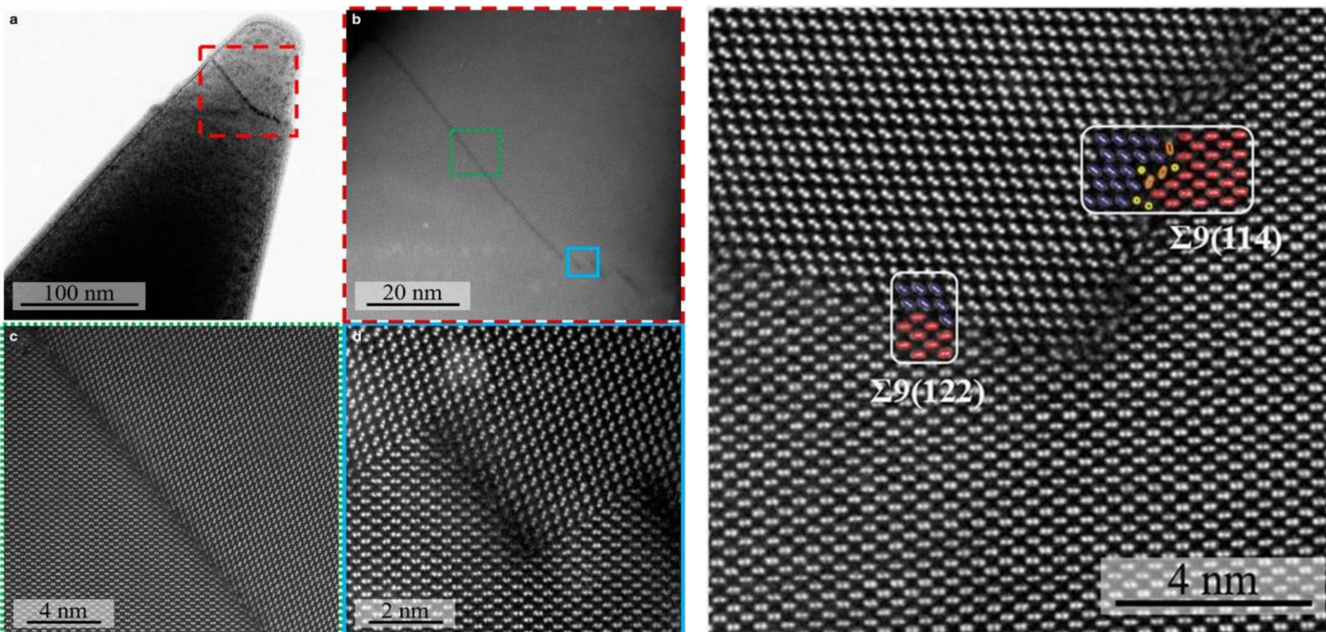
Complementary techniques – (S)TEM on same material

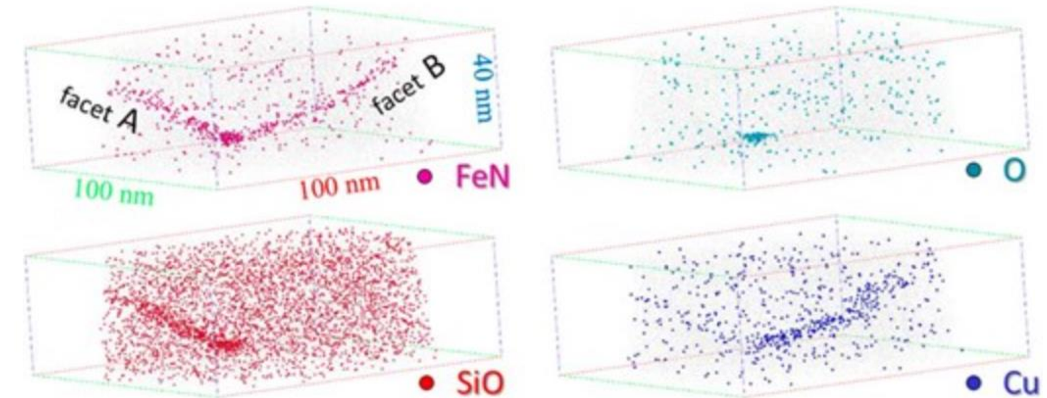
- If nanoscale complementary analysis of a material is required, the easiest approach is to carry out TEM and APT sample preparation on identical regions.
- Atom probe samples are sufficiently thin such that (S)TEM can be carried out on them without additional preparation if mounted on a grid.



Stoffers *et al* Microanal, Volume 23, Issue 2, 1 April 2017, Pages 291–299

- Complementary polycrystalline silicon grain boundary analysis by (S)TEM and APT on the same grain boundary as selected by Electron Beam Induced Current can be carried out on the same sample.



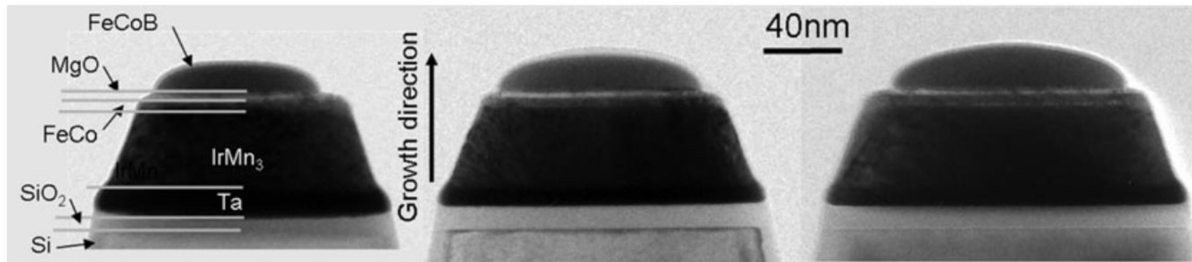


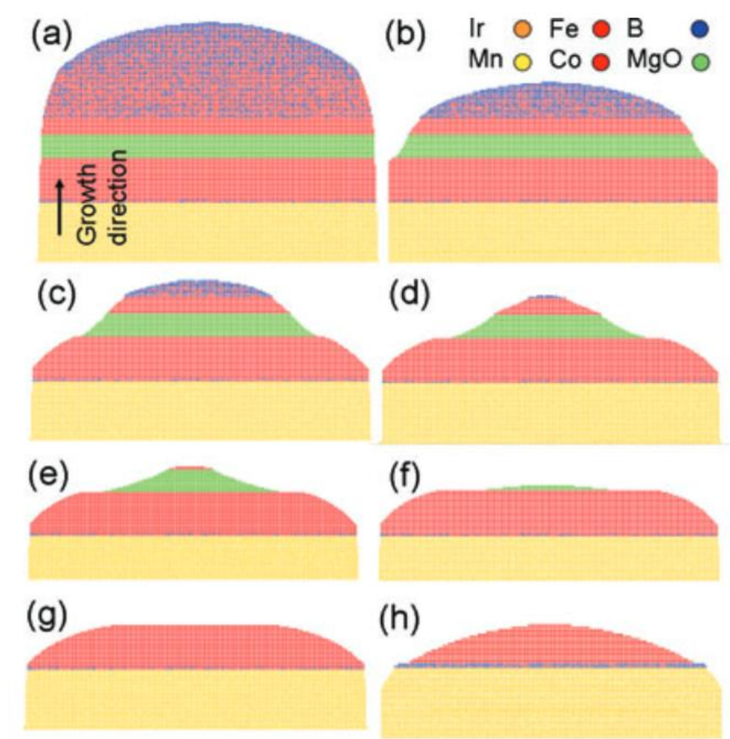
- Allows correlation of location and concentration of recombination linked species as a function of grain boundary misorientation.

Complementary techniques – (S)TEM on APT samples

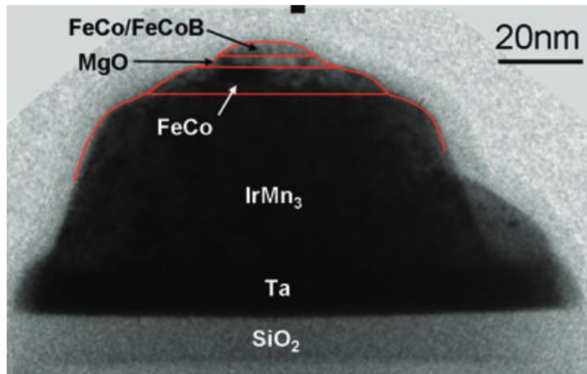
- TEM imaging on an APT tip prior to analysis can give an initial tip radius and thus inform reconstruction parameters.

E. A. Marquis et al Journal of Microscopy, Vol. 241, Pt 3 2011, pp. 225–233



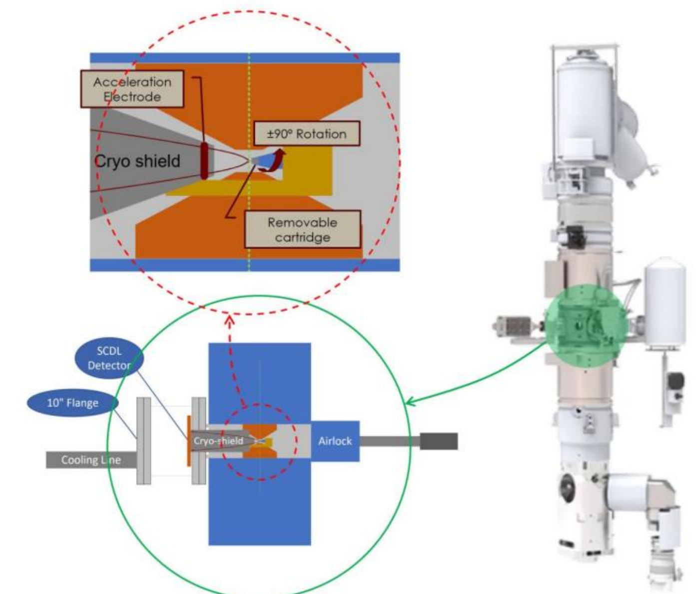


- In the case of a complex microstructure such as a multilayer system, the sample end form dynamically changes due to the variation in evaporation field requirements of the different layers.



- This can inform dynamic reconstruction models in order to guide and improve accuracy of 3D reconstructed volume.

- Combining the capabilities of an atom probe and TEM in a single instrument is ongoing (Project Tomo).

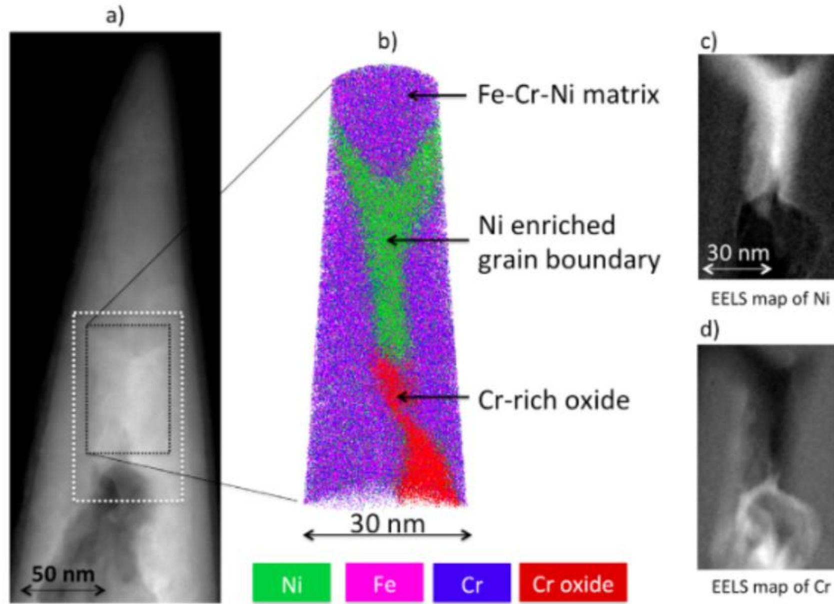


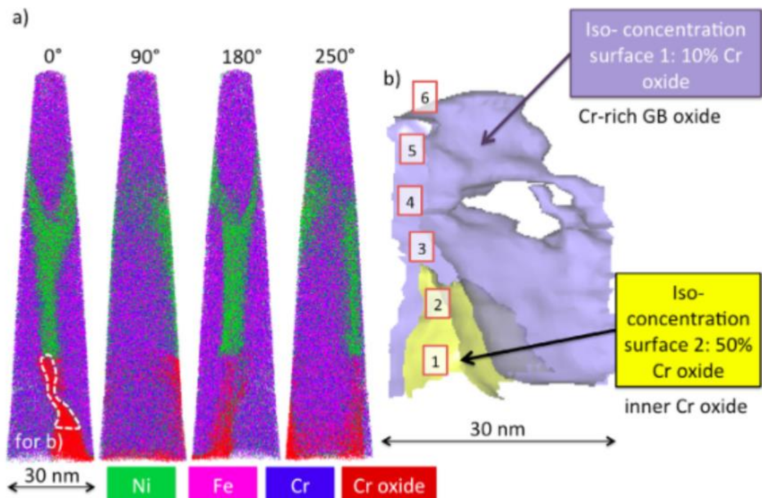
- Pausing APT analysis to transfer to a TEM and take images during analysis is possible but time consuming and can affect yield.

Kelly et al, Microsc. Microanal. 26 (Suppl 2), 2020

Complementary techniques – STEM on APT samples

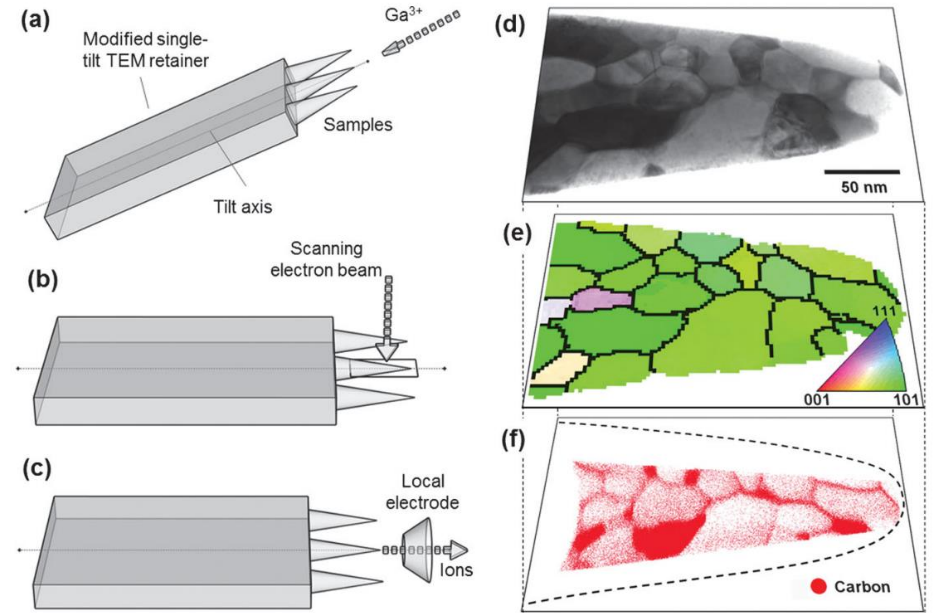
- (S)TEM based imaging, diffraction analysis and spectroscopy also can be carried out prior to APT analysis.

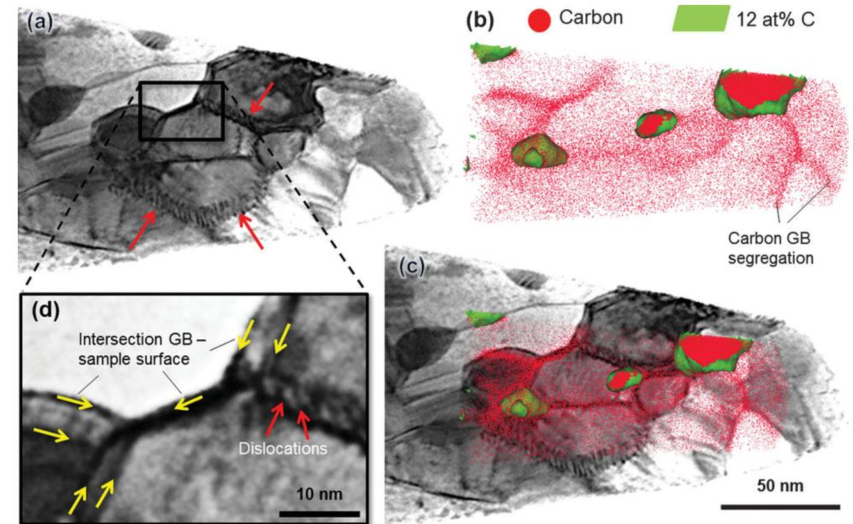




Meisnar et al, Corrosion Science, Volume 98, 2015, Pages 661-671

- APT only collects data from core of the physical sample, (S)TEM increases field of view.
- Local orientation relationships can be obtained purely from APT data but is very material dependent.
- Complementary analysis ideal for materials where features of interest could not be readily distinguished through a single method.





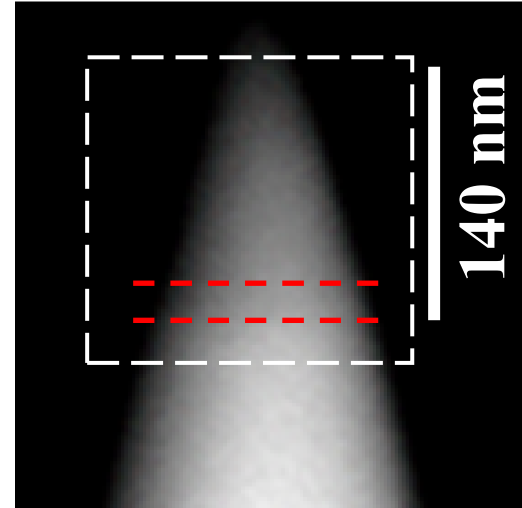
M. Herbig et al PRL 112, 126103 (2014)

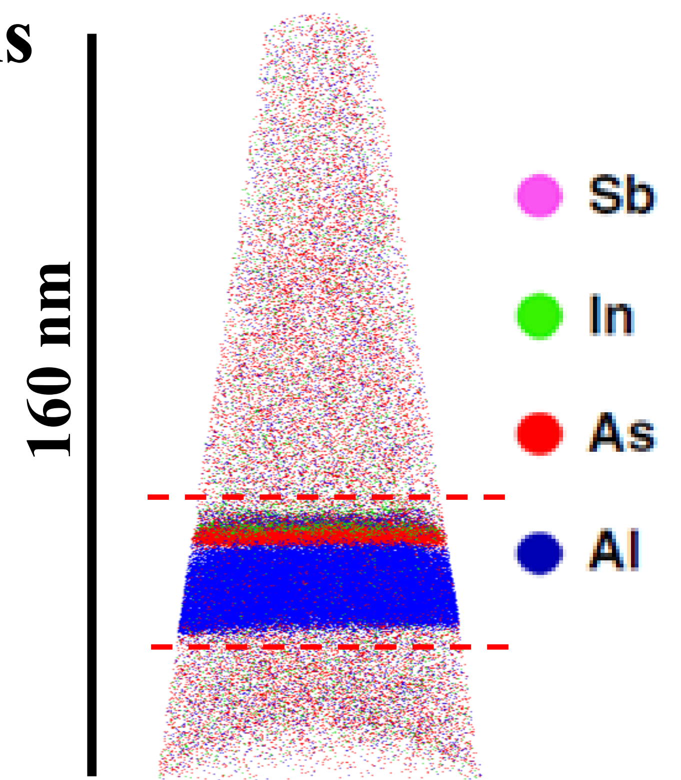
General workflow summary for atom probe analysis

Three main stages of carrying out APT:

Sample preparation: Initial material selection to final tip fabrication.

How representative is my sample?
Does my APT sample have the region of interest within ~50-100 nm of the tip apex.

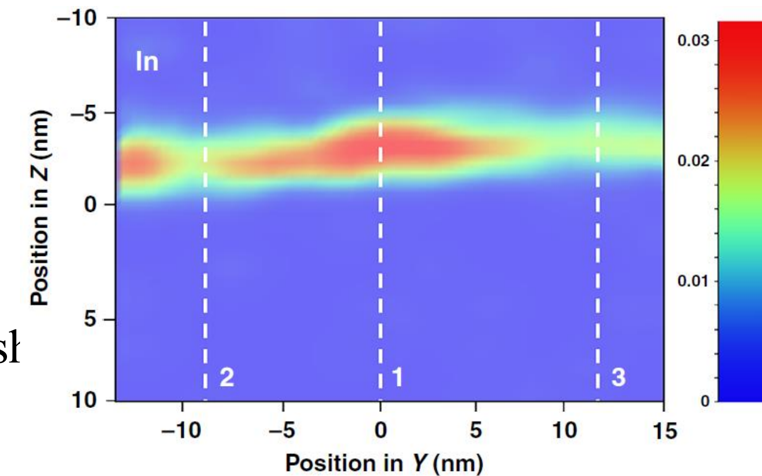




Analysis: Optimisation of analysis parameters for the data required. Obtaining suitable amounts of representative data

How does the method in which the sample is analysed affect the data?
How do I balance high quality data with sufficient amounts of data?

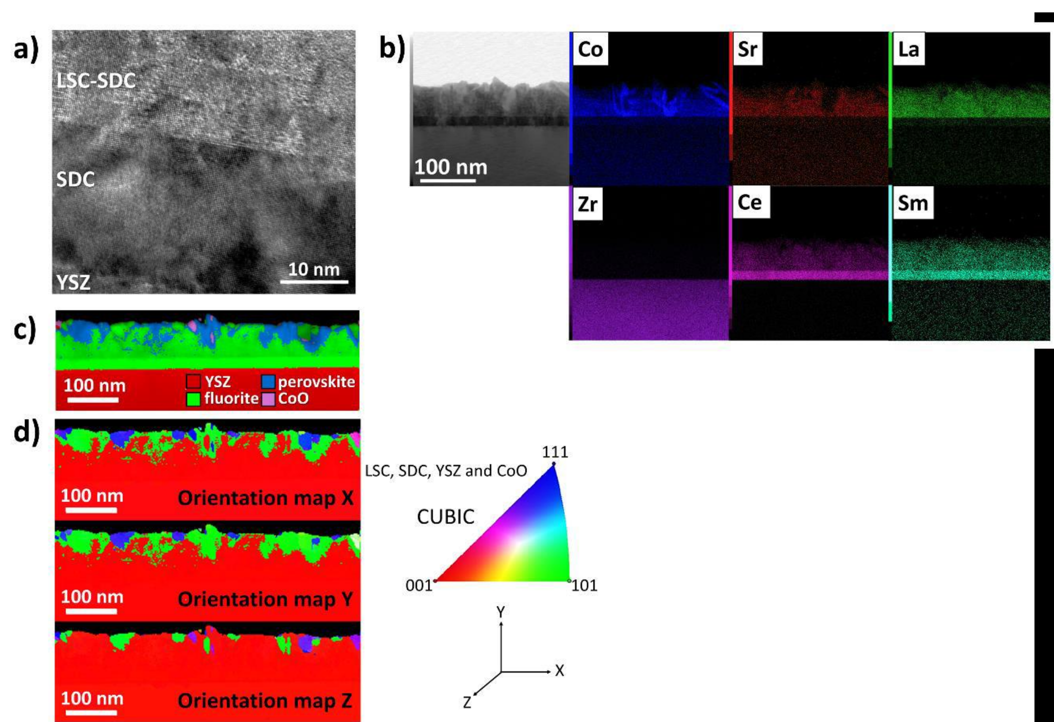
Reconstruction : Putting together 3D volume with reasonable physical parameters. Identification of ionic species in the mass spectra. Determining compositions (bulk and segregated), compositional profiles from selected interfaces, cluster searching, size and sl of features determination of errors and much more…..

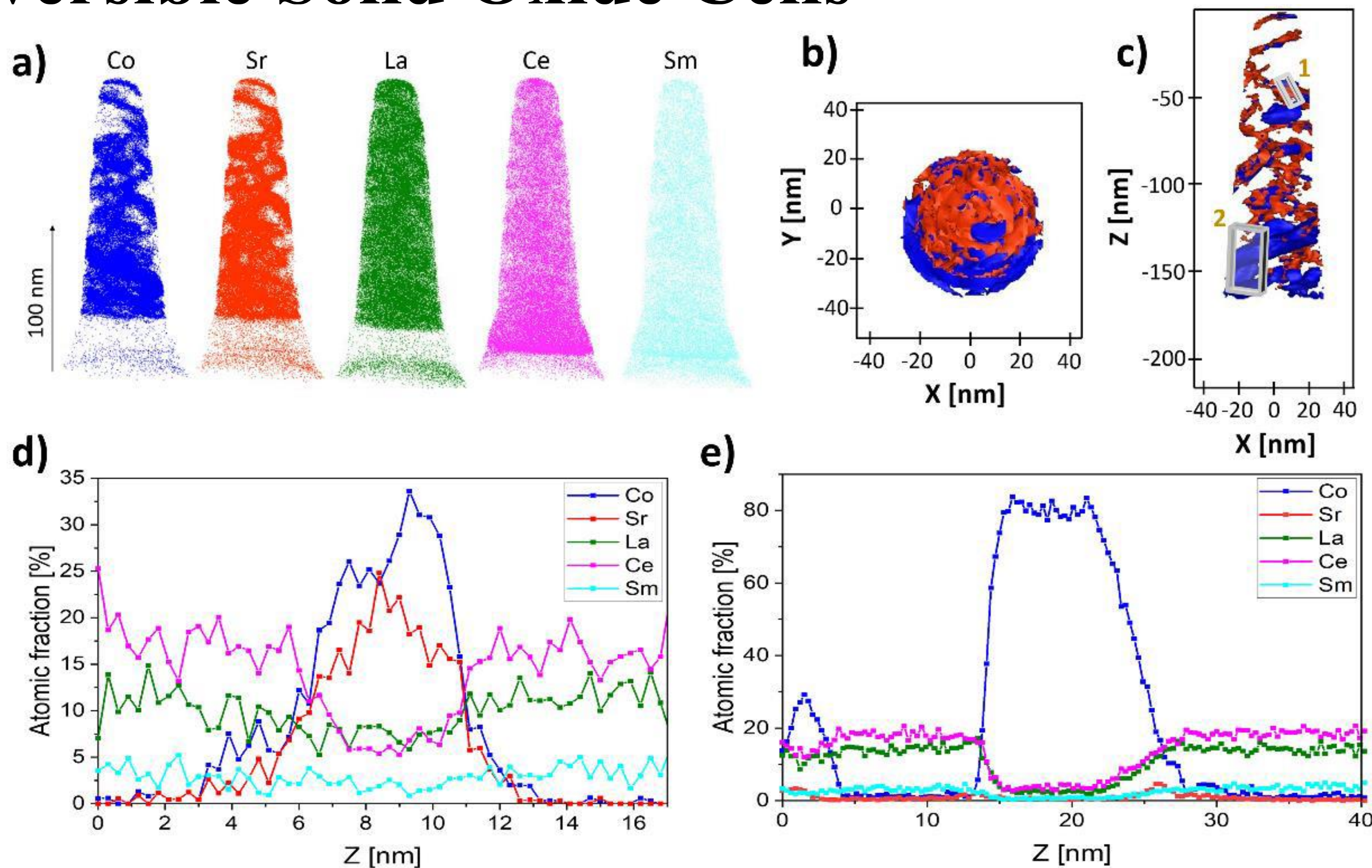


How does the method in which the data is reconstructed affect the interpretation?
Is the data spatially and compositionally representative of the original sample?

Gajjela, R.S.R., Hendriks, A.L., ***Douglas, J.O****. et al. Light Sci Appl 10***,** *125 (2021).*

A Self-Assembled Multiphasic Thin Film as an Oxygen Electrode for Enhanced Durability in Reversible Solid Oxide Cells



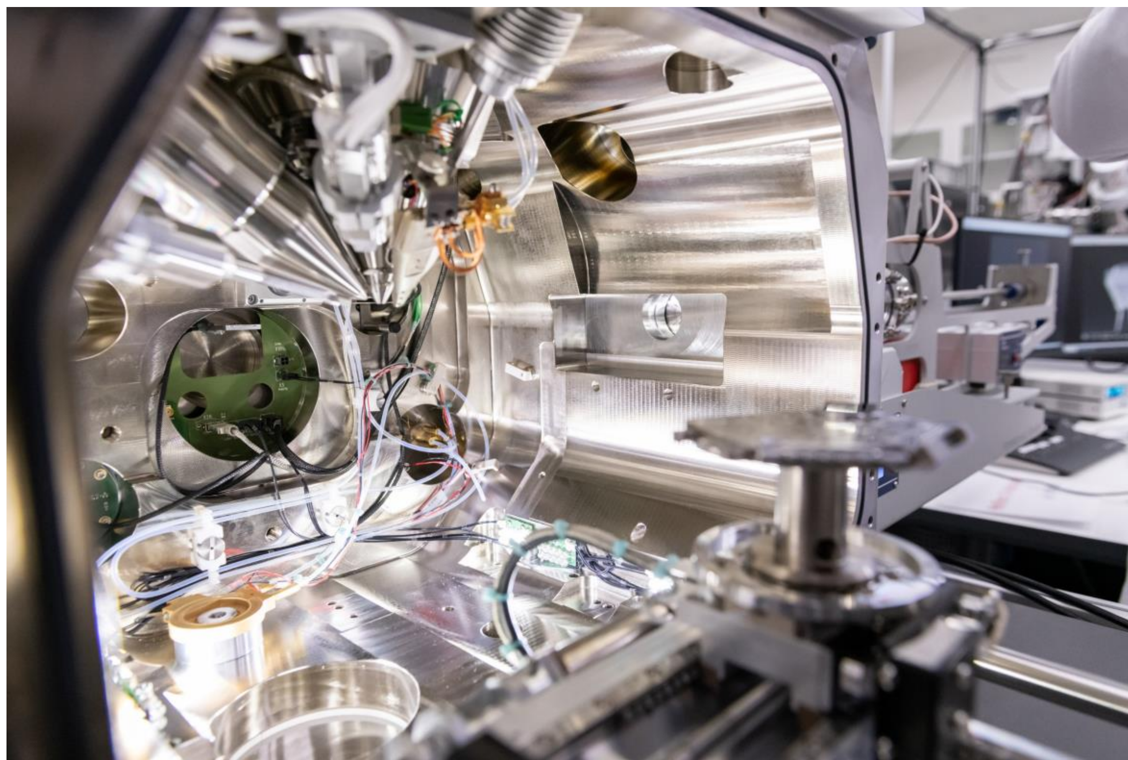


$La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC)-$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) nanocomposite.

Model films fabricated on top of single crystal YSZ substrates.

ChemRxiv. 2024; doi:10.26434/chemrxiv-2024-c29k4

Imperial Centre for Cryo Microscopy of Materials



IMPERIAL
Department of Materials

Max-Planck-Institut
für Eisenforschung GmbH

EPSRC
Engineering and Physical Sciences
Research Council

Questions before starting a proposed atom probe analysis

- What specific material system are you looking to analyse?

- What size and shape of samples have you got that from which you wish to extract out atom probe specimens and how many different materials do you wish to collect data from?

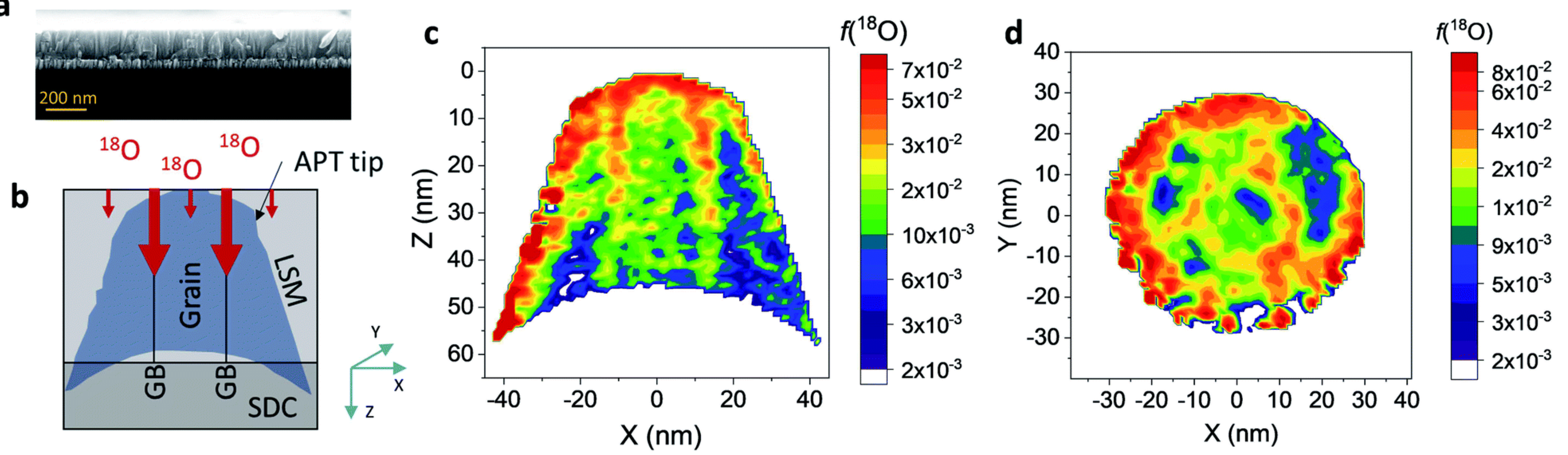
- Do your samples have any form of environmental requirements (air sensitive etc)? The entire process flow should be planned out to ensure sample viability.

- What sort of compositional variation of what elements do you expect in your features/interfaces? Atom probe has the ability to detect all elements equally (with a few caveats) but there are detection limits in the tens of ppm range and issues with certain combinations of elements.

Comparison with SIMS

Where can you do APT

Isotope labelling and tracking



^{18}O fraction is reported in logarithm

DOI: 10.1039/D1TA10538H (Communication) *J. Mater. Chem. A*, 2022, **10**, 2228-2234

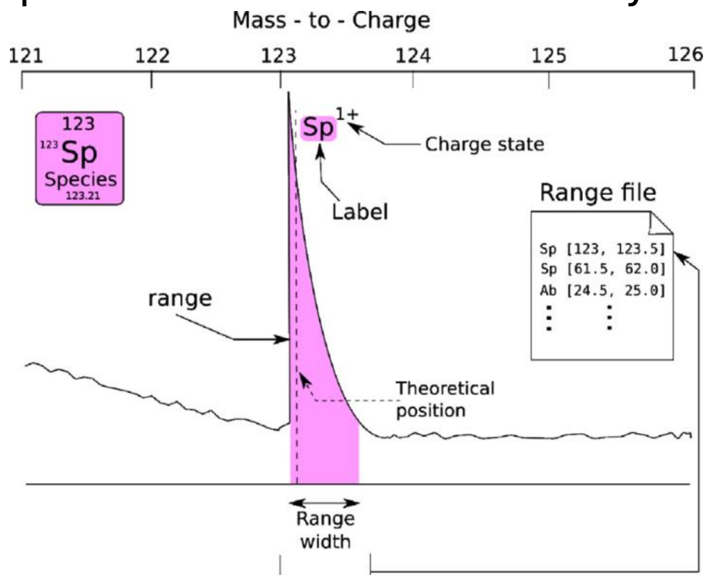
Visualizing local fast ionic conduction pathways in nanocrystalline

Francesco Chiabrera‡ [ab], Federico Baiutti‡ *[ac], David Diercks [d], Andrea Cavallaro [e], Ainara Aguadero [eg], Alex Mora

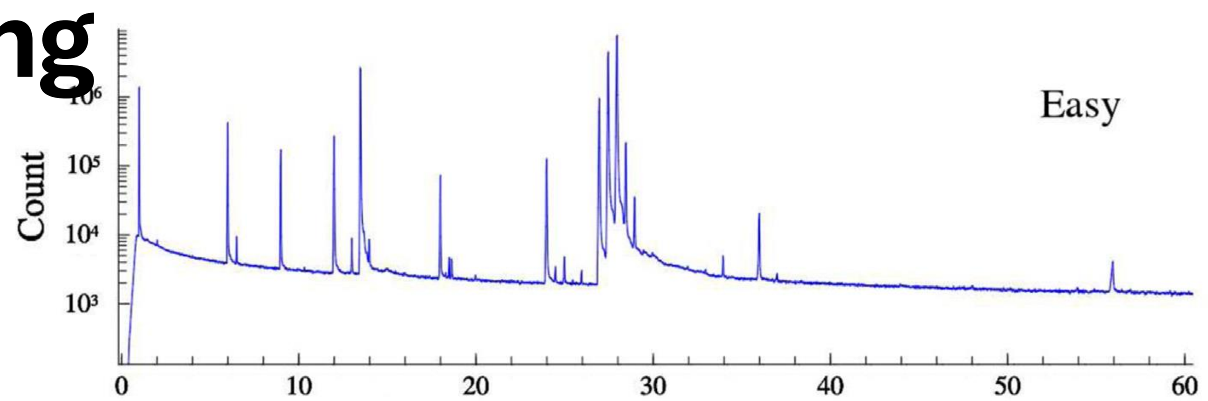
Isotope labelling and trackingc

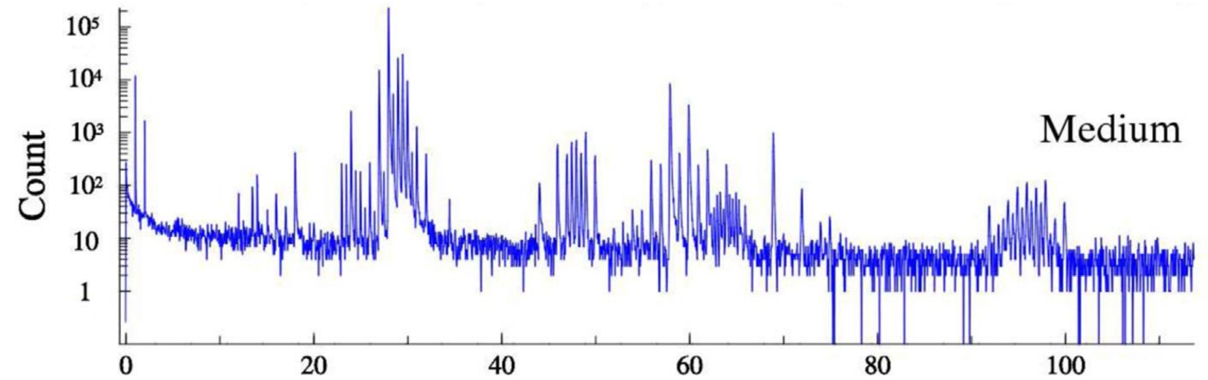
Consistency in Ranging

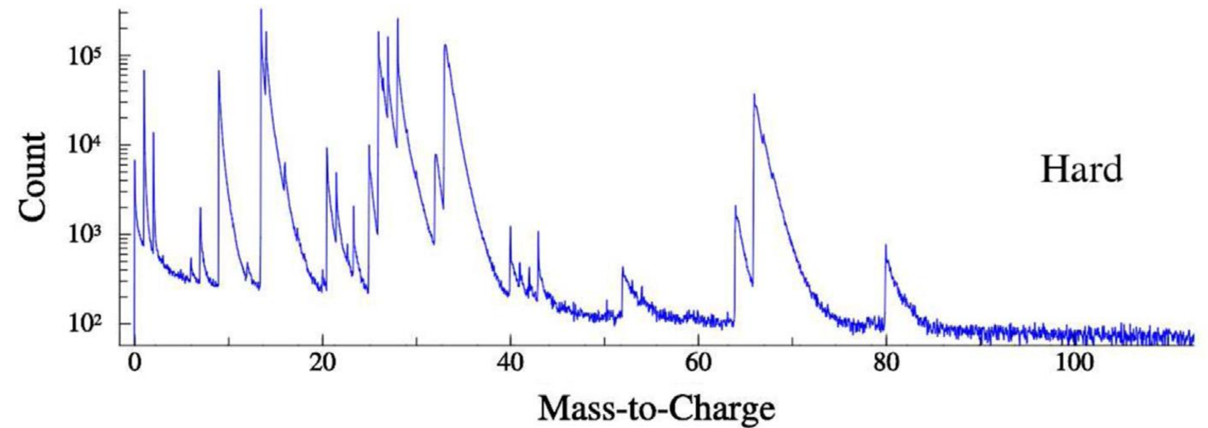
- All APT compositional information is based upon accurate and reproducible ranging of mass spectra peaks.
- Ranging of species is mostly still human driven although automatic systems do exist.
- No regulated way to range, multiple techniques have been used but each material system may require a different approach.
- Consistency is key if comparing similar datasets.
- Large variations in data interpretation between users have been observed, especially with complex mass spectra and lack of consistency in analytical approach.



- Complex mass spectra typically contain multiple overlapping species within difficult to define peak shapes.



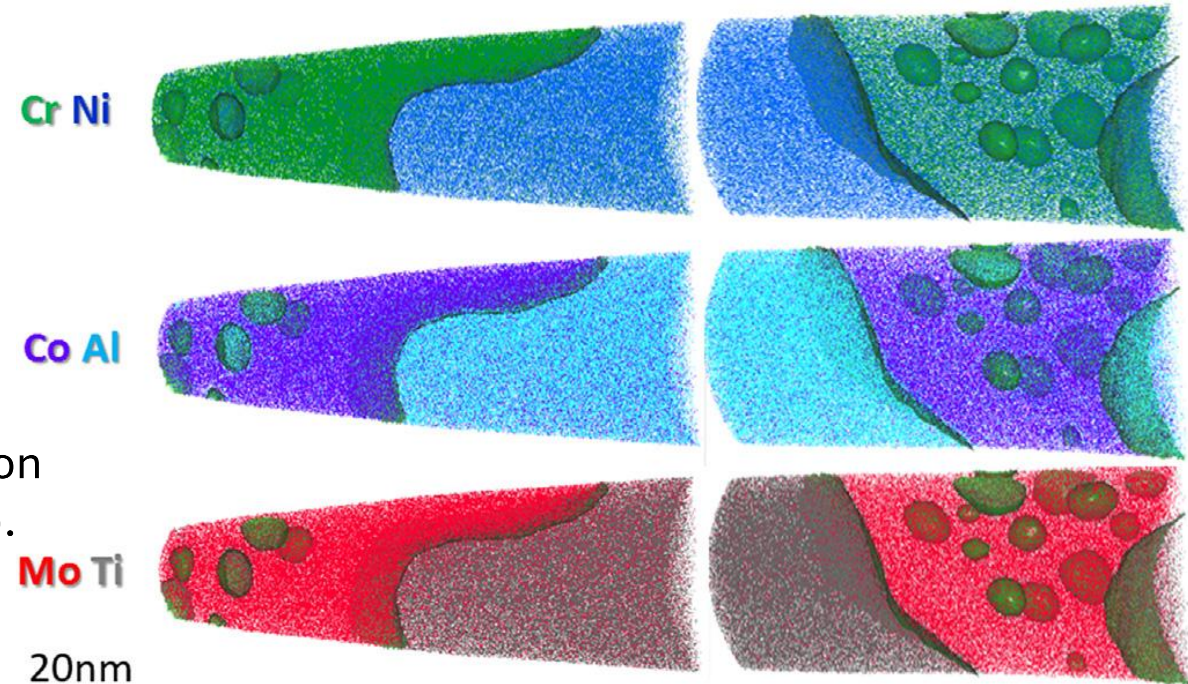


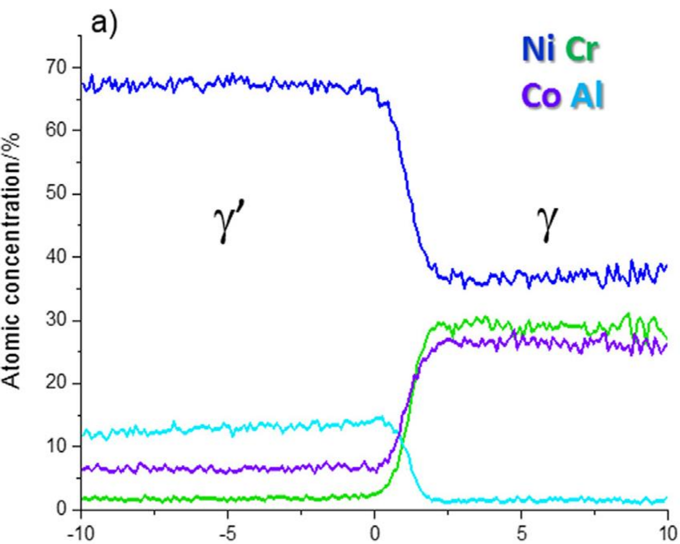


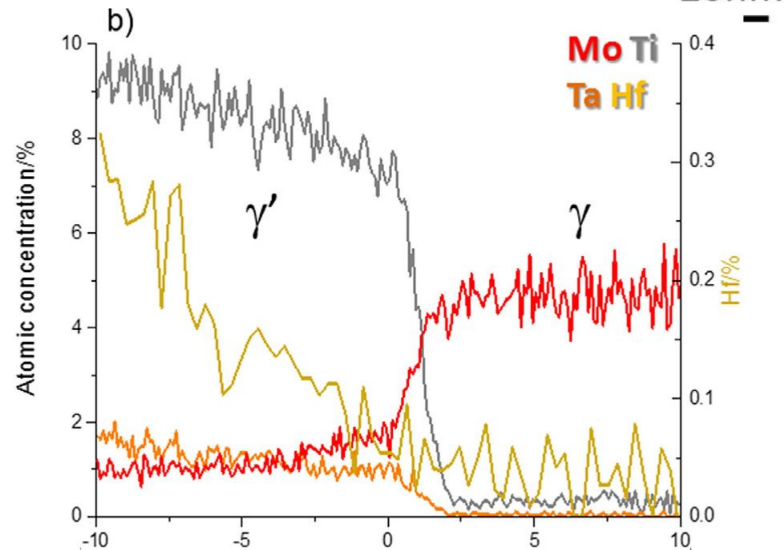
Haley et al, Ultramicroscopy, Volume 159, Part 2, December 2015, Pages 338-345

Iso-surfaces

- Deliniating a surface between two regions is generally carried out using variation in composition or density.
- Specific species of interest are tallied in voxels, voxels are then joined together.
- Measured interfacial width can vary as a function of orientation within tip (due to variation in spatial resolution with direction).





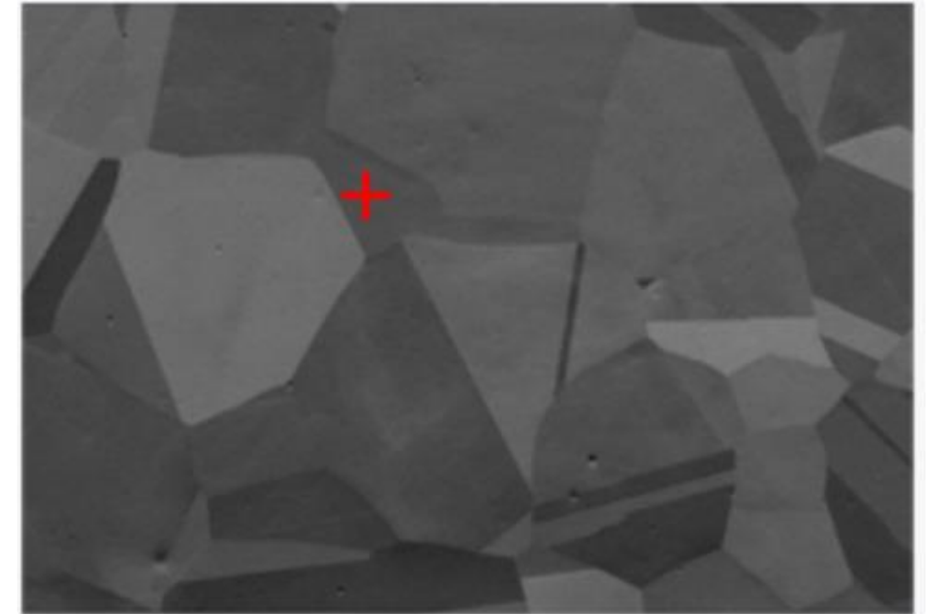


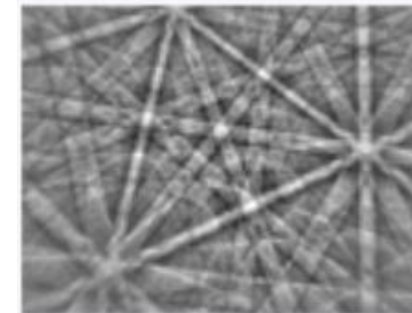
- From these surfaces (which can be summed when small), proximity histograms can be produced.
- Compositional profiles from curved interfaces can show presence of diffusion profiles of specific species.

Bagot et al Acta Materialia 125 (2017) 156-165

Electron Backscatter Diffraction (EBSD)

SEM chamber wall
vacuum
ambient pressure
SEM incident beam
inclined sample
~60°–70°
tube
70°
phosphor screen
low light CCD camera





orientation: 108; 36; 89

- Method of determining crystal structure from surface regions of highly polished specimens.

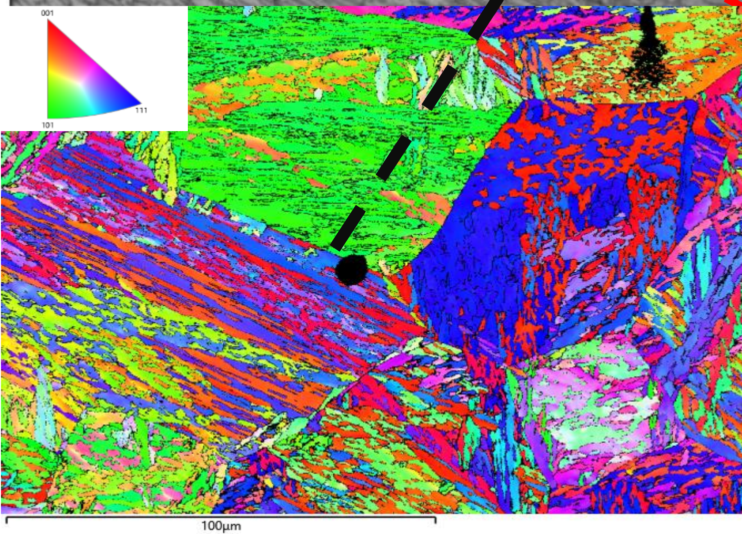
Strains, planes and EBSD in materials science, Materials Today, Volume 15, Issue 9, September 2012, Pages 366-376

Liftout from prior austinite grain boundary in bainitic steel as identified by EBSD

- Electron beam deposition of Pt over grain boundary to provide initial protection.
    - Linear section of grain boundary delineated by thin Pt line.
- Standard Pt protective layer then deposited.

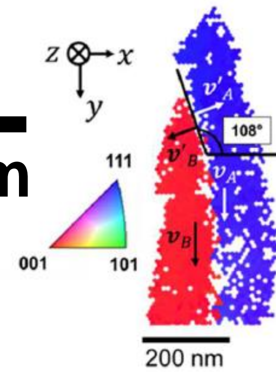
Band Contrast 2

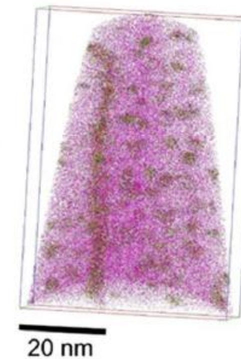
Map Data 2

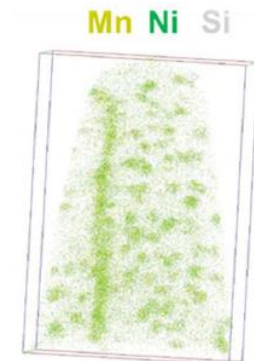


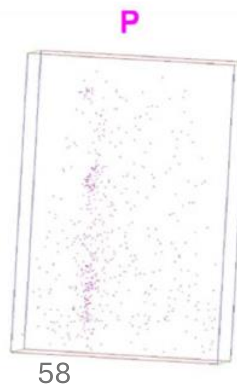
20µm

B.M. Jenkins et al . Applied Surface Science, Volume 528, 30 October 2020, 147011.

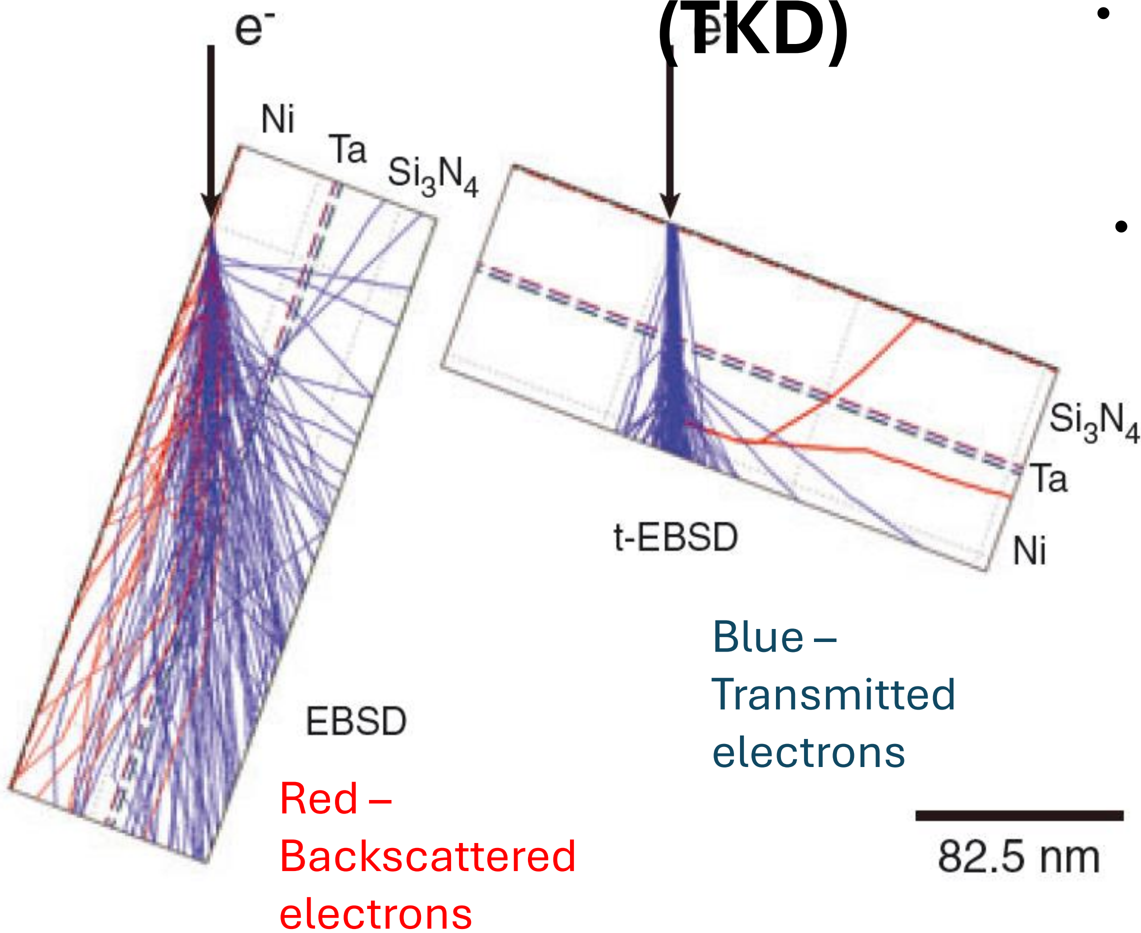






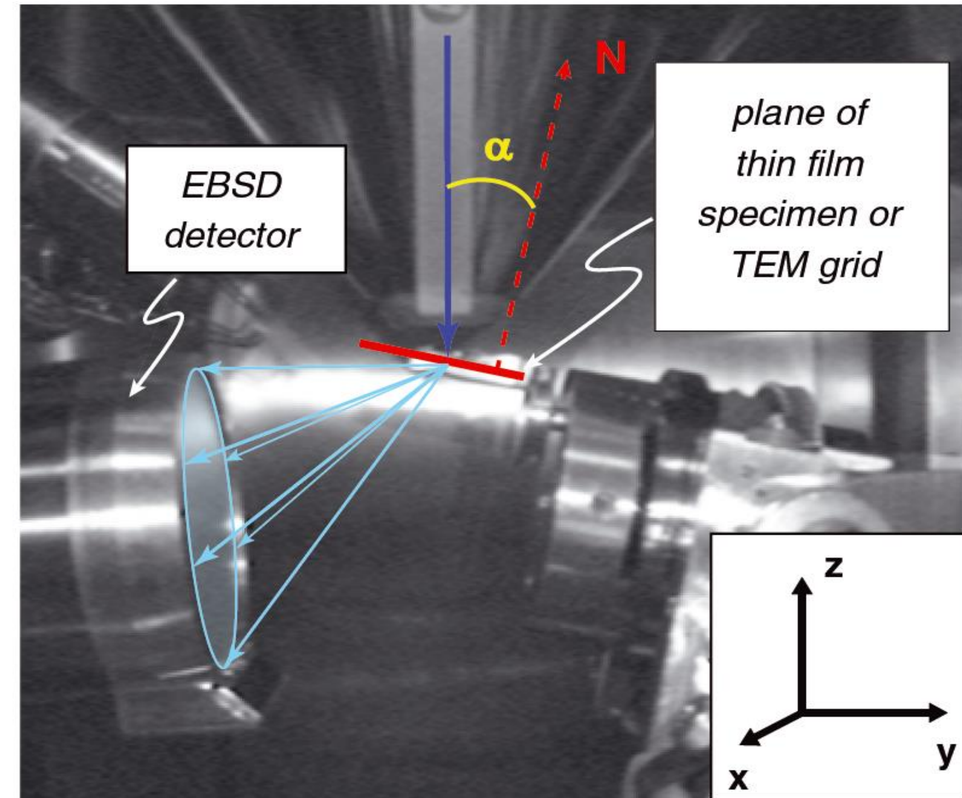


Transmission Kikuchi Diffraction (TKD)

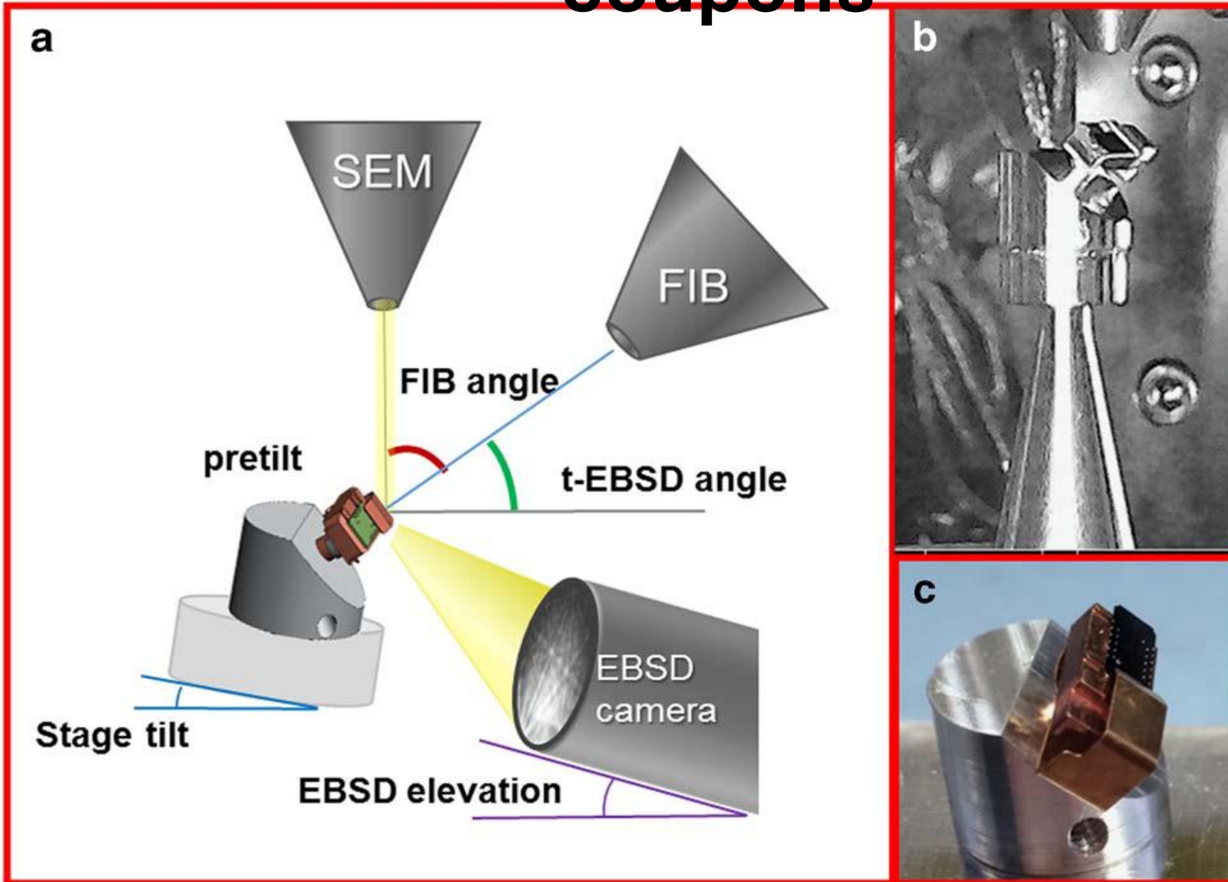


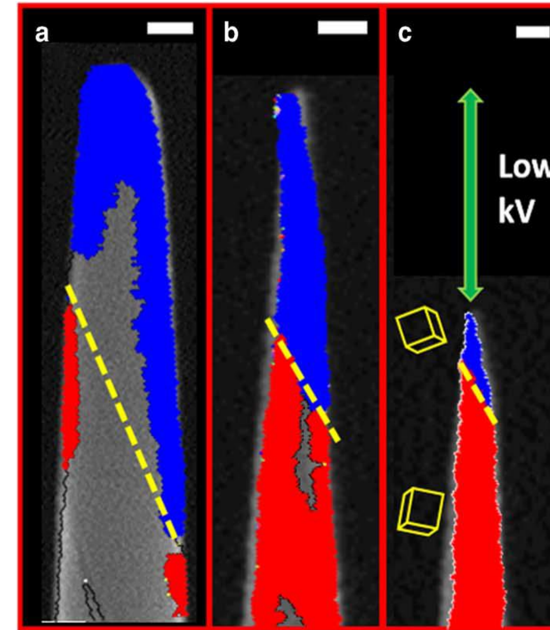
Transmission EBSD from 10 nm domains in a scanning electron microscope, Journal of Microscopy, Vol. 245, Pt 3 2012, pp. 245–251

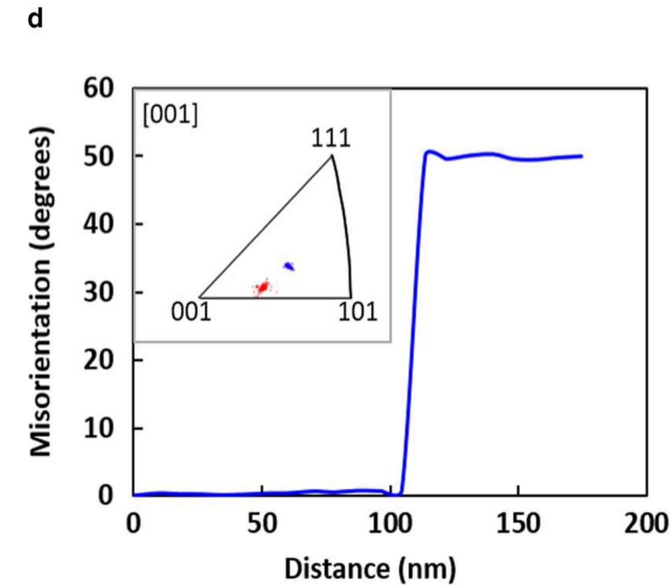
- EBSD is generally carried out on polished surfaces of bulk samples, with backscattered electrons from **the surface** tens of nm forming the diffraction patterns.
- TKD is carried out on thin (tens of nm – a few μm) samples with transmitted electrons from the **exit side** forming the diffraction patterns.



TKD on liftout samples on silicon coupons



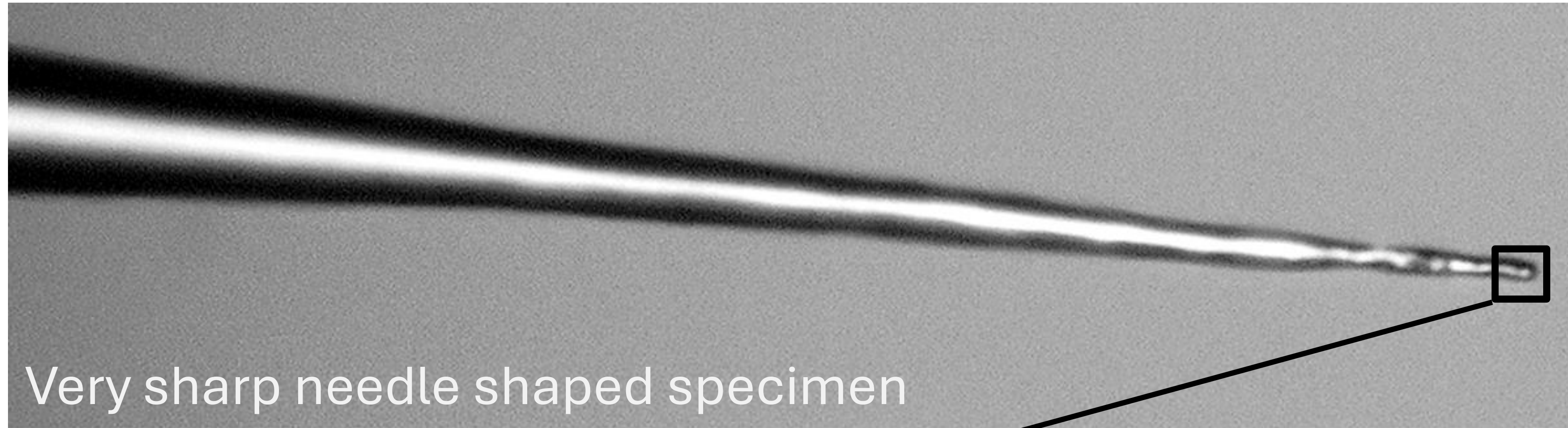


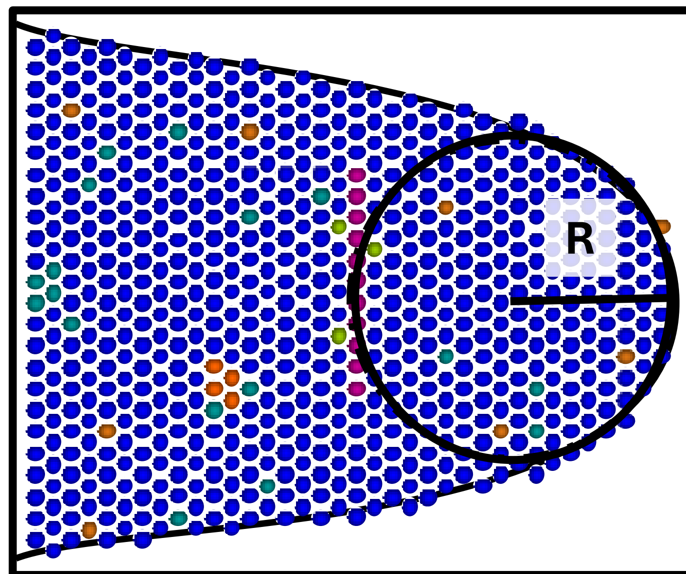


Implementing Transmission Electron Backscatter Diffraction for Atom Probe Tomography, Microsc. Microanal. 22, 583–588, 2016

- Through use of a 45° pre-tilt holder, TKD is possible on samples mounted on outer rows of silicon micropost coupons.
- Mill using 30 kV to get grain boundary within a few hundred nm of surface and then low kV to polish to within suitable distance (scale bar = 200 nm).
- Misorientation angle can be readily calculated and grain boundary placed within 50 nm of apex.

Field ionization -applying electric fields to sharp tips



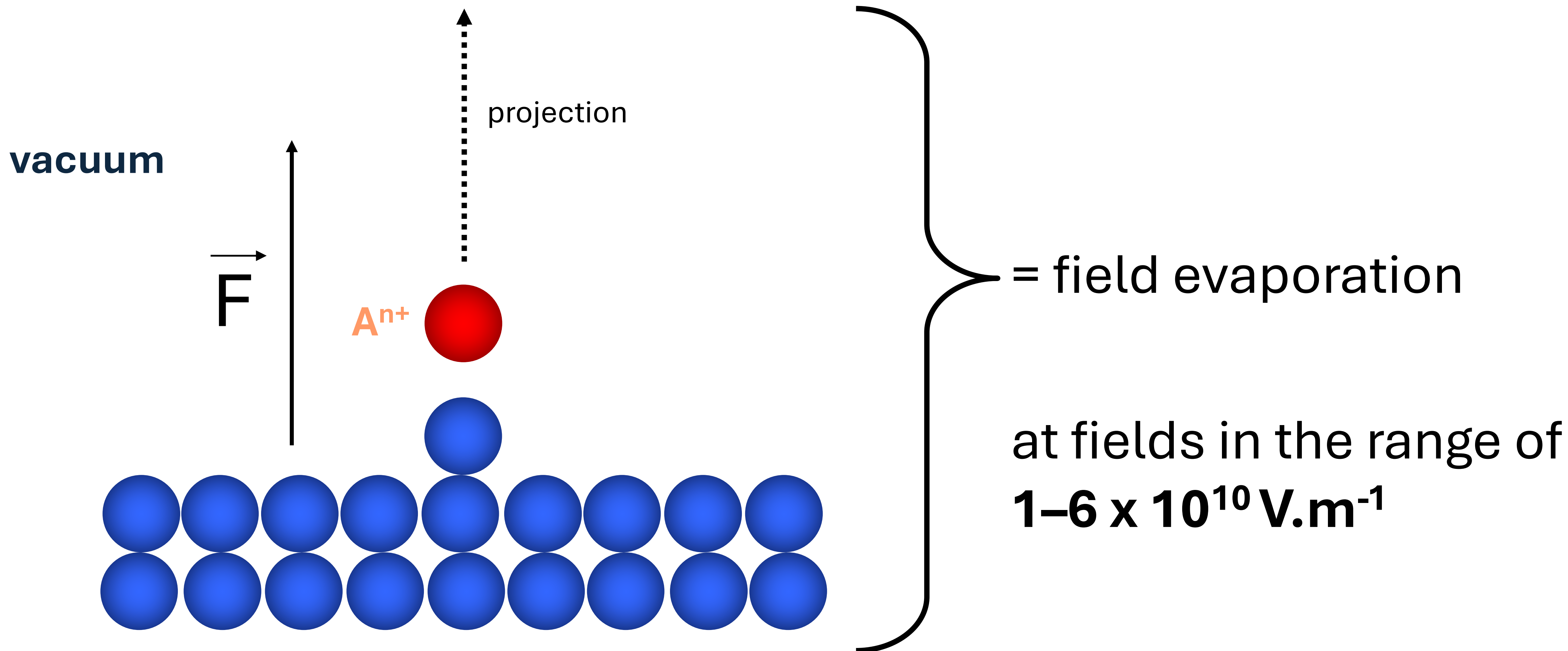


R<100 nm

Application of a DC Voltage (V) produces an intense electric field (F) since:

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

Intense electric field on surface atoms

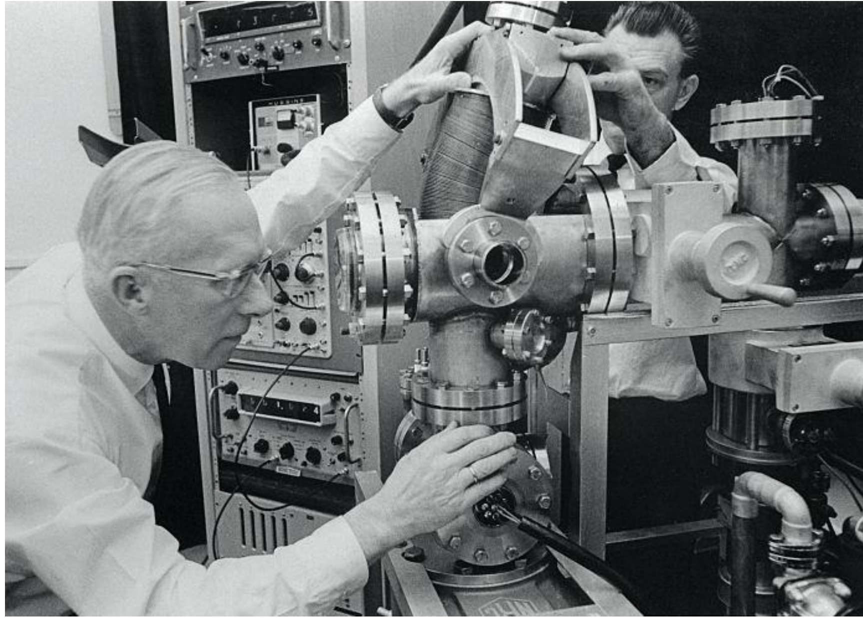


= field evaporation

at fields in the range of

1–6 x 10^{10} V.m^{-1}

Ion emission – Field ion microscopy



- Nanoscale needle-shaped specimen at low temp (10-150 K)

- Insert low pressure of rare gas (He,Ne,Ar)

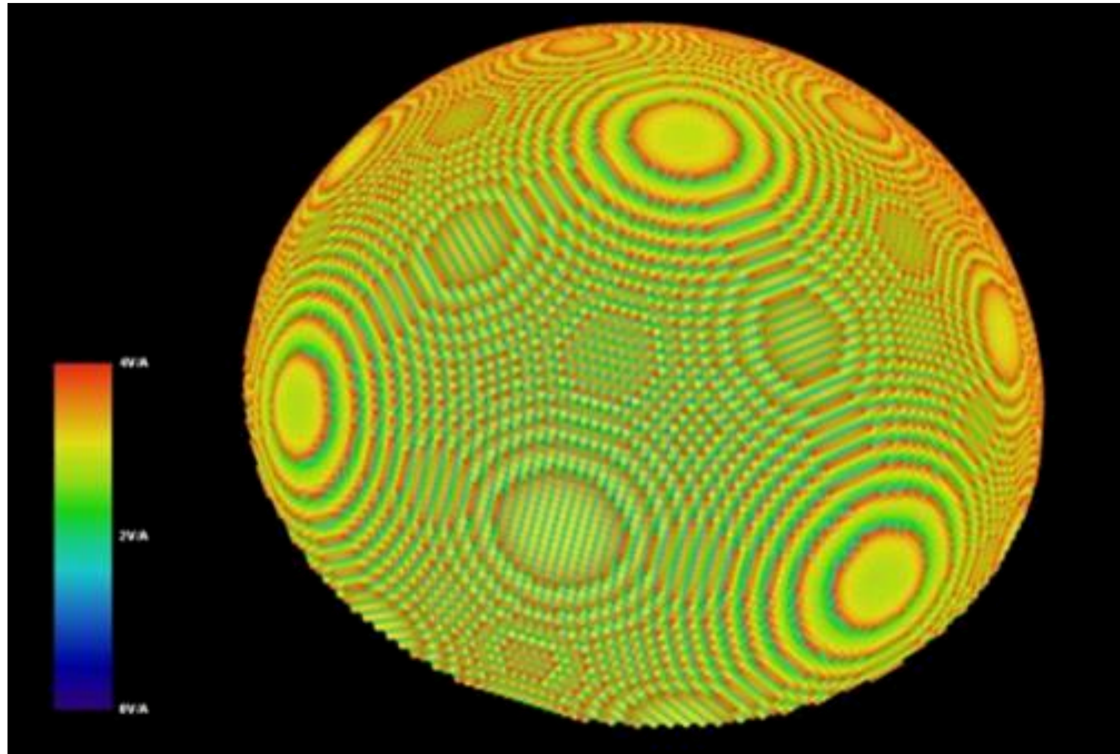
- Add an image intensifier (Multi Channel Plate/phosphor screen)

- Apply a positive voltage to the tip

W, 60 K,
V=0 to 10 kV

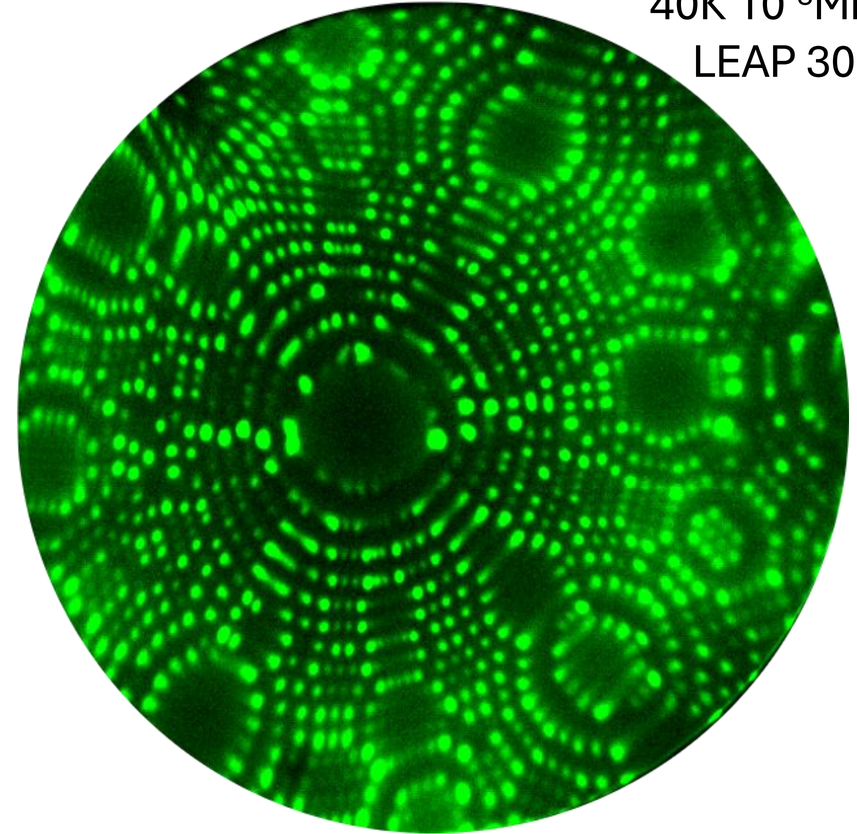
Courtesy of F. Vurpillot and co-workers

Microscopic electric field variations



- Imposing a needle shaped (hemispherical apex) geometry on a crystalline material leads to a terraced surface structure.
- Concentric rings linked to crystallographic pole orientations are visible, with highest field experienced by atoms at kink sites and edge sites.

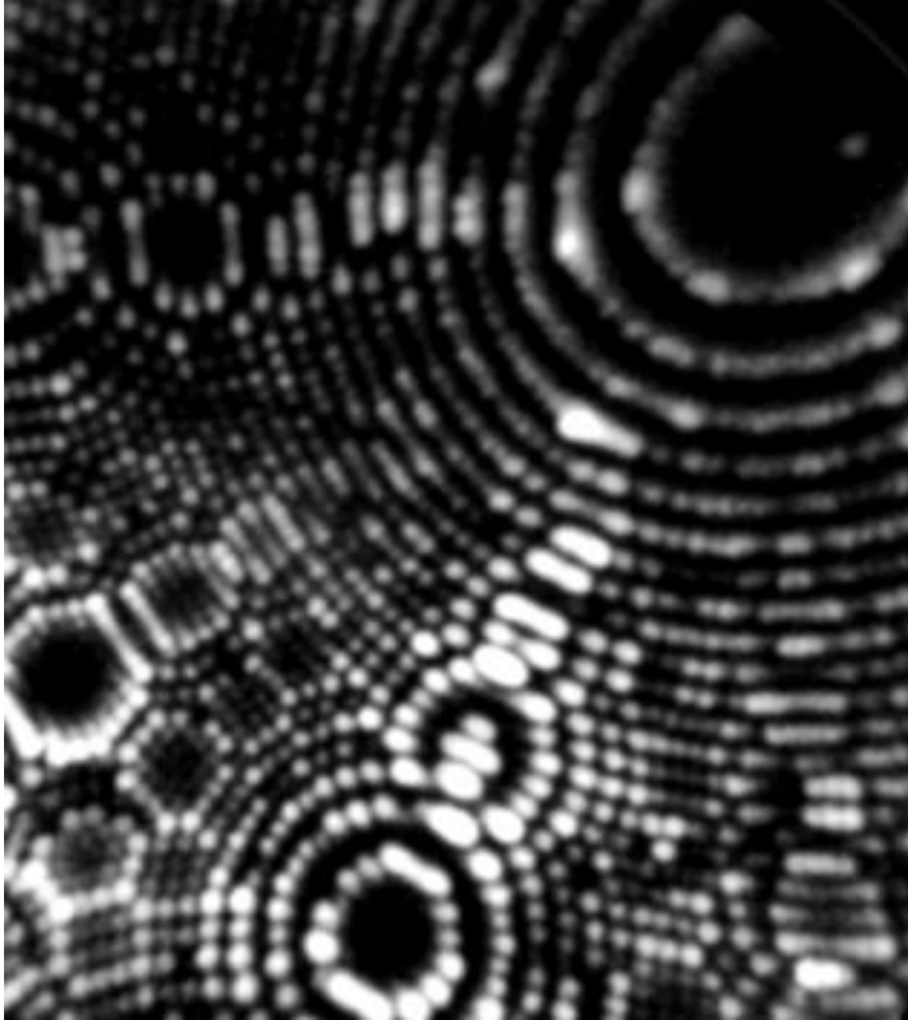
Tungsten, 8 kV
40K 10^{-5}Mbar He
LEAP 3000X Si



- Variation in surface field linked to the local topography can be observed through increased numbers of gas atoms desorbing from them via Field Ion Micrographs.

Courtesy of F. Vurpillot and co-workers

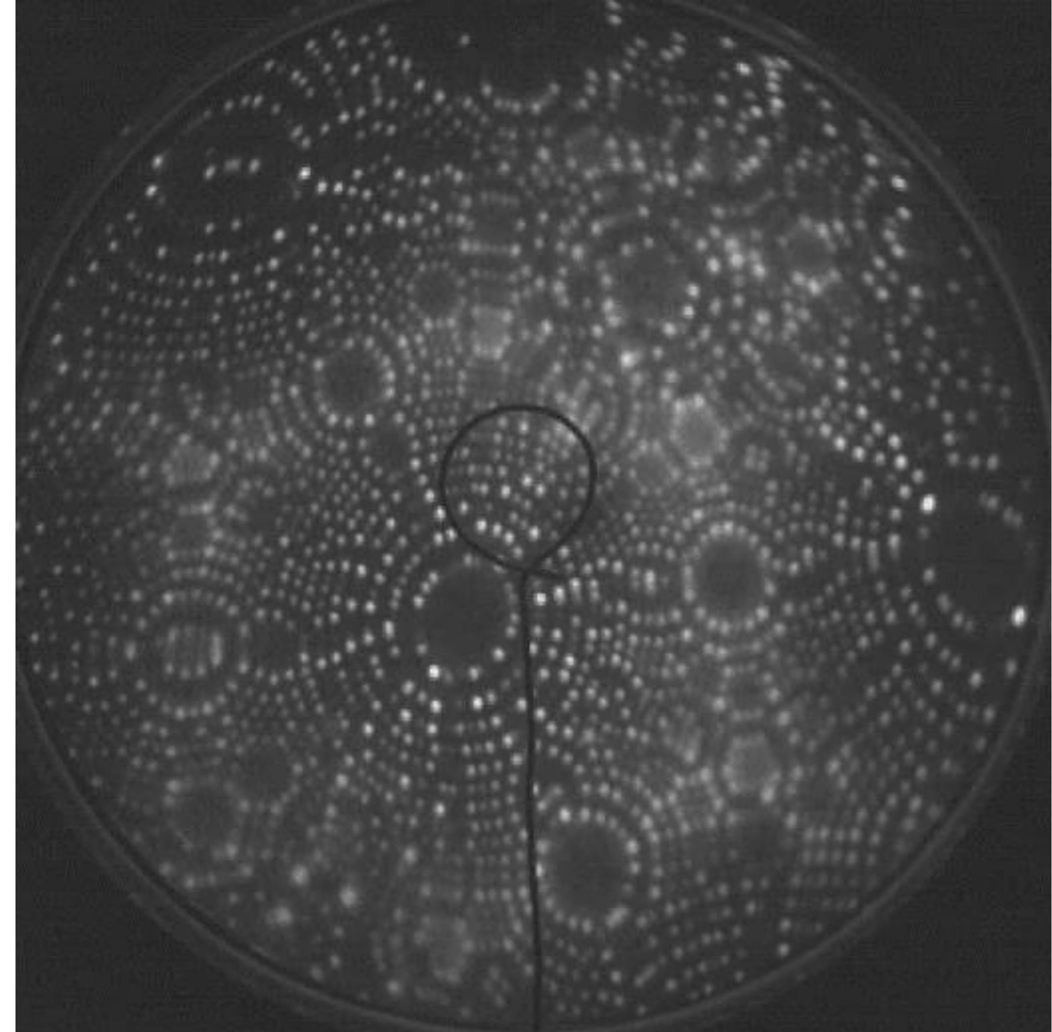
Increase standing voltage or pulse voltage



DC mode

Gold, 10 kV
20K 10^{-5}Mbar Ne

Evaporation rate ~ 10^5 at/s



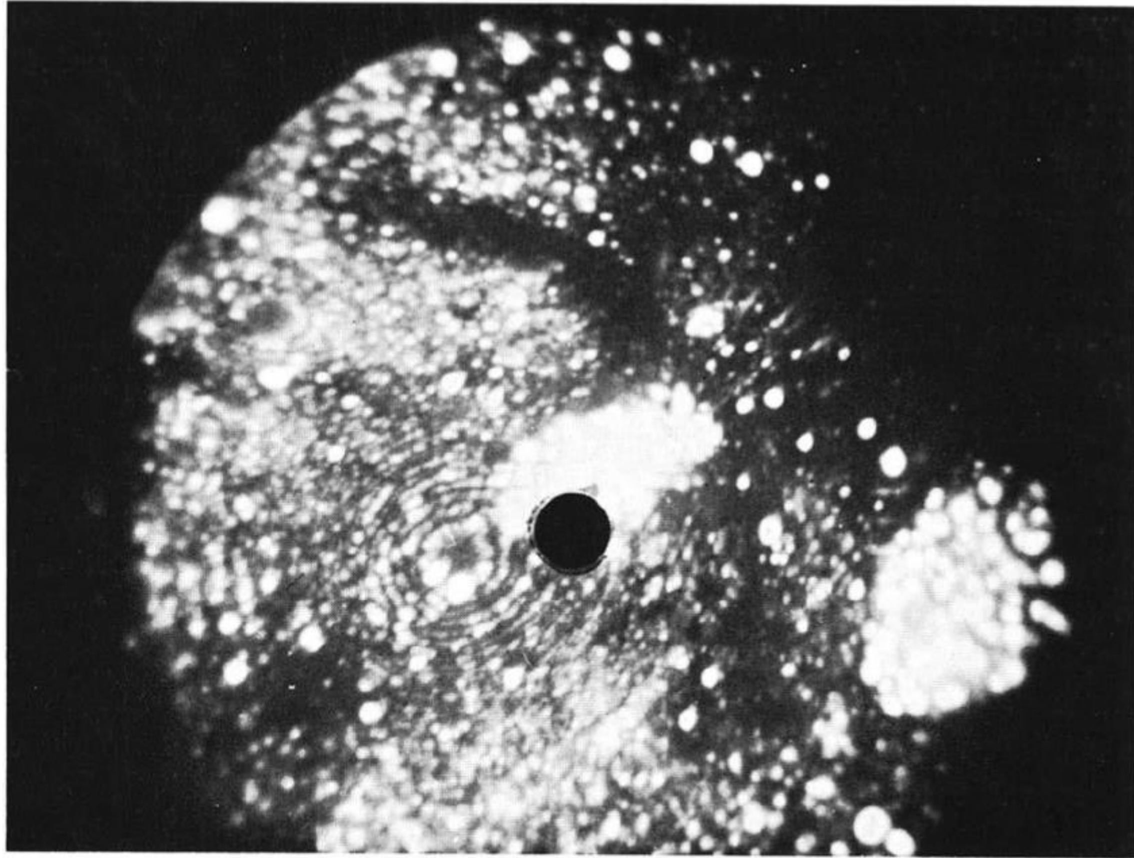
Pulsed mode
tungsten, 8 kV
40K 10^{-5}Mbar He

Field ion Microscopy and Atom Probe

Pt surface imaged using field ion microscopy for catalysis research

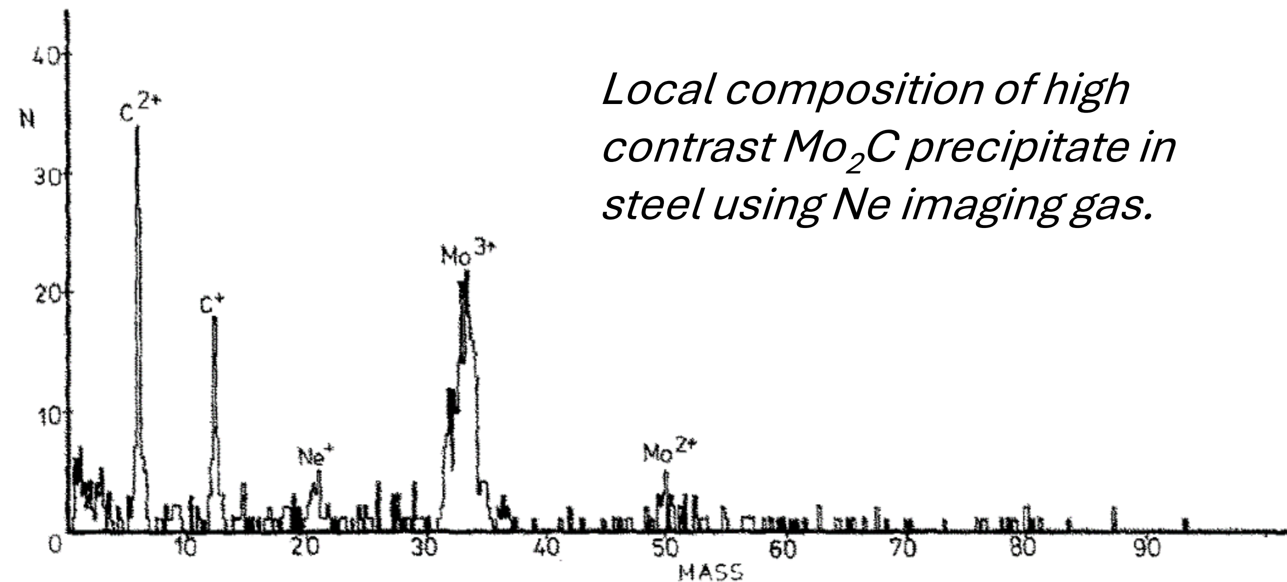
- Professor Erwin Muller pioneered the Field Emission Microscope (later Field Ion Microscope) in the 1950s.
- Through preferential emission of adsorbed gas atoms onto protruding atoms on crystal terraces, allowed first imaging of atoms and still used today for high resolution surface analysis.
- Limited elemental analysis possible through contrast variation. How to improve this?

Field Ion Microscopy and Atom Probe



Turner *et al Surface Science*, vol. 35, pp. 336–344, 1973.

- Early atom probe used a FIM image to select a region of a few nm (black 'pinhole' in FIM image).
- The imaging gas was then removed, sample rotated towards a time of flight detector and high voltage pulsing applied.
- This allowed a 1D concentration profile measured from time of flight mass spectrometry from the selected region.
- Selective analysis of nanoscale features was now possible.

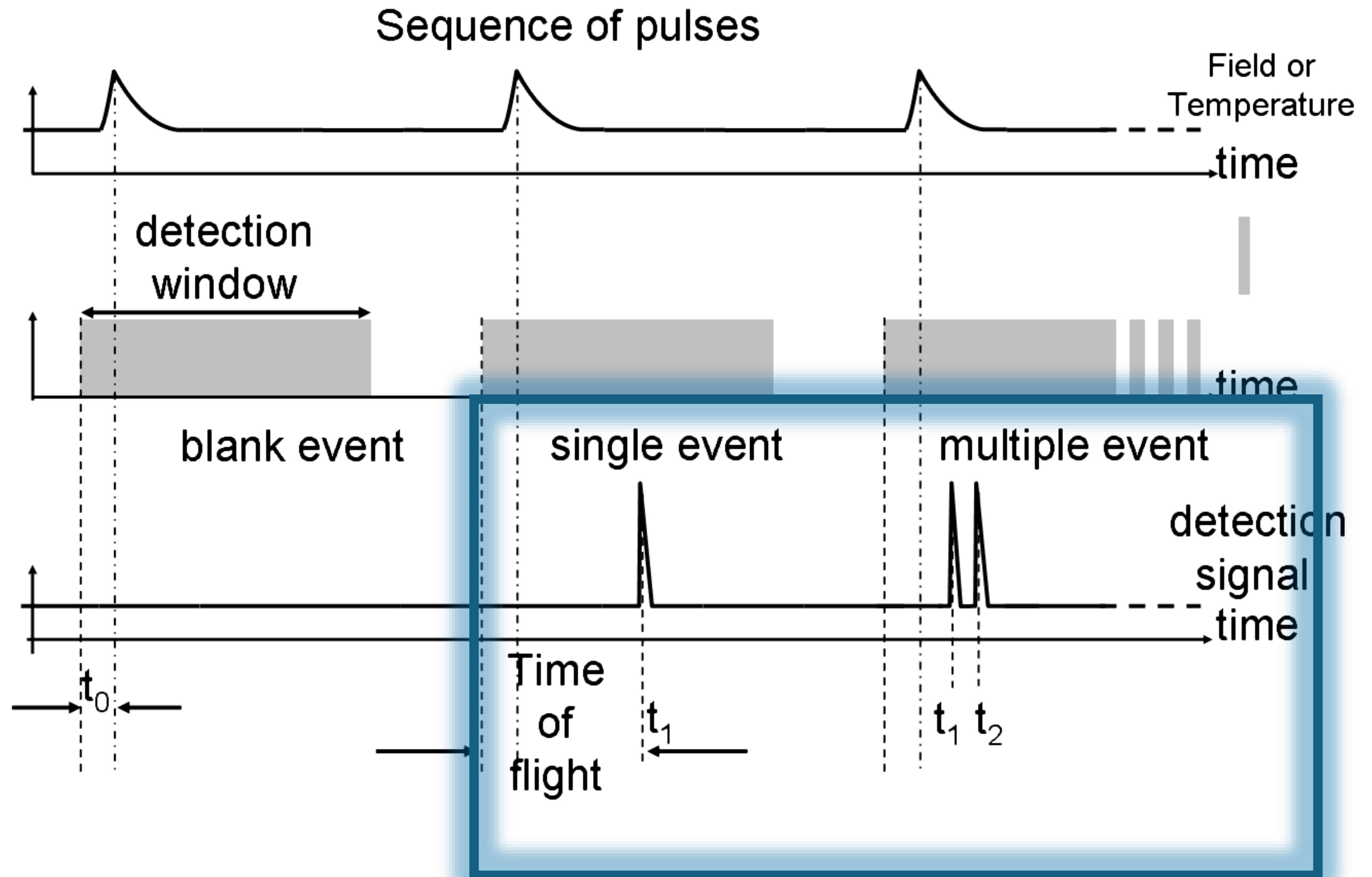


Local composition of high contrast Mo_2C precipitate in steel using Ne imaging gas.

Modern instruments have much increased fields of

Time of flight mass spectrometry - Sequence of detection

- Any ions within the detection window of a pulse are linked to that pulse.
- This gives us the "start" for our time of flight calculations.
- Not all ions emitted at the peak of the pulse, giving spread in times of flight.
- Multiple ions can arrive in the same pulse.



Field vs temperature dependence

electric field

high-voltage / field pulsing

F_{DC}

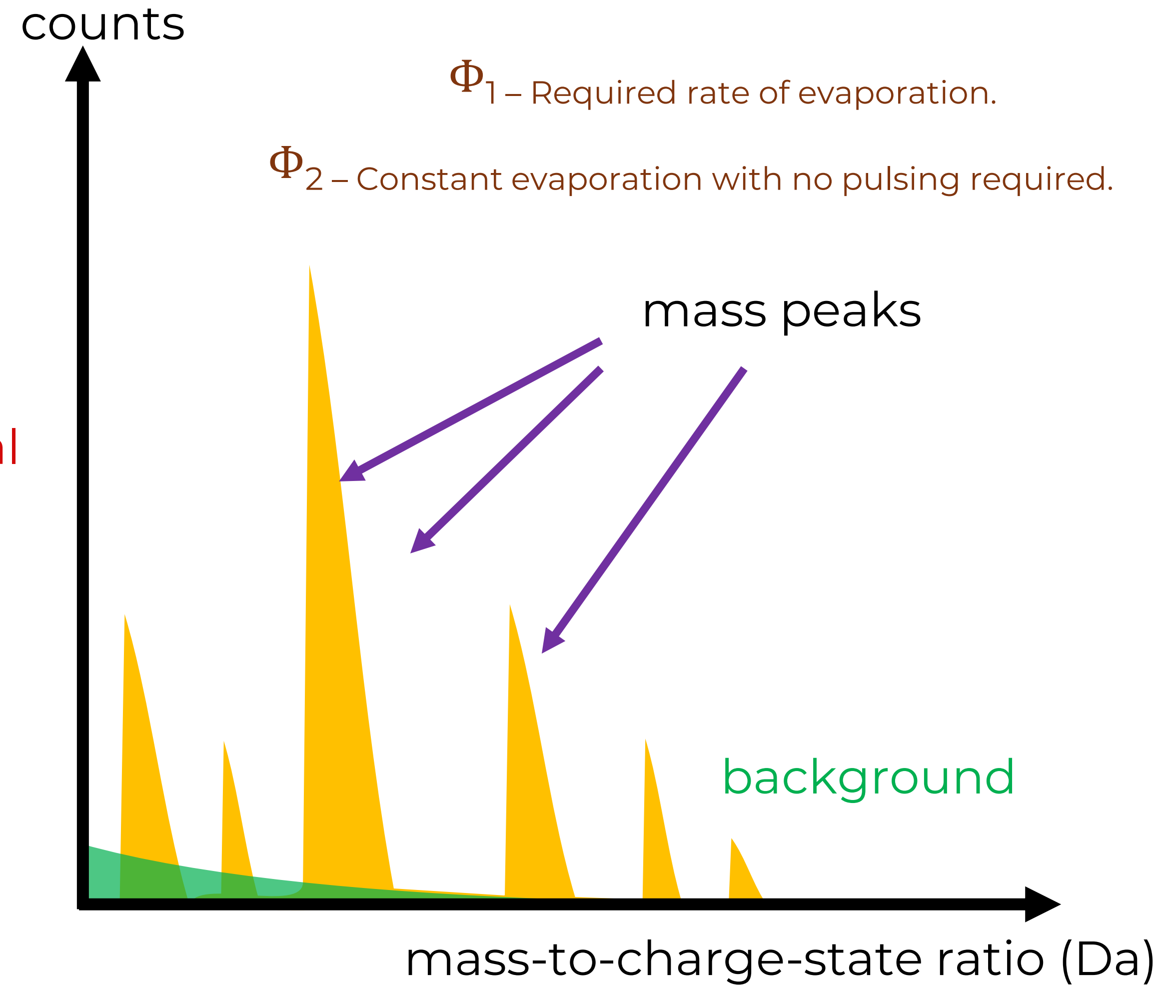
laser / thermal pulsing

$\phi_2 > \phi_1$

ϕ_1

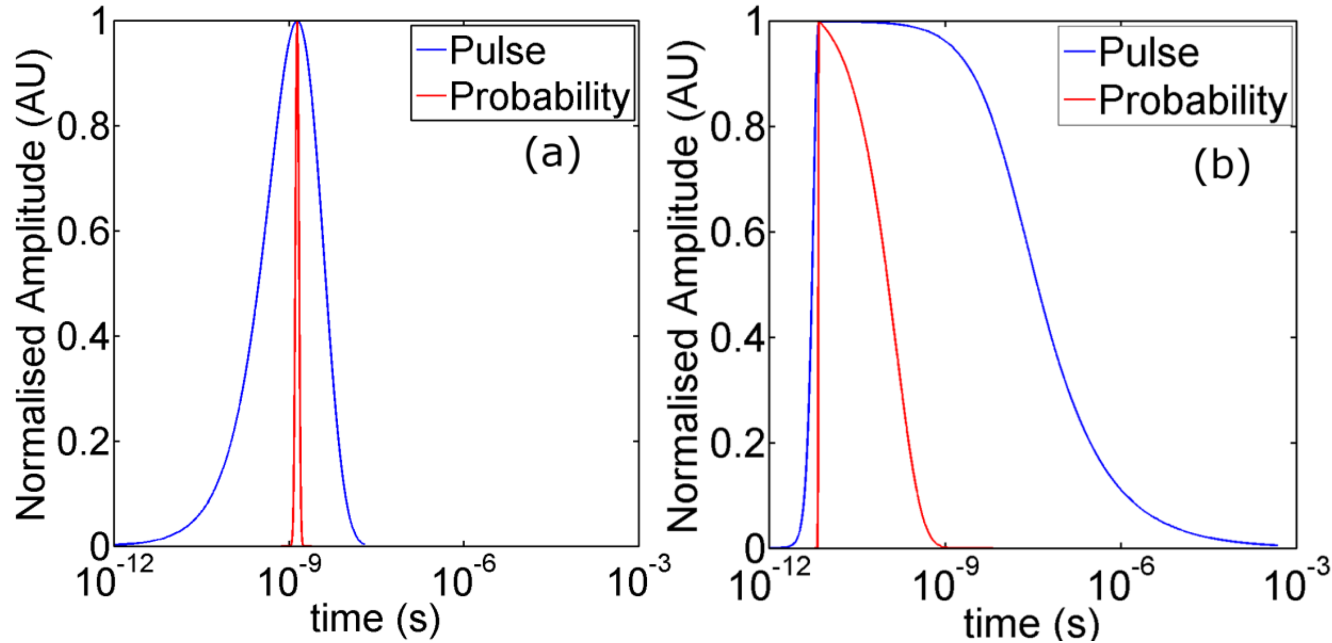
temperature

T_{base}

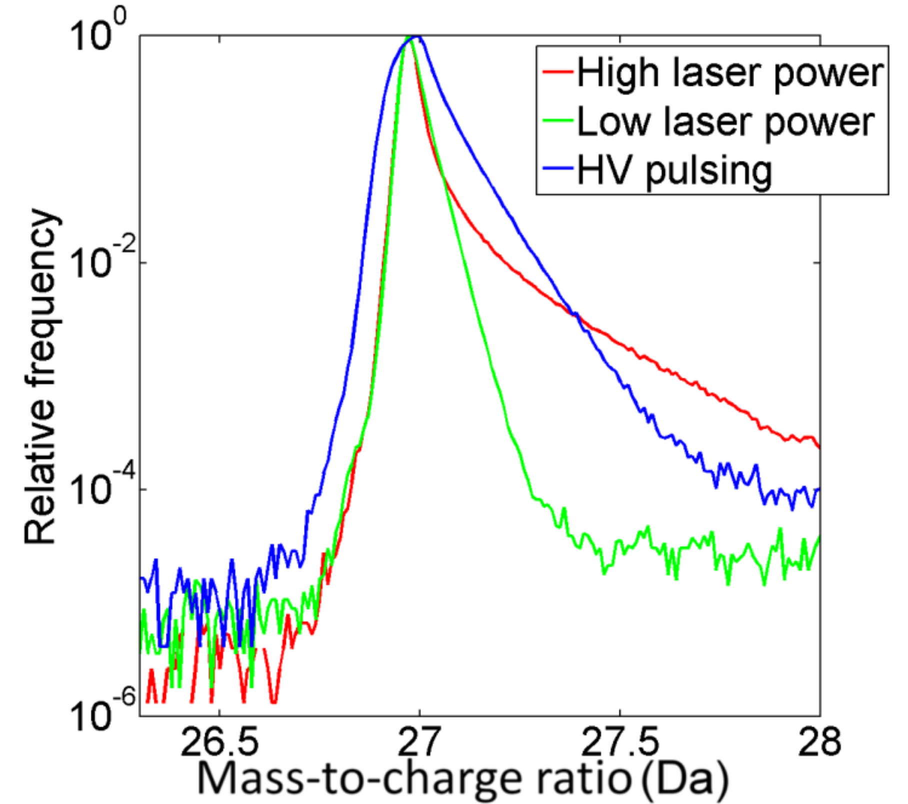


- Typical applied voltages are between 2kV and 10 kV.
- Typical pulse fractions of 15% to 25%.

Spread in time-of-flight and mass resolution



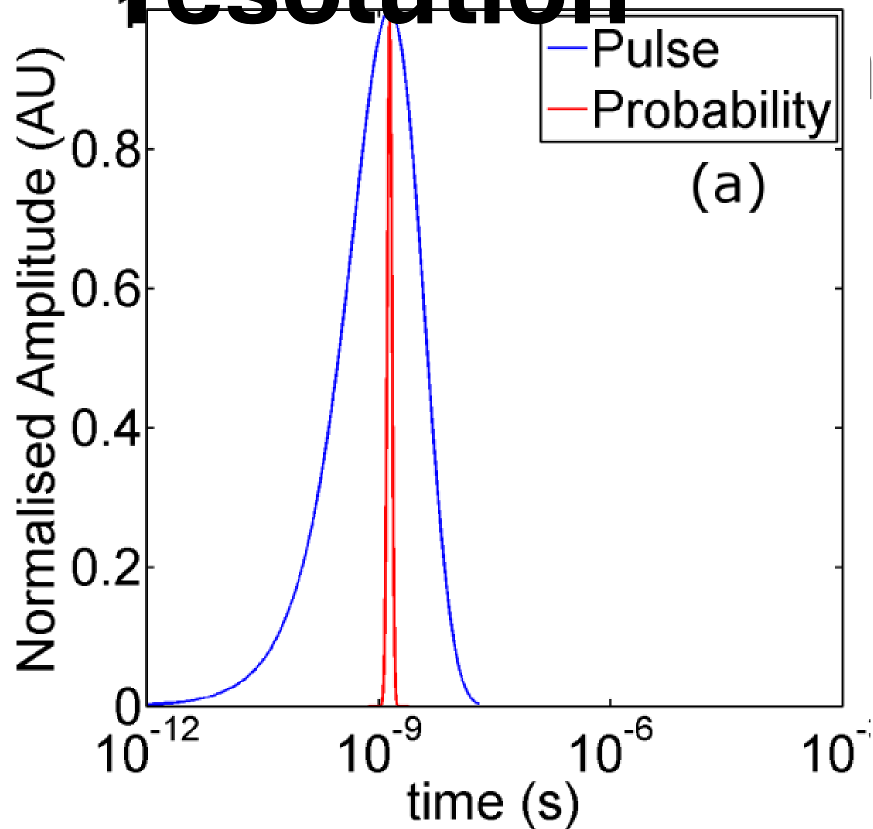
$$P_{evap} \propto \exp\left(-\frac{Q_n(F)}{k_B T_0}\right)$$

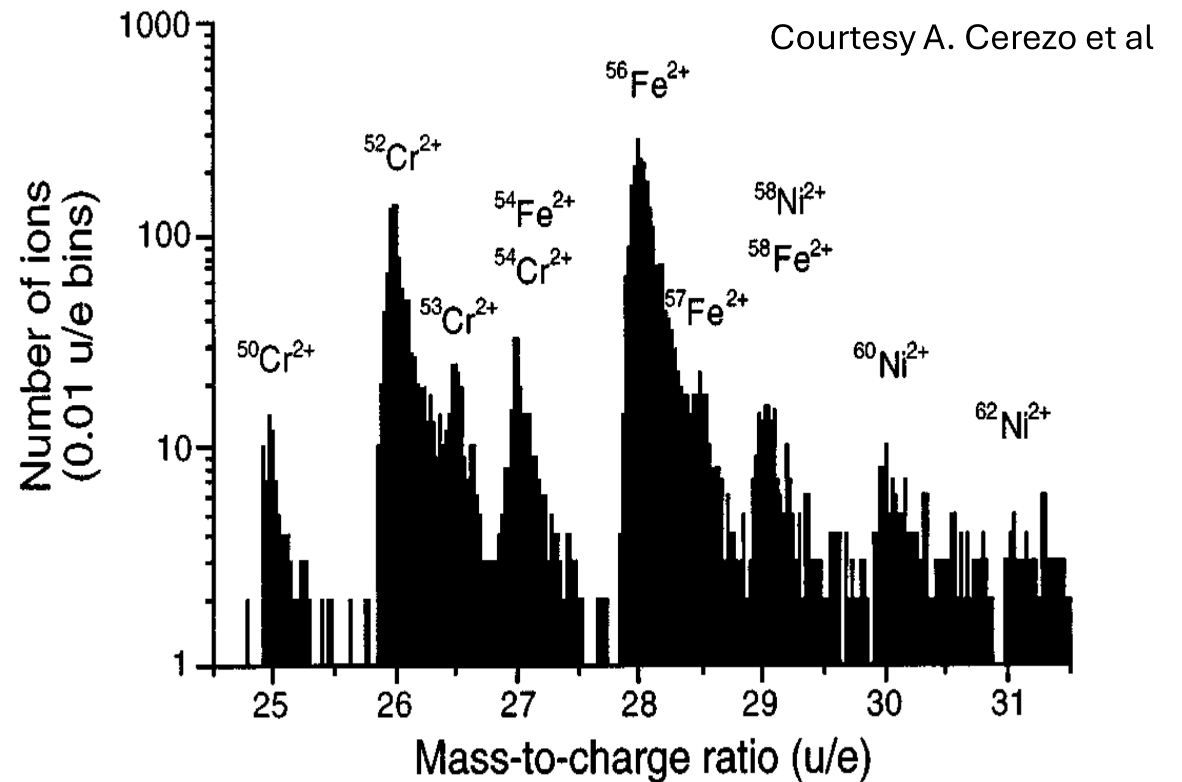


- Pulses are not instantaneous. Ramp and decay are also not always identical.

- Spread in time of flight leads to a spread in mass-to-charge ratio. This leads to peak shapes linked to the physical mechanisms that caused the evaporation.

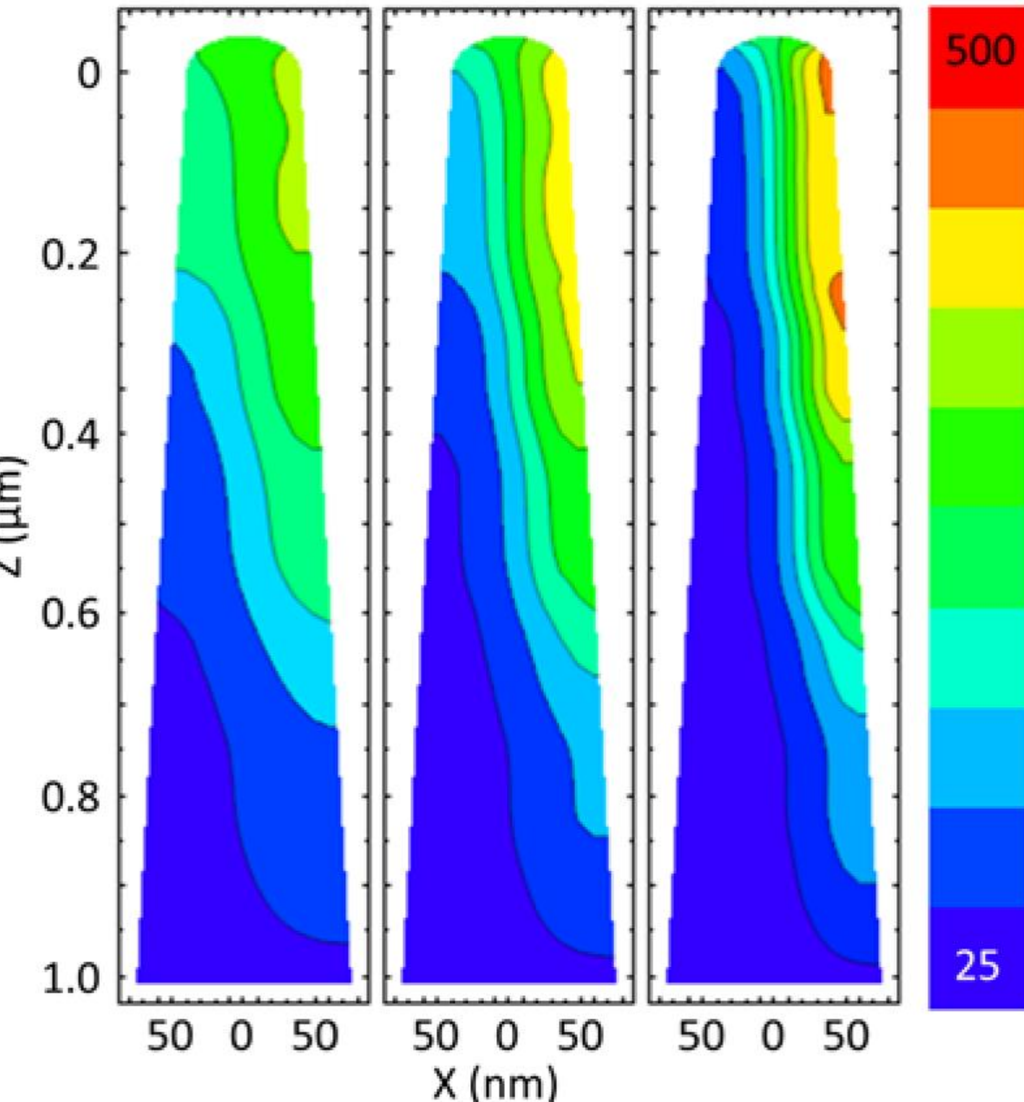
Spread in time-of-flight and mass resolution



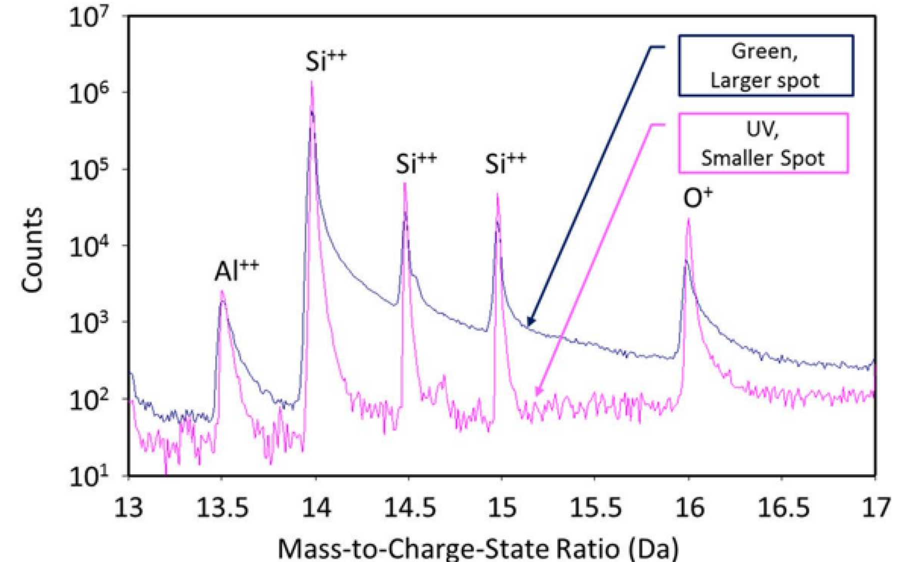


- The spread of possible energies leads to **widening of peaks** in the mass spectrum
- This limits the mass resolving power: resolving two closely spaced peaks or trace elements can be harder.

Introduction of laser pulsing



- Initially, APT analysis was mostly limited to conductive materials as high voltage pulsed was used to initiate evaporation
- Add thermal component to the evaporation process. Reduces the applied standing field and reduces stress
- UV wavelength lasers can be focused to a smaller spot and reduce delayed evaporation events (“thermal tails”).
- Allows (much easier!) analysis of semiconductors and insulators, opening up wider application to geological materials.



Kelly *et al* *Microscopy and Microanalysis*, vol. 18 S02, pp. 584–585,