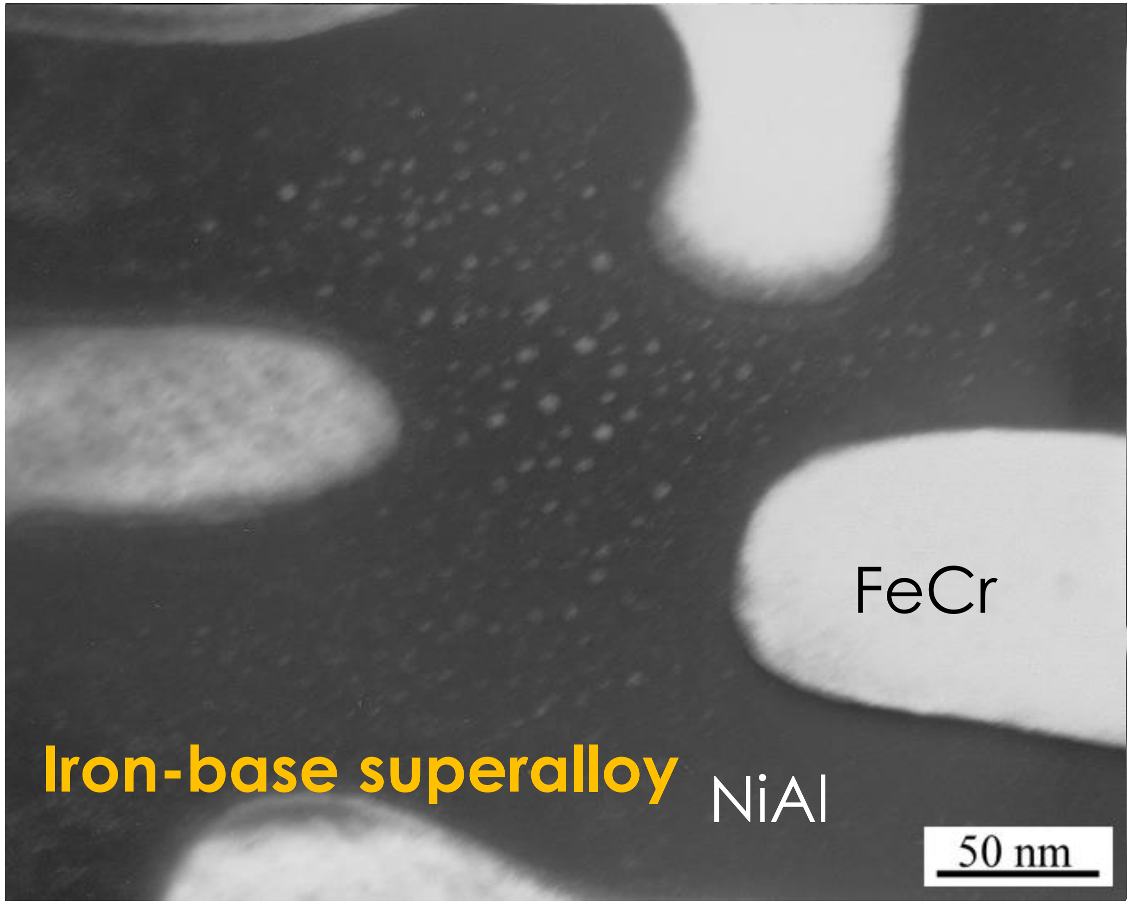
STEAM INSTRUMENTS

Materials Applications of Atom Probe Tomography

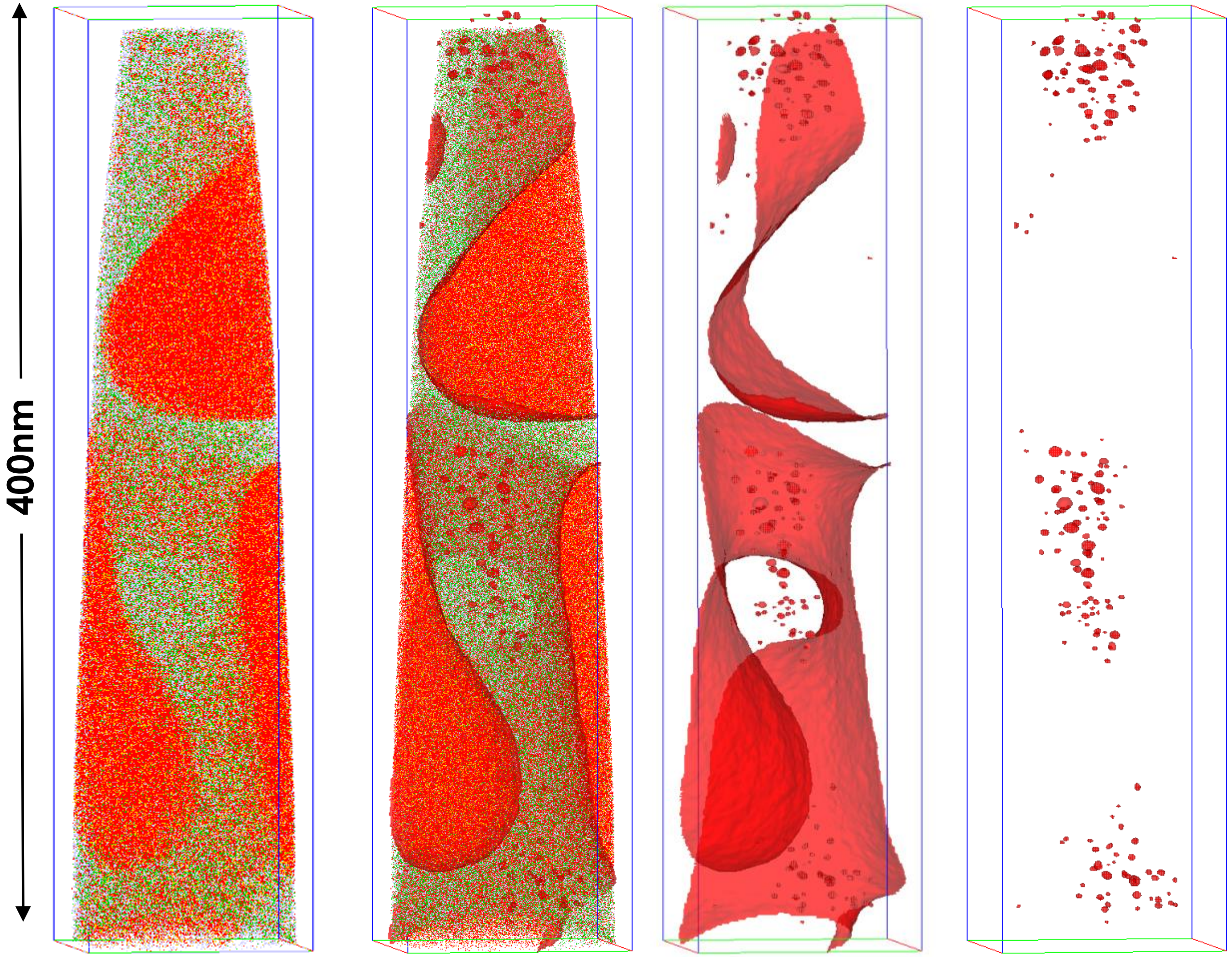
Metals

Correlative Microscopy & Characterization

TEM Dark-field Images

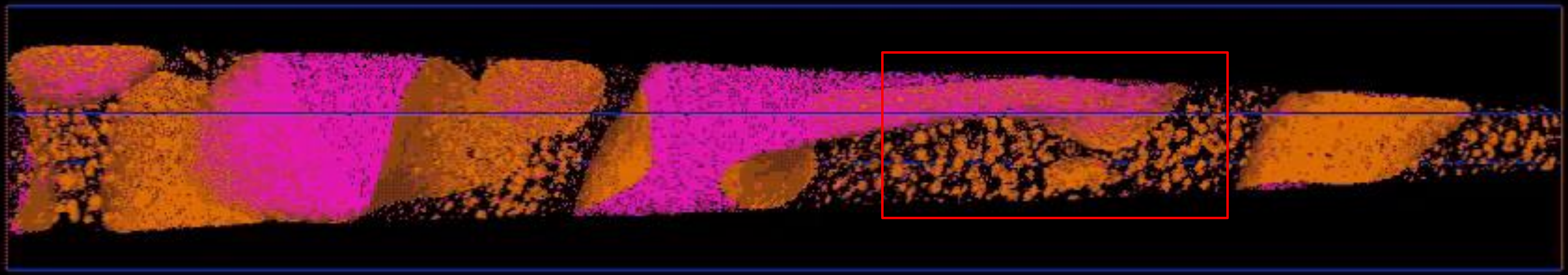


LEAP Tomographs (Fe)



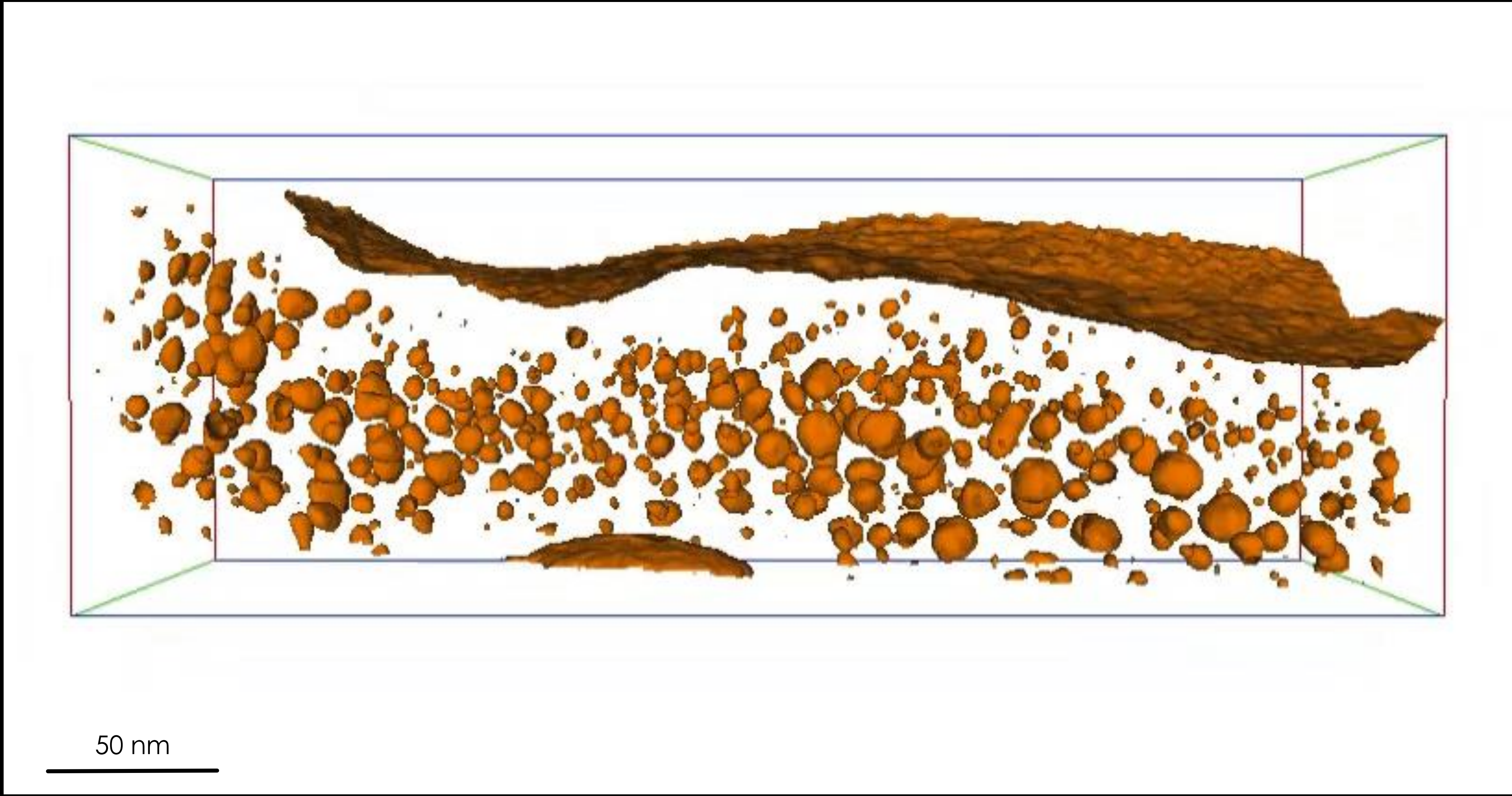
- *C. Stallybrass, G. Sauthoff, A. Schneider, and Y. Degas, Max Planck Institut fur Eisenforschung-Düsseldorf*

APT Provides 3D Analysis



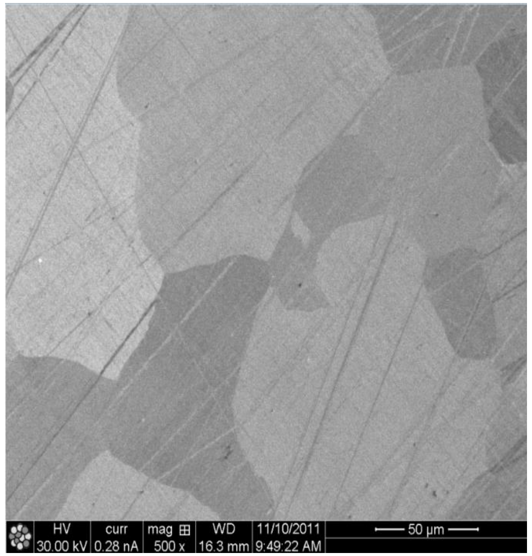
100 nm

There is a lot of 3D detail

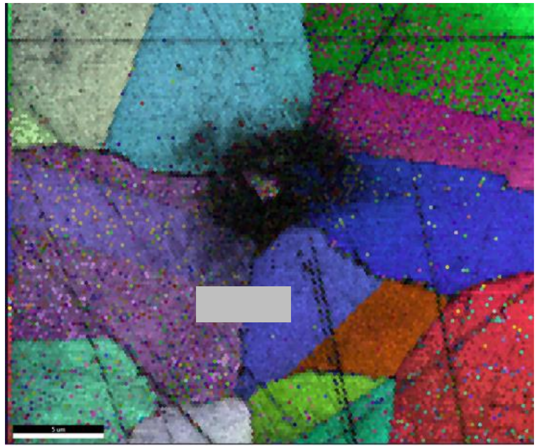


Grain Boundary Analysis

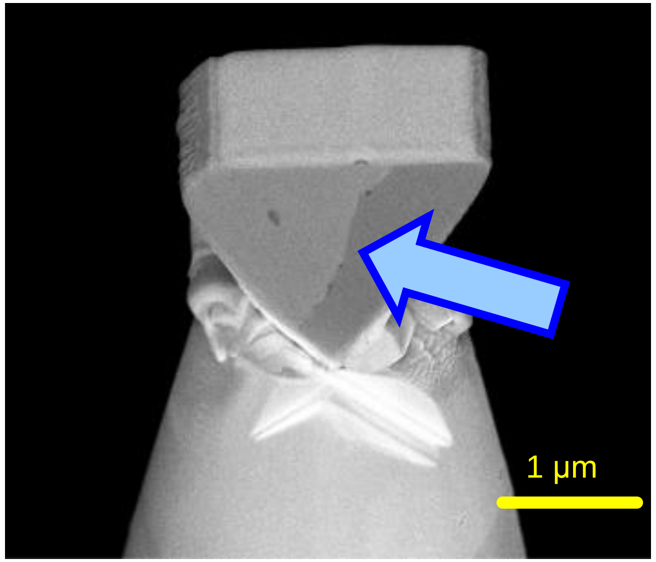
Grain boundary visibility



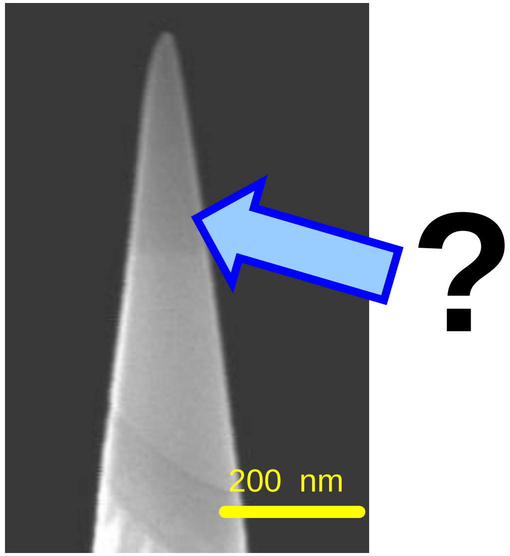
SE/BSE Contrast



EBSD Map



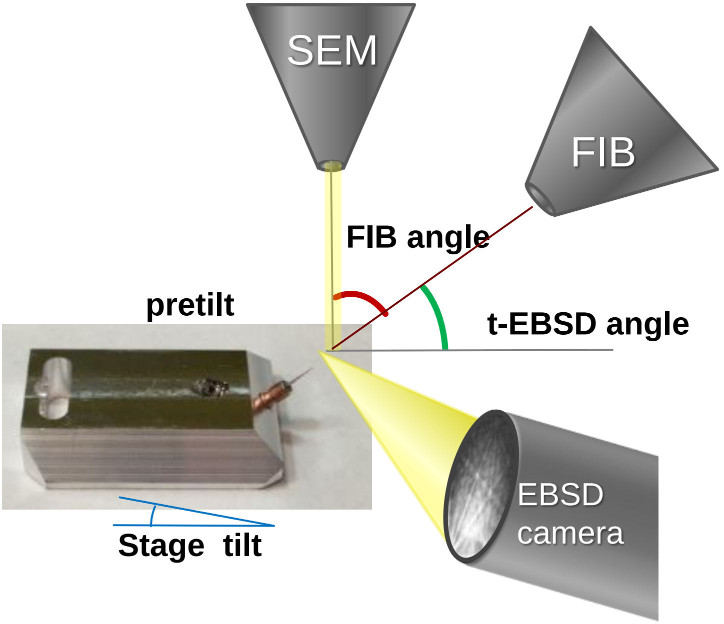
- Mounted wedge prior to sharpening.
- Precipitates visible at the interface.
- Grain boundary is clearly visible.

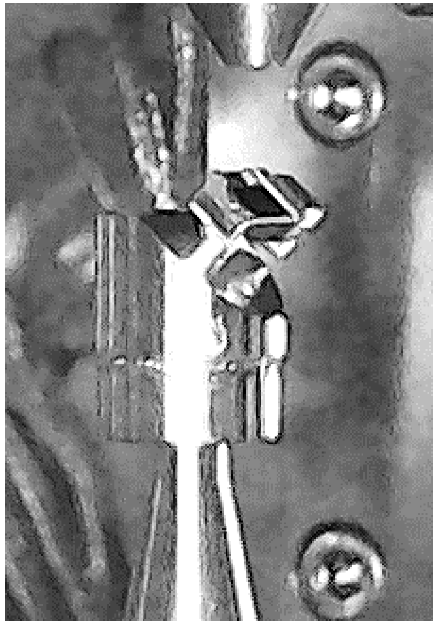


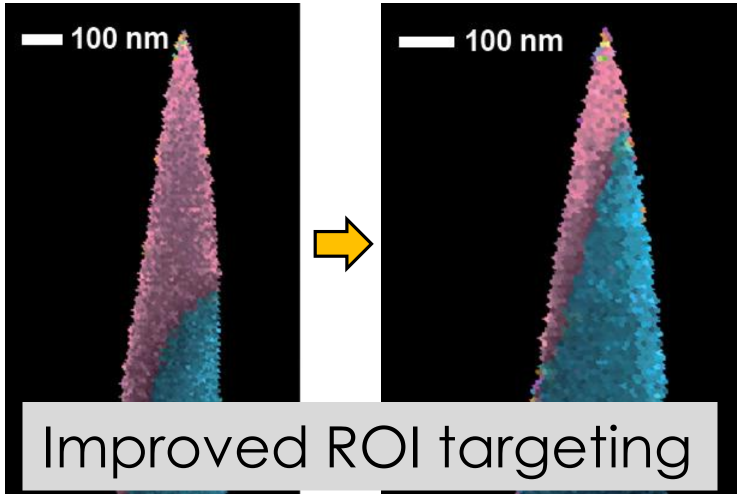
- Final tip shape: grain boundary no longer visible.

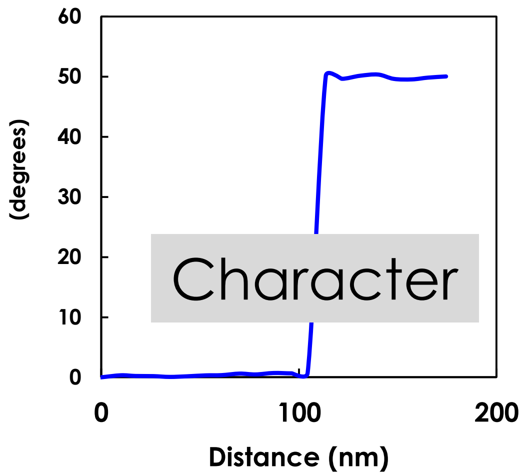
- Without TKD, targeting an ROI can be difficult
- During final tip shaping, often channeling contrast is lost

TKD During APT Specimen Preparation



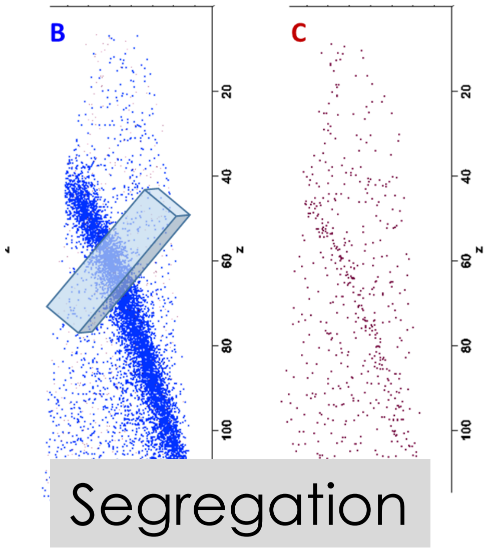


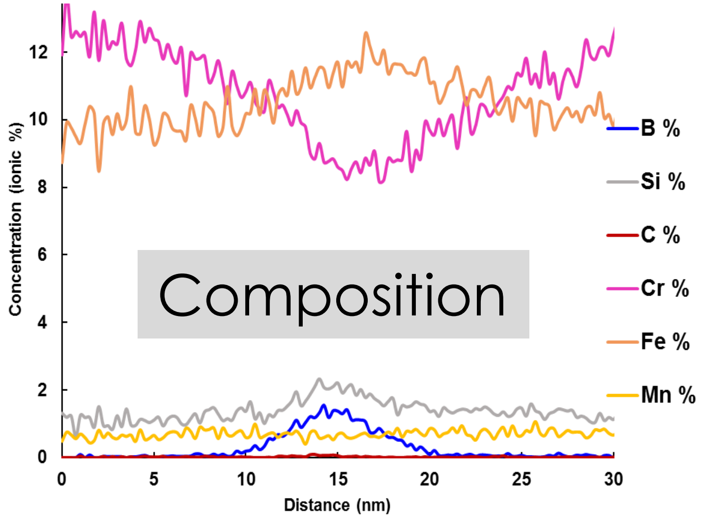




- TKD can be combined with atom probe to provide crystallographic information
- It is quick and easy in the FIB/SEM without needing to move the specimen from the milling position

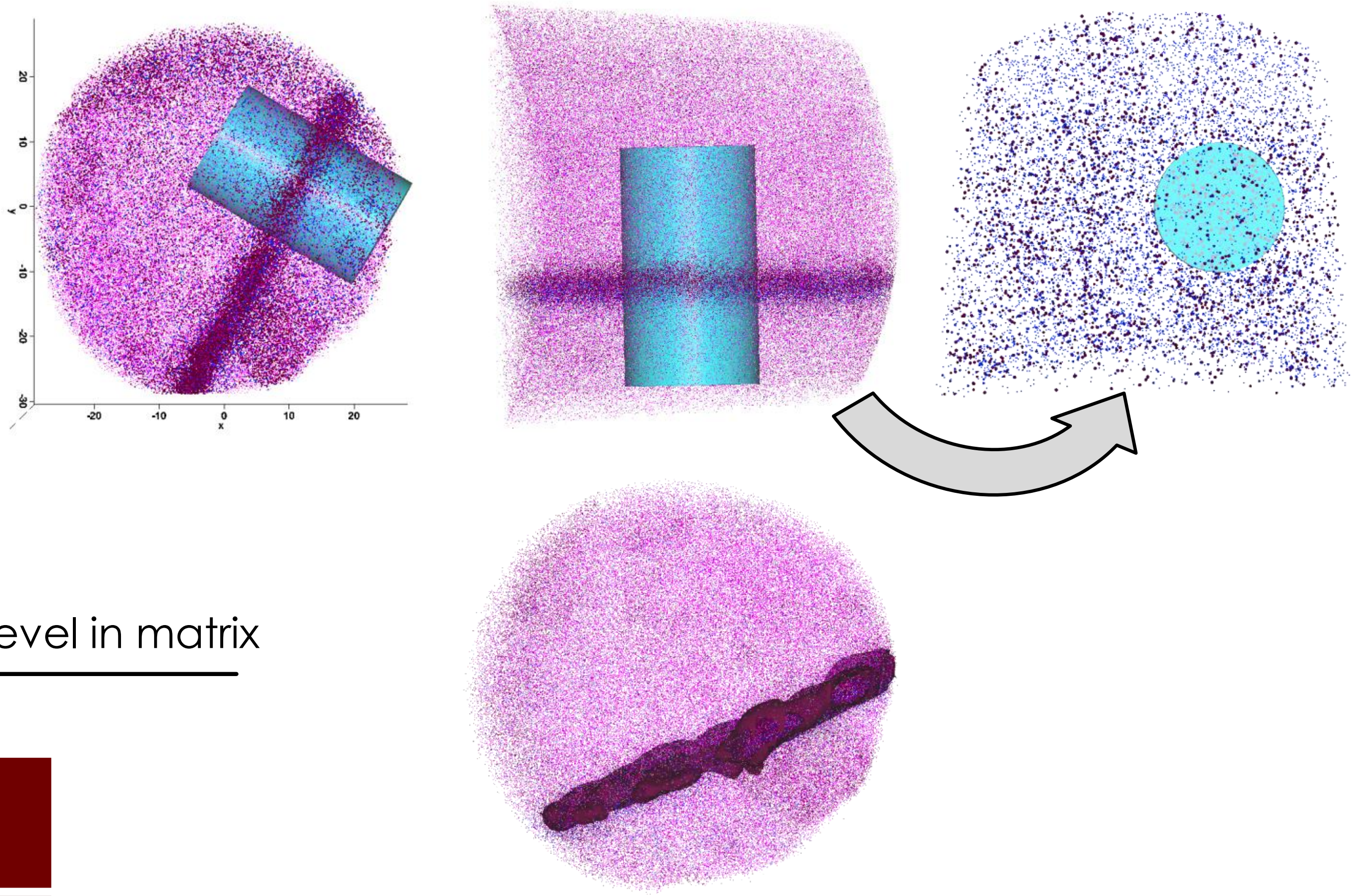
K.P. Rice, R.R. Keller, M.P. Stoykovich, Specimen-thickness effects on transmission Kikuchi patterns in the scanning electron microscope, Journal of Microscopy. 254 (2014) 129–136.





Quantifying Segregation: Interfacial Excess

- Gibbsian Interfacial Excess is a measure of the amount of segregation at a grain boundary, ***normalized by area***[1] (i.e., excess over the concentration in the bulk)
- This allows a measure of segregation to be calculated
- Light elements and heavy elements can be measured simultaneously



$$\textbf{Interfacial excess} = \frac{\text{Species level at GB - Species level in matrix}}{\text{Sampling area}}$$

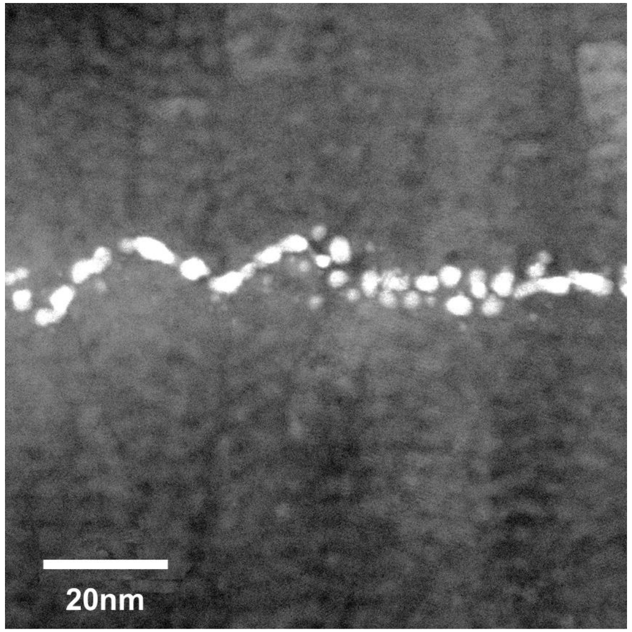
Ion	Interfacial Excess
Carbon	34.5 atoms/ nm^2
Boron	7.6 atoms/ nm^2

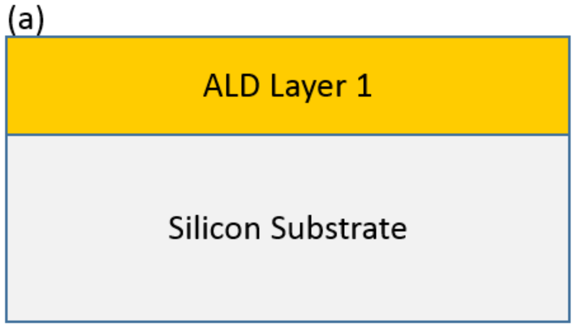
Hellman, O.C., Seidman, D.N., 2002. Measurement of the Gibbsian interfacial excess of solute at an interface of arbitrary geometry using three-dimensional atom probe microscopy. Materials Science and Engineering: A 327, 24–28.

Materials Applications

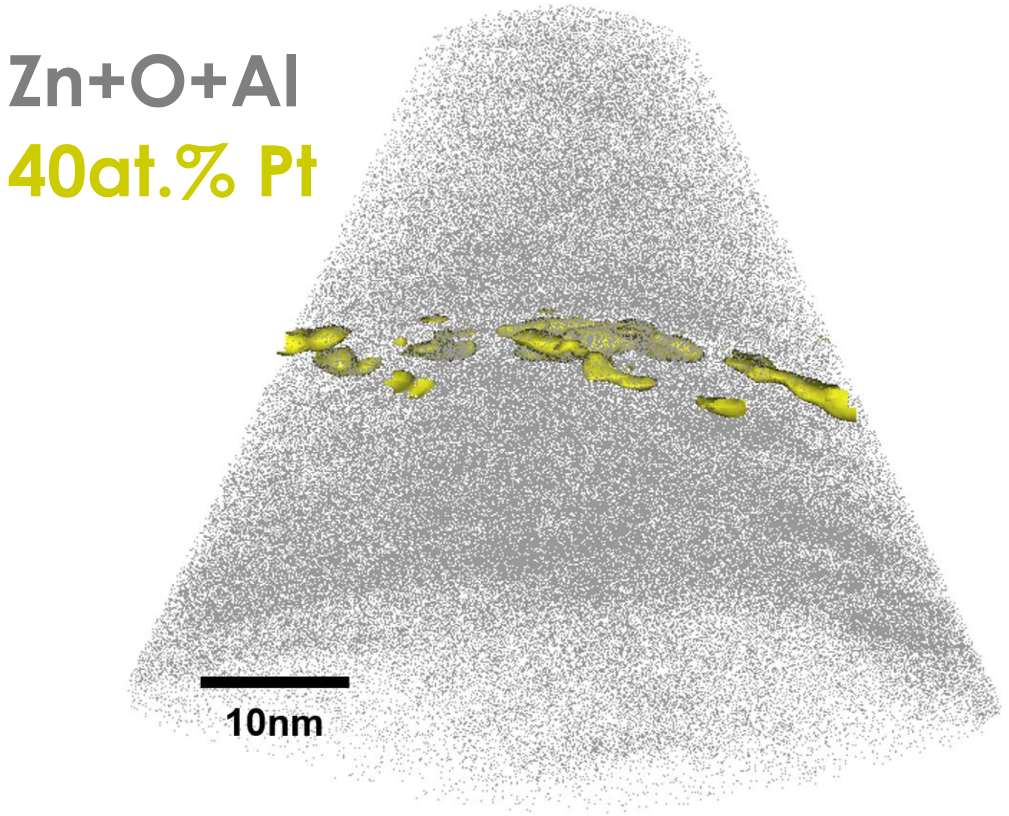
Nanowires and Nanoparticles

Specimen Preparation - Encapsulation

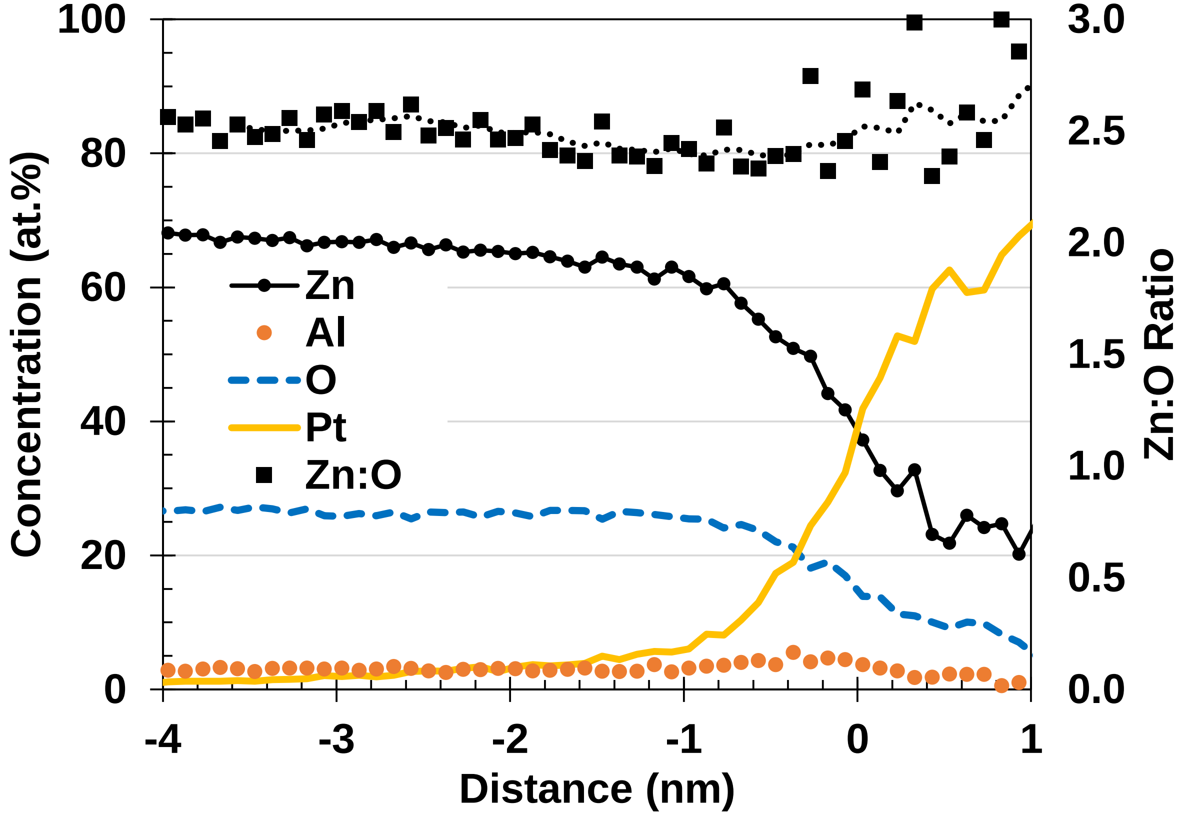




APT of Pt Nanoparticles



Proxigram Analysis [1]



[1] O. Hellman et al., Micro. Microanal. 6 (2000) 437.

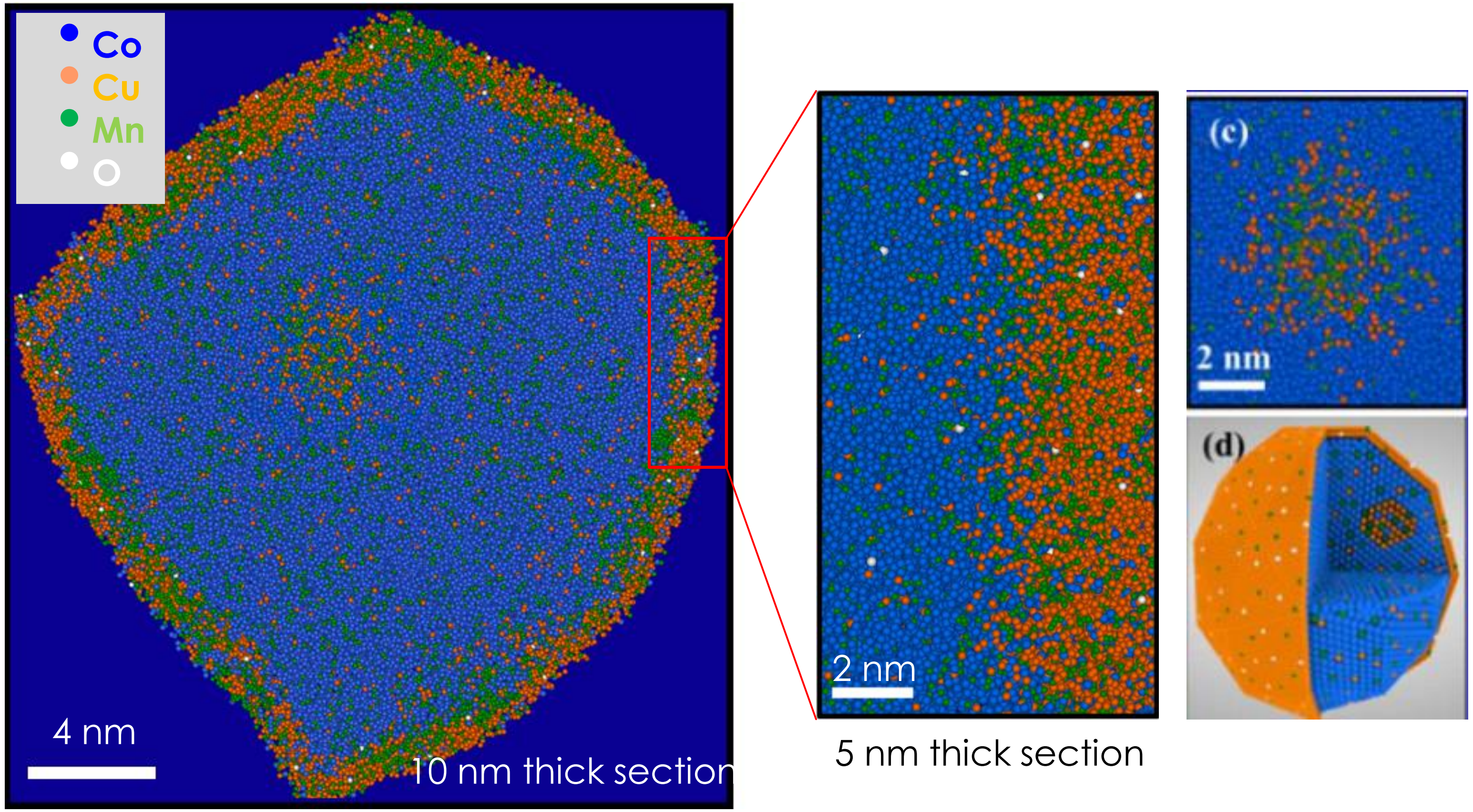
CoCuMn Catalyst Particle

Motivation

- -High efficiency production of Long-Chain Terminal Alcohols

- a Co-rich core structure and a Cu-dominated CoCuMn mixed shell that is highly effective in enabling chain lengthening with terminal alcohol or olefin production

- Sample Preparation was eBeam deposited Pt

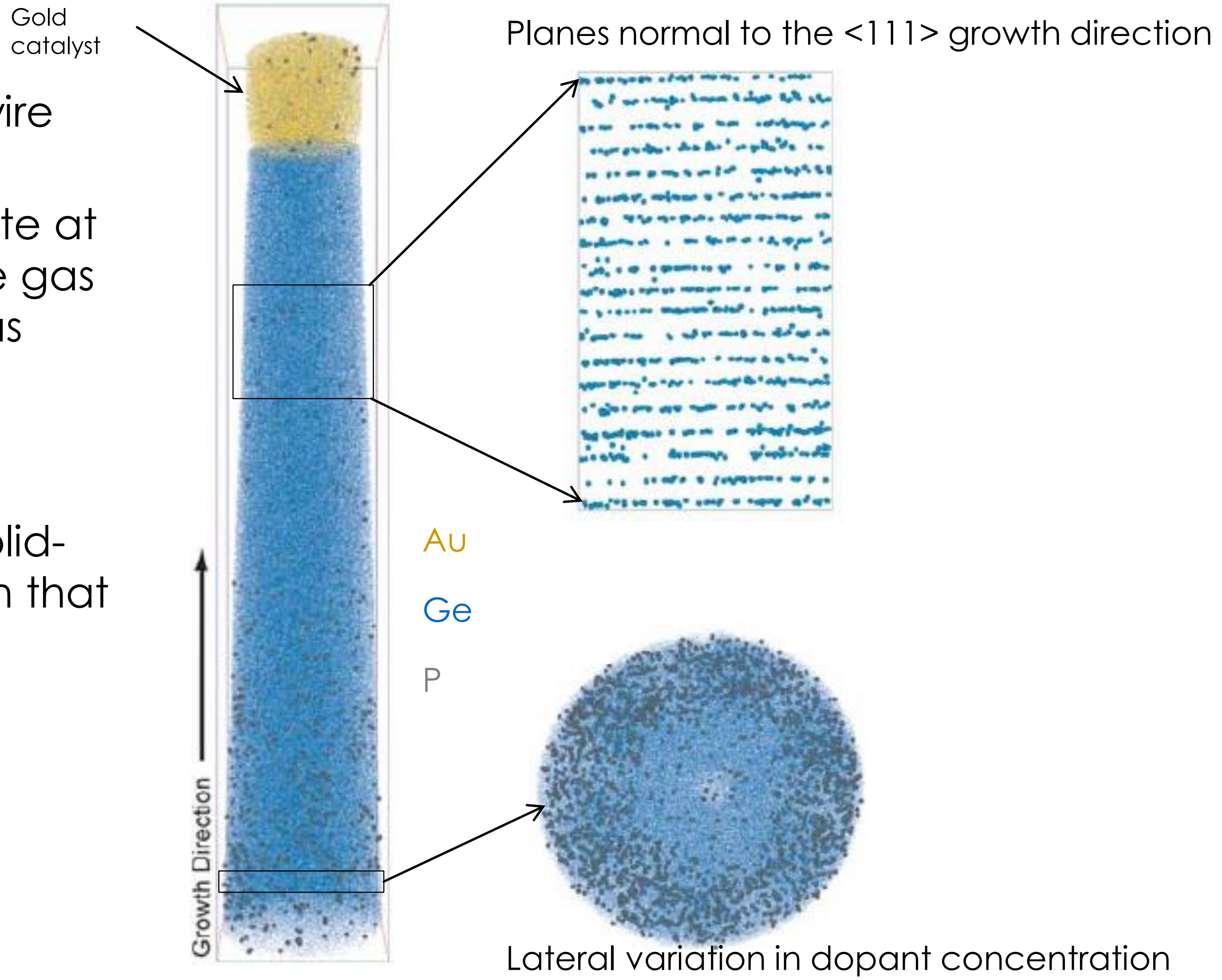


- Images are sections through 3D tomographic reconstructions
  - Faceted core-shell structure that contain intra-core clusters
- Oxygen was distributed throughout the core-shell interface
- Surface contains a high concentration of Cu and Mn

Xiang et al. J. Am. Chem. Soc., 2013, 135 (19), pp 7114–7117.

Nanowires: P-Doped VLS Germanium

- Phosphorous-doped germanium nanowire grown with a gold nanoparticle[2]
- The doping rate is determined by the rate at which the dopant atoms move from the gas phase as precursors to the solid phase as substitutional impurities
  - Quantitative analysis of the mass spectrum showed that the dopant concentration in the vapor-liquid-solid-grown nanowire was much less than that of the gas phase



1. Lauhon, L. J., *MRS Bull.* 2009, *34*, 738-743.
2. Perea, D. E., *Nature Nanotech.* 2009, 315-319

Materials Applications

Geological Materials

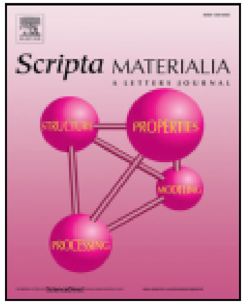
New Review of APT in Geoscience

Scripta Materialia 148 (2018) 115–121

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat



Viewpoint article

Atomic worlds: Current state and future of atom probe tomography in geoscience

Check for updates

D.W. Saxey [a,*], D.E. Moser [b], S. Piazolo [c,d], S.M. Reddy [a,e], J.W. Valley [f]

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[d] *School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK*
[e] *School of Earth and Planetary Sciences, Curtin University, Perth, WA 6102, Australia*
[f] *Department of Geoscience, University of Wisconsin, Madison, WI 53706, USA*

Geochronology and Life on Earth

nature geoscience

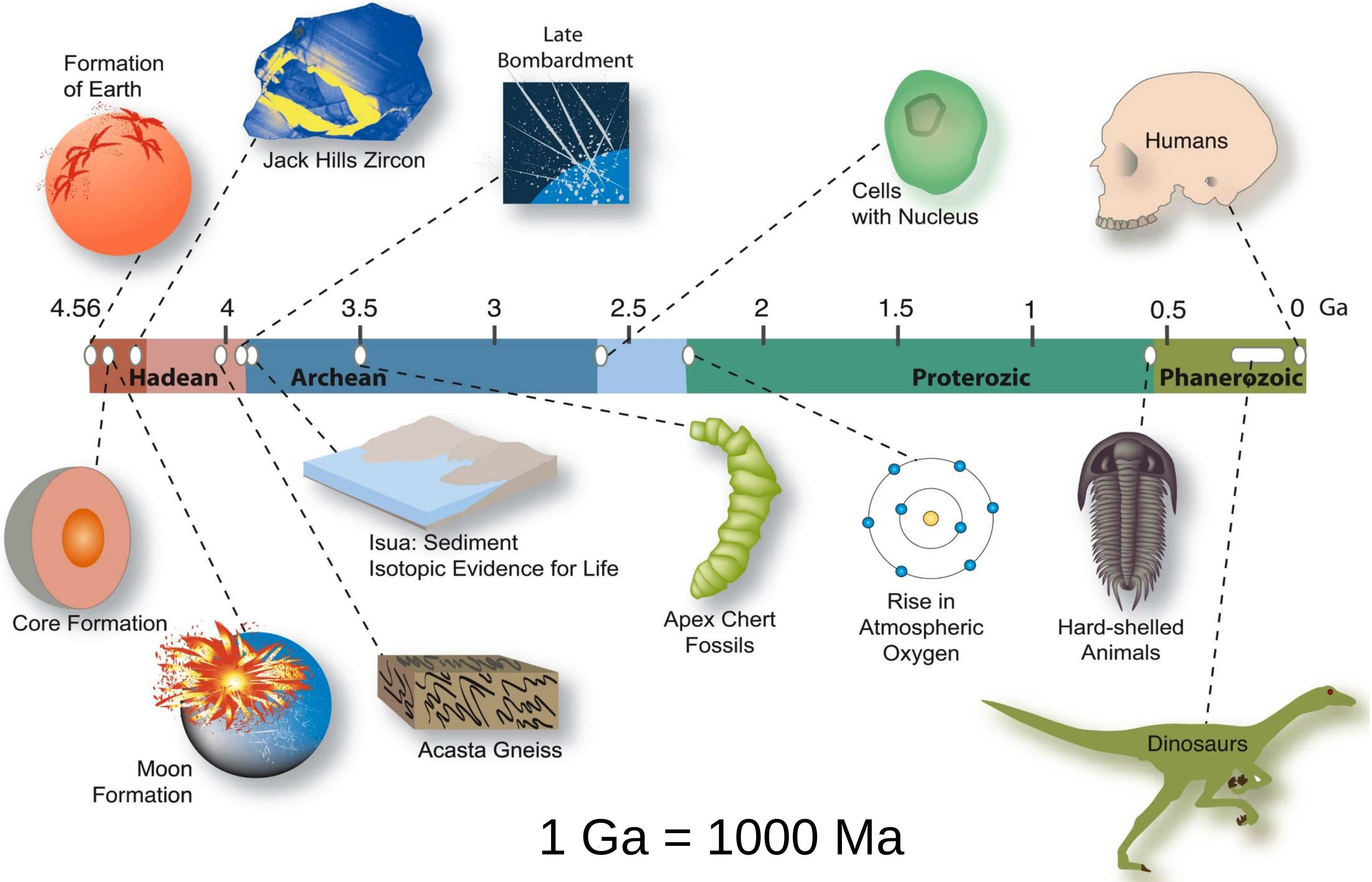
LETTERS

PUBLISHED ONLINE: 23 FEBRUARY 2014 | DOI: 10.1038/NGEO2075

Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography

John W. Valley[1*], Aaron J. Cavosie[1,2], Takayuki Ushikubo[1], David A. Reinhard[3], Daniel F. Lawrence[3], David J. Larson[3], Peter H. Clifton[3], Thomas F. Kelly[3], Simon A. Wilde[4], Desmond E. Moser[5] and Michael J. Spicuzza[1]

Life on Earth



1 Ga = 1000 Ma

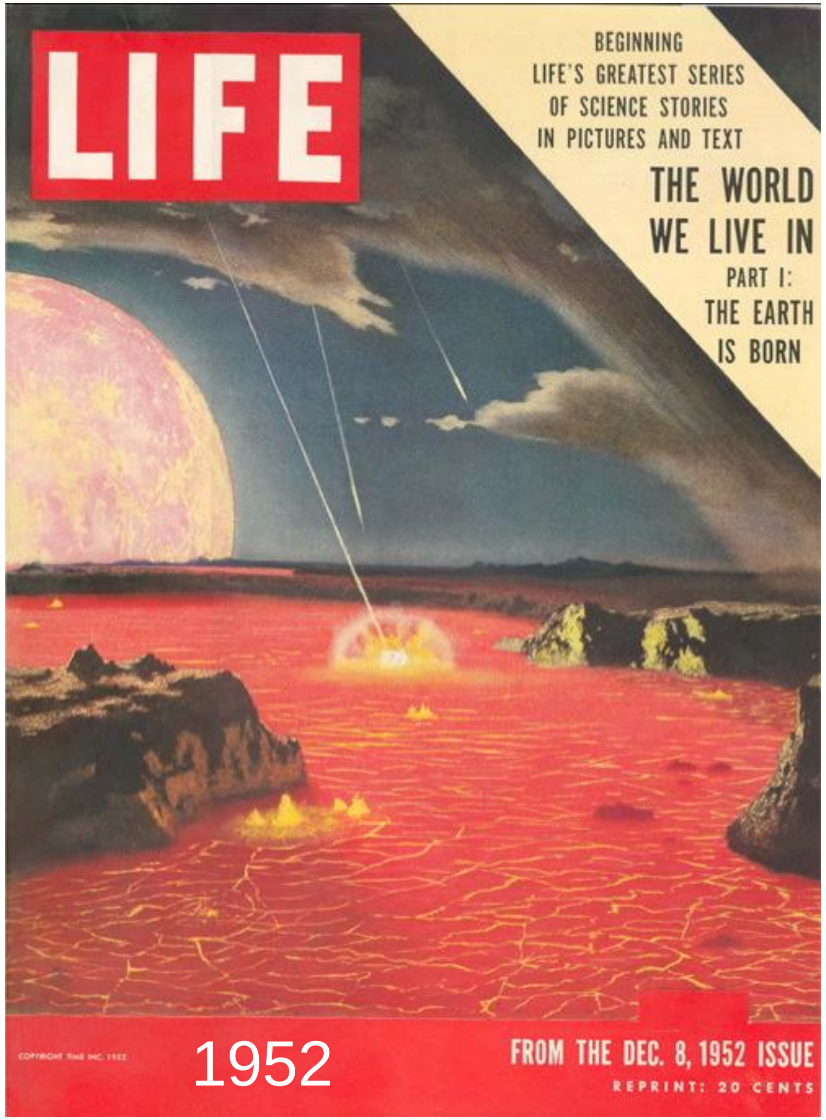
Andrée Valley

Which View is Correct?

Solar System condensed about 4.56 Ga

4.0-4.4 Ga:
Hadean Earth vs.
Cool Early Earth?

Wilde, S.A., Valley, J.W., Peck, W.H. & Graham, C.M., Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago, Nature 409,175–178 (2001).

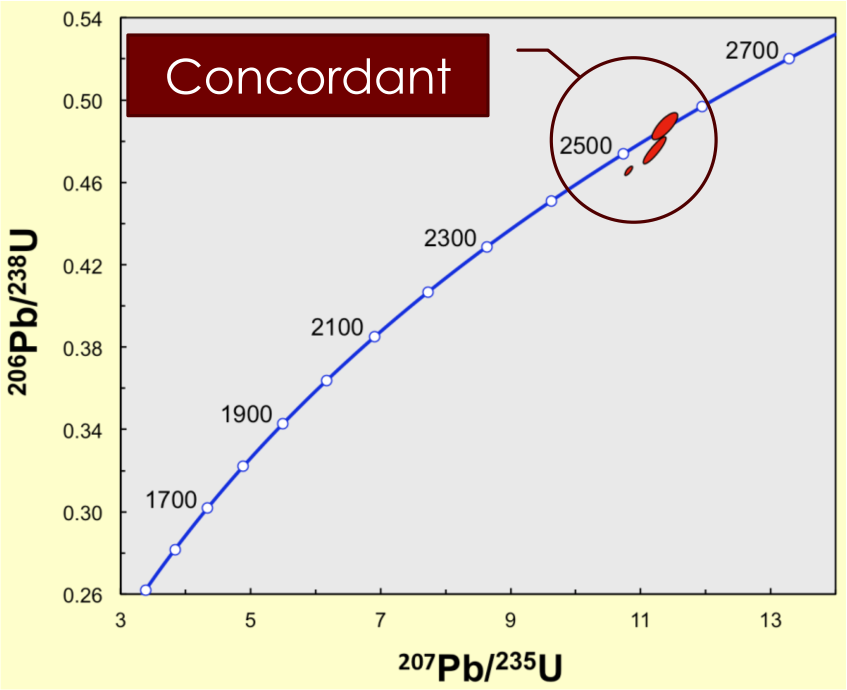


U-Pb Geochronology in Zircon

- When zircons solidify, all Pb segregates to the liquid: (zero Pb in crystal)
- U is typically found at about 500 appm in crystal
- Pb is the final daughter product of both ^{235}U and ^{238}U
  - Any Pb in zircon is radiogenic from U decay
  - Thus, there are two "clocks"
- If both clocks give same date, it is <u>concordant</u> which is imbues confidence

$$\frac{^{206}\mathrm{Pb}^*}{^{238}\mathrm{U}} = e^{\lambda_{238} t} - 1$$

$$\frac{^{207}\mathrm{Pb}^*}{^{235}\mathrm{U}} = e^{\lambda_{235} t} - 1$$



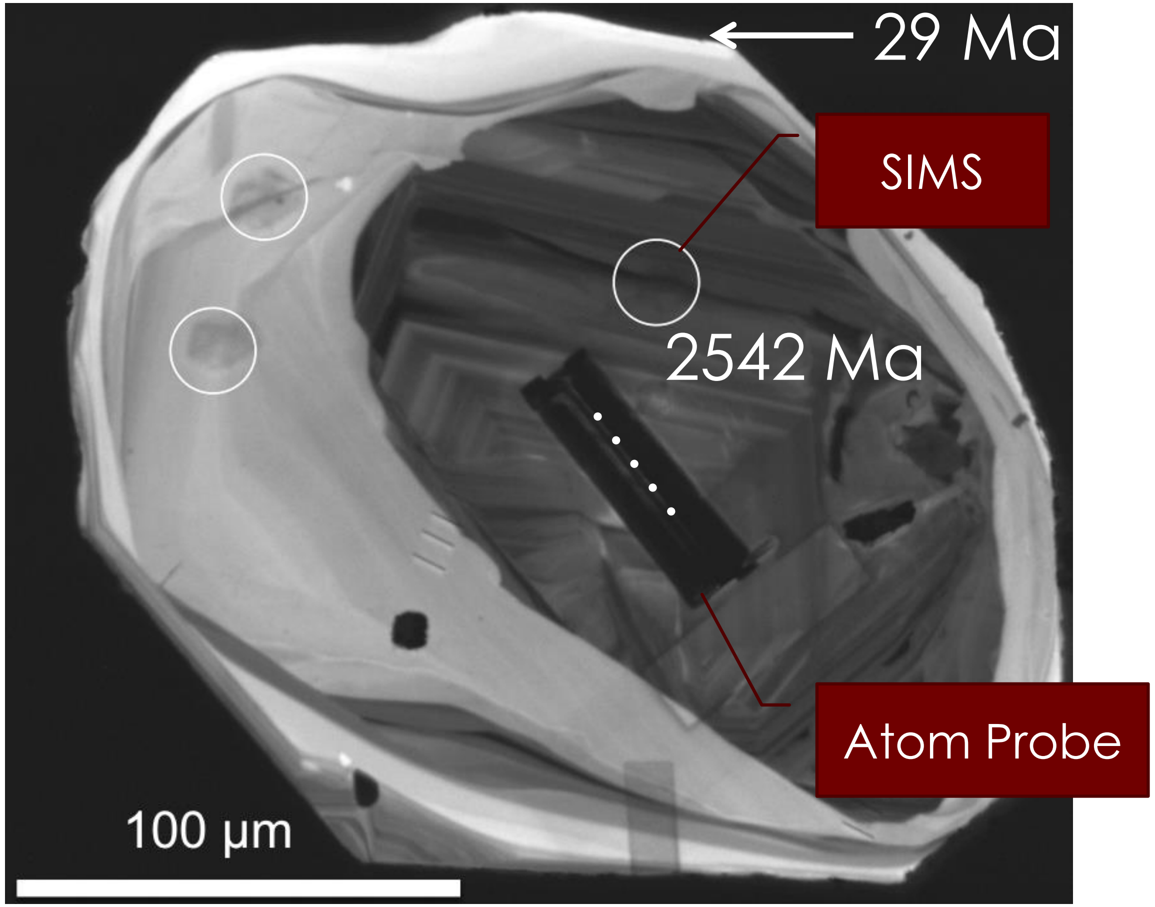
A. Strickland et al. (2011) AJS

Geo Chronometry: APT vs. SIMS

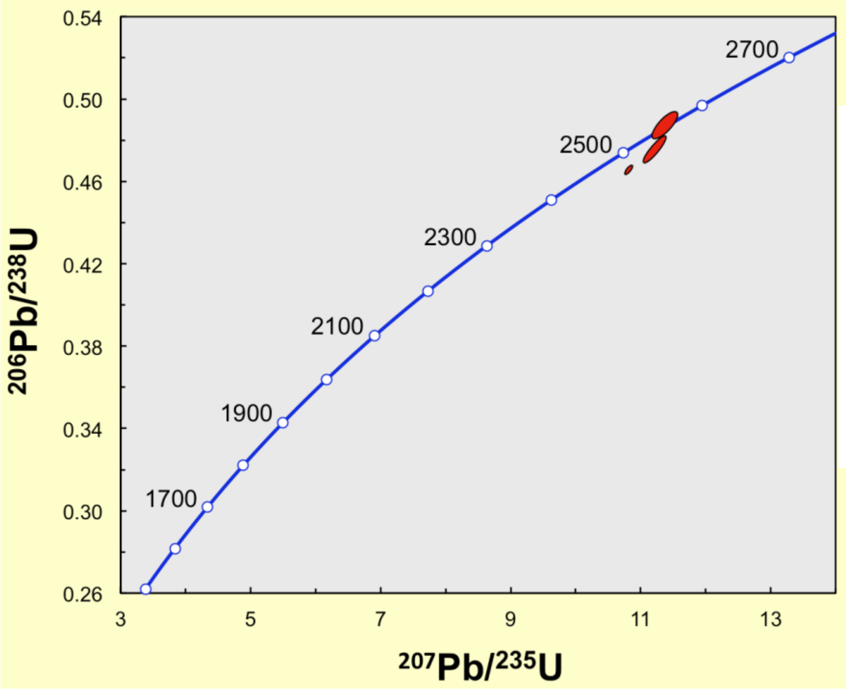
Core = 2542 Ma
97% concordant
U 672 ppm Th 224 ppm

Rim = 29 Ma

Vipont granodiorite, Grouse Creek Mts, UT
Albion, Raft River, Grouse Creek Mts



Atom Probe gets same dates as SIMS



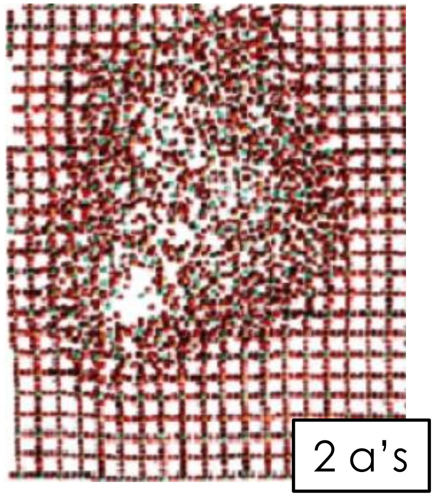
$$\frac{^{206}\mathrm{Pb}^*}{^{238}\mathrm{U}} = e^{\lambda_{238} t} - 1$$

$$\frac{^{207}\mathrm{Pb}^*}{^{235}\mathrm{U}} = e^{\lambda_{235} t} - 1$$

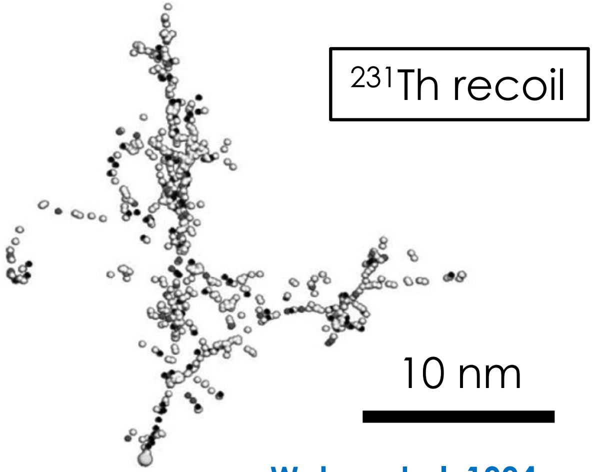
A. Strickland et al. (2011) AJS

a-Recoil Damage in Zircon

a-recoil damage produces defects

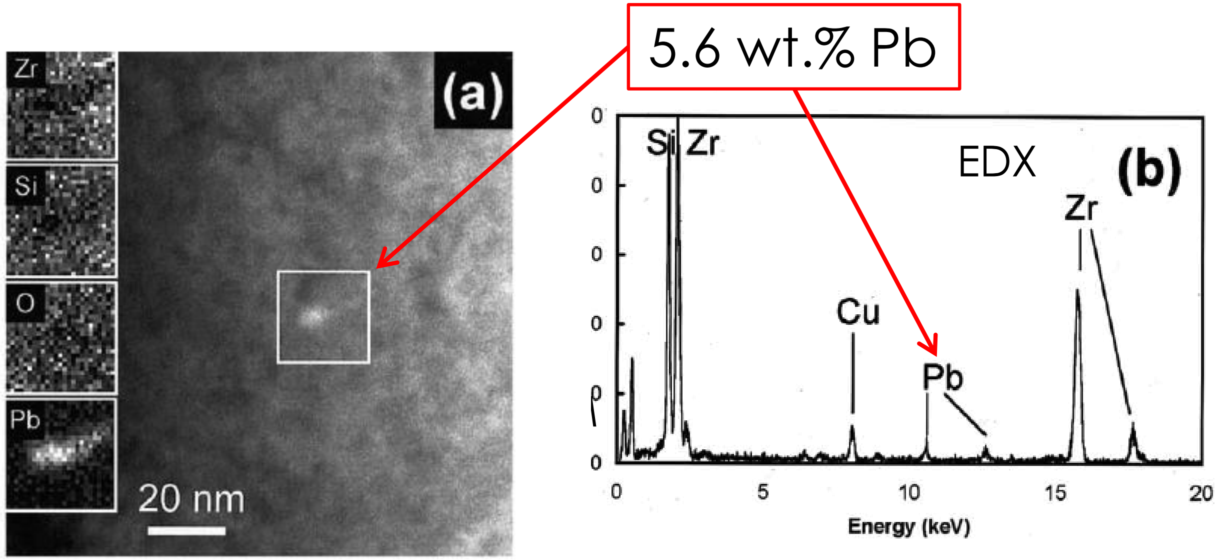


Geisler et al. 2007



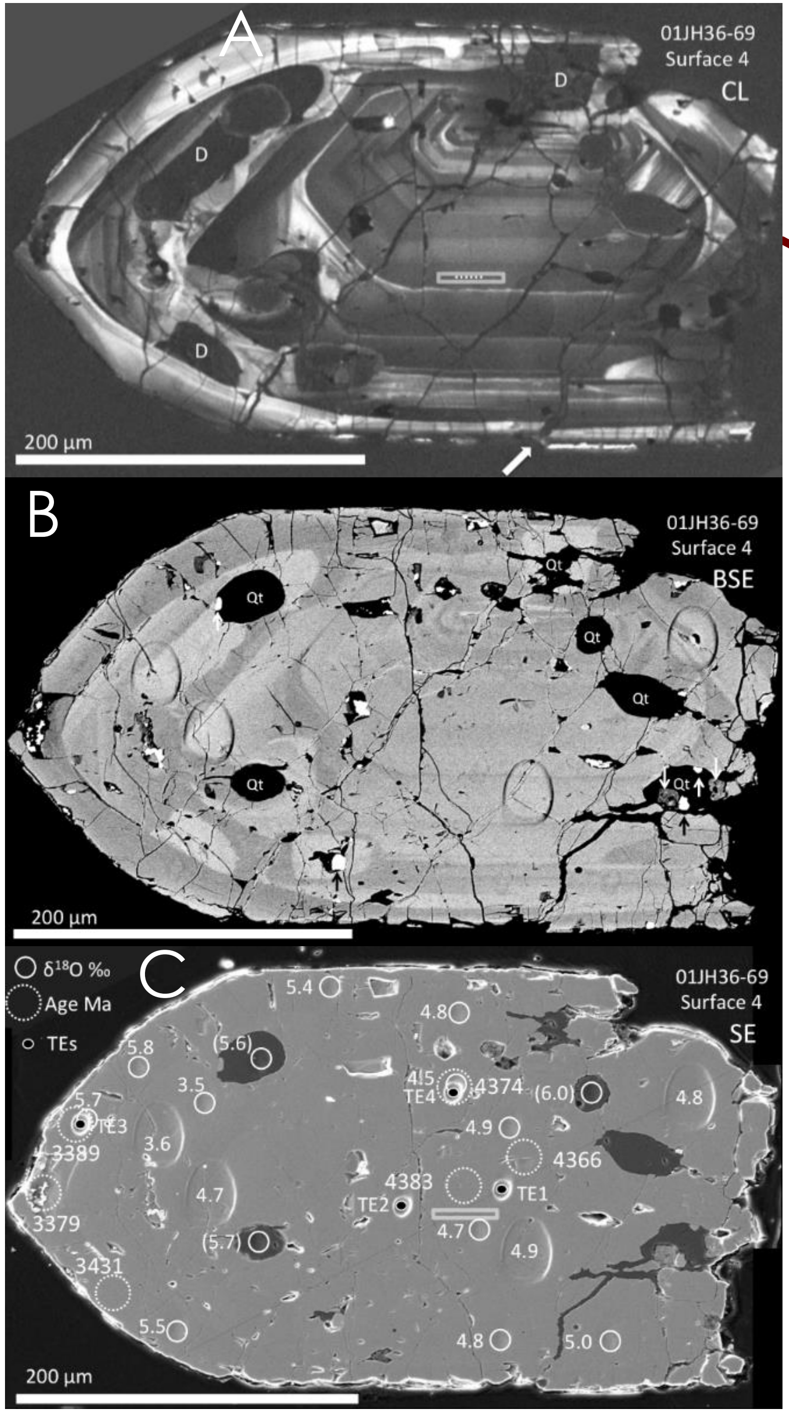
Weber et al. 1994
Ewing et al. 2003

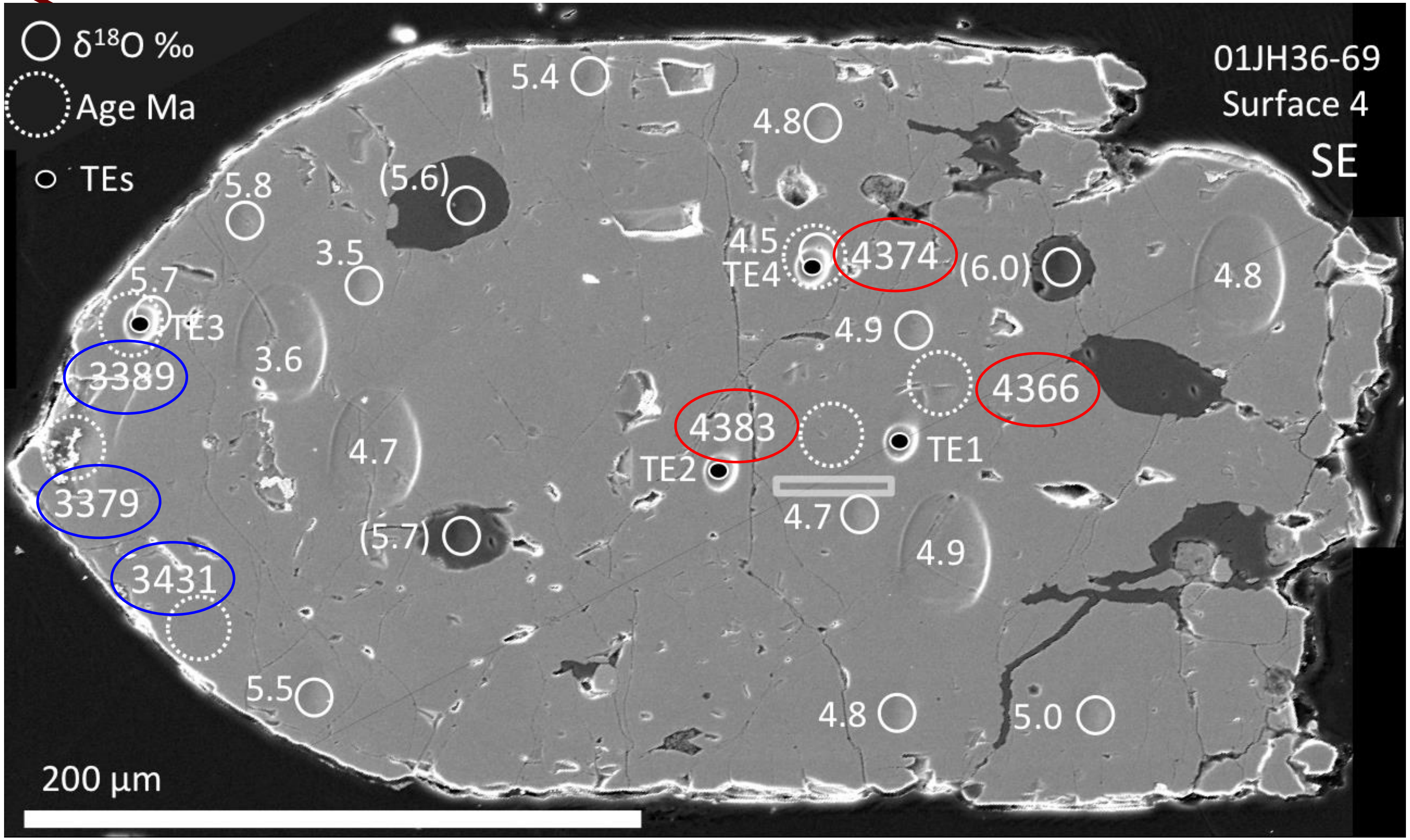
Pb segregation to defects



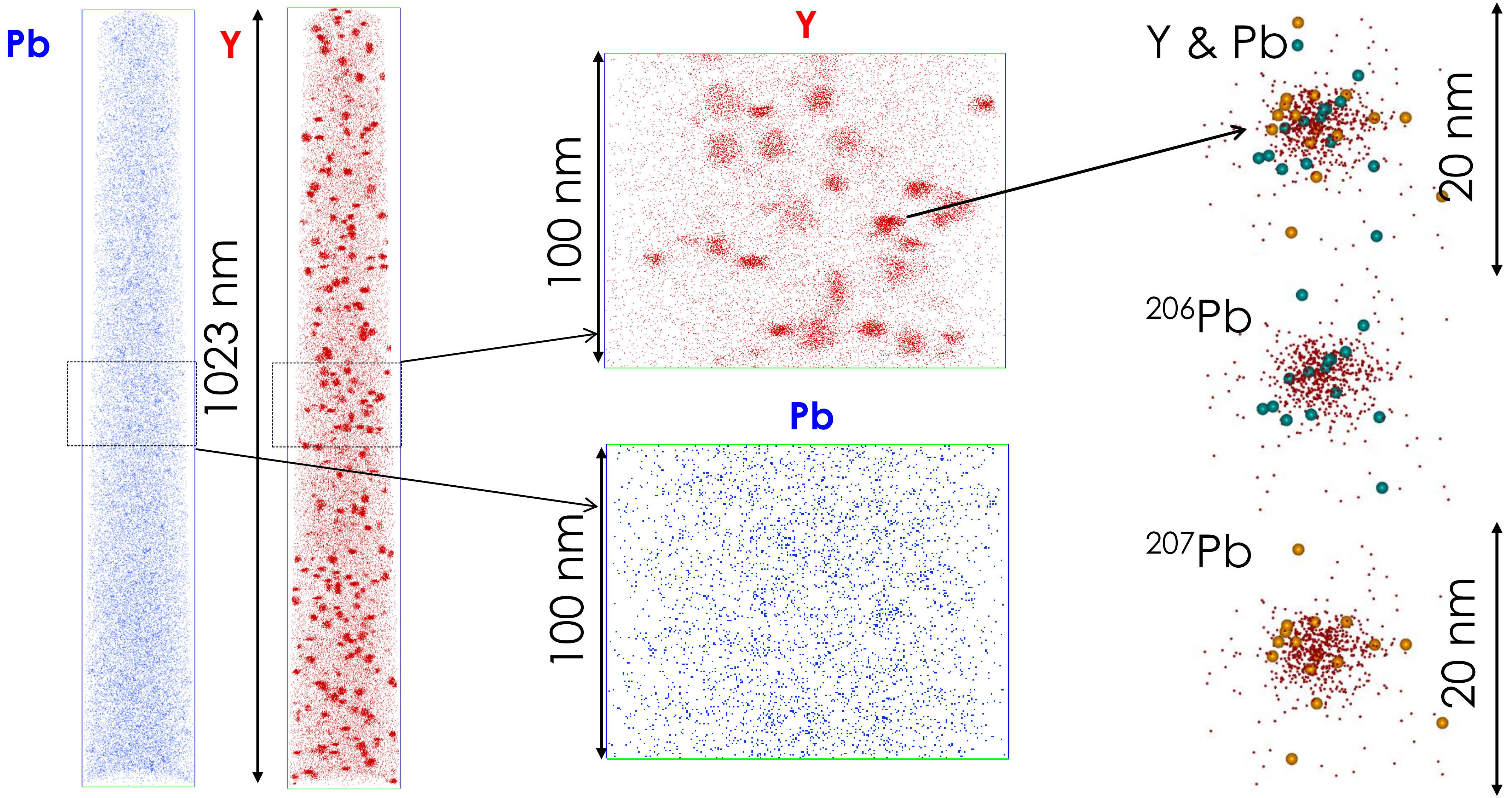
Utsunomiya et al. 2004

Jack Hills 4.4 Ga: Oldest Mineral Known?

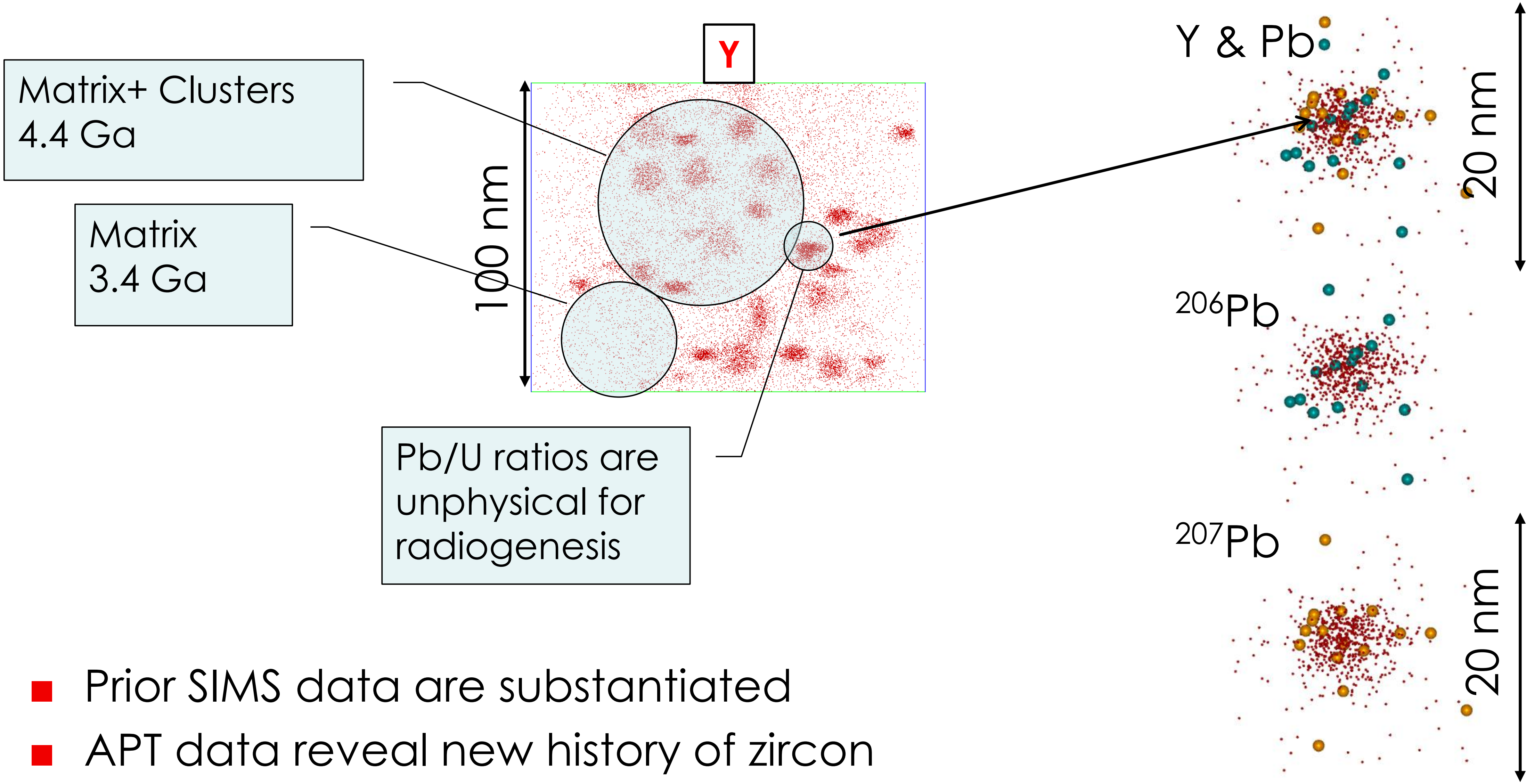




Pb and Y Segregate to Defects



APT Data Tell a New Story



- Prior SIMS data are substantiated
- APT data reveal new history of zircon

Cool Early Earth

Previous SIMS-based conjecture of cool early earth is affirmed

Did life have a chance to start during Hadean Age?

nature geoscience | LETTERS
PUBLISHED ONLINE: 23 FEBRUARY 2014 | DOI: 10.1038/NGEO2075

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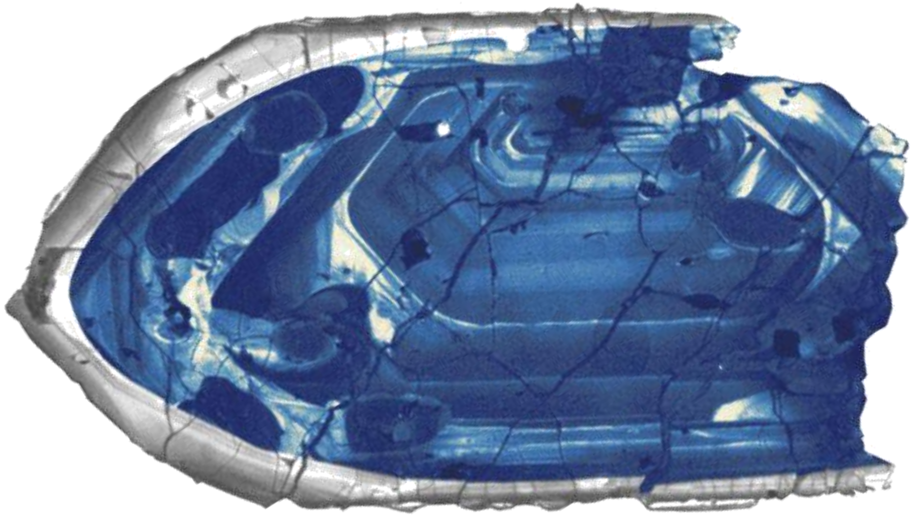
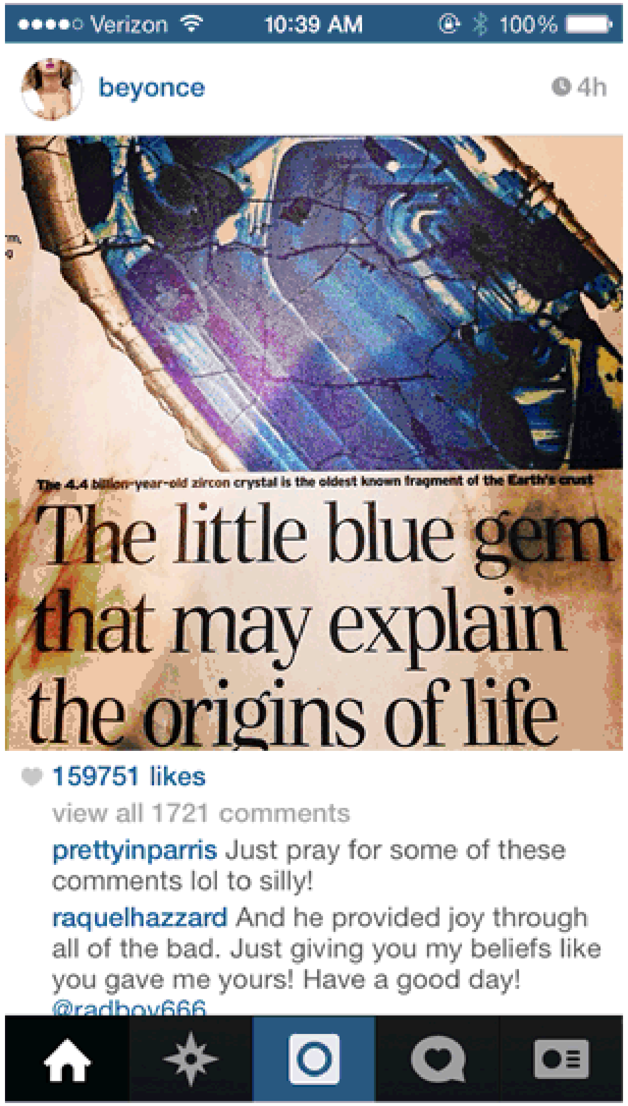
Beyoncé Tweet on Blue Zircon



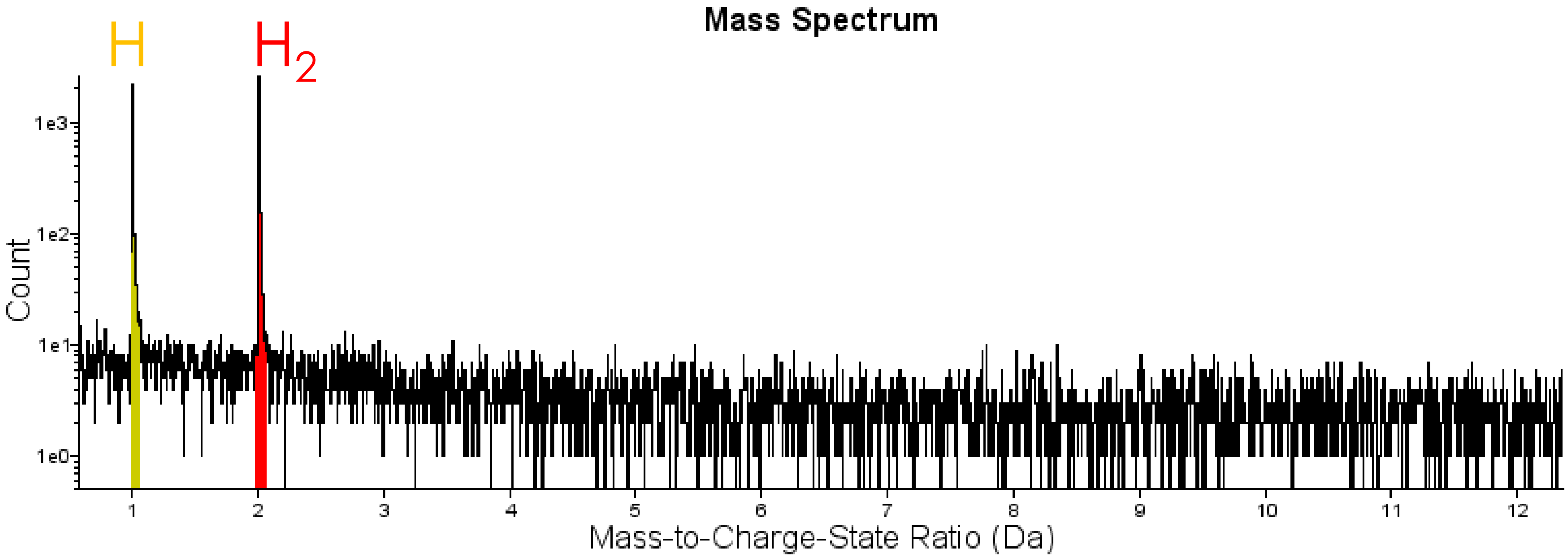


Progress toward Hydrogen Mapping in APT

Hydrogen in APT Mass Spectra

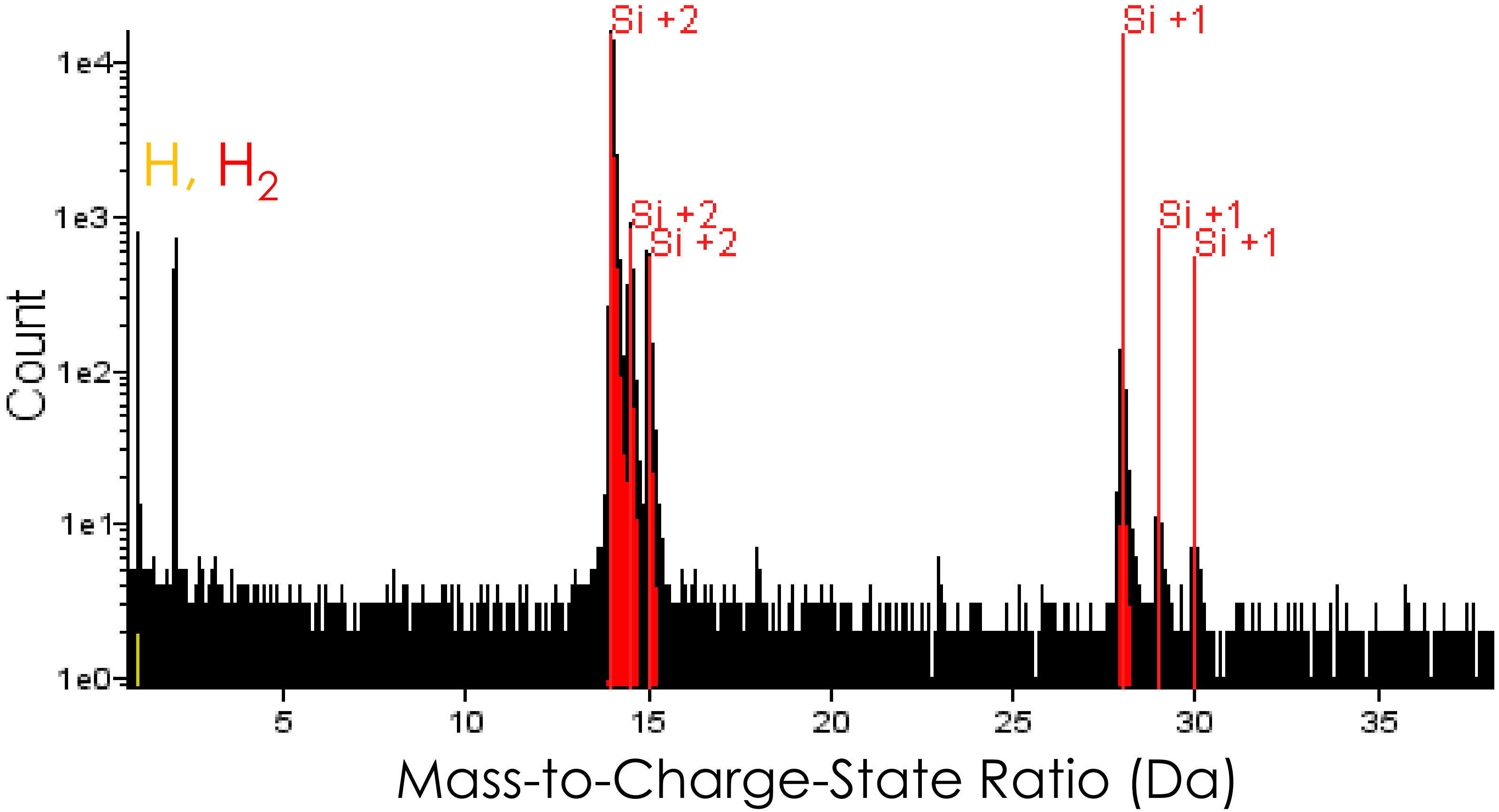
What is the material?

Almost all APT spectra contain hydrogen
– it is a residual gas in the vacuum system.



Hydrogen in APT Mass Spectra – Pure Si

Silicon wafers are VERY pure, they DON'T contain Hydrogen
Hydrogen comes from the vacuum system
This diminishes the quality of quantification for any true hydrogen



H ~ 0.5%

The Hydrogen Challenge for APT

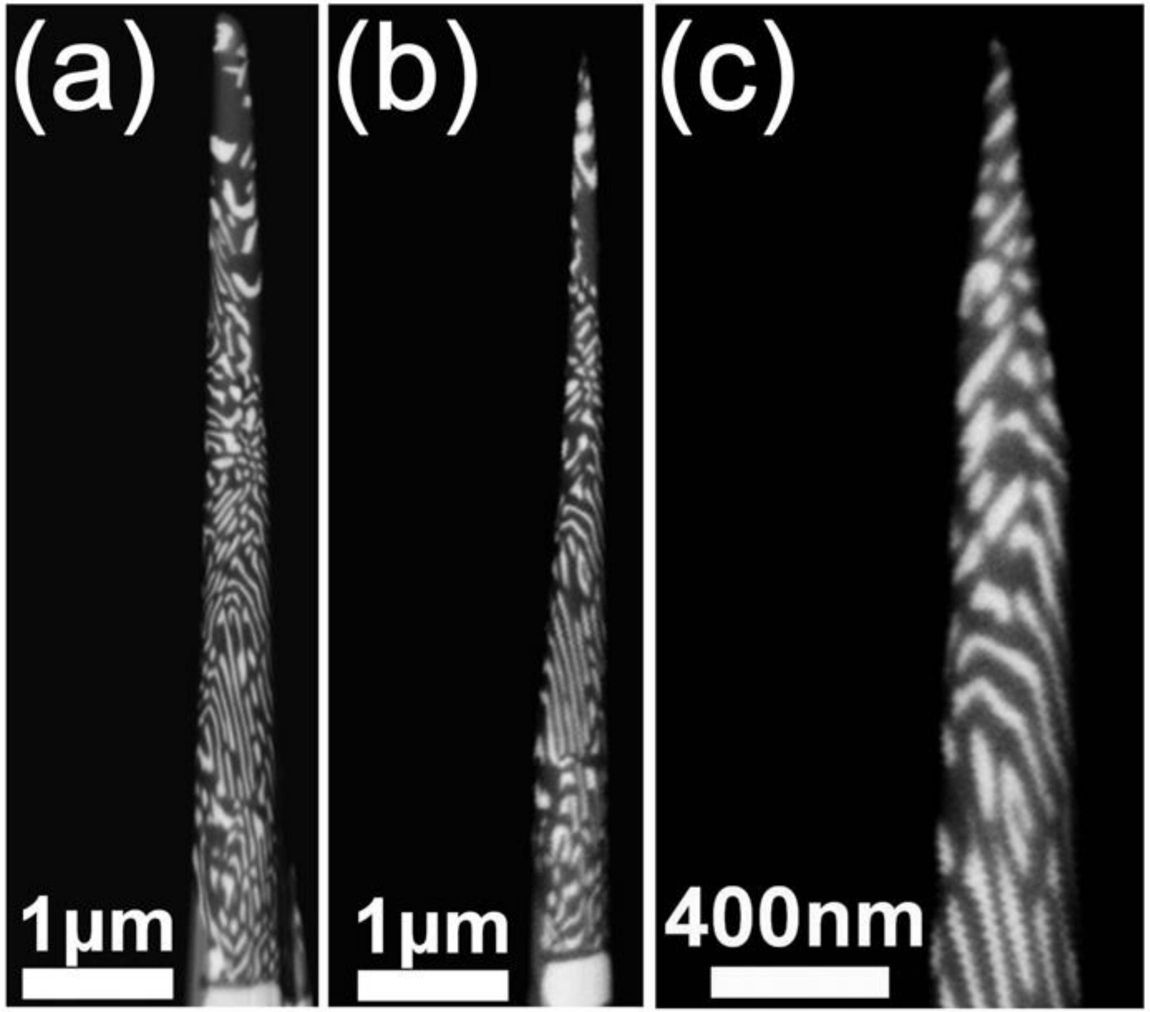
- Residual gas in a vacuum system is 90% H_2
  - H_2 is a difficult gas to pump
  - H_2 outgasses from the steel chamber

- Hydrogen in the analysis chamber leads to:
  - H composition measurement: not quantitative
  - Formation of hydrides which leads to mass interferences
    - AlH^+/Si^+ @28Da
    - SiH^+/P^+ @31Da ….
    - Biological Samples: $C_nH_m^{x+}$

Materials Applications

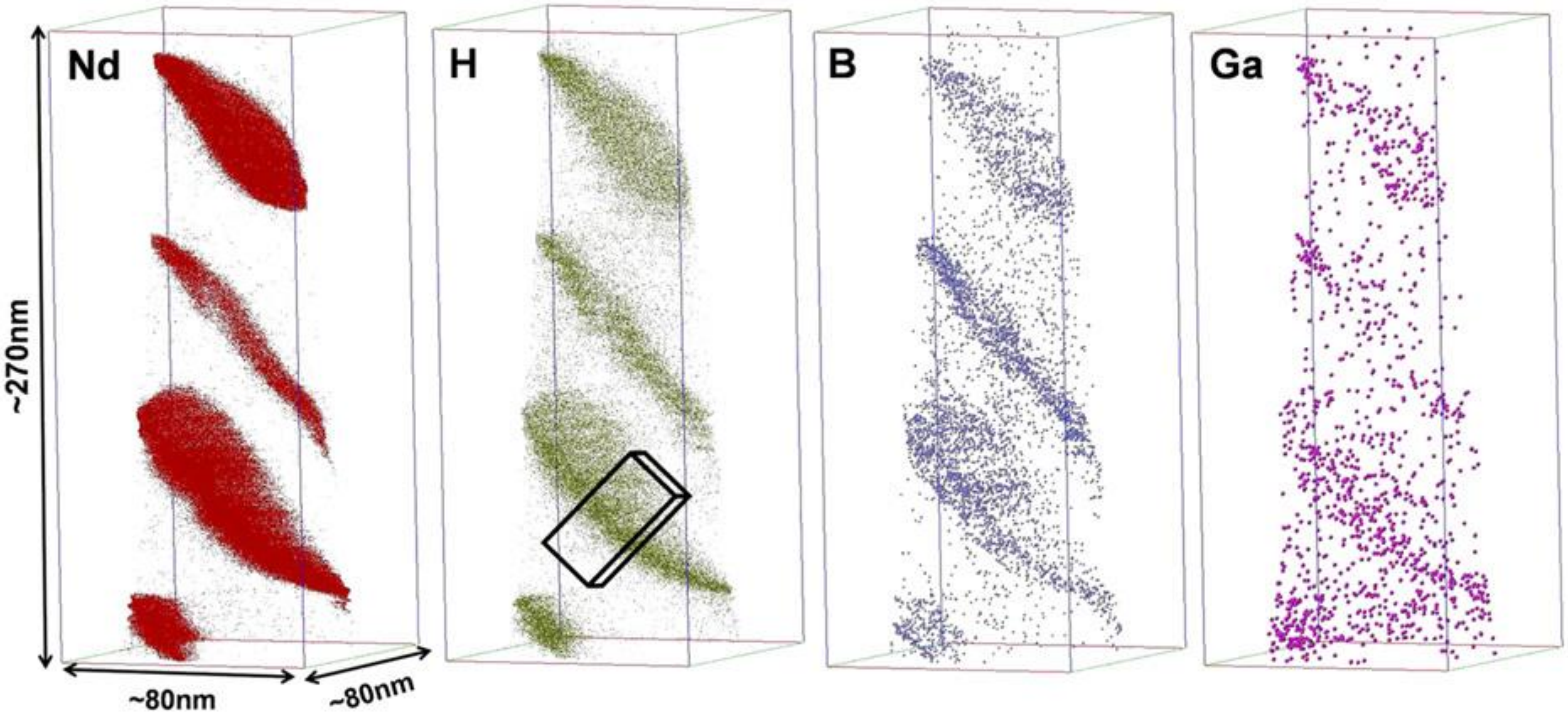
Hydrogen Mapping

Analysis of Hydrides in Hydrogen-Disporportionated Fe-Nd-B Powder



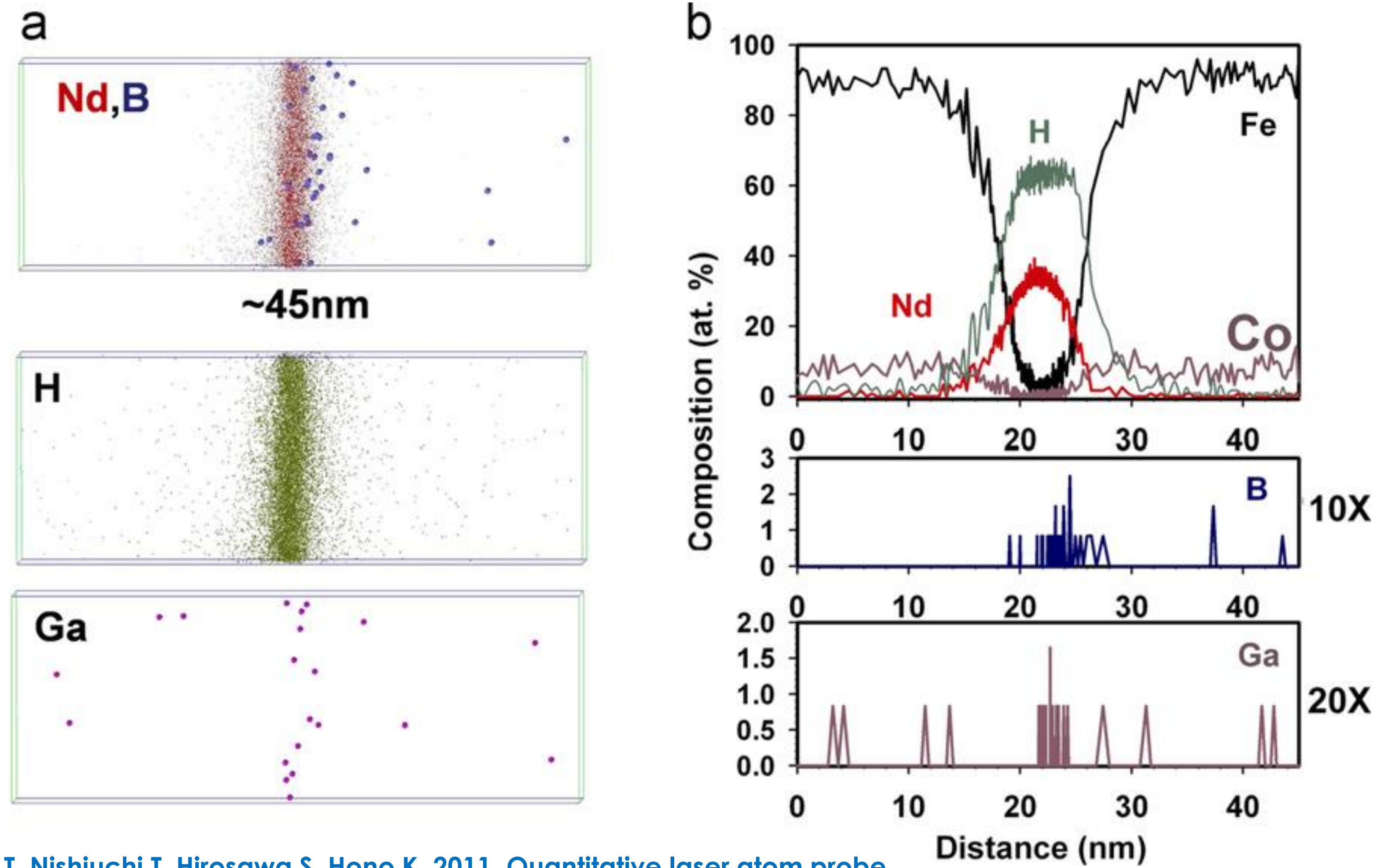
Sepehri-Amin H, Ohkubo T, Nishiuchi T, Hirosawa S, Hono K. 2011. Quantitative laser atom probe analyses of hydrogenation-disproportionated Nd-Fe-B powders. *Ultramicroscopy* 111:615-618.

APT Atom Maps of Fe-Nd-B Powder



Sepehri-Amin H, Ohkubo T, Nishiuchi T, Hirosawa S, Hono K. 2011. Quantitative laser atom probe analyses of hydrogenation-disproportionated Nd-Fe-B powders. *Ultramicroscopy* 111:615-618.

Composition Profile through NdH_2 Precipitate



Sepehri-Amin H, Ohkubo T, Nishiuchi T, Hirosawa S, Hono K. 2011. Quantitative laser atom probe analyses of hydrogenation-disproportionated Nd-Fe-B powders. *Ultramicroscopy* 111:615-618.

Cooperative APT and (S)TEM

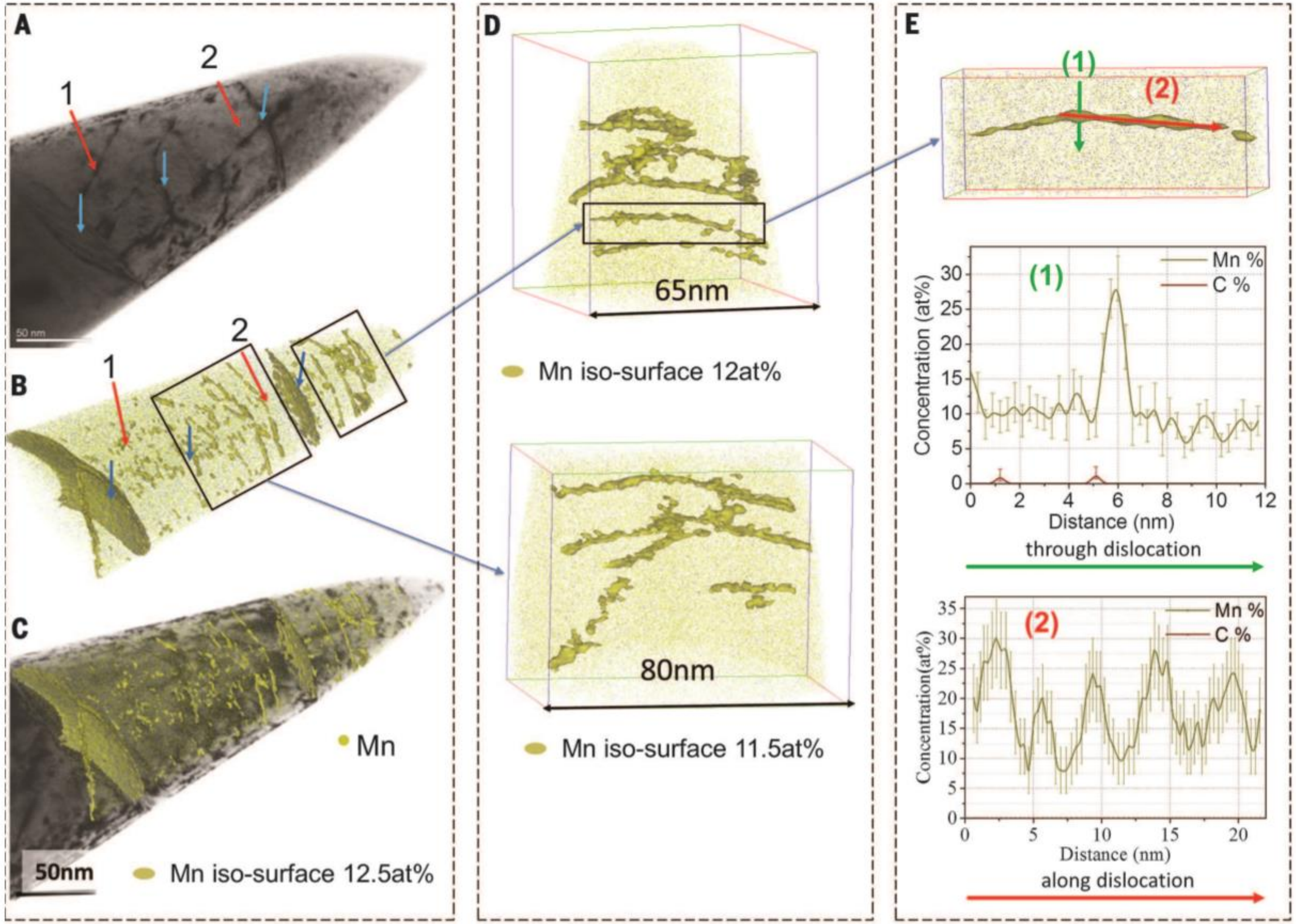
Correlative TEM and APT of Complexions

Linear complexions: Confined chemical and structural states at dislocations

M. Kuzmina, M. Herbig, D. Ponge, S. Sandlöbes, D. Raabe*

sciencemag.org SCIENCE

1080 4 SEPTEMBER 2015 • VOL 349 ISSUE 6252



Atomic-Scale Analytical Tomography

- (S)TEM tomography
  - Full (S)TEM imaging modes
  - Needle-shaped specimens
  - No missing wedge
- EDS adds compositional information
- EELS adds chemical sensitivity
- Diffraction adds atomic structure

+

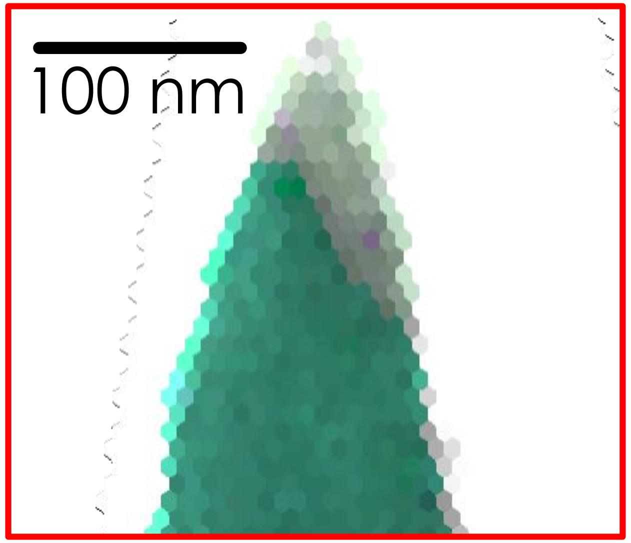
- Atom probe tomography provides 3D atom positions
  - Single atom analytical sensitivity
  - 0.2 nm spatial resolution in 3D
  - Cryo specimen stage (20K)

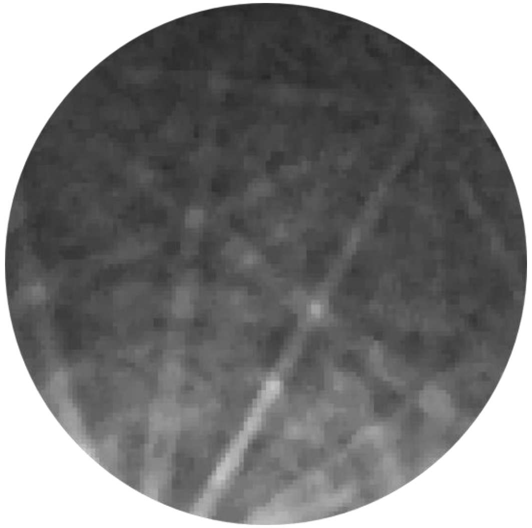
Analytical Tomography
+
Atom Probe Tomography

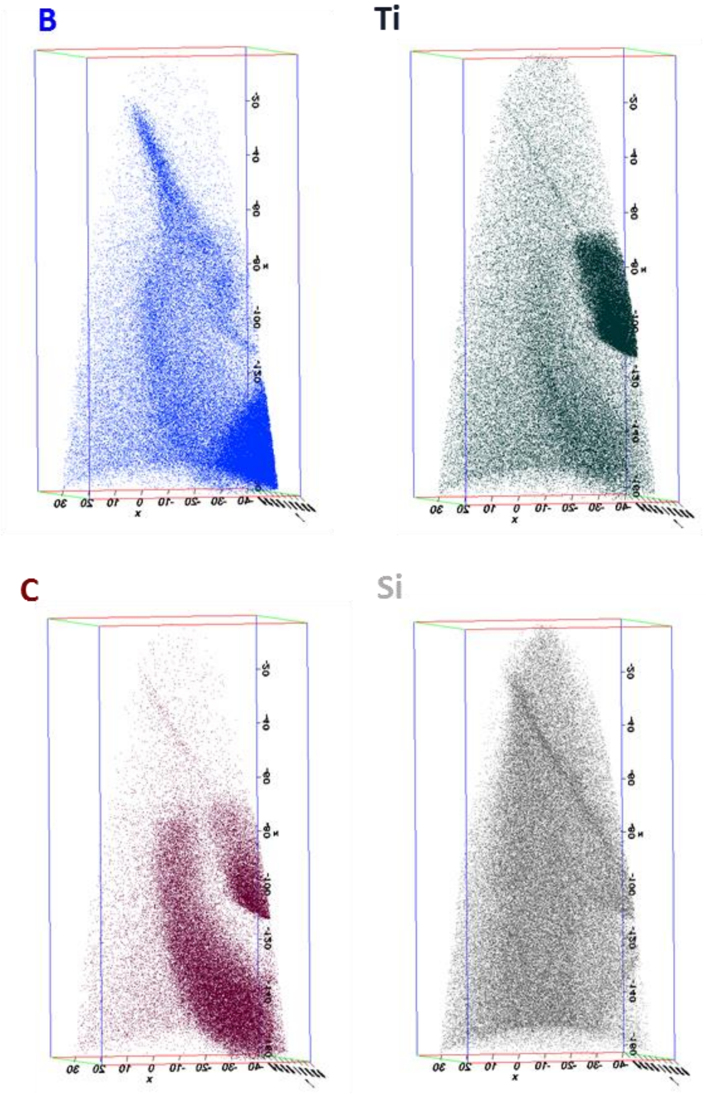
"Atomic-Scale Tomography: A 2020 Vision"
Thomas F. Kelly, Michael K. Miller, Krishna Rajan, and Simon P. Ringer, Microscopy and Microanalysis, Invited Review, vol. 19 (2013) pp. 652 – 664.

"Atomic-Scale Analytical Tomography"
Thomas F. Kelly, Microscopy and Microanalysis, vol. 23 (2017) pp. 34-45.

Illustration of Correlative Imaging Potential



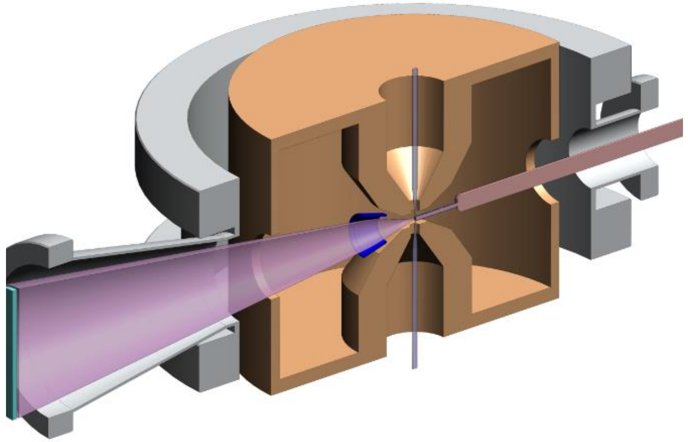




- Ni-base Superalloy
- TKD mapping of atom probe specimen
  - Grain Boundary character
- EELS spectra from grain boundary?
  - What effect does B have on grain boundary chemistry?

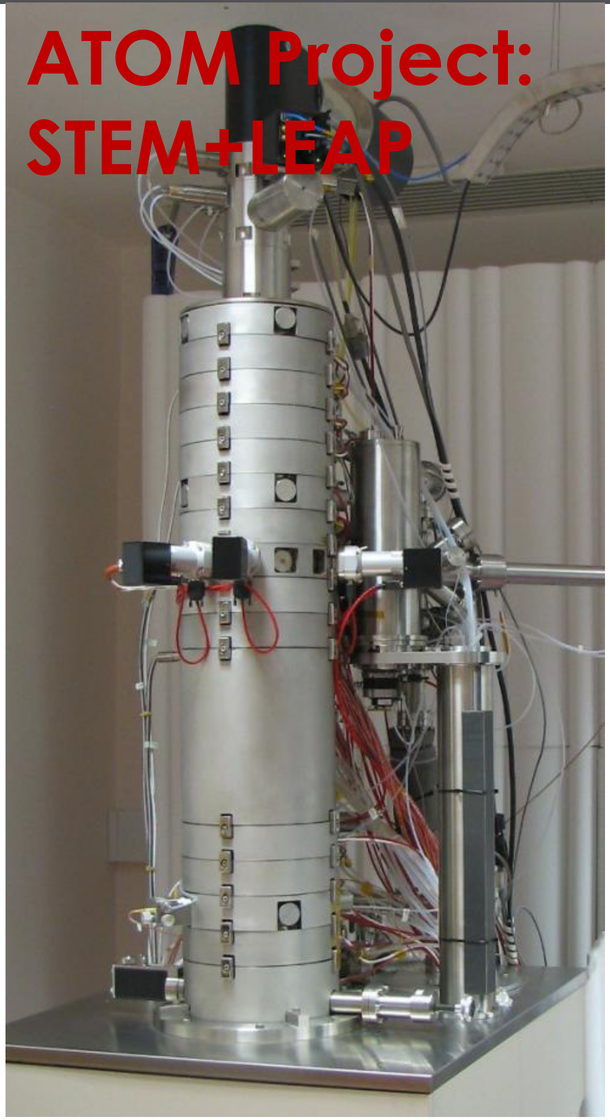
ATOM Project and Project Tomo

Project Tomo: TEM+LEAP

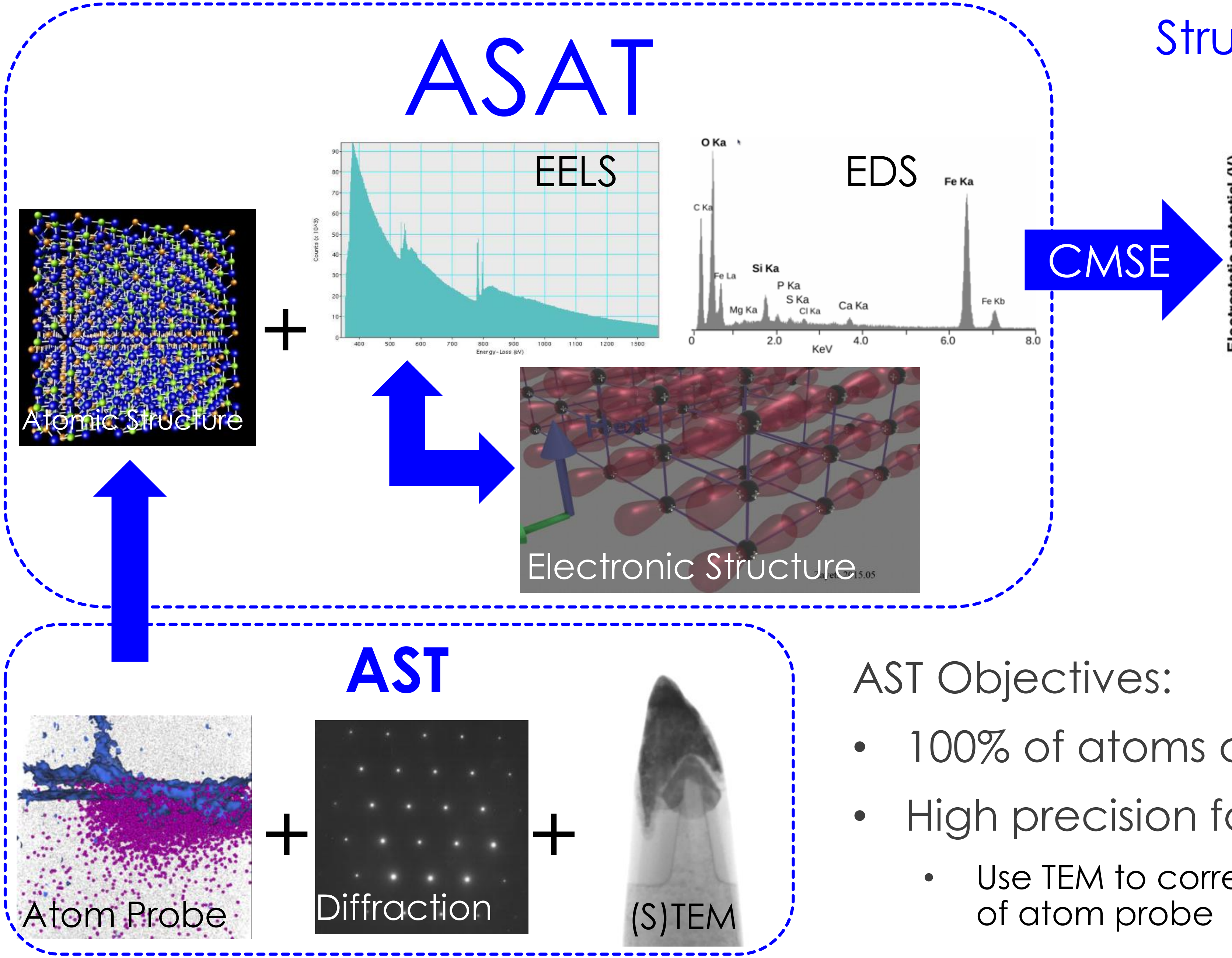


Build objective lens assembly with atom probe inside

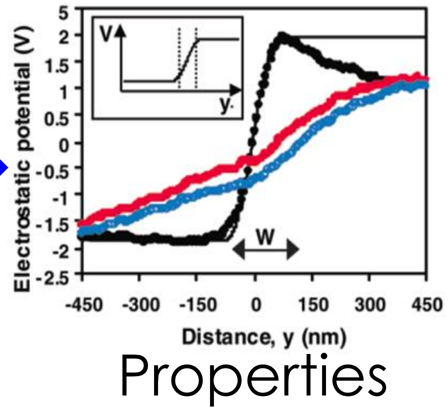
ATOM Project: STEM+LEAP



Collaborators
ATOM Project: Michael Miller, Krishna Rajan, Simon Ringer, Brian Gorman, Ondrej Krivanek and Niklas Dellby
Project Tomo: Rafal Dunin-Borkowski, Joachim Mayer, Dierk Raabe, Max Haider



Structure-Properties Microscopy



AST Objectives:

- 100% of atoms detected
- High precision for atom positions
  - Use TEM to correct trajectory aberrations of atom probe