Atom Probe Tomography (APT)
A new window to nanogeochemistry

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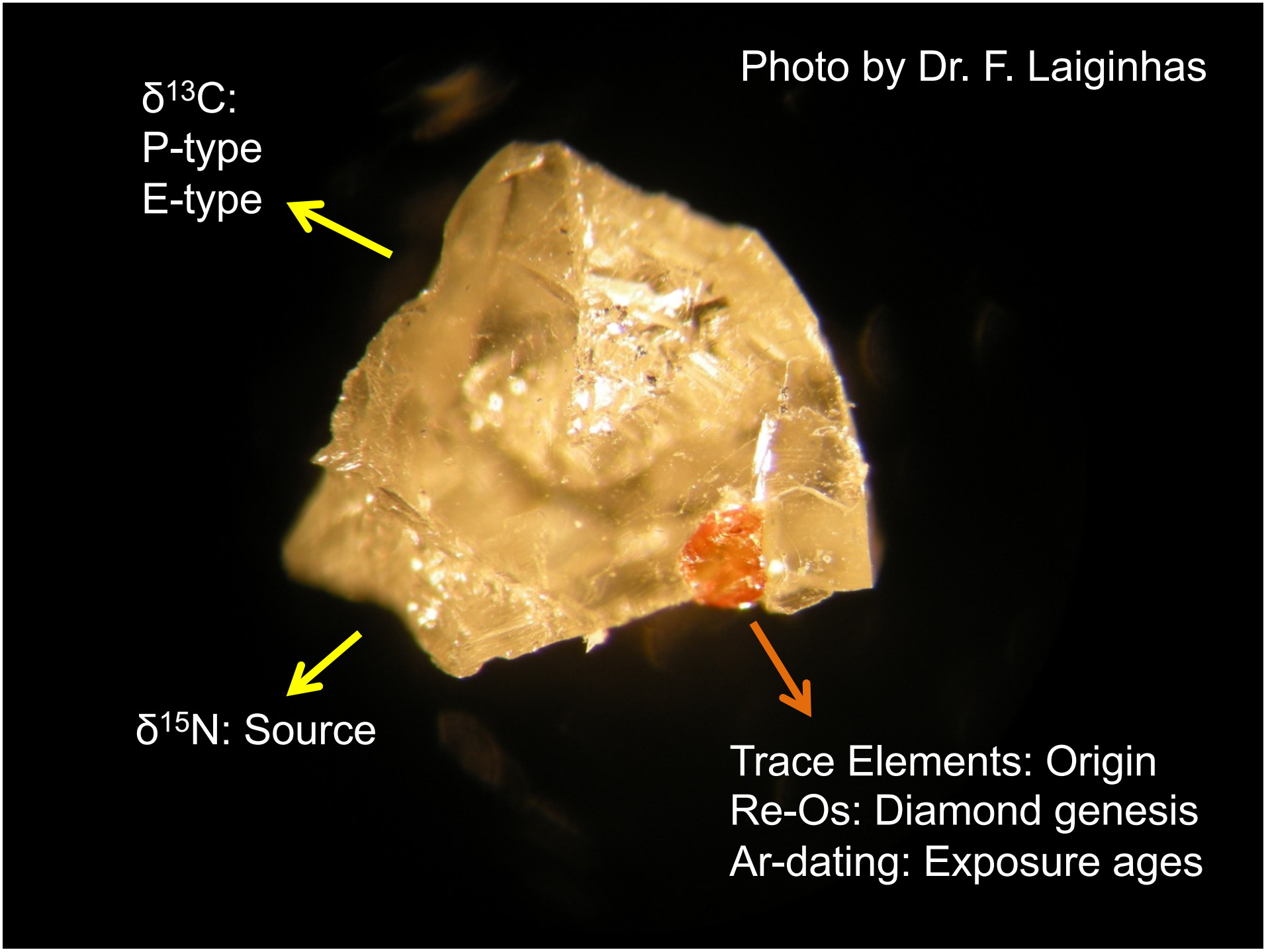
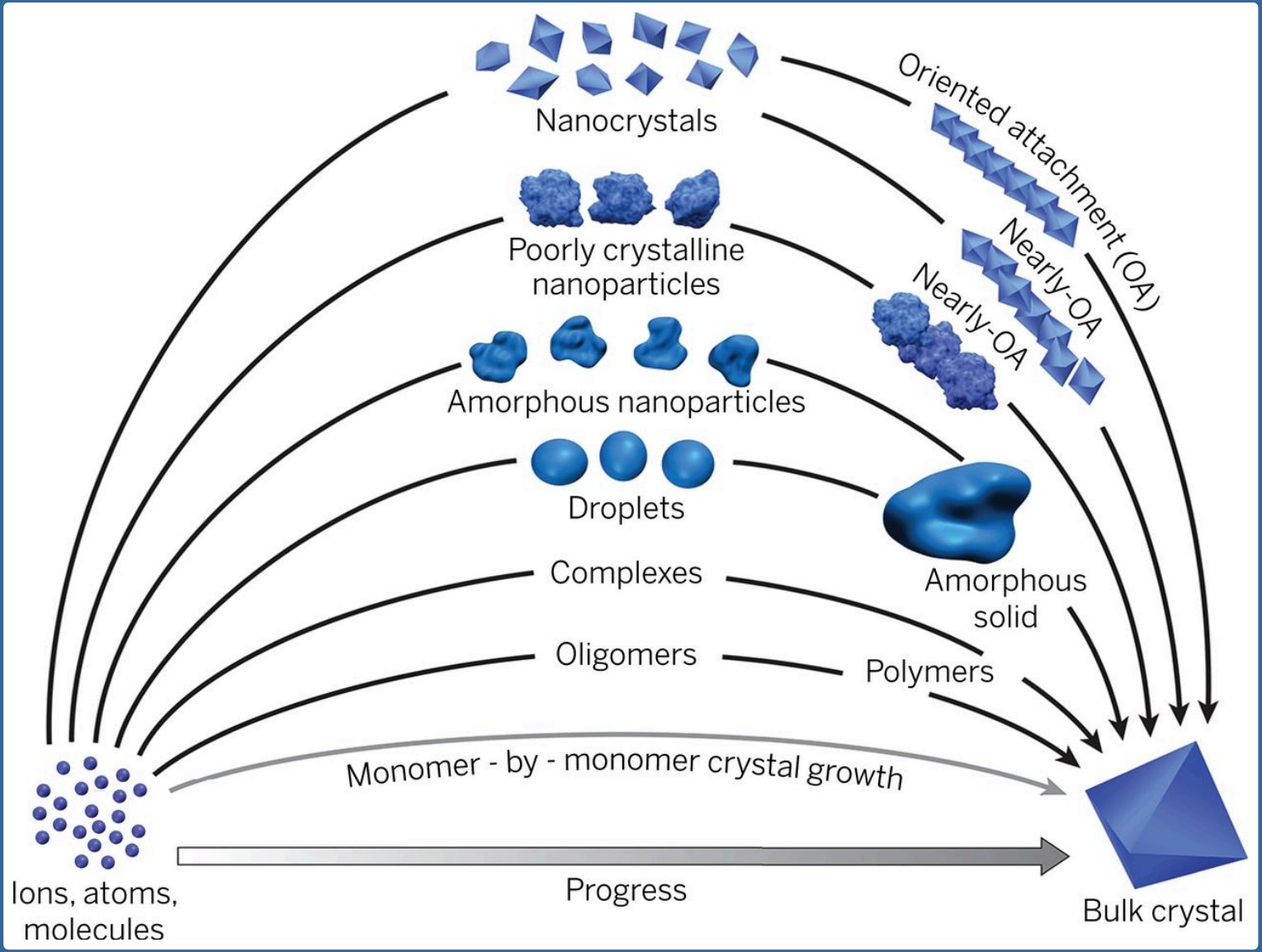
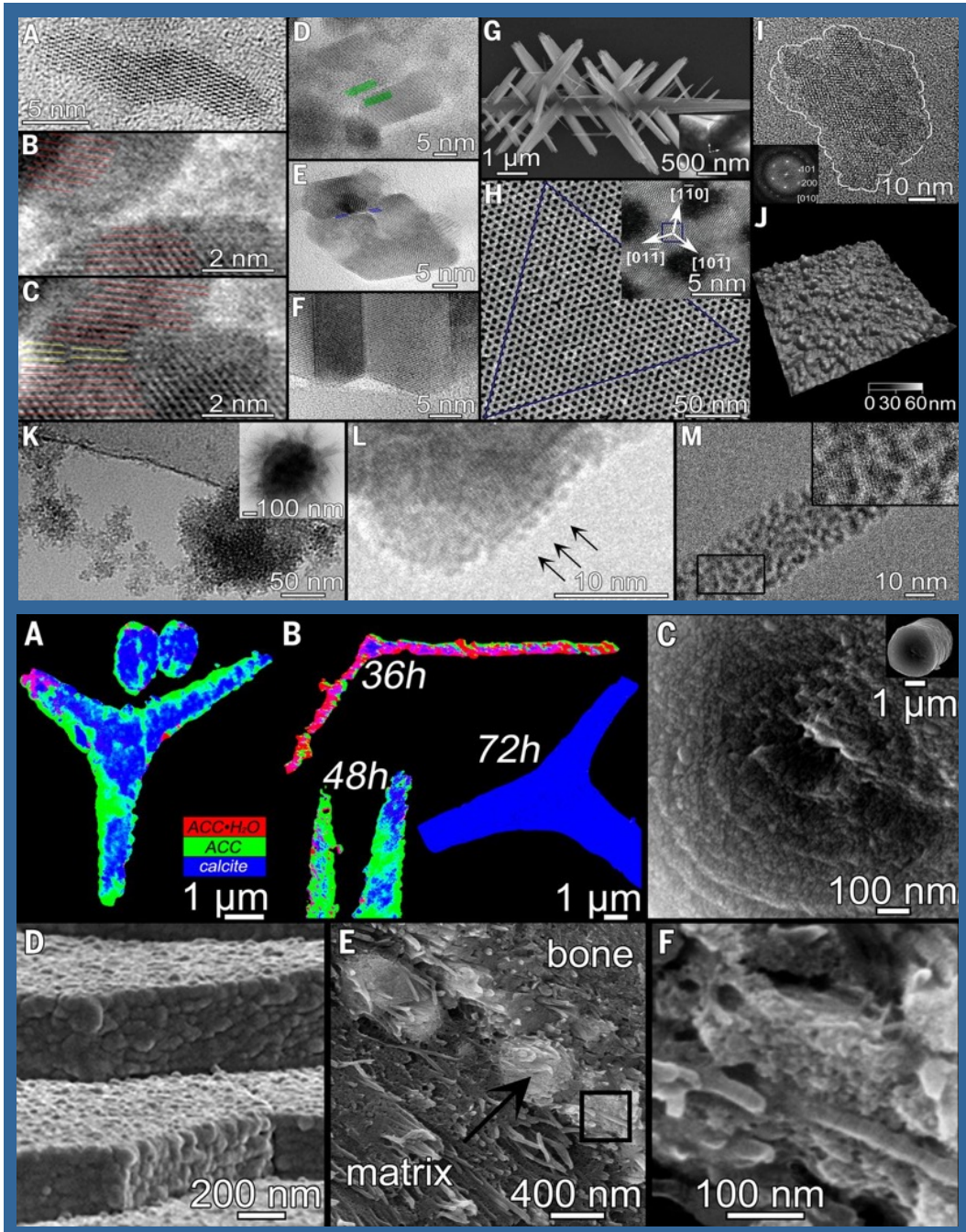


Photo by Dr. F. Laiginhas
δ13C:
P-type
E-type
δ15N: Source
Trace Elements: Origin
Re-Os: Diamond genesis
Ar-dating: Exposure ages

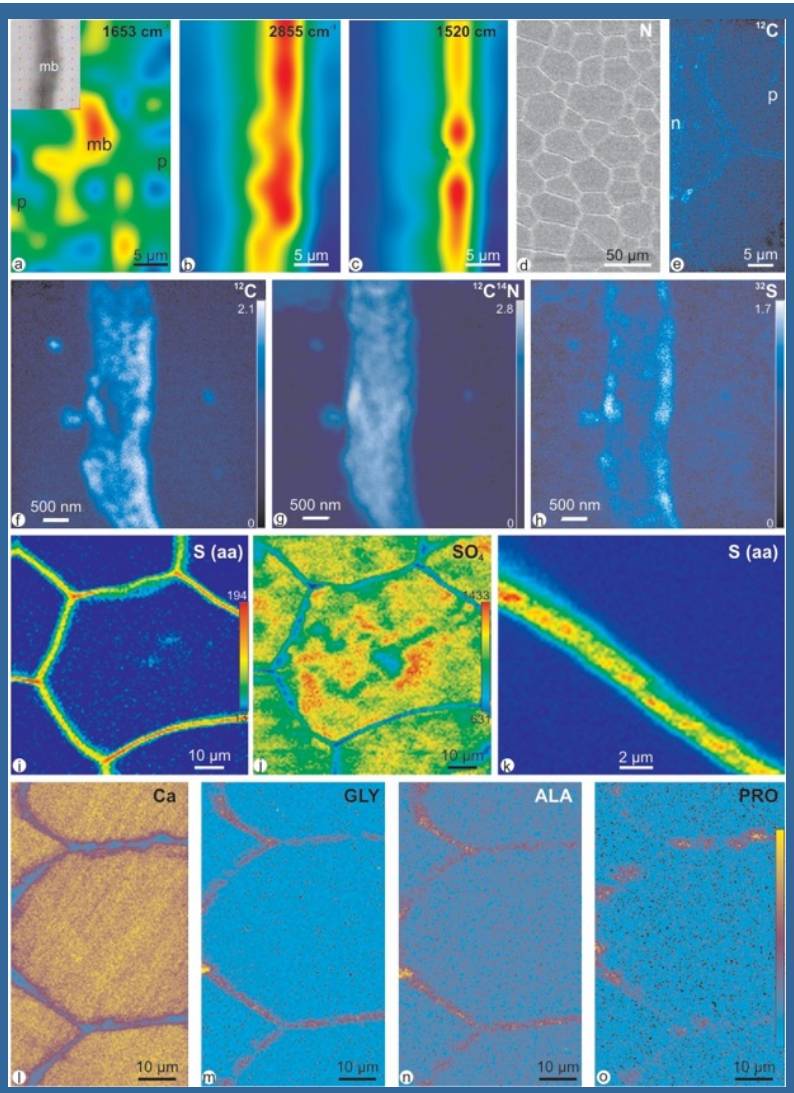
Crystallization Pathways



De Yoreo *et al*. (2015) - Science



De Yoreo *et al*. (2015) - Science

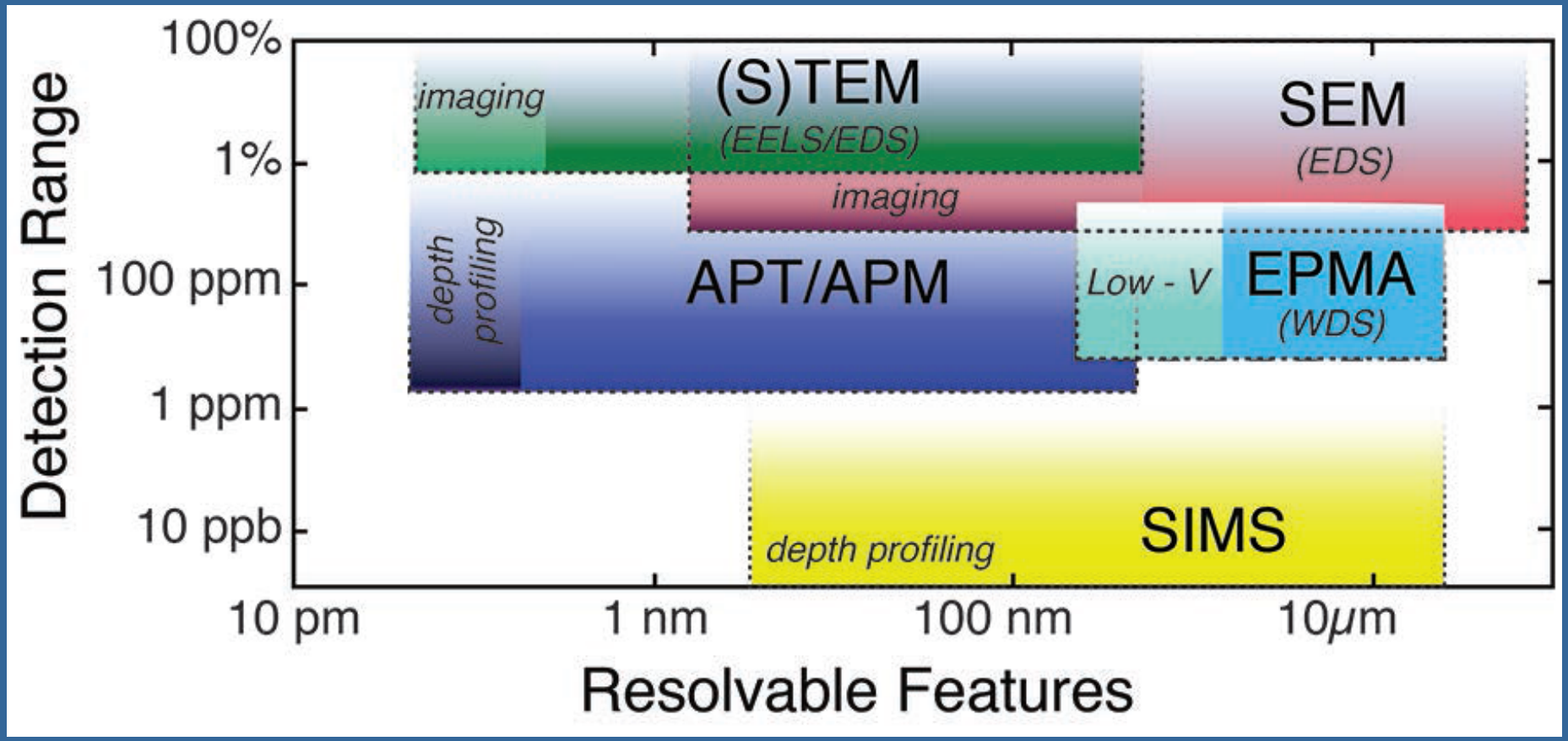


Techniques:

- **FTIR (amide I/II; lipids)**
- **NanoSIMS**
- **XANES**
- **TOF-SIMS**

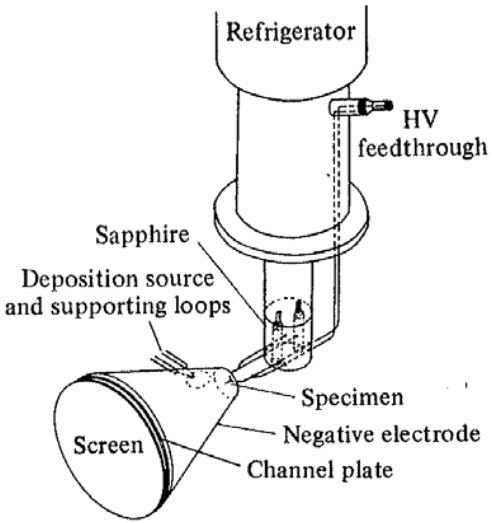
Dauphin *et al.* (2010)-Microscopy & Microanalysis

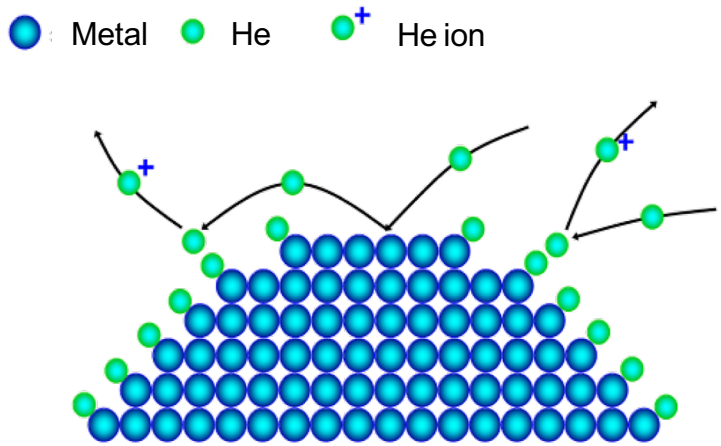
Atom Probe Tomography (APT)

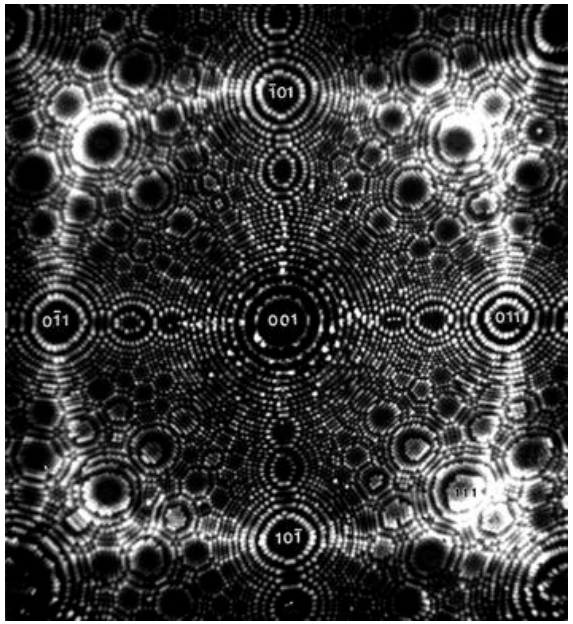


Valley *et al.* (2015) – American Mineralogist

Field Ion Microscopy (FIM)







https://www.researchgate.net/publication/278649966/figure/fig12/Figure-14-4-FIM-001-image-for-platinum-Some-plane-normals-or-poles-are-indexed.png

- Use of an image gas (He and Ne are common) coupled with a very sharp specimen tip that has a standing voltage
- The gas molecule (atom) becomes polarized in the electric field
- Atom is attracted to the specimen surface (field adsorbed)
- Electrons from the adsorbed gas tunnel into the specimen results in the formation of a gas ion and field ionization
- The ion then accelerates to detector (microchannel plate) which creates an electron cascade and projected onto a phosphorus screen yielding an atomic image

From FIM to Atom Probe

- Increasing the voltage will result in the atoms on the surface to field evaporate
- By capturing the atoms (now ions), via a time of flight mass spectrometer with a position sensitive detector, the atom probe is realized!

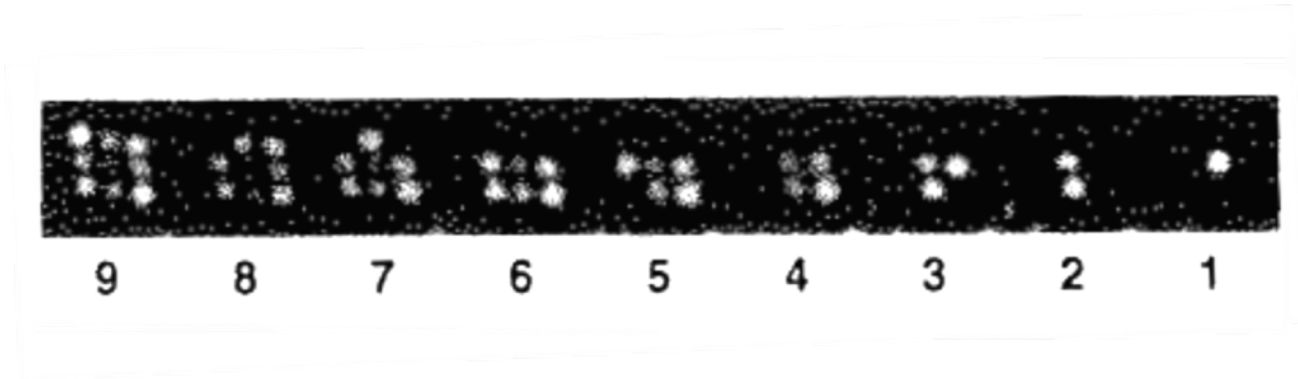
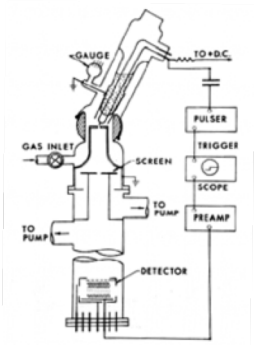
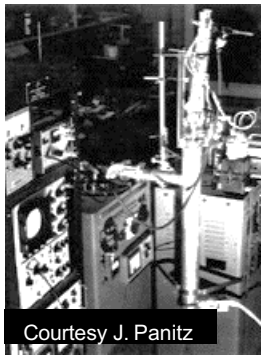


Image of one atom at a time field evaporating from a Ni-Zr catalyst. Takenfrom M.K. Miller Atom Probe Tomography: Analysis at theAtomic Level (2000)

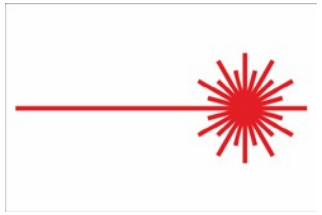
Some Historical Developments of the Atom Probe

1-Dimensional Atom Probe
Mueller, Panitz, McLane Rev. Sci. Instrum. (**1968**)




Courtesy J. Panitz

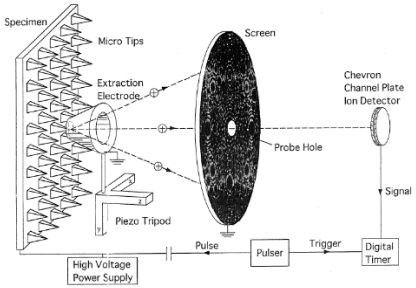
Laser assisted field evaporation
Tsong and Kellogg JAP (**1980**)



Position-Sensitive or 3-Dimensional Atom Probe
G.W. Smith, A. Cerezo - Oxford
M.K. Miller – ORNL
(circa **1986-89**)

http://atomprobe.materials.ox.ac.uk/uploads/images/3dAP.png

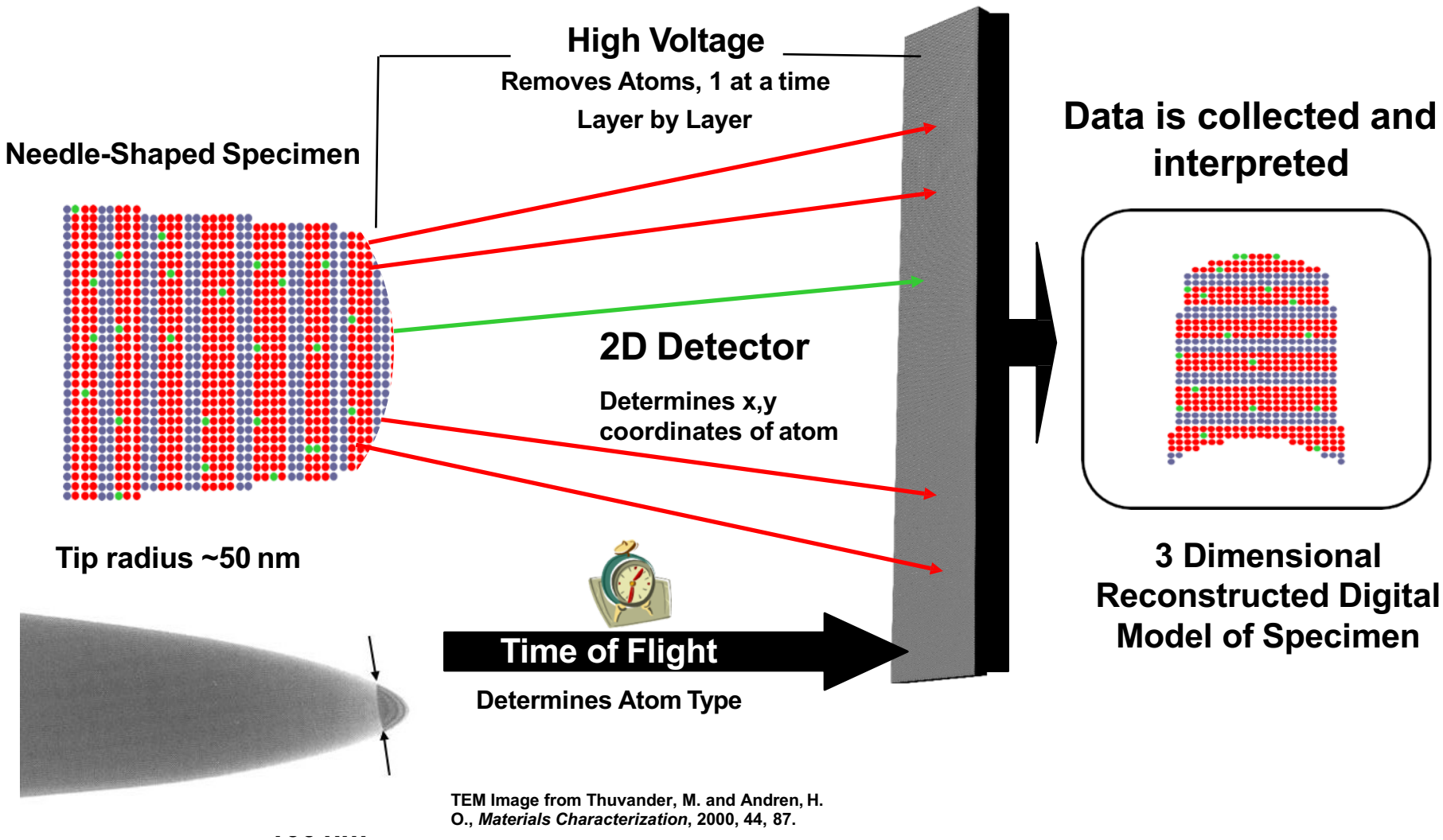
Scanning Atom Probe
Nishikawa, Kimoto
Appl. Surf. Sci. (**1994**)



Local Electrode Atom Probe (LEAP)
T. Kelly et al. (circa **2003**)

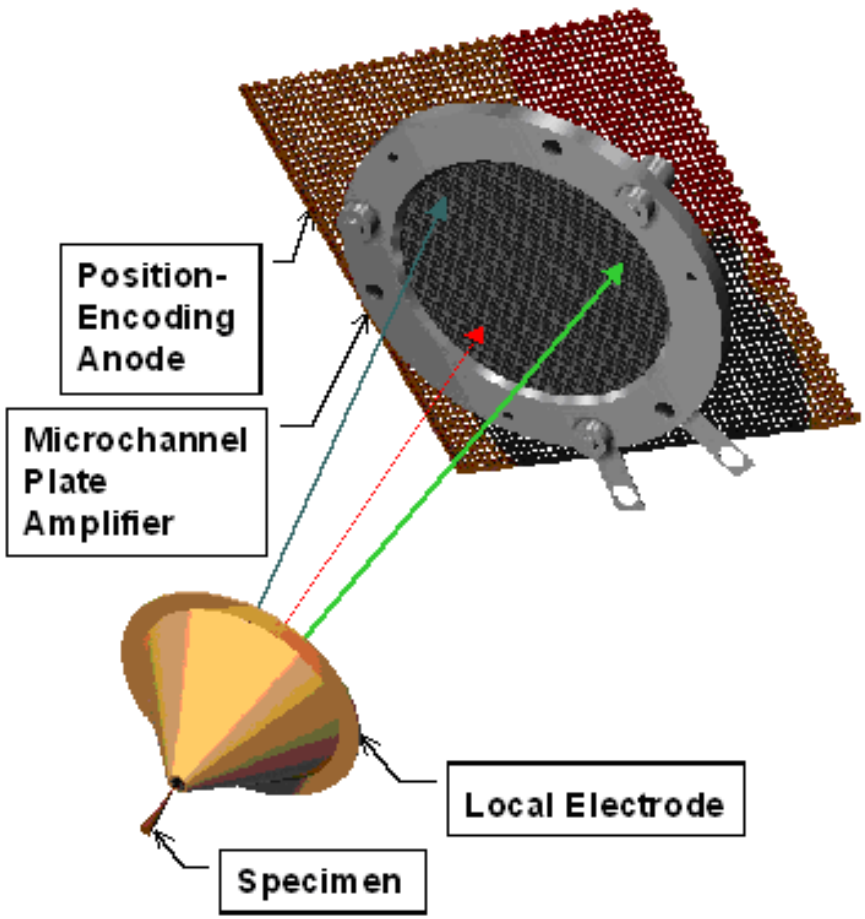
Advanced laser integration and detectors
Cameca 5000-series LEAP (**today**)

How does it work?

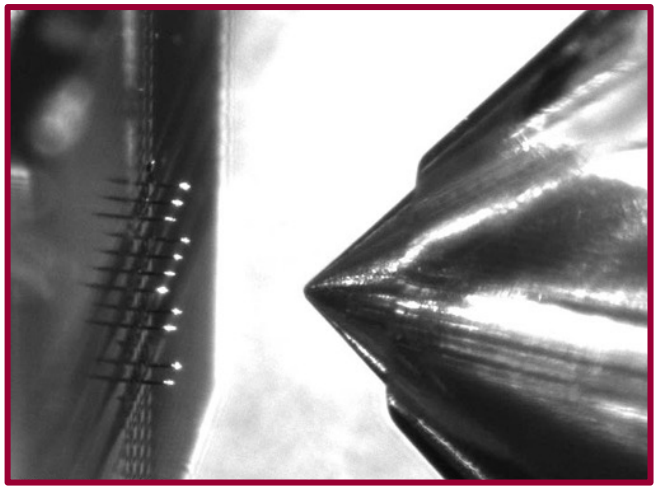


TEM Image from Thuvander, M. and Andren, H. O., *Materials Characterization*, 2000, 44, 87.

Why a Local Electrode?

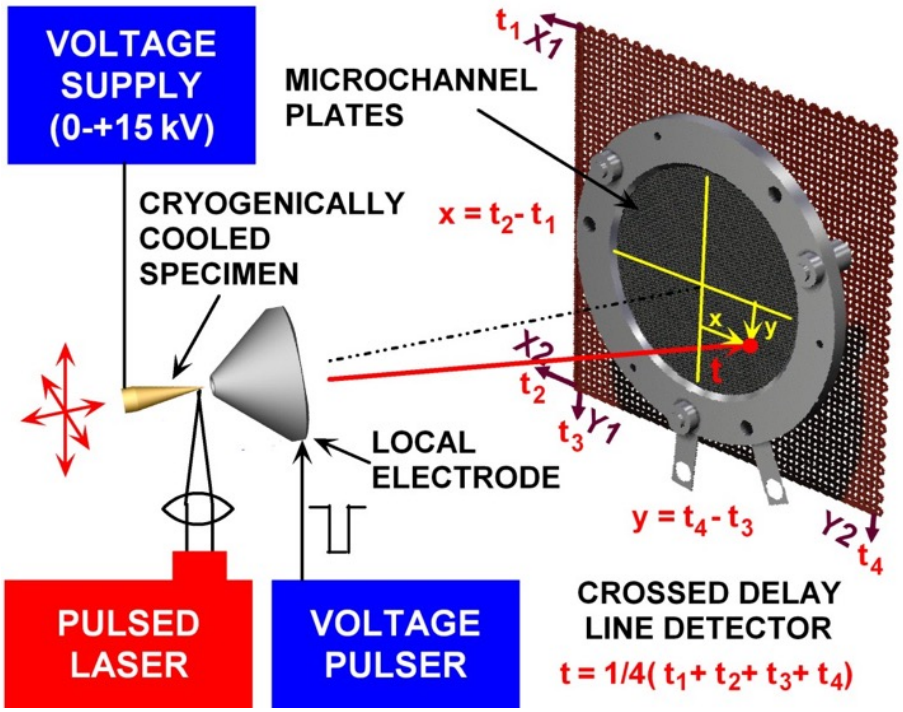


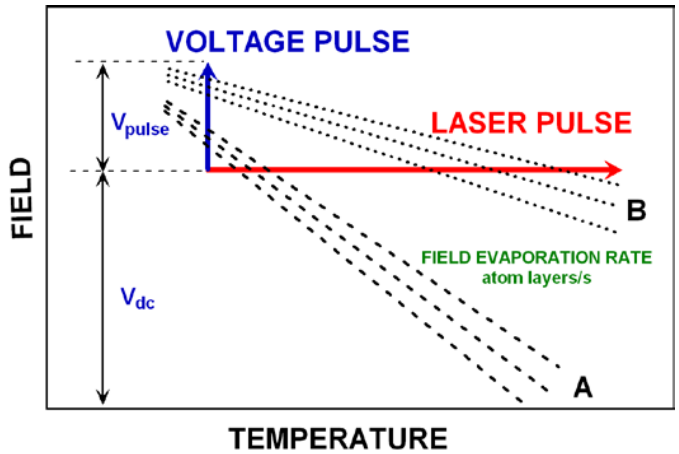
- Step-and-repeat analysis
- **Wide field-of-view**
- Conical cone enhances the fields resulting in lower applied voltage → **Higher data collection rates** (1.5 kHz to 200+ kHz)
- Good mass resolution (> 1/500 FWHM)
- High speed (up to 20,000 atoms/second)
- Cone also serves as a Faraday cage and shields ions from time-varying field effects from pulse



Laser Pulsing

Extending the capability to more materials



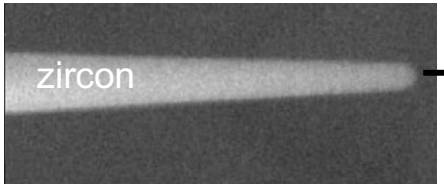


- Instead of applying a voltage pulse to field evaporate atoms, a short duration laser pulse is used to momentarily heat the specimen so that field evaporation occurs on the standing voltage.
- An additional advantage of laser pulsing is that under the correct experimental conditions, an improvement in the mass resolution may be obtained.
- **Low electrical conductivity materials now accessible**

Slide text and figures courtesy of MK Miller, ORNL

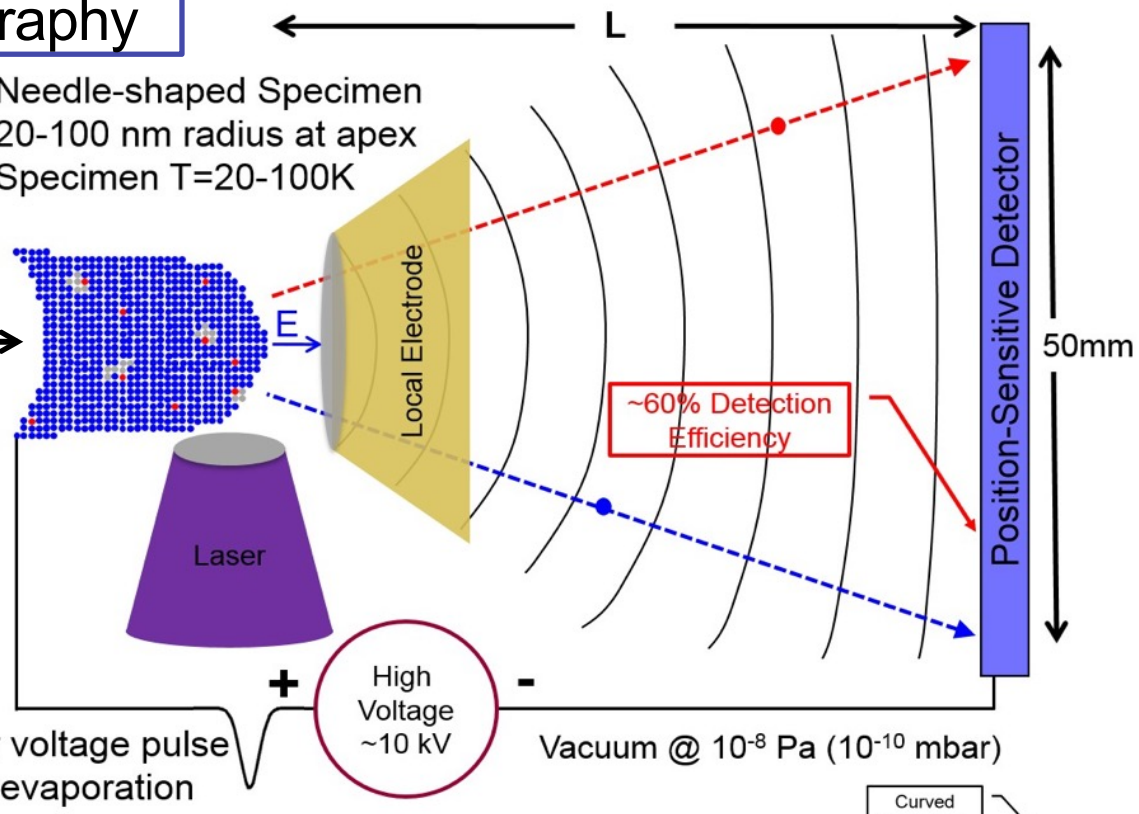
Atom Probe Tomography

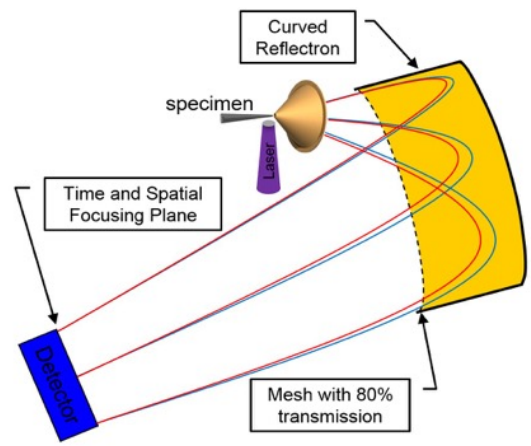
Sample zircon



100 nm

Valley et al. 2015 Am Min

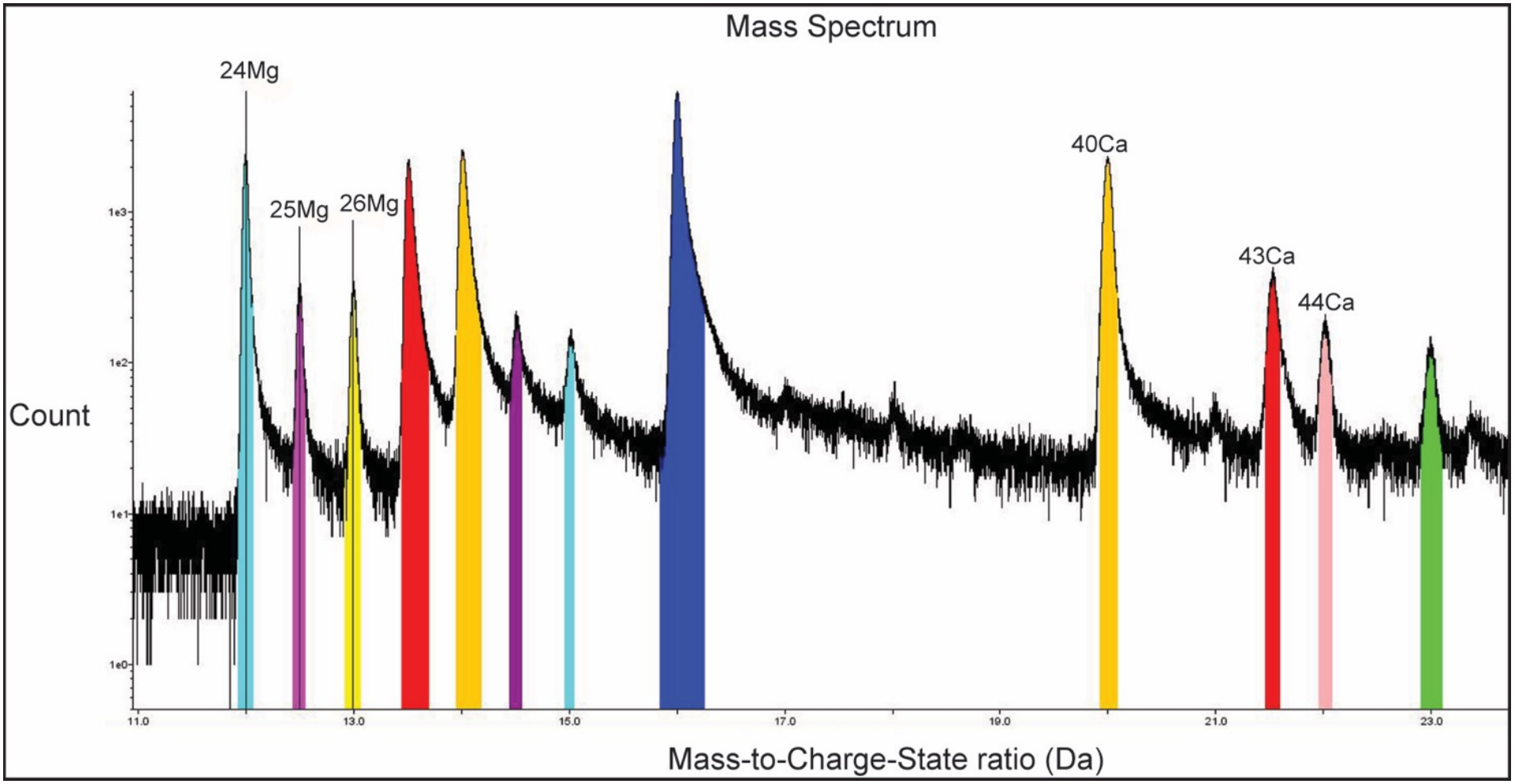


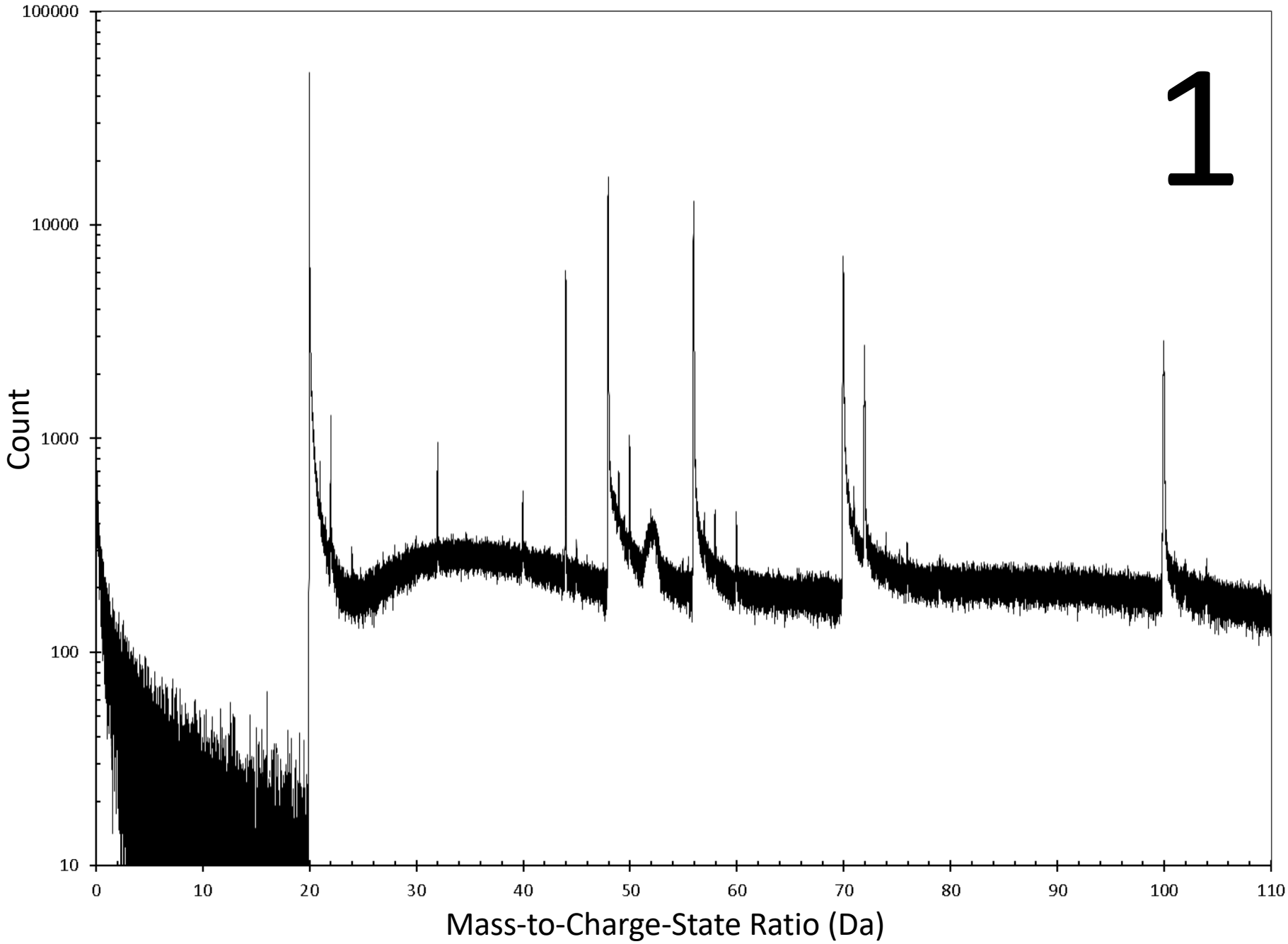


CAMECA

J.W. Valley, Geosciences Atom Probe Tomography (APT) Workshop,
University of Alabama, Jan. 29 -30, 2016

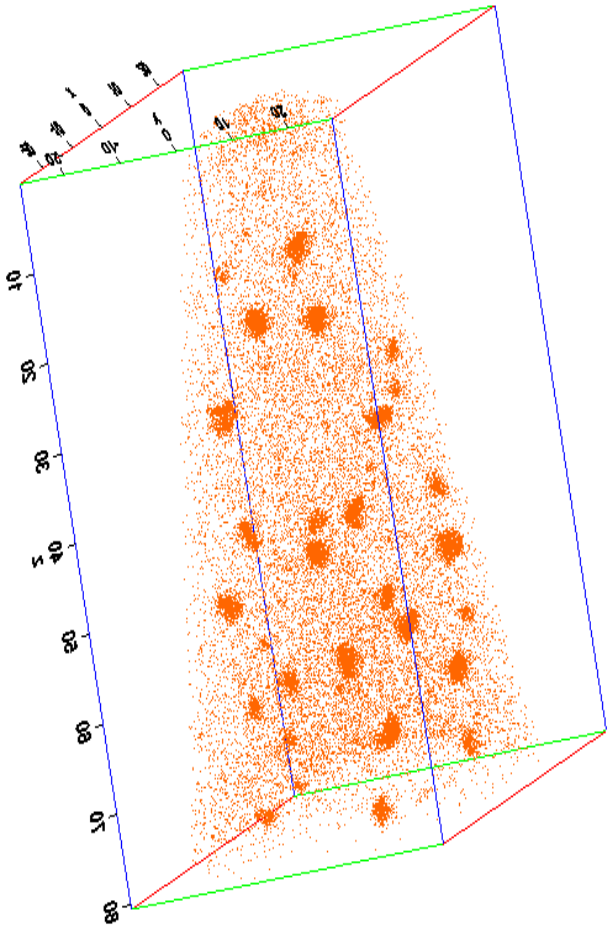
How does data look like?




1
Count
100000
10000
1000
100
10
0
10
20
30
40
50
60
70
80
90
100
110
Mass-to-Charge-State Ratio (Da)

VISUALIZATION: Atom Maps

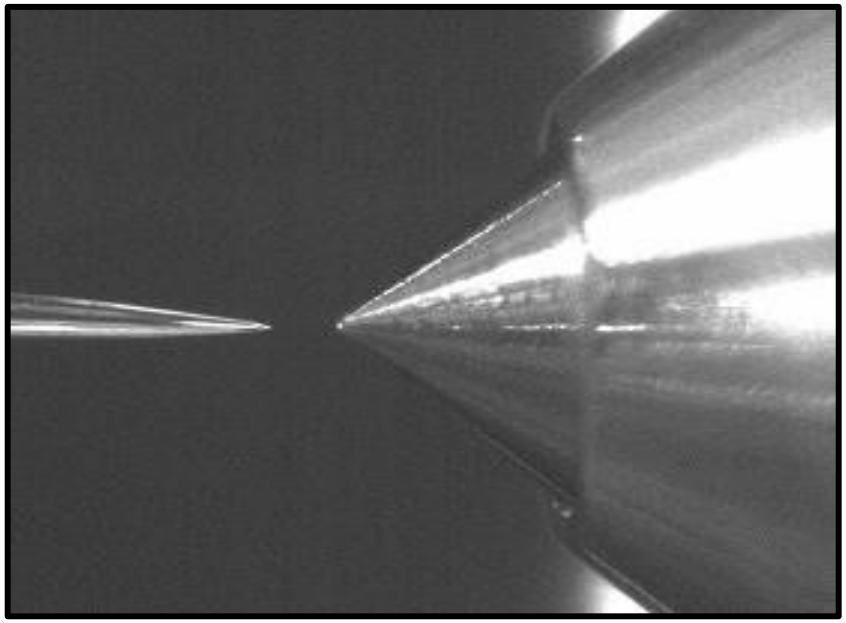
Cu

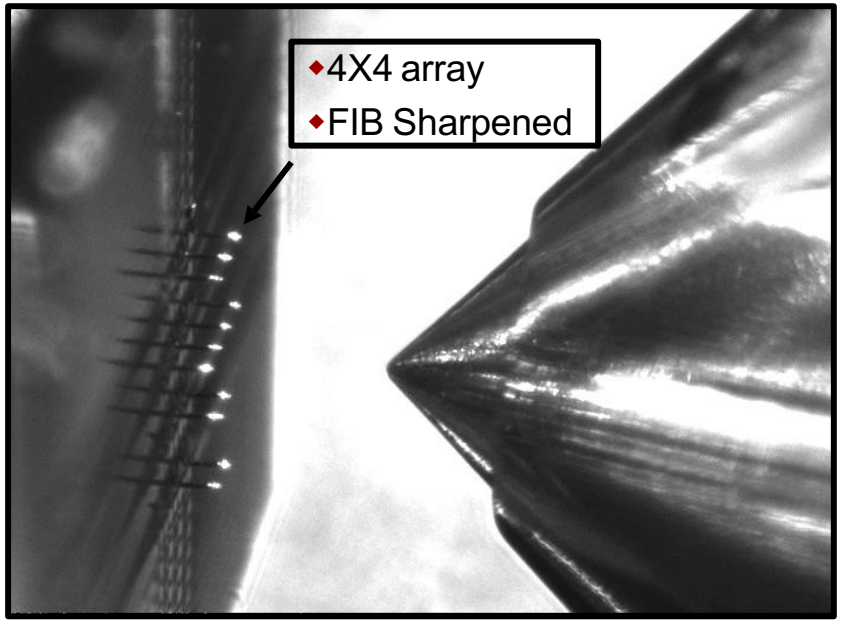


$(Co_{0.95}Fe_{0.05})_{88}Zr_6Hf_1B_4Cu_1$

- Atom maps are reconstructed from thousands of slices each containing a few atoms.
- Each atom is represented by a sphere, user selects the color choice and size.
- Atom probe tomography (APT) permits the reconstruction of a small volume by determining the spatial coordinates and the mass-to-charge ratios of the atoms in the volume.

Sample Preparation





Needle

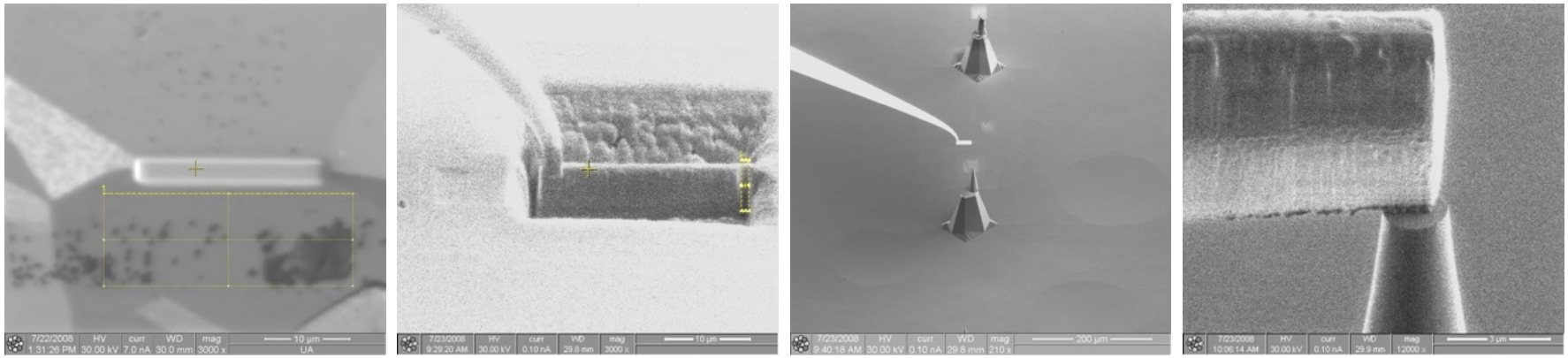
Tip radius ~50 nm

Microtip Array

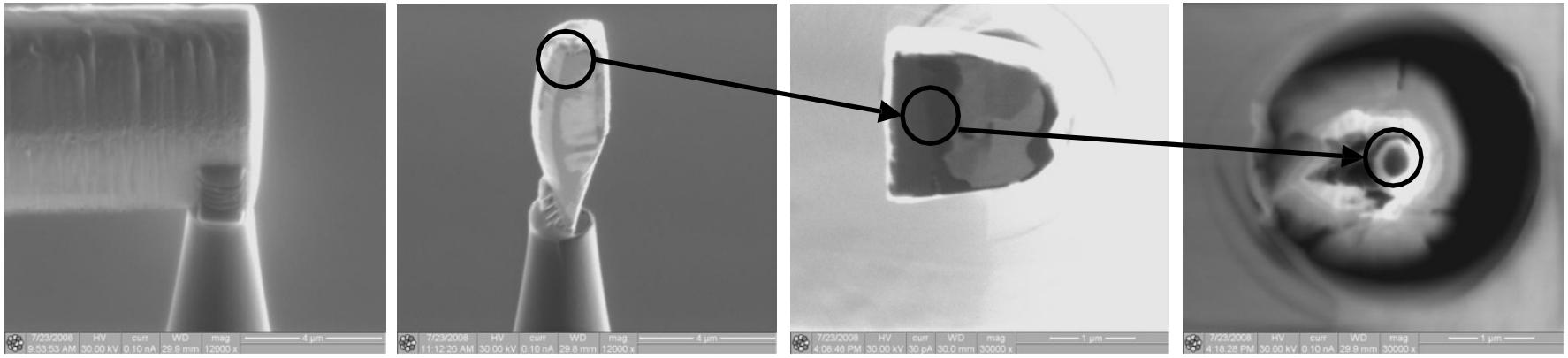
Local electrode "localizes" field, both needles and microtips can be analyzed

TESCAN LYRA XMU FIB/FE-SEM

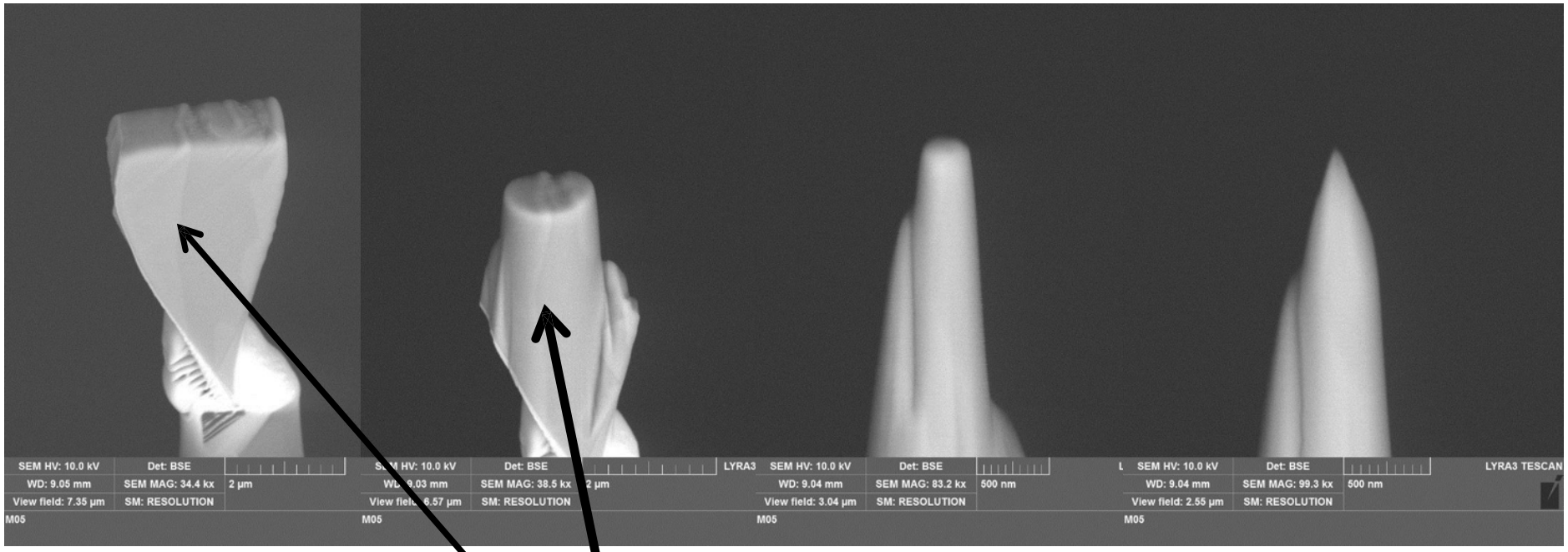
Focused Ion Beam (FIB)



Select GB area, mill away section for in-situ lift out, position wedge to Si substrate

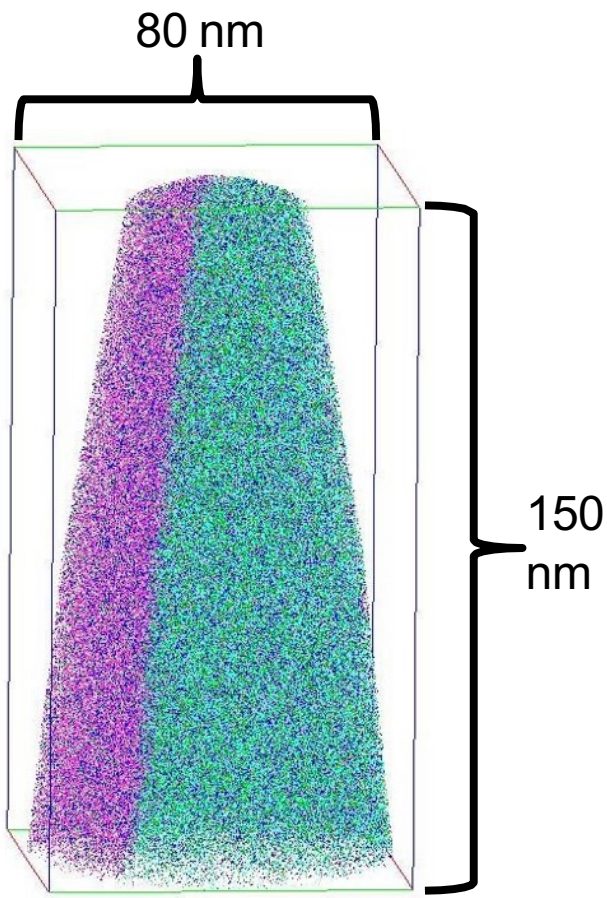


Attach wedge, image side and top w/ ion beam reveals GB, FIB mill AP specimen along GB

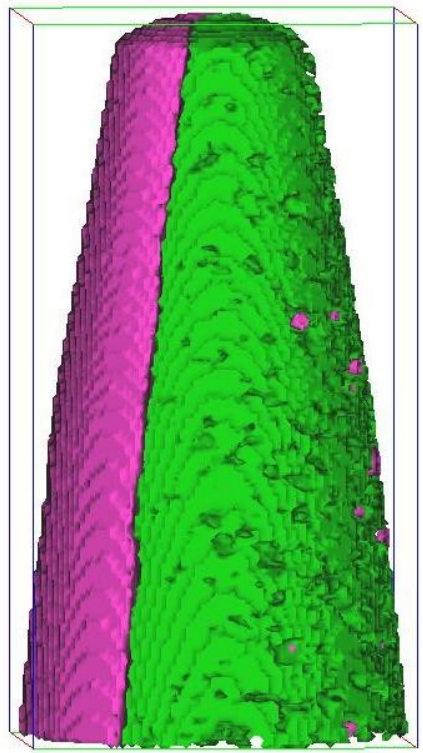


Section of wedge before milling

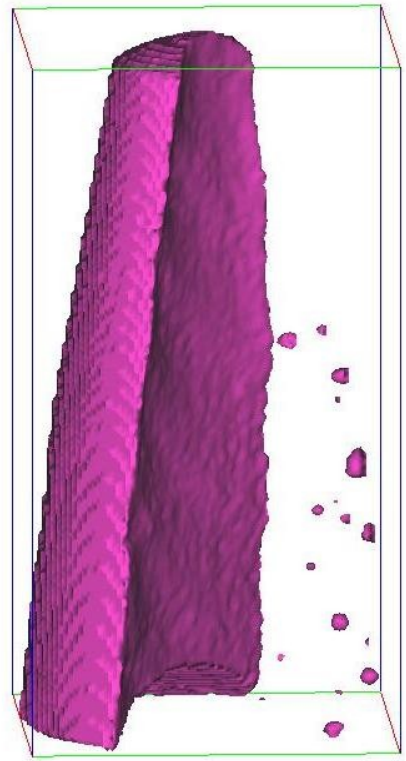
Annular mill using FIB to produce needle shaped Atom Probe specimen, notice grain boundary at apex



Cr/Ni atoms



Cr/Ni “iso-surface”

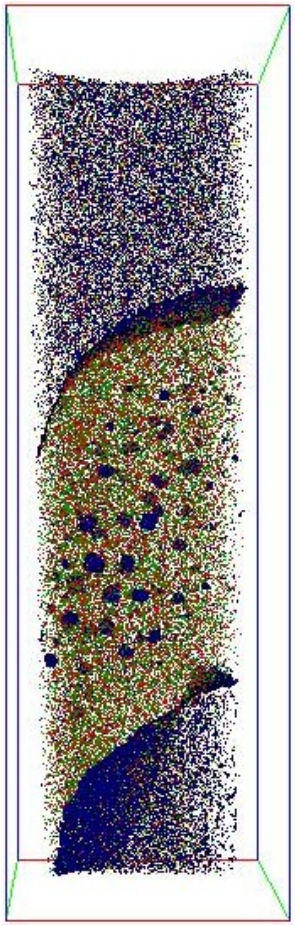


Cr-rich side “iso-surface”

Grain boundary, normal incidence to analysis direction

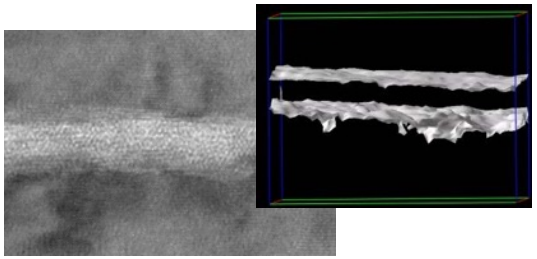
Applications of Atom Probe Tomography

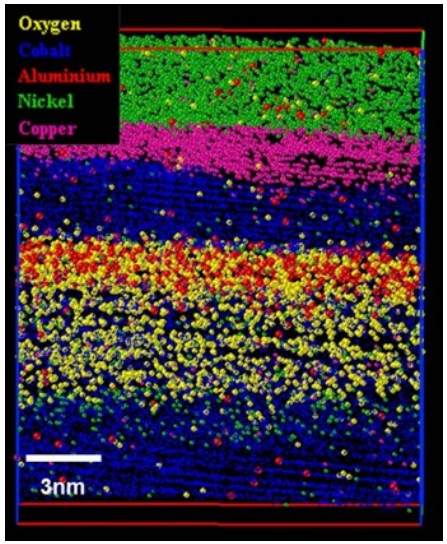
Ferritic Superalloys



C. Stallybrass, G. Sauthoff and A. Schneider, Max Planck Institute fur Eisenforschung, Dusseldor

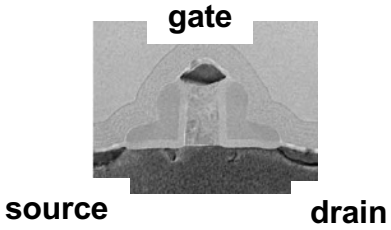
Magnetic Sensors

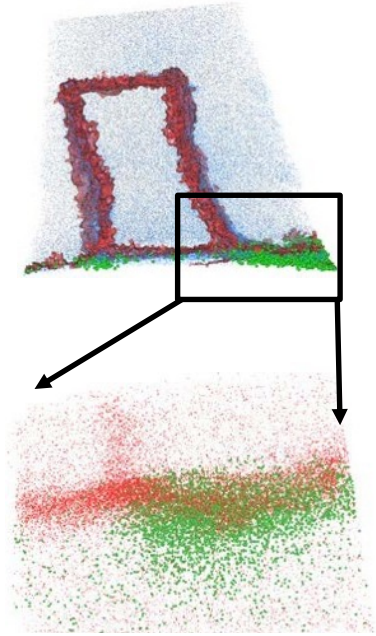




AK Petford-Long, et al., *Journal of Applied Physics* 98 (2005) 124904

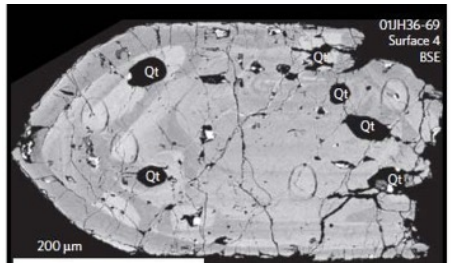
Semiconductor Transistors

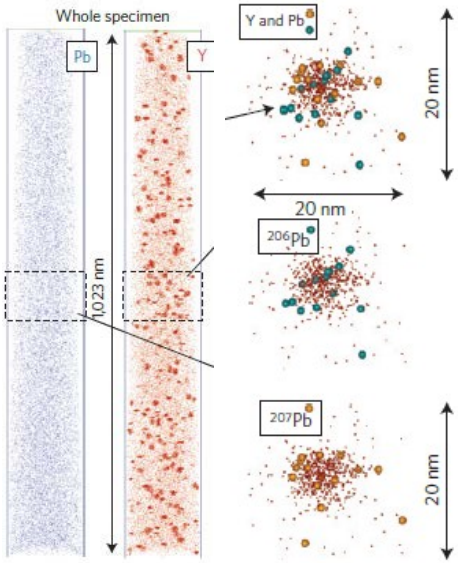




K. Jones, et al.,"Atom Probe Characterization of Magnetic and Semiconductor Device Structures"

4.4 Gyr Zircon





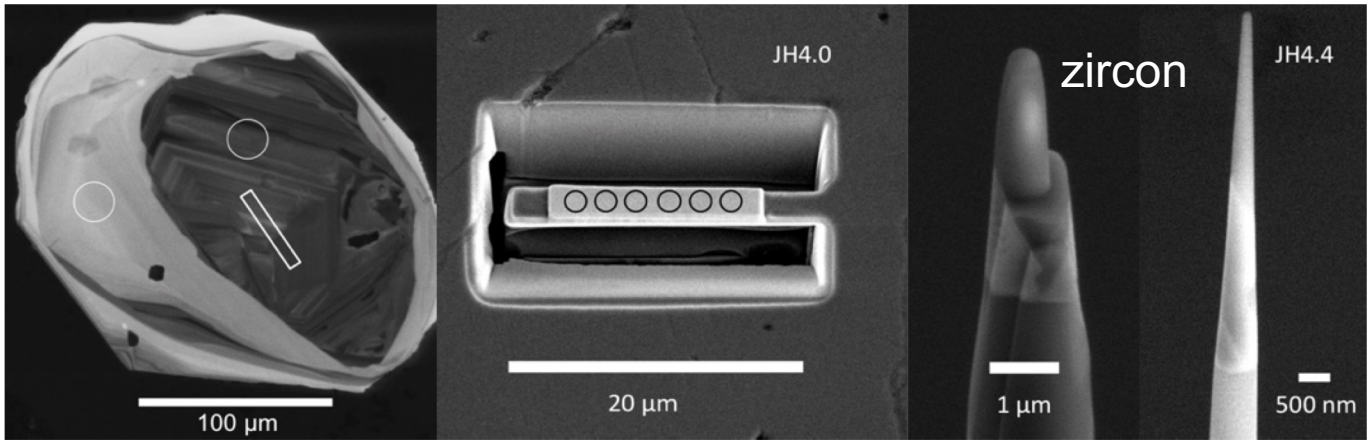
JW Valley, et al., *Nature Geoscience* (2014) **7**

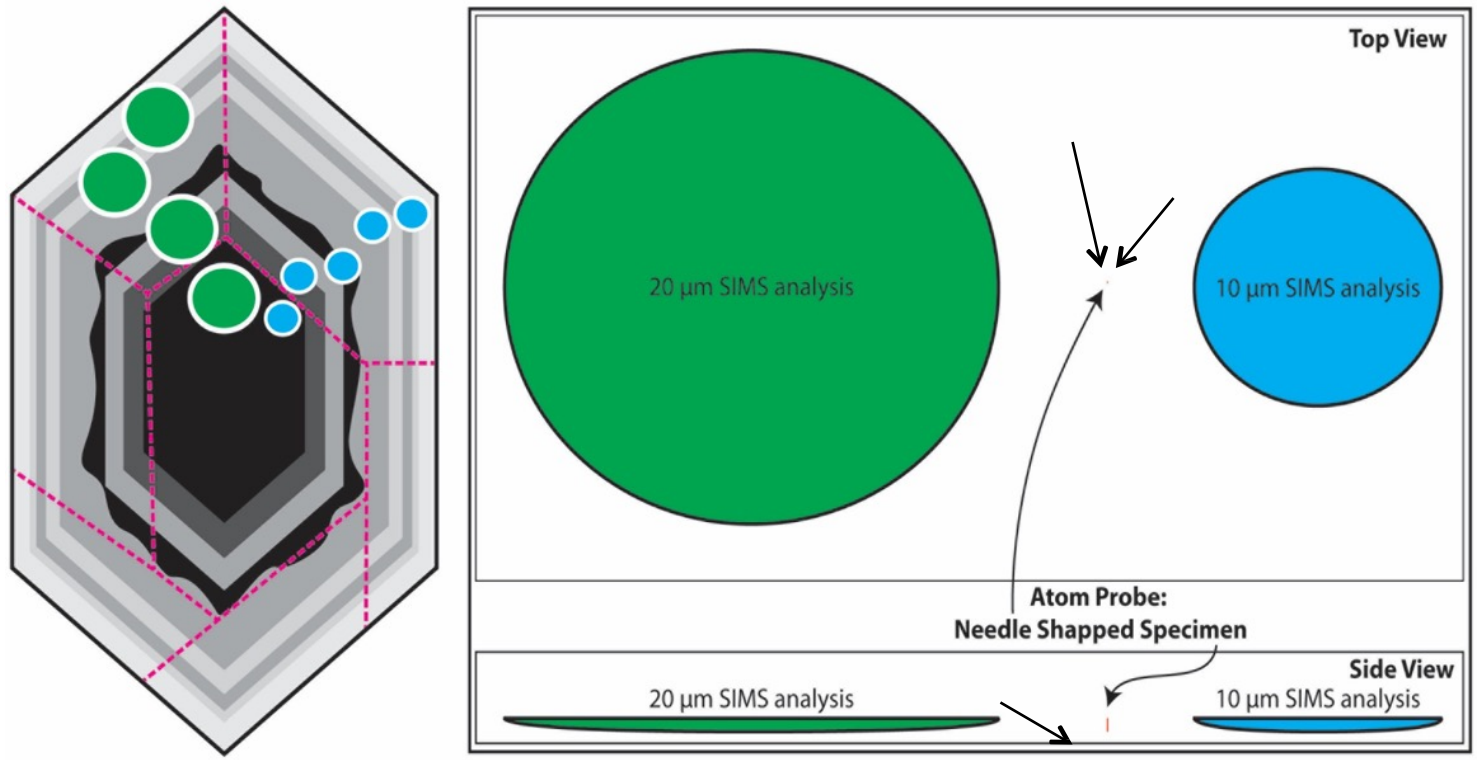
Geological Applications

Zircons

Work by John Valley (Wisconsin-Madison)

Nature Geosciences (2014), American Mineralogist (2015)

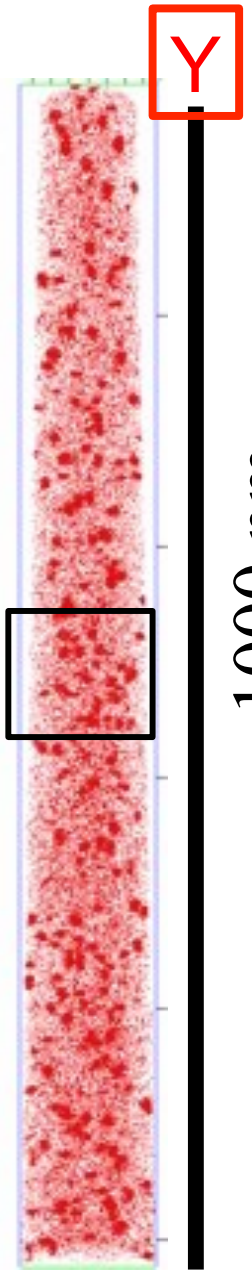




J.W. Valley, Geosciences Atom Probe Tomography (APT) Workshop, University of Alabama, Jan. 29 -30, 2016

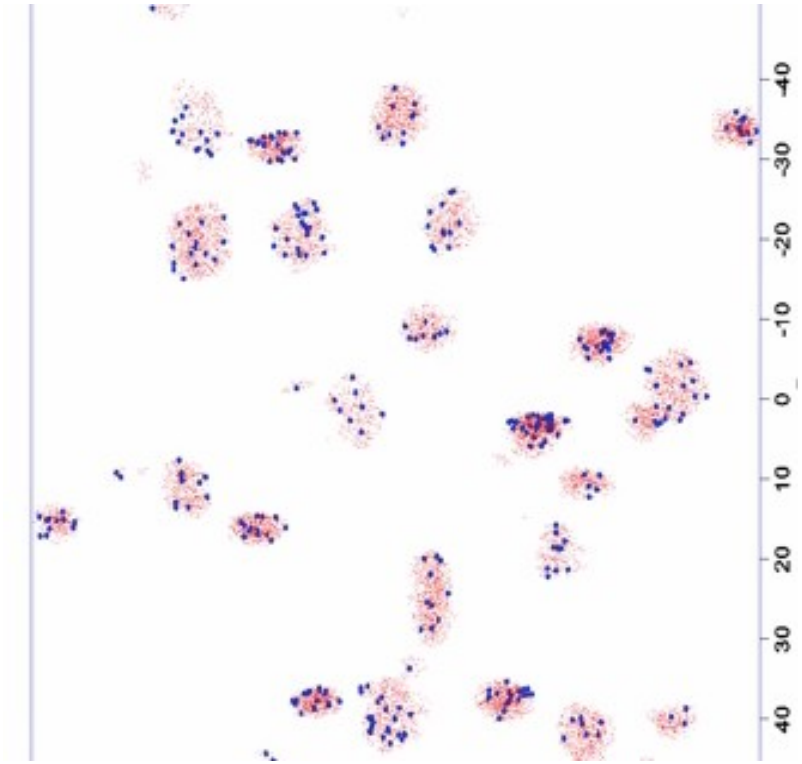
Clusters- APT

4.4 Ga zircon, Jack Hills

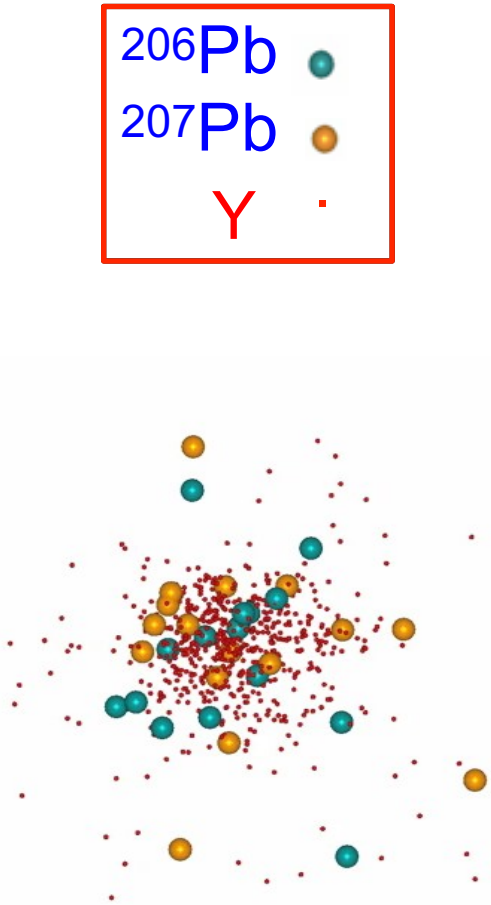


1000 nm

Y & Pb



100 nm

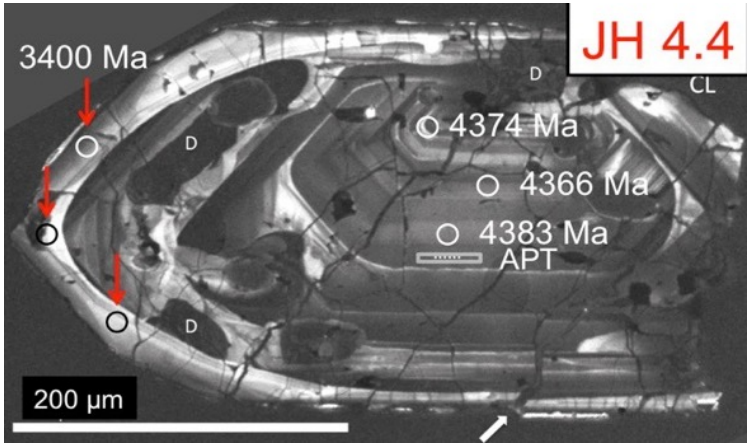


Valley et al. 2014, 2015

10 nm

J.W. Valley, Geosciences Atom Probe Tomography (APT) Workshop, University of Alabama, Jan. 29 -30, 2016

Jack Hills	SIMS $^{207}Pb/^{206}Pb$	APT $^{207}Pb/^{206}Pb$
JH 4.4 Ga		
(10,255 Pb atoms)		
4374 Ma core	0.548	0.52
inside clusters		1.2
outside clusters		0.30
3400 Ma rim	0.291	



APT: Archean/Hadean zircons

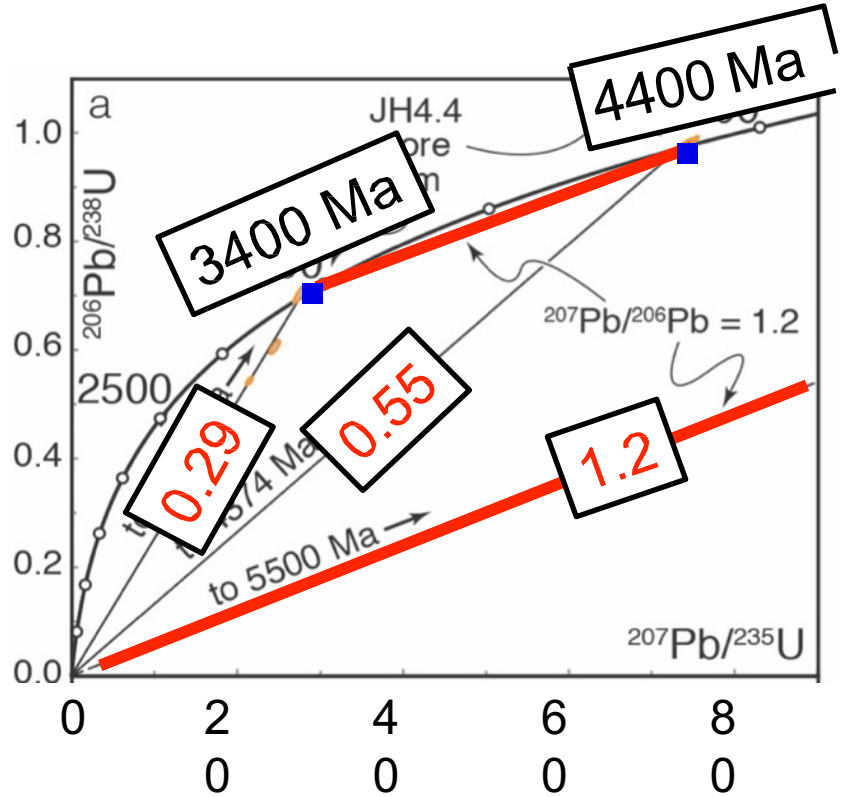
Pb mobility < 50 nm
- Linked to radiation damage

Compositions reintegrated by SIMS
- SIMS ages are accurate

Clusters date reheating events

Confirms 4.4 Ga zircon from Jack Hills

Valley et al. 2014, 2015



Sample Preparation

Optimization

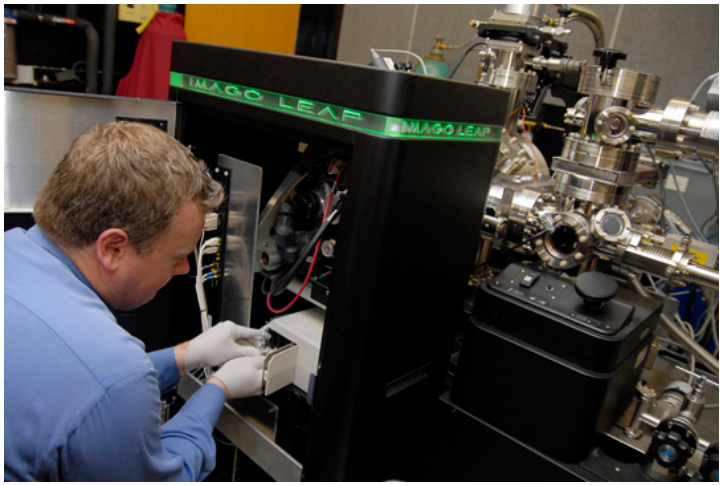
UA GeoAPT

http://uageoapt.ua.edu

Biomineralization

Nanogeosciences

LEAP Instrument



LEAP 3000

LEAP 5000 XS

Sample Preparation

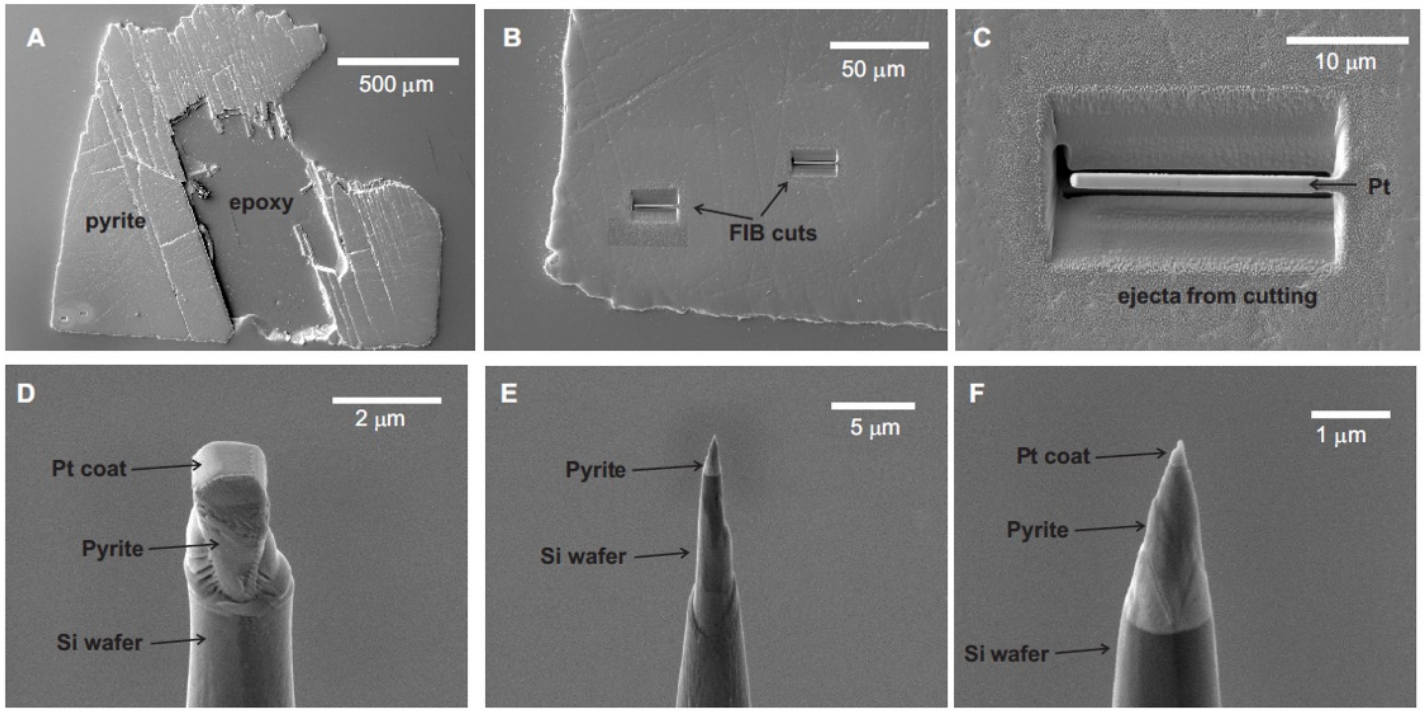
Optimization

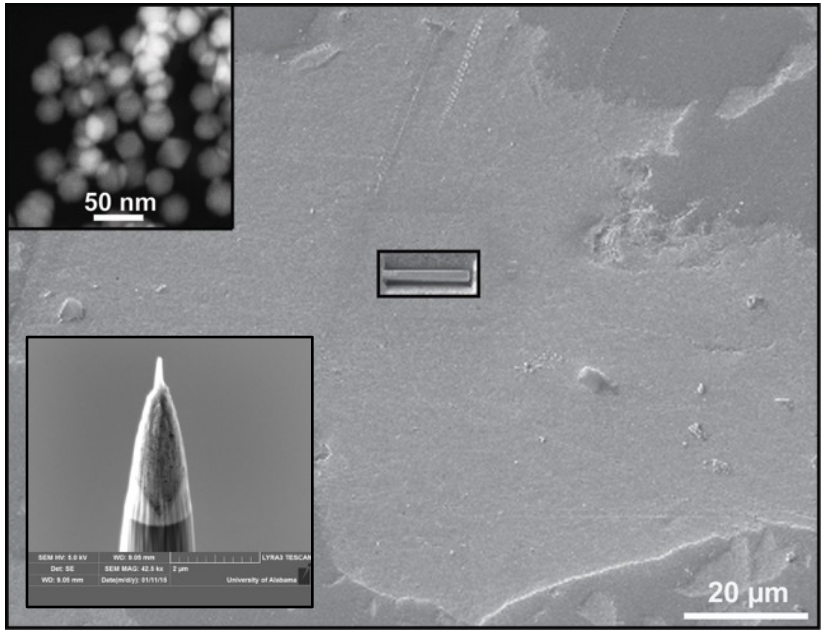
UA GeoAPT

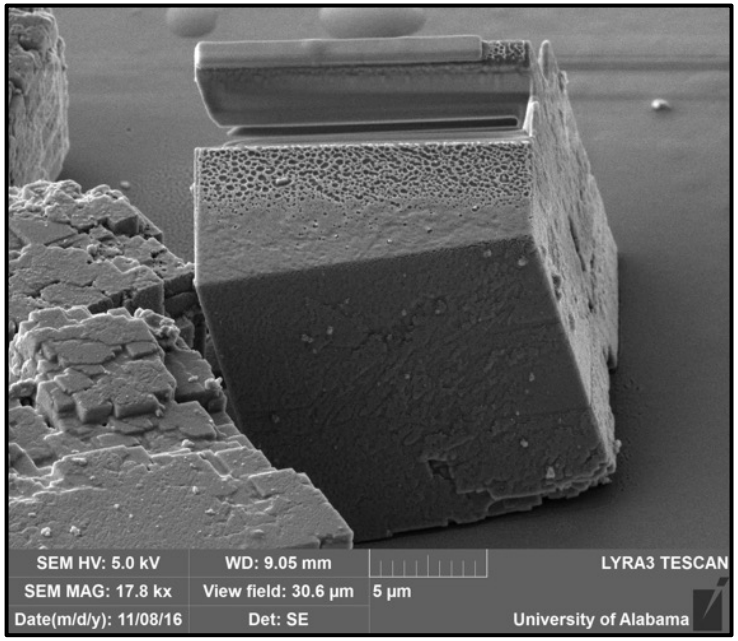
http://uageoapt.ua.edu

Biomineralization

Nanogeosciences


A
500 µm
pyrite
epoxy
B
50 µm
FIB cuts
C
10 µm
Pt
ejecta from cutting
D
2 µm
Pt coat
Pyrite
Si wafer
E
5 µm
Pyrite
Si wafer
F
1 µm
Pt coat
Pyrite
Si wafer


50 nm
20 µm


SEM HV: 5.0 kV
WD: 9.05 mm
LYRA3 TESCAN
SEM MAG: 17.8 kx
View field: 30.6 µm
5 µm
Date(m/d/y): 11/08/16
Det: SE
University of Alabama

Sample Preparation

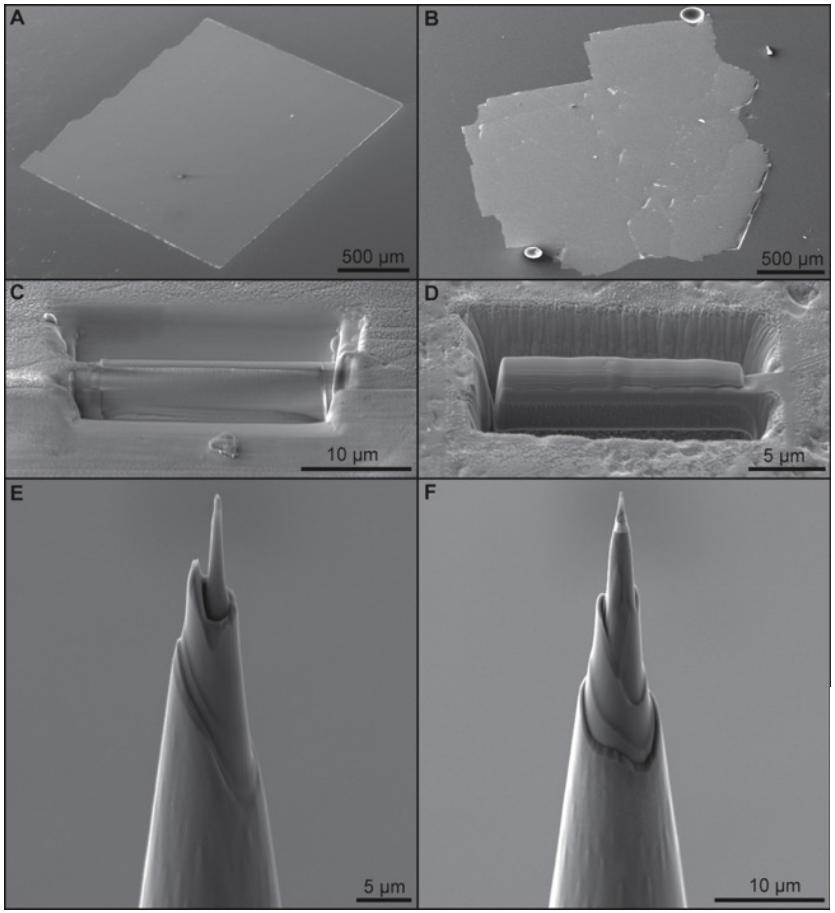
Optimization

UA GeoAPT

http://uageoapt.ua.edu

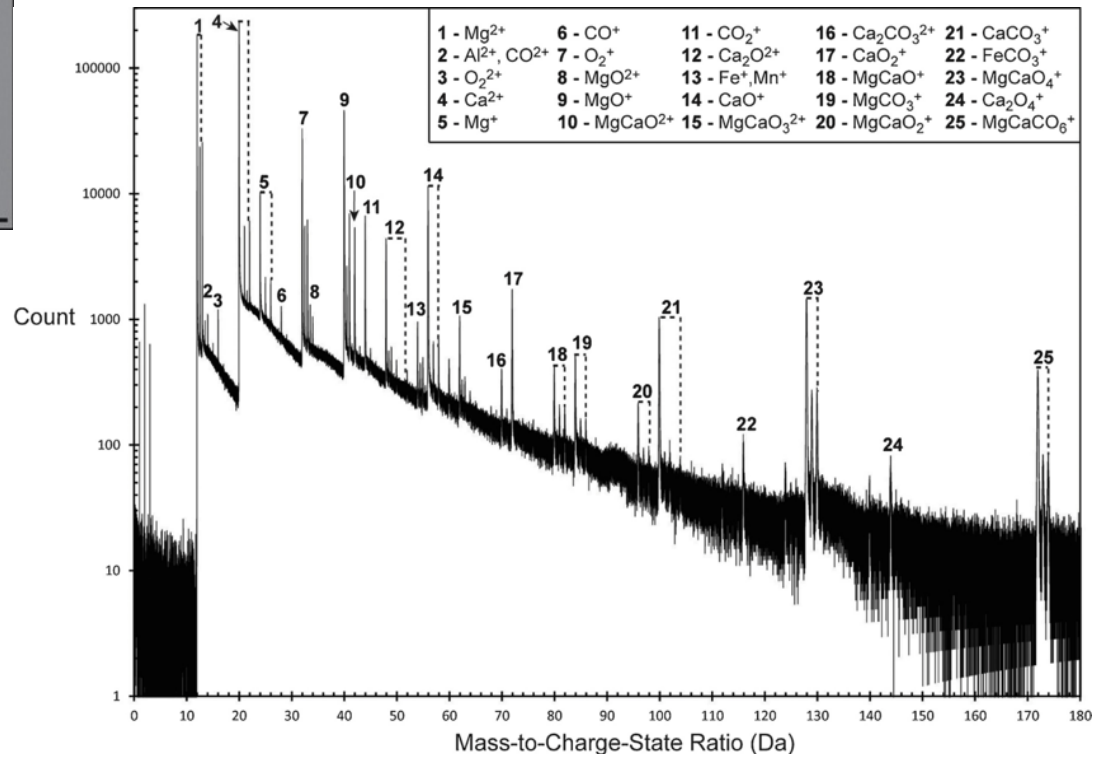
Biomineralization

Nanogeosciences

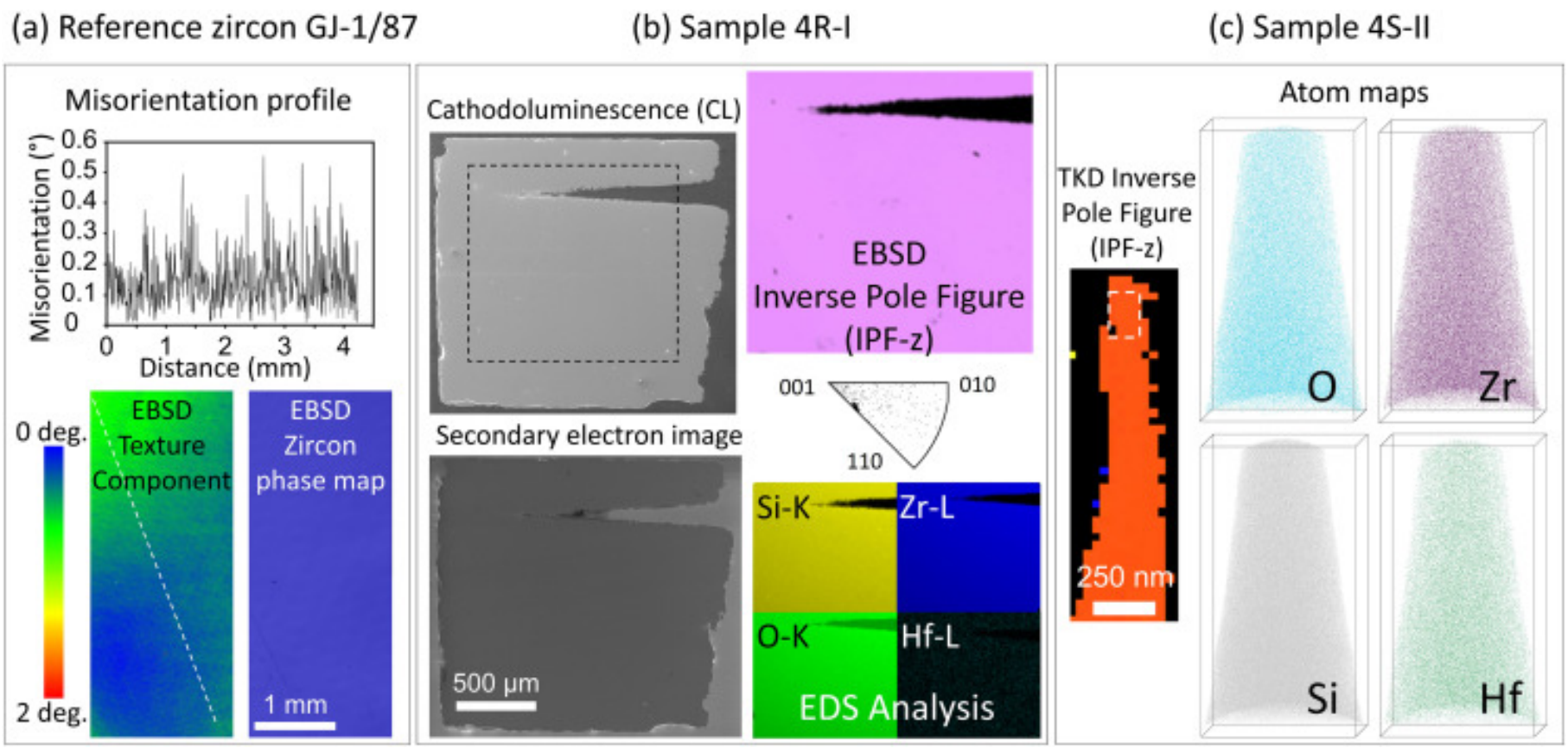


Carbonates

- pJ laser needed and base temperature dependent
- Spectra complexity different for calcite and dolomite, with matching stoichiometry for calcite
- APT underestimates amount of oxygen
- Great detection of chemical impurities (e.g. 0.16 atomic % of Mn in dolomite)



Perez-Huerta *et al.* (2016) - Micron



La Fontaine *et al.* in press – Chemical Geology

Sample Preparation

Optimization

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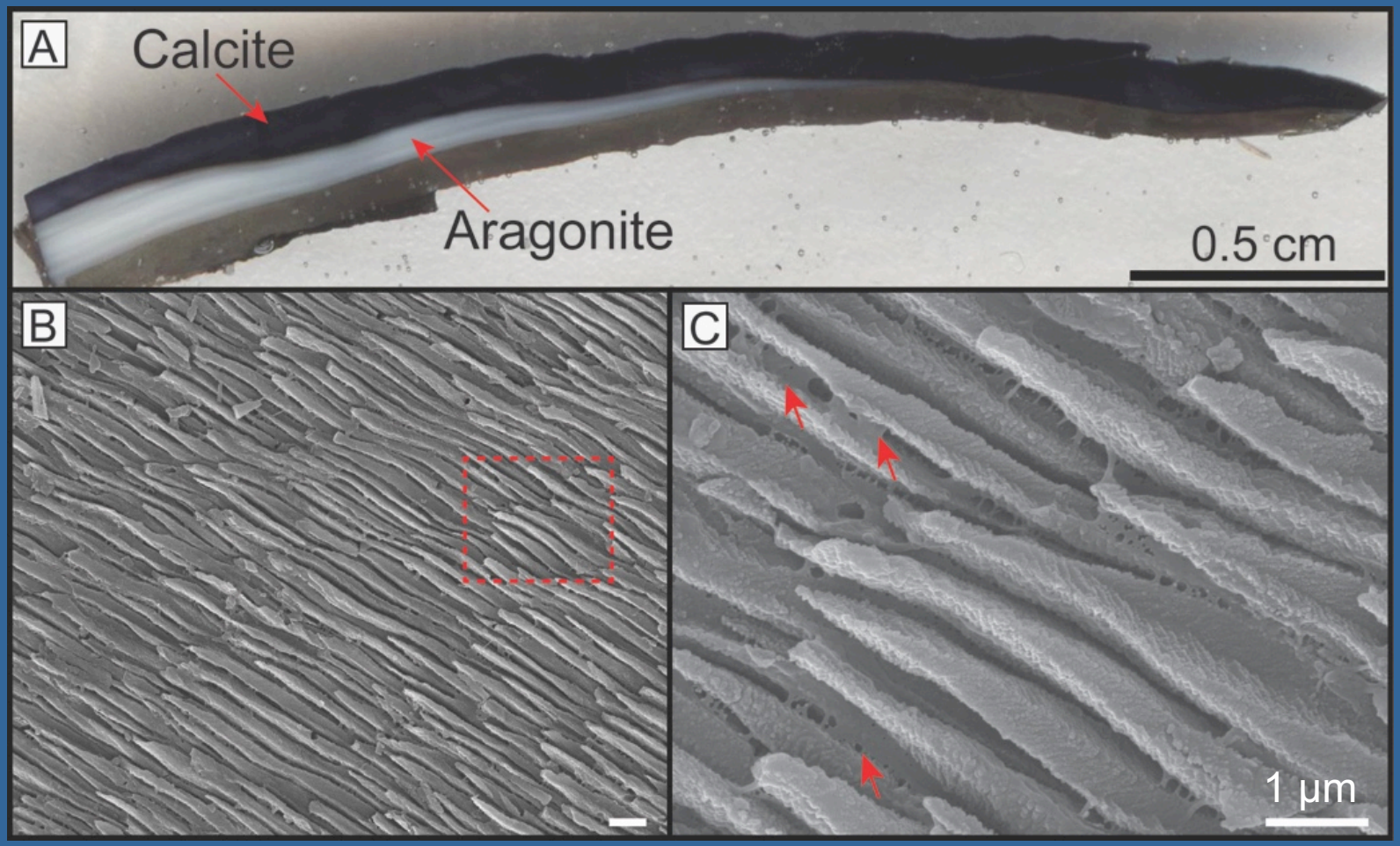
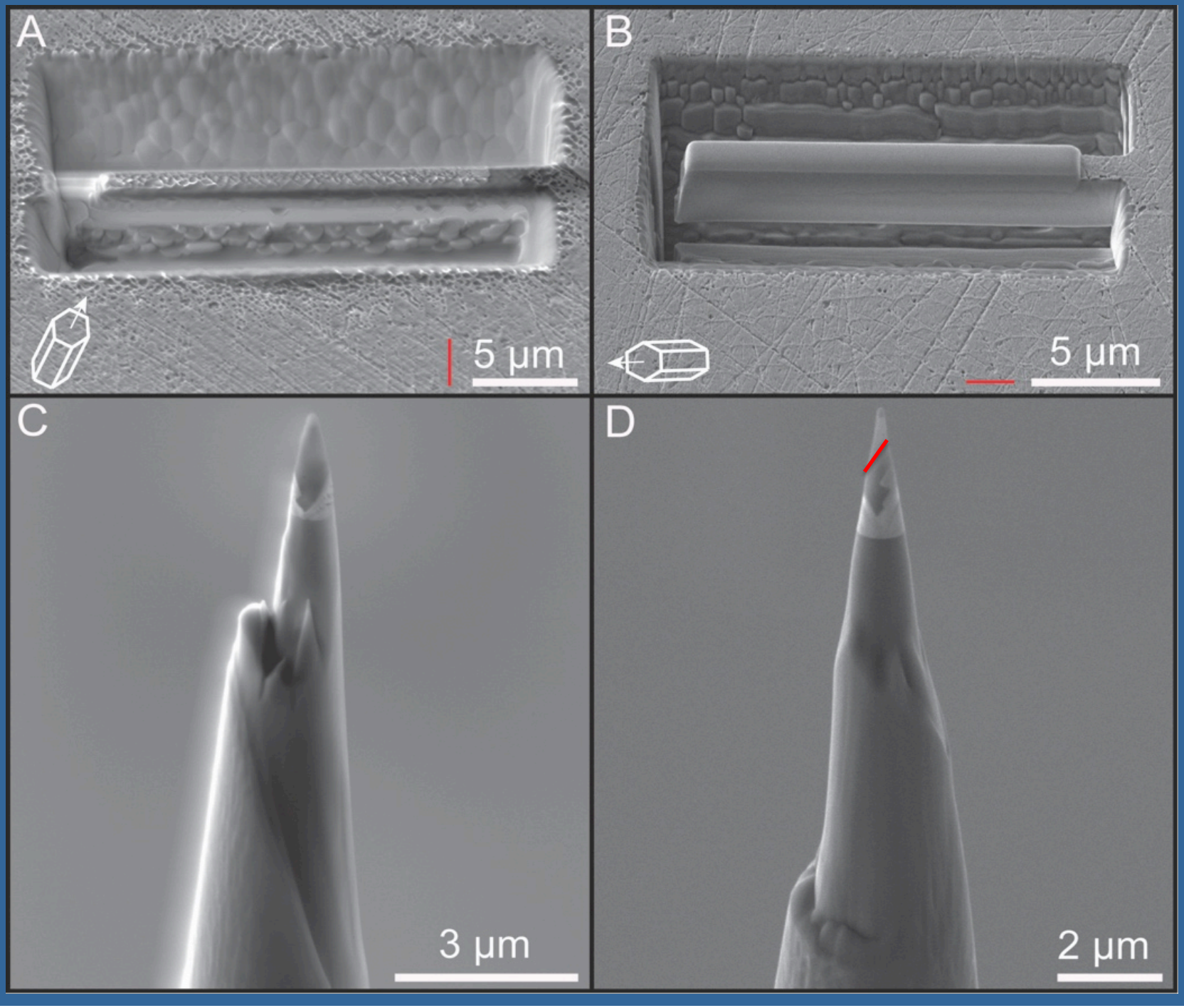
Biomineralization

Nanogeosciences


A
Calcite
Aragonite
0.5 cm
B
C
1 µm

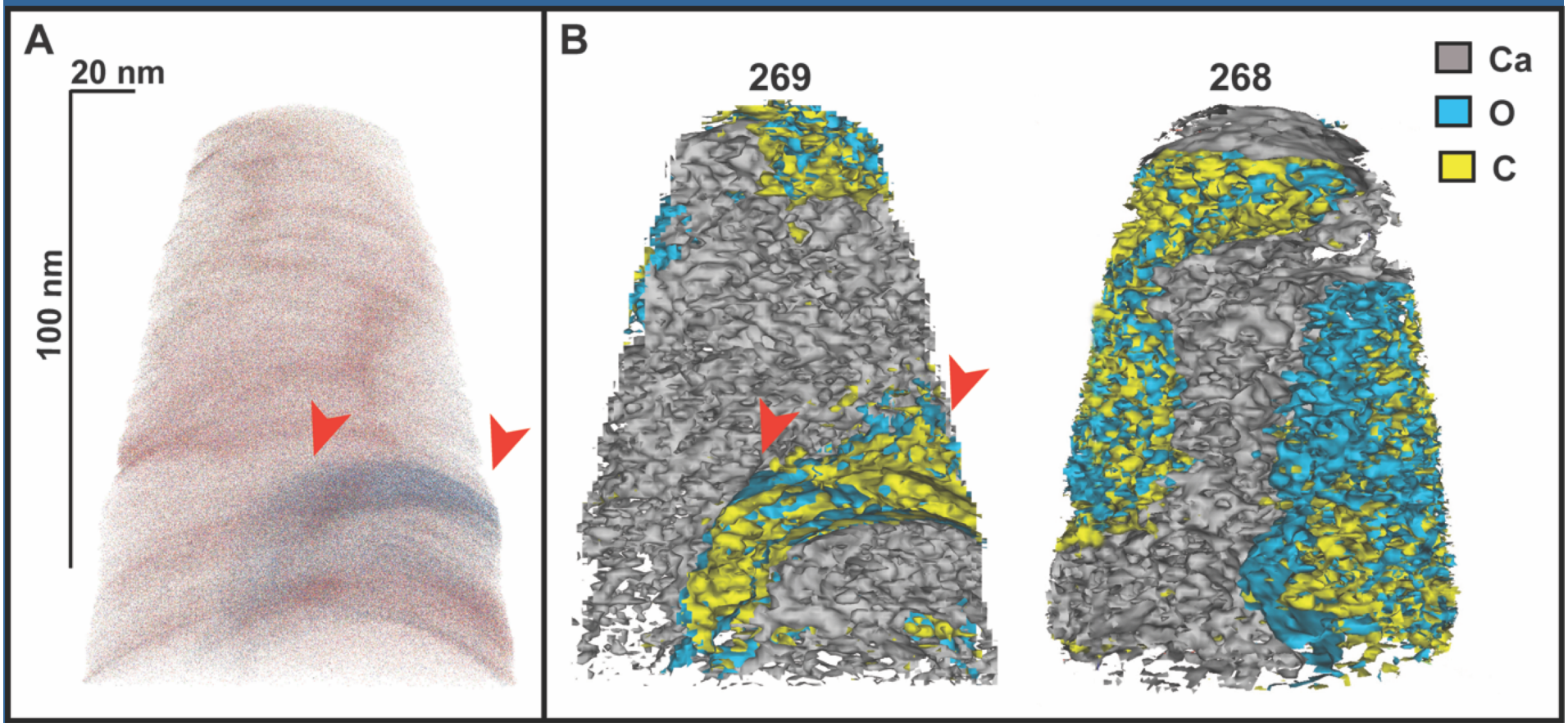

A
5 µm
B
5 µm
C
3 µm
D
2 µm

Biogenic Calcite

Regions enriched in light isotopes (^{16}O and ^{12}C)

Average Na concentration of 0.31 atomic % (n = 5; 2σ = 0.06)

Average N concentration of 0.03 atomic % (n = 3; 2σ = 0.002)



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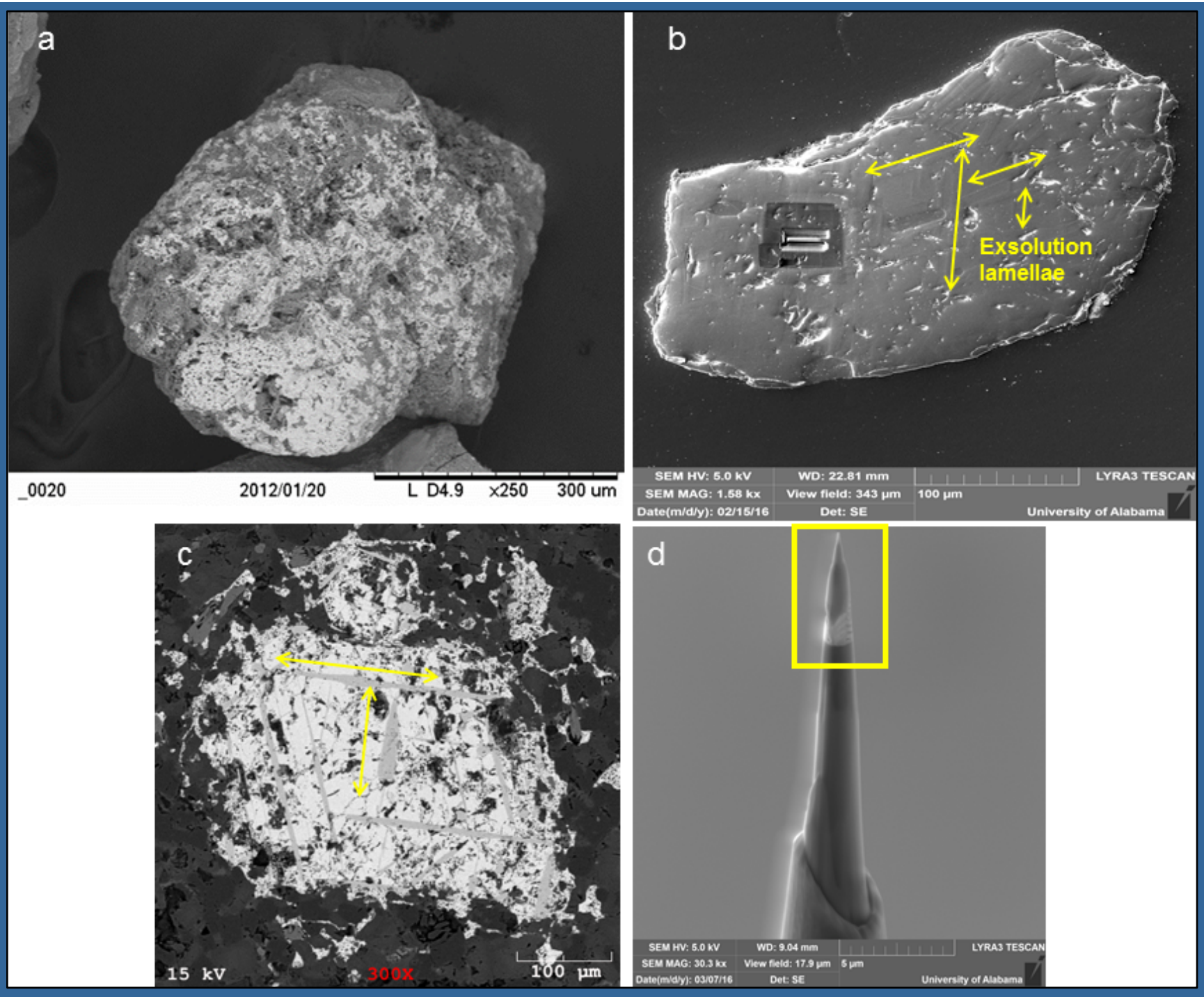
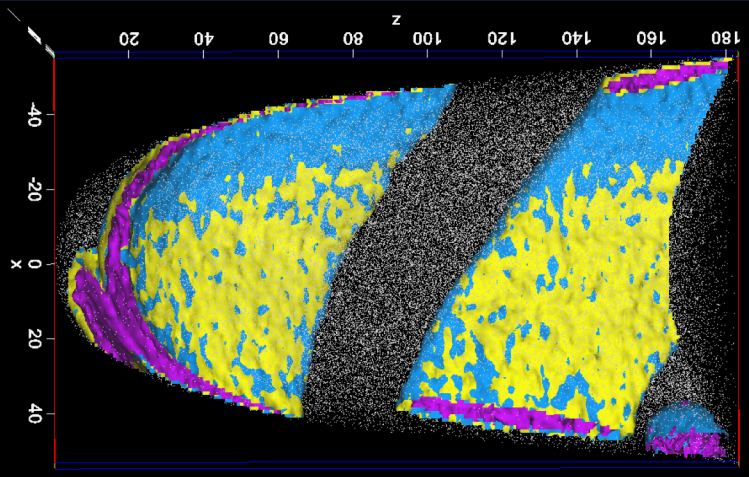
Biomineralization

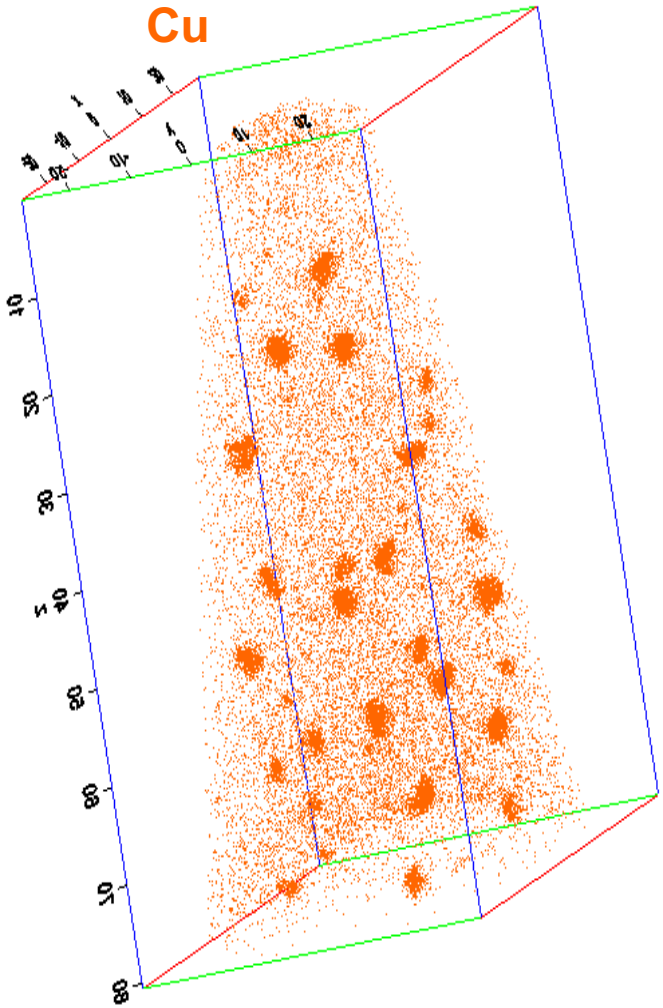
Nanogeosciences


a
_0020
2012/01/20
L D4.9 x250 300 um
b
Exsolution lamellae
SEM HV: 5.0 kV
WD: 22.81 mm
LYRA3 TESCAN
SEM MAG: 1.58 kx
View field: 343 µm
100 µm
Date(m/d/y): 02/15/16
Det: SE
University of Alabama
c
15 kV
300X
100 µm
d
SEM HV: 5.0 kV
WD: 9.04 mm
LYRA3 TESCAN
SEM MAG: 30.3 kx
View field: 17.9 µm
5 µm
Date(m/d/y): 03/07/16
Det: SE
University of Alabama



Genareau et al. – In prep.

Atom Probe Tomography Highlights



$(Co_{0.95}Fe_{0.05})_{88}Zr_6Hf_1B_4Cu_1$

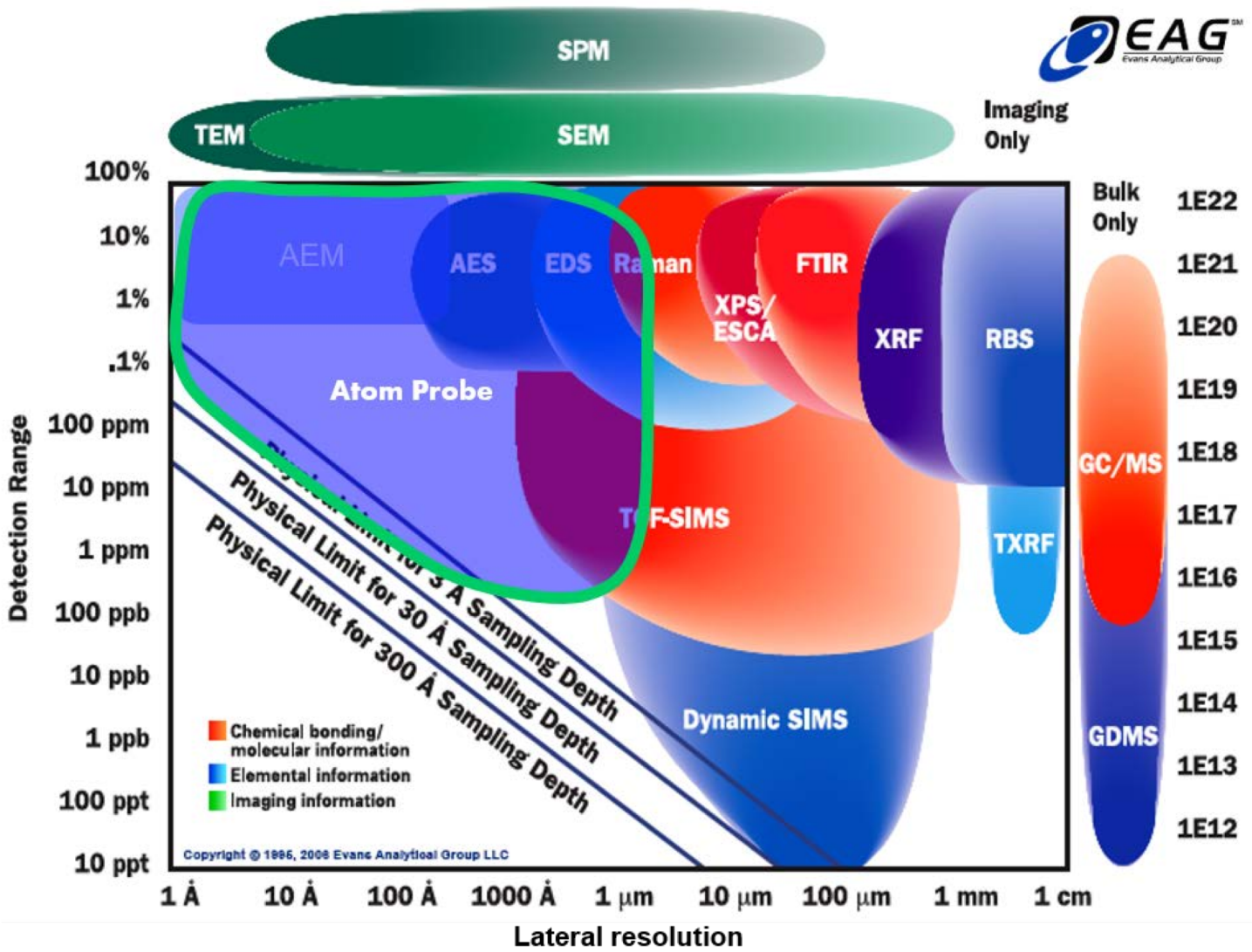
The advantages ☺

✓3D technique
✓ Very high spatial and chemical resolution
✓ Equally sensitivity for all elements
✓ Instrument improvements=rapid data analysis
✓ 10s of ppm resolving power

The disadvantages ☹

✓ Only 50-80% atom efficiency
✓'Complex' species (*i.e.* oxides, etc) evaporate 'complexly' – identification issues
✓Reconstruction technique – do I really have it correct?

The Atom Probe's Niche



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- Dr. Fernando Laiginhas (Postdoctoral Researcher)