# Atom Probe Tomography (APT)
## Geosciences Applications

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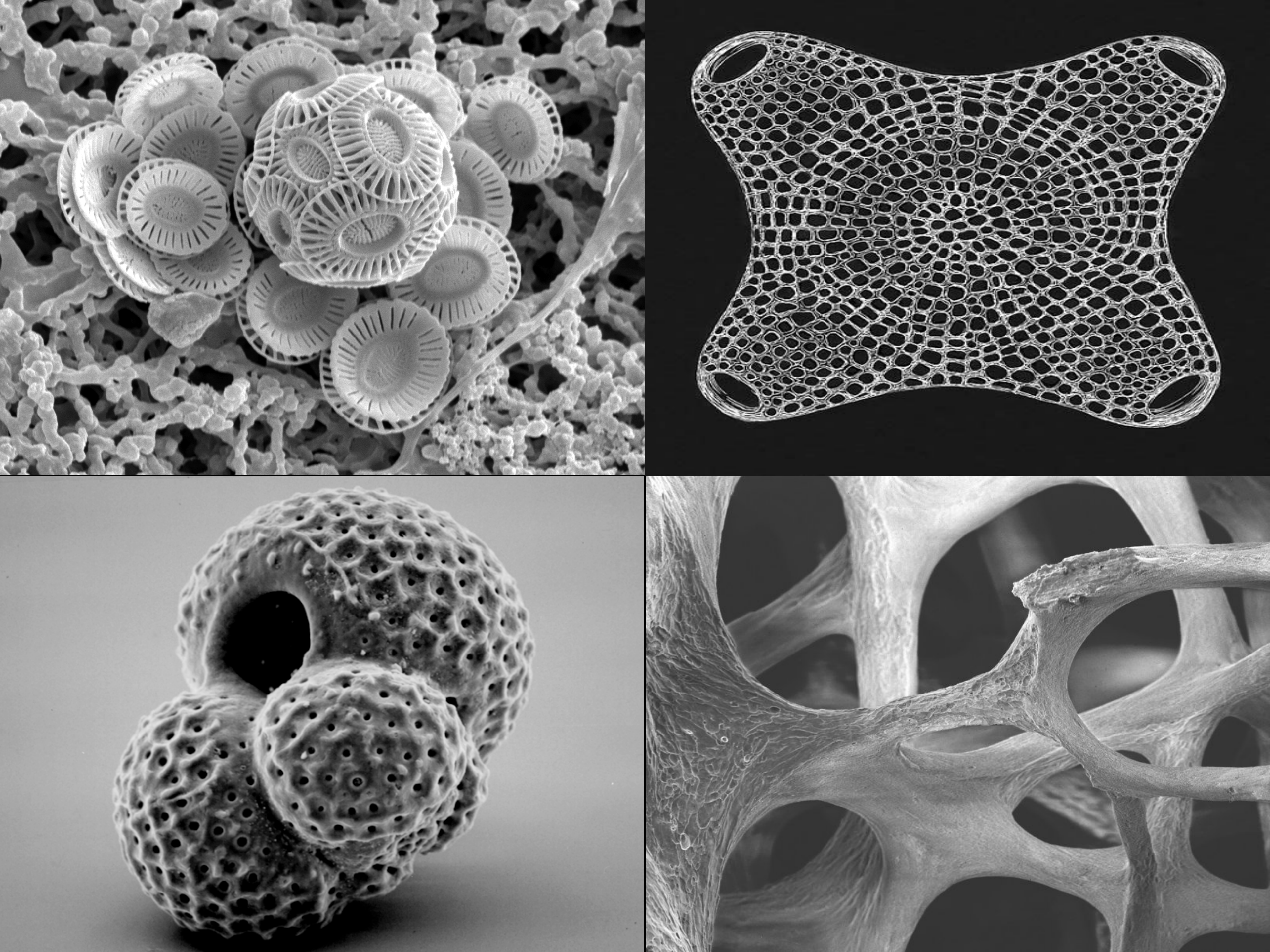
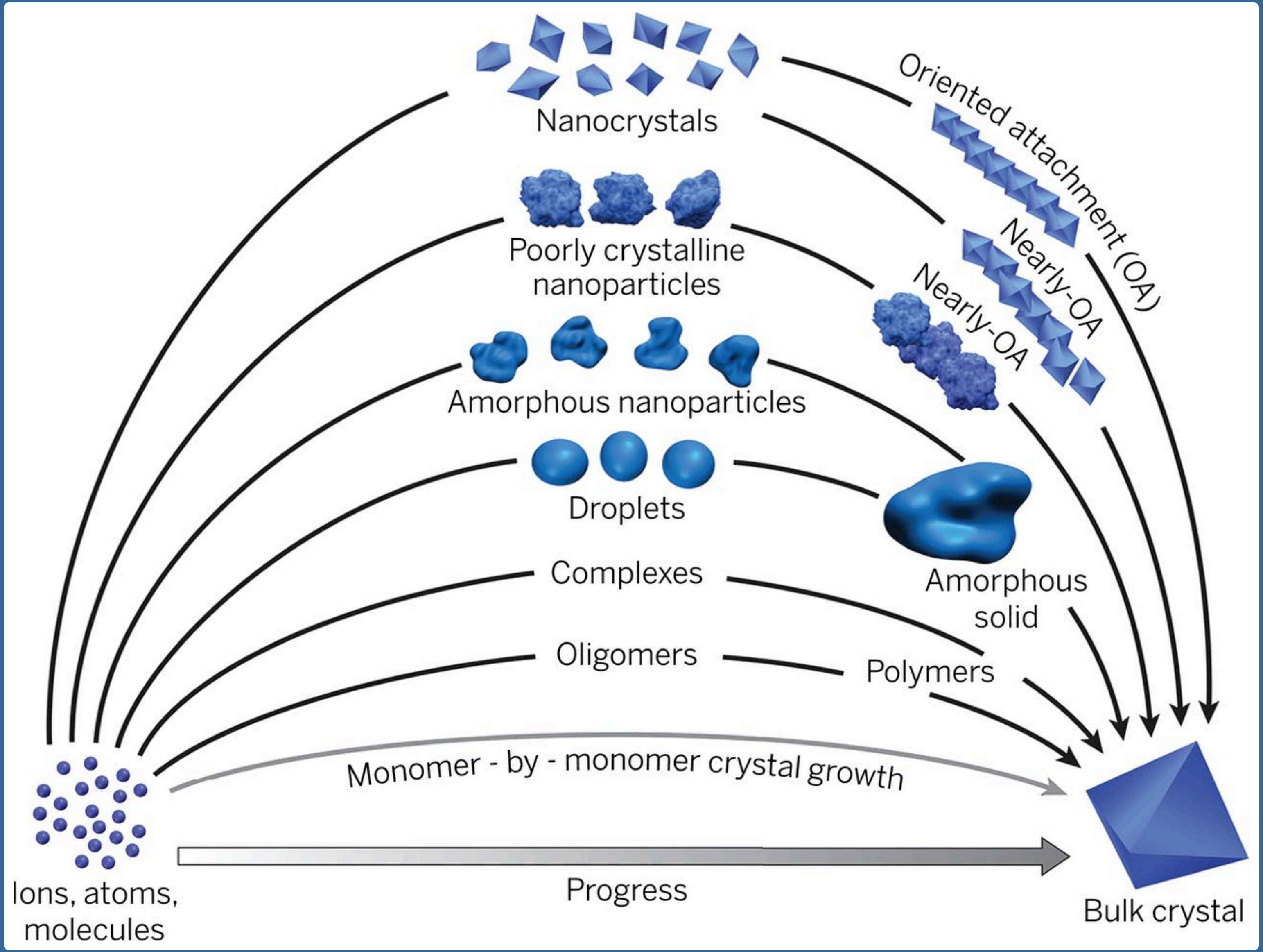
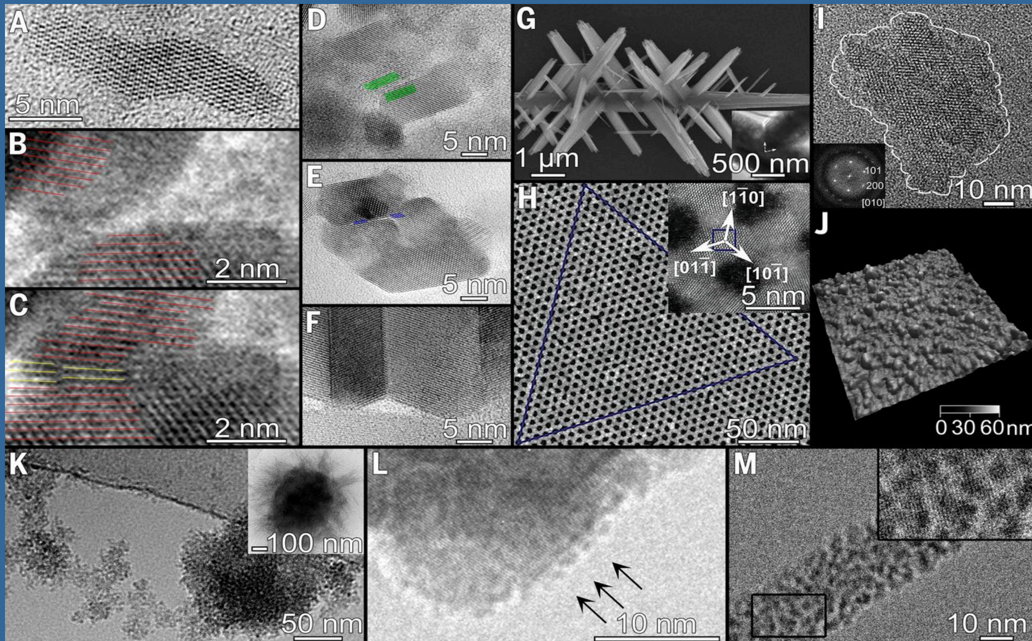
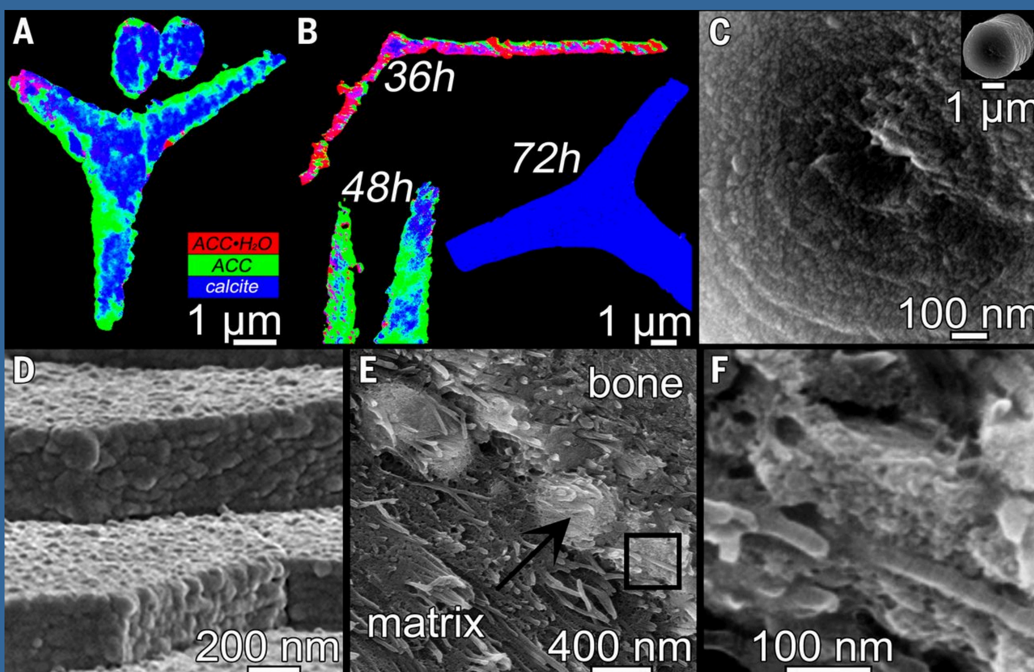


# Crystallization Pathways

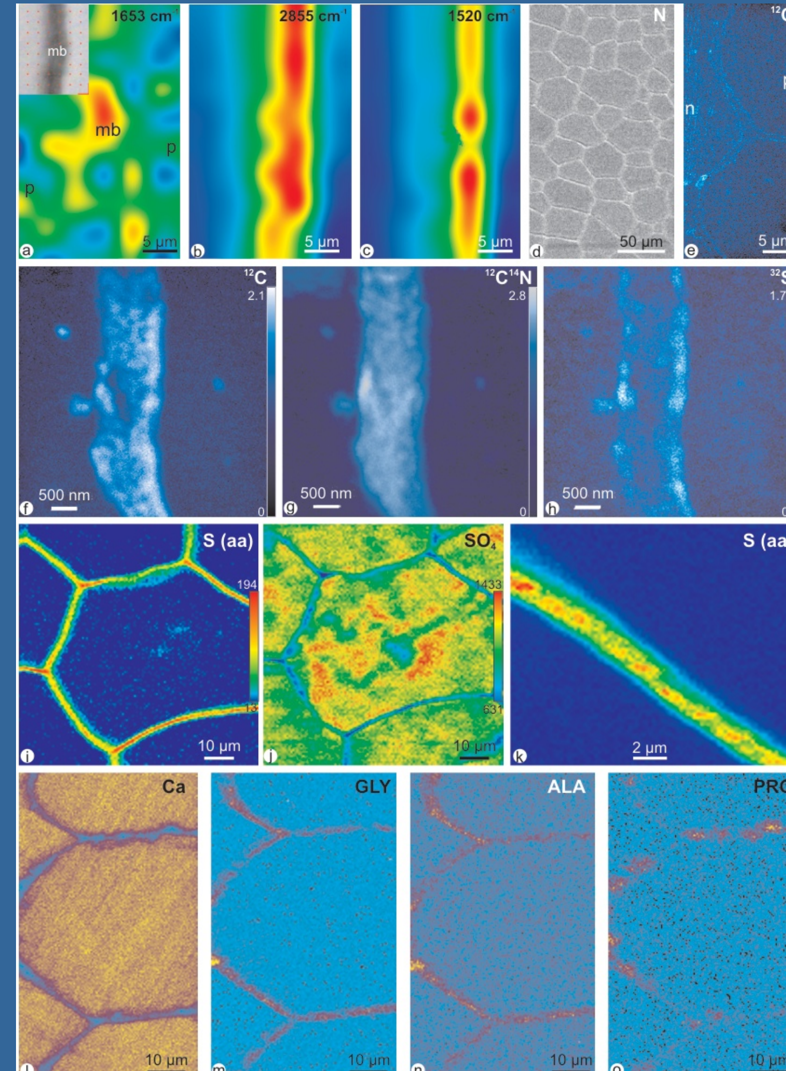



De Yoreo *et al*. (2015) - Science



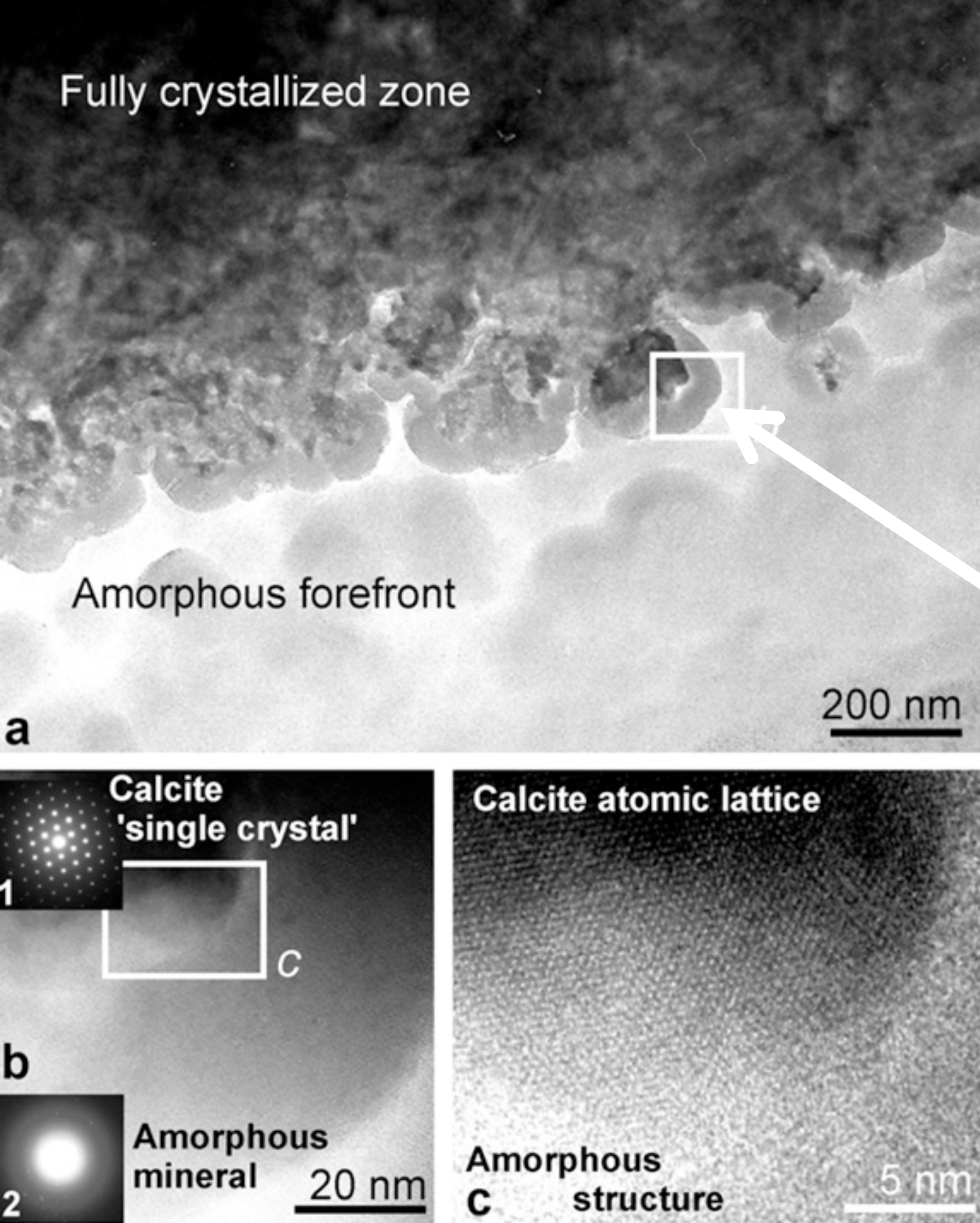

**De Yoreo *et al.* (2015) - Science**




**<u>Techniques</u>:**

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

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

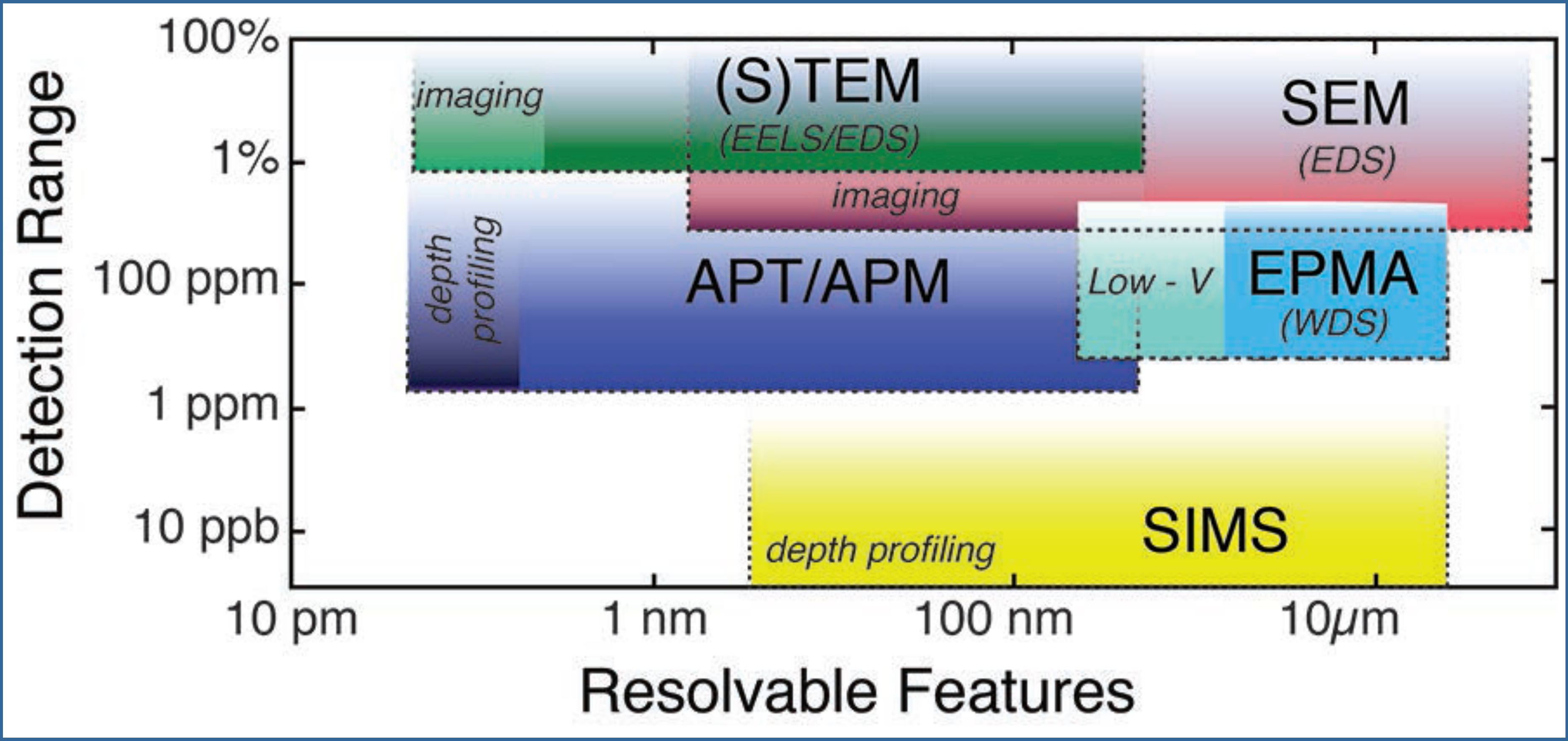



*Pearl oyster*
*Pinctada margaritifera*

# Chemistry?

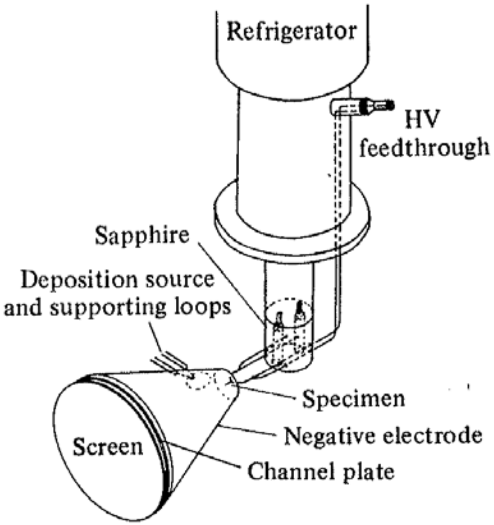
**Baronnet *et al.* (2008) Mineralogical Magazine**

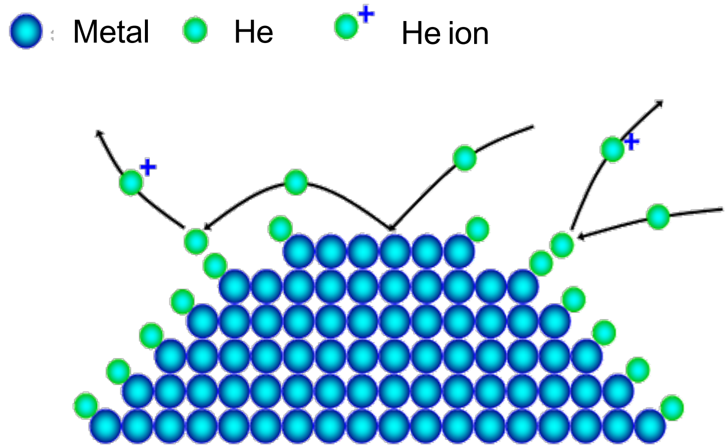
# Atom Probe Tomography (APT)



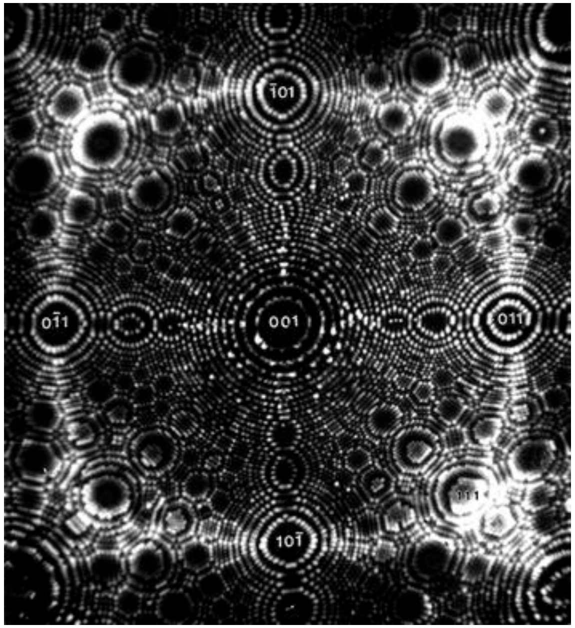

Valley *et al.* (2015) – American Mineralogist

# Field Ion Microscopy (FIM)




- 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




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

# 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!

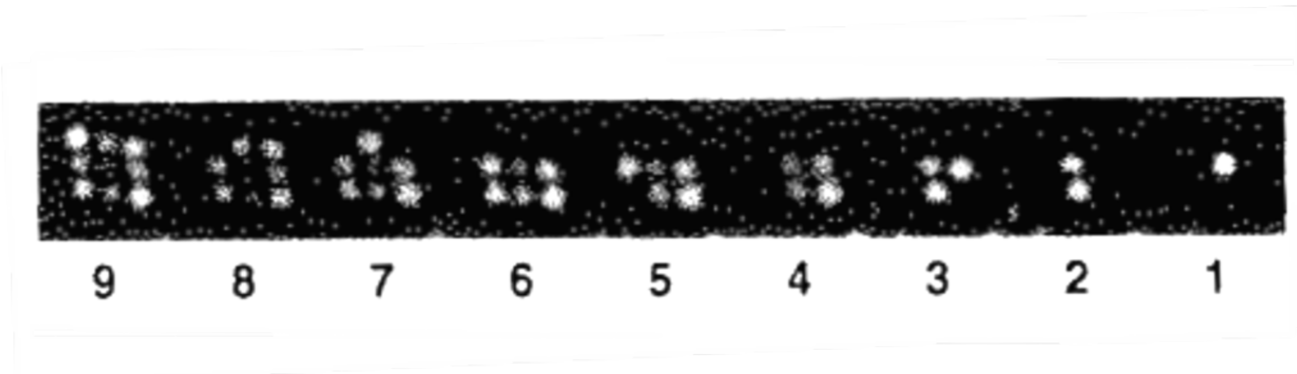
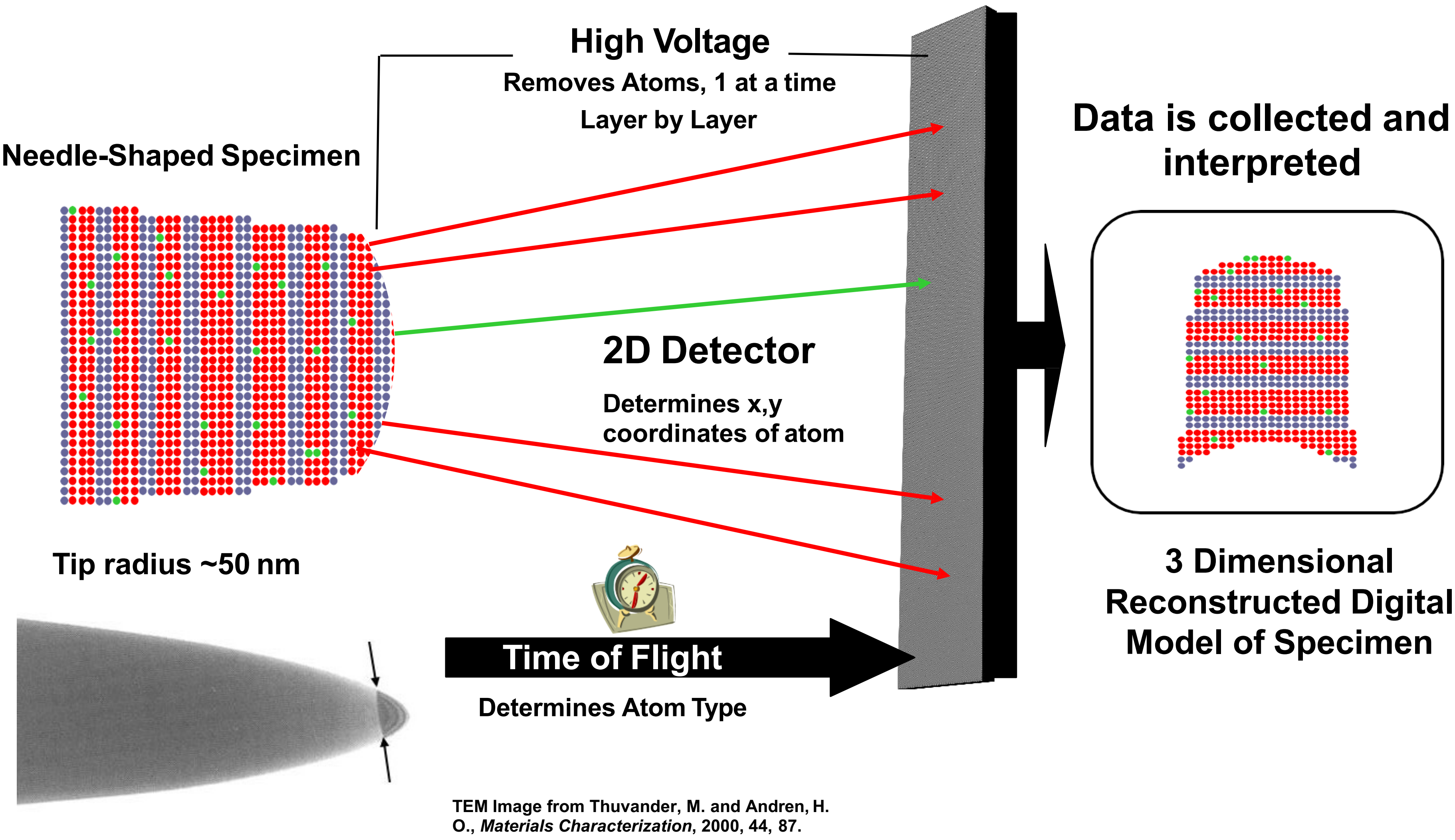


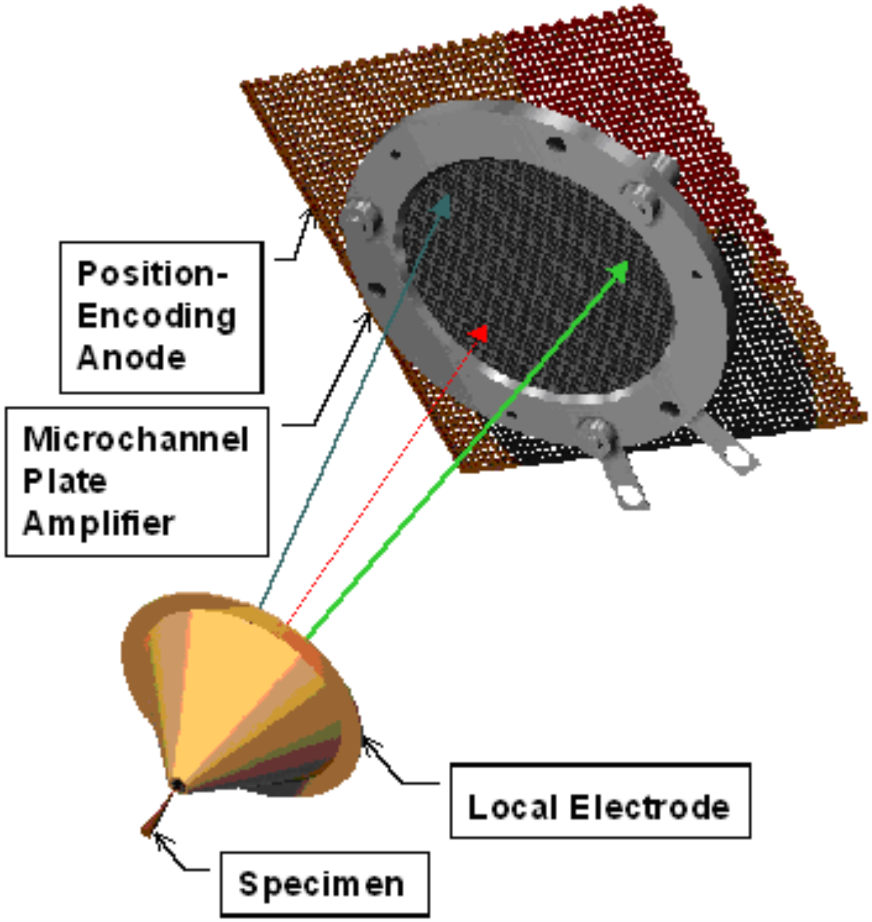

Image of one atom at a time field evaporating from a Ni-Zr catalyst. Taken from M.K. Miller Atom Probe Tomography: Analysis at the Atomic Level (2000)

# How does it work?

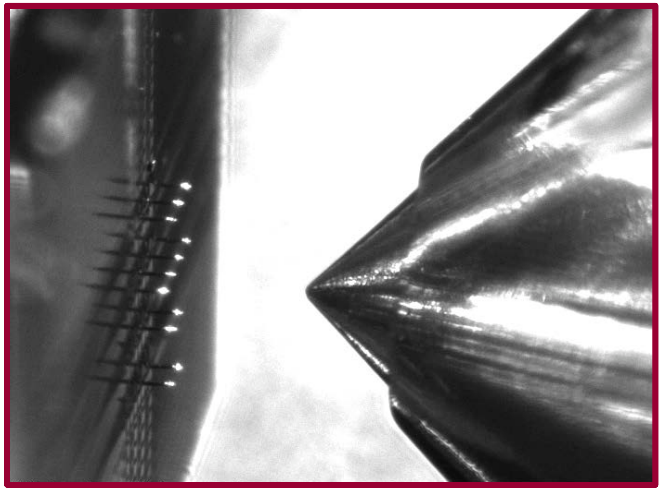



TEM Image from Thuvander, M. and Andren, H. O., *Materials Characterization*, 2000, 44, 87.

# Why a Local Electrode?

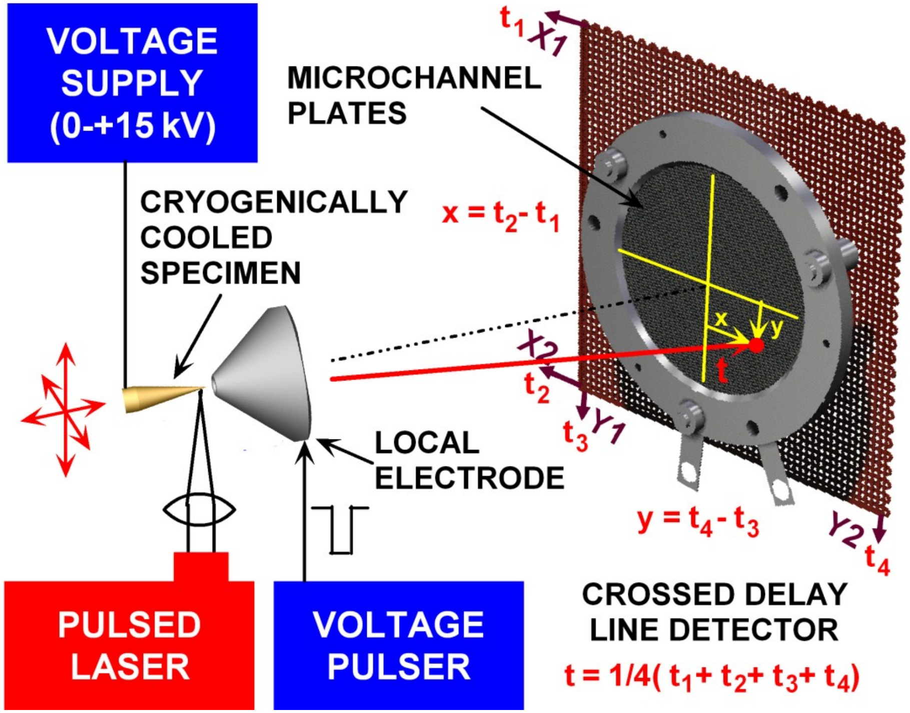


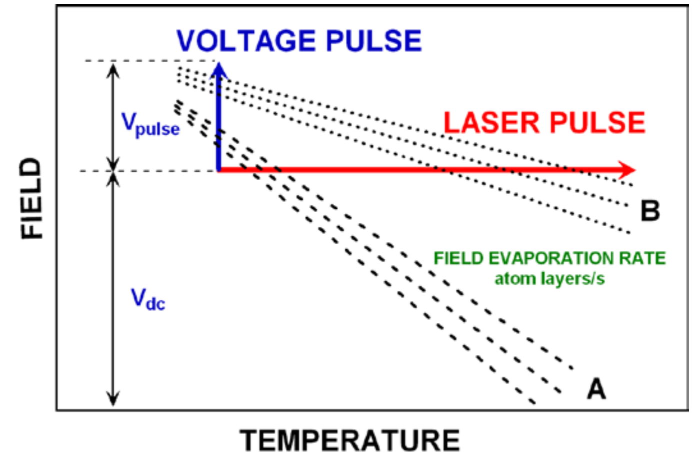

- Step-and-repeat analysis
- **Wide field-of-view**
- Conical cone enhances the fields resulting in lower applied voltage → **Higher data collection rates** (1.5 kHz to 200+ kHz)
- Good mass resolution (> 1/500 FWHM)
- High speed (up to 20,000 atoms/second)
- Cone also serves as a Faraday cage and shields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



# Laser Pulsing

## *Extending the capability to more materials*

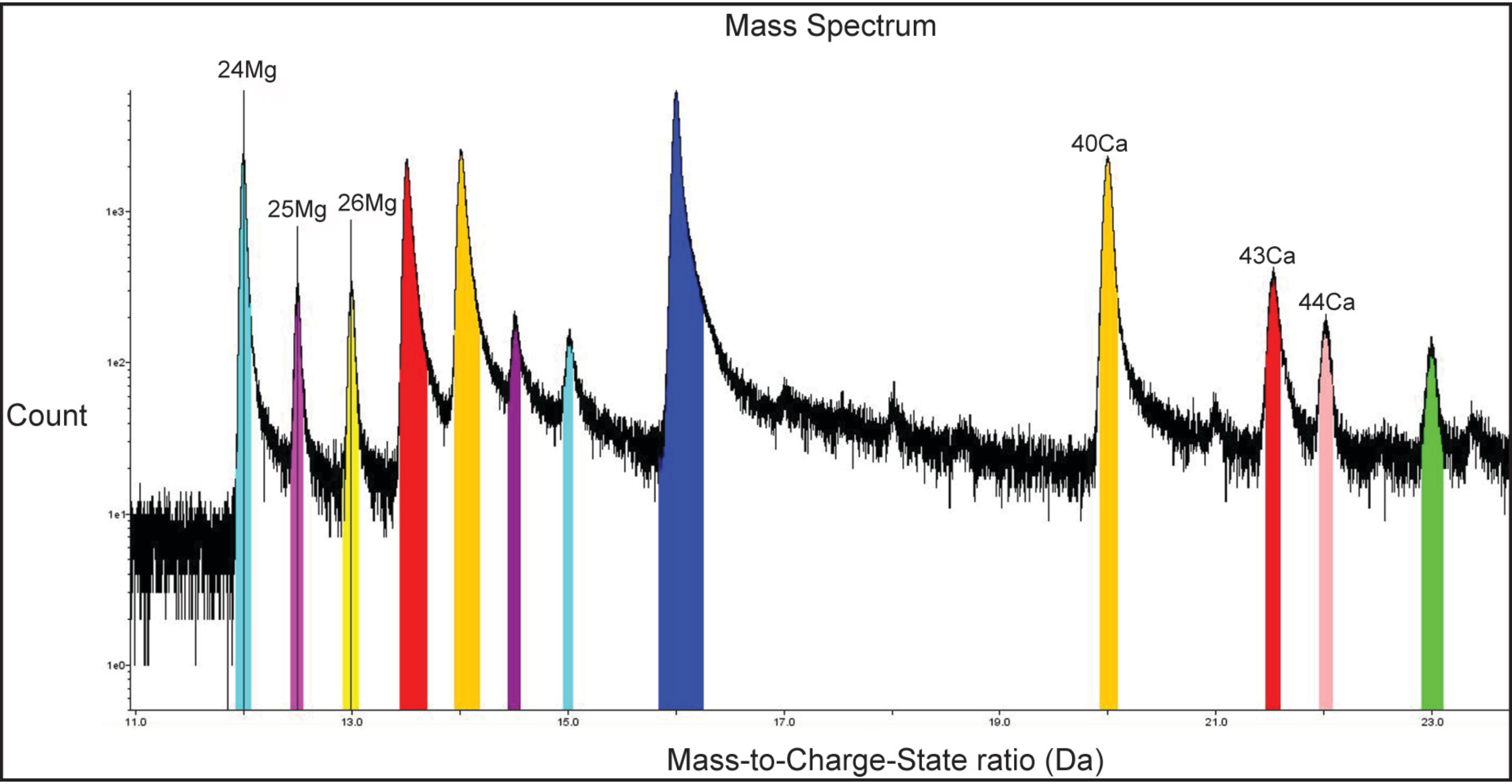



- Instead of applying a voltage pulse to field evaporate atoms, a short duration laser pulse is used to momentarily heat the specimen so that field evaporation occurs on the standing voltage.
- An additional advantage of laser pulsing is that under the correct experimental conditions, an improvement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

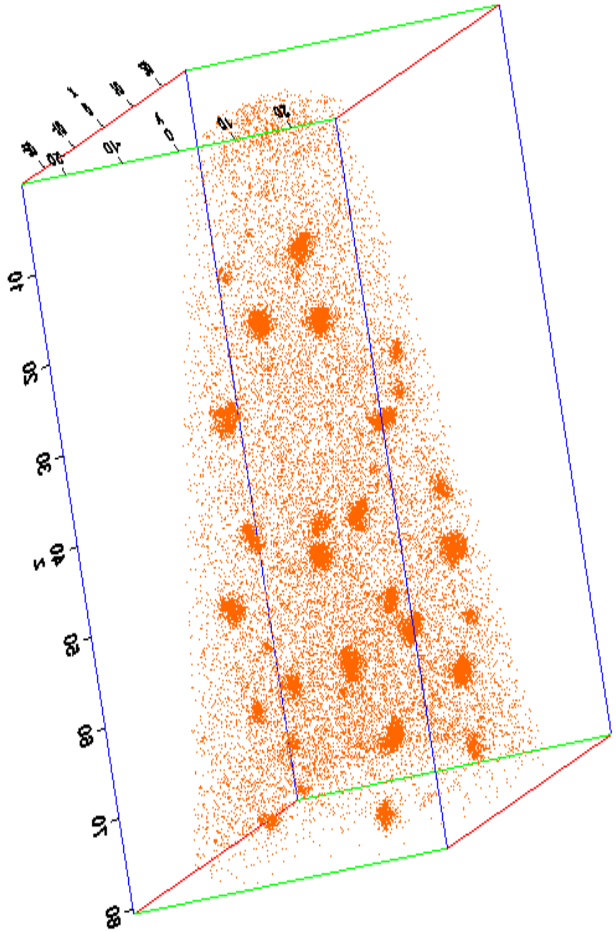
*Slide text and figures courtesy of MK Miller, ORNL*

# How does data look like?



# VISUALIZATION: Atom Maps

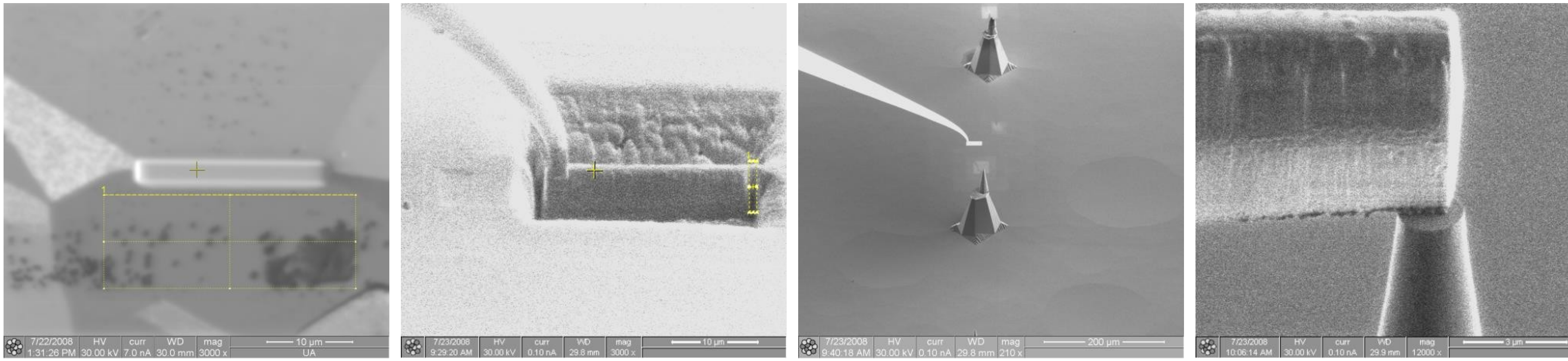
Cu



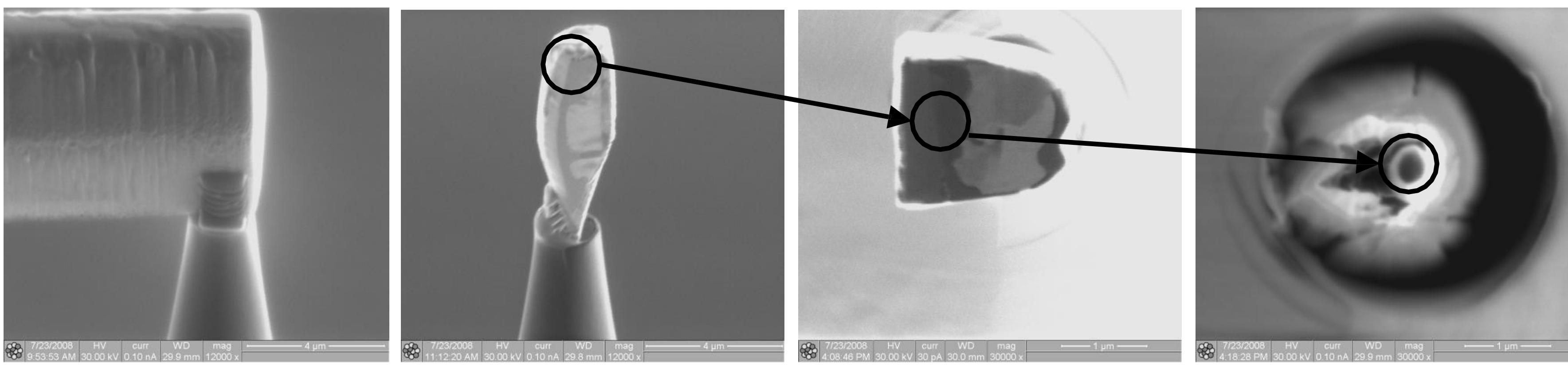
$(Co_{0.95}Fe_{0.05})_{88}Zr_6\mathit{Hf}_1B_4Cu_1$

- 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.

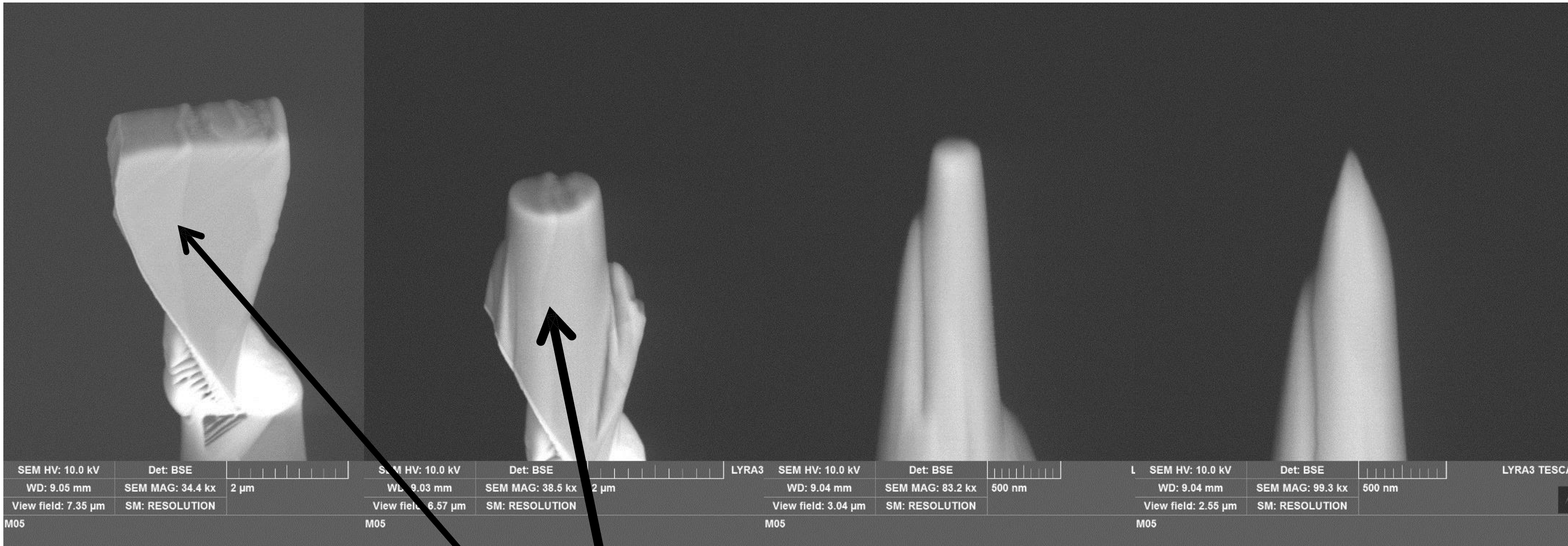
# Focused Ion Beam (FIB)



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

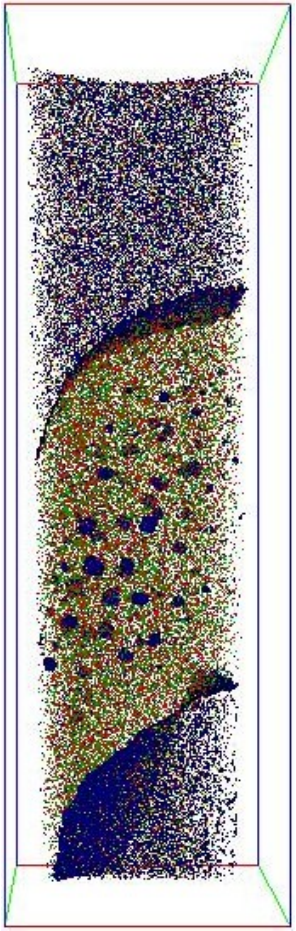



Section of wedge before milling

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

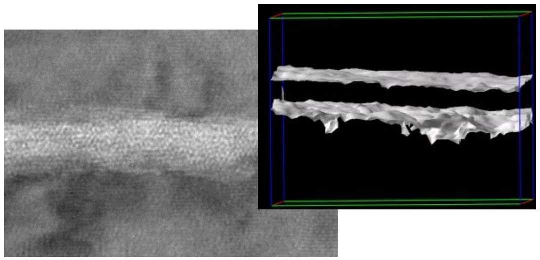
# Applications of Atom Probe Tomography

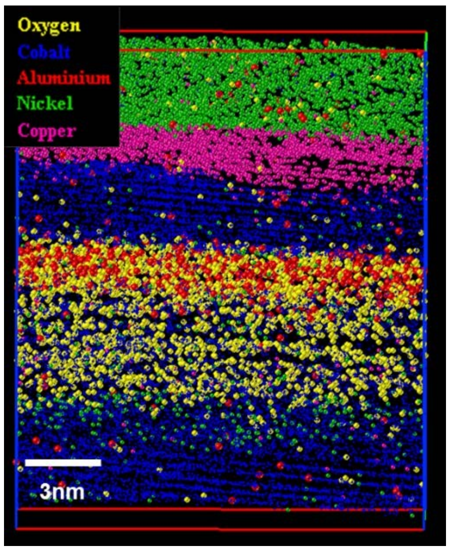
## Ferritic Superalloys



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

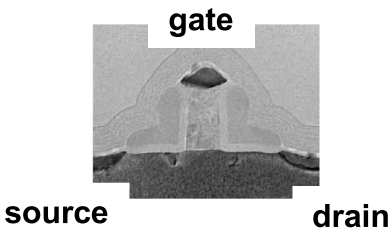
## Magnetic Sensors

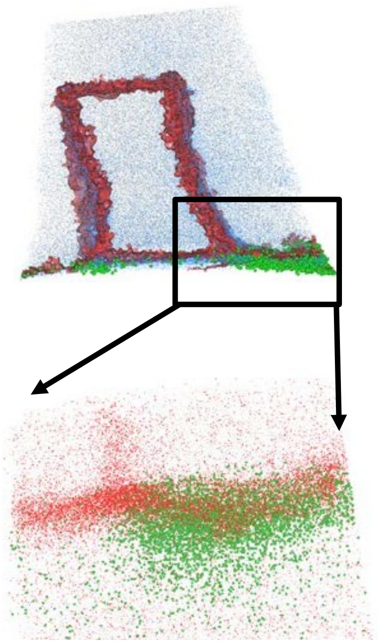





AK Petford-Long, et al., *Journal of Applied Physics* 98 (2005) 124904

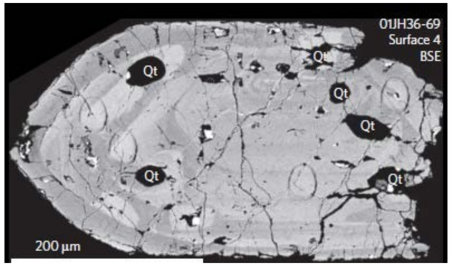
## Semiconductor Transistors

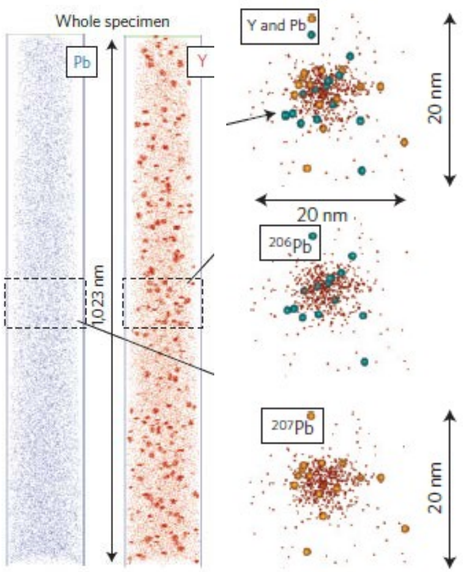


K. Jones, et al.,"Atom Probe Characterization of Magnetic and Semiconductor Device Structures"

## 4.4 Gyr Zircon

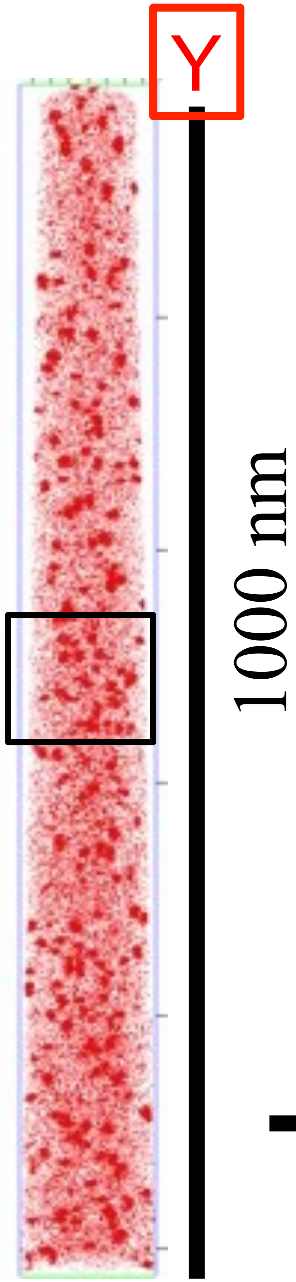


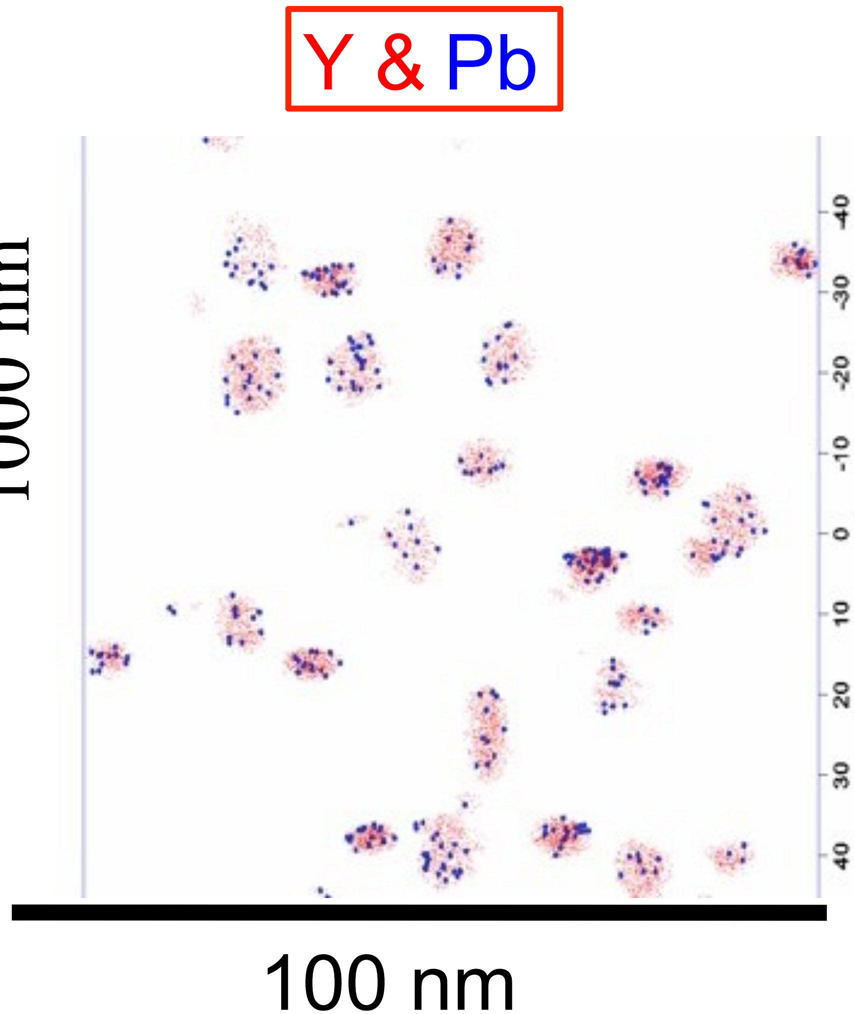



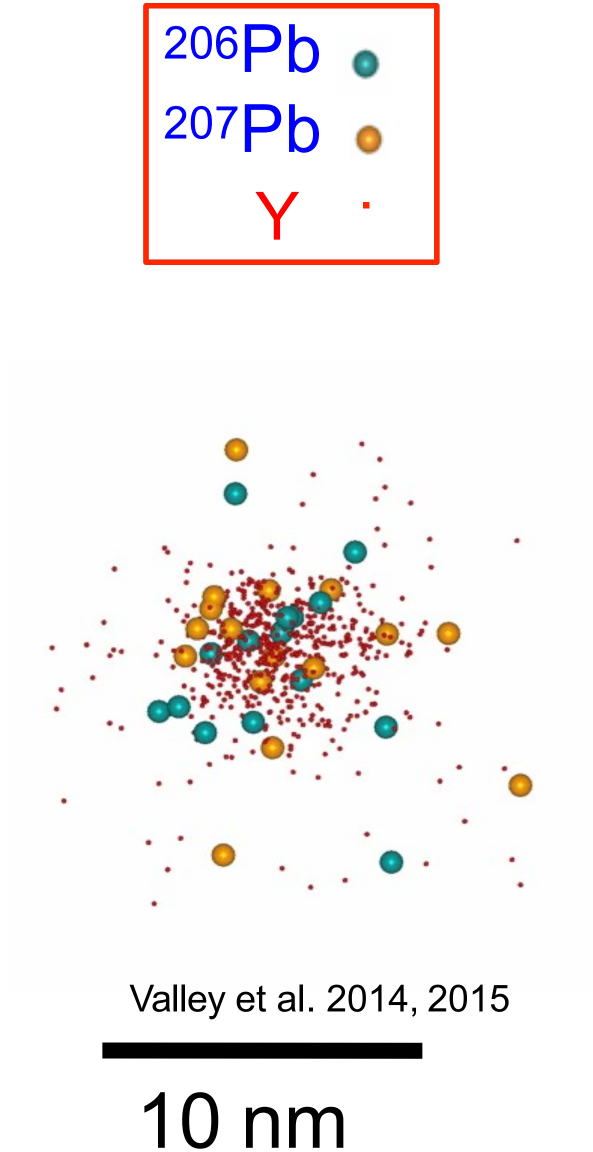

JW Valley, et al., *Nature Geoscience* (2014) **7**

# Clusters- APT

## 4.4 Ga zircon, Jack Hills



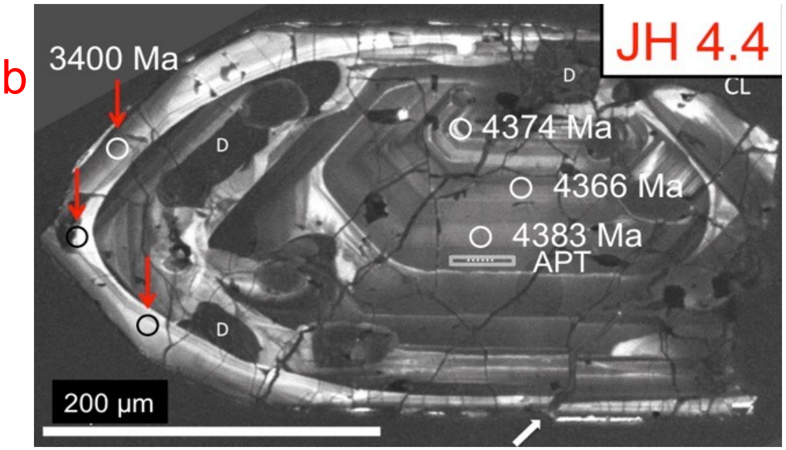




Valley et al. 2014, 2015

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

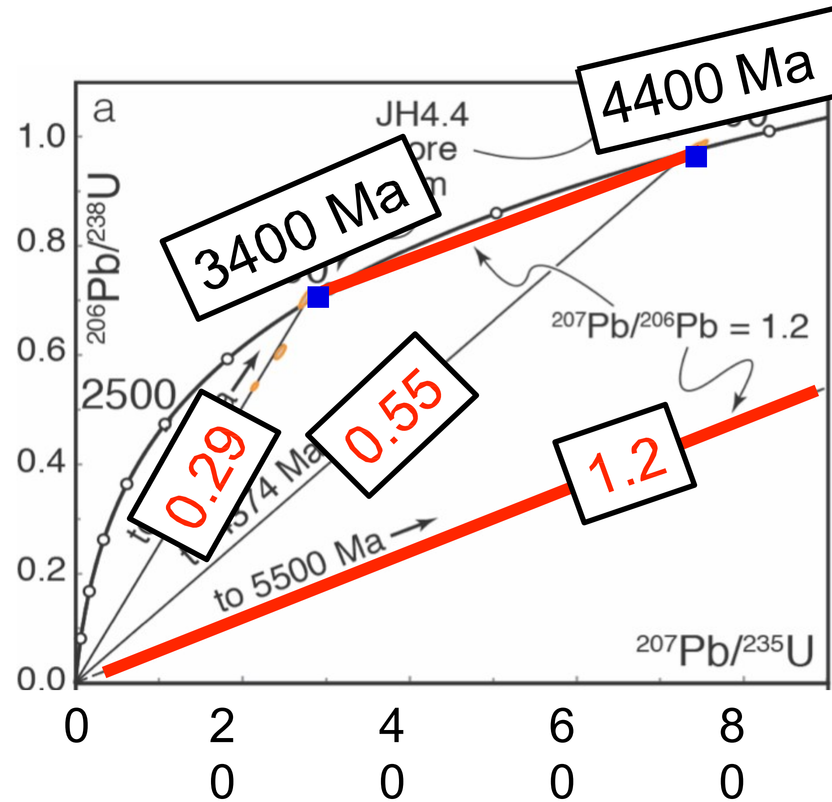
Linked to radiation damage

Compositions reintegrated by SIMS

SIMS ages are accurate

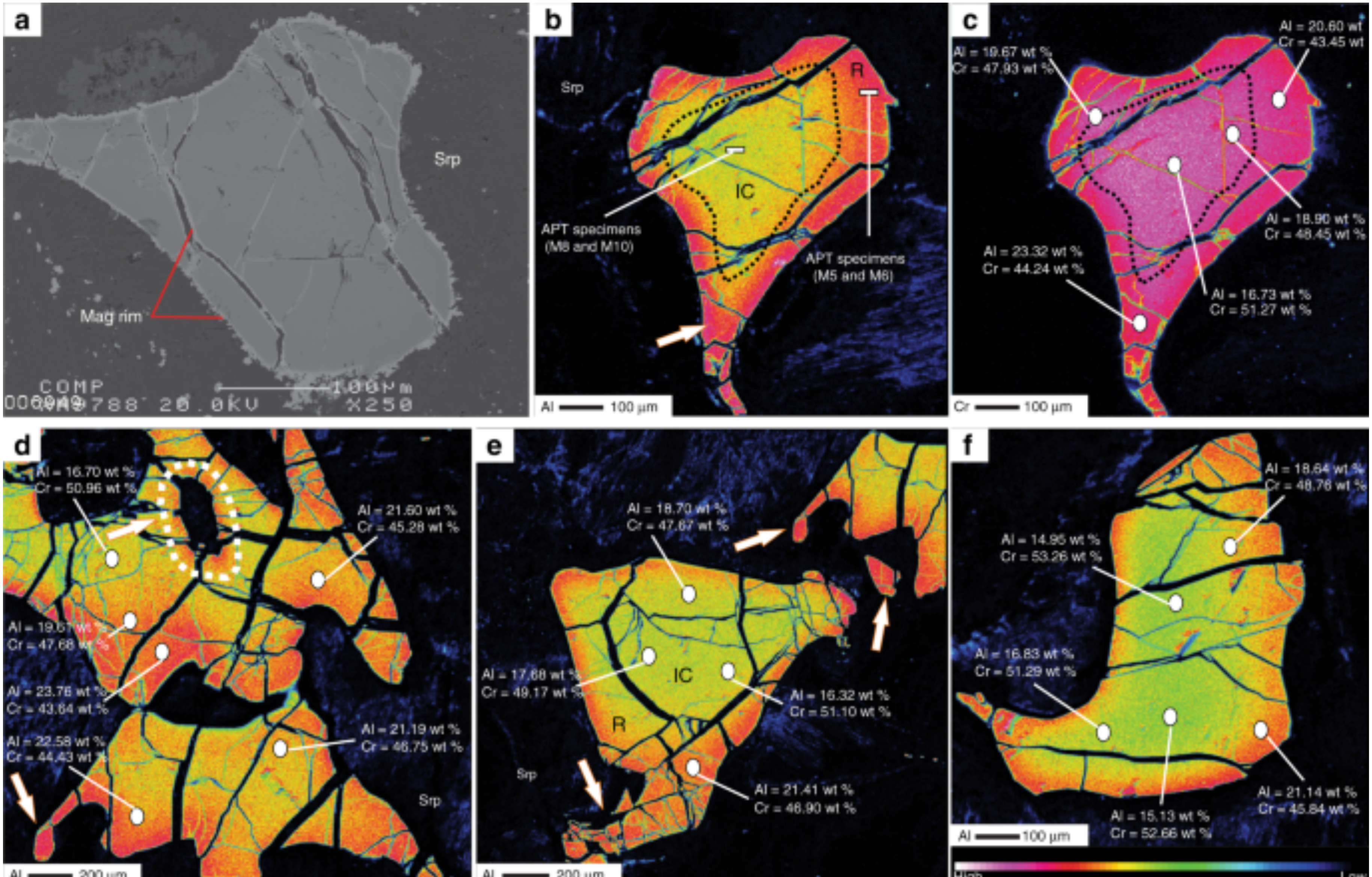
Clusters date reheating events

Confirms 4.4 Ga zircon from Jack Hills

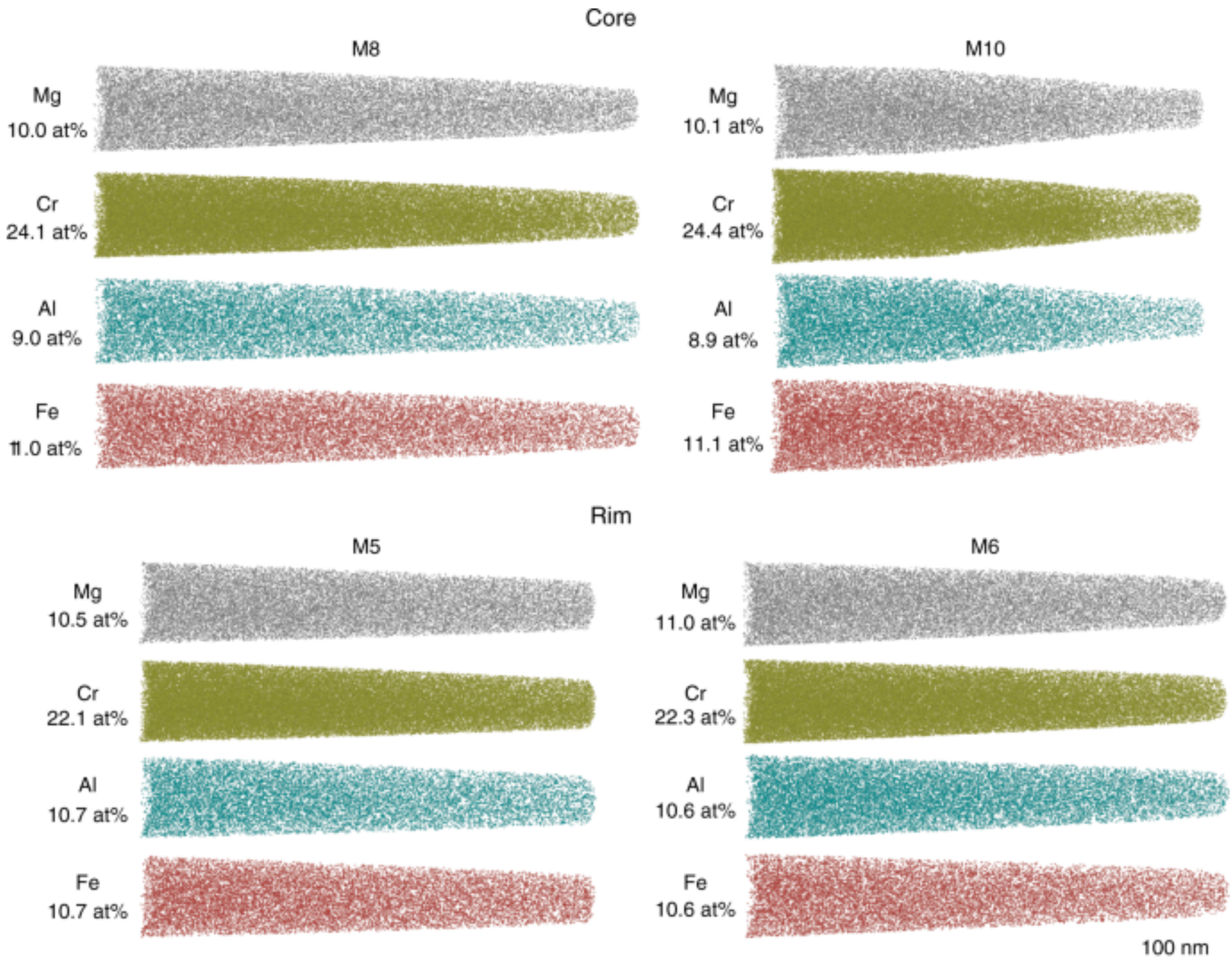


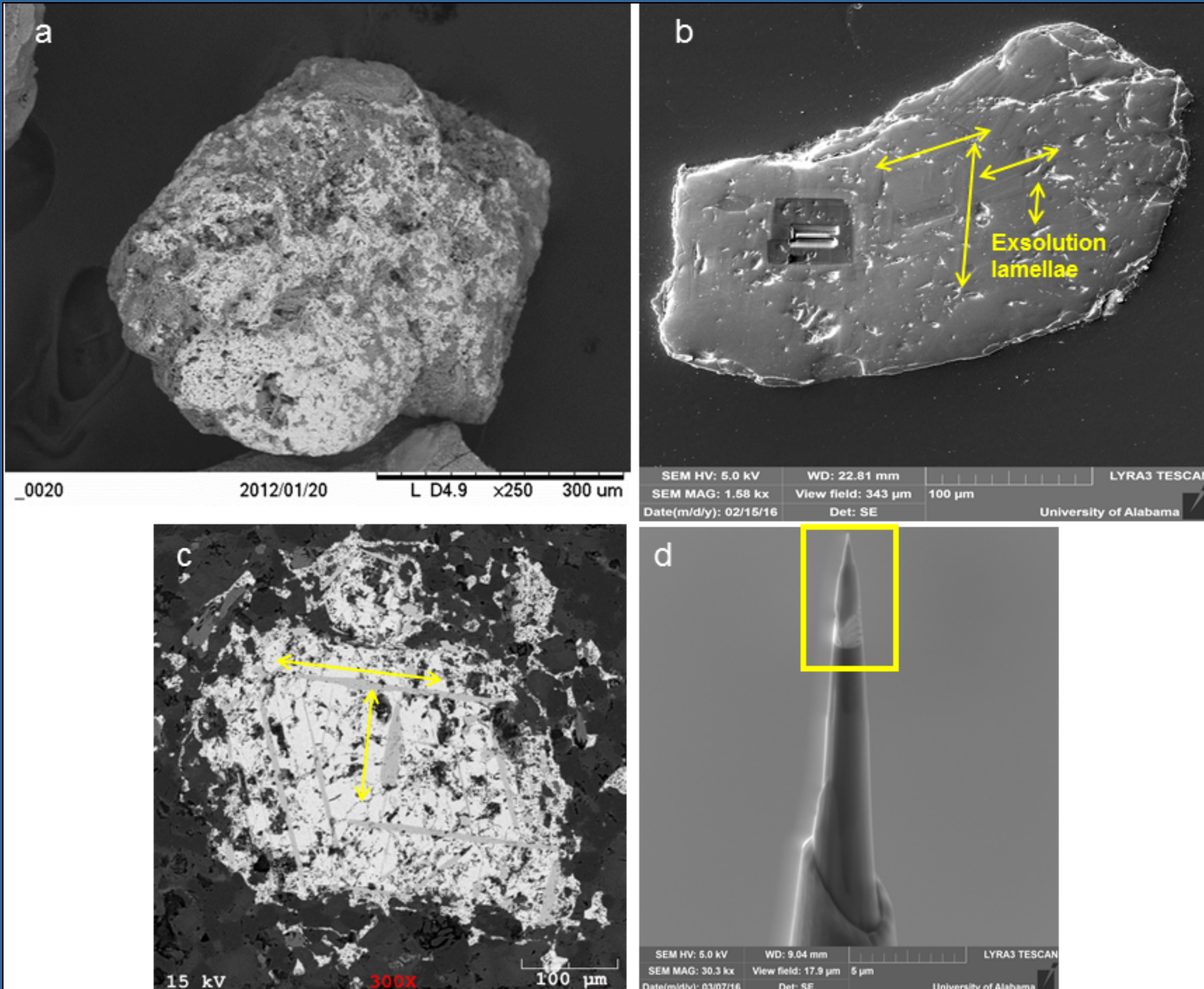

Valley et al. 2014, 2015

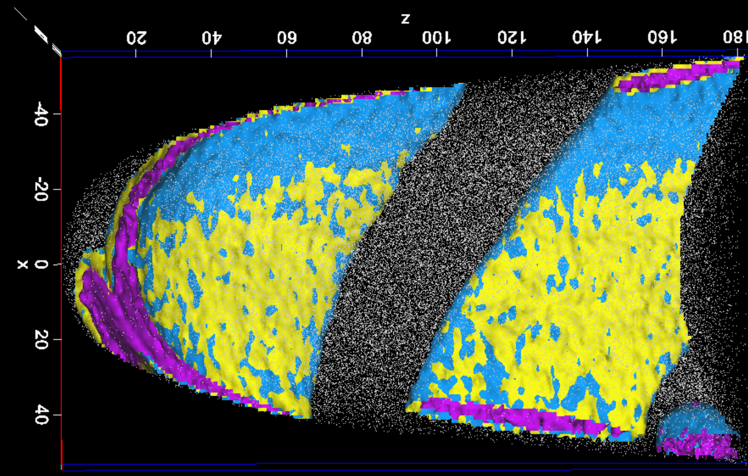
# Spinel
# Cr/Al ratios for Temperature

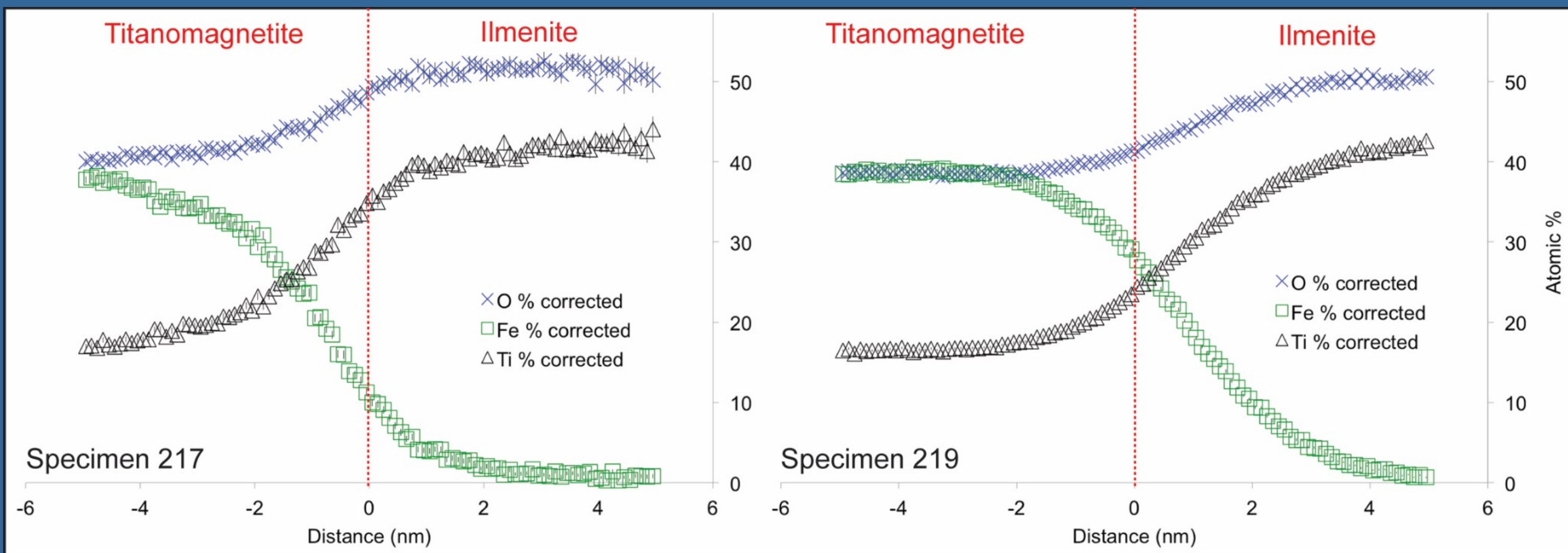



**Gamal El Dien *et al.* (2019) – Nature Communications**

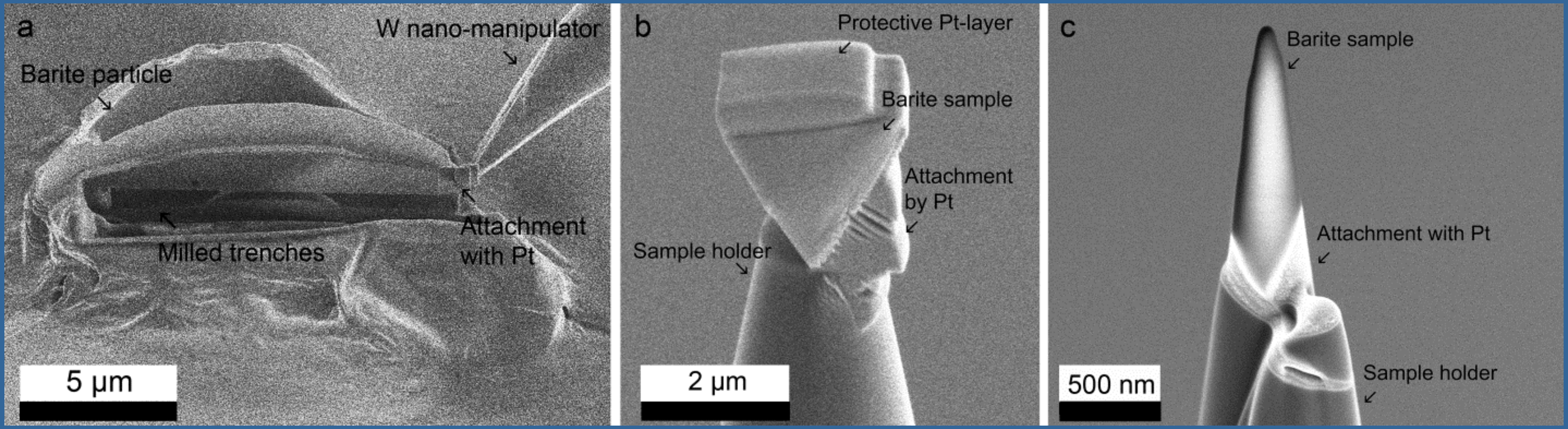

Core
M8
Mg
10.0 at%
Cr
24.1 at%
Al
9.0 at%
Fe
11.0 at%
M10
Mg
10.1 at%
Cr
24.4 at%
Al
8.9 at%
Fe
11.1 at%
Rim
M5
Mg
10.5 at%
Cr
22.1 at%
Al
10.7 at%
Fe
10.7 at%
M6
Mg
11.0 at%
Cr
22.3 at%
Al
10.6 at%
Fe
10.6 at%
100 nm


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

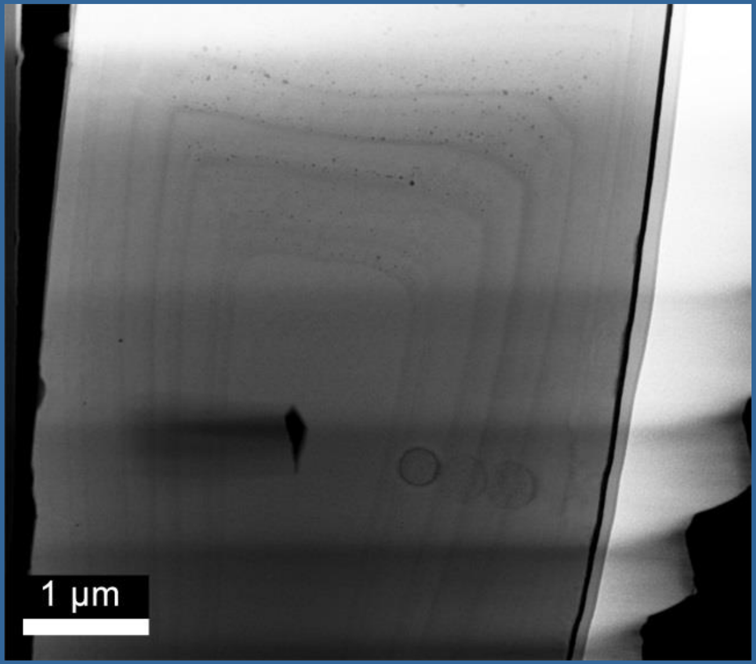


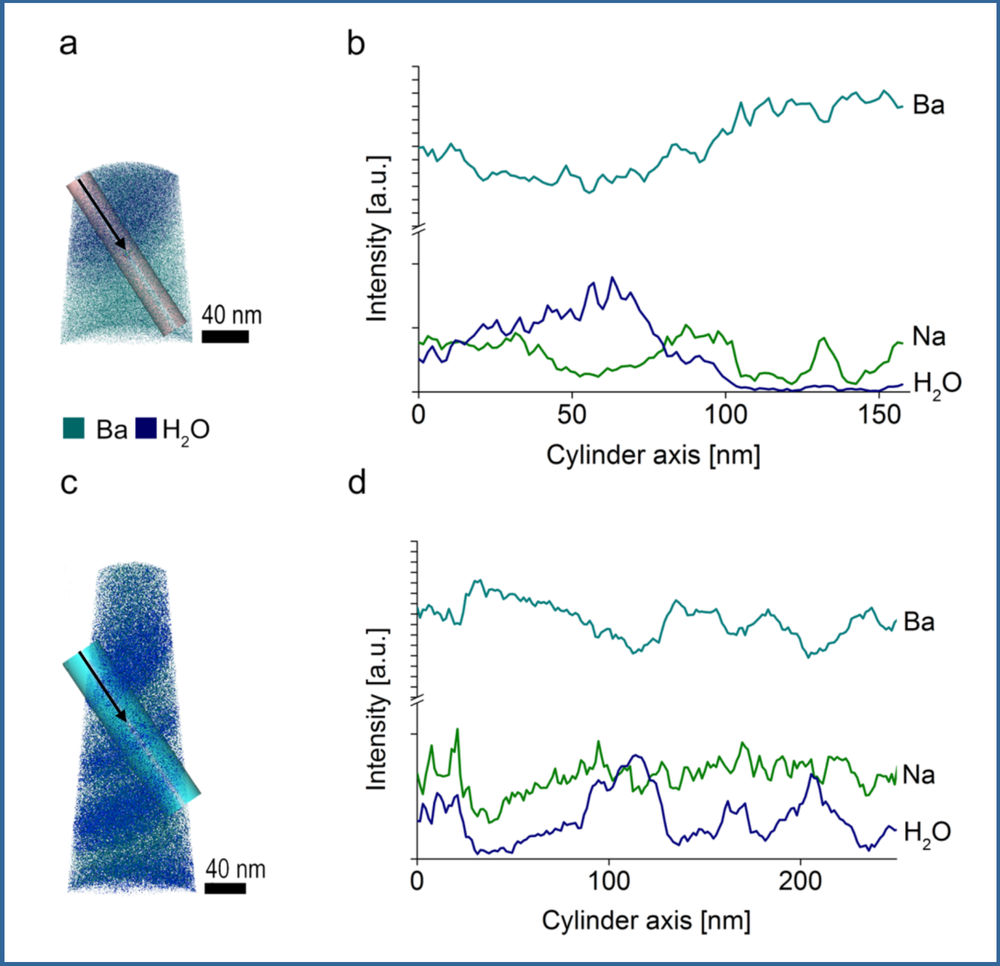




Genareau, Perez-Huerta & Laiginhas (2019) - JoVE

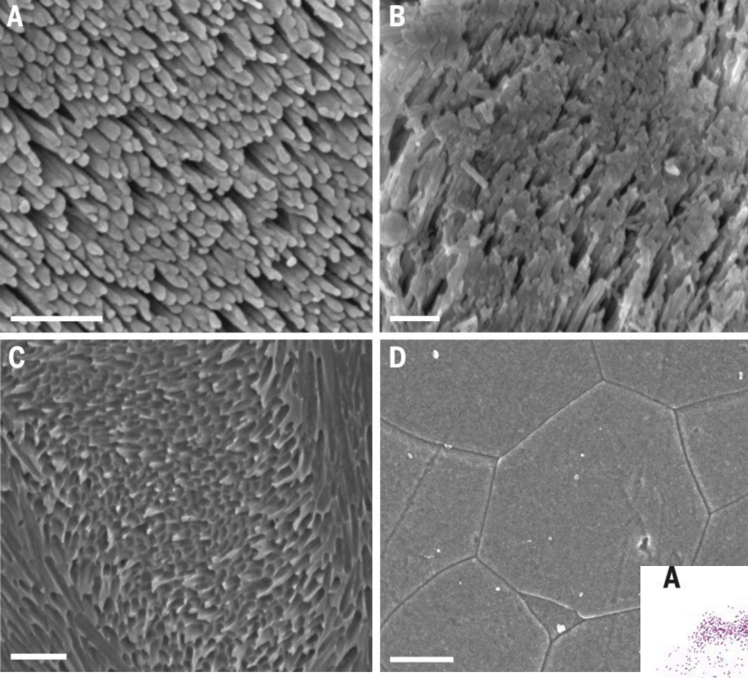



# Barite Crystal – TEM Image

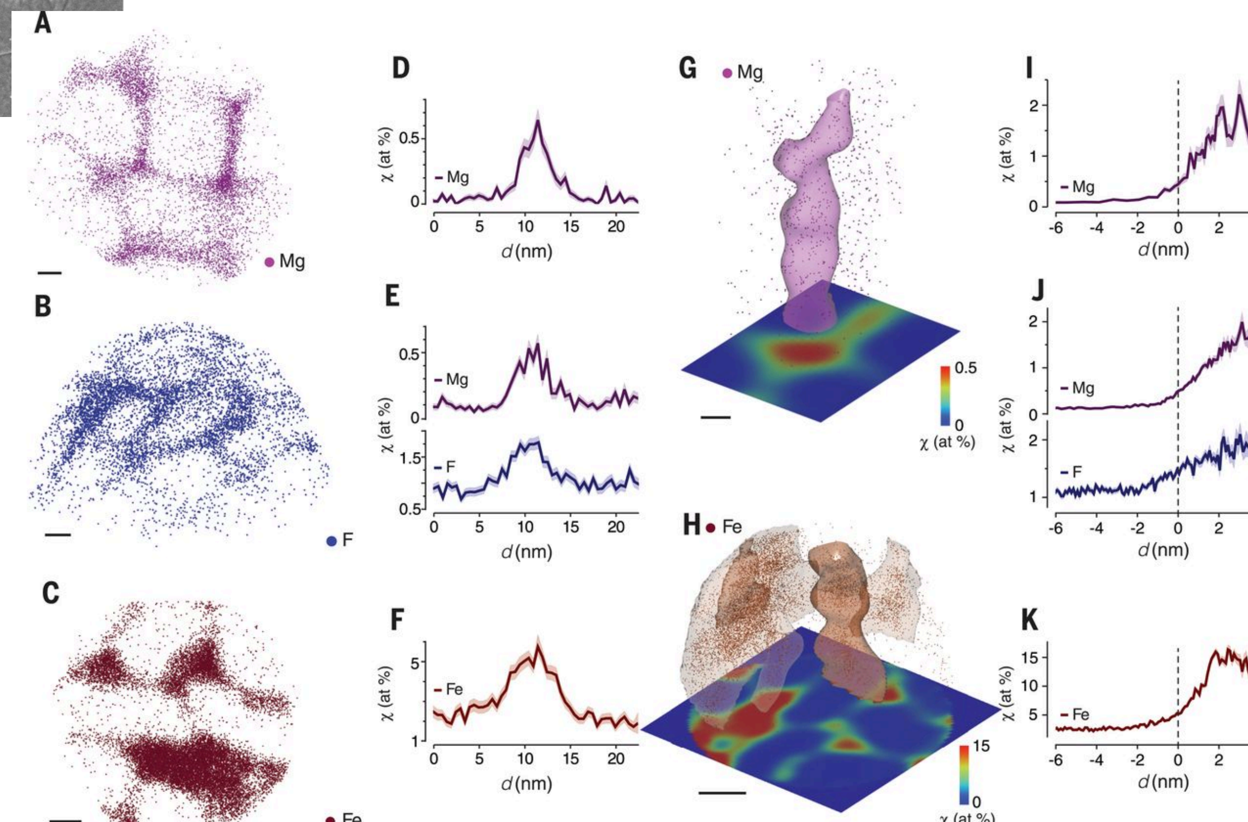


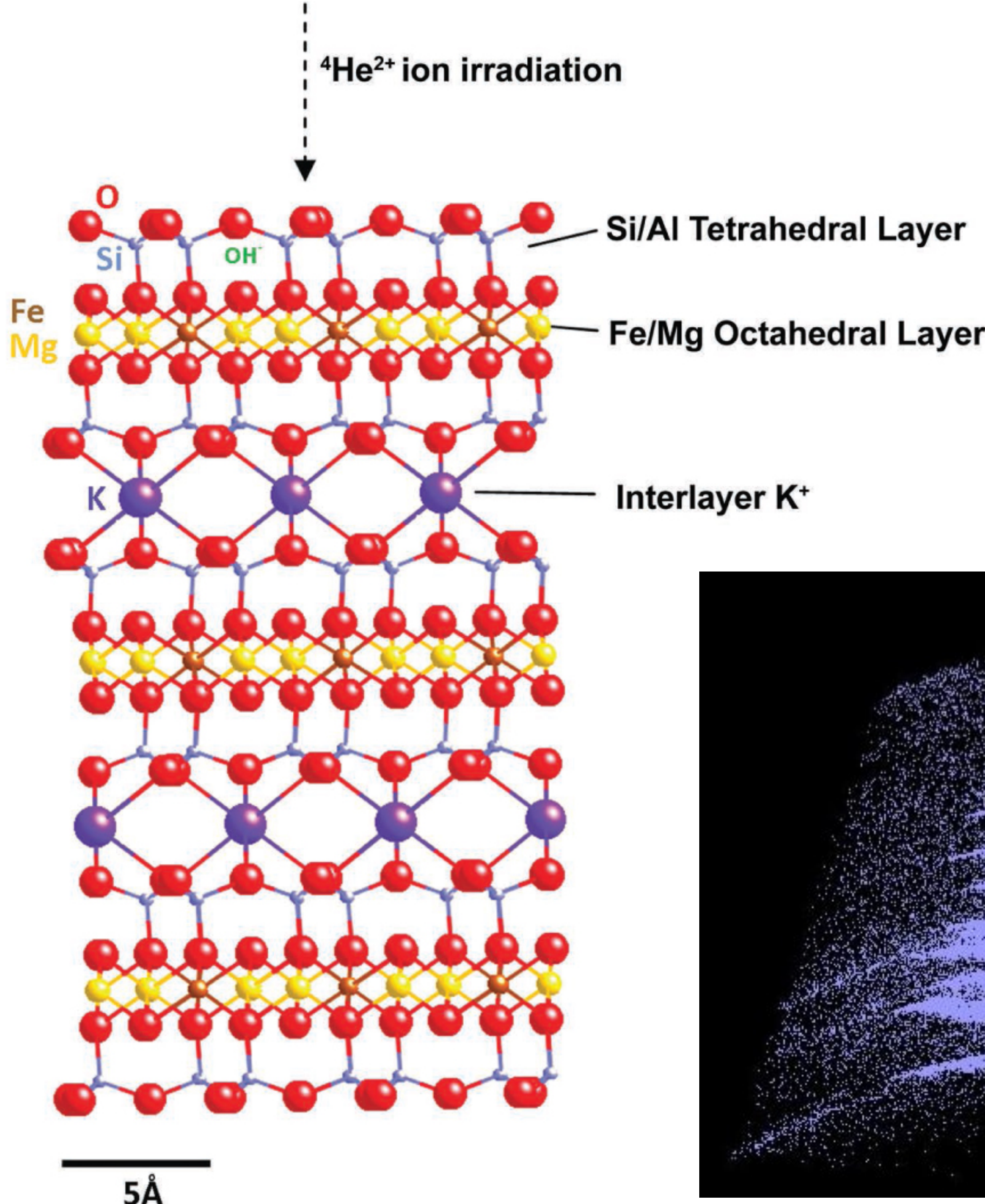




Webber *et al.* (2016) – Chemical Geology



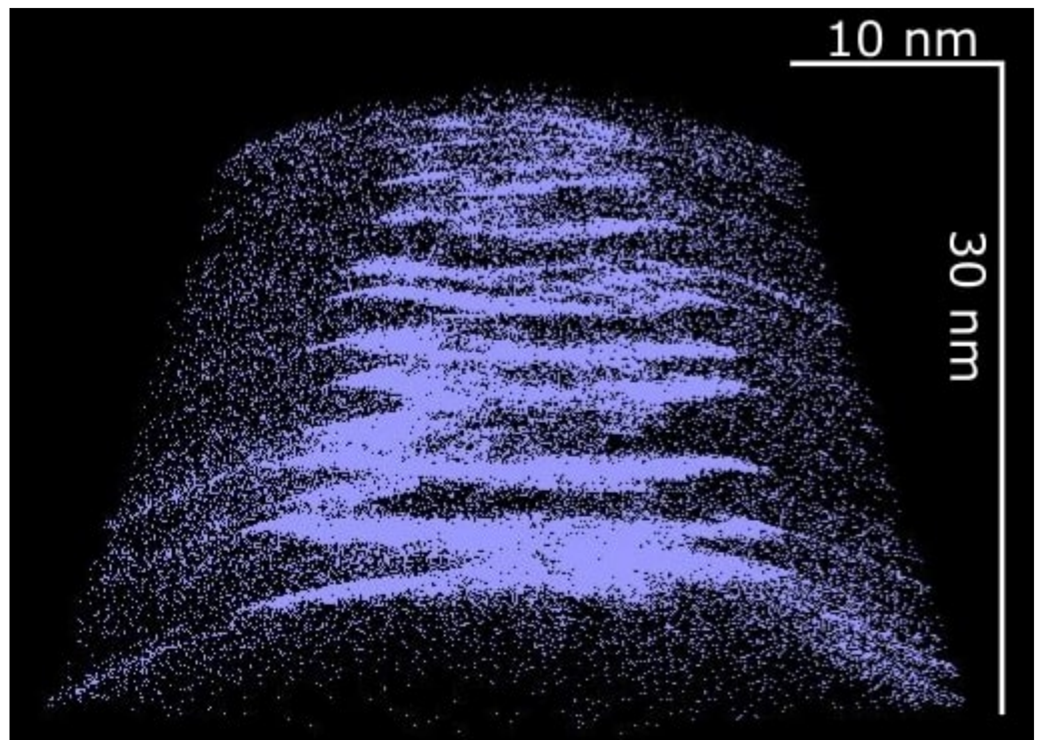

Gordon *et al.* (2015) – Science



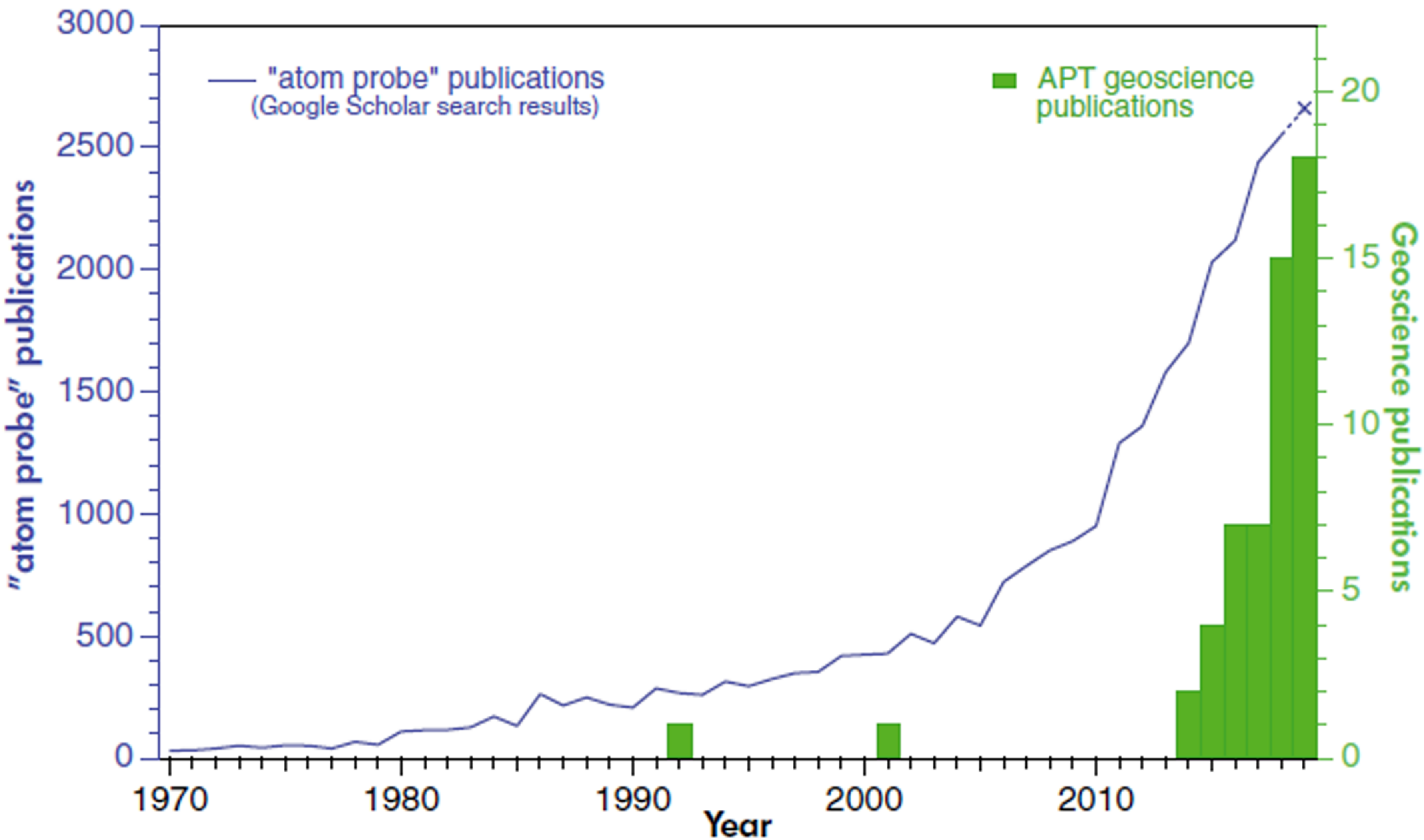


$^4He^{2+}$ ion irradiation
O
Si
$OH^-$
Fe
Mg
K
Si/Al Tetrahedral Layer
Fe/Mg Octahedral Layer
Interlayer $K^+$
5Å


© geology.com

10 nm
30 nm




**Reddy *et al.* (2020) – Geostandards and Geoanalytical Research**

Sample Preparation

Optimization

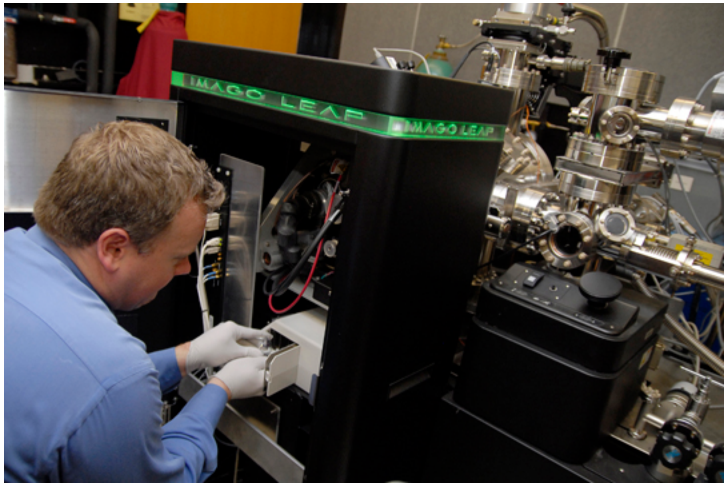
# UA GeoAPT

http://uageoapt.ua.edu

Biomineralization

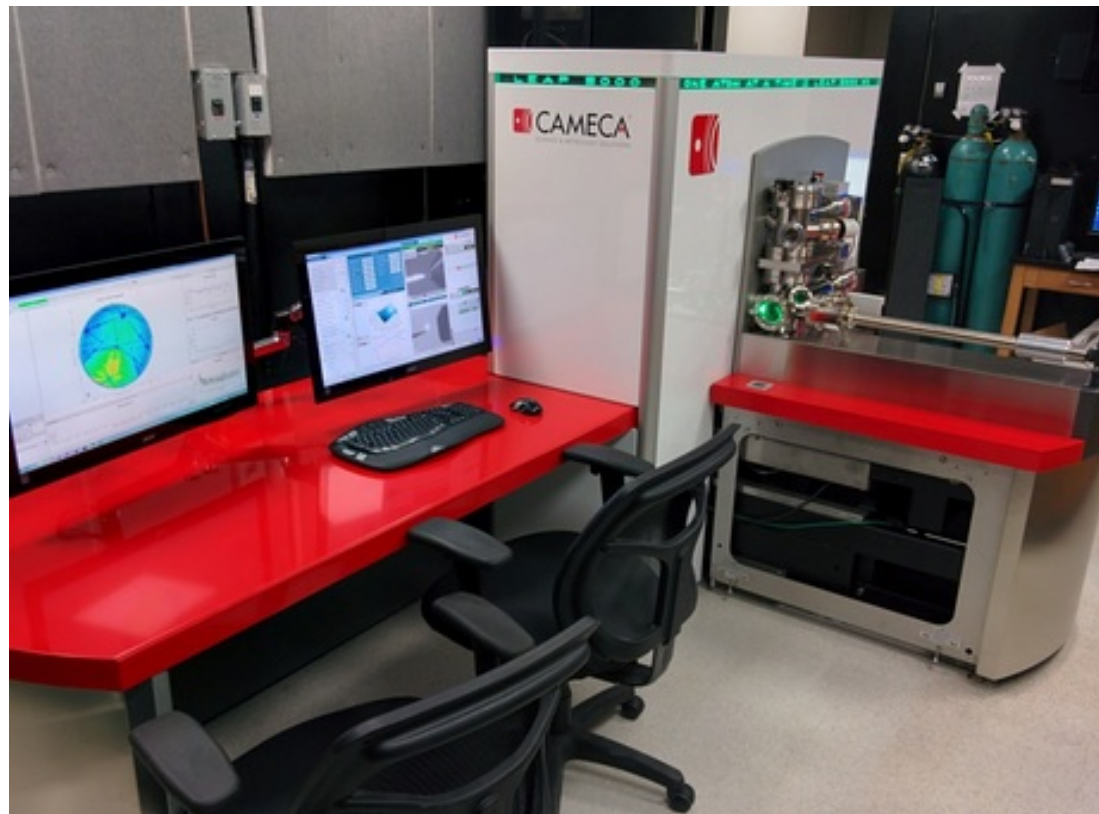
Nanogeosciences

# LEAP Instrument

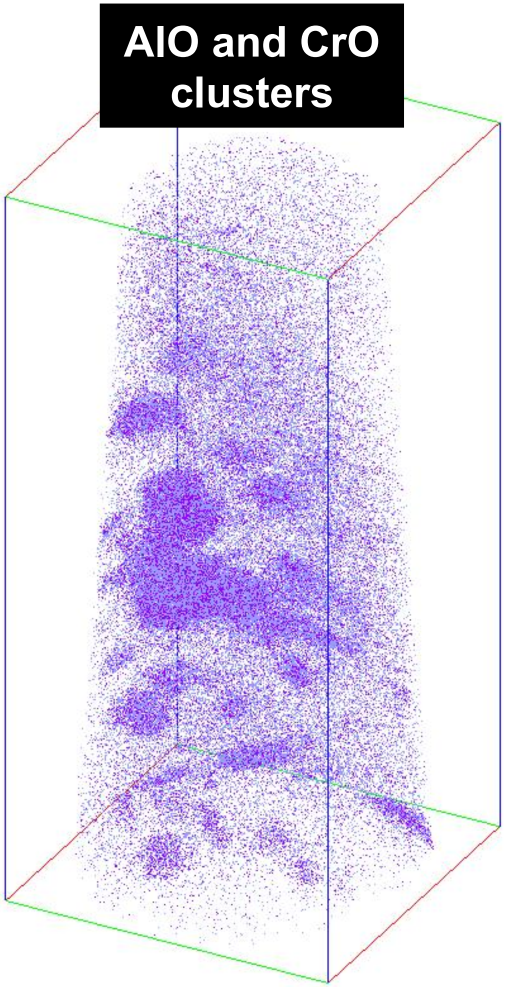



LEAP 3000 XS

LEAP 5000 XS



# Atom Probe Tomography Highlights




CV3 Allende Meteorite

## 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 (already detected 1-2 ppm of Hf)
✓Isotopes?

## The disadvantages

✓ Only 50-82% atom efficiency
✓'Complex' species (*i.e.* oxides, etc) evaporate 'complexly' – identification issues (peak overlaps)
✓Reconstruction technique – do I really have it correct?

# Acknowledgements

- Dave Mogk and NNCI Workshop Organizers
- National Science Foundation (NSF-EAR-IF) for funding [EAR #1647012, 1560779, 1402912]
- Dr. Gregory B. Thompson and Mr. Rich L. Martens at UA, and John Valley (UW-Madison) for slides
- Dr. Fernando Laiginhas and Dr. Chiara Cappelli (Postdoctoral Researchers)