Nanoanalysis of Metamorphic Magnetite using Field Ion Microscopy and Three-Dimensional Atom Probe

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Outline of Discussion

- Short tutorial on Field Ion Microscopy / 3D Atom Probe and why these techniques are interesting for geology and geomicrobiology.
- Discussion of sample preparation techniques for geological samples.
- Presentation of recent results of FIM and 3DAP of a metamorphic magnetite.

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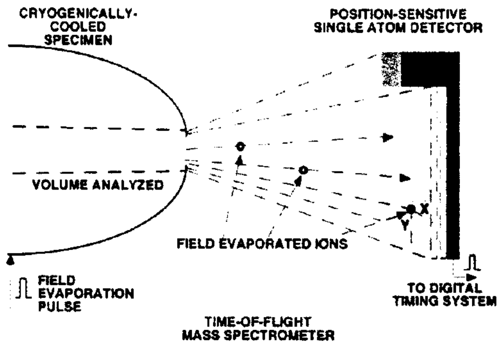
Schematic Illustration of APFIM Analysis



From Miller, et al. (1996) <u>Atom Probe Field Ion Microscopy</u> Oxford University Press

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Schematic Illustration of LEAP Microscopy

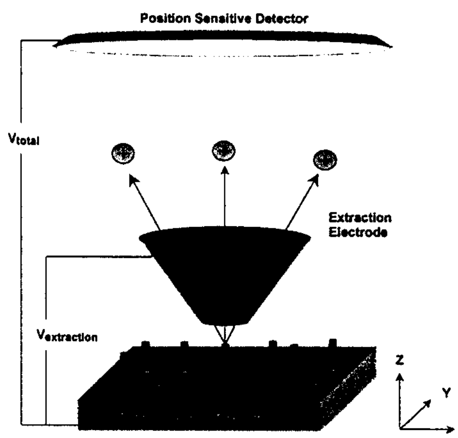

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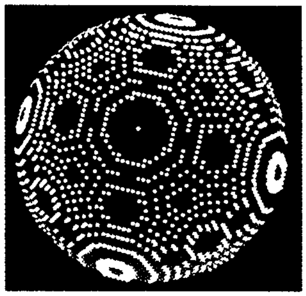
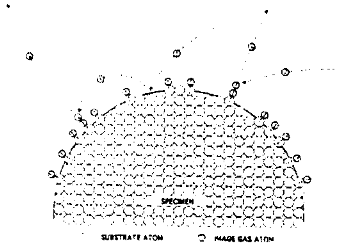
Image Formation in the Field Ion Microscope (FIM)





The ball model illustrating the origin of FIM image contrast. The white atoms indicate sites above which field ionization occurs preferentially. The model is fcc with the (001) plane at the center and {111} planes on the edges.

Image gas atoms (e.g. He, Ne, Ar, etc.) are polarized by the strong electric field, drawn to the surface, becoming field adsorbed. Electrons from the gas atoms tunnel into the metal and become field ionized. These image gas ions are then repelled from the sample towards the detector.

From Miller, et al. (1996) Atom Probe Field Ion Microscopy Oxford University Press

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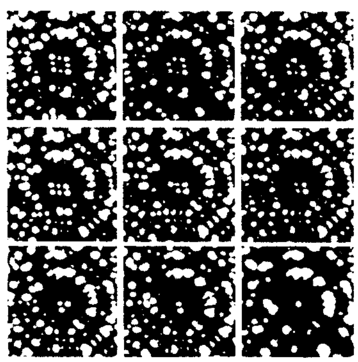
Evaporation of Single Atoms



Sequence of FIM images showing evaporation of single atoms of a nickel zirconium intermetallic specimen from the topmost atomic plane.

From Miller, et al. (1996) Atom Probe Field Ion Microscopy Oxford University Press

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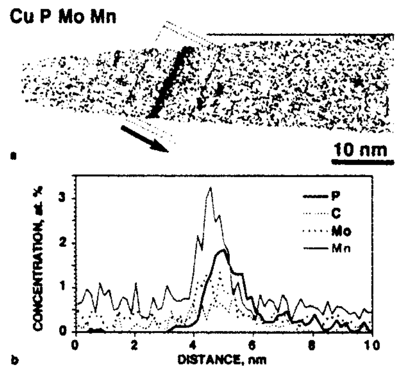
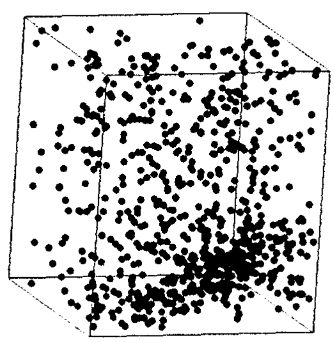
Analytical Capability of 3DAP



Atom probe analysis in the vicinity of an interface in a pressure vessel steel. Enrichments of P, C, Mo and Mn are evident.

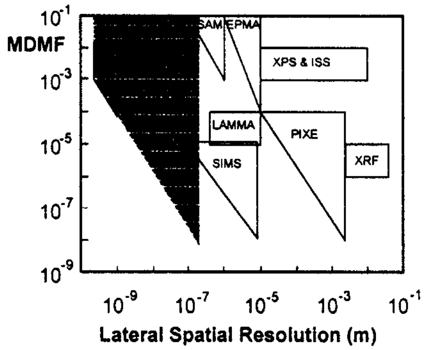
From Miller (2000) Atom Probe Tomography : Analysis at the Atomic Level, Plenum Publishing Corporation.

Analytical Capability of 3DAP



A three-dimensional image of stainless steel showing low levels of boron (red), carbon (green), and phosphorus (blue) at a grain boundary. This analysis was done using the conventional three-dimensional atom probe (3DAP) at Oak Ridge National Laboratory. Other elements (e.g. iron) have been left out of the image for clarity.

Extending the Limits of Detection and Spatial Resolution



- Improvement in Minimum Detectable Mass Fraction (MDMF).
- Increase in Spatial Resolution compared to Secondary Ion Mass Spectrometry (SIMS).

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Objectives of this work

- A 3D near-atomic scale elemental map of a geological sample.
- Demonstrate the planetary science potential of the Local Electrode Atom Probe (LEAP).
  - Potential of LEAP analysis for non-conductive samples:
    - Terrestrial geology and geomicrobiology,
    - Apollo samples from the Moon,
    - Samples returned by the Stardust, Genesis and Mars missions.
- Demonstrate the potential of the Mini-LEAP for the *in-situ* analysis of planetary materials.
  - NASA is currently developing a prototype Mini-LEAP at JPL.

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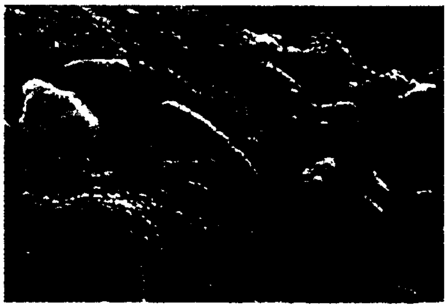
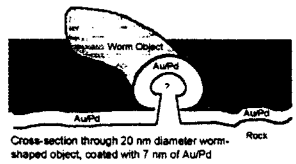
"Nanobacteria"
How do you characterize it?



An SEM micrograph of the "fossil nanobacteria" found in ALH84001 by McKay, et al. [1996].



A schematic diagram of a possible cause of the "fossil nanobacteria" found in ALH84001 by McKay, et al. (1996) as discussed by Steele, et al. (1998) and Bradley, et al. (1997).

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Why Magnetite?

- A common mineral on Earth, the Moon and Mars.
- One of the more conductive minerals.
  - Resistivity = 52 x 10^{-4} ohm-cm.
- This particular magnetite contains disk-shaped exsolutions approx. 40 nm in diameter, 1-3 nm thick and about 10^4 platelets/μm^3.
- EDS shows Mn and Al concentrated in these precipitates.
- Quantitative analysis has been limited by the thickness of this second phase.

Atom Probe is a technique that can potentially quantify the composition of these precipitates.

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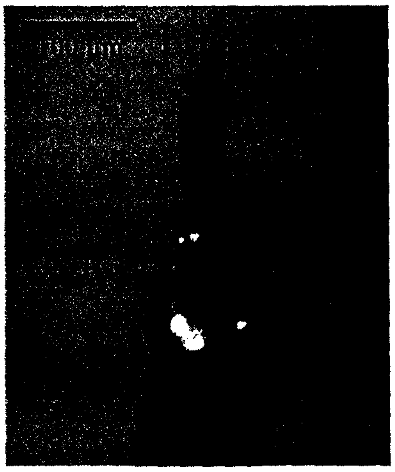
"Method of Sharp Shards"



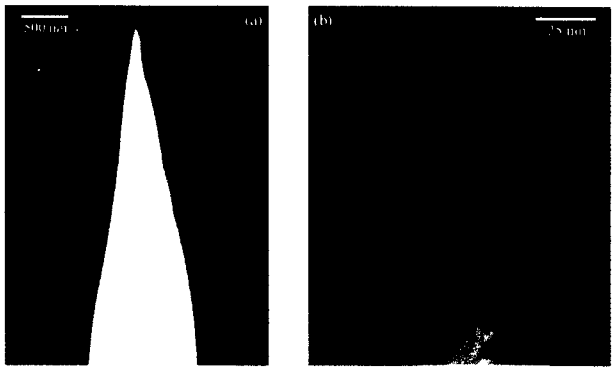
- Introduced by Camus, Melmed & Banfield in 1991.
- Magnetite grains >2 mm in diameter were crushed at random to make sharp fragments 50 μm across and 250 μm long.
- A single fragment is attached to a stainless steel insect pin using two-part, conductive silver epoxy.

Sample Shaping Using a FIB

Sample as mounted with Pt deposition at the base to improve electrical connection.

Sample after extensive ion milling using various beam currents and orientations.

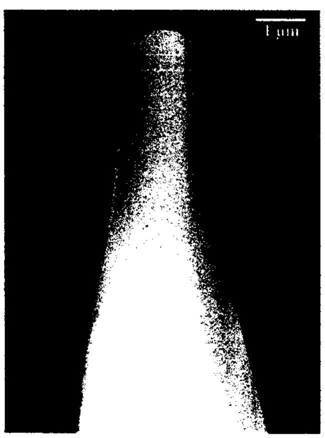
Magnetite Field Emission Tip Prepared with a FIB



a) Profile of tip illustrating the smooth shank obtained. b) Sample tip showing radiation damage due to the 25 keV Ga beam.

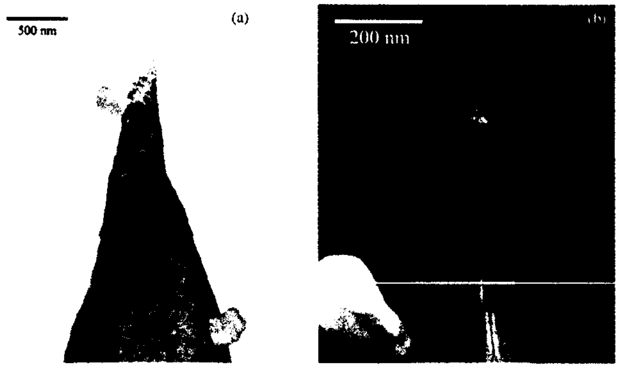
Note that the damage decreases in thickness further down the shank of the sample.

Post-Mortem Analysis of Magnetite Sample



- TEM of sample 031300E after first analysis in the ECOPoSAP.
- Sample was analyzed to the voltage limit of 16 kV.
- Sample "flashed" near end of run.
- Note the slight roughness at the tip.

Recovery of a Magnetite Field Emission Tip



Surface after Field Evaporation

TEM of sample 031300E after resharpening with a Gatan ion mill with 5 keV Ar and gun tilt = 40°. a) Bright field image showing precipitates and bend contour. b) High magnification image of the tip and precipitates seen in FIM images. The line indicates the surface obtained after field evaporation.

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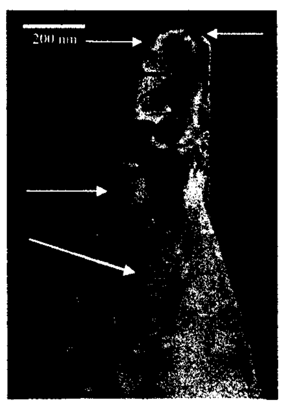
Post Evaporation TEM Analysis of Magnetite LP204-1

Disk-shaped precipitates normal to the beam.



Precipitates seen in FIM images. The location of this surface is indicated on previous slide.

Electron diffraction pattern indicates that this view is normal to the [100].

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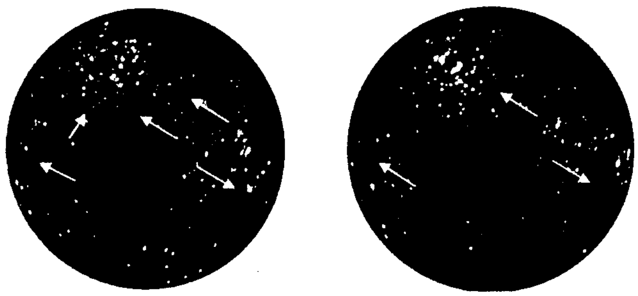
Field Ion Micrographs of Magnetite LP204-1



16 kV 16.5 kV

Note the clarity of the {111} poles and the precipitates running directly through the pole at right of the images.

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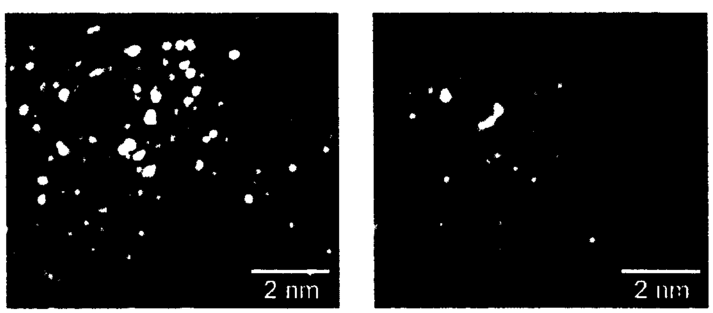
Six-fold Symmetry of the {111} Planes



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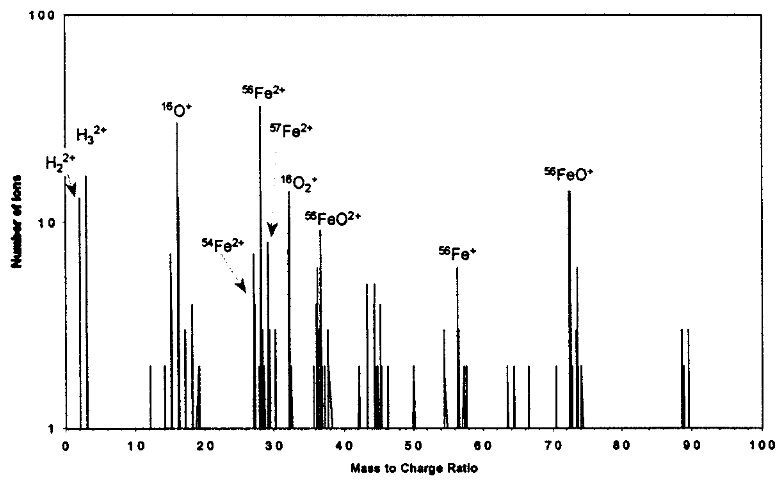
First Mass Spectra from a Geological Material using Atom Probe



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Conclusion

- First high quality FIM images of a bulk mineral.
- Preliminary APFIM analysis of magnetite:
  - Mass spectra have been obtained showing isotopes of Fe and O as well as FeO.
  - Singly and doubly charged ions are observed.
  - A preliminary mass spectrum taken from a precipitate contains both Mn and Al, as expected from previous analysis of magnetite LP204-1 by Sitzman, et al.
- Traditionally non-conductive samples ***CAN*** be imaged and analyzed using APFIM.

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