Correlative Microscopy & Characterization

TEM Dark-field Images

Iron-base superalloy

FeCr

NiAl

50 nm

LEAP Tomographs (Fe)

400 nm

- C. Stallybrass, G. Sauthoff, A. Schneider, and Y. Degas, Max Planck Institut fur Eisenforschung-Düsseldorf
APT Provides 3D Analysis
There is a lot of 3D detail
Grain Boundary Analysis
Grain boundary visibility

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

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

• Final tip shape: grain boundary no longer visible.
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.

Gibbsian Interfacial Excess is a measure of the amount of segregation at a grain boundary, normalized by area (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.

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

<table>
<thead>
<tr>
<th>Ion</th>
<th>Interfacial Excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>34.5 atoms/ nm²</td>
</tr>
<tr>
<td>Boron</td>
<td>7.6 atoms/ nm²</td>
</tr>
</tbody>
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Materials Applications

Nanowires and Nanoparticles
Specimen Preparation - Encapsulation

(a) ALD Layer 1

Silicon Substrate

20nm
APT of Pt Nanoparticles

Zn+O+Al
40 at.% Pt

Proxigram Analysis [1]

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

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

Materials Applications

Geological Materials
Viewpoint article

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

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

John W. Valley¹*, Aaron J. Cavosie¹,², Takayuki Ushikubo¹, David A. Reinhard³, Daniel F. Lawrence³, David J. Larson³, Peter H. Clifton³, Thomas F. Kelly³, Simon A. Wilde⁴, Desmond E. Moser⁵ and Michael J. Spicuzza¹
Life on Earth

1 Ga = 1000 Ma
Which View is Correct?

Solar System condensed about 4.56 Ga

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

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 concordant which is imbues confidence
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

\[ \frac{206^{\text{Pb}}}{238^{\text{U}}} = e^{\lambda_{238}t} - 1 \]
\[ \frac{207^{\text{Pb}}}{235^{\text{U}}} = e^{\lambda_{235}t} - 1 \]

A. Strickland et al. (2011) AJS
α-Recoil Damage in Zircon

α-recoil damage produces defects  

Pb segregation to defects

Geisler et al. 2007

Weber et al. 1994
Ewing et al. 2003

Utsunomiya et al. 2004

5.6 wt.% Pb
Jack Hills 4.4 Ga: Oldest Mineral Known?
Pb and Y Segregate to Defects

Atom Probe Tomography
Umbrella Winter School

December 12, 2018
APT Data Tell a New Story

Matrix+ Clusters
4.4 Ga

Matrix
3.4 Ga

Pb/U ratios are unphysical for radiogenesis

- 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?

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

John W. Valley1,2, Aaron J. Cavaosia1,2, Takayuki Ushikubo3, David A. Reinhart4, Daniel F. Lawrence4, David J. Larson3, Peter H. Clifton5, Thomas F. Kelly3, Simon A. Wilde4, Desmond E. Moser5 and Michael J. Spicuzza1

Atom Probe Tomography - Umbrella Winter School
Beyoncé Tweet on Blue Zircon

The little blue gem that may explain the origins of life

159,751 likes
view all 17,211 comments
prettyinparris: Just pray for some of these comments lol to silly!
raquelhazard: And he provided joy through all of the bad. Just giving you my beliefs like you gave me yours! Have a good day!
@krayney656
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.

Mass Spectrum

[Diagram showing mass spectrum with peaks at H and H₂]
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, H₂

H ~ 0.5%
The Hydrogen Challenge for APT

- Residual gas in a vacuum system is 90% H₂
  - H₂ is a difficult gas to pump
  - H₂ 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: CₙHₘₓ⁺
Materials Applications

Hydrogen Mapping
Analysis of Hydrides in Hydrogen-Disproportionated Fe-Nd-B Powder

Composition Profile through NdH$_2$ Precipitate

Cooperative APT and (S)TEM
Linear complexions: Confined chemical and structural states at dislocations

M. Kuzmina, M. Herbig, D. Ponge, S. Sandlöbs, D. Raabe

sciencemag.org  SCIENCE

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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”

“Atomic-Scale Analytical Tomography”
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?
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
Atom Probe Tomography - ASAT

**AST Objectives:**

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

**Properties**

- Atomic Structure
- Electronic Structure
- EELS
- EDS
- Diffraction
- Atom Probe (S)TEM

**Structure-Properties Microscopy**

**CMSE**