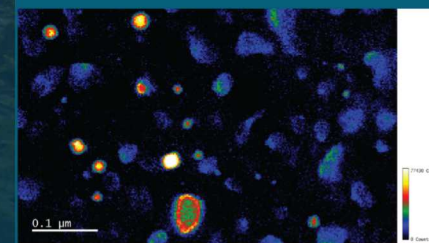




Using EELS to Determine He Pressure Inside Nanometer-Scale Bubbles



PRESENTED BY

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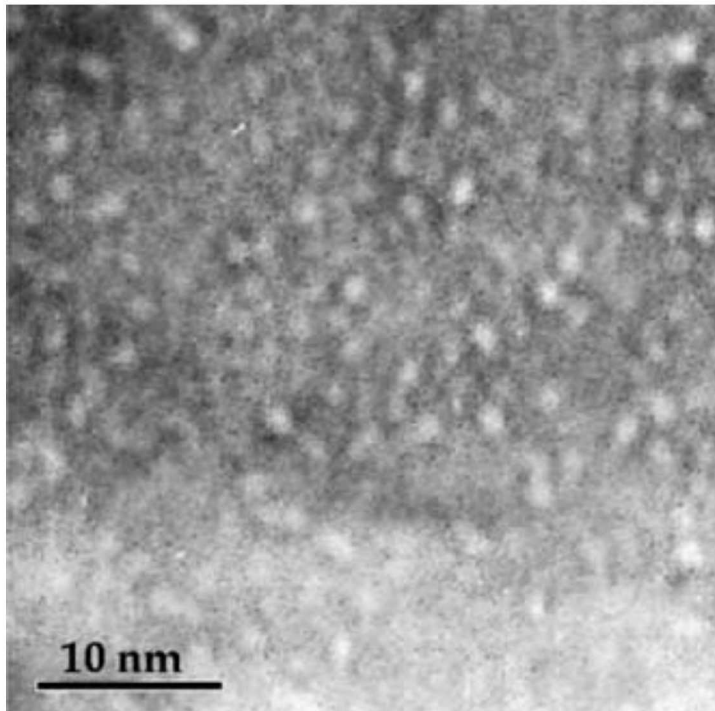
Acknowledgements

- Suzy Vitale – Carnegie Institute of Washington
- Warren York – Sandia National Laboratories, Livermore, CA
- E. Lynn Bouknight and Kirk L. Shanahan – Savannah River National Lab

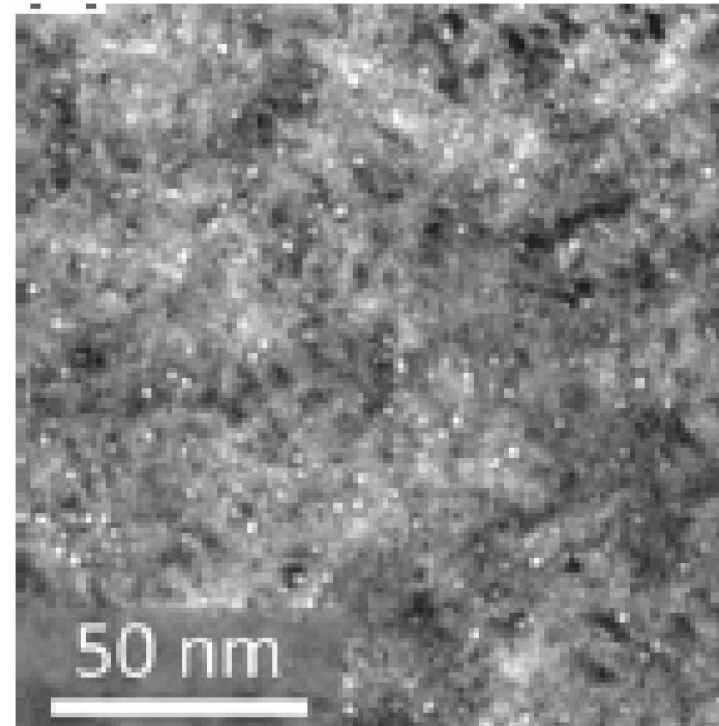


3 Helium Nanobubbles in Metals

^3H Decays into ^3He and forms bubbles in tritium storage materials



A. Fabre et al., 8-month Pd tritide
J. Nuc. Mater. 342 101 (2005)



J. R. Jeffries et al., Pu-Ga alloy
J. Nuc. Mater. 410 84 (2011)

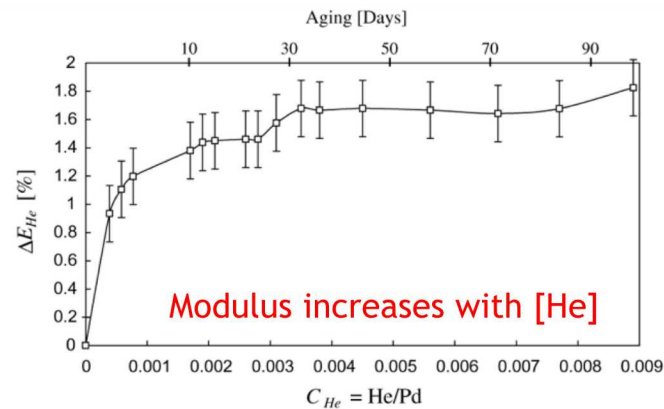
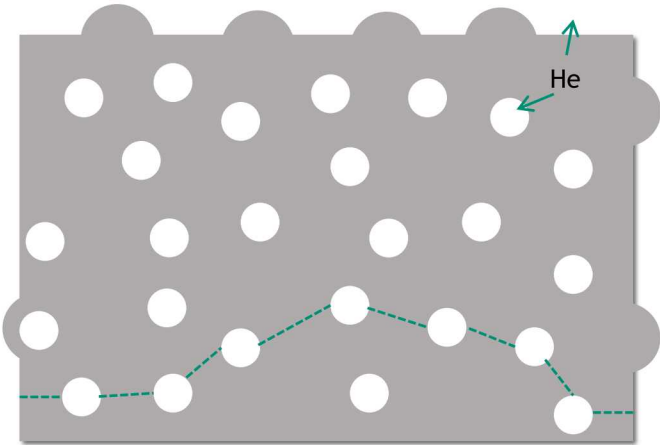
This phenomena also occurs

- Nuclear Reactor Materials - M.S. Blackmur, *et al.*, *Scripta Materialia* **152** (2018); M. Klimenkov, *et al.*, *Micron* **46** (2013)
- Magnetron Sputtering of Si - R. Schierholz, *et al.*, *Nanotechnology* **26** (2015)
- Nuclear Waste Disposal Materials - A.M. Seydoux-Guillaume, *et al.*, *Earth and Planetary Science Letters* **448** (2016)

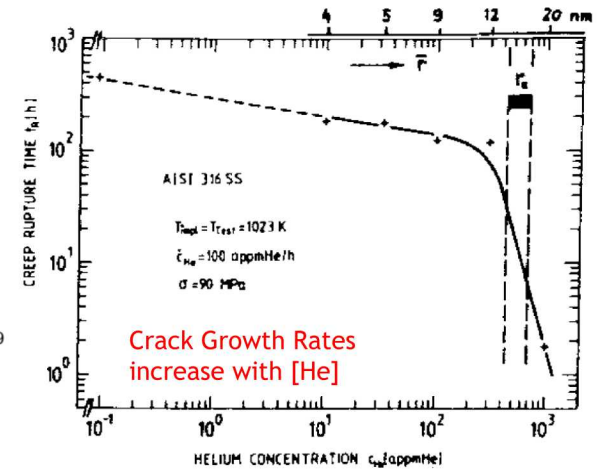


5 ^3He bubbles degrade mechanical properties in metal tritides

- Bubbles create fracture paths, swelling/deformation depending on pressure
- ^3He may escape at surfaces (and fracture surfaces), through grain boundary paths



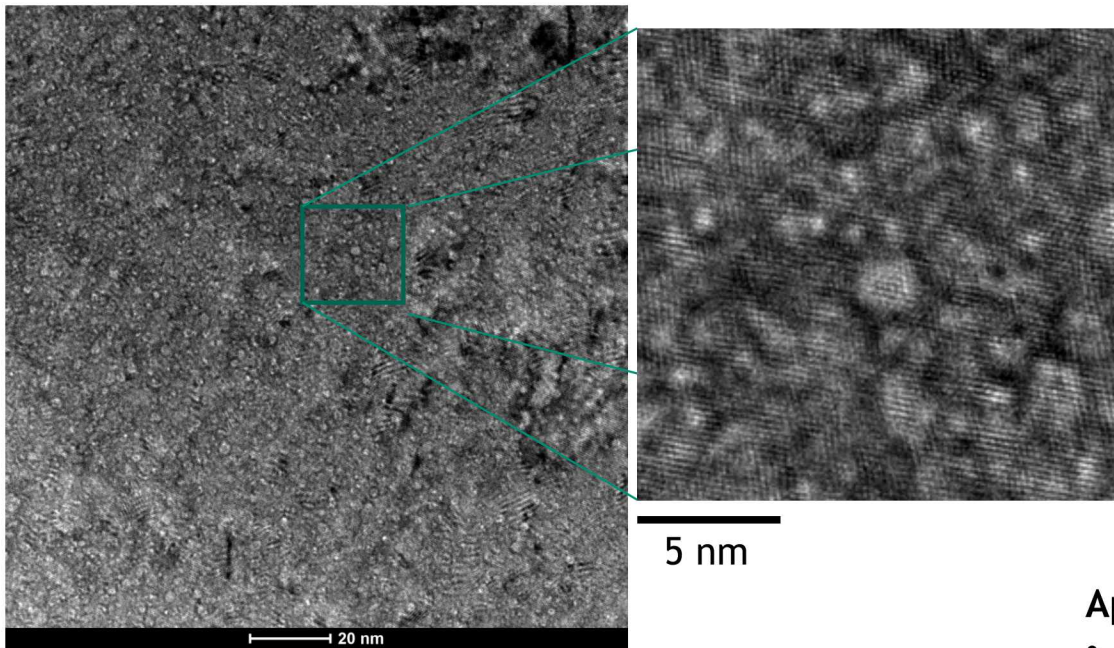
A. Fabre et al., 8-month Pd tritide
J. Nuc. Mater. 342 101 (2005)



H. Trinkaus and B.N. Singh, *Journal of Nuclear Materials* **323** (2003)

Material functionality is destroyed if rupture occurs

6 Helium Bubbles in Metals



Bubbles are a few nm diameter, tens of nm apart.

Questions

- When did bubbles form?
 - Early nucleation or continual
- Where did the He come from?
 - Surrounding volume, coalescence, or ripening
- How much He is in each bubble?
 - Pressure

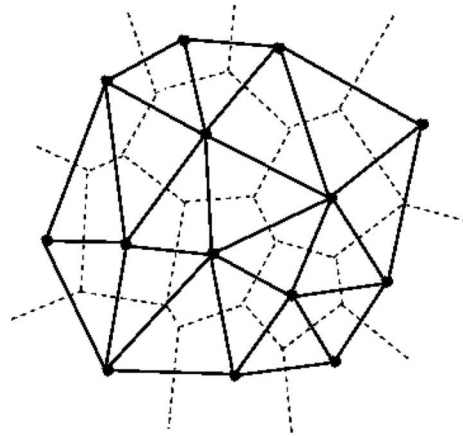
Approach

- Map bubbles in 3D using electron tomography
 - Eliminates 2D projection issues
- Use EELS to measure the pressure of He and to understand growth mechanisms

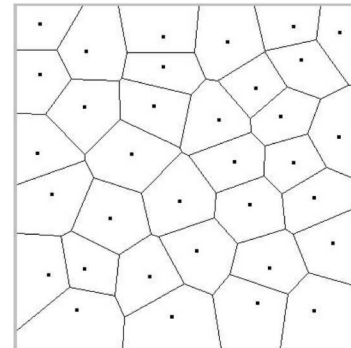
Goal: To develop improved models of helium bubble nucleation and growth, and better predict swelling, fracture, and ^3He release.

7 Capture Volume Theory

- If all bubbles nucleate at a same early time and their growth is diffusion limited, then they should contain the He generated in a capture region geometrically nearest each bubble.
- Capture volume is described by Voronoi tessellation.



2D Voronoi tessellation

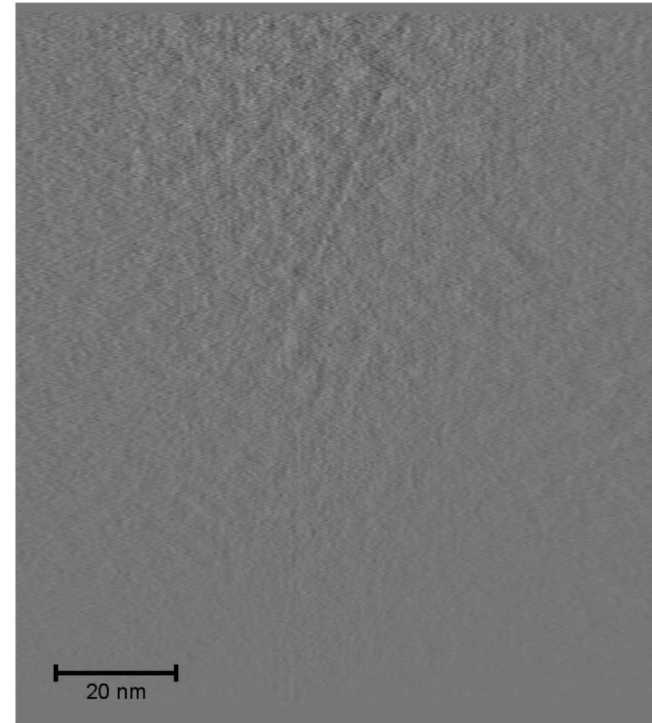
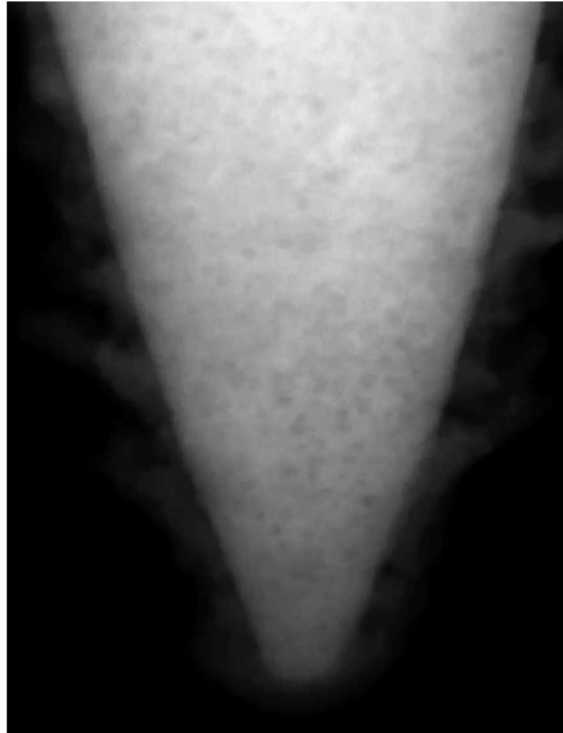


small capture area \Rightarrow small bubble?

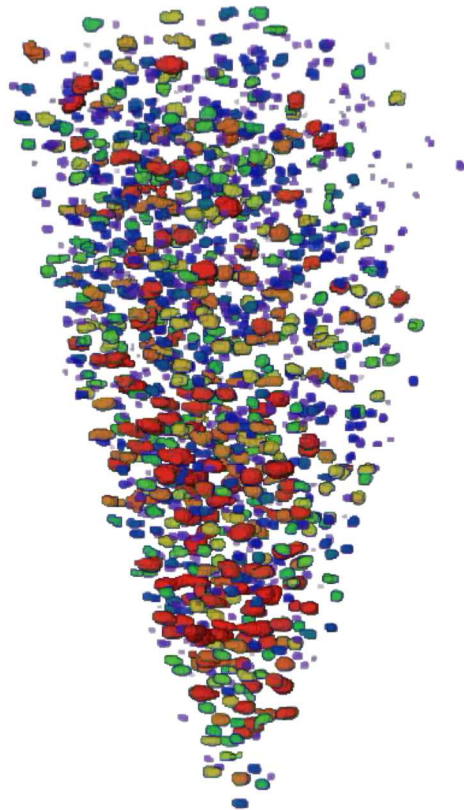


8 Dark field (HAADF) STEM Electron Tomogram

- Tritiated for 3.8 years (from a SRNL Pd-5 at.% Ni ribbon).
- No Grain Boundaries
- Estimated He/Pd = 0.12
- Bubbles are dark, ~2 nm diameters.
- Images taken from -70° to 70° (increment 1°).



Reconstruction of the 3D Bubbles



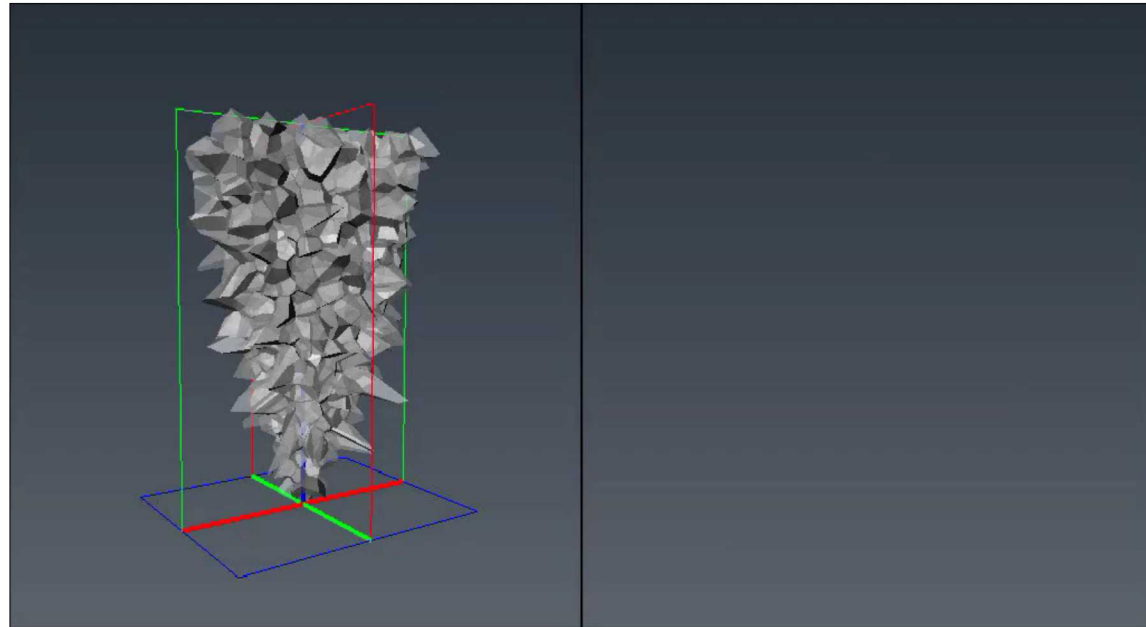
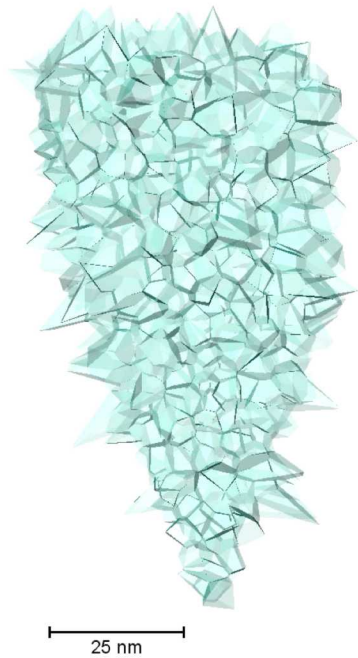
25 nm

- 3D bubbles are reconstructed from images using the “*Weighted Back Projection*”
- ~1500 bubbles with average diameter 2 nm
- Bubbles can be elongated due to reconstruction artifacts
- Red bubbles are large, blue bubbles are small.



Reconstruction of Capture Volumes

2D voronoi tessellation

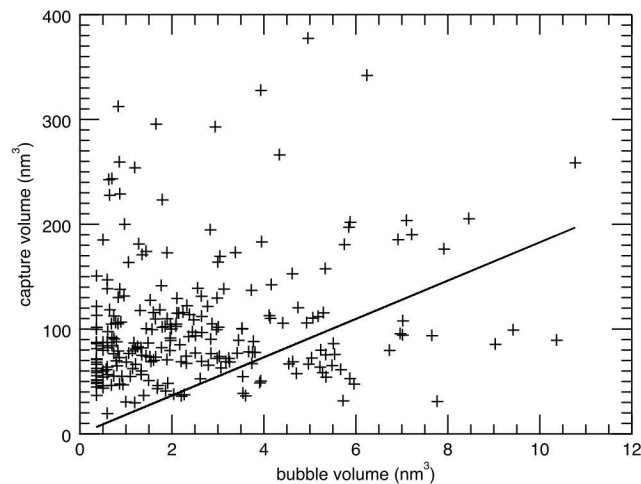


- Determined by 3D Voronoi tessellation of bubbles
- Outer layer of surface-crossing volumes is omitted from further analysis



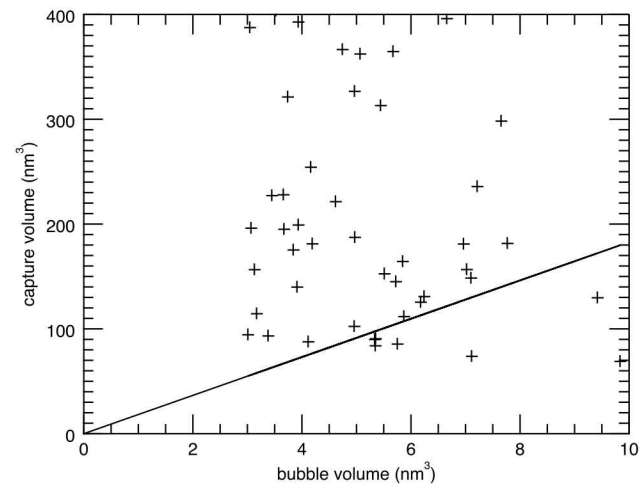


Individual Capture Volume



Solid line: expected for 3.8 year of tritium decay (He/Pd = 1.2) if bubbles have 5GPa pressure based on the loop punching growth

Individual Capture Volume

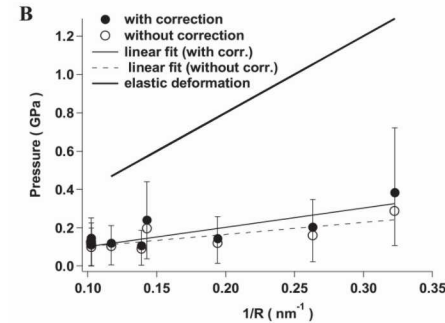
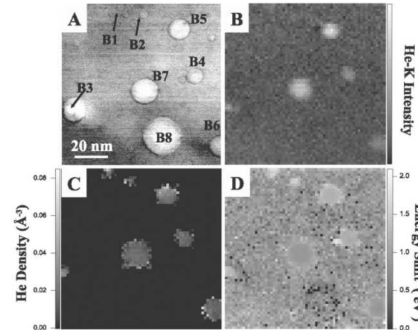
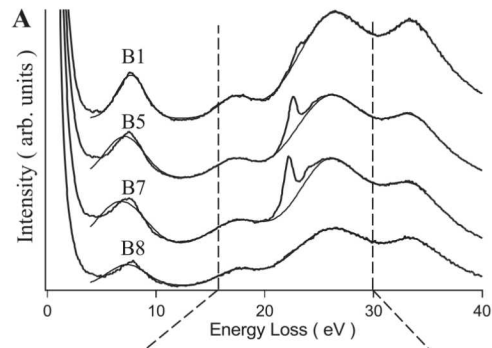


Exclude bubbles smaller than 3 nm³

Still no correlation!

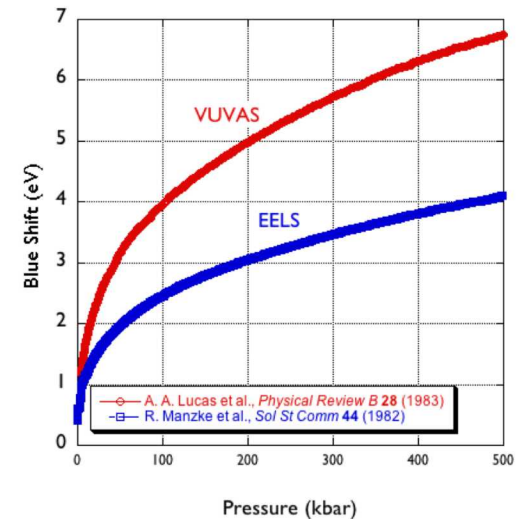
No bubble and capture volume correlation is found!

EELS measurements of pressure will help determine which bubbles grow



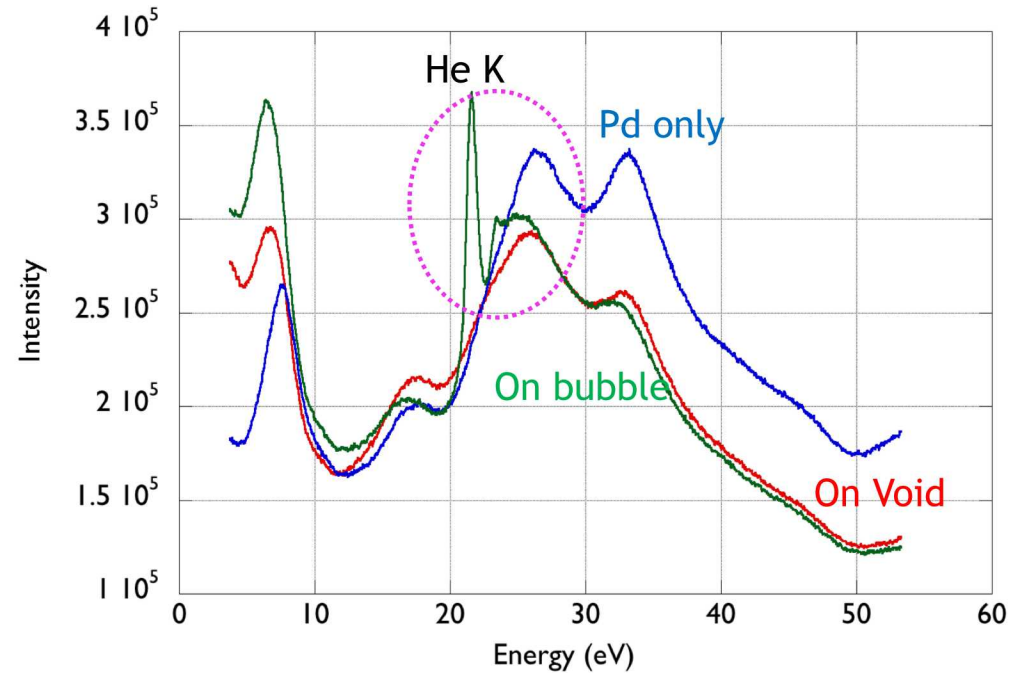
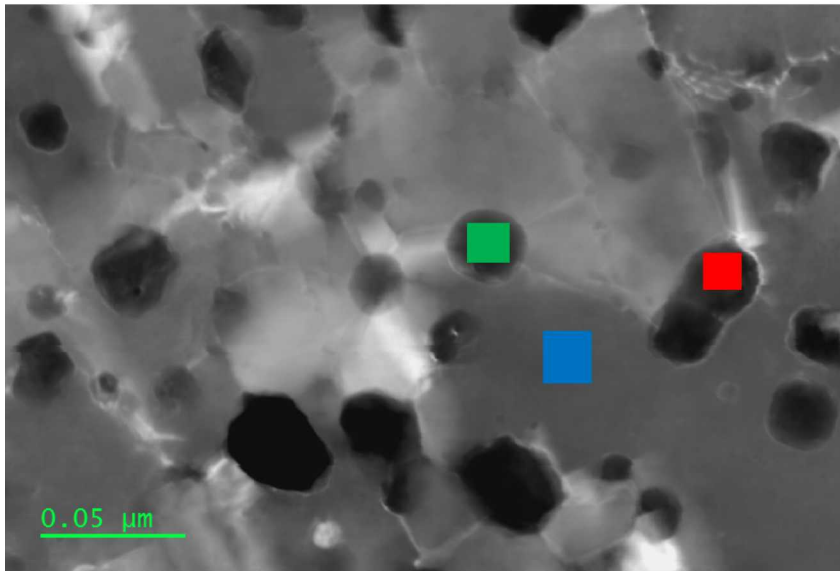
D. Taverna et al., PRL
100 035301 (2008)

- Why was the pressure of the bubbles lower than expected in this case?
- Why did the bubble size distribution appear to be so much larger than our bubbles
 - 5-20 nm diameter after 8 months of aging
 - 1-4 nm after 3.8 years



S.E. Donnelly, *Radiation Effects* **90** (1985)

Differentiating Bubbles from Voids Proves Challenging



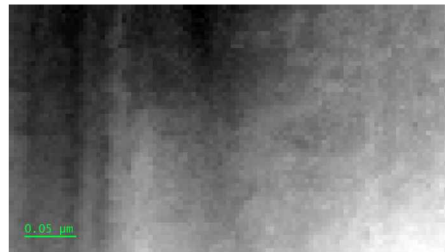
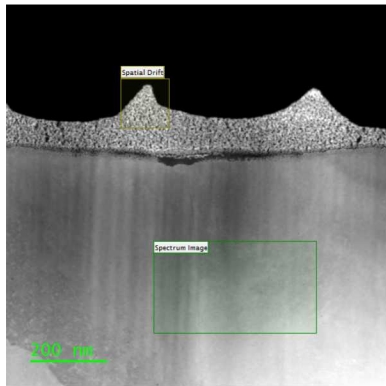
He ion implanted $1e17$ ions/cm²
Annealed 600°C 2 h
ADF STEM image

25 eV plasmon peak increases in intensity over voids and is difficult to separate from the intensity from He, especially for low signal (small bubbles)

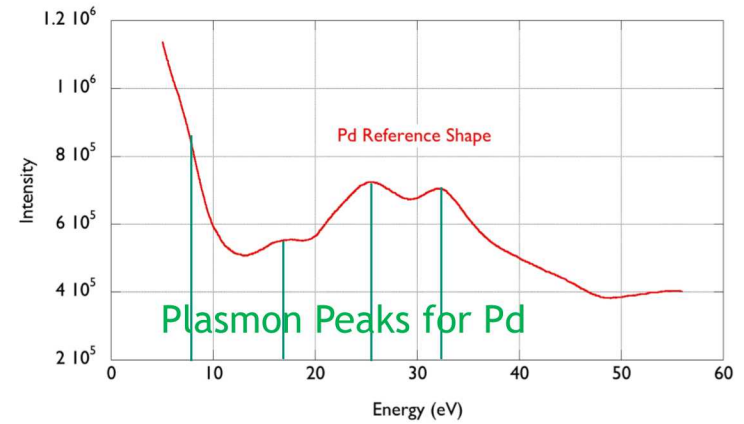
Robust fitting routine is needed!

2 Step Fitting with Pure Pd Reference and Gaussians

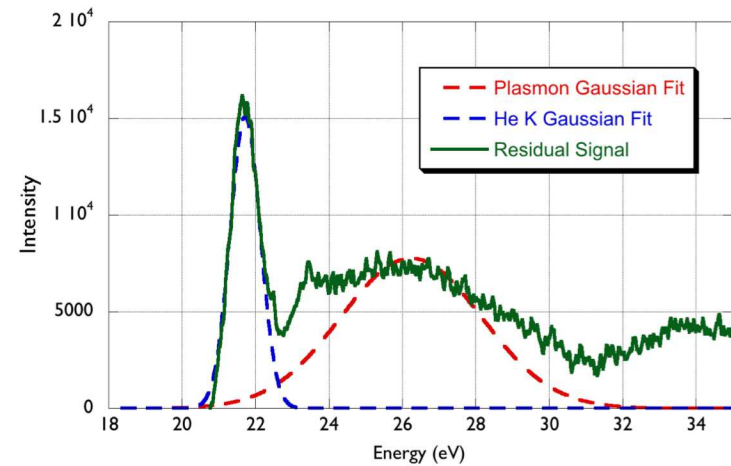
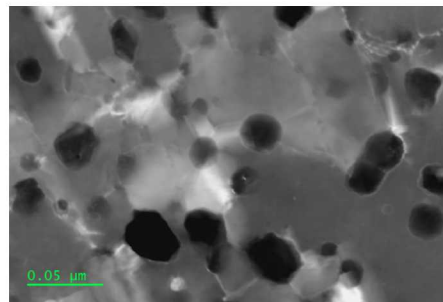
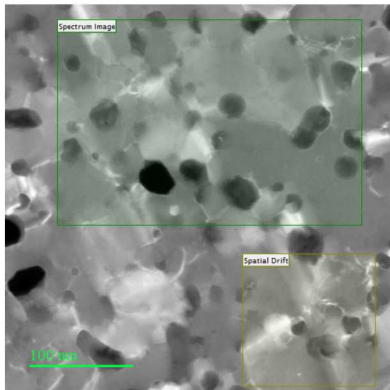
Step 1: Get Residual Signal After MLLS fit with Pd ref

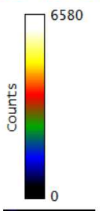
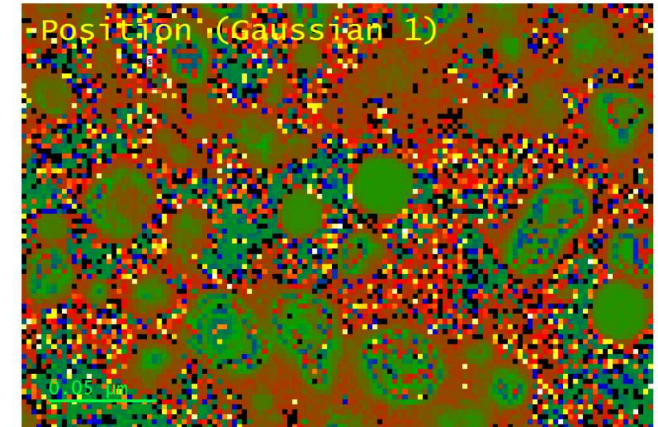
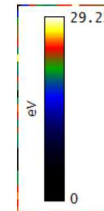
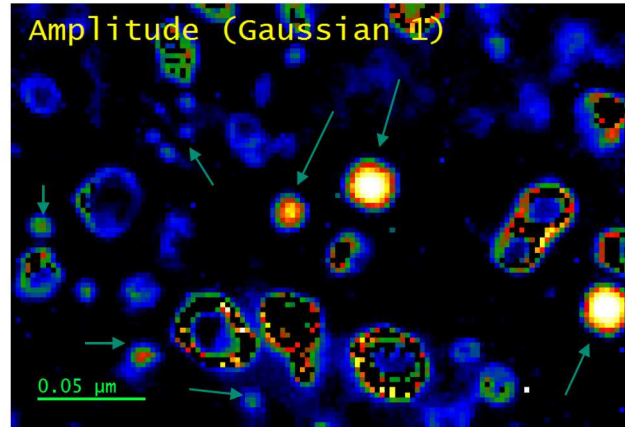
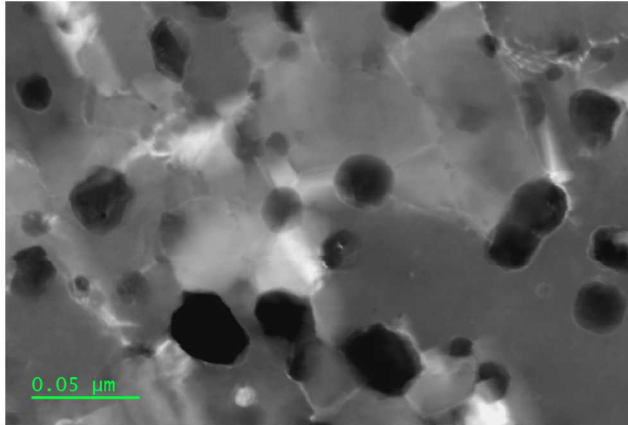


Annealed Pd Wire



Step 2: Fit Residual with 2 Gaussians

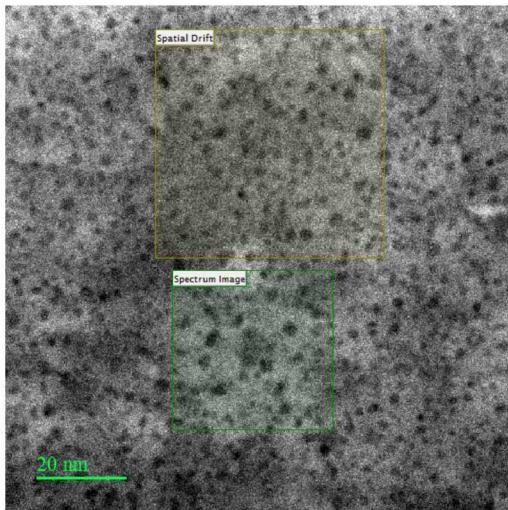




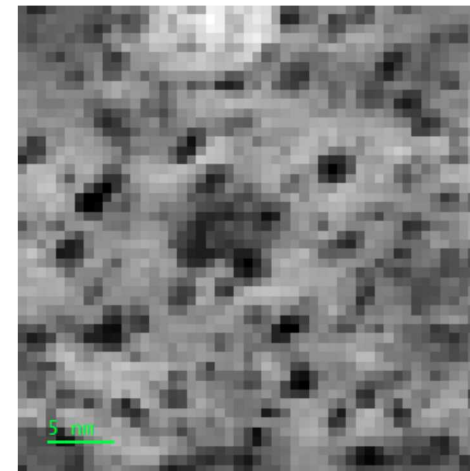
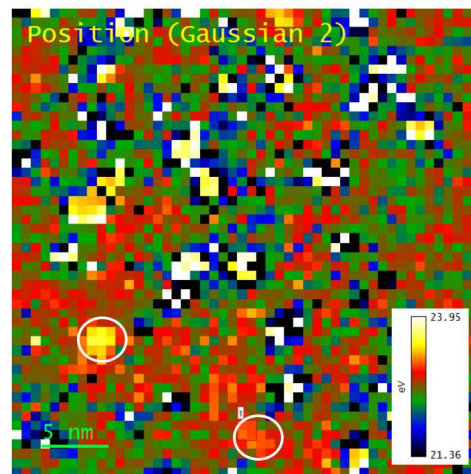
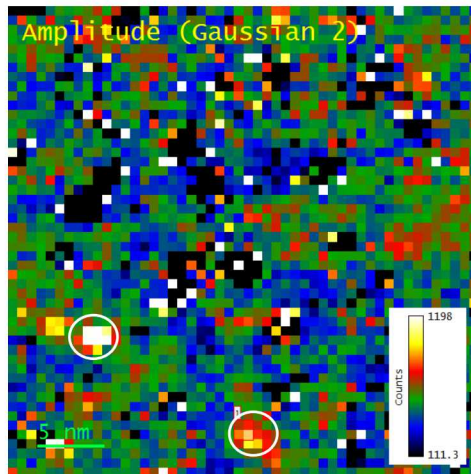
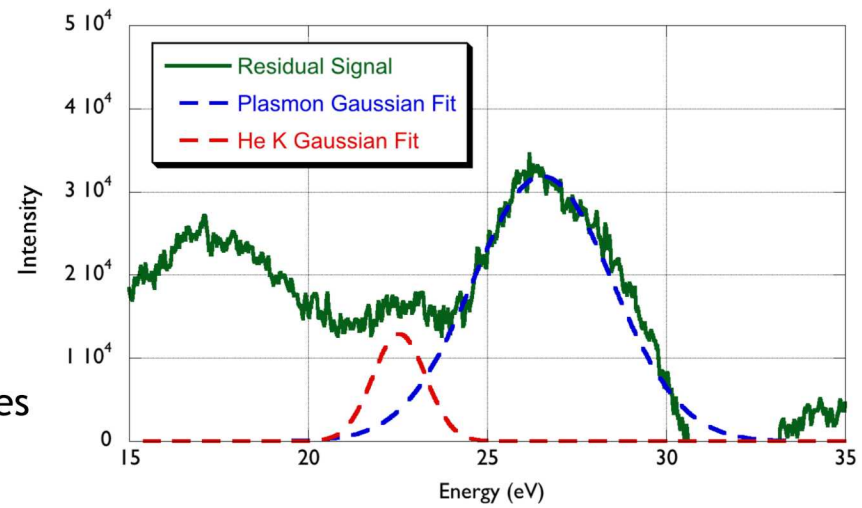
The Rules

- Amplitude has to increase from perimeter to center and can't have missing pixels
- Position must have region with similar pixel values, can be random and noisy

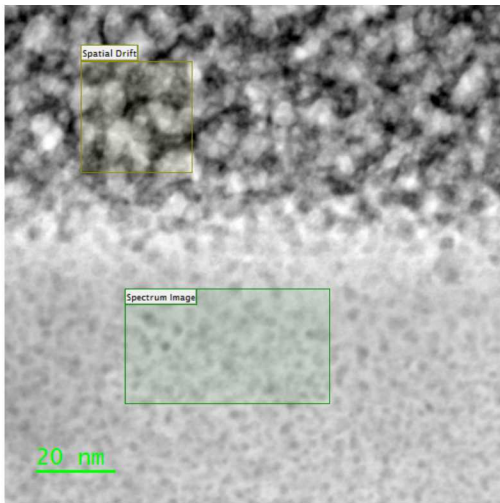
Smaller Bubbles Are Far Less Obvious and Rarely Filled (JEOL F200 Cold-FEG)



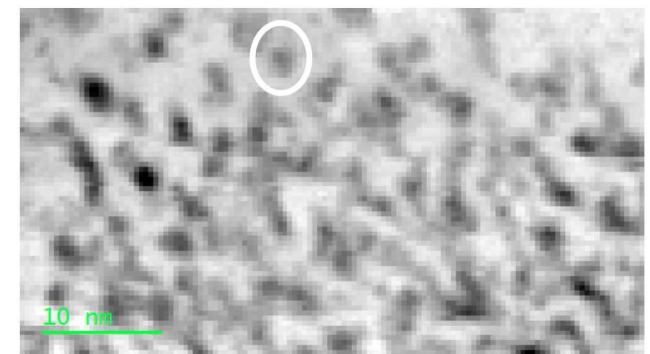
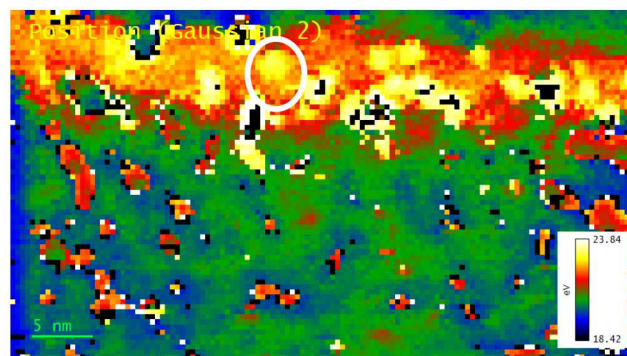
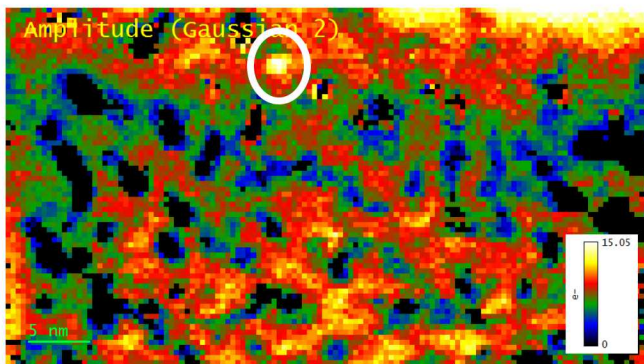
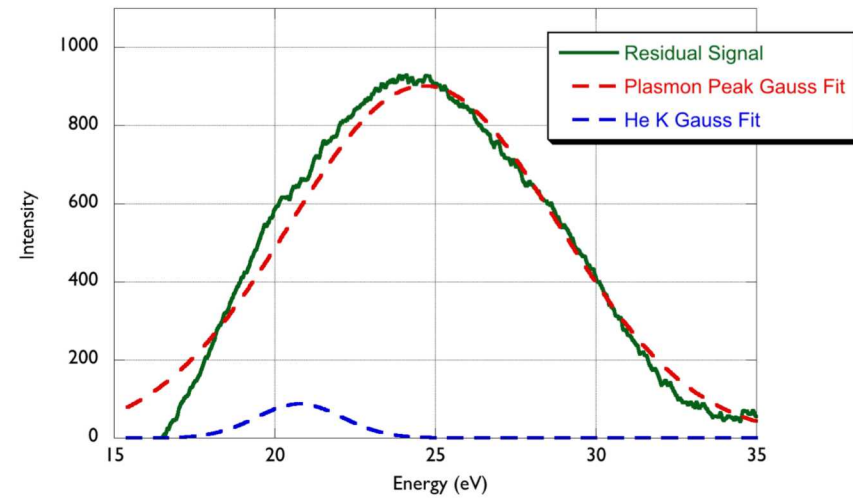
- Most of the bubbles appear unfilled



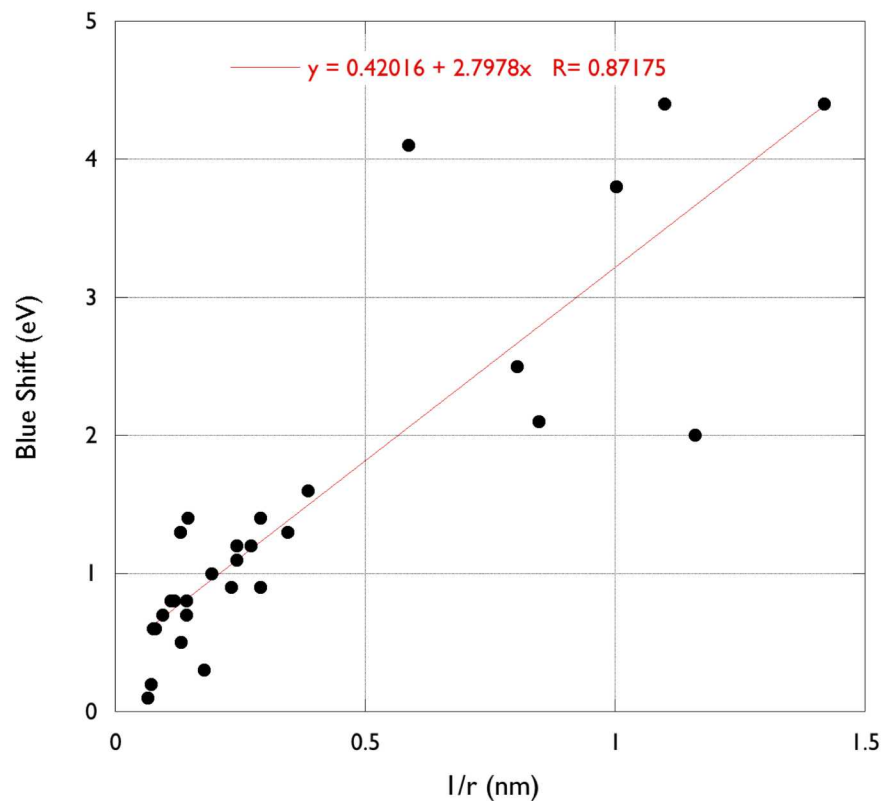
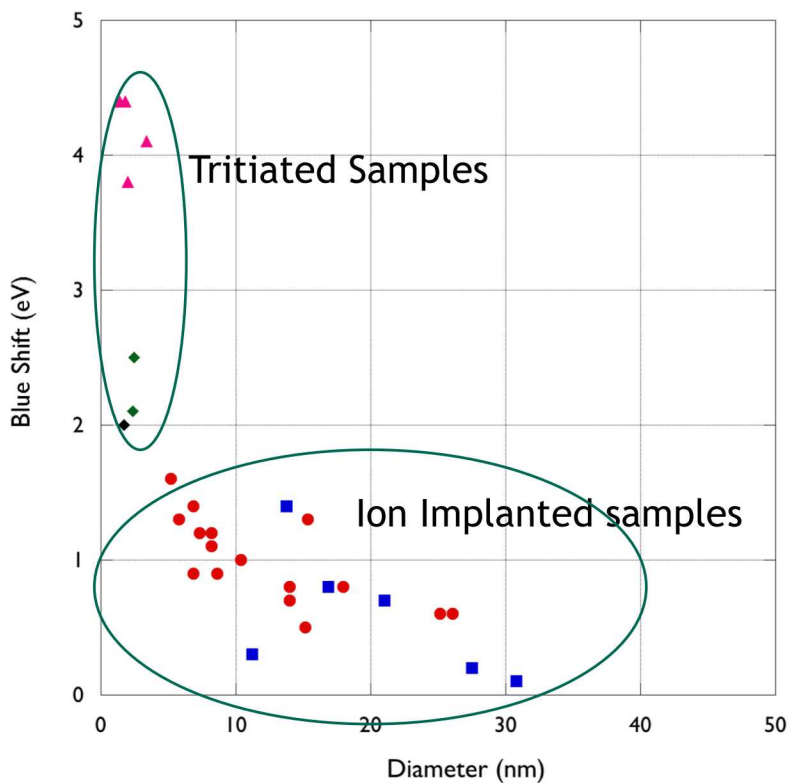
Smaller Bubbles Are Far Less Obvious and Rarely Filled (FEI Titan Themis Z)



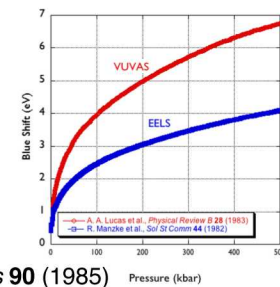
- One bubble satisfies both my rules



19 Bubble Pressure and Size Has Expected $1/r$ Dependence



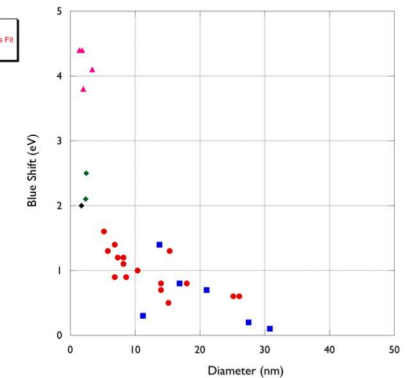
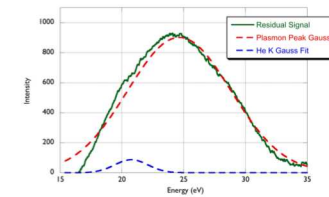
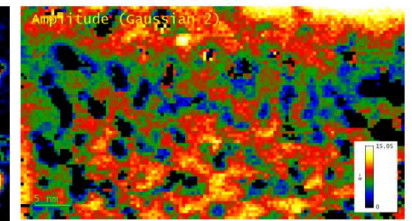
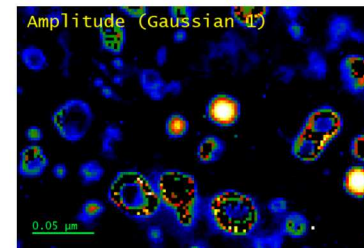
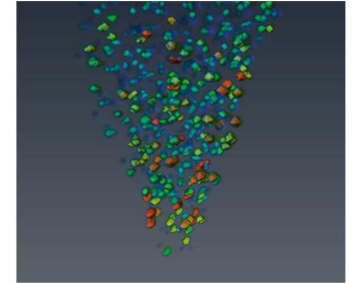
- Most of the observed bubbles are pressurized to approximately 5 Gpa



S.E. Donnelly, *Radiation Effects* 90 (1985) Pressure (kbar)

Summary

- The three dimensional size and location distribution of He bubbles in aged Pd-Ni after tritium decay shows no correlation between bubble size and capture volume size
 - Bubble nucleation occurs throughout aging process
- He bubble pressure can be measured with EELS for a distribution of bubble sizes
 - Fitting routines were developed that could differentiate bubbles from voids
 - We find that most small diameter bubbles (< 5nm) do not remain filled during the FIB prep or observation process
- When strict rules are followed for identifying bubbles, the bubbles follow the expected trend for pressure vs size
- We finally measure GPa pressures in nanometer scale bubbles



- 3D Electron Tomography and EELS provides critical information for understanding and refining models of gaseous bubble formation in metals
- Finally we can detect He atoms in nanoscale bubbles and it is an exciting time because we can quantitatively check classic theories of radiation damage in materials

