# He Retention in Tritides: Importance of Bubble Location and Spacing Distribution

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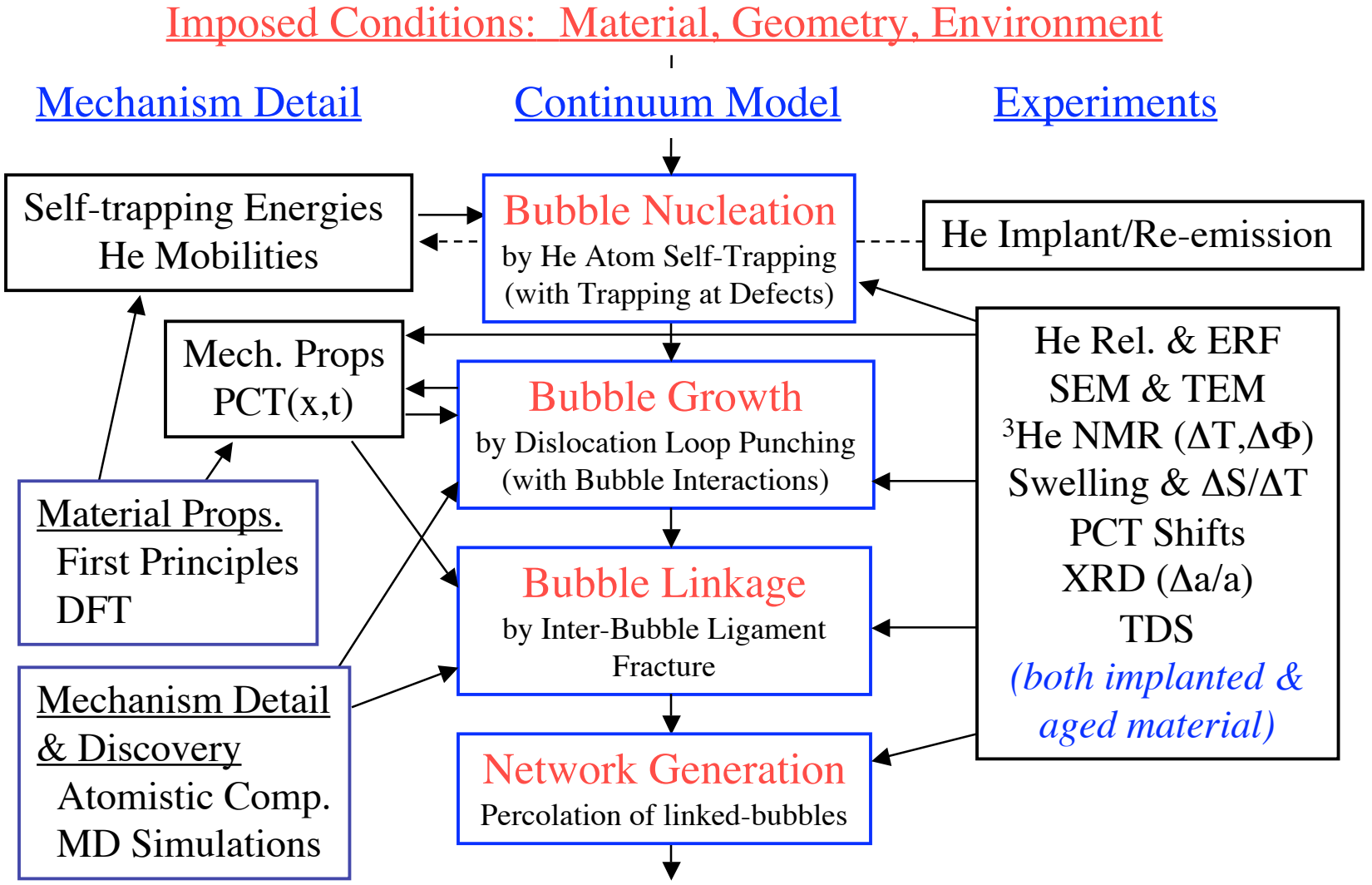
H and He in Materials Workshop, Albuquerque, Feb 6-7, 2007

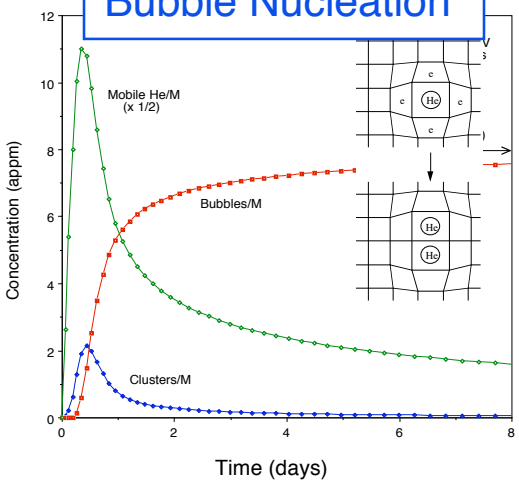
- Helium Bubble Linkage and the Transition to Rapid He Release in Pd Tritide
  (SAND 2006-7779)
- Effects of the Beta-Induced Reactivity of Er Tritide: Simulation Experiments

# The Bubble Evolution Model

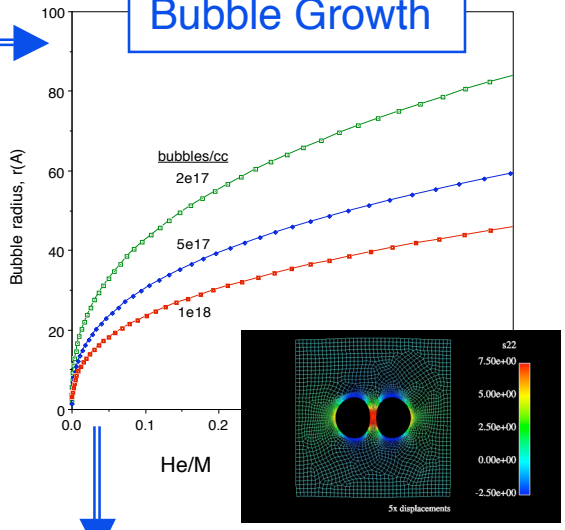


# Model predicts bubble characteristics and He the release spectrum.

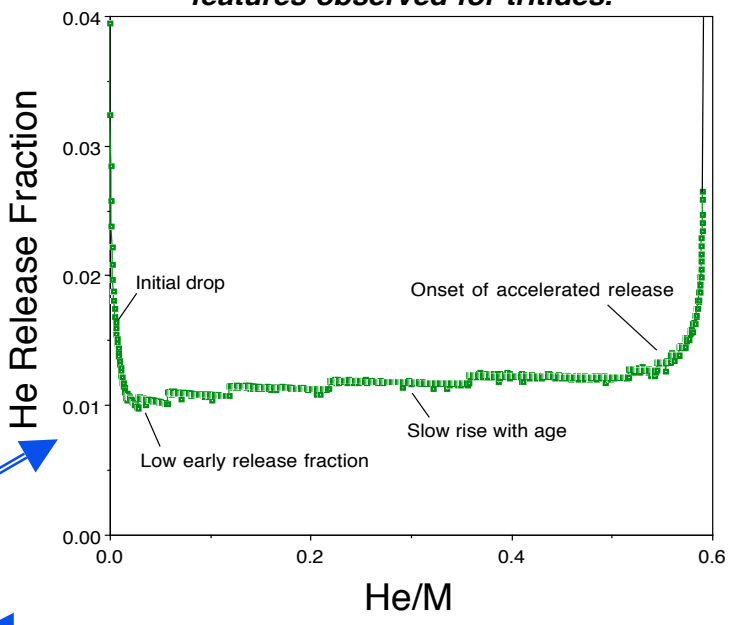
## Bubble Nucleation



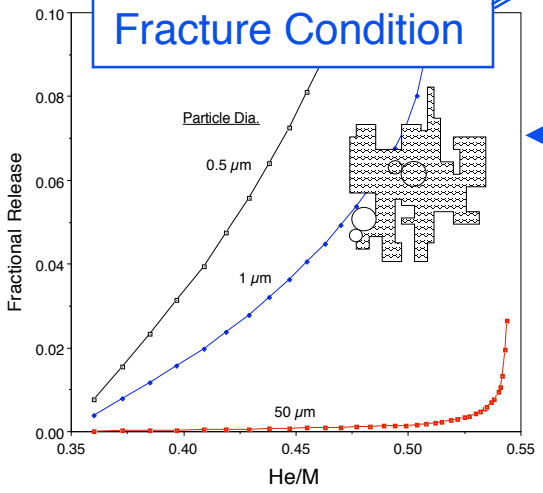

## Bubble Growth



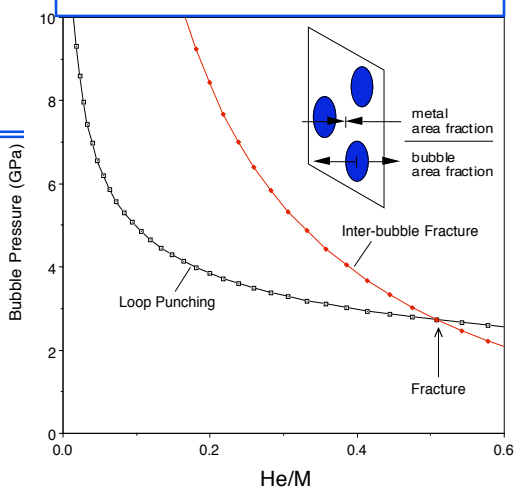

***Computed He release shows all the features observed for tritides.***




## Percolation of the Fracture Condition



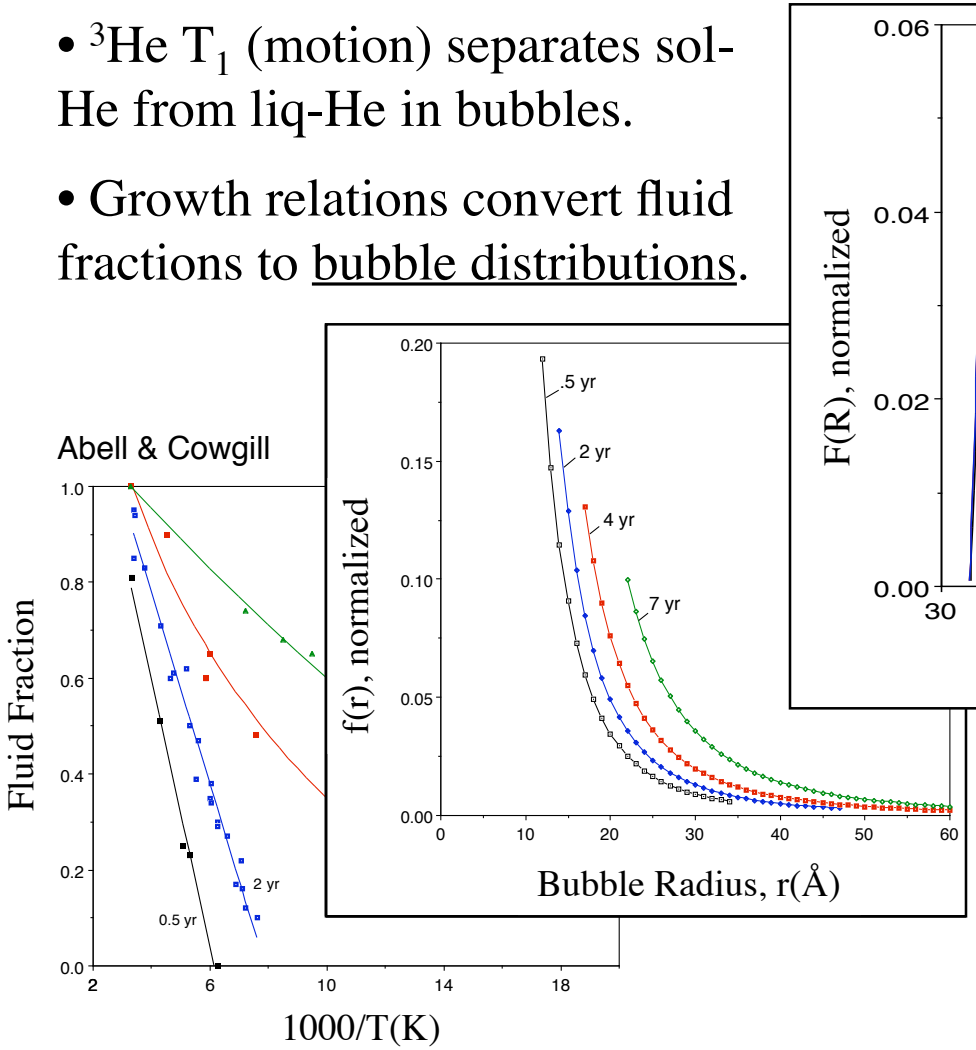

## Inter-Bubble Fracture

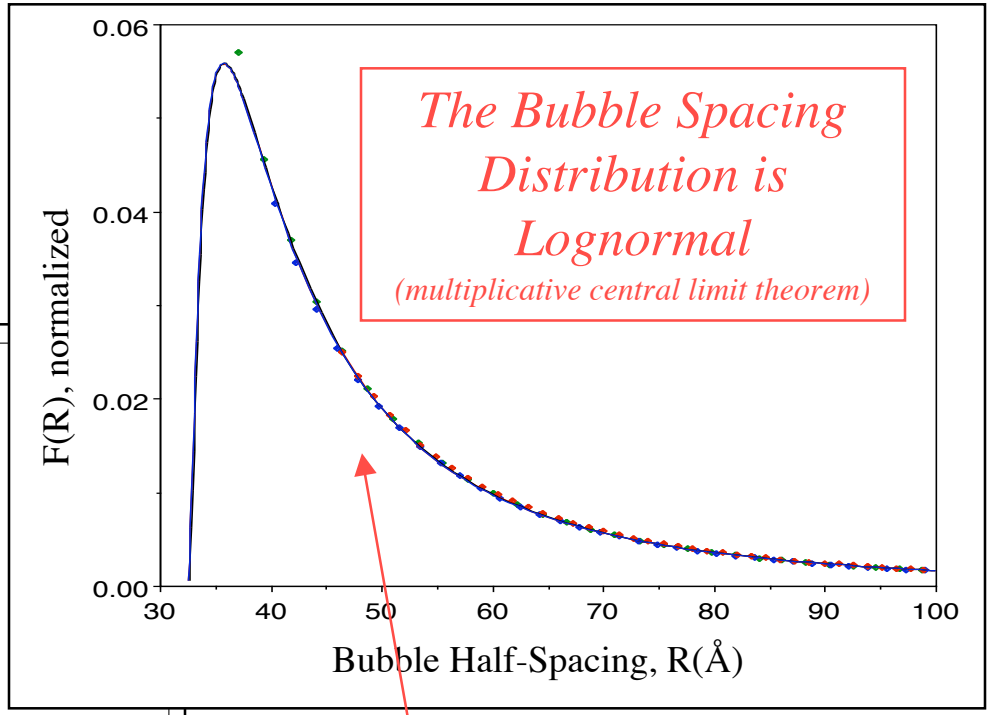



***The He release spectrum is critically dependent on the bubble spacing distribution.***

# The bubble spacing distribution in PdTx was determined by $^3$He NMR.

- $^3$He $T_1$ (motion) separates sol-He from liq-He in bubbles.
- Growth relations convert fluid fractions to bubble distributions.

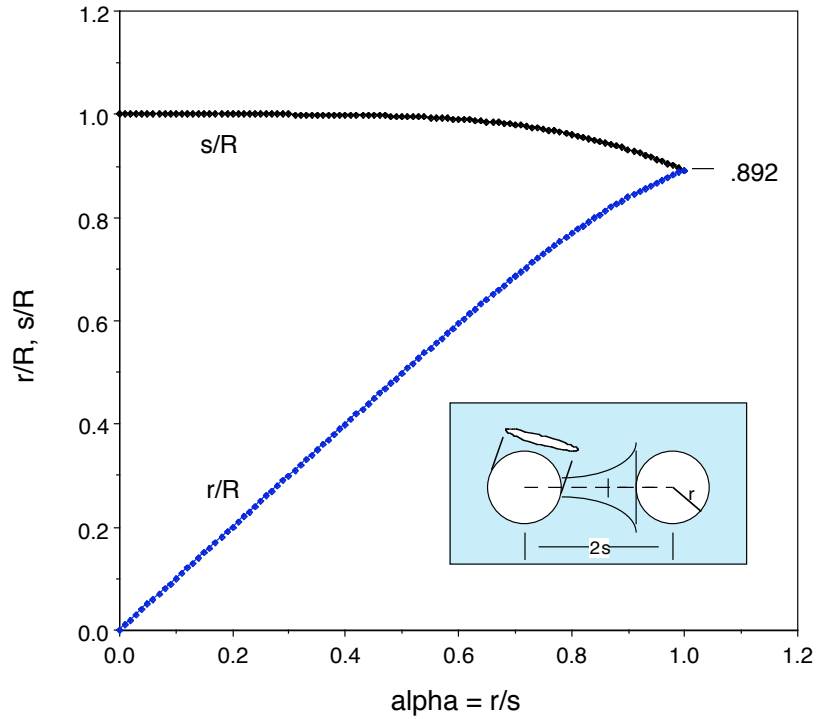


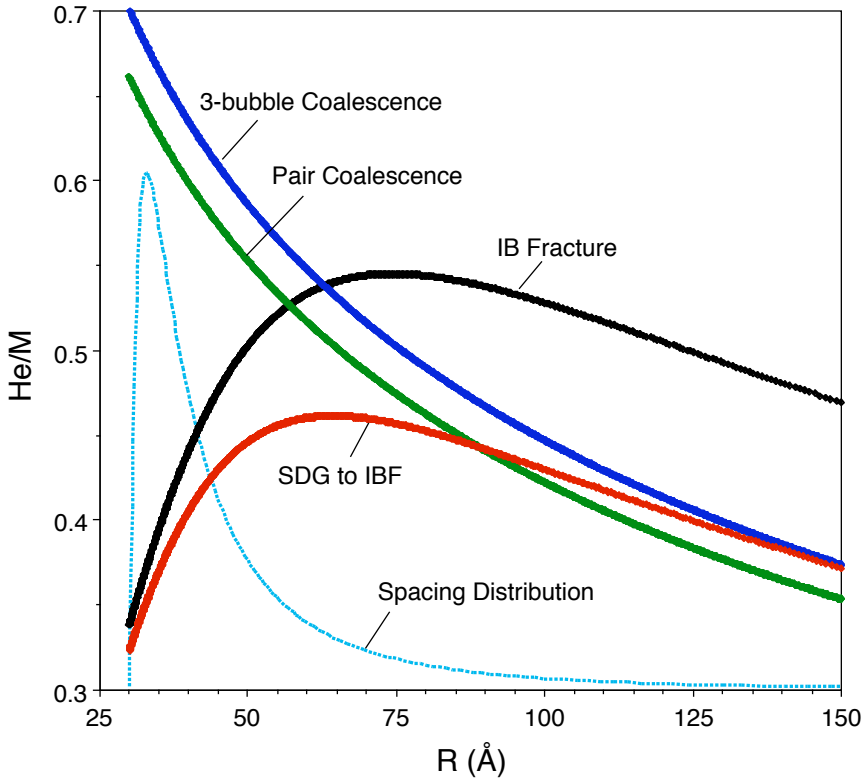




*The constant spacing distribution*
*- verifies nucleation has stopped*
*- provides a sensitive test of the nucleation and growth models.*

# The Critical He/M for Bubble Linkage depends on bubble spacing.

- Stress created by neighbors leads toward bubble coalescence.
- Stress-directed bubble growth occurs only for non-symmetric arrays.
  - requires a spacing distribution.



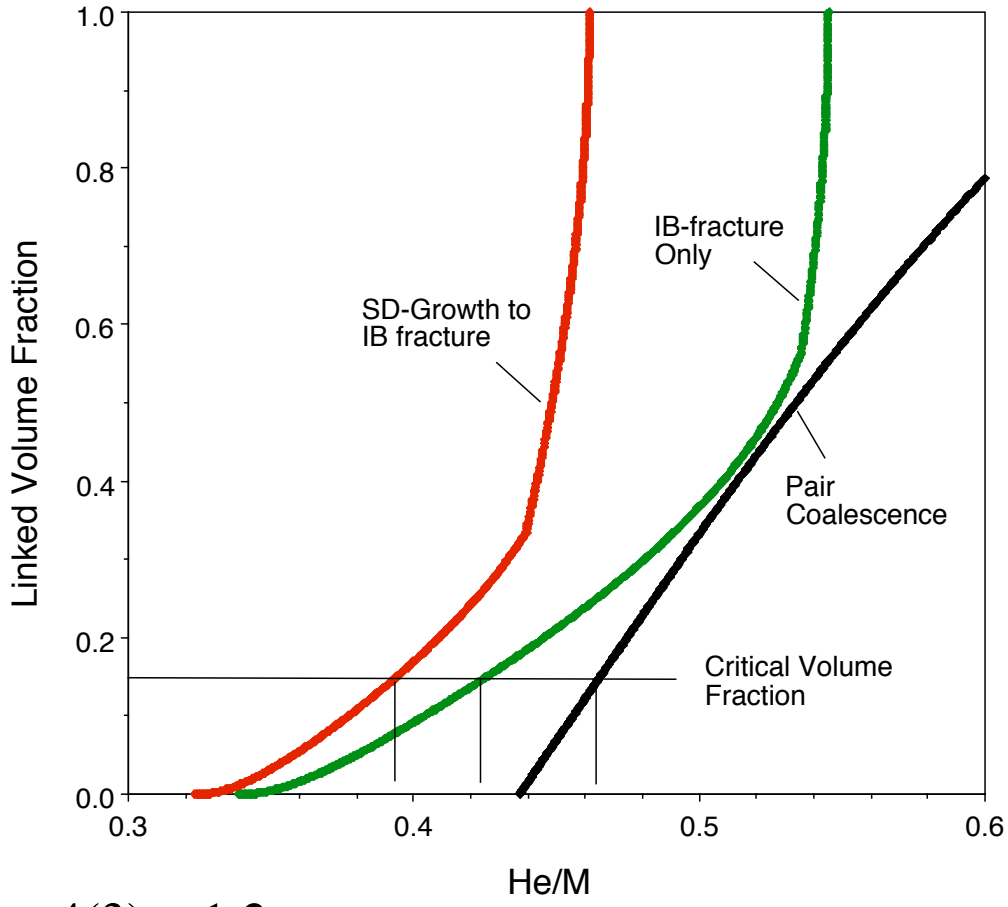




- SD-growth is interrupted by inter-bubble ligament fracture.
  - linkage starts with closely-spaced bubbles.

# Linked Volume Fraction increases with He/M concentration

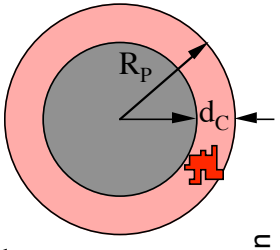
- Linkage by SD-growth to IB-fracture
  - begins at .32 He/M
  - at .44He/M, incorporates widely-spaced bubbles
  - at .39 He/M, reaches the Critical Volume Fraction for infinite percolation:
- From classical percolation theory in 3d, $V_C = .15$
- In "rapid release", the release rate is 1-2 times the generation rate:

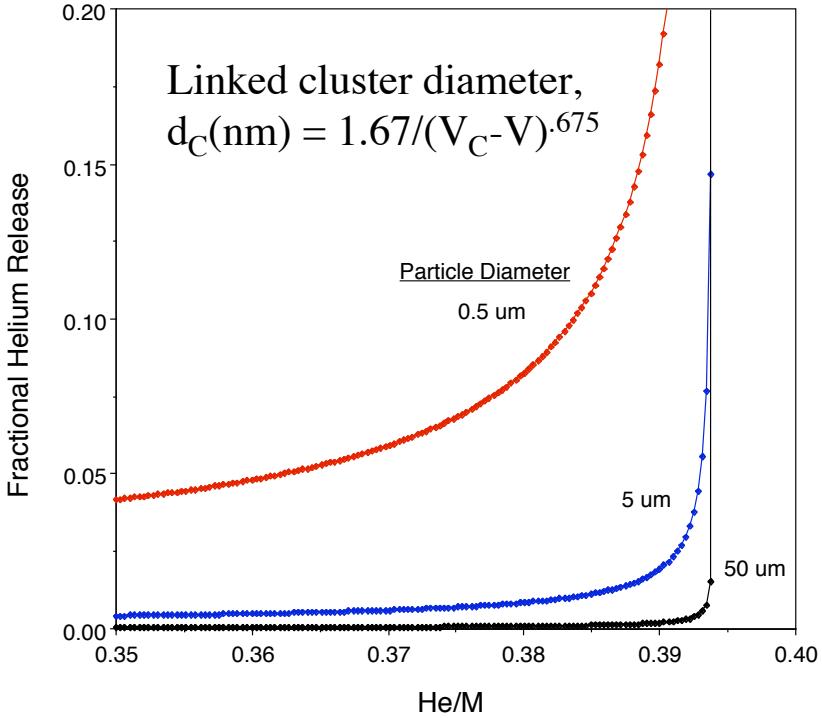
$$\text{Rel/Gen} = (\text{He/M})\frac{dV}{d(\text{He/M})} \approx .4(3) = 1.2$$

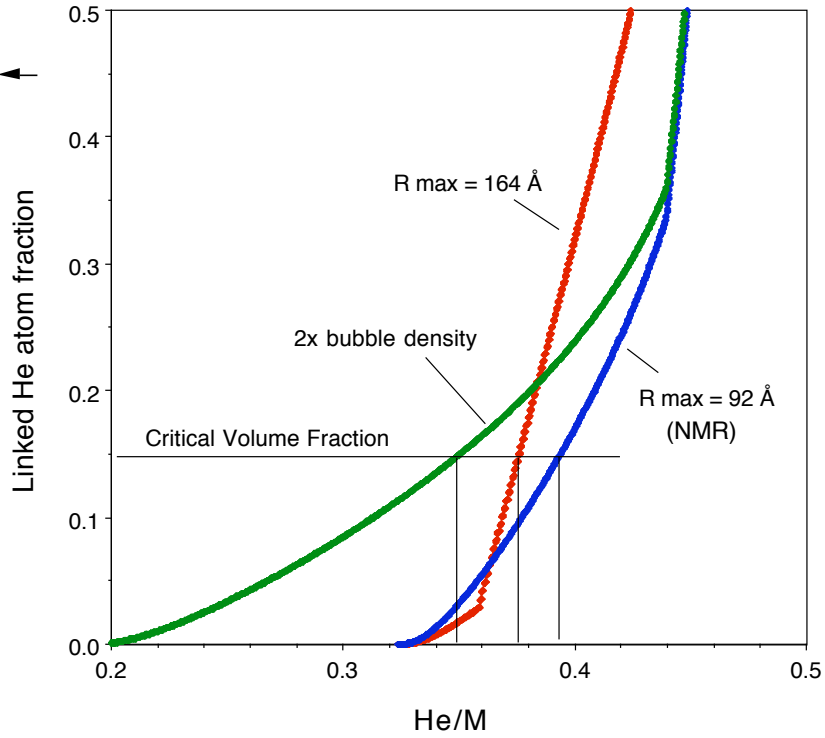


# Percolation of surface-connected, linked-bubble clusters gives the *transition* to rapid release.

- Fractional He release:
  - spherical particles
    $V_P = V\,[1-(1-d_C/R_P)^3]$
  - films (thickness L) on substrates
    $V_F = V\,(d_C/L)$




- Linkage percolation is sensitive to details of the bubble spacing distribution.

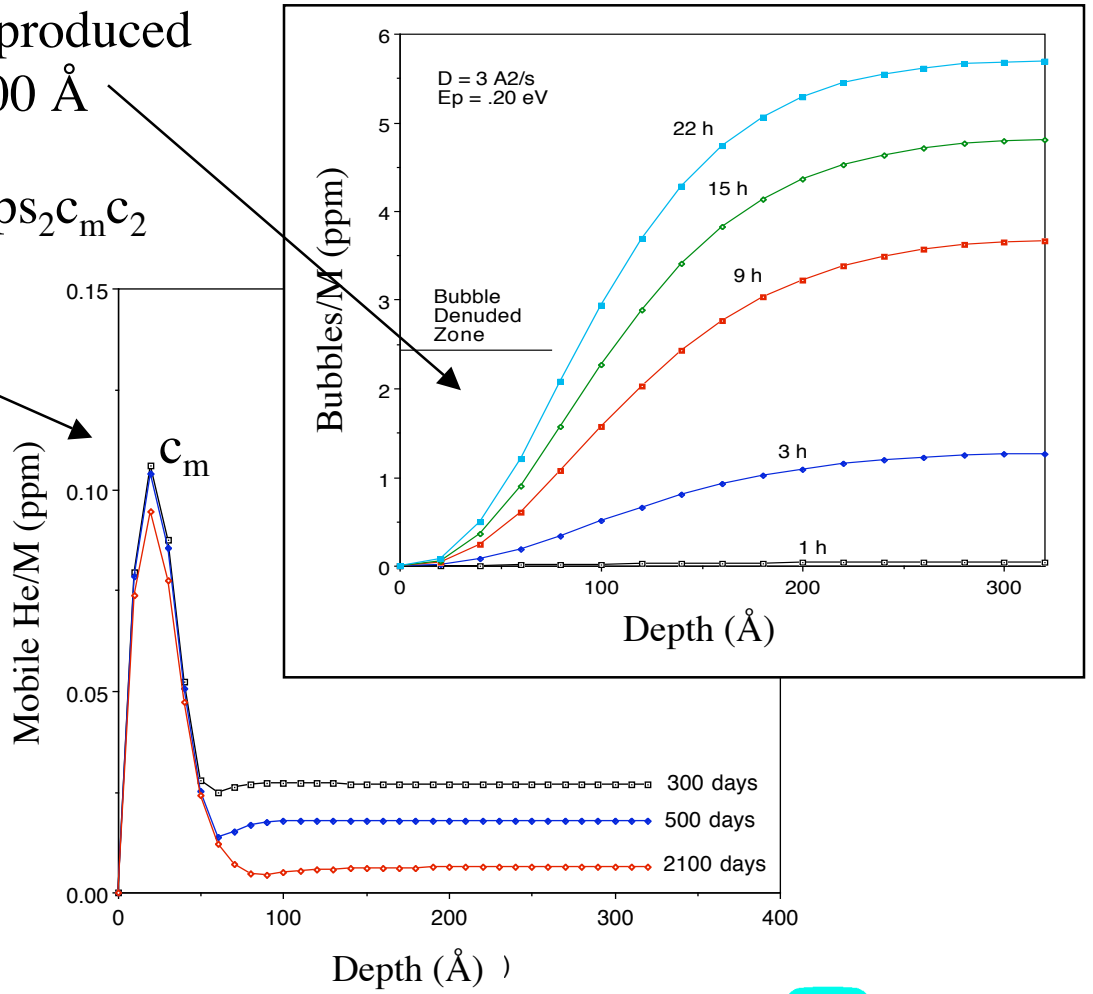
# Early He release depends on the bubble density and defect trapping near surfaces.

- Bubble denuded zone $d_Z$ produced by He self trapping: 50-100 Å

$$dc_2/dt = ps_1c_m^2 - q_2c_2 - ps_2c_mc_2$$

- The mobile Helium concentration near the surface is too low to nucleate bubbles.

- The He escape length $\lambda_{esc} \approx d_Z/2$ produces an early release fraction.
  - For PdT, $\lambda_{esc} \approx 40$Å



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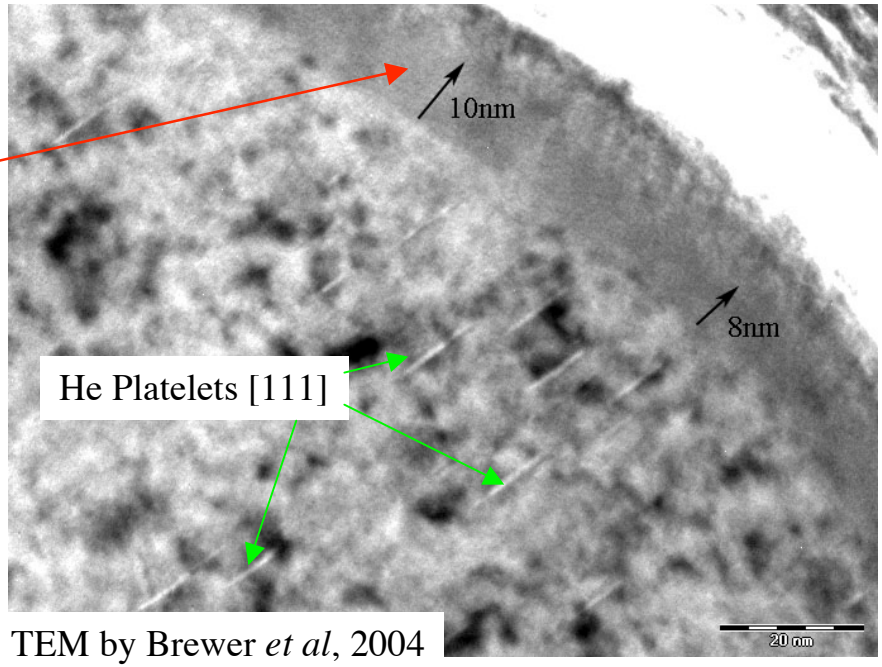
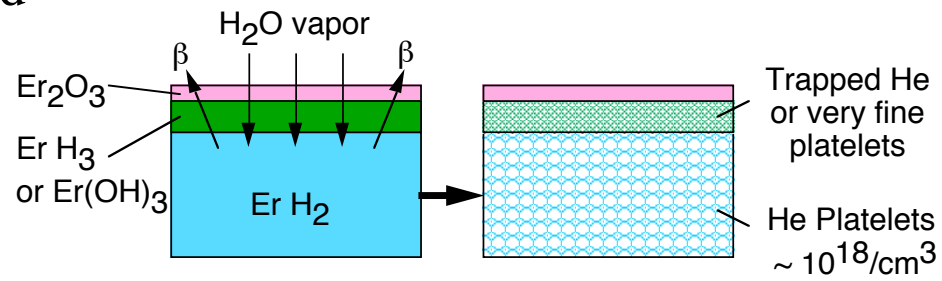
# However, for Er tritide films, only $^3$He born within the *top monolayer* escapes!

- He escape depth from [111] oriented $ErT_2$ films = 1.8 Å (Snow *et al,* 2006)
- What makes He immobile in this layer?
  1) Trapping at $Er_2O_3$ precipitates?
     - requires O/Er ~1 in "hydride"
  2) Trapping within $Er(OT)_3$ layer?
  3) $Er(H,T)_3$ near-surface layer?
     - produced by $H_2O$ oxidation
     - He migration blocked by H
- Testing (3) using $ErH_2$ films, exposed to water vapor in the ALS (LBNL).
  - radiation-enhanced oxidation
  - H-pickup (resistivity, TDS)
  - effect on He migration (HeIRE)
  - work in progress




TEM by Brewer *et al*, 2004



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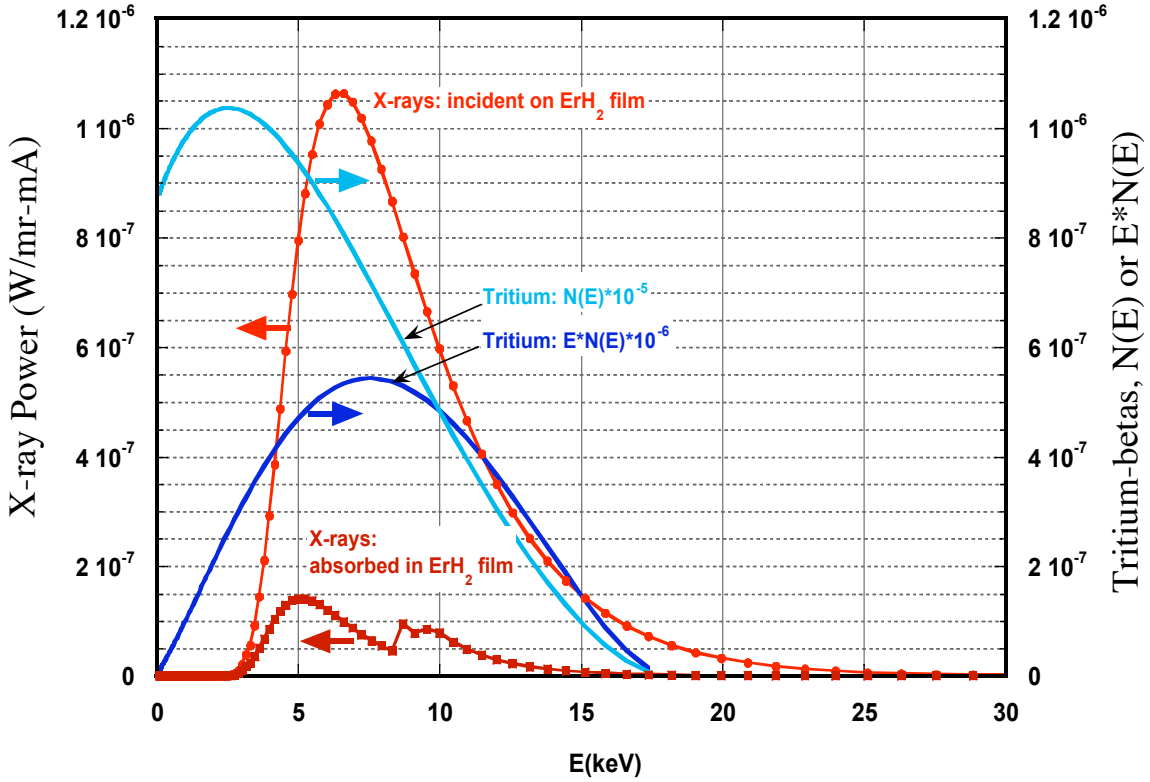
# Energy deposition by synchrotron-based X-rays is similar to tritium betas.

Comparison of Energy Deposition Spectra

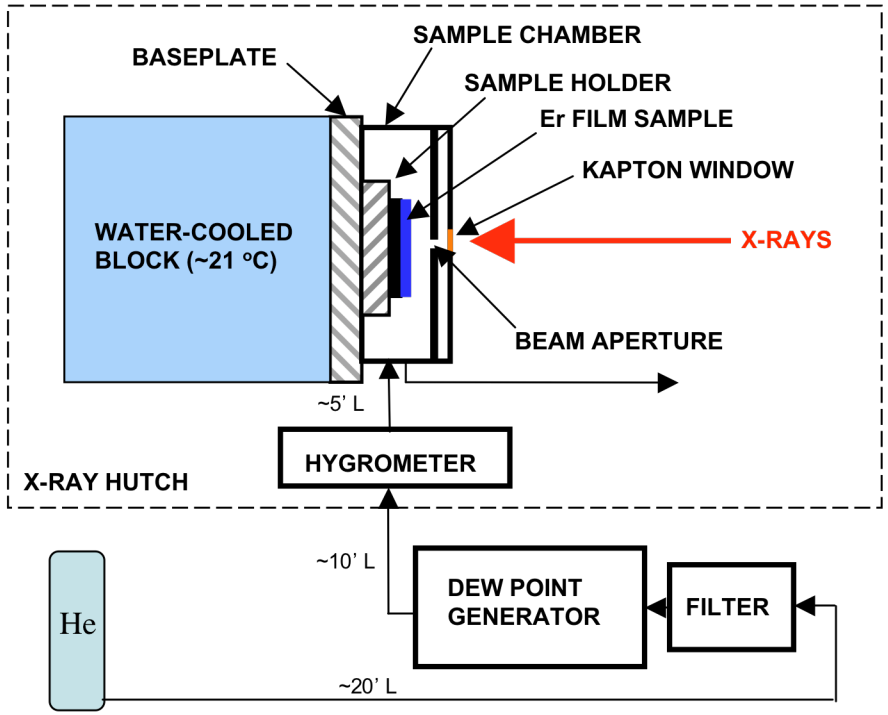
Tritium=blues, X-rays=reds (LEX-D code)



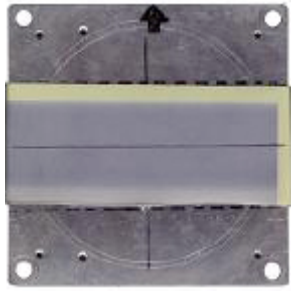

- Same average energy of 5-10 keV.
  - Power deposited by tritium betas is E*N(E)
- Energy is deposited uniformly throughout the film
  - Only 10% of incident energy is absorbed,

# X-ray exposures of $ErH_2$ films were done at the Advanced Light Source synchrotron (LBNL)

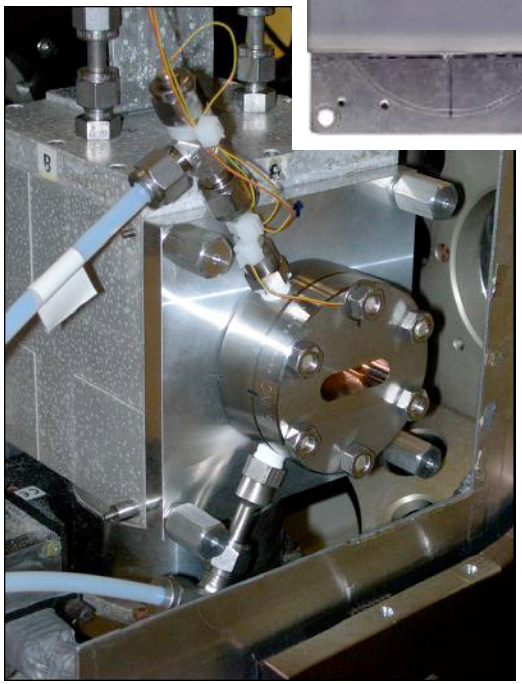
- Experimental Arrangement:




Vertically Scanned



Beamline 3.3.2



Sample Cell
on Scanner Cooling Block

- Environment: Water vapor in flowing He.
  - Eliminated ozone produced by X-rays in air.



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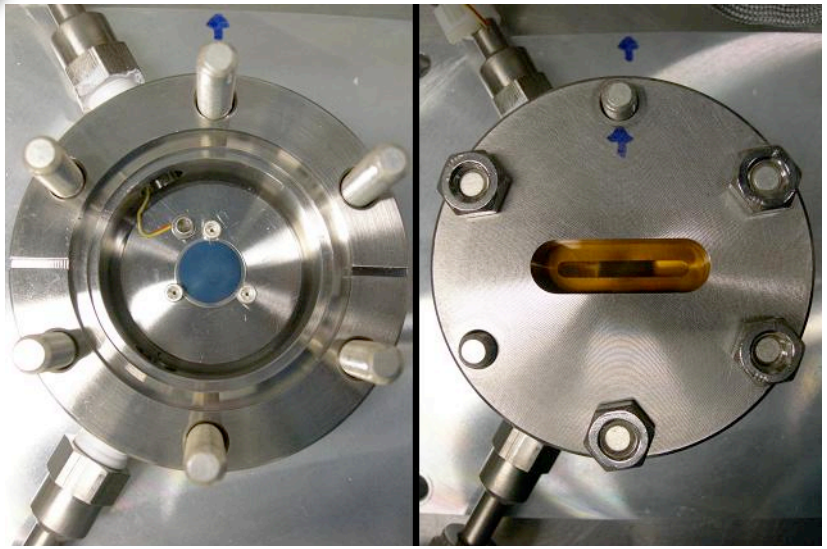
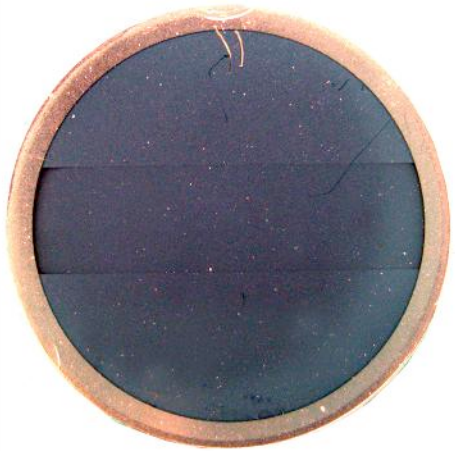
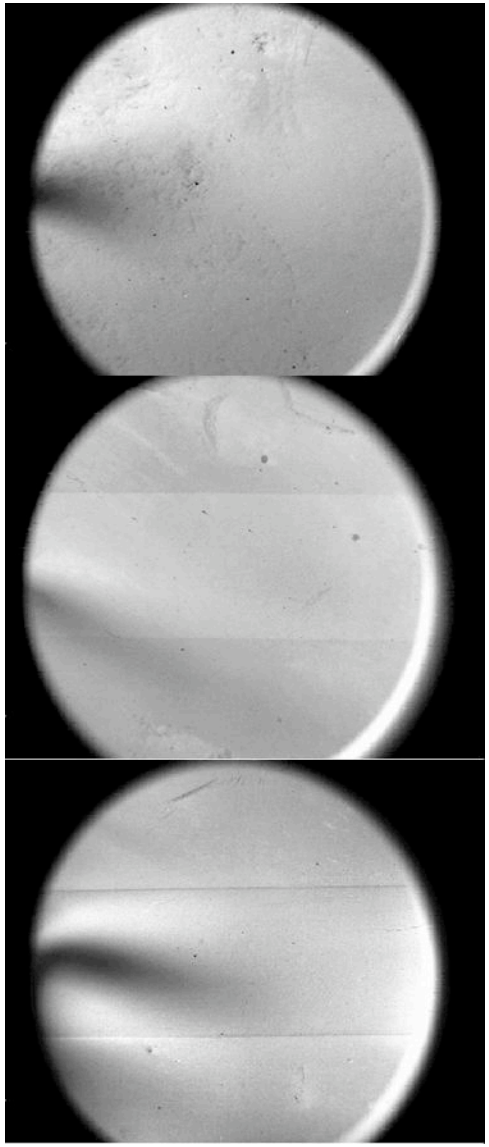
# We exposed a stripe across the samples.





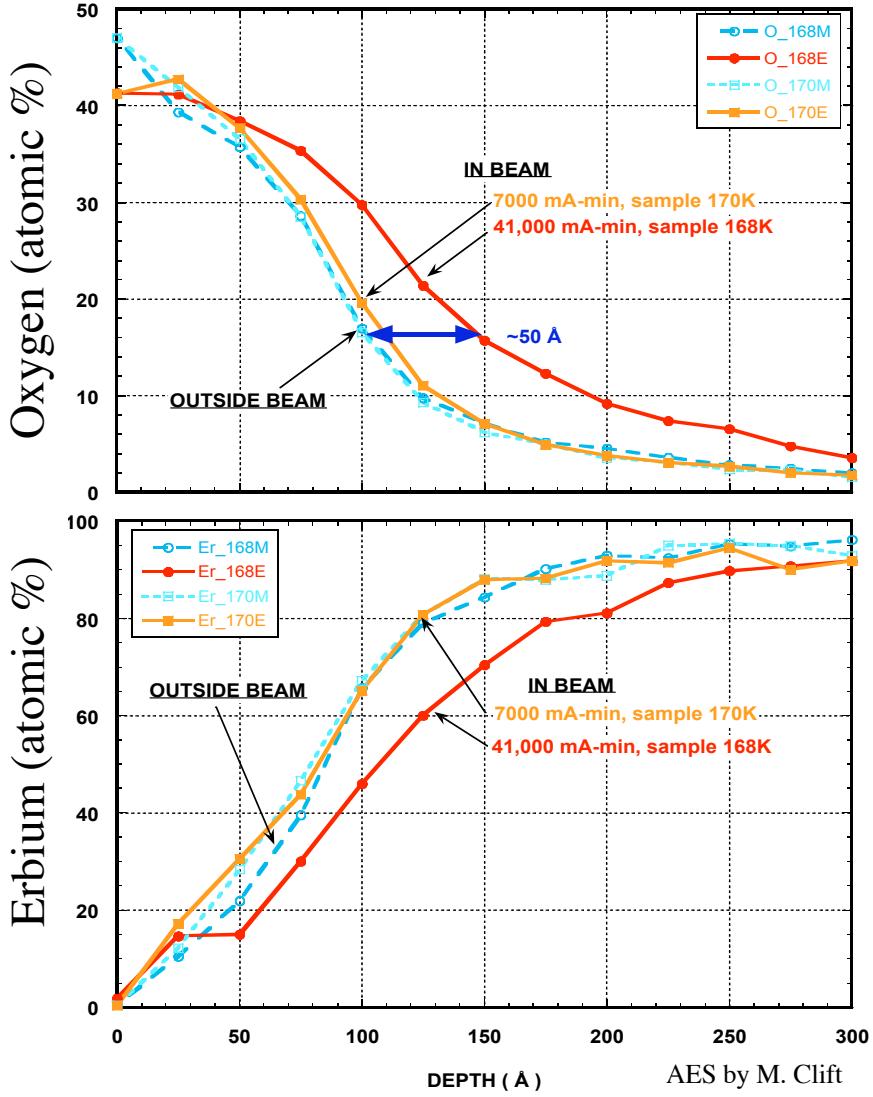


#108K
1.3 hr
.17 Torr, 0.8% RH
120 ma-hr

#170K
1.5 hr
10 Torr, 48% RH
120 ma-hr

#168K
7.5 hr
9.5 Torr, 45% RH
680 ma-hr

# X-ray exposures in $H_2O$ vapor increased the oxide thickness, similar to betas.



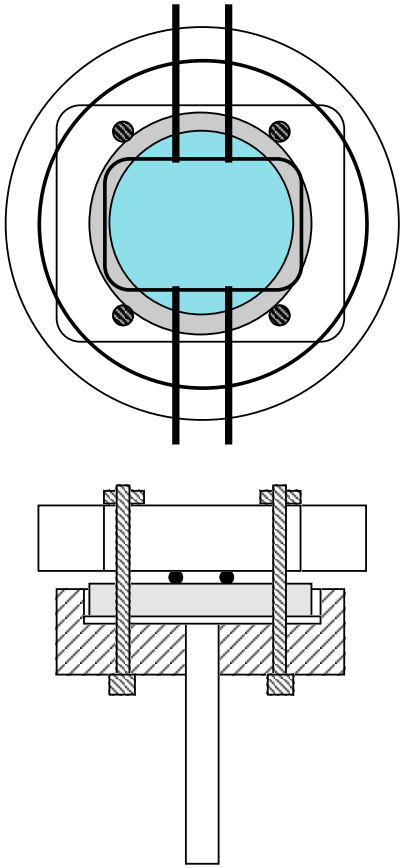

AES by M. Clift

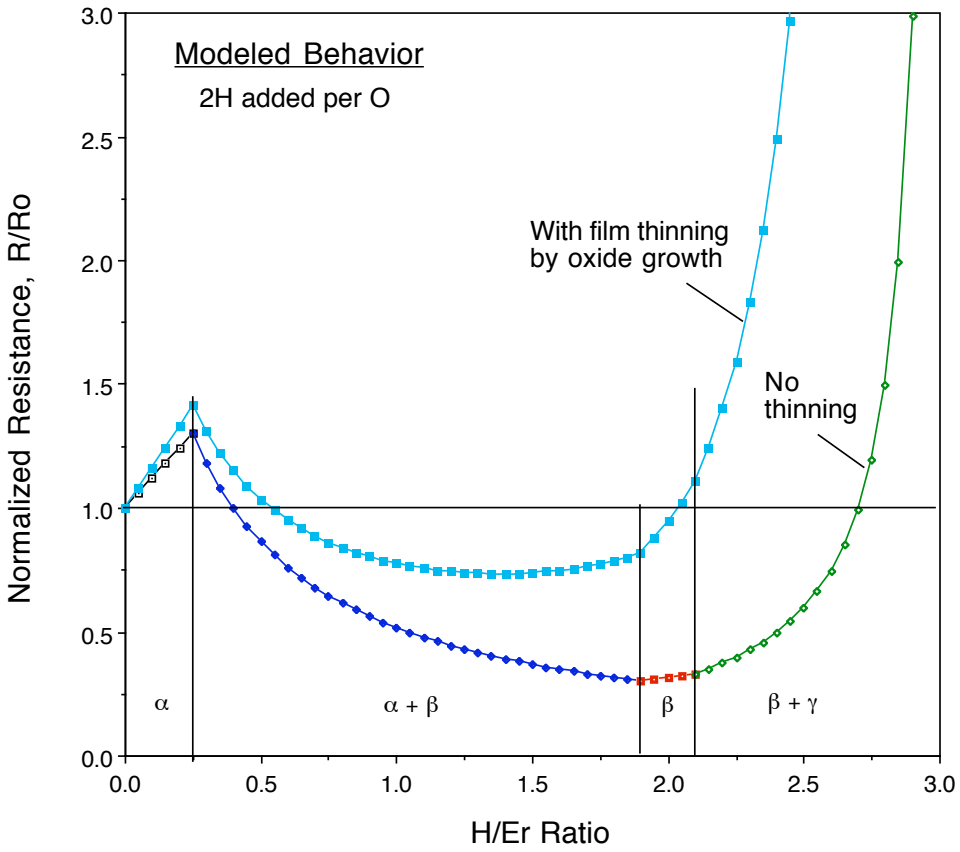
- Nascent-H pickup is expected to be too small to discern by thermodesorption.

- Plans (delayed by funding):
  - Use $D_2O$
  - Expose larger $ErH_2$ area
  - Quantify nascent-D by NRA or TDS

# Hydrogen pickup can be deduced *in-situ* from the change in electrical resistivity of the film.

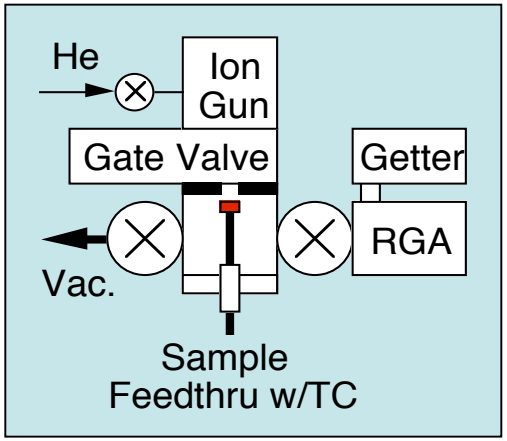
- 4-point resistance probe uses films on quartz discs.

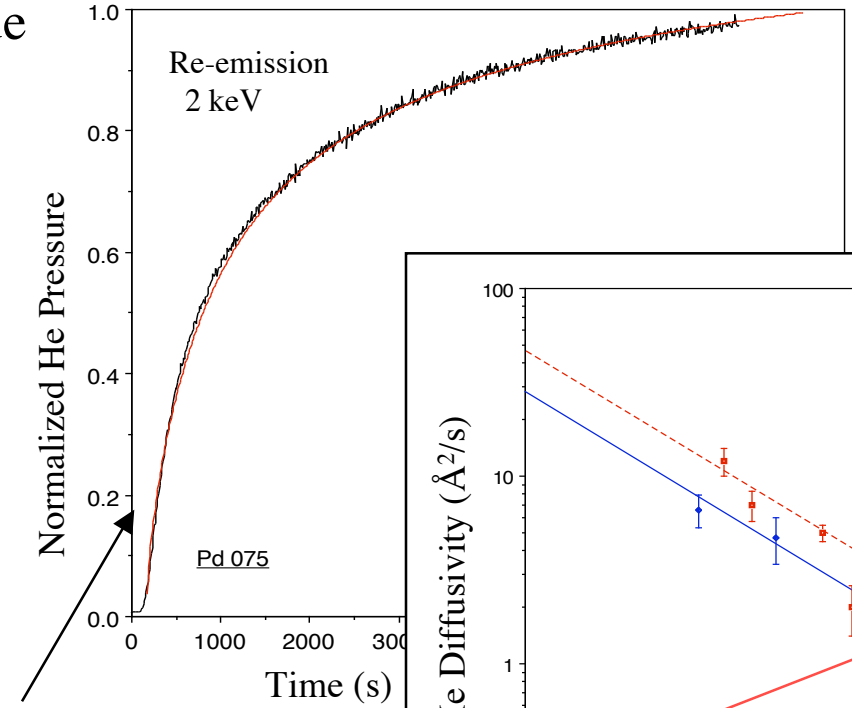


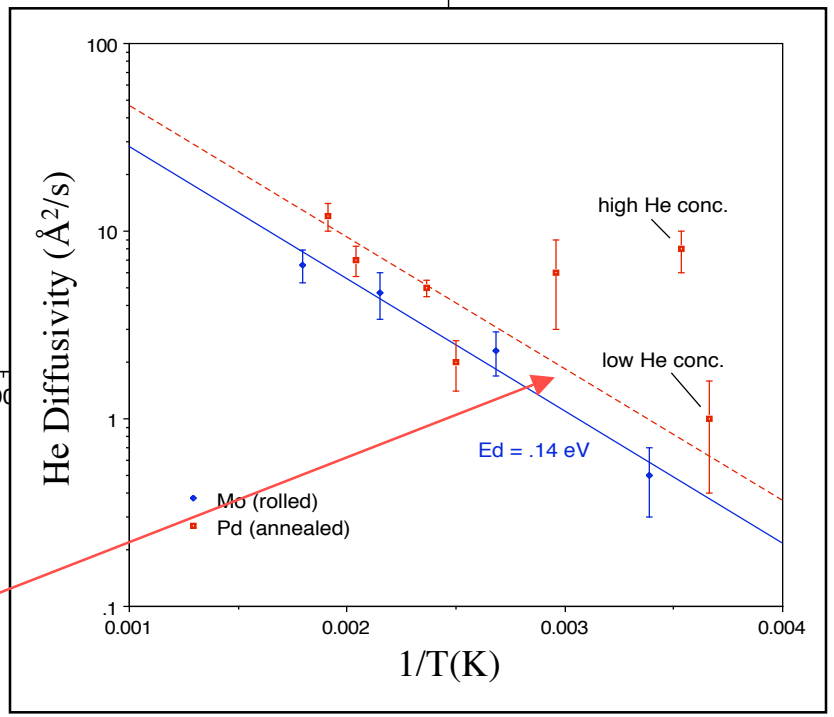


# Near-surface He diffusion and trapping parameters are measured by Implant/Re-emission.

- The HeIRE technique uses small volumes & rapid valve timing.




- He re-emission is fit to diffusive release with self-trapping.

*Measured diffusivity in Pd agrees with model value for average bubble density.*



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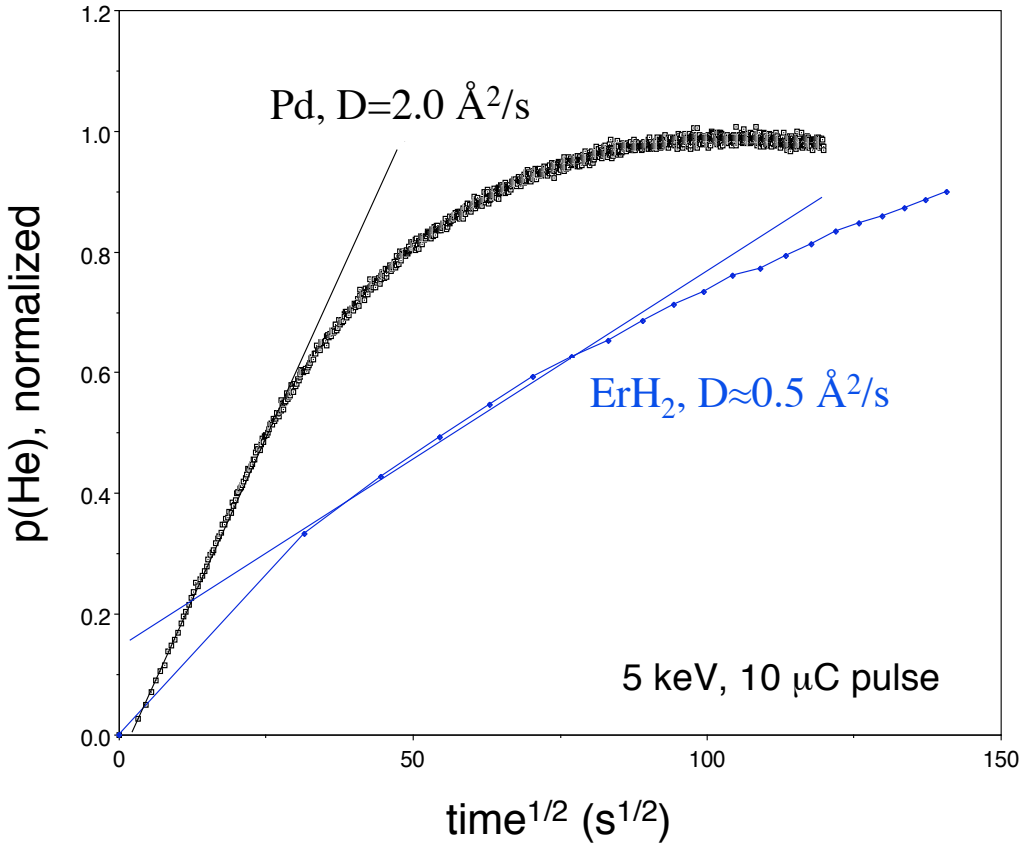
# Experiments with $ErH_2$ films show lower diffusivity and significant He trapping at RT.

- He diffusion through $Er_2O_3$ is assumed rapid.
- Early time dependence is approximated by draining of slab (L=$He^+$ range, SRIM):

$$p(He) \approx [4Dt/\pi L^2]^{1/2}$$

- The re-emission fraction indicates lots of low-energy traps:

| T(°C) | release/implant |
|---|---|
| 27 | .018 |
| 100 | .06 |
| 150 | .17 |
| 200 | .38 |



# The cause of low early He release from Er tritide films remains a mystery.

- Films appear to possess a "hydride phase" layer with significant He trapping.

  Er films have an $Er(OH)_3$ layer over $Er_2O_3$.

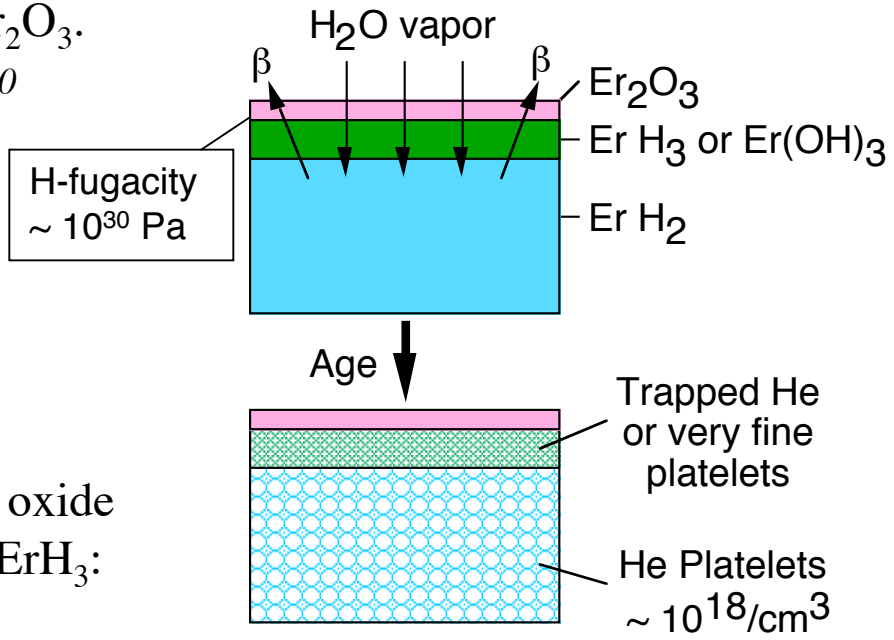
  *(Y.G. Wu et al., Proc. SPIE 4086 (2000) 360 & observed by Roland Schulze, LANL)*

  Tritide betas appear to assist
  - migration of OH through oxide
  - conversion of $Er(OH)_3$ to $Er_2O_3$?

  *$Er(OH)_3$ - 326.8 kcal/mole*
  *$Er_2O_3$ - 453.6 kcal/mole*

  Reaction of OH with $ErH_2$ beneath the oxide should produce more $Er_2O_3$ & stable $ErH_3$:

  *$9\ ErT_2 + 3\ OH = Er_2O_3 + 7\ Er(H,T)_3$*




- The beta-enhanced surface chemistry of tritides can be simulated using synchrotron X-rays on hydrides. -- We have observed oxide growth.

- Effects on He migration can be examined by implant/re-emission techniques.