A continuum-scale model of hydrogen precipitation and bubble growth in metals

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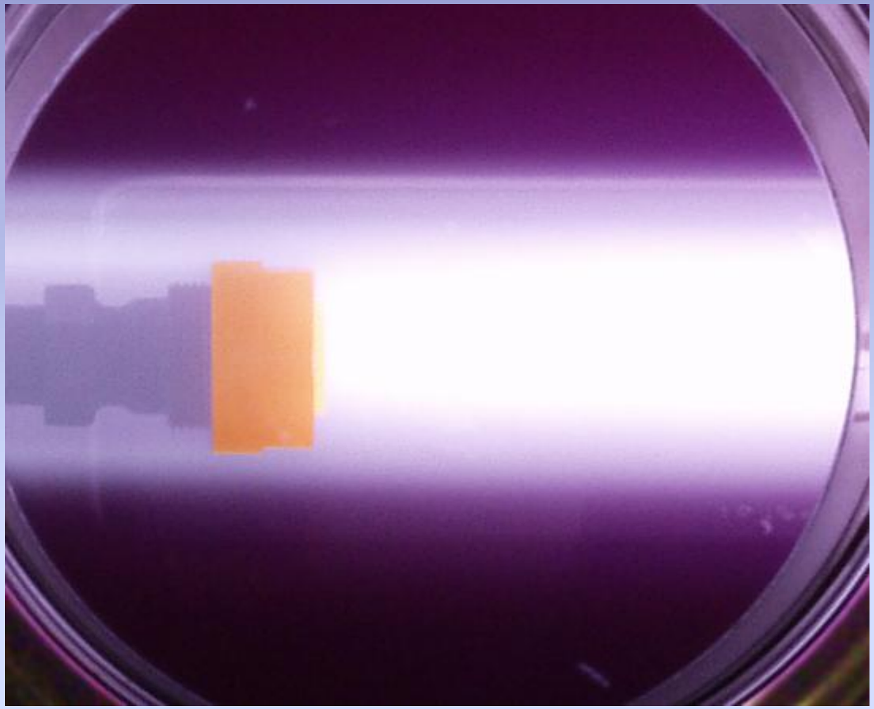

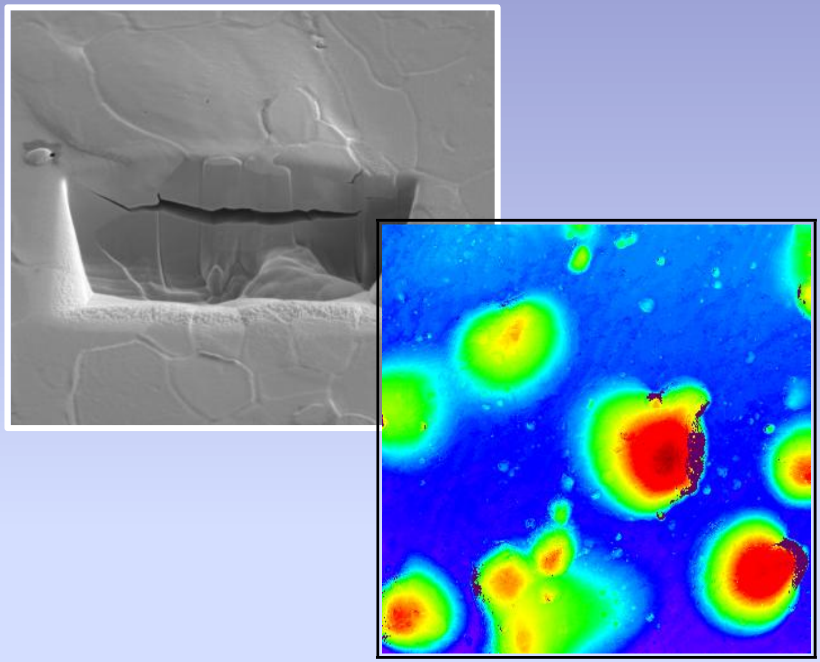

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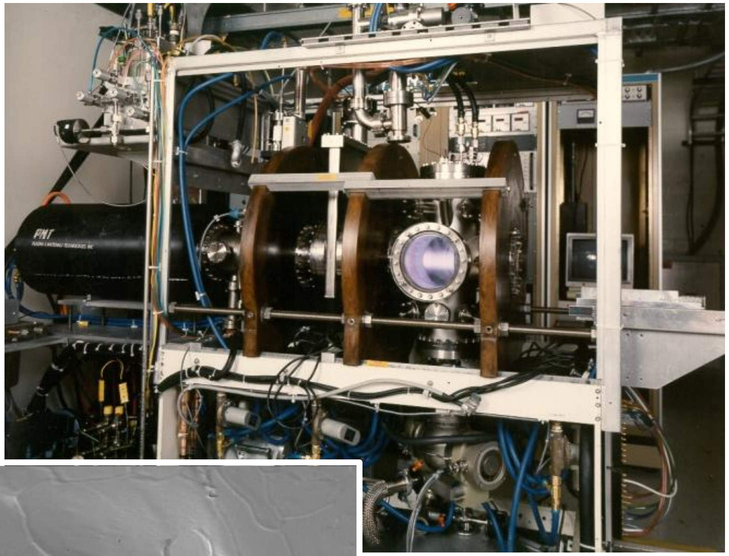
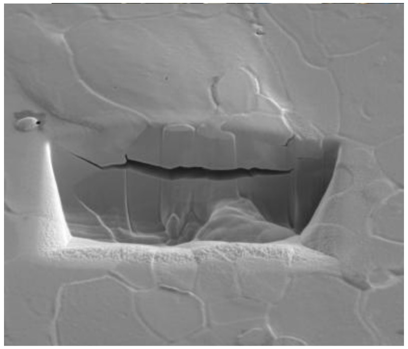
Overview

Hydrogen interaction with materials is relevant to:

- Tritium storage
- Hydrogen energy infrastructure
- Magnetic fusion energy

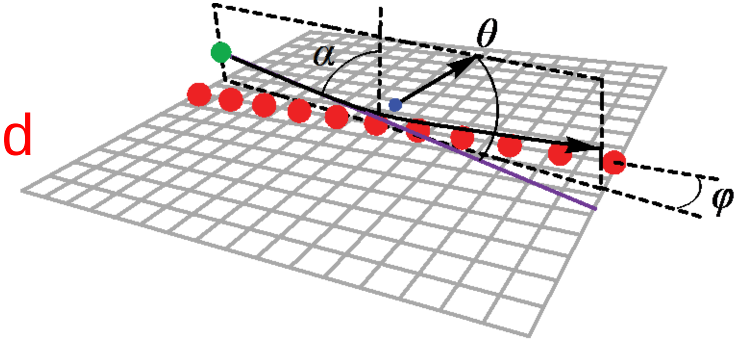




In this talk, I will discuss:

- Tritium retention in metals
- Experimental motivation
- Continuum-scale bubble model

The basic physics governing how hydrogen behaves in different materials can be applied to a wide range of systems.

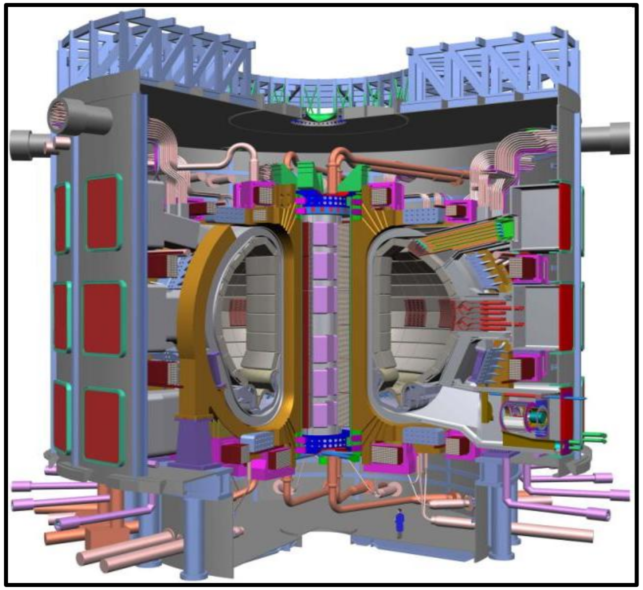


Magnetic fusion energy program couples with other hydrogen research at Sandia

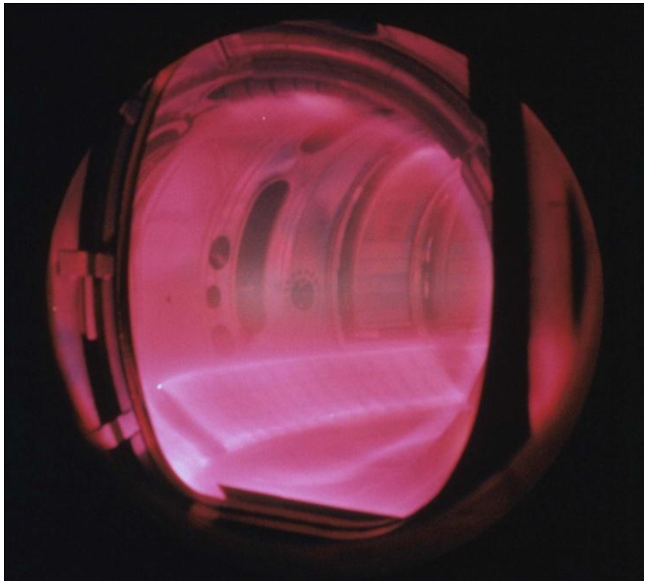
Basic concept:
Same as hydrogen bomb

ITER:
international fusion project (€ 15 billion)

Key issue:
Trapped tritium



ITER baseline design



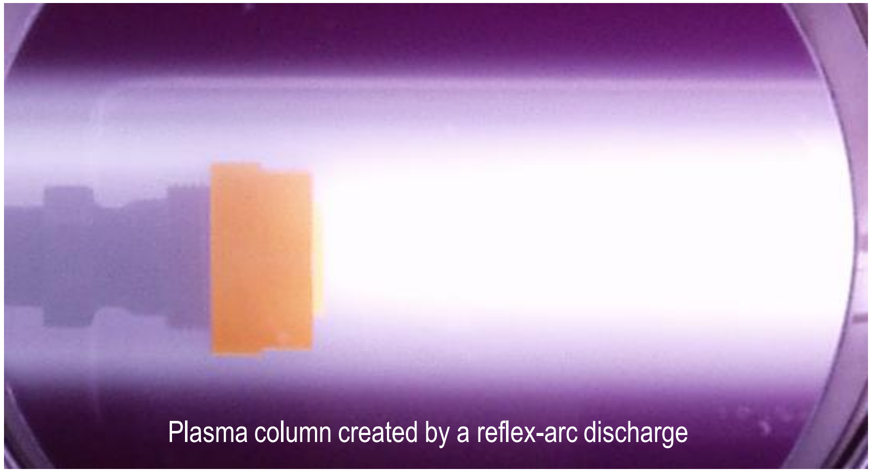
Interior view showing plasma discharge

We leverage Sandia tritium and GTS expertise for fusion:
- Simulate neutron damage
- Understand tritium trapping
- Model bubble growth

Common interest benefits the science behind GTS:
- Fosters collaboration
- Provides access to international expertise
- Outside funding to enhance capabilities

Experimental motivation: Understanding tritium retention in metals

- Implant high concentrations of tritium into materials
- Study **tritium trapping** and **permeation**
- Joint experiment between **Sandia** and **Idaho National Laboratory (INL)**



Plasma column created by a reflex-arc discharge

TPE glove box

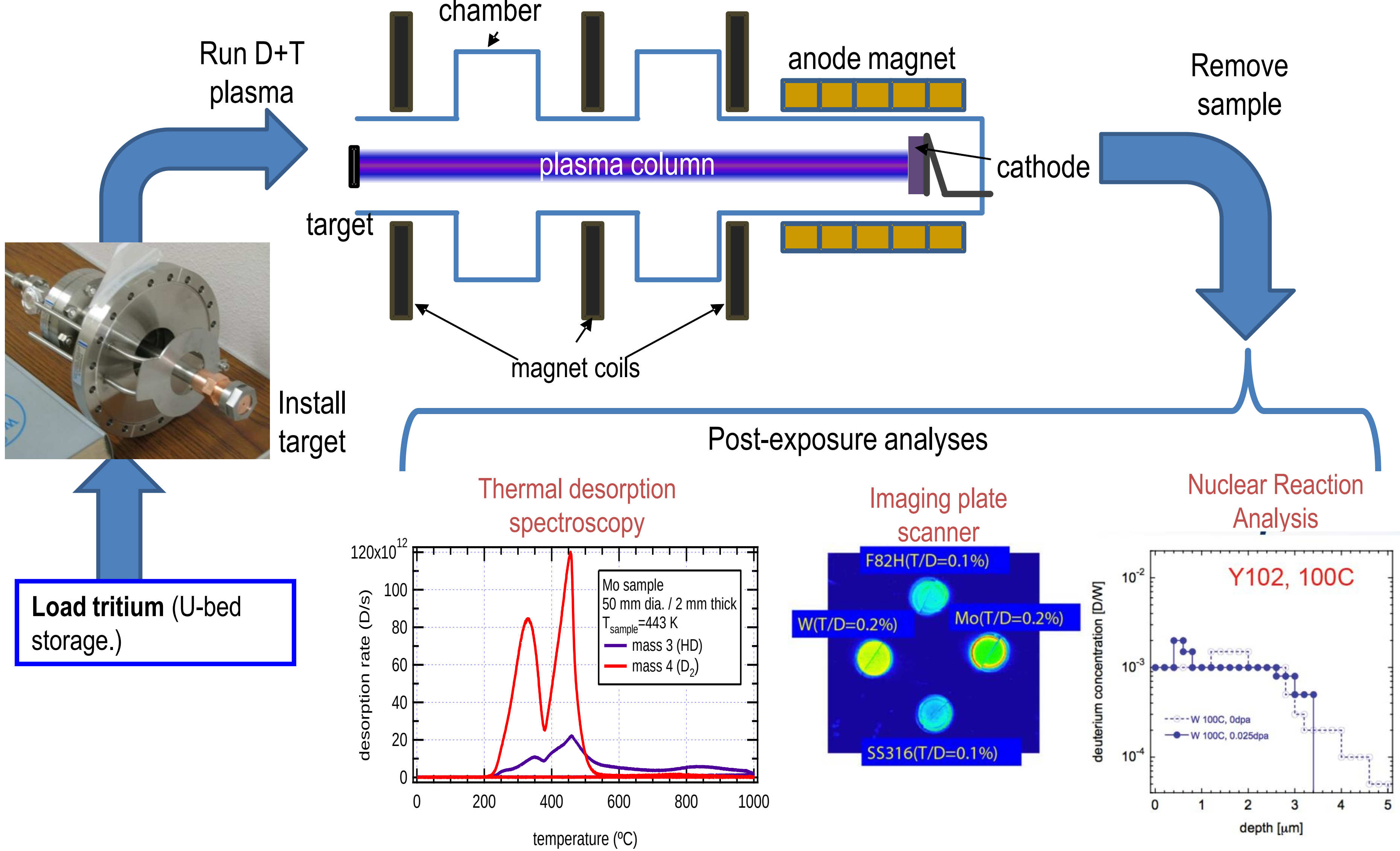
Unique features

- Only high-flux tritium plasma generator in the world
- Handles **neutron irradiated samples**
- Plasma-driven permeation
- Tritium surface/depth profiling

Experiment History:

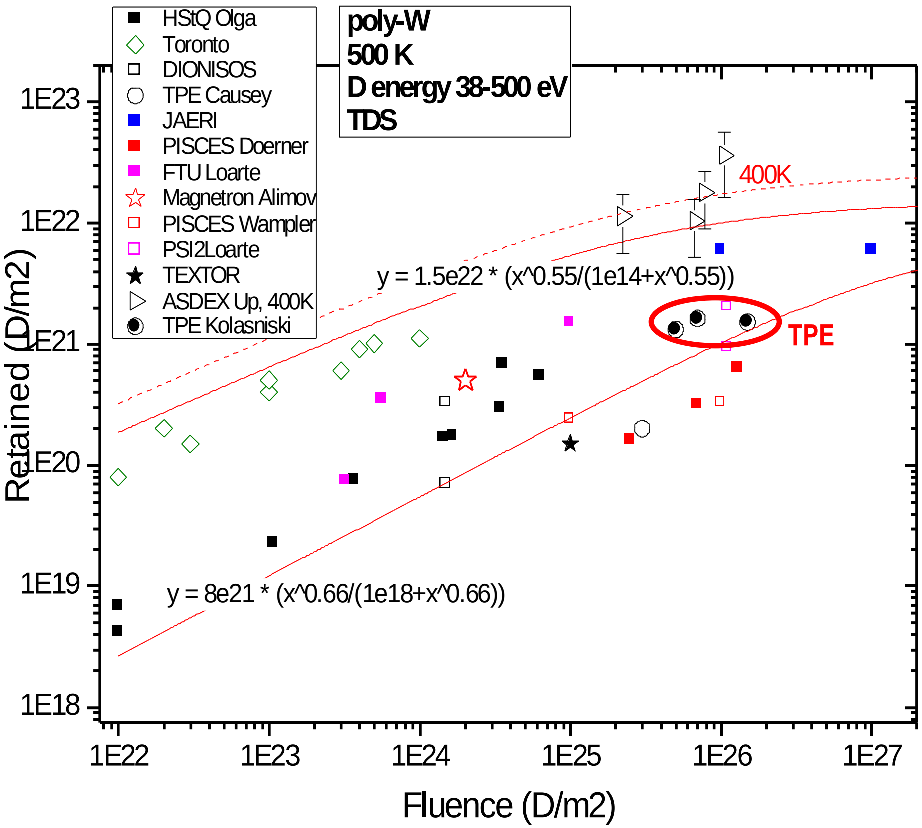
- Developed at SNL, later moved to INL (2002).

Thermal desorption spectroscopy enables us to measure the total tritium inventory



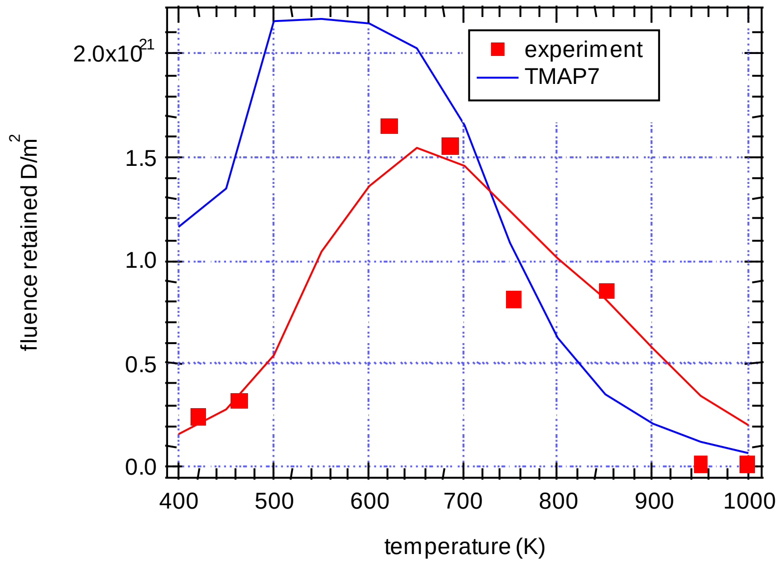
TPE contributes to understanding tritium retention at high concentrations

Retention measurements: Used to predict tritium accumulation in reactors



Tritium inventory as a function of ion beam fluence.

Retention variation with temperature:

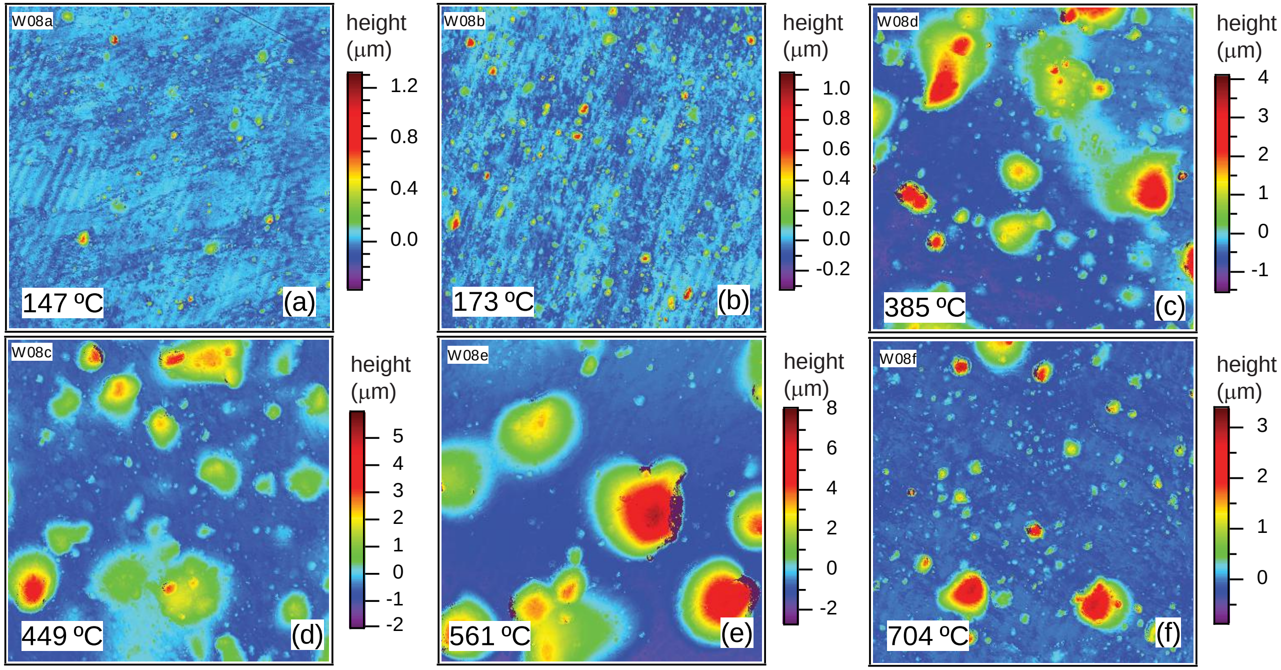


- Existing models over-predict retention
- Extrapolations to higher fluence questionable

What materials science are we missing?

PROFILOMETERY REVEALS THAT SMALL HYDROGEN BUBBLES HAVE GROWN

<u>Note</u>:
Each panel depicts a 500 µm × 500 µm area.

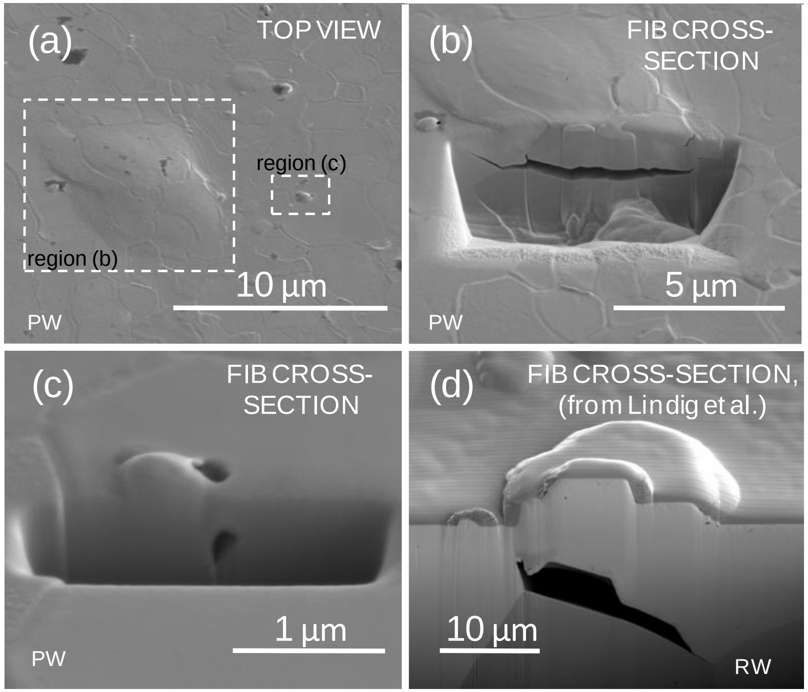


- Difficult to keep hydrogen in solution in W.
- **Precipitation** of H_2 in bubbles preferred.
- Trapping by bubbles inhibits permeation.
- Standard models (TMAP7, DIFFUSE) don't account for bubble growth and precipitation.

Hydrogen precipitate growth in tungsten: experimental findings

<u>*Focused ion beam (FIB) results*</u>:

- Profiled PLANSEE W previously exposed in TPE:
  - 70 eV D^+ ions
  - $\Phi = 1.1 \times 10^{18}$ $cm^{-2}s^{-1}$
  - $F = 8.7 \times 10^{21}$ cm^{-2}
  - $T = 385$ ° C.
- Large blister in (b) enlarged by crack growth.
- Small blister in (c) has grown by dislocation loop punching.
- FIB profile of re-crystallized tungsten exposed under similar conditions shown in (d). Image from [Lindig et al., *Phys. Scr.* (2009).] Growth mechanism also appear to be due to dislocation loop punching.



<u>*Bubble growth mechanisms*</u>:

- Crack propagation
- Dislocation loop punching
- Vacancy clustering

Continuum-scale finite difference model enables simulations of bubble growth

Precipitation affects hydrogen diffusion in metals [W.R. Wampler, *Nucl. Fusion* (2009)]

Motivation for further model development:

- DFT, MD, and Kinetic Monte Carlo reveal key nucleation and growth mechanisms.
- Incorporate insight into continuum approach to model experimental environment
- Existing continuum models (TMAP, DIFFUSE) exclude important physics (e.g. precipitation)

❑ We leverage metal tritides expertise at Sandia from **^{3}He bubble** growth models [D.F. Cowgill, *Fusion Sci. & Technol.* (2005)]

❑ Altered to simulate hydrogen bubbles:

  - Different nucleation process [Henricksson *Appl. Phys. Lett.* (2008).]

❑ Use experiments to refine model.

Diffusion and trapping were modeled using a continuum-scale approach

Diffusion:

Basic 1-D diffusion equation assuming uniform temperature.

Point defects:

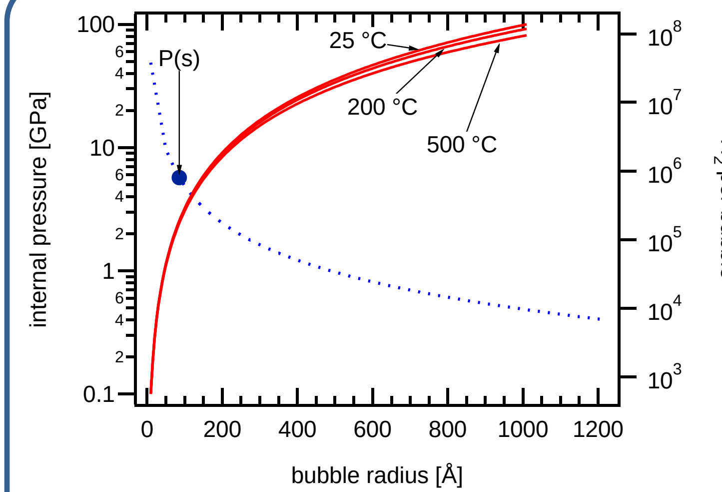
Point defects modeled as 1.4 eV saturable traps (not permitted to serve as nucleation sites for bubbles.) Used approach of Ogorodnikova [*J. Nucl. Mater.* 2009] to address trapping and release:

$$\partial C_t(x,t)/\partial t = (2Da/3)[C_m(N_t - \delta C_t) - (12\delta C_t / a^3)\exp(-E_t / kT)]$$

δ = inverse trap saturability; N_t = trap density; C_t = H concentration in traps.

Trapping by bubbles:

Modeled using a simple approach developed by Mills [J. Appl. Phys. (1959)].



Bubble growth by loop punching

Loop punching condition:

$$p_{LP} \geq 2\gamma/r_b + \mu b/r_b$$

γ = surface energy r_b = bubble radius

b = Burgers vector μ = shear stress

Plot above shows the p_{LP} for W. For small bubbles, p_{LP} is >10 GPa. Need equation of state to calculate H_2 per bubble from loop punching stress.

Internal pressure within bubbles can exceed 1 GPa

H_2 equation of state (EOS):

Very high pressures (>1 Gpa) expected within small hydrogen bubbles.

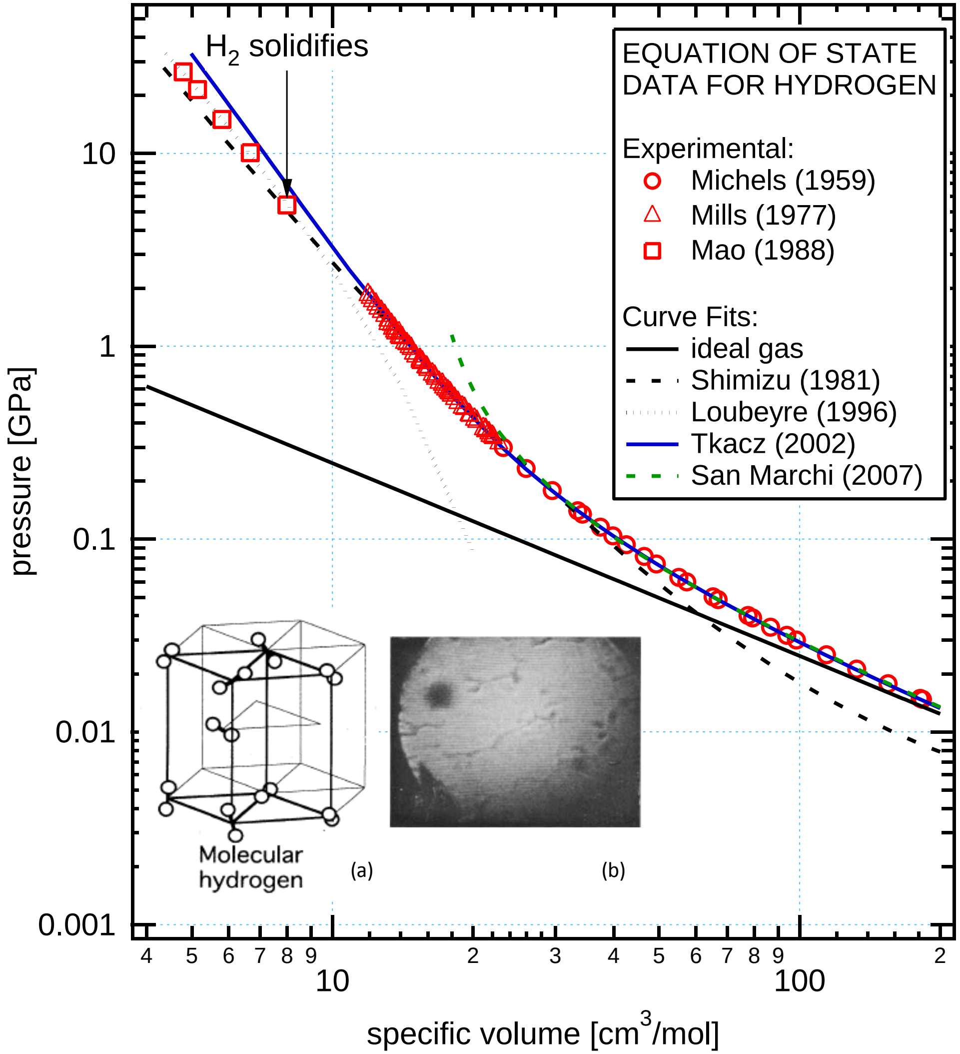
At **25 ° C**, H_2 solidifies at ***p*=5.7 GPa**, forming an hexagonal close-packed molecular solid.

- Over the range of pressures of interest for this work, we found Tkacz's [J. Alloys & Compounds (2002)] EOS to provide the best fit:

$$v = Ap^{-1/3} + Bp^{-2/3} + Cp^{-4/3} + (D + ET)p^{-1}$$

- San Marchi's simplified EOS is also quite accurate at lower pressures:

$$v = \frac{RT}{p} + b$$



Equilibrium conditions dictate when the bubbles will grow

Calculation of equilibrium pressure:

When will the precipitate gas be in equilibrium with the hydrogen in solution?

- Equate the **chemical potentials** of the gas phase and solution.
- Account the non-ideal behavior of the gas in bubbles by incorporating hydrogen **fugacity**:

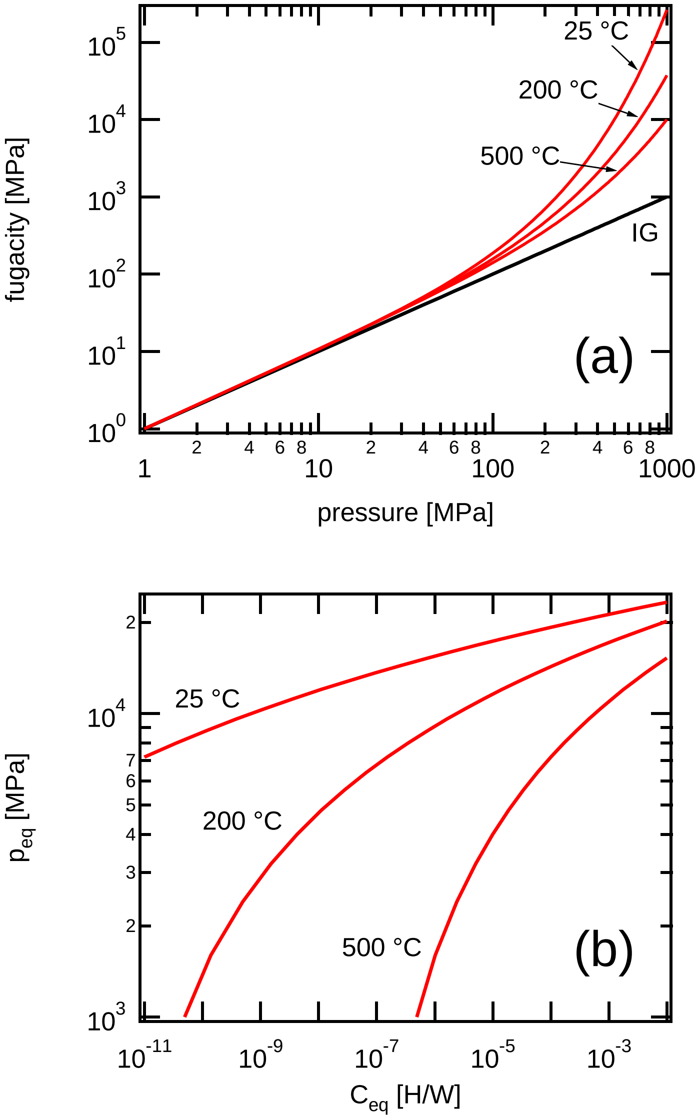
$$\ln(f/p) = \int_0^p (v(p,T)/RT - 1/p)dp$$

- The **equilibrium concentration** is then given by the following expression:

$$C_{eq} = \sqrt{f}\, S_0 \exp(-H_S/RT)$$

S_o and H_s are solubility parameters from Frauenfelder [*J. Vac. Sci. & Tech.*, 1969].

Equilibrium conditions predict when precipitation is favorable.



Continuum-scale approach enables rapid solution of diffusion equation

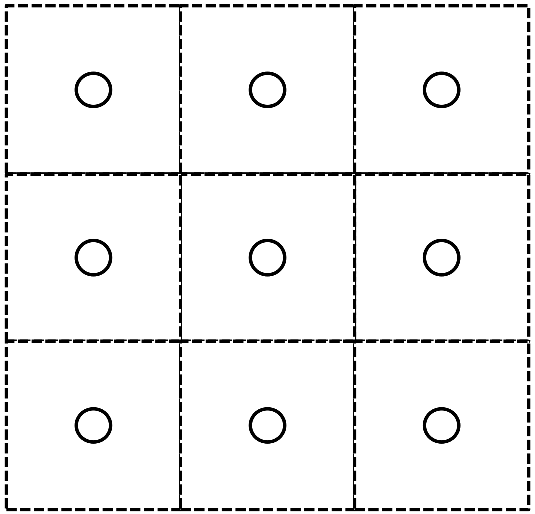
Assume:

(a)Point defects saturable, do not behave as bubble nucleation sites.

(b)Array of evenly-spaced sperhical bubbles.

(c)Bubble diameter smaller than inter-bubble spacings

(d)Slow thermal ramp (quasi-equilibrium is satisfied.)



Array of evenly-spaced spherical bubbles.

Basis for finite difference model: need to integrate three coupled PDE's

Governing equation (1-D diffusion w / 2 sink terms):

$$q_T = \partial u_T(x,t)/\partial t$$

$$\partial u(x,t)/\partial t = D(t)\,\partial^2 u(x,t)/\partial x^2 - q_T(x,t) - q_B(x,t)$$

Flow into or out of the bubbles determined by local eq. conc.

$$q_B = \partial u_B(x,t)/\partial t = 4\pi D(t) r_B(x,t) N_B(x)\left[u(x,t) - u_{eq}(x,t)\right]$$

Concentration at bubble surface determined by Sievert's Law:

$$u_{eq}(x,t) = \sqrt{f} S_0 \exp(-E_s/RT)$$

Fugacity (requires aforementioned EOS):

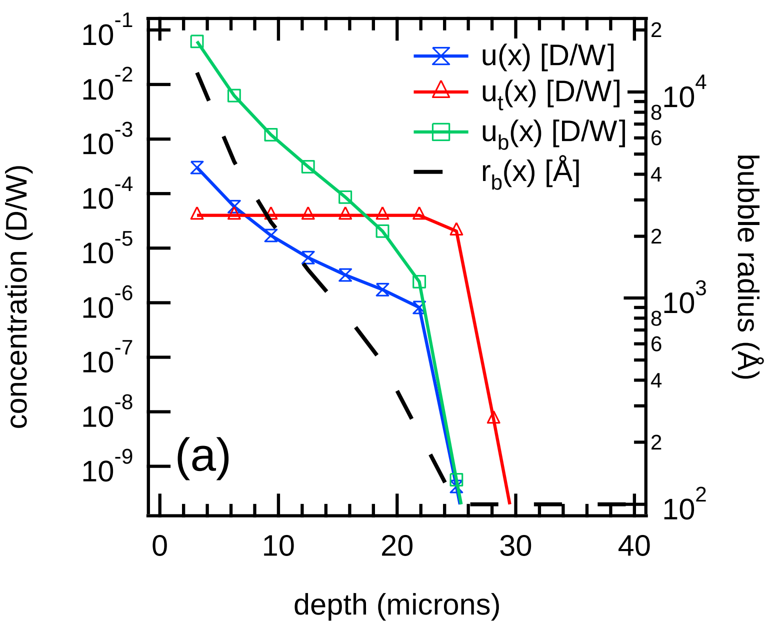
$$\ln(f/p) = \int_0^p (v(p,T)/RT - 1/p)\,dp$$

SIMULATED BUBBLE SIZES CONSISTENT WITH EXPERIMENTAL FINDINGS

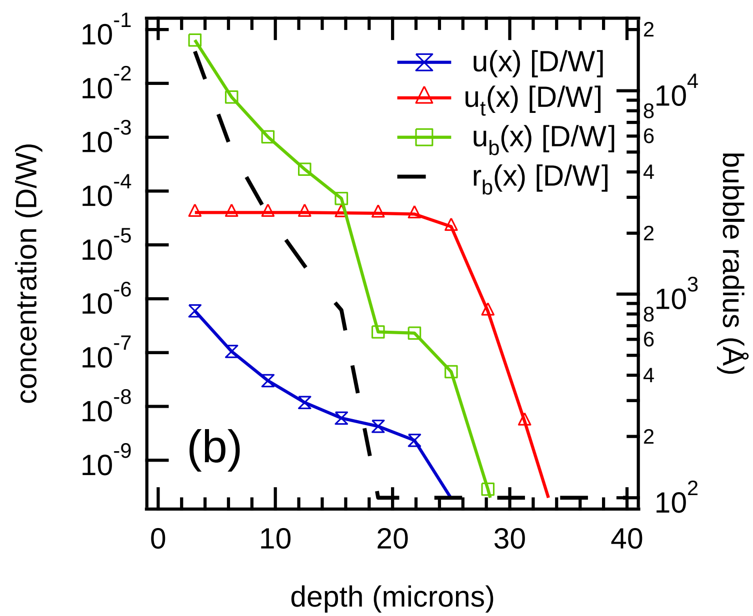
- Assumed a pre-existing concentration of nucleation sites (eventually growing into bubbles.)
- Traps fill first, followed by bubble growth.
- Using realistic input conditions, depth profiles consistent with experimental findings.

$N_t = 4\times10^{-5}$ W^{-1}
$N_b = 10^{-12}$ W^{-1}
$F = 10^{18}$ D/cm^2-s, calculated near-surface conc. at the end of range from $F = Du/r$.
$r = 2.5$ nm for 100 eV D^+ ions

300 K



500 K



Concluding remarks

We have studied….

- *Tritium trapping in metals*
  - TPE used to implant a large amount of hydrogen
  - Observed hydrogen bubble growth in tungsten
- *Hydrogen bubble growth*
  - Successfully adapted metal tritides code
  - Model accurately predicts bubble growth conditions
  - Further work:
    - Implementation of fast DAE solver
    - Modeling of thermal desorption from precipitates
    - Experiments to validate the model predictions
    - Application to high-temperature hydrogen attack.

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