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Deuterium retention at displacement damage in tungsten

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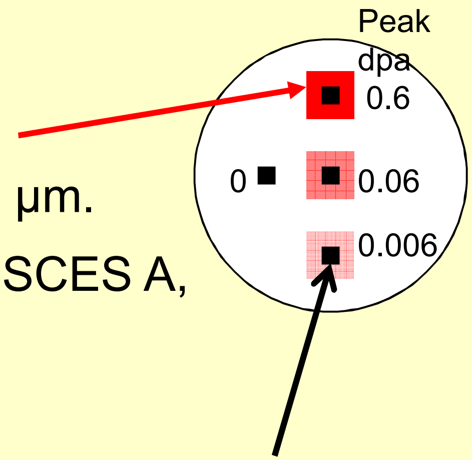
Introduction

- Fusion neutrons cause atomic displacements (vacancies & interstitials).
- In ITER ~ 0.7 dpa in W from 0.4 MW/m^2 for 0.63 FPY by end-of-life.
- DT from plasma diffuse rapidly in tungsten and are atomically bound (ie. trapped) at vacancies.
- Therefore damage may increase tritium inventory in tungsten components.

Key issues:

1. How many traps/dpa? <<1 because defects diffuse & anneal.
2. How quickly and to what depth are traps filled by exposure to plasma.
3. Temperature dependence
   - Experiments
   - Model

Experimental approach

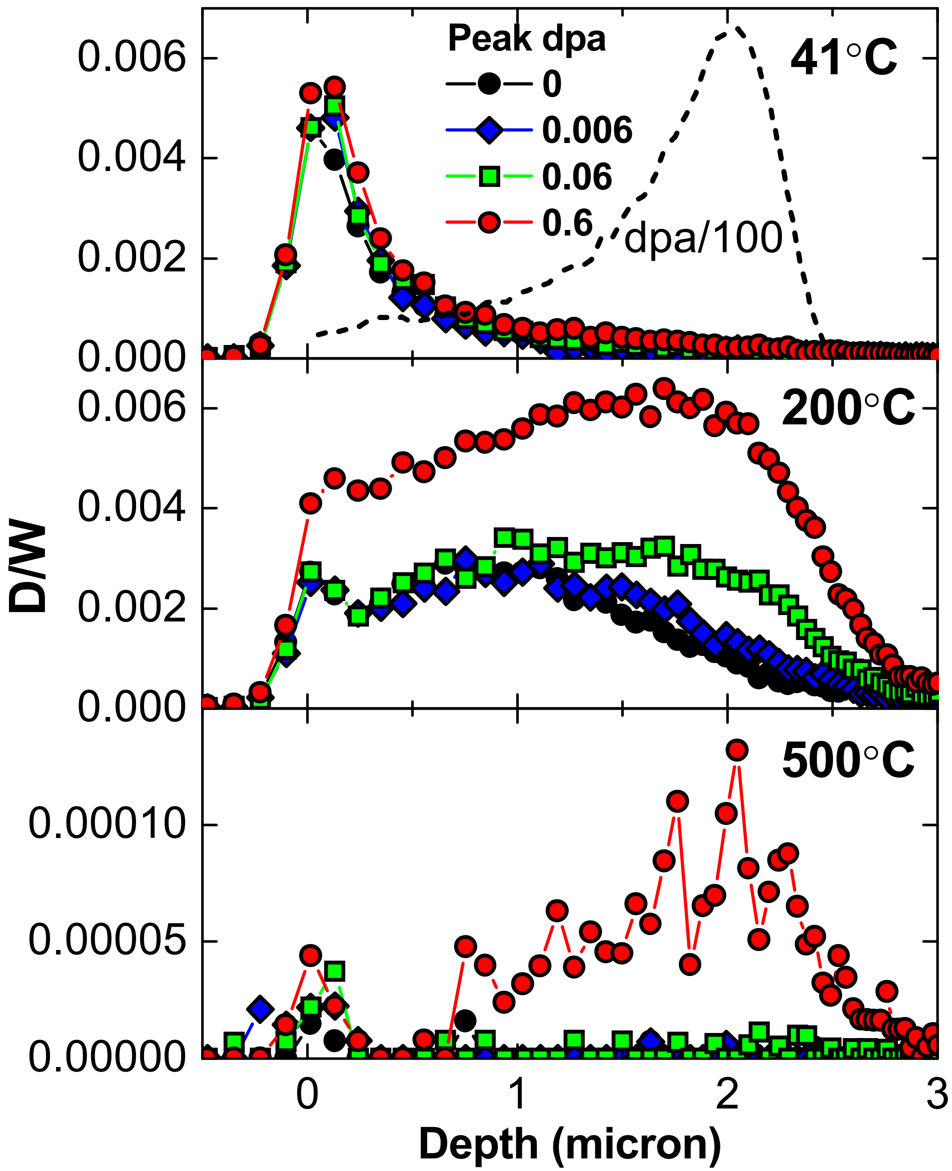


1. Simulate neutron damage using 12 MeV Si ion irradiation.
   Produces ~ 7500 displacements per ion, up to 0.6 dpa at 2 μm.
2. Simulate exposure to divertor plasma using D plasma in PISCES A,
   (by R.P. Doerner at UCSD)
   low energy (~100eV), high flux (2×10^{18} D/cm^{2}s)
   & fluence (10^{22} D/cm^2), at T = 40 to 500°C.
3. Measure resulting D concentration vs depth to 3μm by D(^{3}He,p)α NRA.
4. Material: Plansee tungsten 99.97%

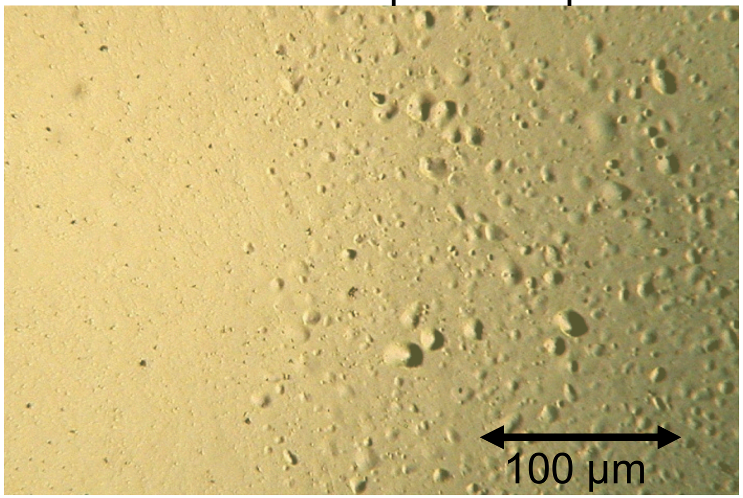
Experiments:

1. Damage & D plasma, T=40, 200, 500°C.
2. Damage & D + 5% He plasma, T=200, 300, 400, 500°C
3. Damage & D + 5% He plasma at 200°C after 500°C anneal.

D retention at damage with D plasma

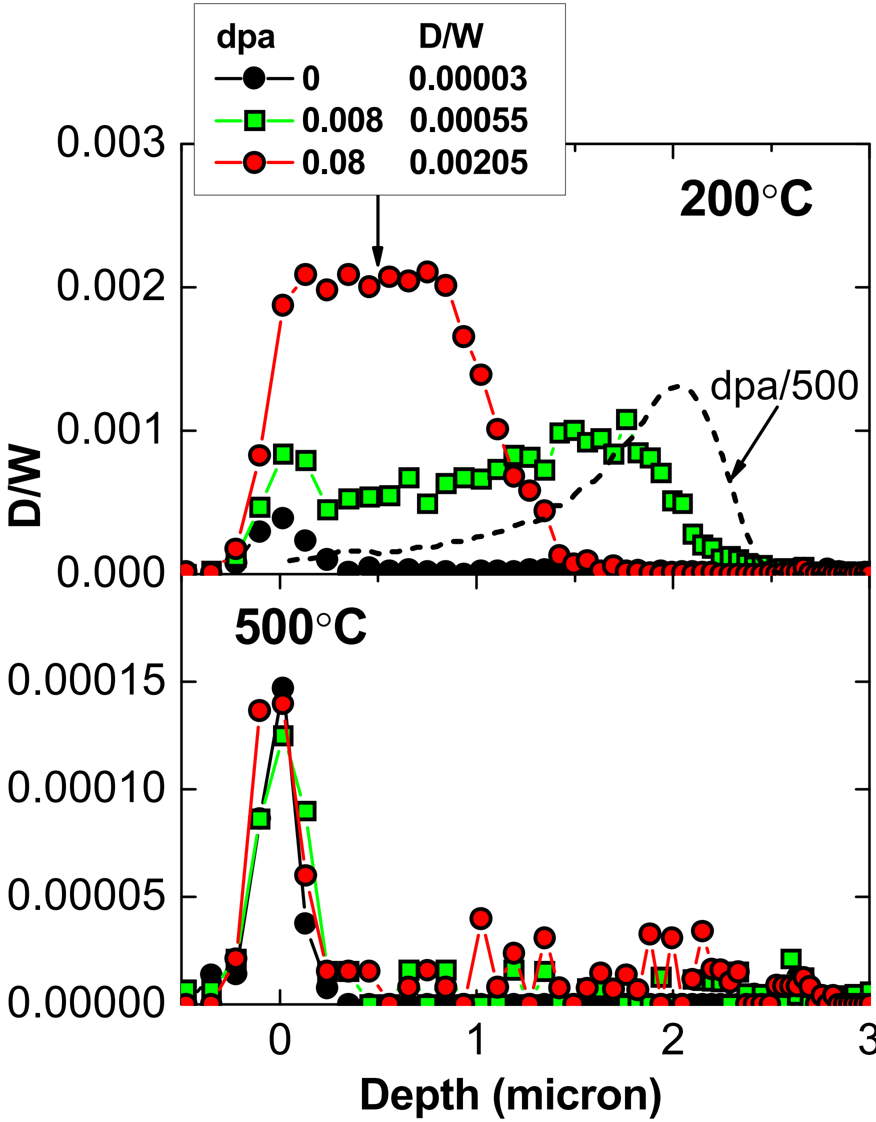


Blisters on W exposed at 200°C
Shadowed from / Exposed to plasma



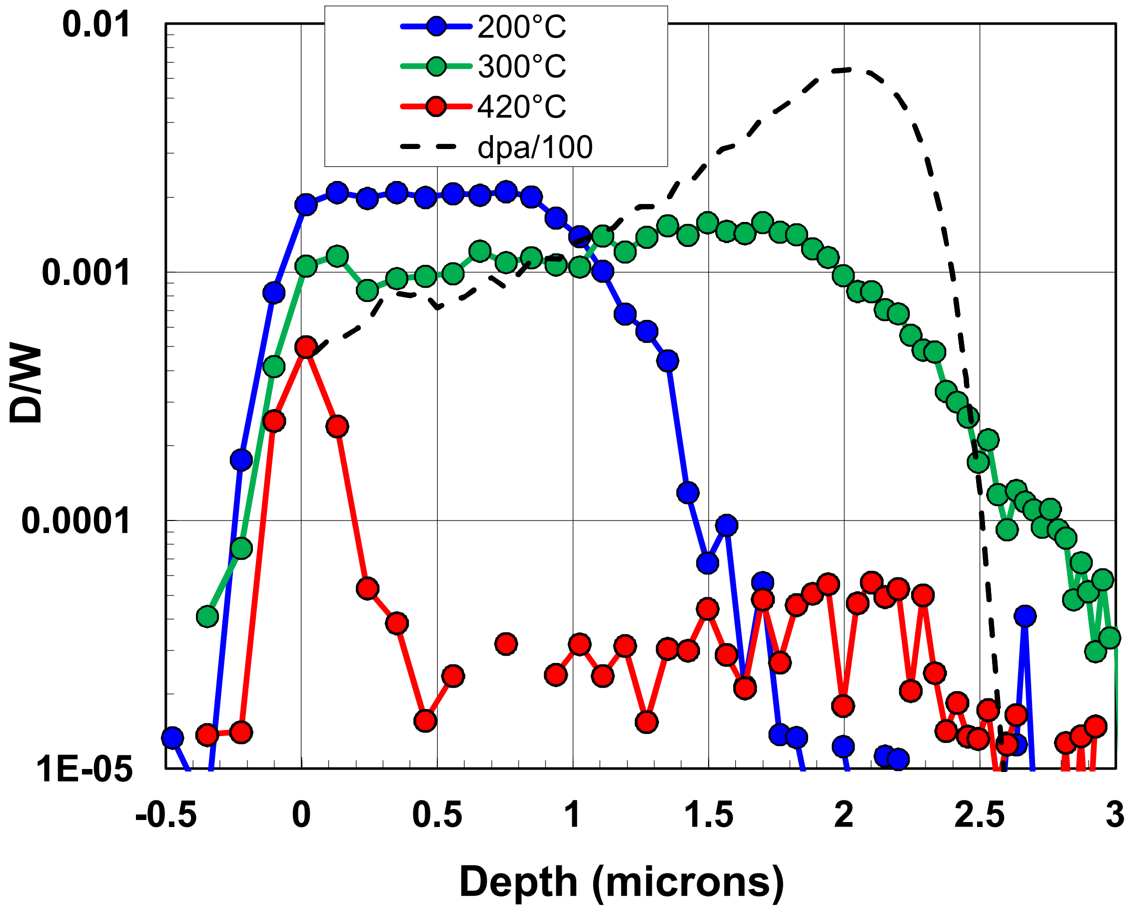
- **D precipitates near the surface, in damaged and undamaged W:**
  0.5 µm at 41°C
  2 µm at 200°C
  no precipitation at 500°C.
- **Damage increases D retention.**
- **Increase in D/W at damage peak:**
  small at 41°C,
  largest at 200°C.

D retention at damage with D + 5% He plasma



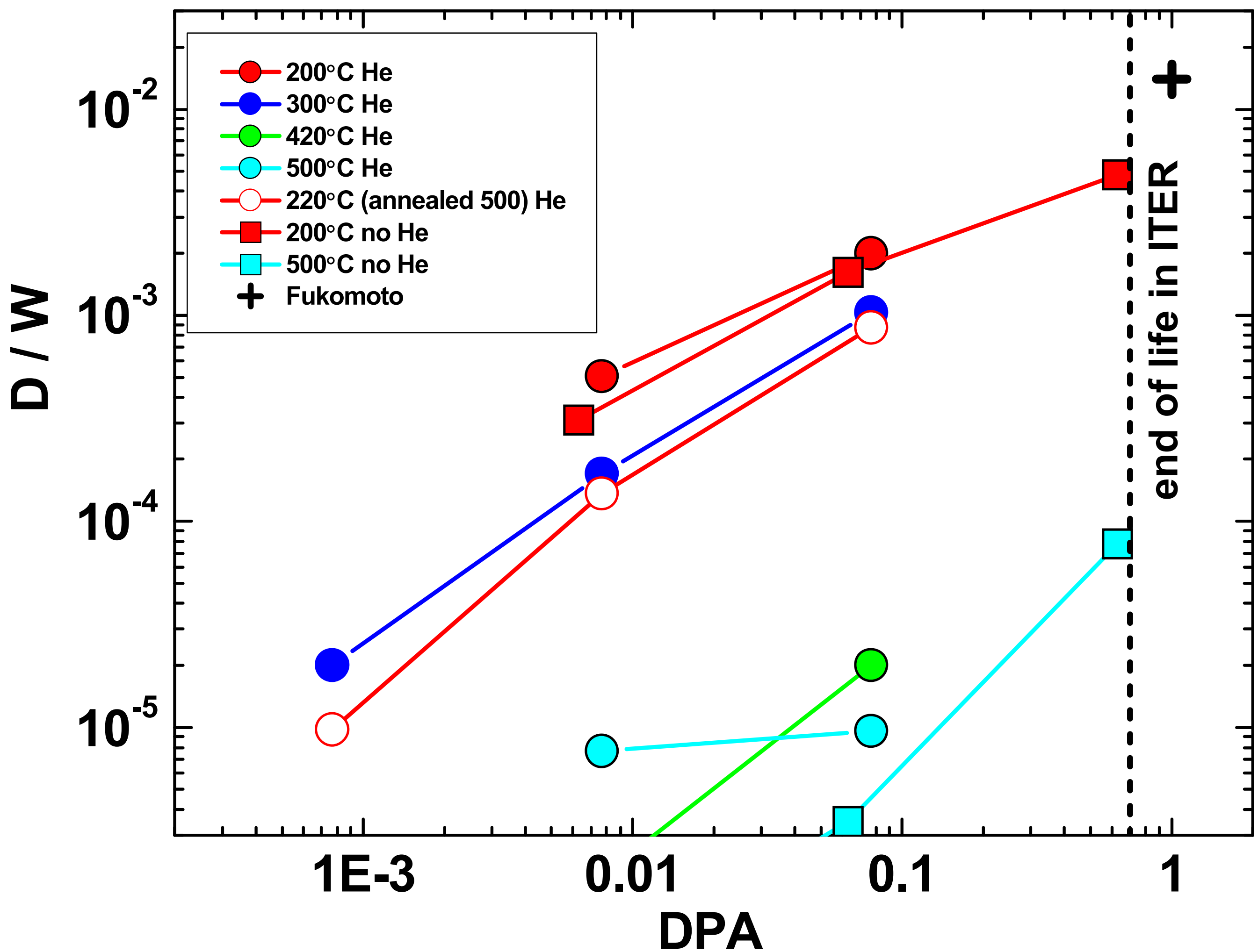
- He reduces D retention by precipitation (eg. by ~ 35x at 200°C in undamaged W).
- No blistering.
- He in the plasma creates small bubbles near the surface (Miyamoto) which hinder D precipitation at greater depths, but D is still trapped at displacement damage.
- Increase in D retention from damage is similar with & without He, but now not to full depth of damage because of kinetics.

Large decrease in trapped D between 300 & 420°C



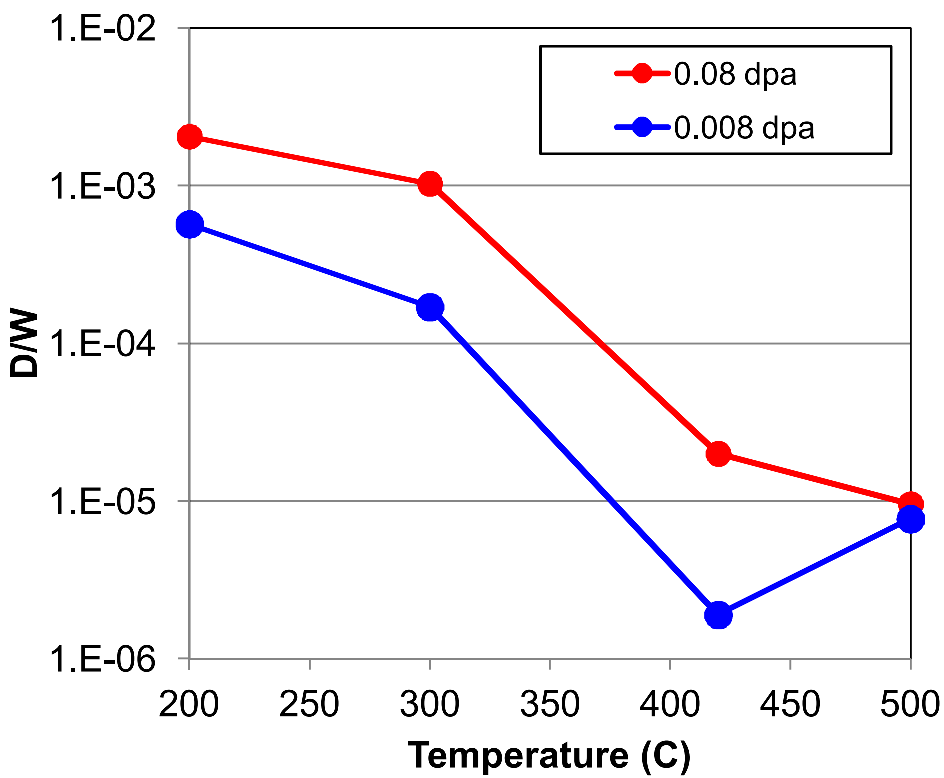
Deuterium depth profile in tungsten with 0.6 dpa peak exposed to D+5%He plasma in PISCES

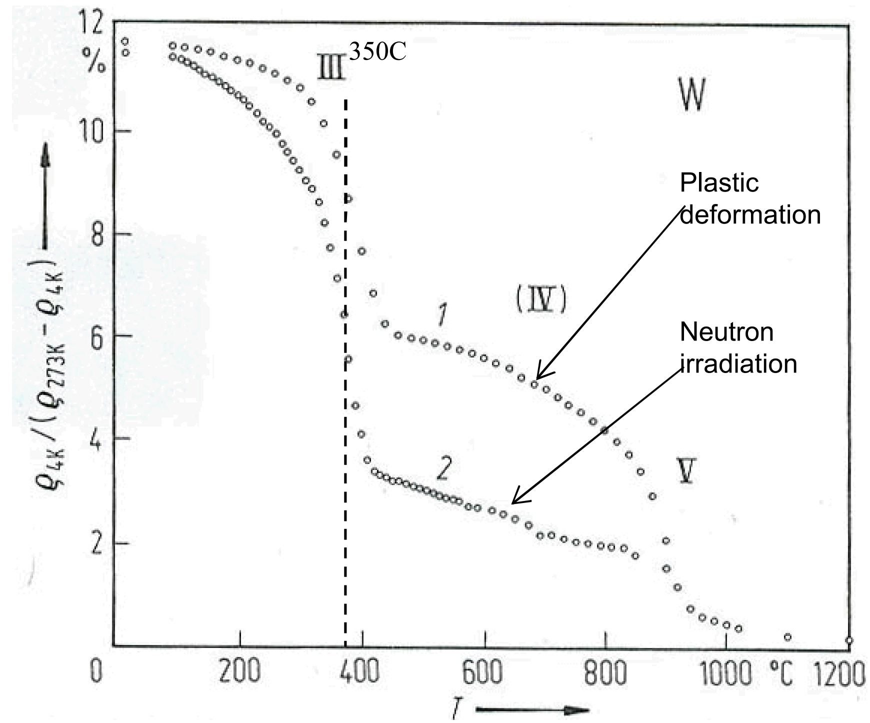
Concentration of trapped D vs dpa & T



- D/W for dpa from end-of-life neutron fluence in ITER ~0.005 at 200°C.
- D/W~100x lower at 500°C than at 200°C.

Large decrease in trapped D between 300 & 400°C.
Is this due to vacancy annealing?





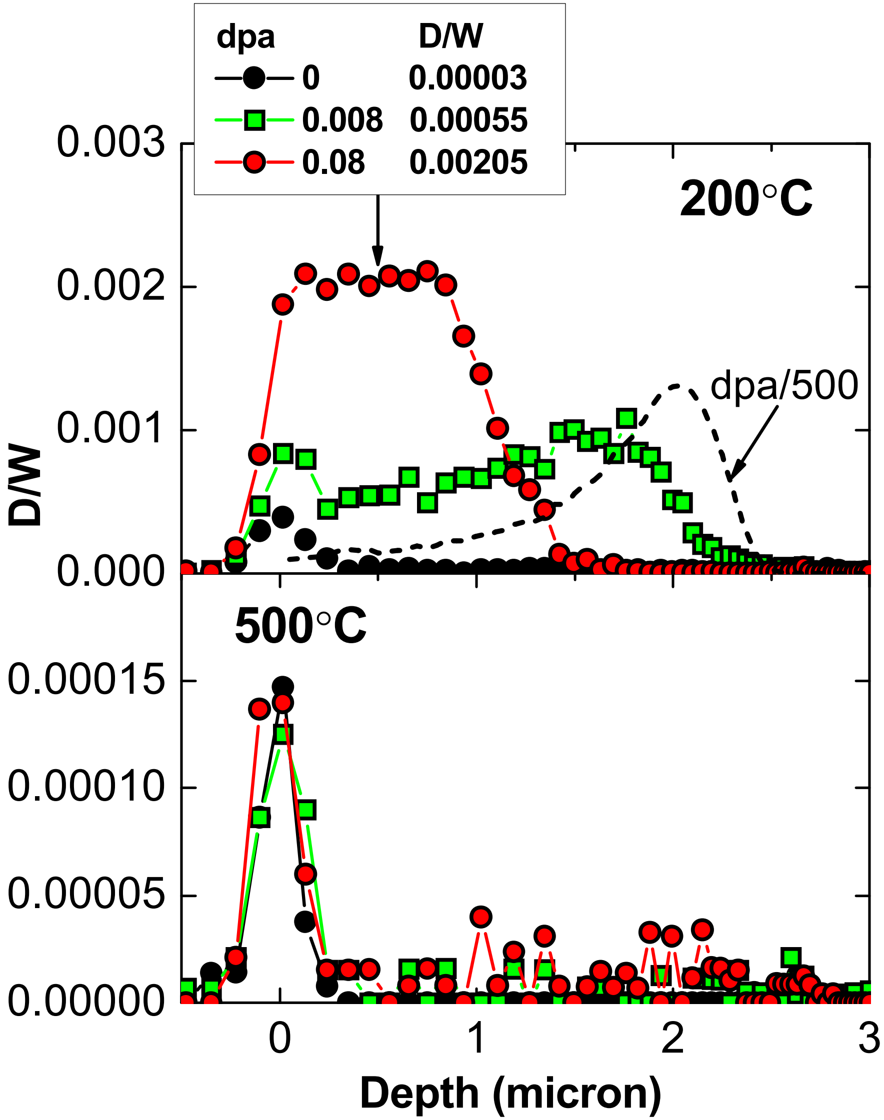
Vacancies anneal (stage III) near 350C,

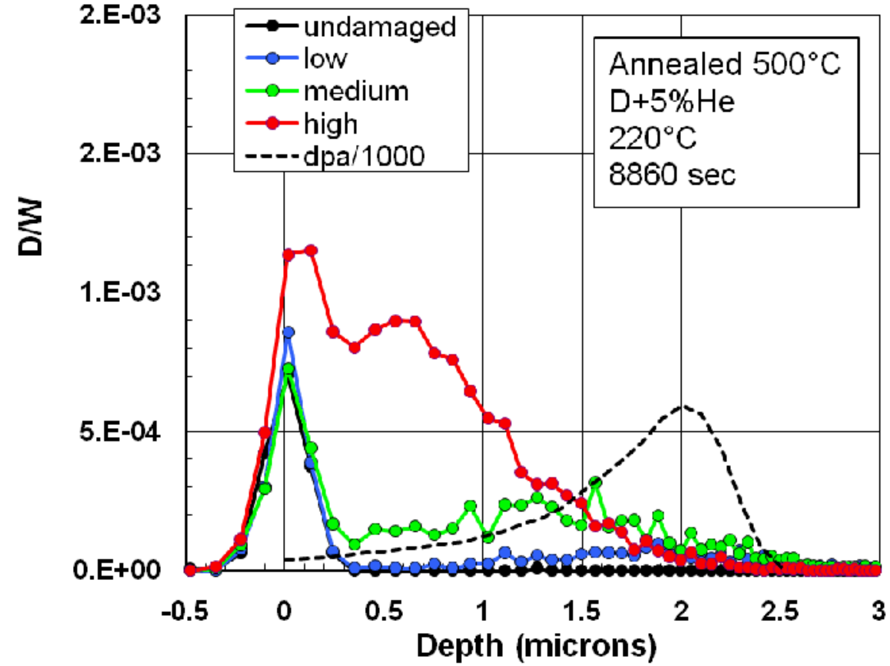
Vacancy clusters anneal (stage IV) near 900C
in neutron or ion irradiated tungsten.

Also seen by positron annihilation.

Reduction in D/W could be due to vacancy annealing

Anneal at 500ºC reduced D trapping at 220ºC by ~2x.

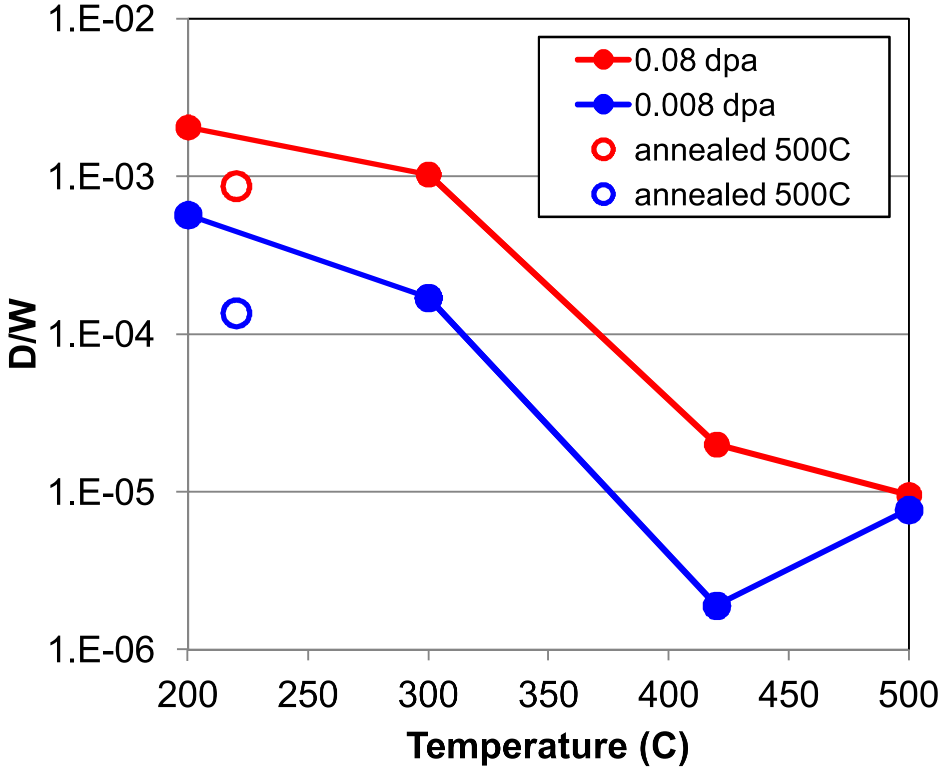




Q: Is lower D/W at 500°C due to vacancy annealing or weak trapping?

Test : Anneal damaged tungsten at 500°C for 1 hour, then expose to plasma at 200°C to see if traps have annealed.

A: Many traps are still present implies that the lower D/W at higher T is mainly from weak binding to traps.



Model for D retention at displacement damage

1. Diffusion-limited release would give near-surface concentration:
   $C_s = \Phi\, x/D\, N_o$.

2. Precipitation reduces the near-surface concentration of mobile D in solution.

3. Fractional occupation σ of traps in equilibrium with concentration C_s is given by:

$$\frac{\sigma}{1-\sigma} = \frac{C_s}{z} \exp\left(-\frac{Q_t}{kT}\right)$$

4. Saturable traps (eg. monovacancies or vacancy clusters)
   fill by diffusion from the near-surface:

$$N = C_T\, x = \sqrt{2Dt\, C_S\, \sigma\, C_T}$$

Model for D retention at displacement damage

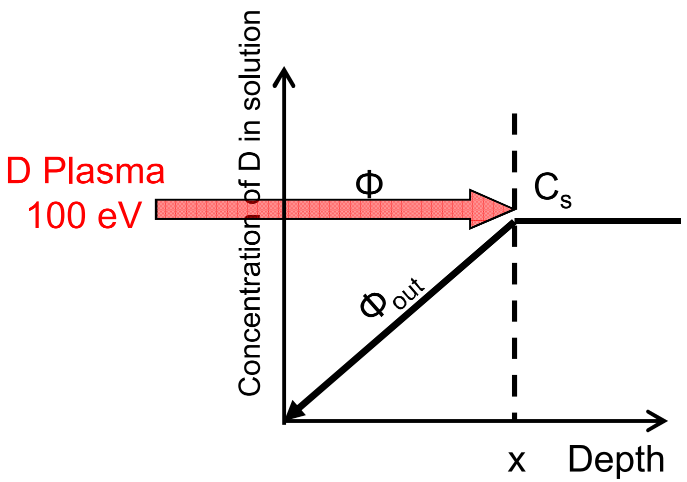
1. Diffusion-limited release would give near-surface concentration Cs = Φ x/D No .

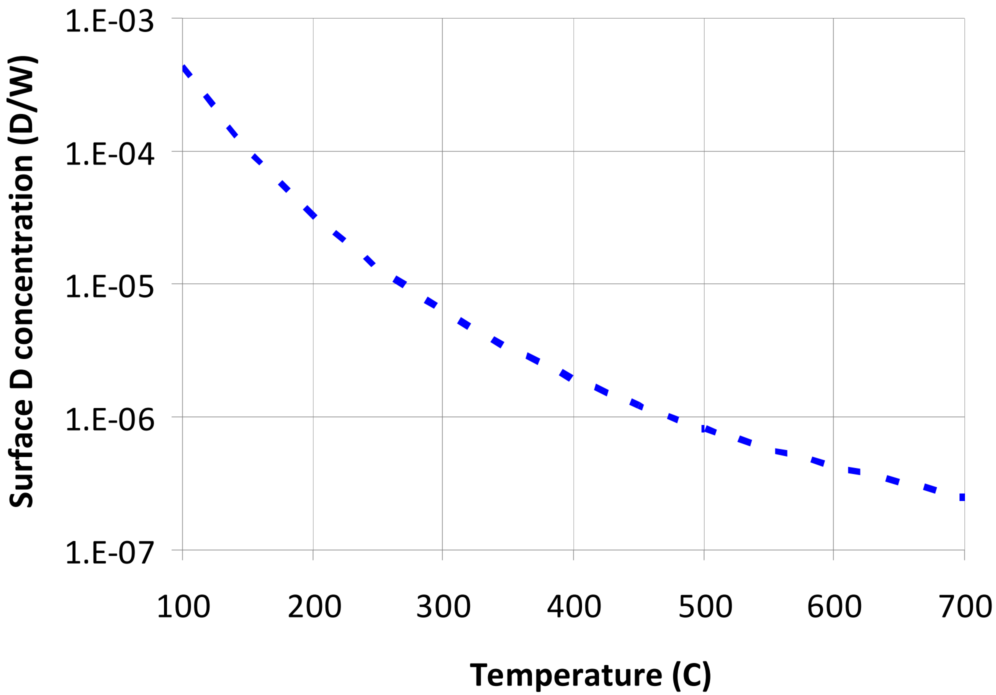
Plasma injects D into solution sites

Near-surface D concentration from diffusion-limited release:

$\Phi \approx \Phi_{out} = D\, C_s\, N_o / x$

$C_s = \Phi\, x / D\, N_o$





Diffusivity from Frauenfelder,

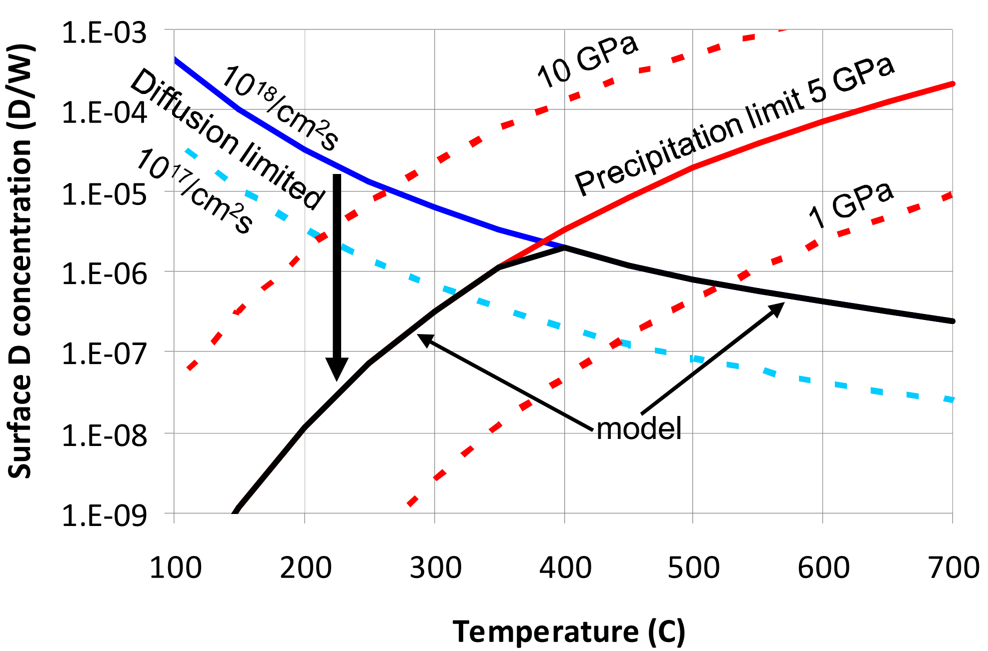
$N_o = 0.63 \times 10^{23}$ tungsten atoms/cm^3,

$\Phi = 2 \times 10^{18}$ D/cm^{2}s , x≈3 nm for PISCES plasma

Model for D retention at displacement damage

2. **Precipitation** reduces the near-surface concentration of mobile D in solution.

Gas pressure required for void growth by dislocation production is
$P_{max} \sim \mu b/r \sim$ 1-10 GPa for r = 10-100 nm.
Corresponding concentration of D in solution is
$C_{max}=S\ (P^*_{max})^{1/2}$, where solubility $S=S_0\ \exp(-Qs/kT)$.
Equilibrium gas pressure P_{eq} and fugacity P* are related by the equation of state†, P~P* for P<0.1GPa (ideal gas EOS).
If $C>C_{max}$, D will flow into voids increasing their volume by plastic deformation, ie. gas precipitates. Bubble nucleation depends on microstructure.
Precipitation limits the chemical potential, and the concentration of D in solution, and hence the permeation to greater depths.

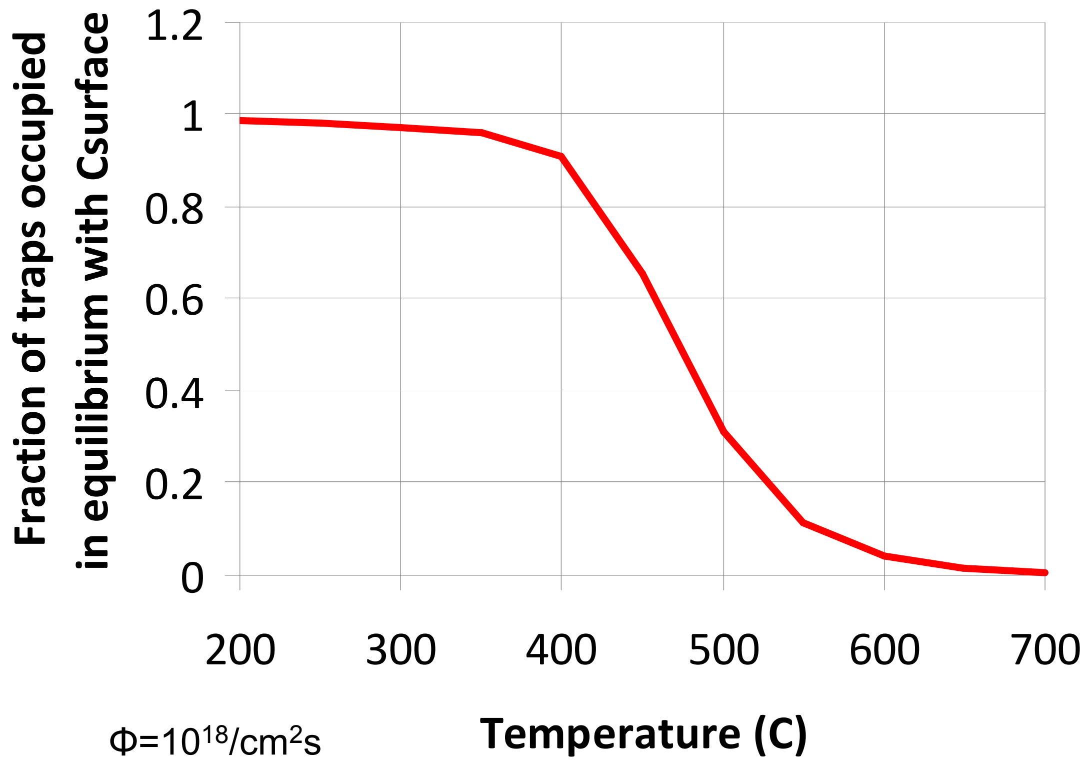


† *Tkacz and Litwiniuk, J. Alloys and Compounds* <u>*330-332*</u> *(2002)89.*

Model for D retention at displacement damage

3. Fractional occupation σ of traps in equilibrium with concentration Cs is given by:

$$\frac{\sigma}{1-\sigma} = \frac{C_s}{z} \exp\left(-\frac{Q_t}{kT}\right)$$



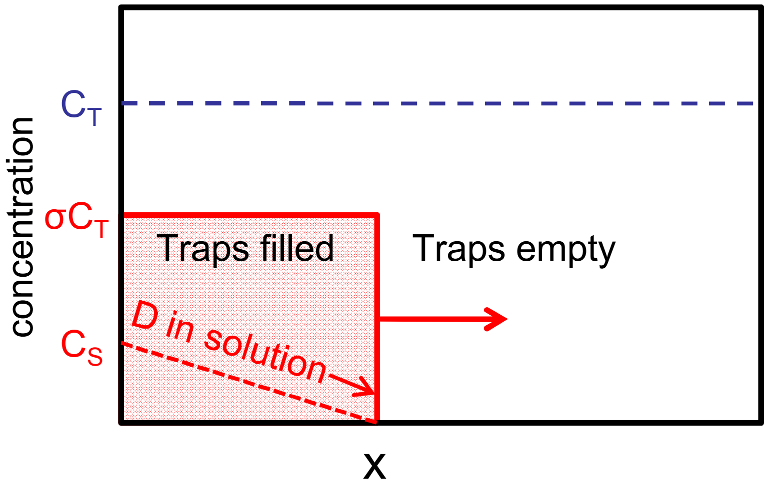
$\Phi=10^{18}/cm^2s$
P_{max}=5GPa
Q_t=1eV [*Eleveld and Van Veen, JNM* ***191-194*** *(1992) 433*]

1eV traps are not effective above~ 500°C

Model for D retention at displacement damage

4. Saturable traps (eg. monovacancies or vacancy clusters) fill by diffusion from the near-surface:

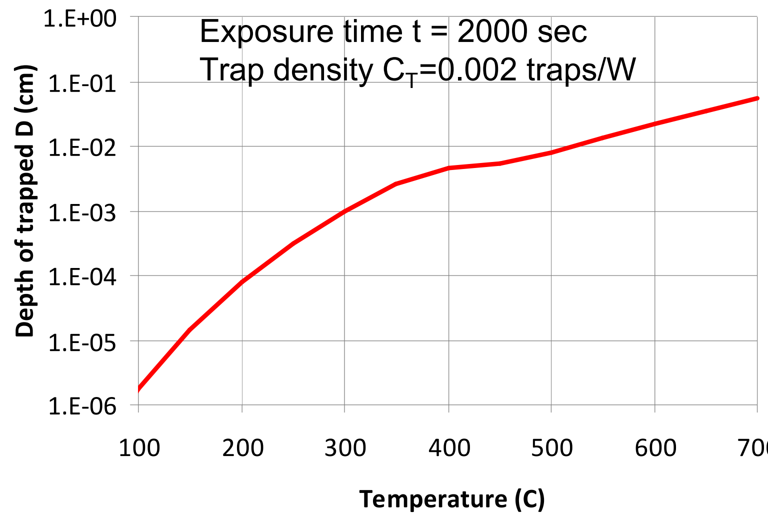
Traps are filled to depth x and empty at greater depth.

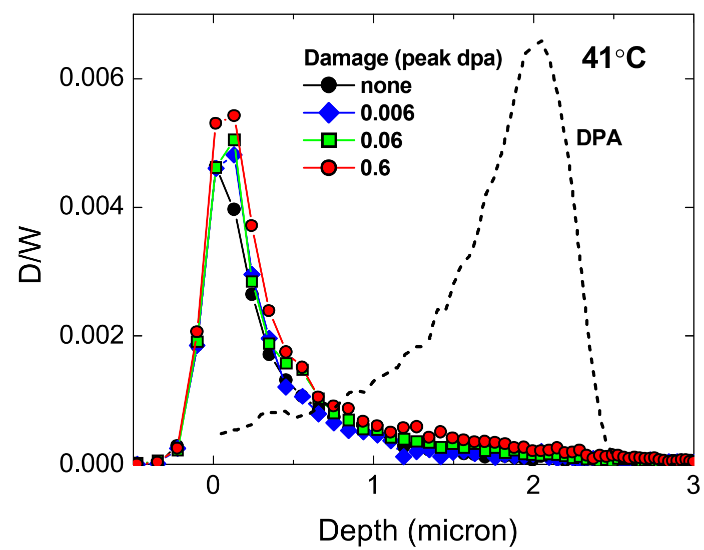


Flux to moving interface: $$D\frac{C_S}{x} = \sigma C_T \frac{dx}{dt}$$

Depth to which traps are filled: (uniform trap concentration) $$x = \sqrt{2Dt\frac{C_S}{\sigma C_T}}$$

Trapped D: $$N = \sigma C_T\, x = \sqrt{2Dt\, C_S\, \sigma C_T}$$

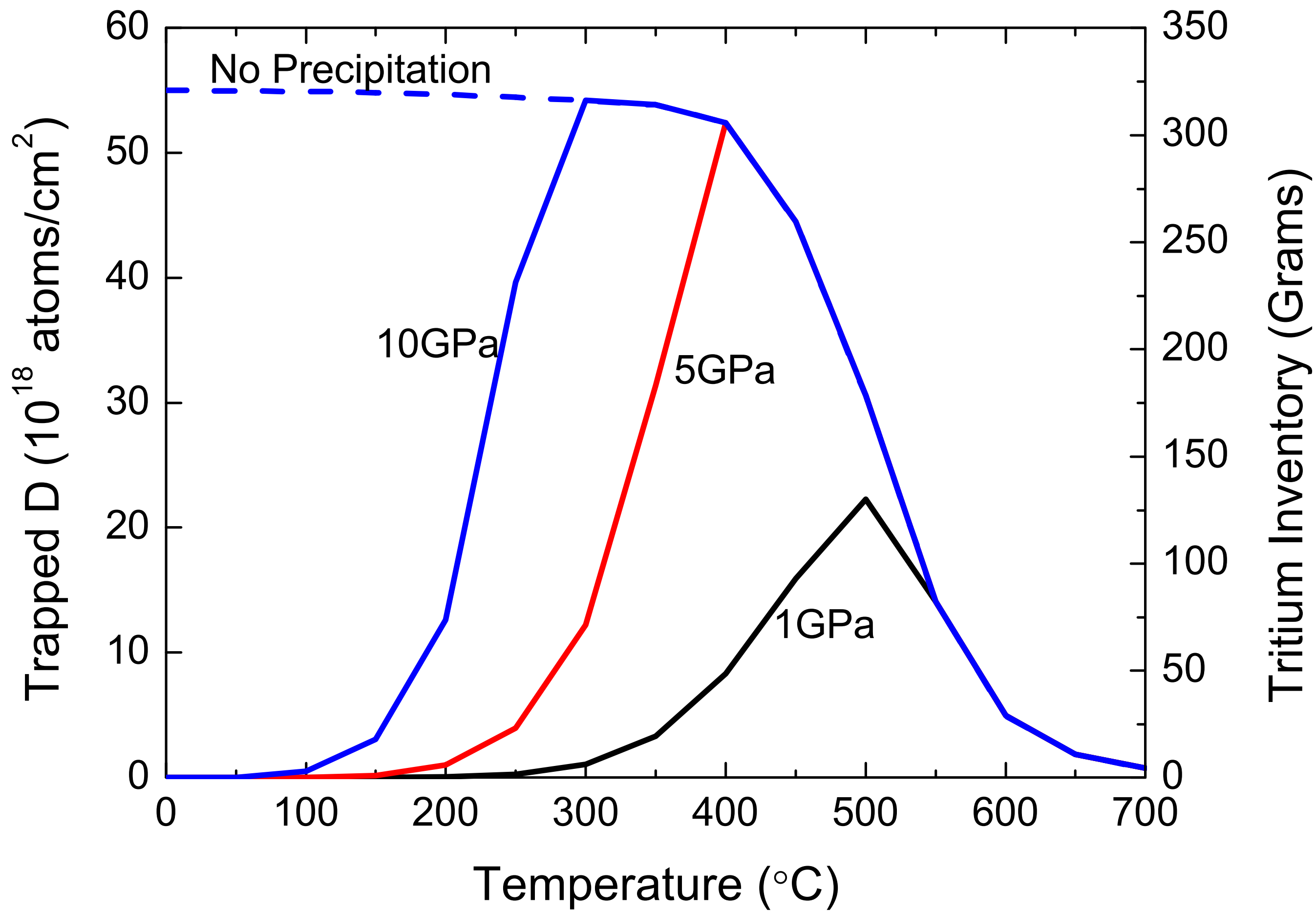




At T=41°C D precipitates
- damage does not increase retention
- D does not reach traps at 2 microns

Implications for tritium inventory in ITER

DT retention is limited by precipitation at T<300°C, and by trap binding at T>400°C



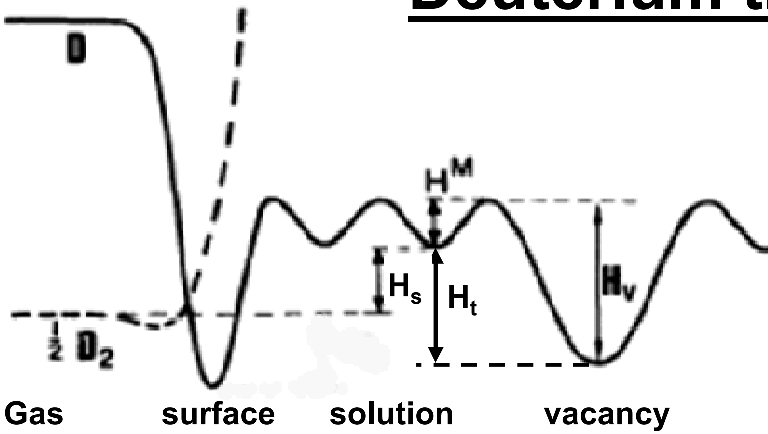
Flux=2E18 D/cm^{2}s
Exposure time=2x10^7 sec (ITER end of life)
Trap concentration=0.002 traps/W
Binding energy to traps Q_t=1eV
50%T, 140 m^2 tungsten

Conclusions

- Exposure to plasma causes D retention by precipitation (near-surface) plus trapping at damage.
- D in solution from implantation at high flux and low temperature has high chemical potential which drives precipitation.
- Precipitation reduces the near-surface D concentration and hence the permeation to greater depths.
- D retention at $T<200^{o}C$ is small due to slow kinetics, ie. permeation.
- D retention at $T>400^{o}C$ is small due to weak binding of D to traps.
- D retention may be maximum near 300-400ºC where traps fill and permeation is fast enough to extend to greater depths.
- The model for D retention presented here includes effects of trapping and precipitation, and the dependence on temperature, incident flux, trap strength needed for extrapolation to other conditions (eg. ITER).

Extra Slides

Deuterium trapping - Energetics



Trapping: D bound to vacancy

Precipitation: formation of gas from solution

Enthalpies:

H^M = 0.39 eV migration

H_s = 1.04 eV solution

*Frauenfelder JVST **6** (1969) 388*

H_v = 1.43 eV dissociation from trap

$H_t = H_v - H^M$ = 1.04 eV binding to trap (vacancy)

*Eleveld and Van Veen, JNM **191-194** (1992) 433*

Chemical potential

solution $$\mu_s = H_s - TS_s + kT\ln\left(\frac{C}{6-C}\right)$$

traps $$\mu_t = H_t - TS_t + kT\ln\left(\frac{\sigma}{1-\sigma}\right)$$

gas $$\mu_g = \frac{1}{2}\left[H_g - TS_g + \int_{P_0}^{P} V\,dP\right]$$

$$\mu_g = \frac{1}{2}\left[H_g - TS_g + kT\ln\left(\frac{P^*}{P_0^*}\right)\right]$$

Fugacity (=pressure for ideal gas)

$$P^* = \exp\left(\frac{1}{kT}\int V\,dP\right)$$

Equilibrium condition

$$C = S\sqrt{\frac{P^*}{P_0^*}} \quad \text{and} \quad S = S_0 \exp\left(-\frac{H_s}{kT}\right)$$

S_0 ~0.01 D/W/atm$^{1/2}$

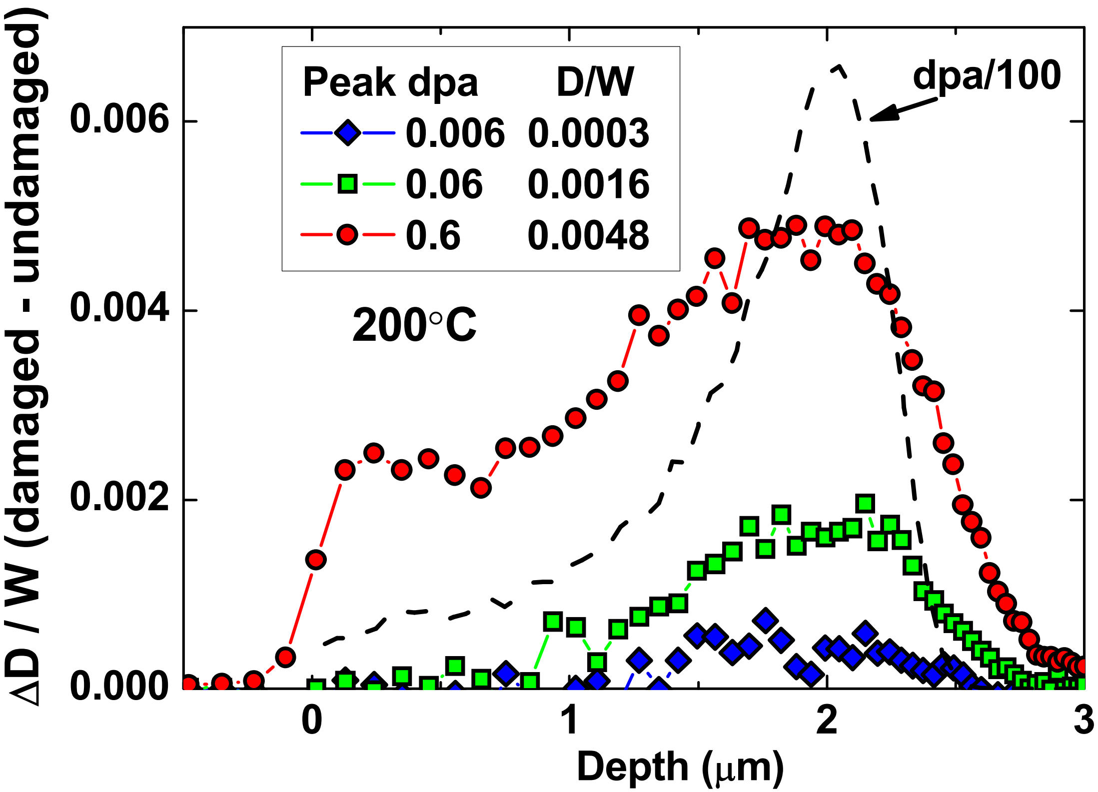
$$P_t = \left[\left(\frac{\sigma}{1-\sigma}\right)\frac{1}{L_0}\exp\left(-\frac{(H_t - H_s)}{kT}\right)\right]^2$$

assuming $S_s = S_t$

$$\frac{\sigma}{1-\sigma} = \frac{C}{z-C}\exp\left(-\frac{H_t}{kT}\right)$$

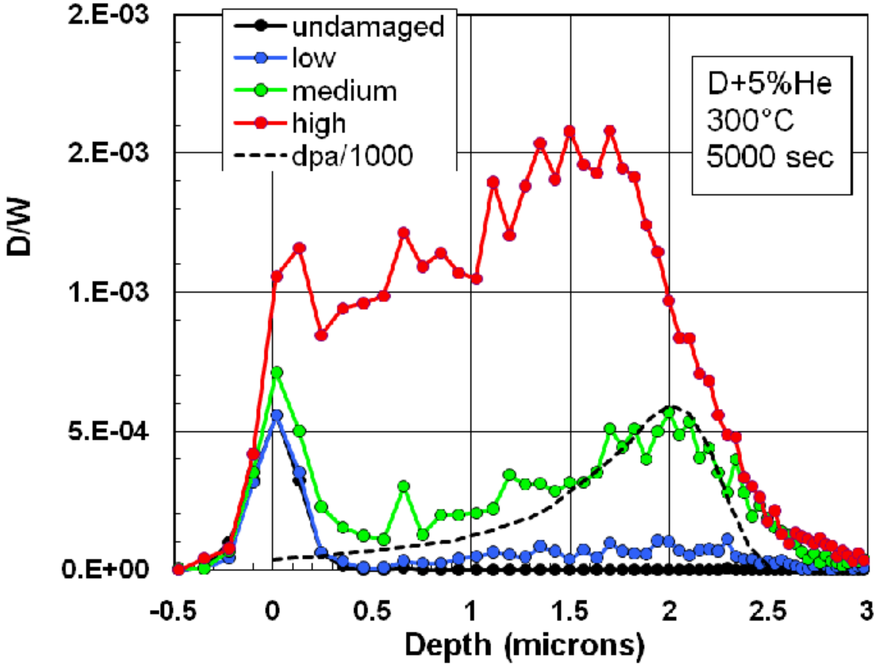
z=6 solution sites per metal atom for bcc lattice

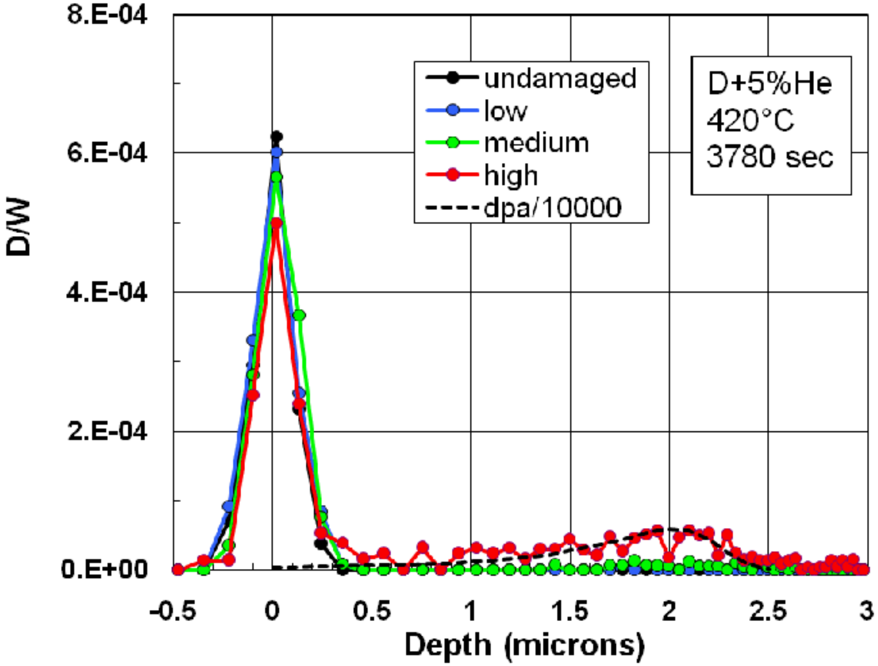
D is retained at displacement damage



- Subtracting D profile in undamaged W shows D retained at displacement damage.
- D retention increases with damage and is highest at the depth of the damage peak (2 μm).
- D retention at damage is saturating, probably because damage saturates near 1%, 3x more D from 10x more damage.

D retention at damage with D + 5% He plasma





Large decrease between 300 & 400C.