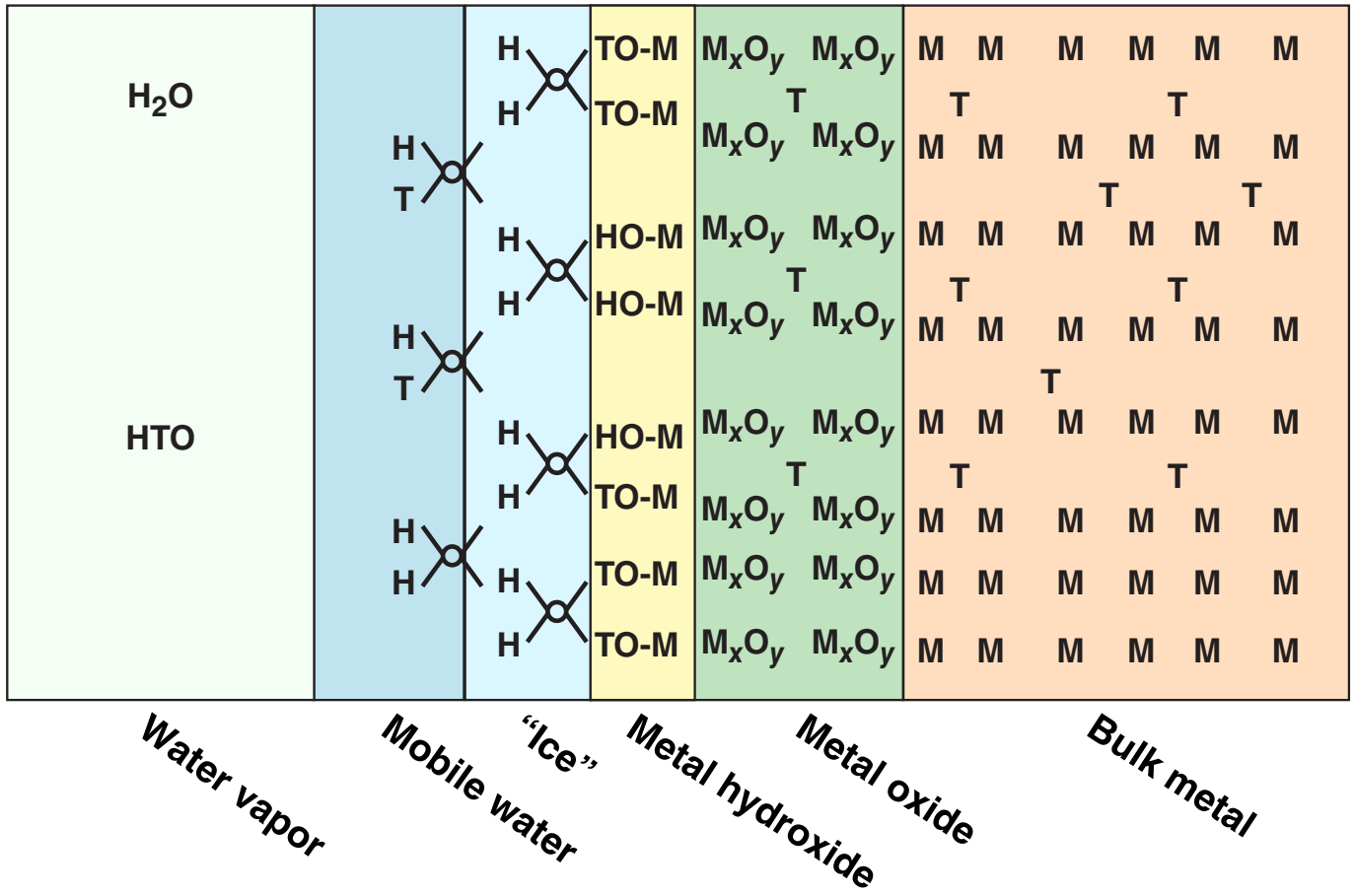
Modeling Tritium on Metal Surfaces



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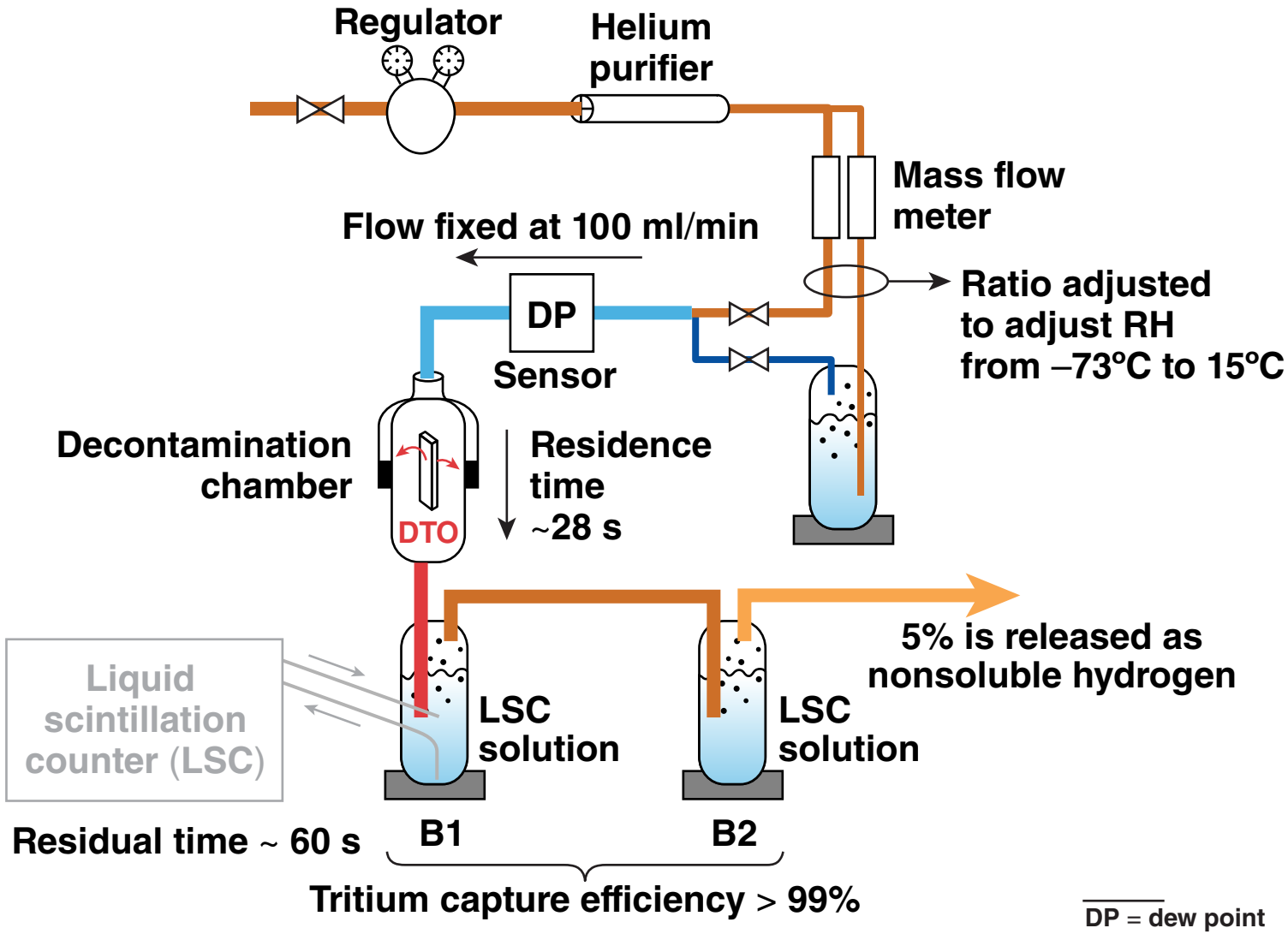
Summary/conclusions

- Two techniques have been used to study tritium in metals:
  - Linear thermal desorption
  - Pulsed RF Tonks-Langmuir plasmas
- Tritium concentrates in the water layers covering metal surfaces
- Surface water layers pump tritium from the bulk
- Regrowth of surface activity is
  - rapid and
  - Controlled by diffusion from the bulk metal

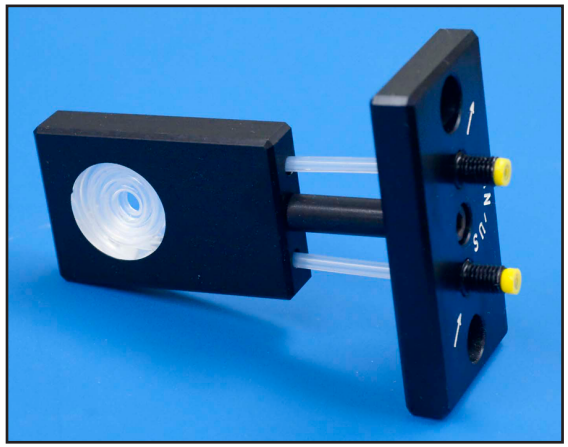
DTO is transferred from contaminated samples to the detection system using humid carrier streams



DP = dew point
RH = relative humidity

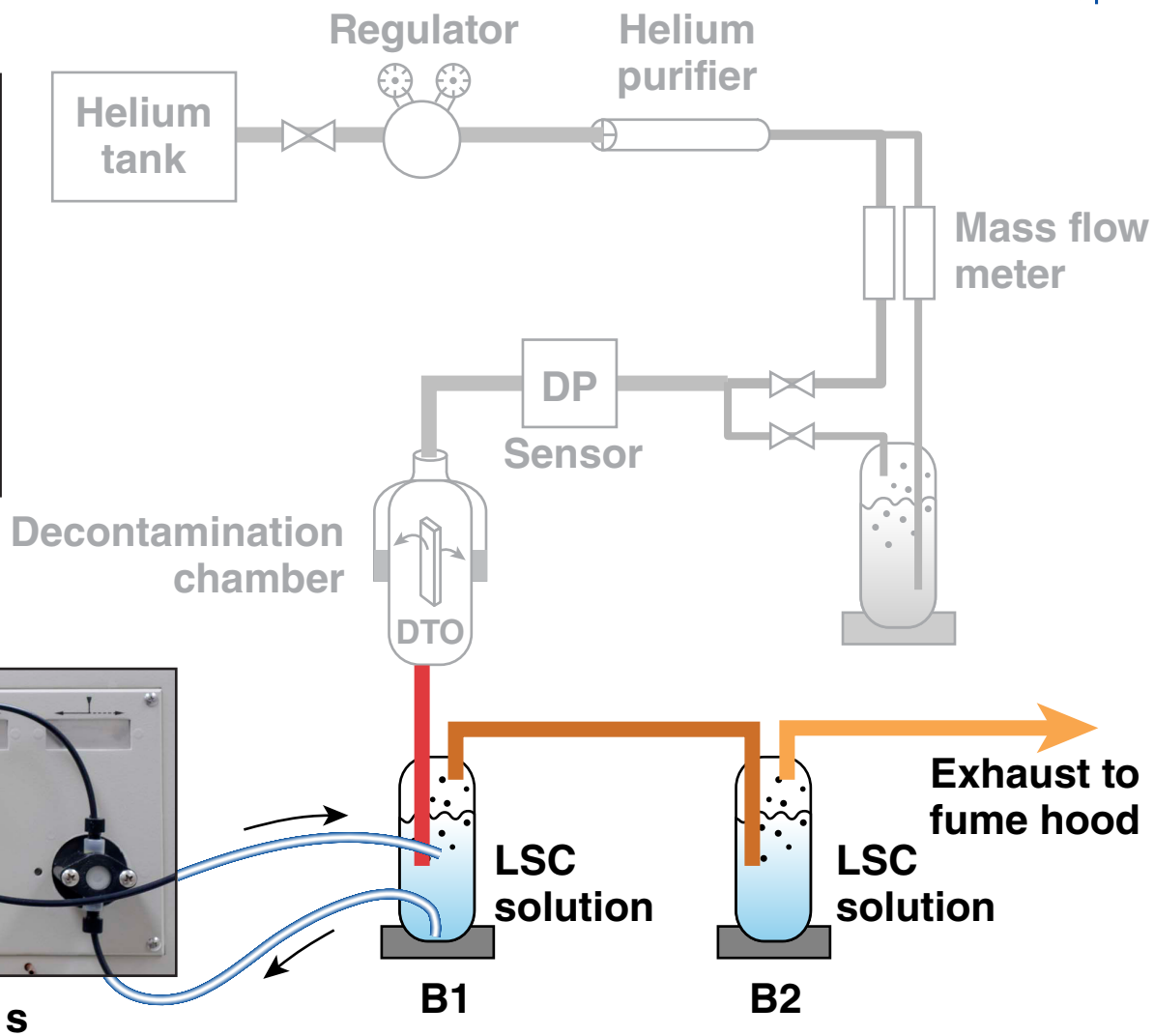
E18737b

The liquid scintillation counter measures the activity in the first wash bottle in real time



LSC

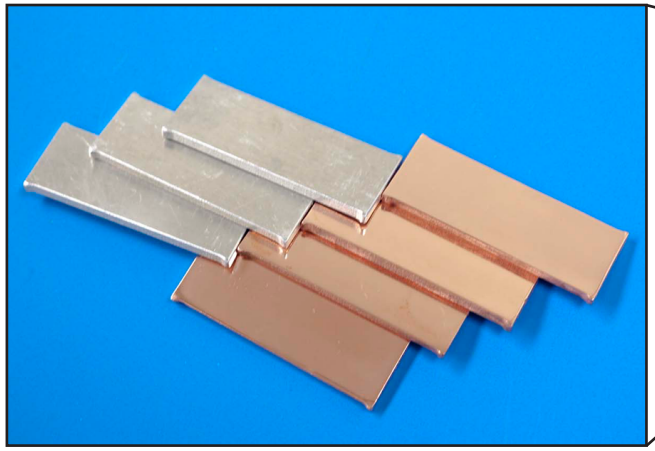
Residence time ~60 s

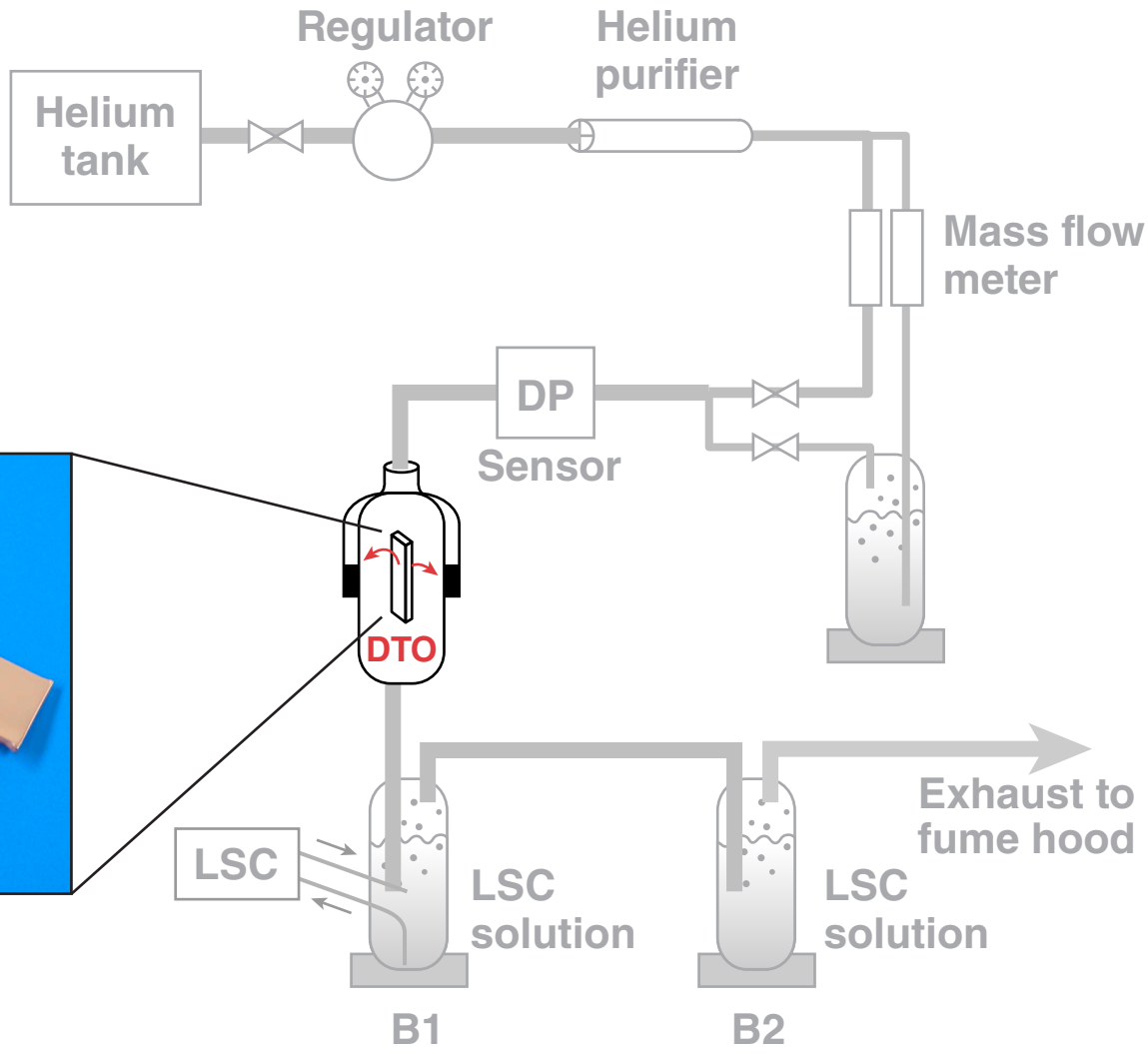


E18740b

The samples are exposed to DT gas and stored in dry helium at 1 atm and room temperature (RT)

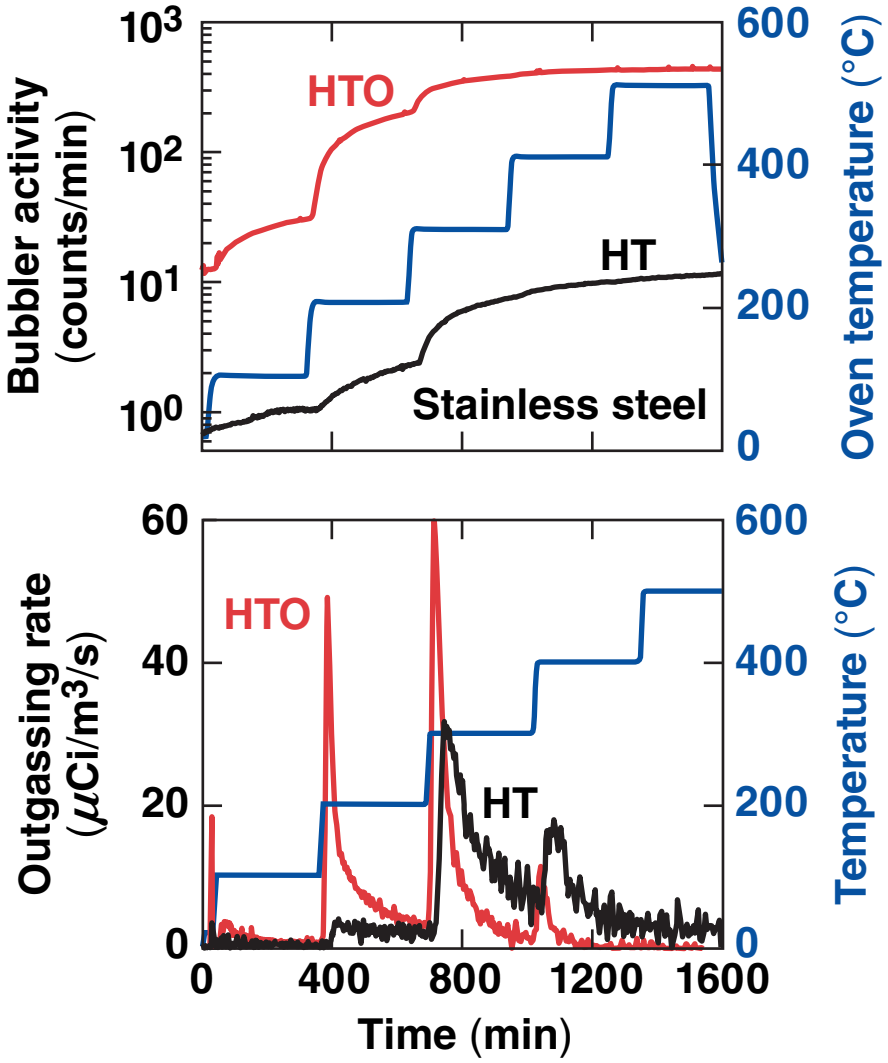
- **Samples 5 × 1.8 × 0.3 cm**
- **Stainless steel exposed to 690 Torr DT for 23 h at RT**
- **Cu exposed to 729 Torr DT for 96 h at RT**

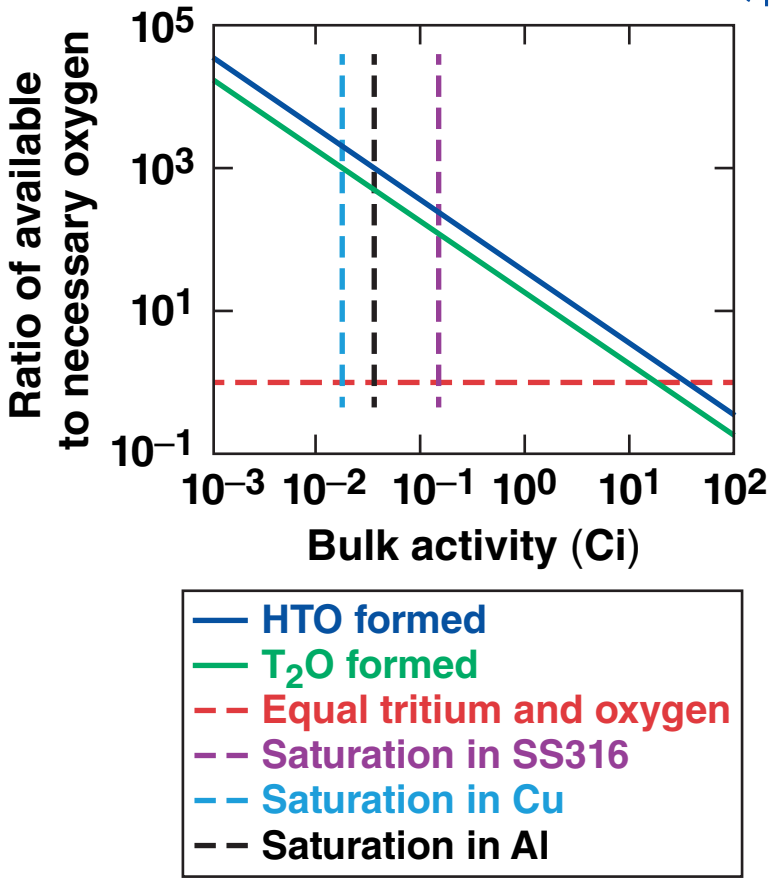




E18738b

Linear thermal desorption provides a good measure of the total tritium absorbed in the metal

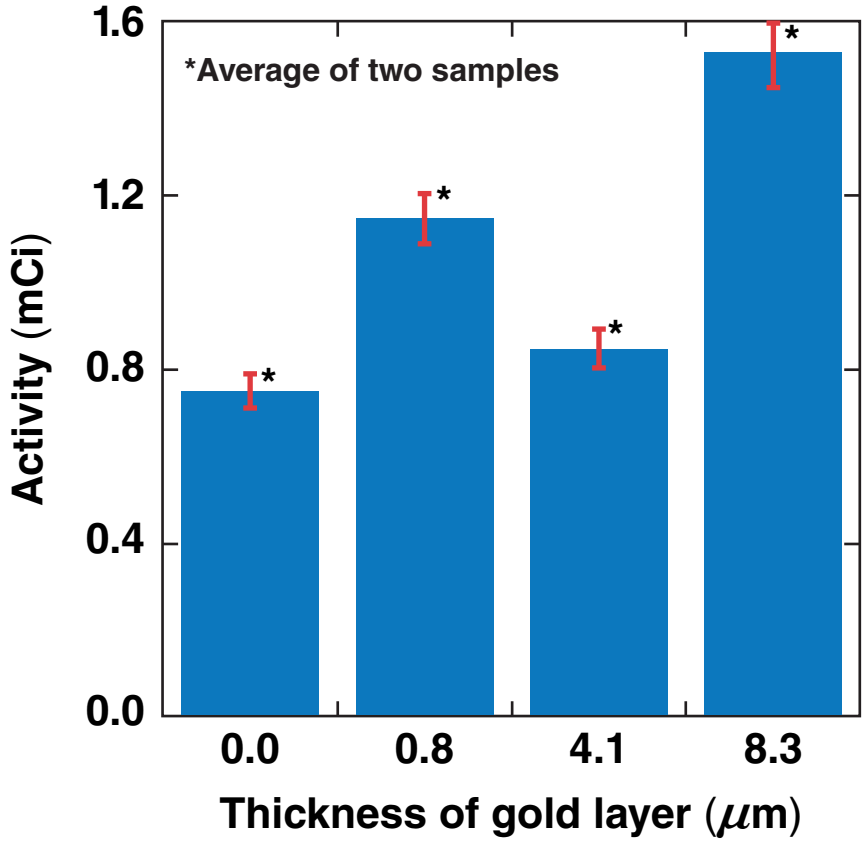




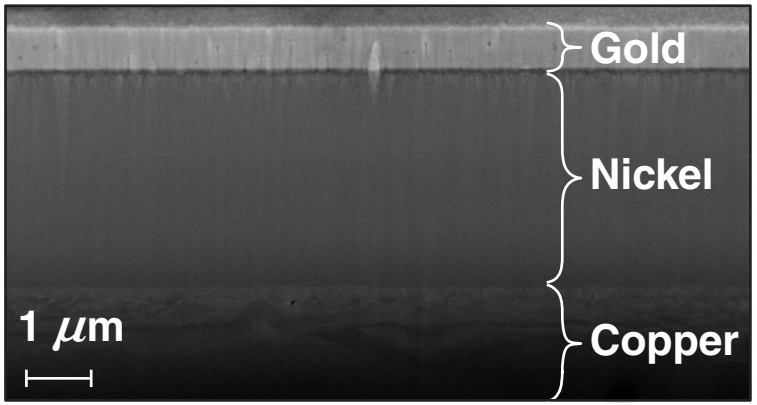
- Tritium release from metals is dominated by HTO under most typical exposure conditions

E24692

The effectiveness of electrolytic deposition of gold layers may not lower tritium inventories in metals

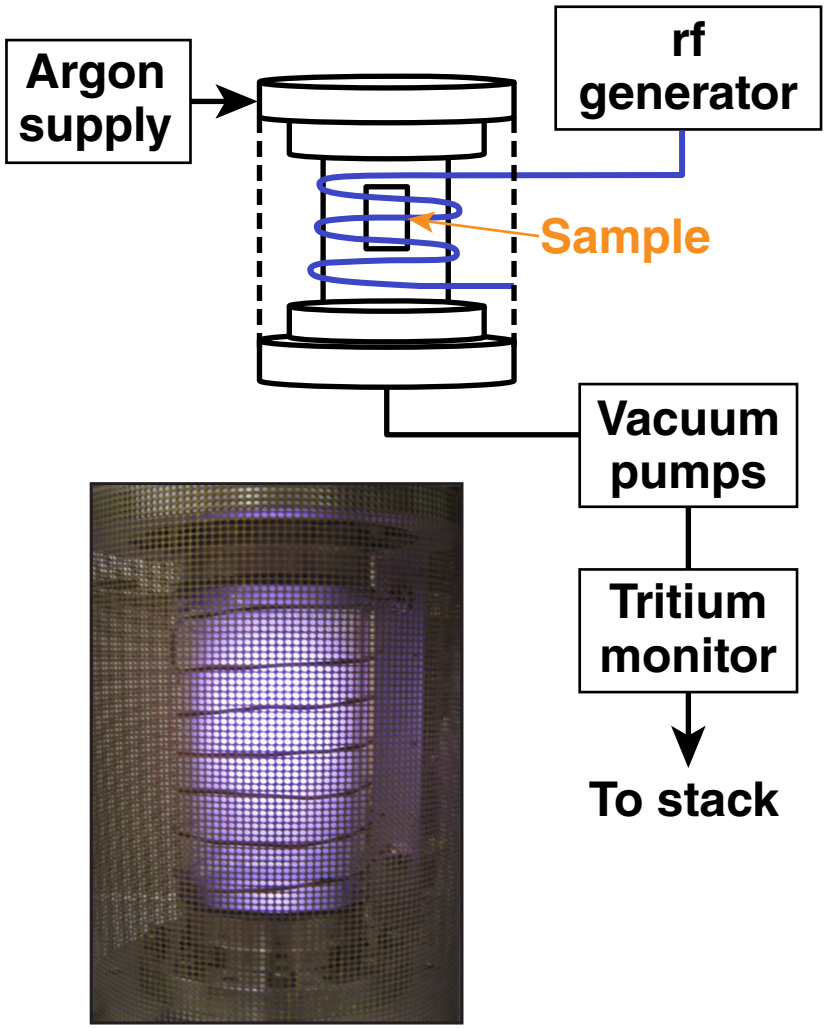


- An increase in the total tritium inventory at low gold layer thicknesses implies asymmetric permeation
- Increased inventory at higher gold layer thicknesses implies that the solubility of gold exceeds stainless steel



E24693

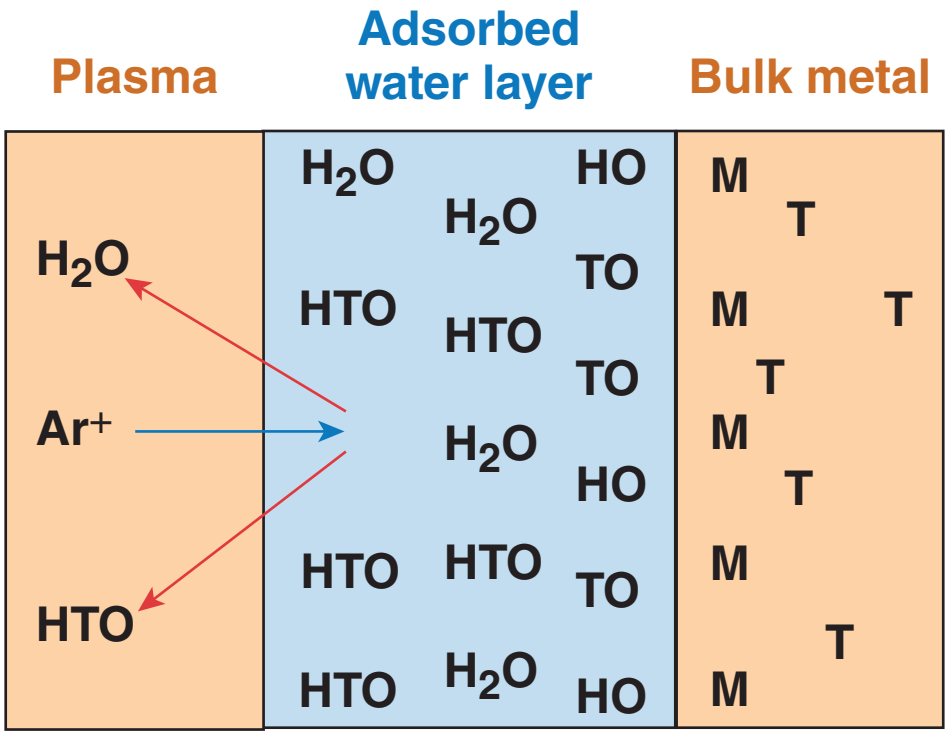
Radio-frequency–generated argon plasma was used to desorb tritium from metals into a flowing gas stream



- A plasma was ignited in argon by passing a 13.56-MHz ac current through a copper coil
- The sample floated at the plasma potential
  - ionic flux = electron flux
- Tritium released from the sample was purged into a downstream in-line tritium monitor
- Base pressure ≈ 10^{-4} Torr
  - trace water in the vacuum system redeposits on the metal surface within 15 s

E24695

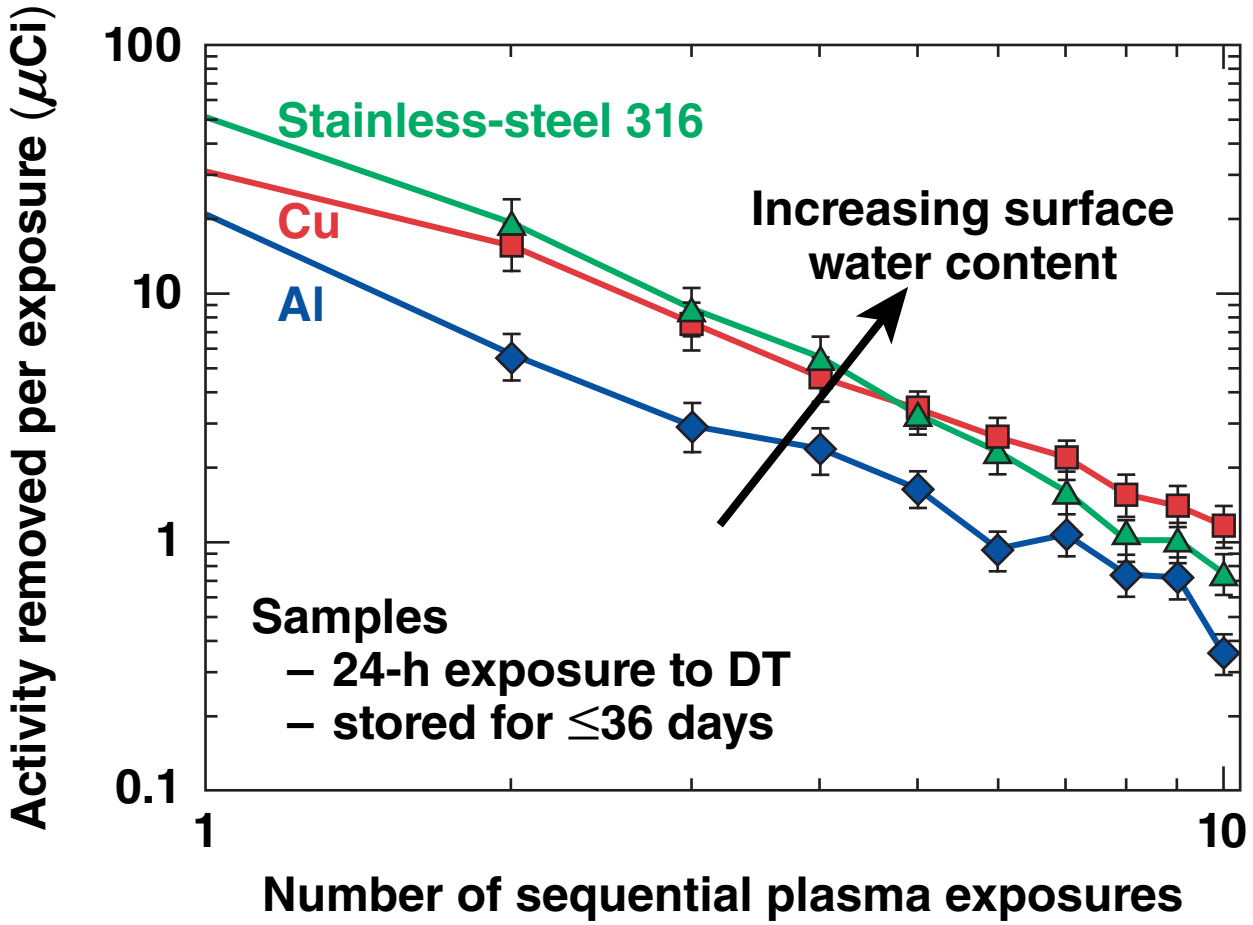
Water was removed from the sample surface using a series of 2-s plasma bursts



- Metal surface comprises
  - hydroxyl layer
  - proton bonded "ice" layer
  - mobile Van der Waal bonded water
- Adsorbed water layer regrows between exposures
- Tritium migrates into freshly formed tritium-free water layer

E24696

Total removable surface activity increases with the number of monolayers of adsorbed water at a fixed relative humidity

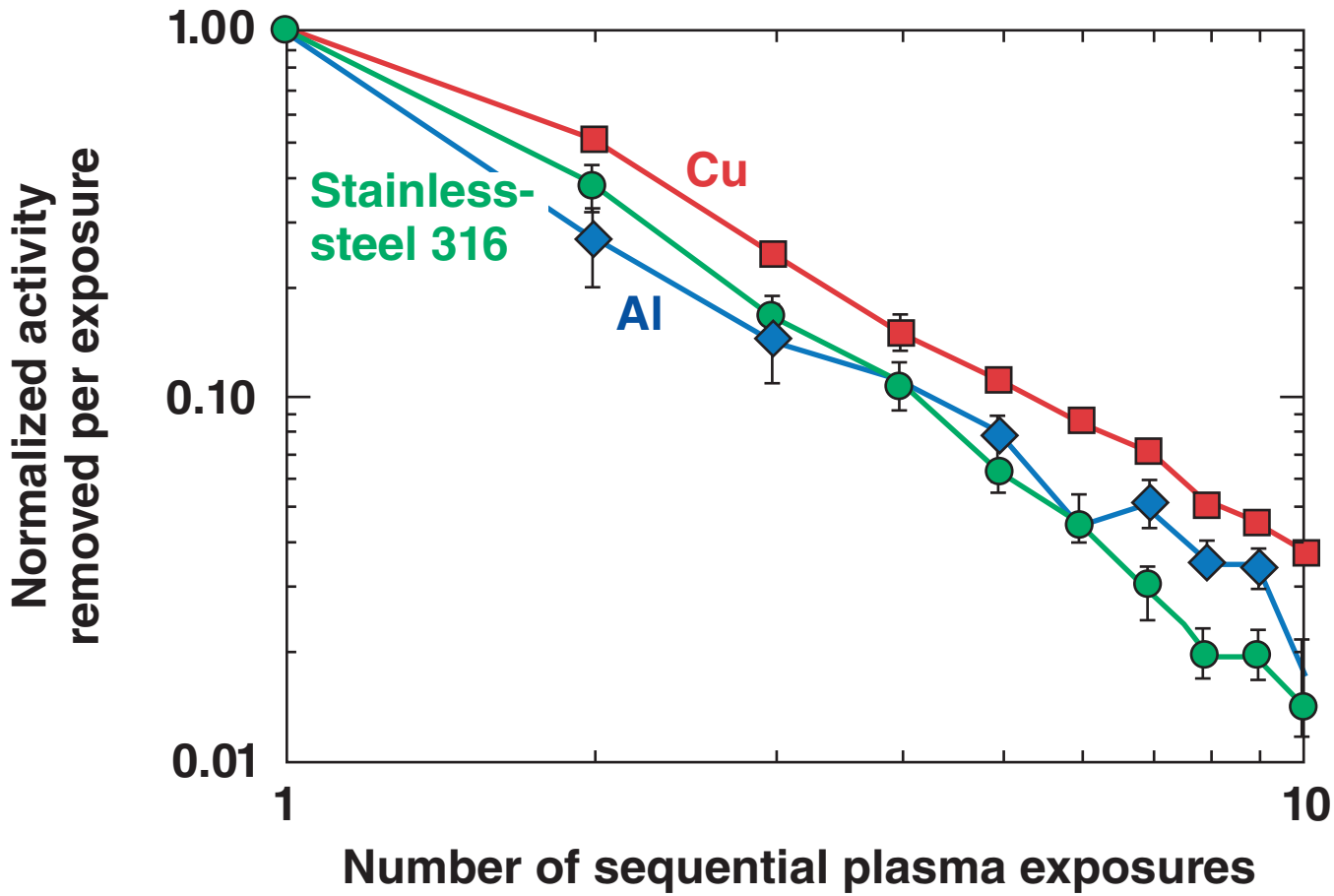


Water isotherm references

- Aluminum: H. A. Al-Abadleh and V. H. Grassian, Langmuir 19, 341 (2003).
- Copper: S. P. Sharma, J. Vac. Sci. Technol. 16, 1557 (1979).
- Stainless steel: T. Ohmi et al., Rev. Sci. Instrum. 64, 2683 (1993).

E24697

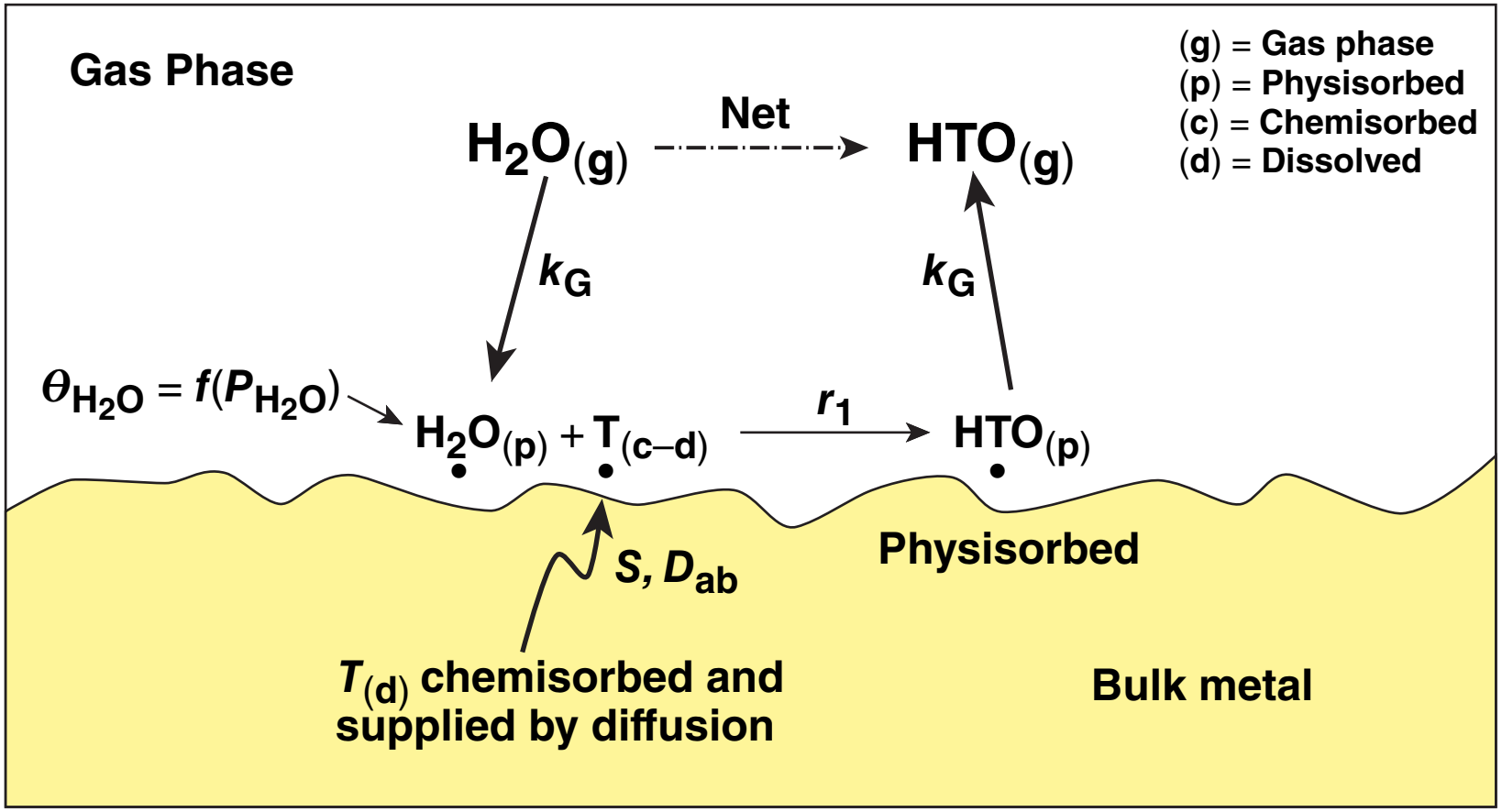
Activity removed from stainless steel, copper, and aluminum follows the same trend for all three metals



- Data were normalized to the initial amount removed

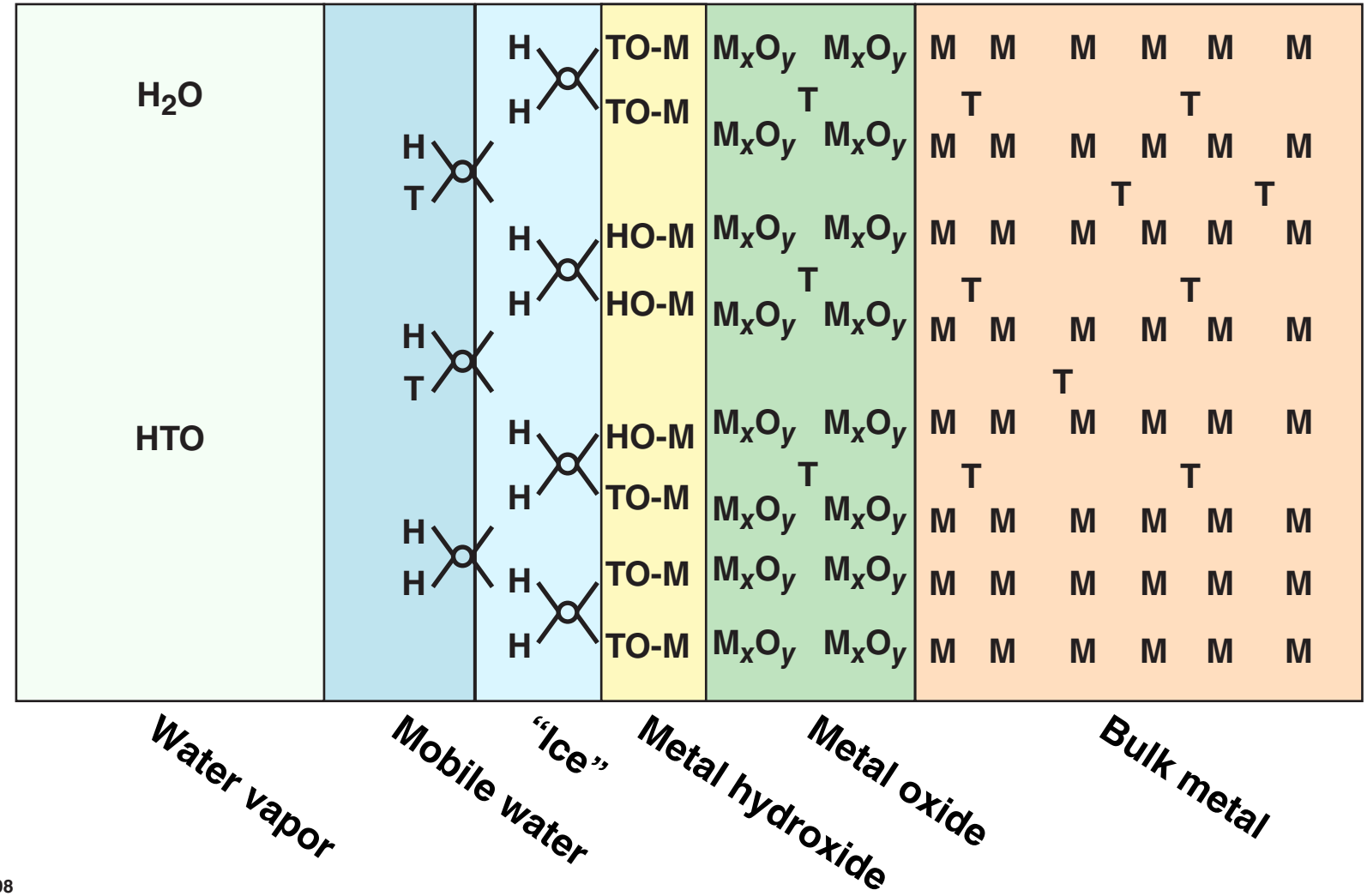
E23847a

The reactions among adsorbed species introduce a nonlinear behavior with respect to humidity



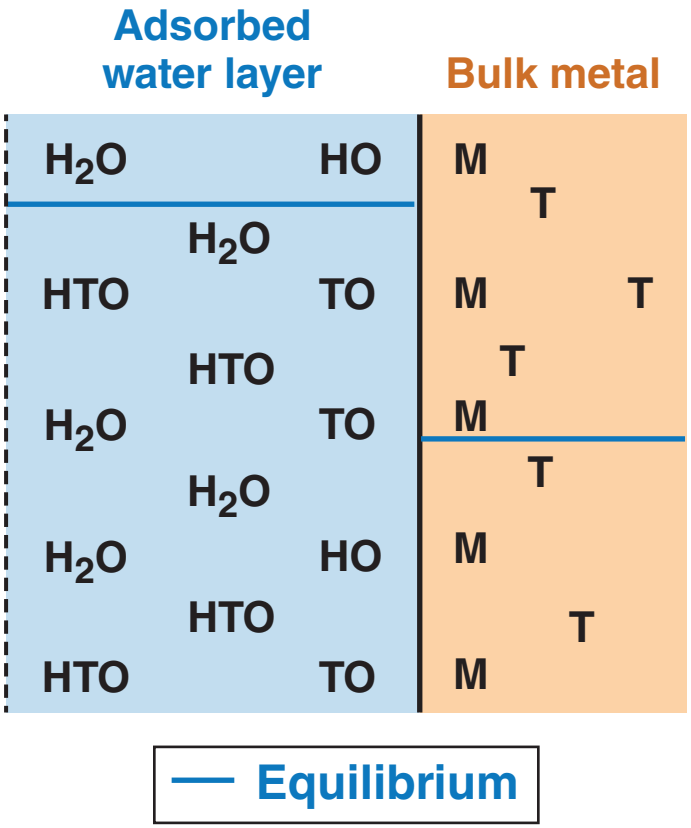
E18726b

Clean metal surfaces comprise layers of oxide, hydroxide, rigidly bound water, and mobile water in equilibrium with water vapor above the metal



E24698

Tritium migration to the surface is described by Fickian diffusion through the bulk driven by a rapid equilibrium across the surface bulk interface



Assumptions

- Surface and bulk concentrations are related through the equilibrium constant
  - rapid equilibrium across the interface

$$c_{bulk} \longleftrightarrow c_{surface}$$

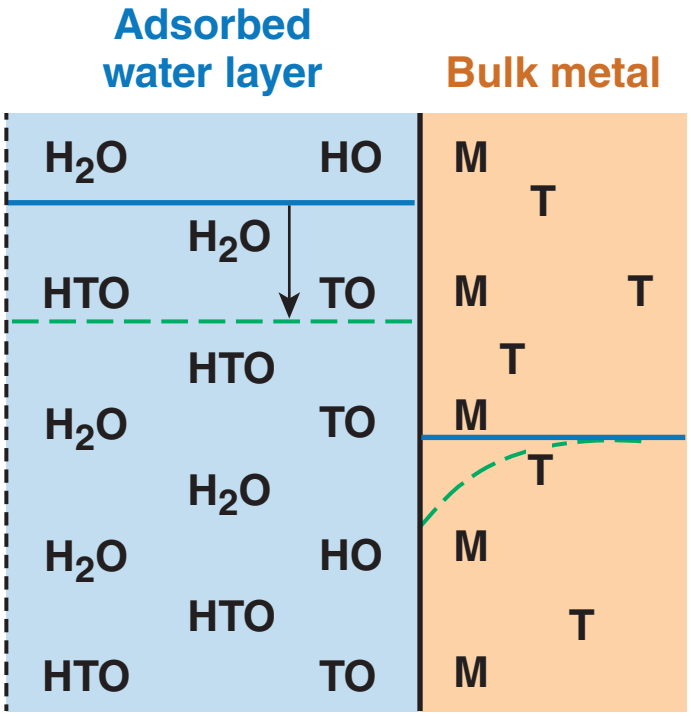
$$K_{eq} = \frac{c^{eq}_{surface}}{c^{eq}_{bulk}} = \frac{S_{surface}}{S_{bulk}}$$

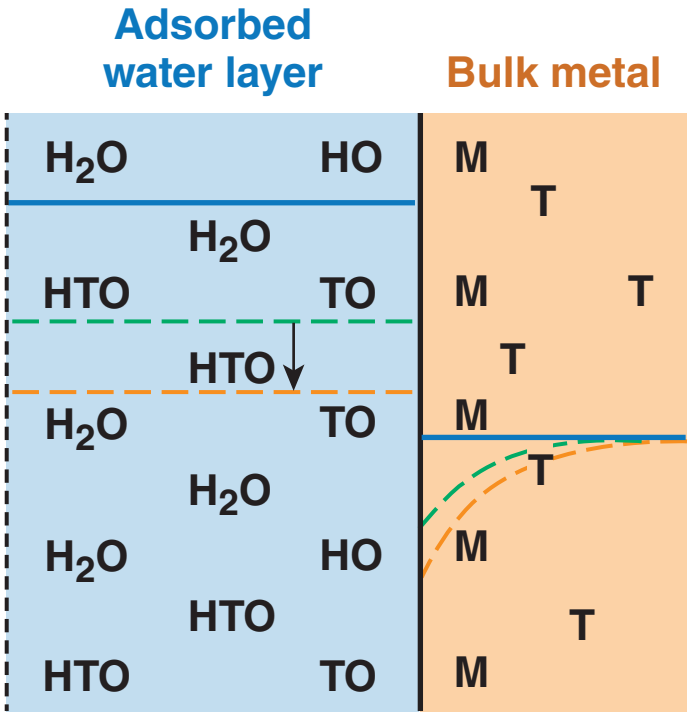
- Rapid equilibrium in the adsorbed water layer

E23848d

A drop in the tritium concentration in the adsorbed water layer perturbs the equilibrium across the interface

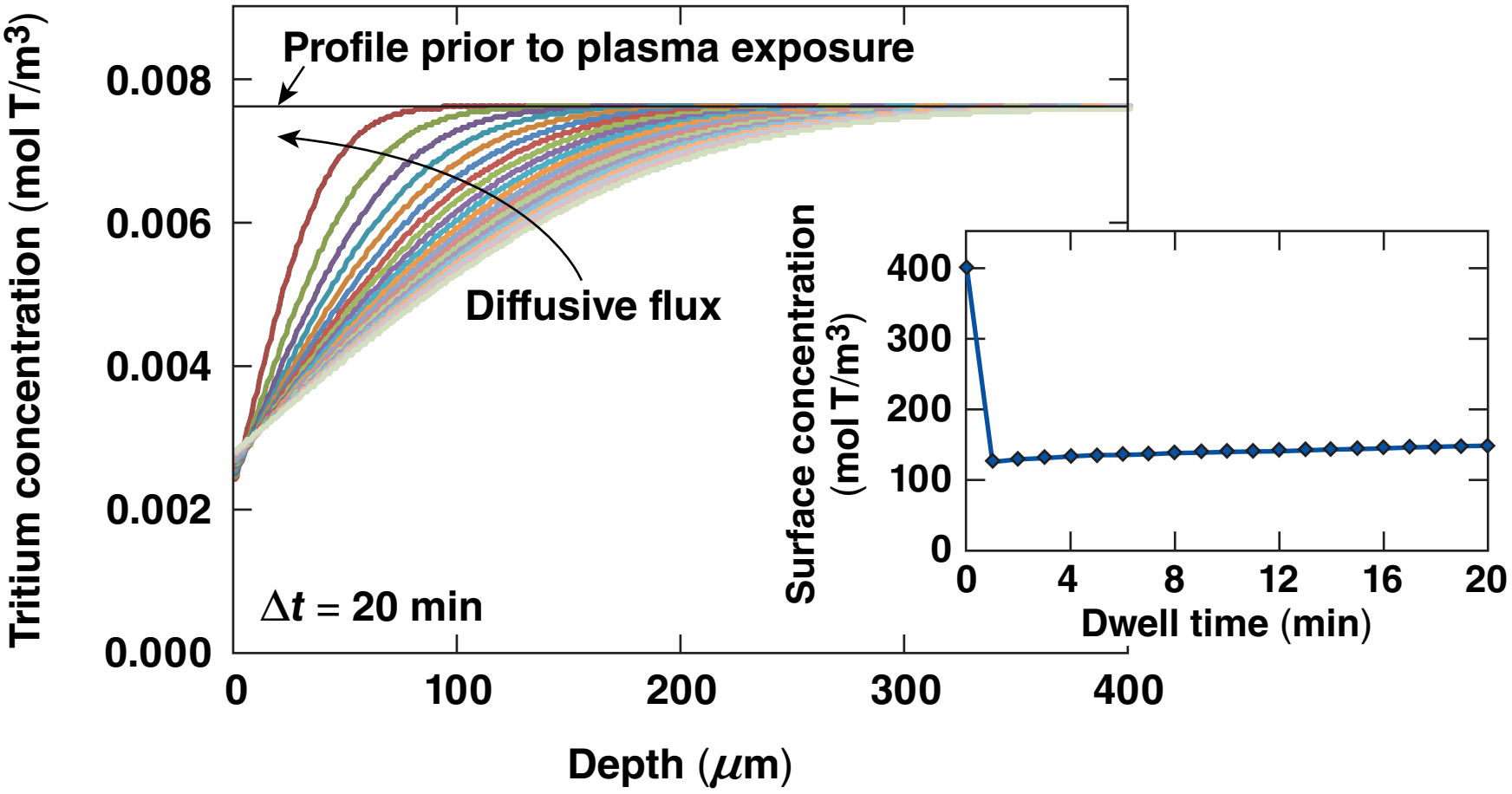
- Tritons are drawn from the bulk to return to equilibrium across the interface





E23848e

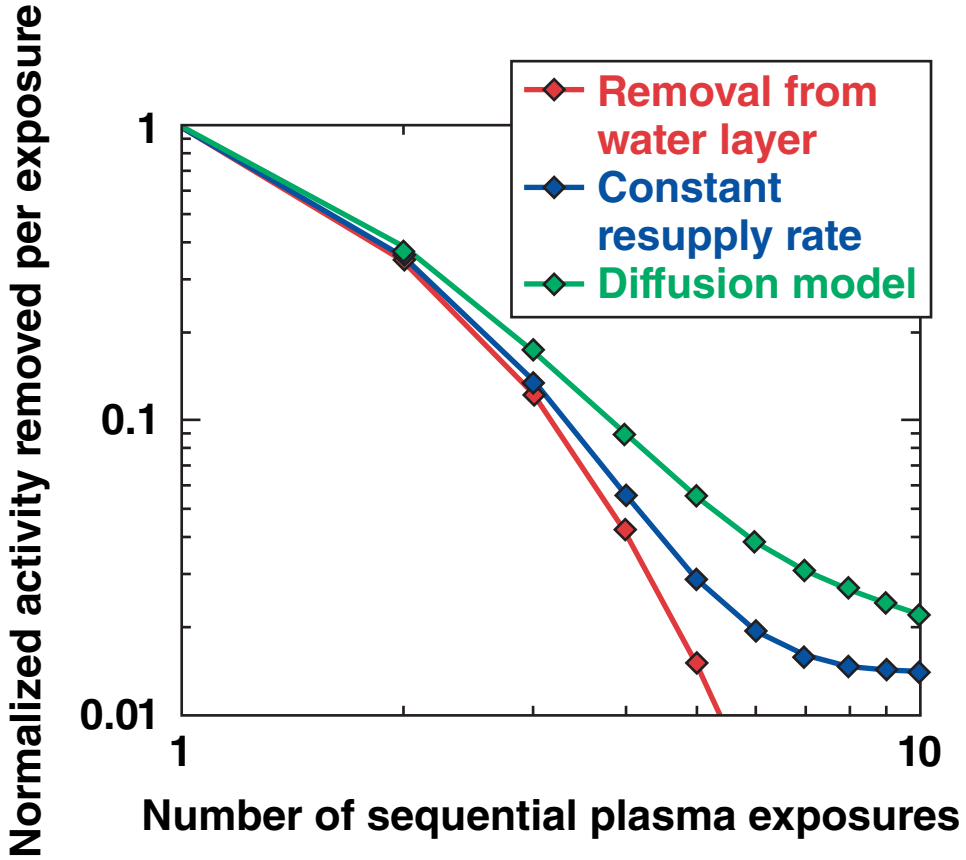
Tritium concentrations re-equilibrate after a plasma exposure removes surface activity



- Model utilizes a finite difference solution
  - concentration in each "cell" determined by flux balance

E24699

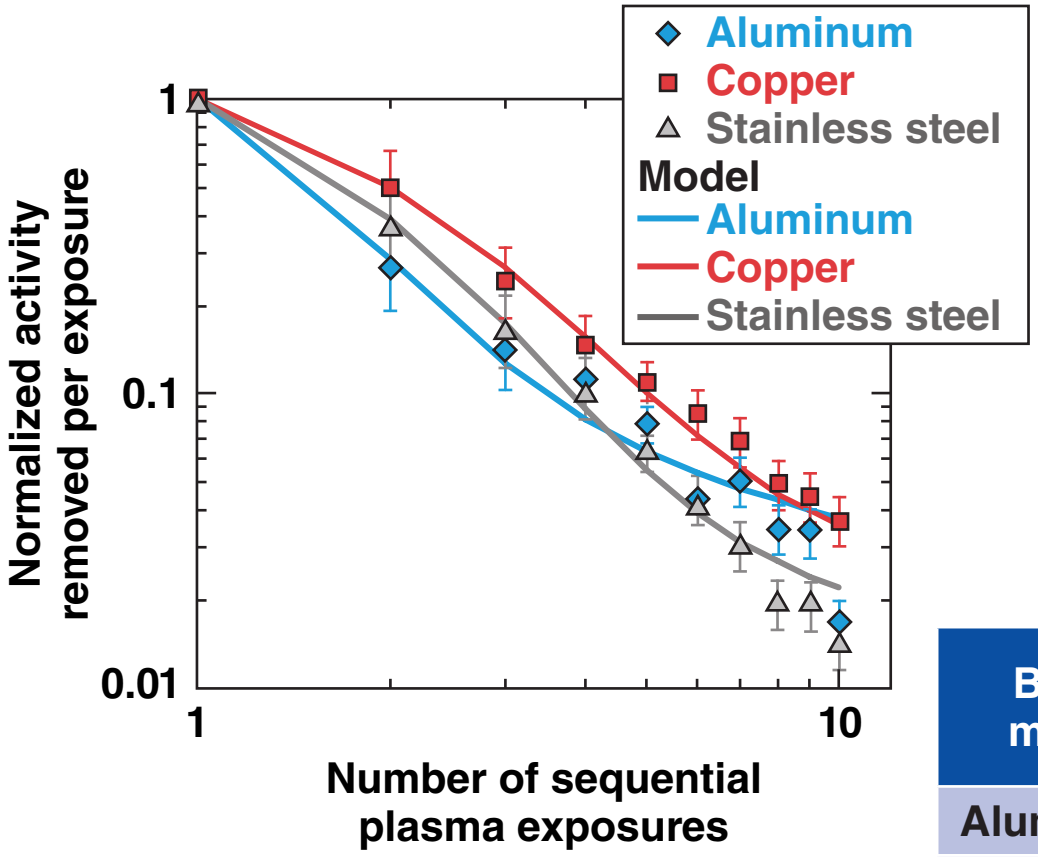
Simulated activity removed suggests the first three exposures contain activity originated on the surface



- Each simulation assumes different mechanisms of regrowth
  - surface tritium alone
  - constant resupply rate
  - diffusion-limited resupply
- Simulations assume an overall efficiency = 0.65
- Trends begin to diverge at the third plasma exposure
  - sum of first three exposures is a good indication of initial surface activity

E24700

Diffusion model can predict quantity of tritium removed during a series of plasma exposures

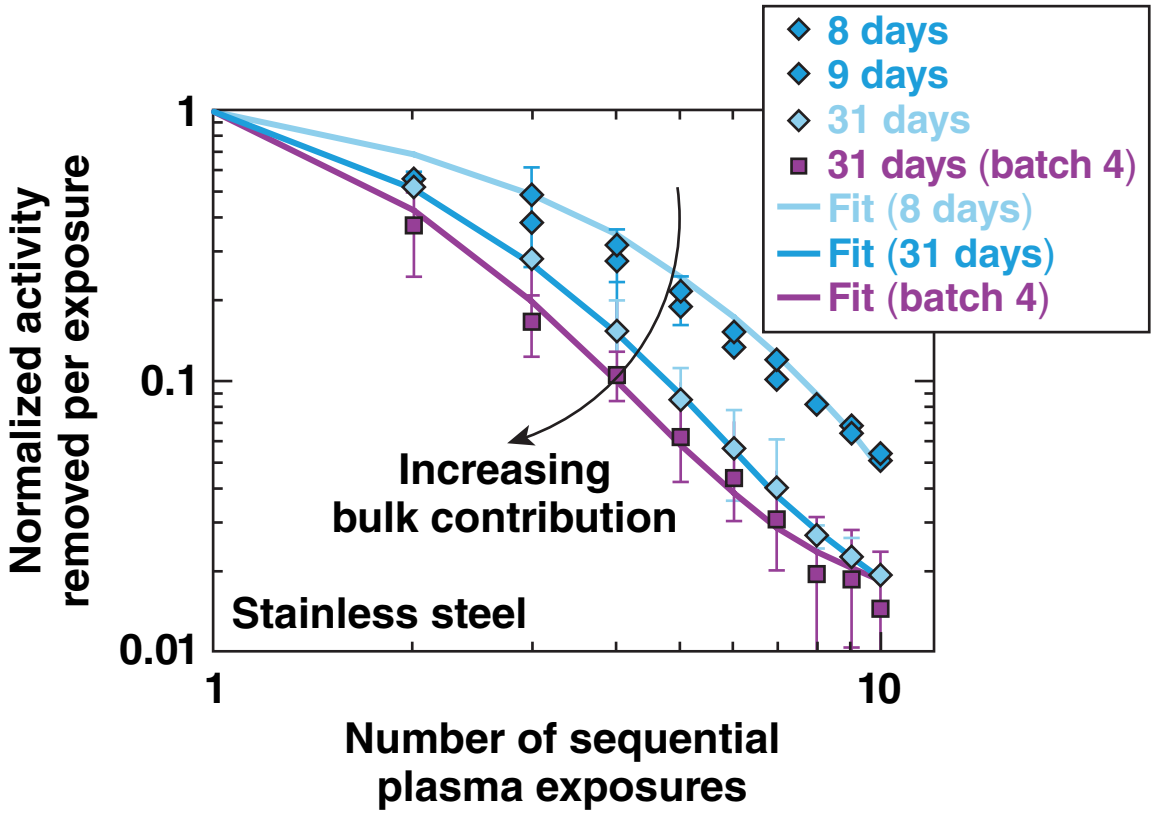


- Diffusion model fit to data by varying solubility ratio and overall efficiency
- Similar surface solubilities expected if tritium is primarily dissolved in adsorbed water

Base metal	Surface-layer solubility (kmol T/m^3)	Overall efficiency
Aluminum	53±5	0.85
Copper	50±5	0.56
SS316	17±1	0.66

E24711

The solubility ratio relaxes toward the equilibrium value

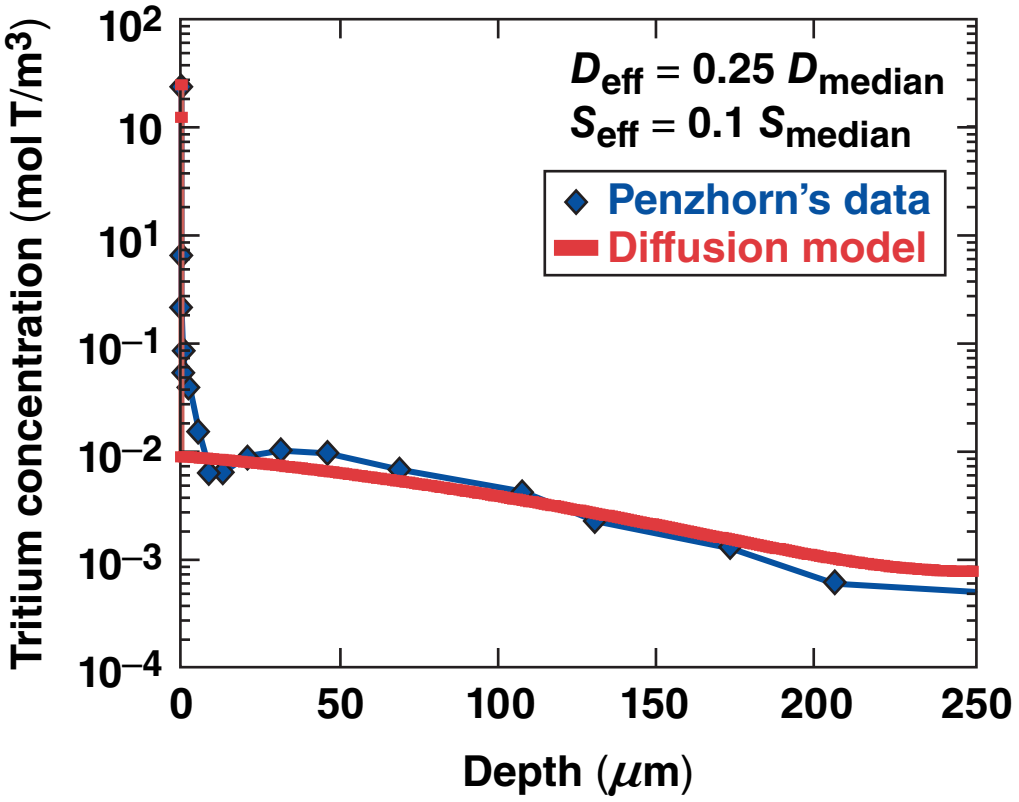


Storage time (days)	Solubility ratio	Overall efficiency
8	120,000	0.3
31	28,000	0.5
31 (batch 4)	20,000	0.6

- Samples stored for shorter periods show an exponential trend
  - removal is predominantly from the surface
- Longer storage periods lower the surface fractions removed
  - migration into bulk depletes accessible tritium

E24702

The diffusion model reproduces the previously measured concentration profiles by others

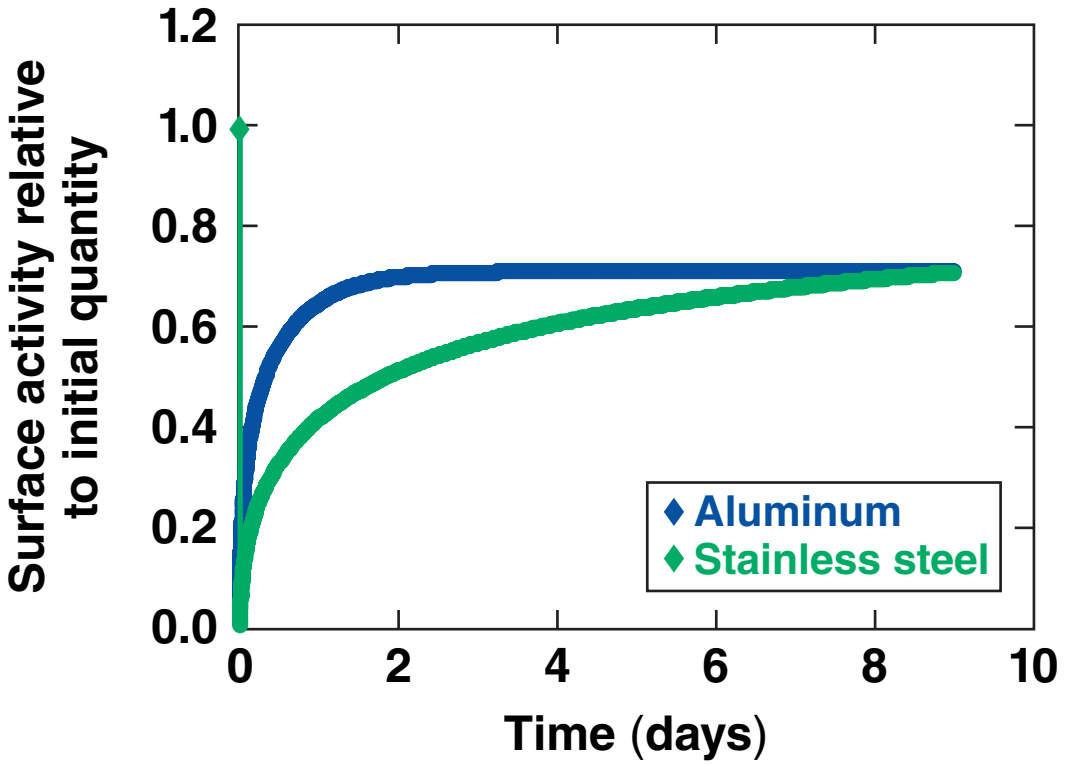


- Profiles measured by Penzhorn *et al.** using acid etching
- Median parameters were determined from the literature survey
  - effective parameters are still within the reported spread
- The model uses simplifying assumptions
  - no grain boundaries
  - no tritium loss to the air
  - does not reproduce the subtle details

*R. D. Penzhorn *et al.*, J. Nucl. Mater. 353, 66 (2006).

E24712

Bulk-metal diffusion determines the surface activity regrowth rate



- Initial concentration profiles are assumed to be in equilibrium in the metal and across the interface
- The surface activity was removed at $t = 0$
- Concentration profiles were then allowed to recover from the perturbation
  - assume no tritium is lost from the sample

Surface concentrations regain ~70% of the initial activity after nine days.

E18722b

Summary/conclusions

- Two techniques have been used to study tritium in metals:
  - Linear thermal desorption
  - Pulsed RF Tonks-Langmuir plasmas
- Tritium concentrates in the water layers covering metal surfaces
- Surface water layers pump tritium from the bulk
- Regrowth of surface activity is
  - rapid and
  - Controlled by diffusion from the bulk metal