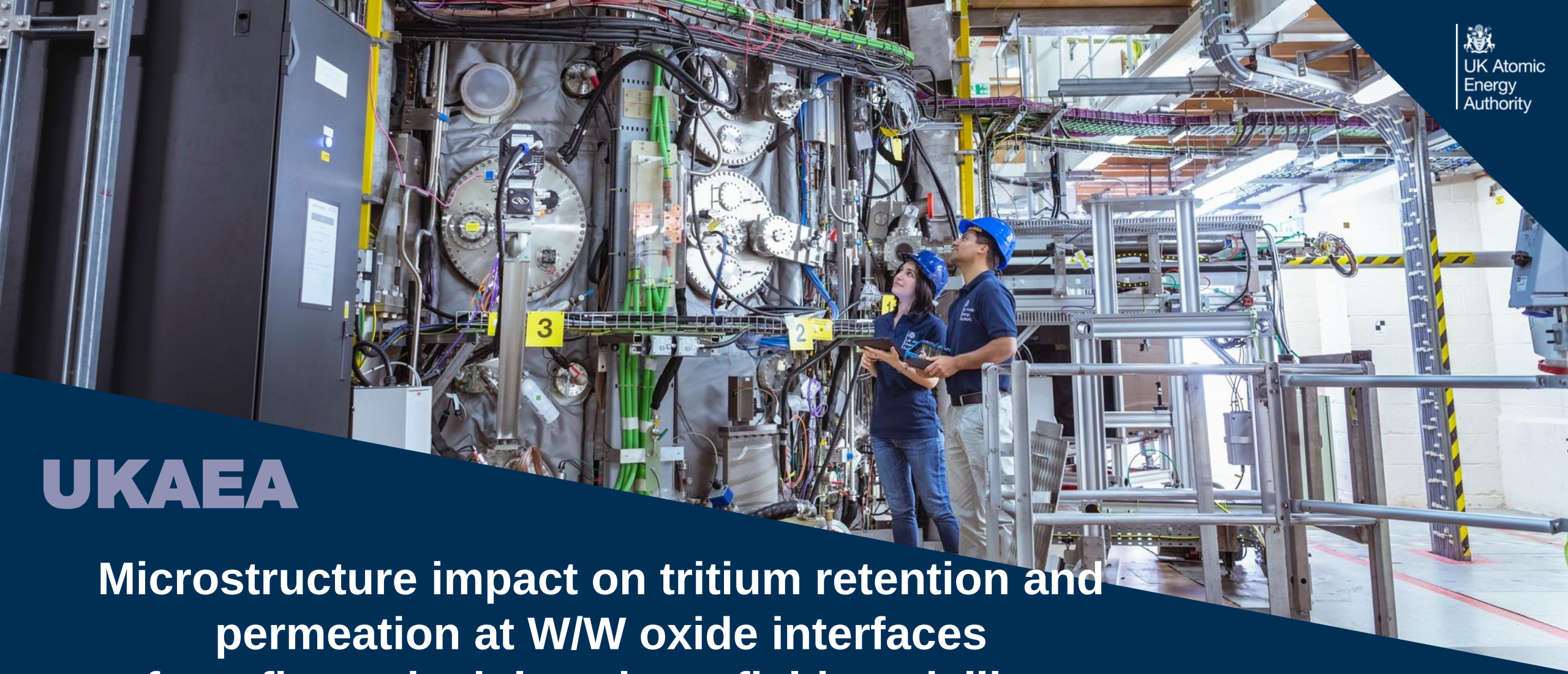


UK Atomic Energy Authority

UKAEA

Microstructure impact on tritium retention and permeation at W/W oxide interfaces from first-principles phase field modelling

D. Nguyen-Manh[a], K. Starkey[b], M. Christensen[b], E. Wimmer[b], C. Geller[b] and M..R. Gilbert[a]

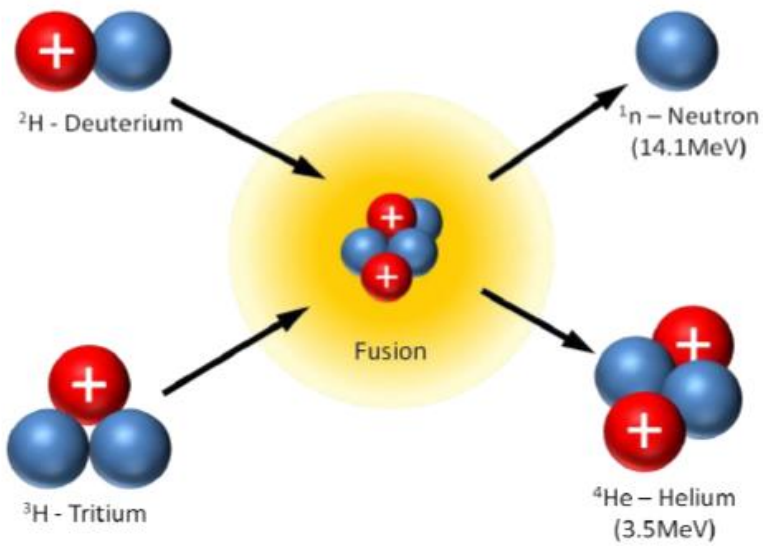
a) United Kingdom Atomic Energy Authority and b) Materials Design Inc.

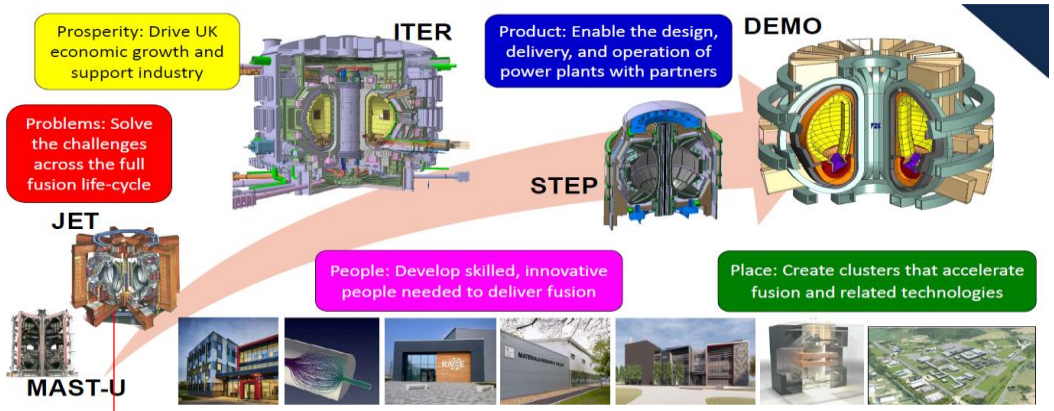
7th International Workshop on MoD-PMI, Vienna, May 26-28, 2025

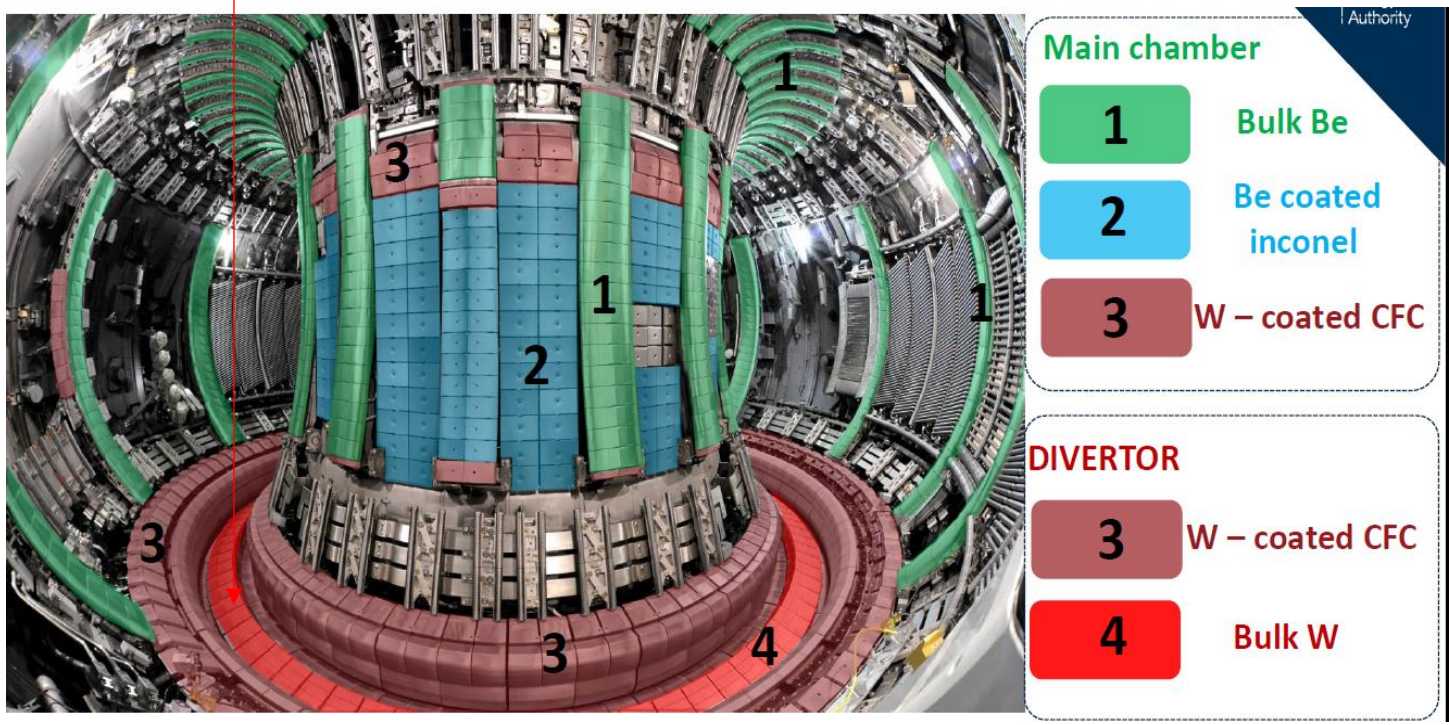
Outline

- Motivation
- Tritium thermodynamics and kinetics in tungsten (W) and its oxides
- MLPs developments for interfaces W/W oxides
- First-Principles Phase Field (FPPF) prediction of detritation from W/W oxide interface modelling
- Summary and Outlook

Motivation: Deuterium and Tritium in fusion devices



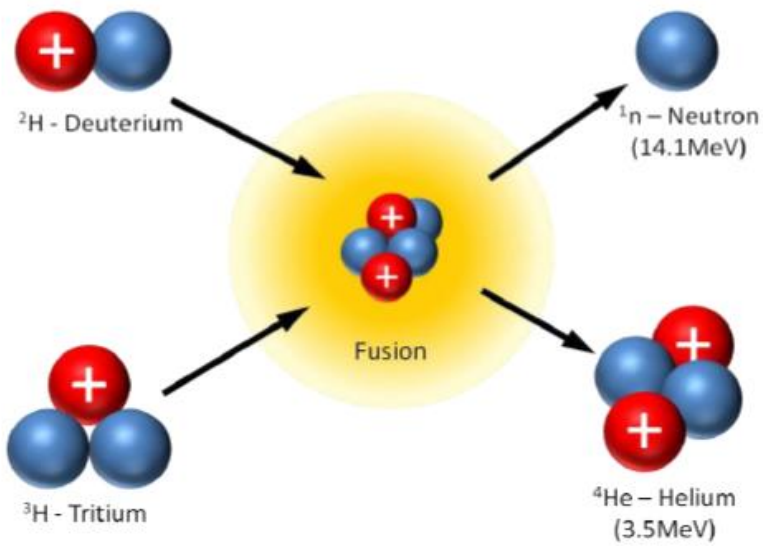


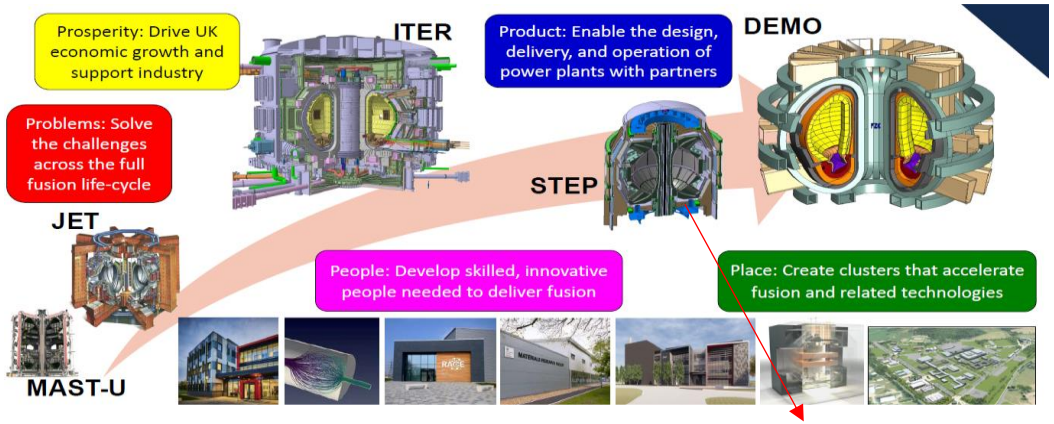


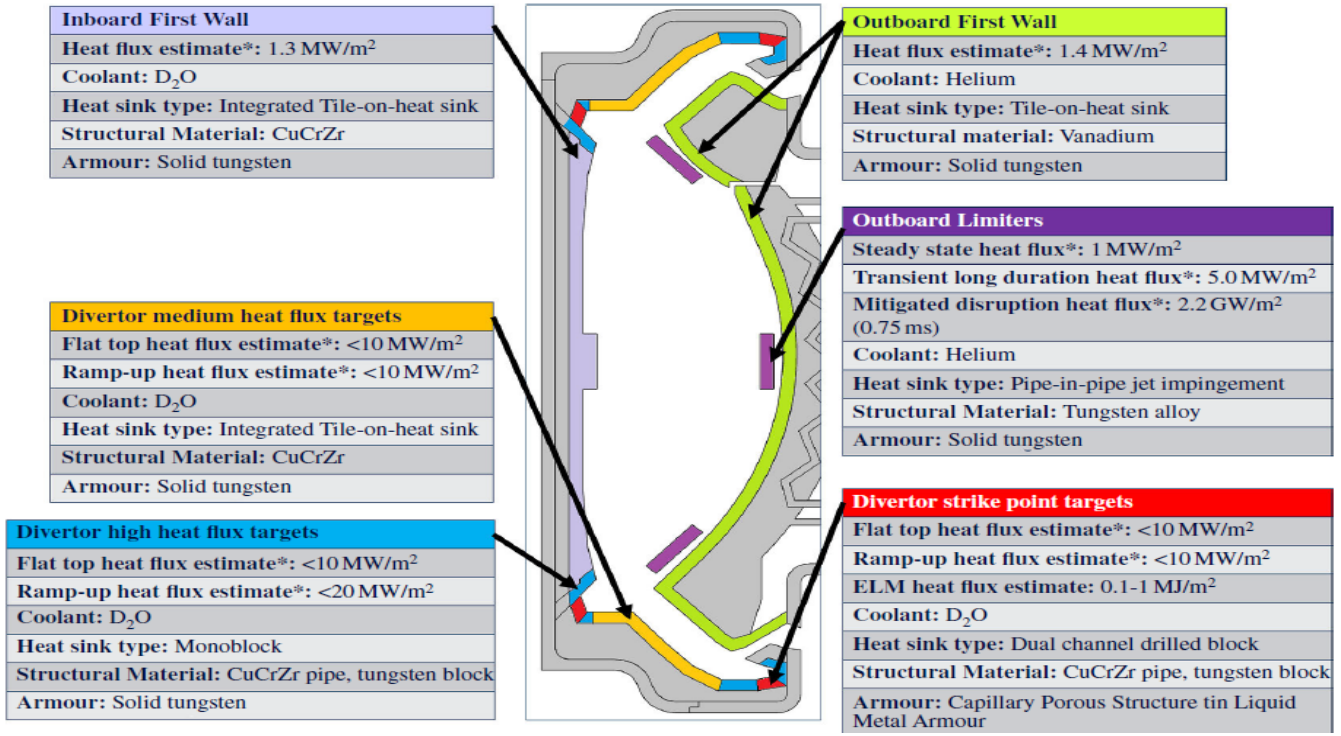
As one of the most promising materials for plasma-facing components, there are extensive experimental studies of detritiation in Tungsten (W) for designing future fusion devices such as ITER, STEP and DEMO as well as for JET decommission and repurposing (JDR)

D. Nguyen-Manh, et al., Microstructure impact on tritium retention and permeation in tungsten/oxide interface, 7th International workshop on MoD-PMI, Vienna, May 2025

Motivation: Deuterium and Tritium in fusion devices







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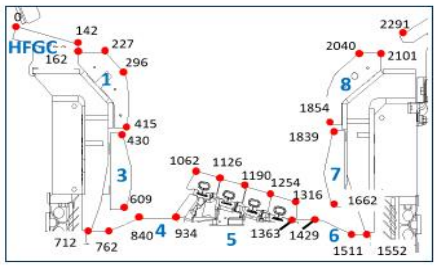
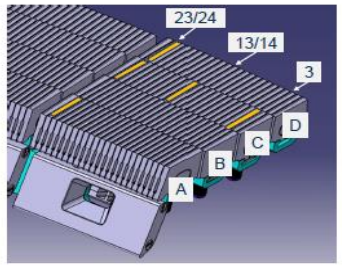
D. Nguyen-Manh, et al., Microstructure impact on tritium retention and permeation in tungsten/oxide interface, 7th International workshop on MoD-PMI, Vienna, May 2025

Hydrogen isotopes (HI) in plasma-facing materials: Oxidation and detritiation of tungsten

UK Atomic Energy Authority

JET ITER-like wall divertor

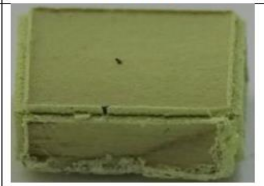
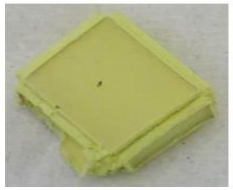




$(D + D \rightarrow 1.01\ MeV\ T + 3.03\ MeV\ p)$

Where D is deuterium, T is tritium and p is a proton.

JET Decommissioning Repurposing (JDR)
Materials Detritiation Facility (MDF)
Tritium Analysis Laboratory (TAL)

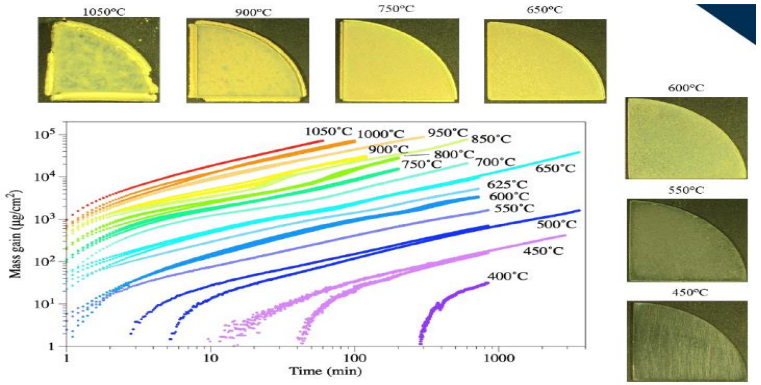
Post 650°C	Post 750°C (1)	Post 750°C (2)
21SID182	21SID187	21SID191
2.081	2.112	2.14
		

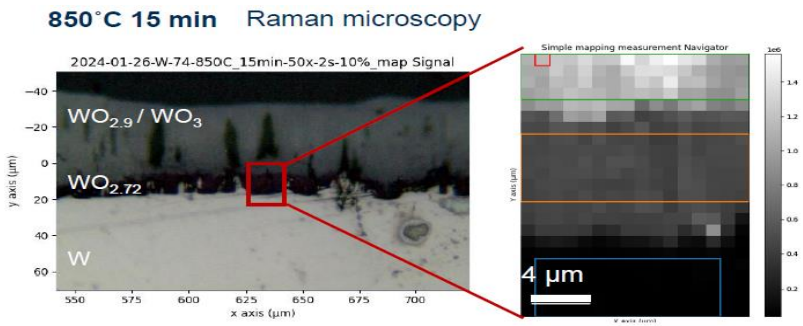
$F = 1 - C_f / C_0$

$DF = 1/(1 - F)$

Extraction Factor (F)	0.88 ± 0.1
Detritiation Factor (DF)	8.063 ± 1.11

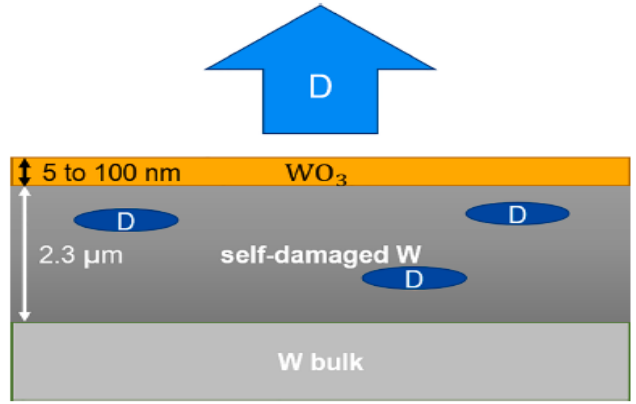
The oxidation behaviour of fusion materials under maintenance, waste handling environment or in accident scenarios and impact on tritium recovery and storage

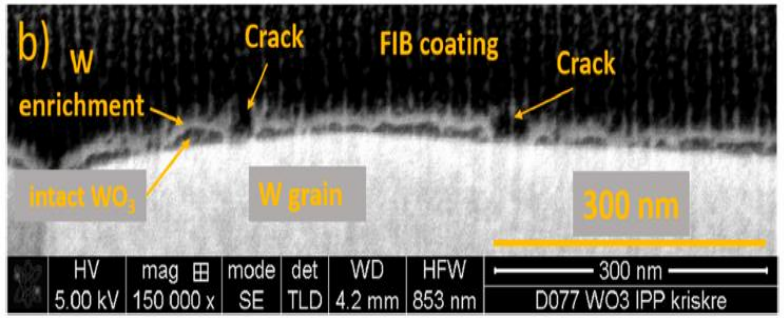




E. Prestat, STEP Report, 2024

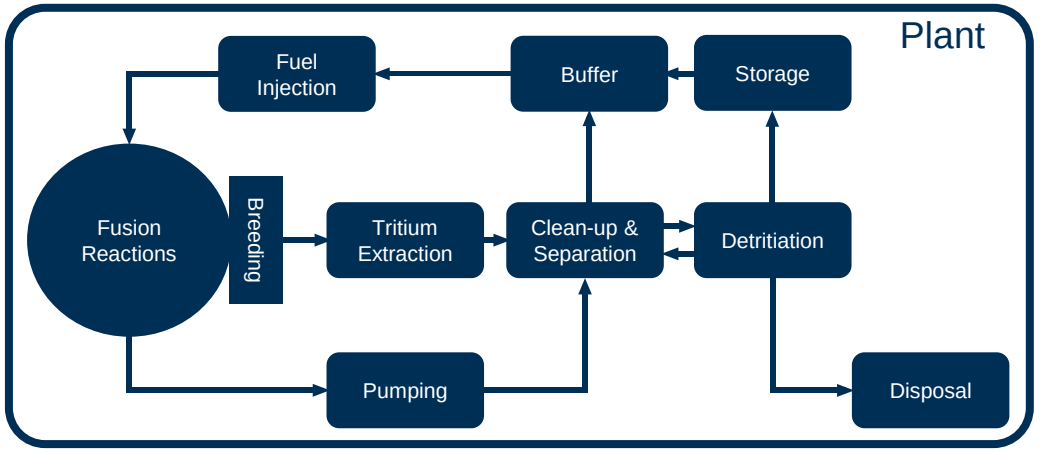
Influence of thin surface oxide films on HI release from self-ion irradiated tungsten

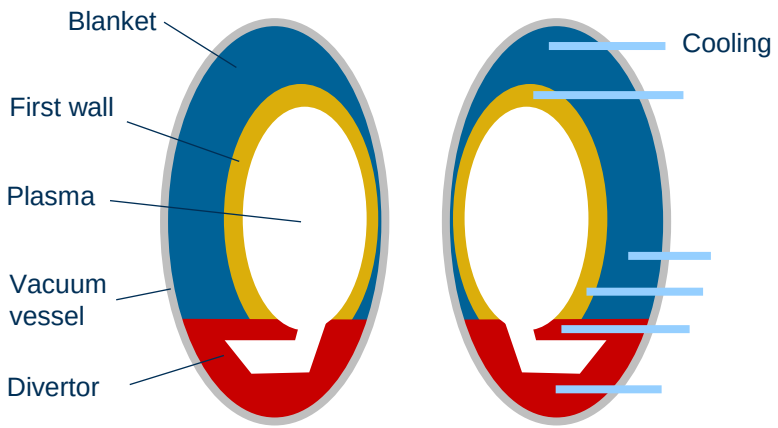


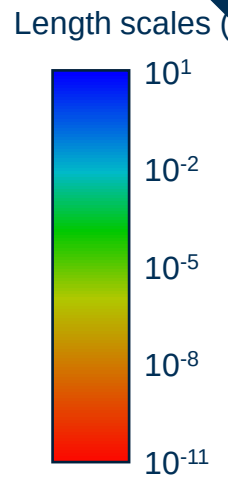


K. Kremer et al. (2021, 2022, 2023)

Tritium Inventory Modelling (TIM): Multi-Systems, Multi-Physics and Multi-Scale Problems







WP0: Process Architecture Modelling Modular approach, optioneering and analysis of full tritium cycle

Fuel Cycle BC
Plasma modelling, regulation

WP1: Process Technologies Modelling
Dynamic subsystem response

Pilot Plants AGHS, H3AT

WP2: Multi-physics Modelling
Component level, gradients in operating conditions

Lab-scale Experiments (other projects)
Permeability, desorption

WP3: Diffusion and Trapping Mechanisms
Irradiation damage, microstructure, temperature and stress

WP4: Ab-Initio Models
Fundamentals of retention, isotopic effects

WP5: Model Interfacing, UQ and Analysis
Linking different models, improving model understanding, efficiency

WP6: Computational Frameworks and tools
Code maintainability, scalability, computational resourcing

Multi-physics HI diffusion model suitable to scale-up at engineering component level

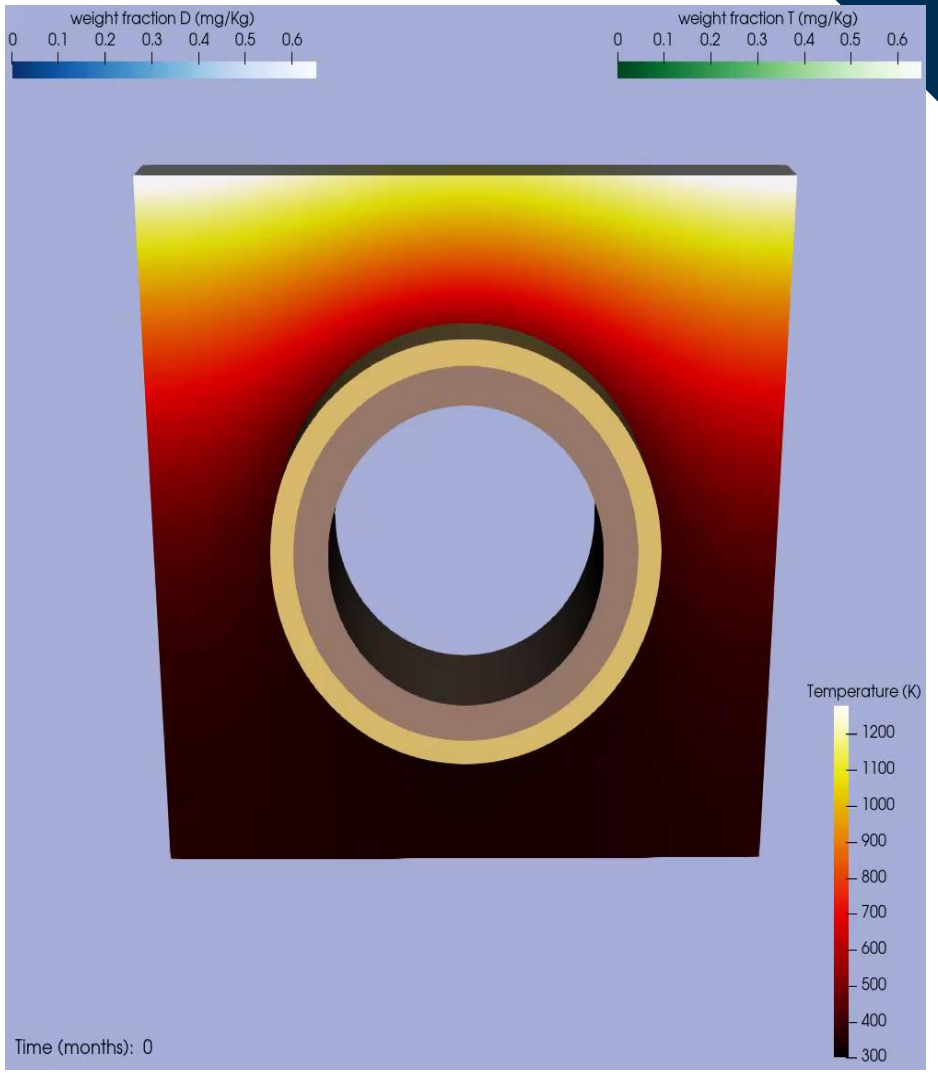
UK Atomic Energy Authority

➢PALIOXIS code developed within TIM program at UKAEA for finite-element hydrogen-isring otope modelling of diffusion and retention in metallic materials from first-principles ab-initio calculations for use with MOOSE

❑**multi-trap** from extensible as DFT/MLEP database extends
❑**multi-gas** allows for He-HI interaction with chemical potentials
❑**multi-occupancy** correct thermodynamics for trapping energies
❑**multi-dynamics** long-lived transients & steady state together

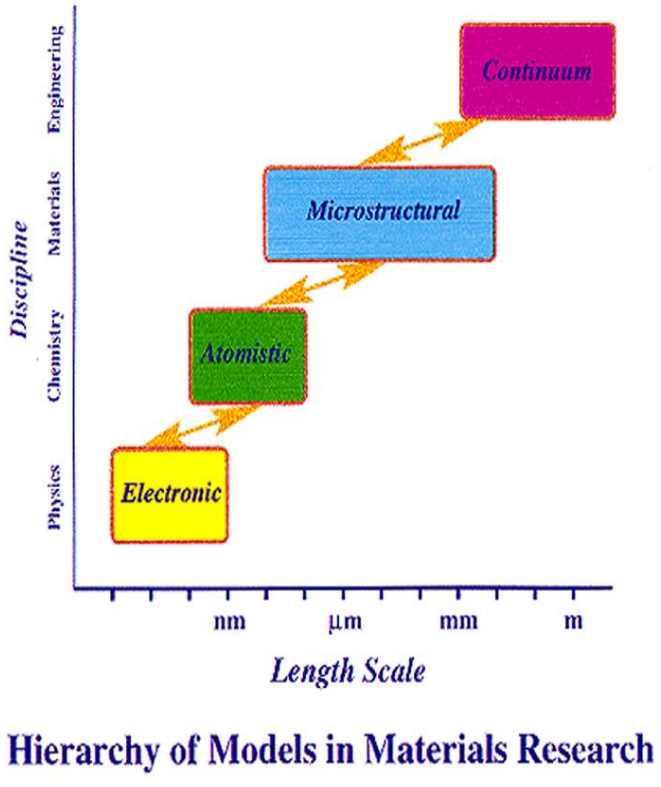
➢PALIOXIS is a new multi-scale modelling HI transport code based on ab-initio input database and not TMAP/FESTIM clone
➢ See Sanjeet Kaur talk

➢**Movie:** 3D mono-block multi-isotopes and multi-occupancy test simulations with 0.1 at. % of mono-vacancy for W/Cu-Cr-Zr/Cu layers with equal flux of D and T at surface (10^{19} ions/m2/s), head load of 8MW/m2, inside pipe convective cooling to water at 320K



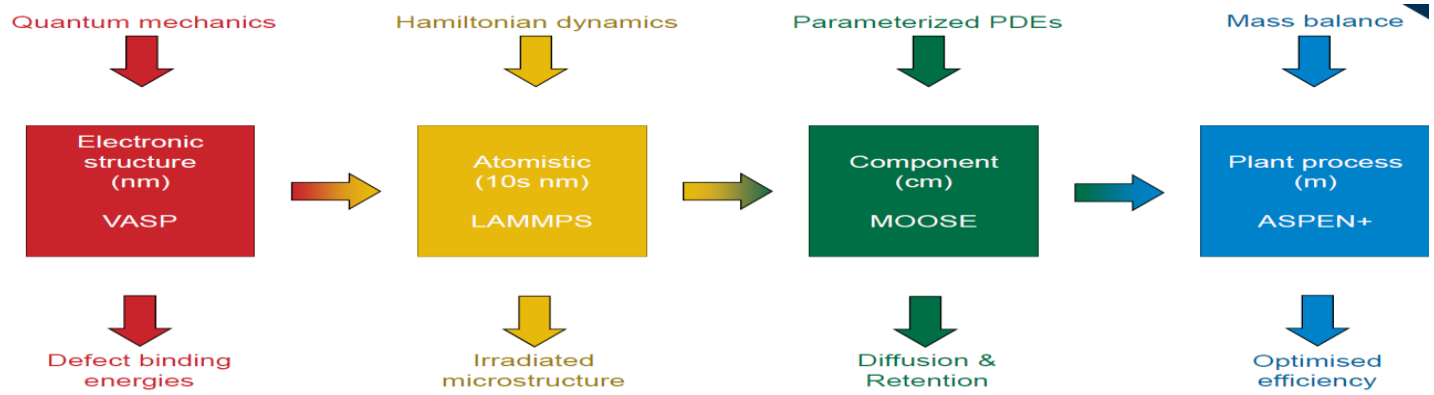
D. Nguyen-Manh et al., Microstructure impact on tritium retention and permeation in tungsten/oxide interface, 7th International workshop on MoD-PMI, Vienna, May 2025

Multi-scale, multi-physics modelling of HI retention & diffusion from first principles

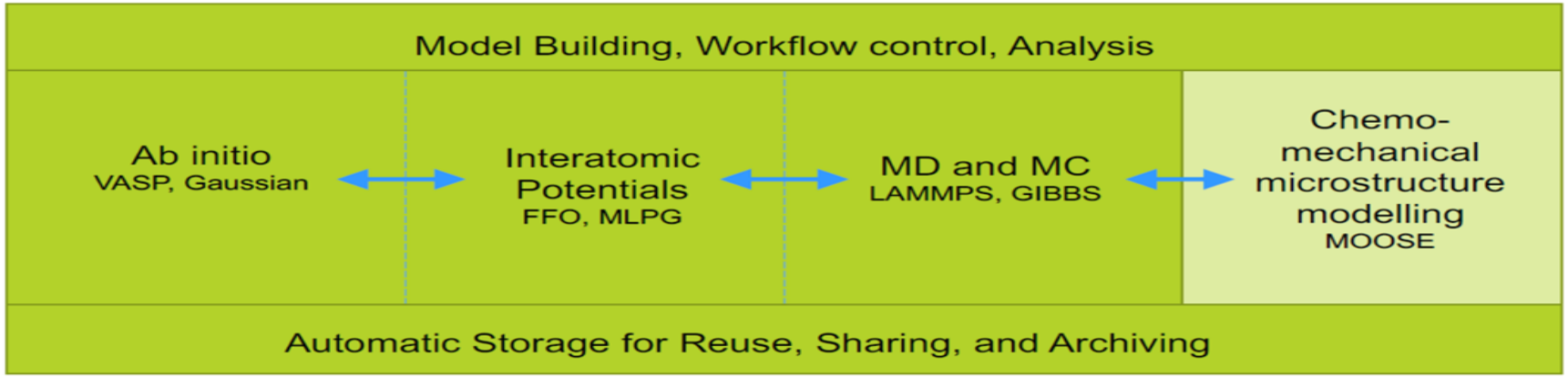


Hierarchy of Models in Materials Research

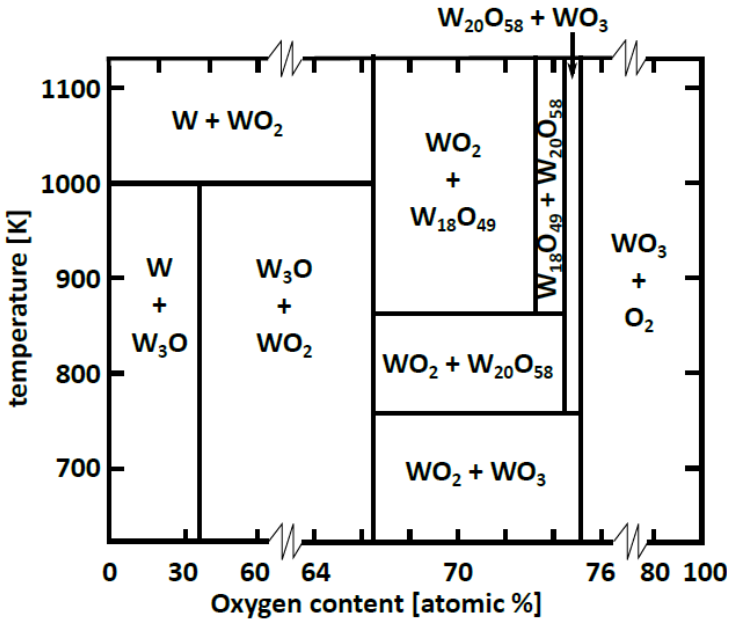
DNM et al., Phil. Trans. Royal Soc. London, 315, 529 (1995)

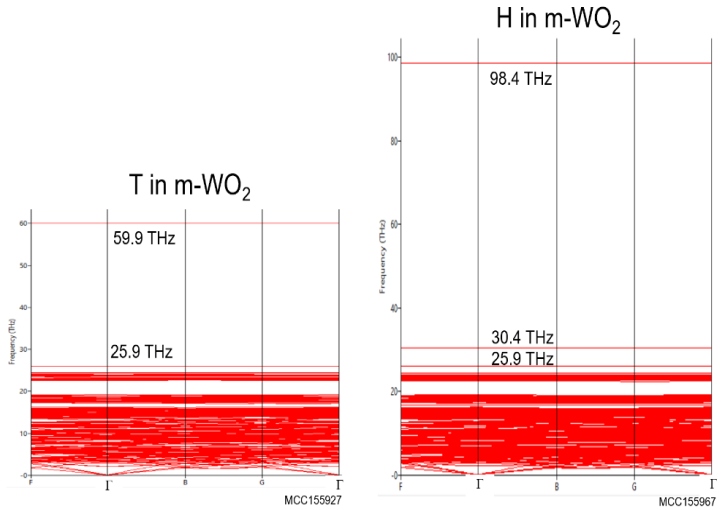


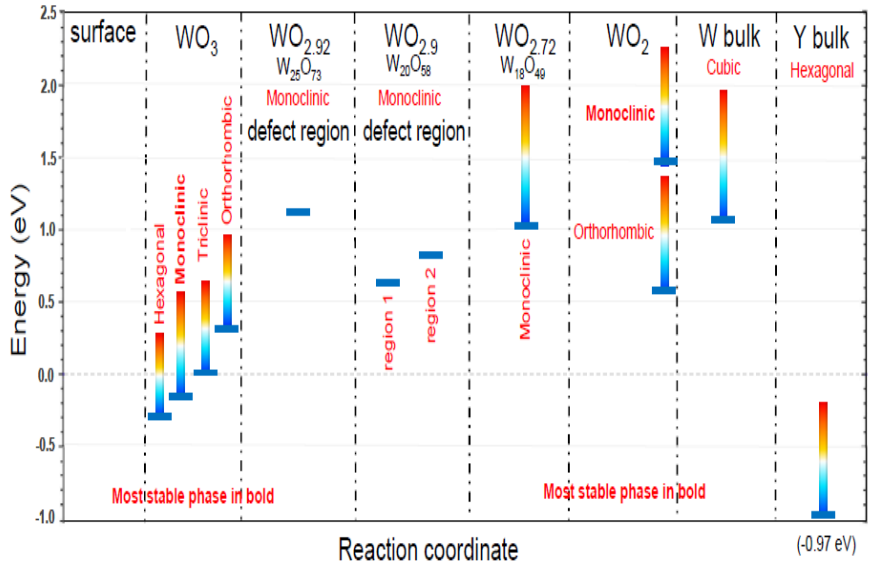
PALIOXIS code developed at UKAEA (see Sanjeet Kaur talk)

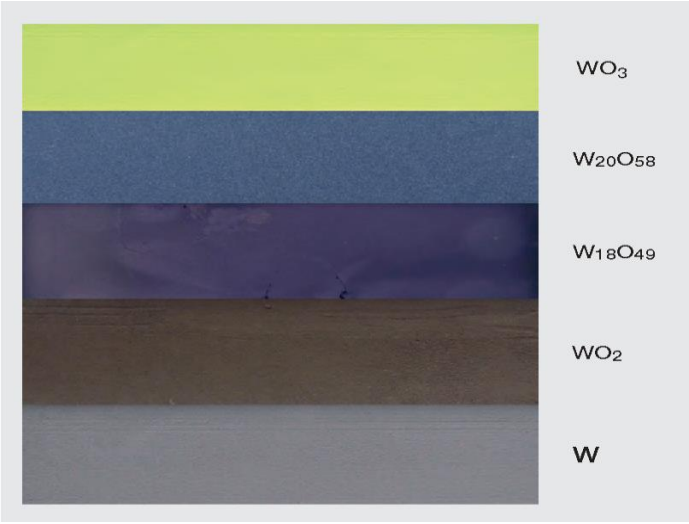


Tritium (solubility) thermodynamics in W and W oxides









	O-H (THz)	O-D (THz)	O-T (THz)
bcc-W	35.2, 45.8	24.9 32.4	20.5, 26.5
WO_2 (monoclinic)	22.8, 30.4, 98.4	17.3, 21.8, 71.4	11.1, 15.6, 19.2, 59.9
WO_2 (orthorhombic)	34.5, 40.6, 42.6	24.8, 29.5, 32.1	20.9, 24.6, 28.6
$W_{18}O_{49}$ (monoclinic)	16.3, 29.6, 99.5	14.0, 19.7, 72.3	10.5, 17.1, 60.5
WO_3 (monoclinic)	20.9, 37.1, 88.9	16.1, 27.1, 64.2	14.3, 22.0, 54.5
WO_3 (orthorhombic)	23.0, 38.9, 84.2	16.3, 27.5, 59.6	14.4, 23.7, 51.8
WO_3 (hexagonal)	6.4, 29.6, 110.8	4.5, 20.9, 78.4	3.7, 17.2, 64.3
WO_3 (triclinic)	12.7, 31.5, 107.8	9.0, 22.3, 76.3	7.4, 18.3, 62.5

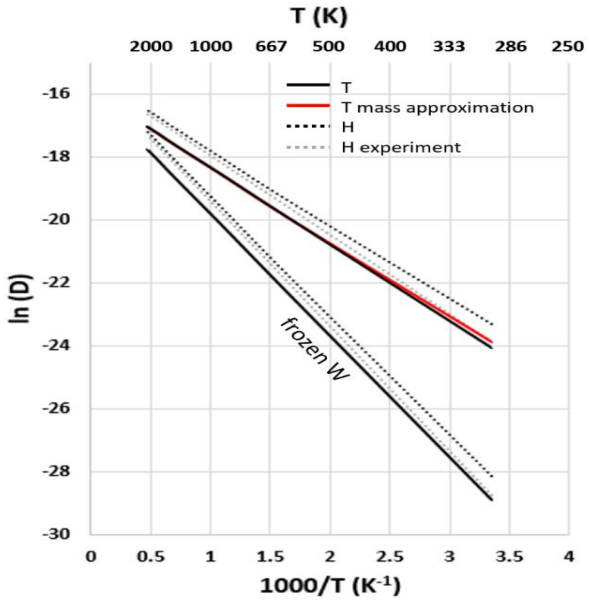
Active Raman modes of H, D, T in W-O phases

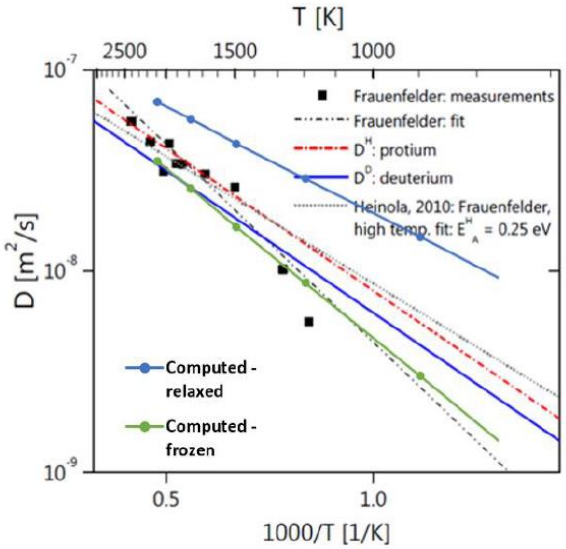
Exothermic reaction of T(H) in monoclinic WO3 at T=0K.

Free energy of insertion of H and T in m-WO3 becomes positive as function of temperature in an excellent agreement with experimental data at T=0K

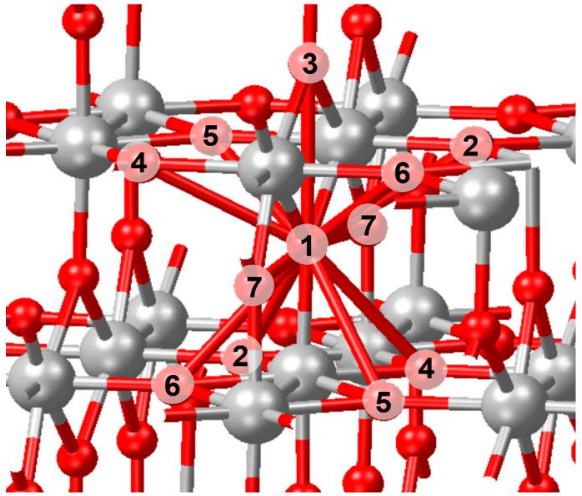
D. Nguyen-Manh et al., Microstructure impact on tritium retention and permeation in tungsten/oxide interface, 7th International workshop on MoD-PMI, Vienna, May 2025

Tritium kinetics in W and W oxides





- The Arrhenius plot gives a pre-factor of D_0 = **2.06×10^{-7} m²/s** and **effective barriers E_A of 0.20 eV** and 0.33 eV (frozen lattice), respectively
- The ab-initio computed plots are in excellent agreement with experimental data recently compiled by Holzner et al. (2000) for H in W



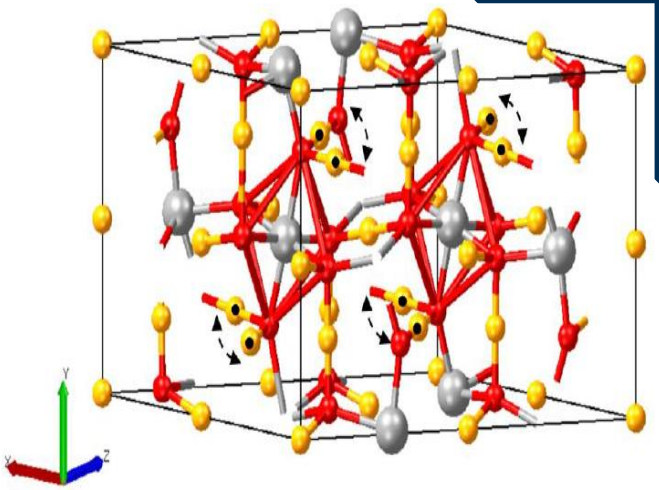


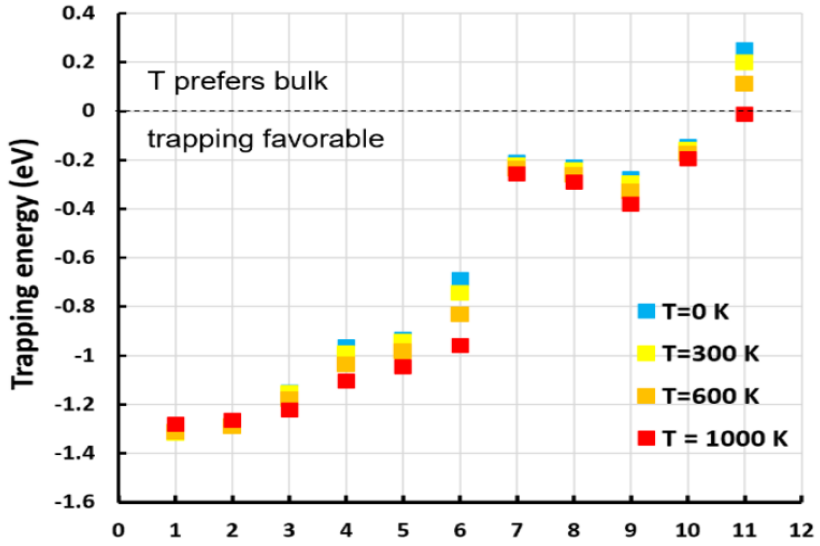
Table 5-3. Computed diffusion barriers for T(H) in m-WO_2. The jumps refer to the site labels in Figure 5-33. The values include zero-point energies.

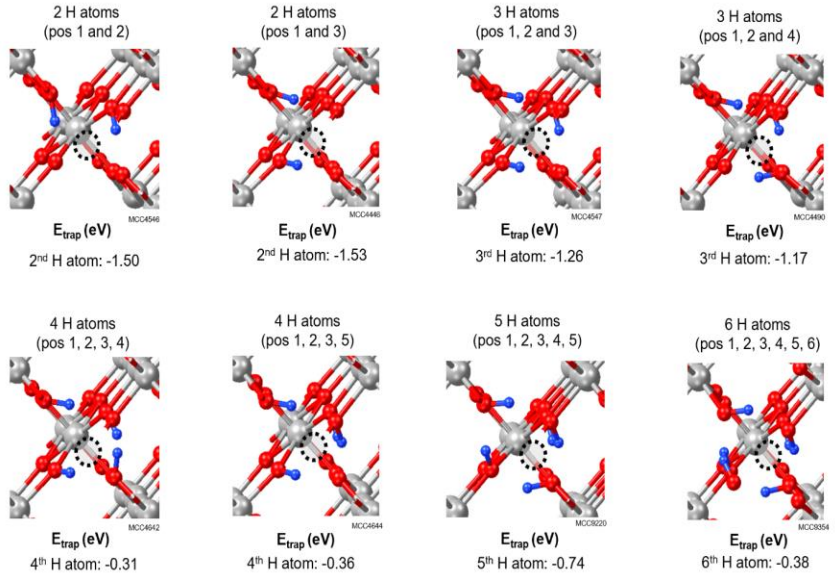
Jump	*Barrier for H (eV)*	*Barrier for T (eV)*
1→2,4,5,6	0.77	0.81
1→3	1.01	1.06
1→7	0.96	1.03

Table 5-4. Diffusion barriers for tritium in m-WO_3. The values include zero-point energy. Entries indicated by "small" are just a few hundredths of eV.

Jump	1	2	3	4	5	6	7	8	
Barrier (eV)	small	0.81	0.71	0.86	0.40	0.51	small	0.77	
Jump	9	10	11	12	13	14	15	16	
Barrier (eV)	0.62	0.62	0.88	0.59	0.66	small	0.69	0.80	
Jump	17	18	19	20	21	22	23	24	25
Barrier (eV)	0.73	0.72	small	0.74	0.64	small	small	0.78	0.73

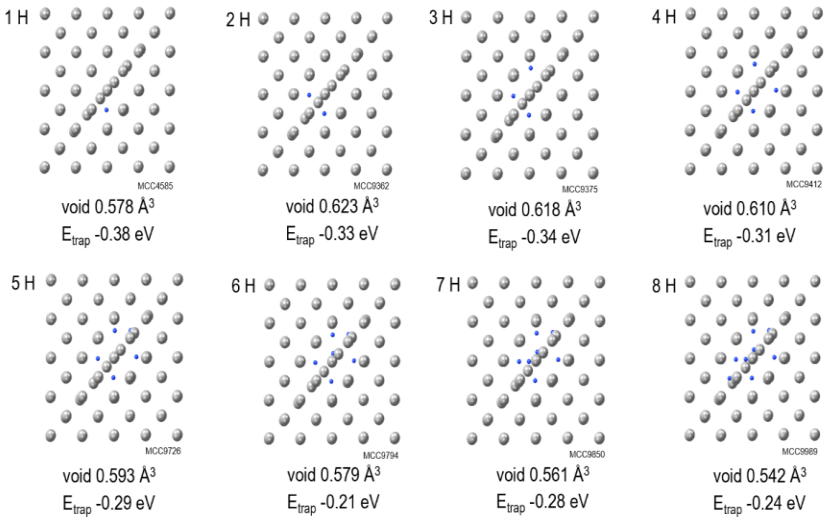
T trapping by defects in W and W oxides



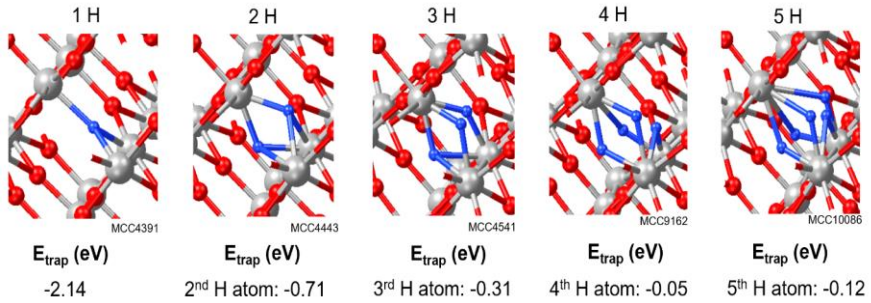


Free energies of trapping of T(H) by O vacancy in m-WO3

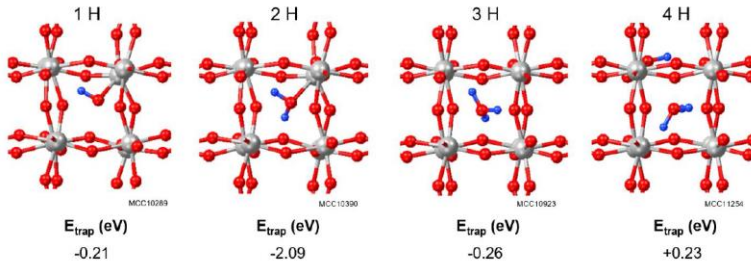
Temperature (K)	E_{trap} for T (eV)	E_{trap} for H (eV)
0	-0.88	-0.92
300	-0.94	-0.98
600	-1.07	-1.10
1000	-1.28	-1.30



Trapping of multiple H atoms (1-6) by W vacancy in m-WO_2.

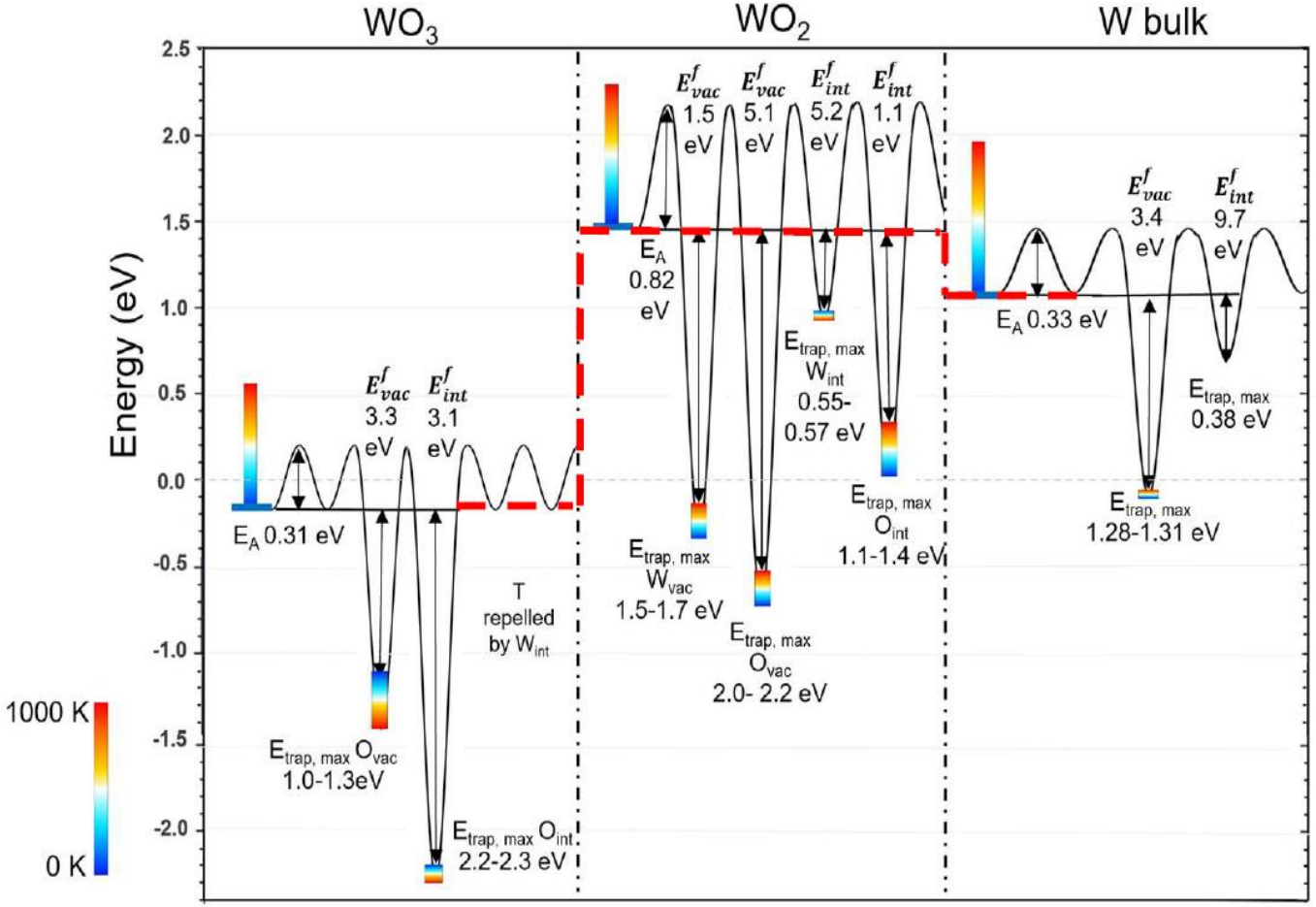


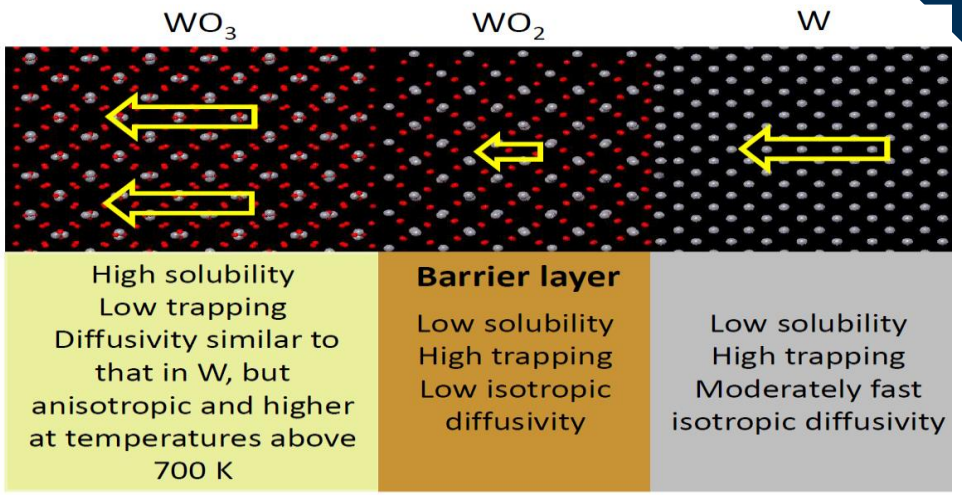
. The O vacancy can accommodate 3 H atoms

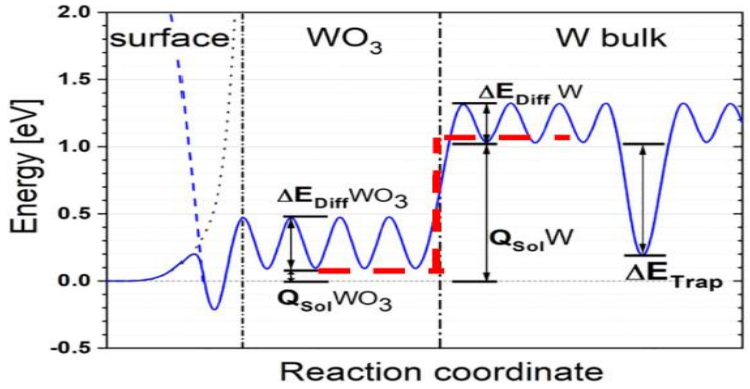


Trapping of H at O interstitial in m-WO3. Water (H2O) molecule is formed with 2H atoms

First principles prediction vs. empirical model: Important role of WO2 phase for T retention and diffusion

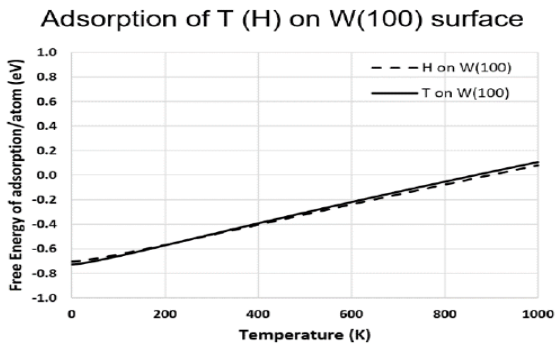


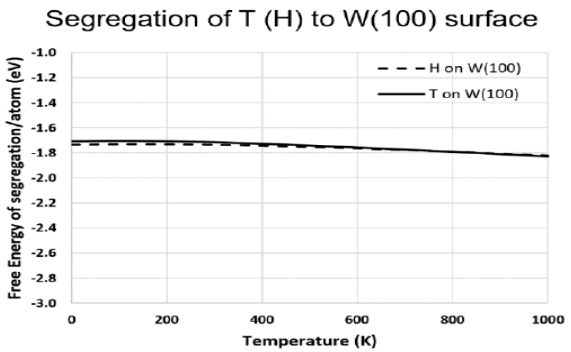


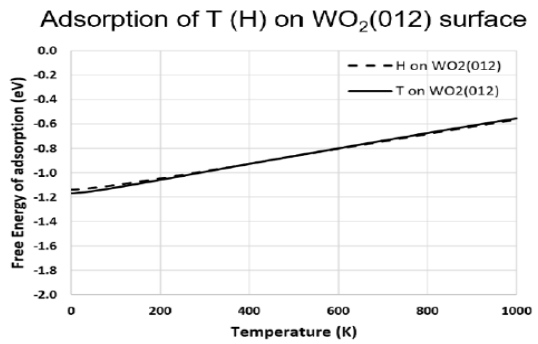


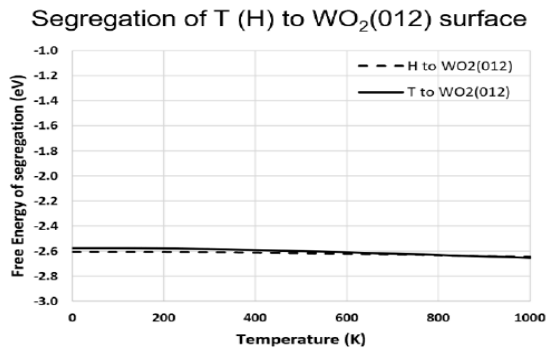
M. Christensen et al., Nucl. Mater. Energy, 38 (2024) 101611

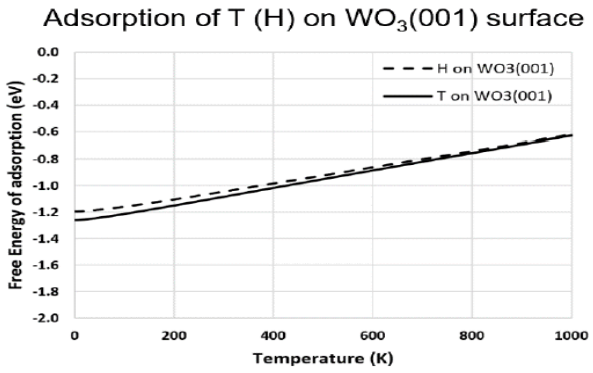
HI adsorption and surface segregation in W and W oxides

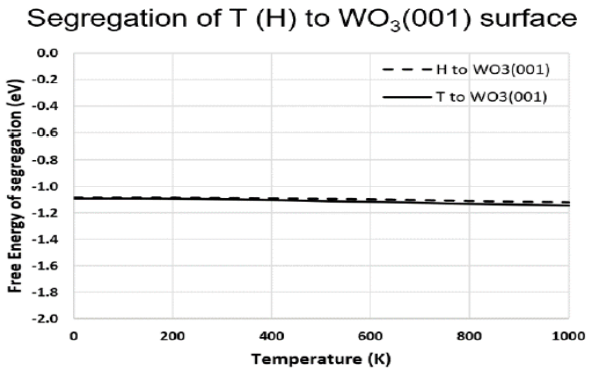






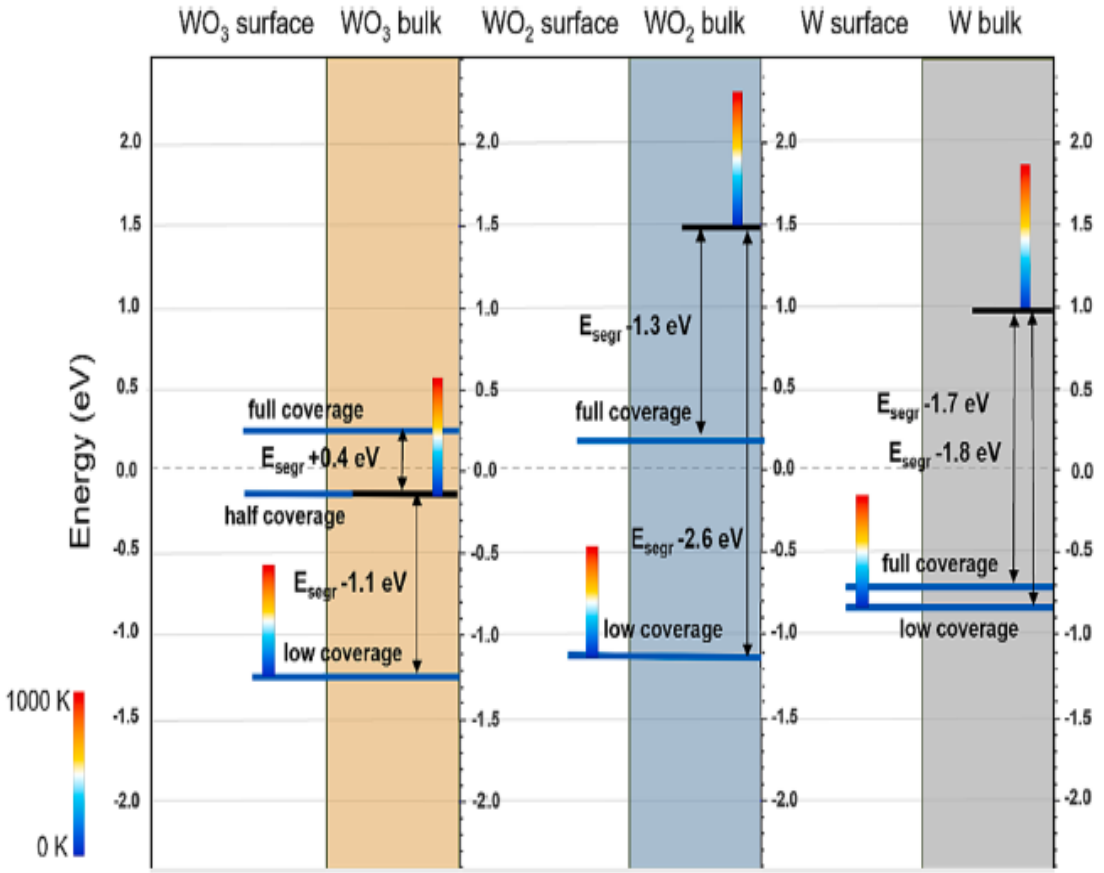






$$E_{ads} = E_{surf,\ H} - E_{surf} - \tfrac{1}{2}\ E_{H2}.$$

$$E_{segr} = E_{surf,H} + E_{bulk} - E_{surf} - E_{bulk,H}$$



H segregation to WO_3 (010)/(001) grain boundary

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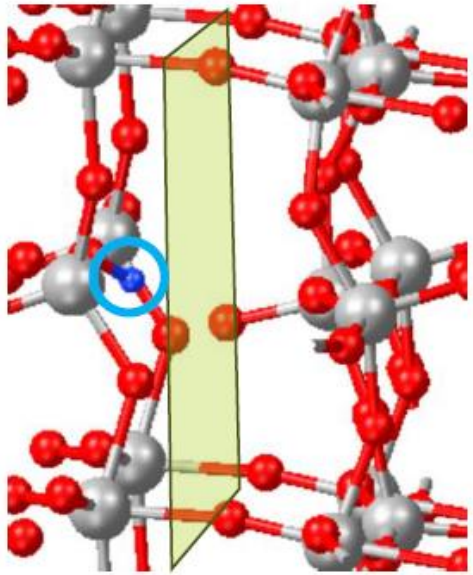
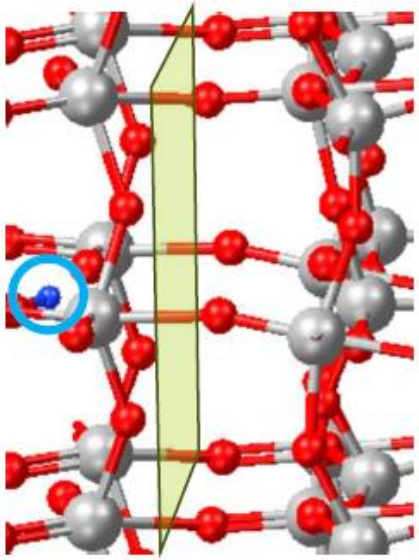
Grain boundary 1 (WO-O terminated)

site 1



$E_{segr.}$ = -1.09 eV

site 2

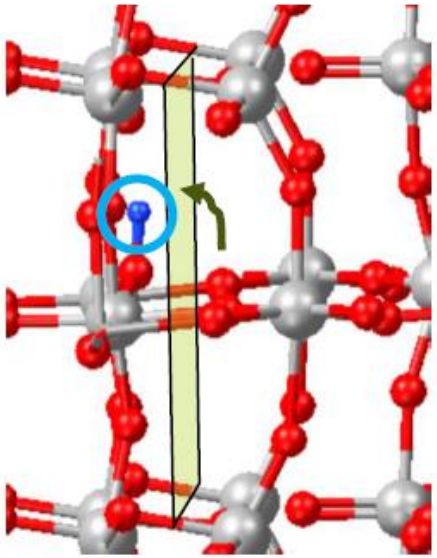


$E_{segr.}$ = -2.12 eV

H rotates in towards

Grain boundary 2 (WO-WO terminated)

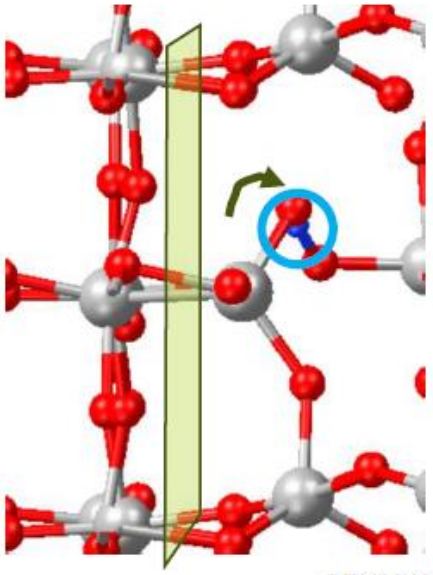
site 1



$E_{segr.}$ = 0.10 eV

H rotates in from GB

site 2



$E_{segr.}$ = 0.24 eV

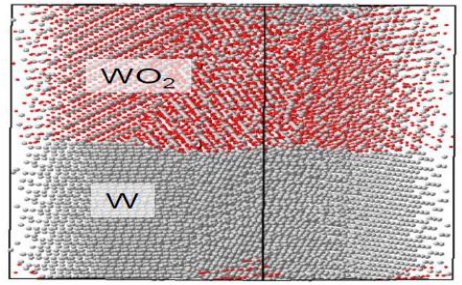
H rotates in from GB

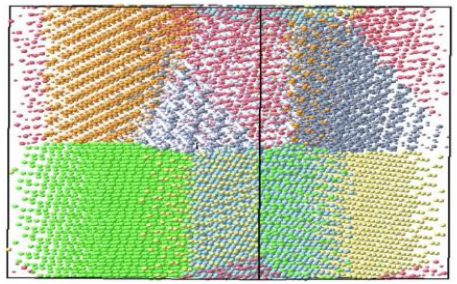
Training set of structures for W and W oxides and their interfaces for MLPs: 17,000 DFT data of configurations

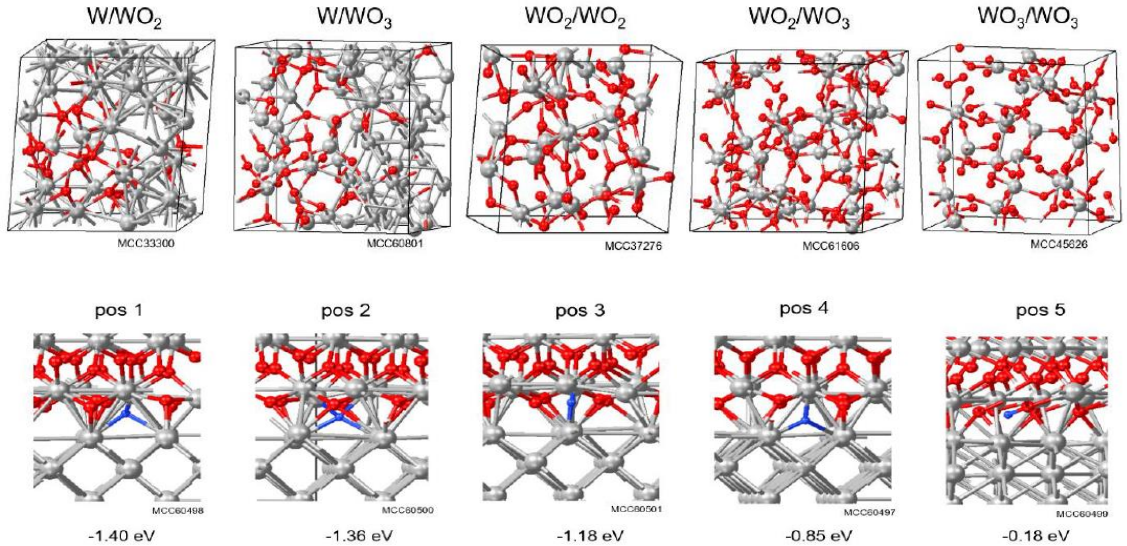
System	Number of structures
H_2	102
W-H	3747
WO_2-H	5109
WO_3-H	3455
W-WO_2-H (interfaces)	3359
W-WO_3-H (interfaces)	882
WO_2-WO_3 (interfaces)	428

MLP	Training set	Number of structures	Type	Energy RMSE (eV/atom)	Forces RMSE (eV/Å)	Applied to systems
C97664.frc	C97664.fts	5362	q-SNAP	0.0532	0.0236	O diffusion in W
MCC106376.frc	MCC106376.fts	570	q-SNAP	0.0142	0.0205	O diffusion in $W_{18}O_{49}$
MCC115118.frc	MCC115118.fts	4485	q-SNAP	0.0340	0.0199	T diffusion in WO_3
MCC107484.frc	MCC107484.fts	6561	q-SNAP	0.0374	0.0232	T diffusion in $W_{18}O_{49}$, Void formation in WO_3
MCC106378.frc	MCC106378.fts	5932	q-SNAP	0.0490	0.0237	Interface energies

The construction of polycrystalline models is based on a Seed & Growth algorithm and Voronoi decomposition.

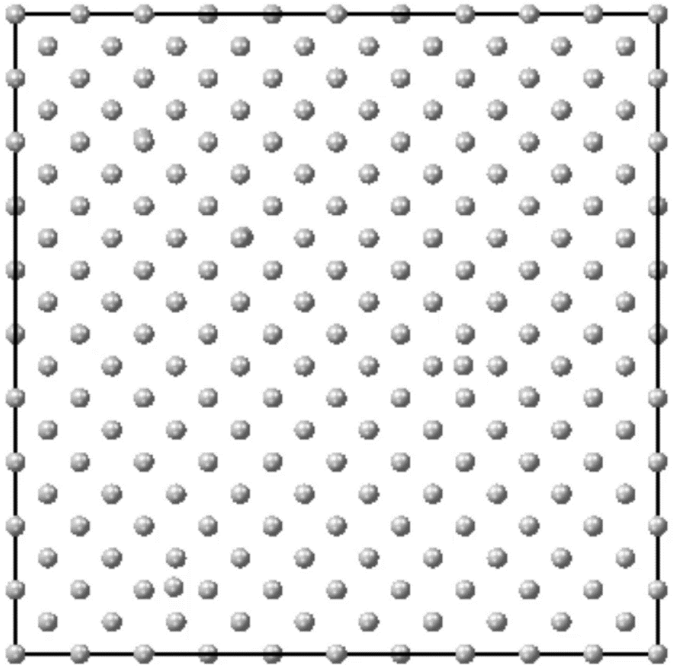


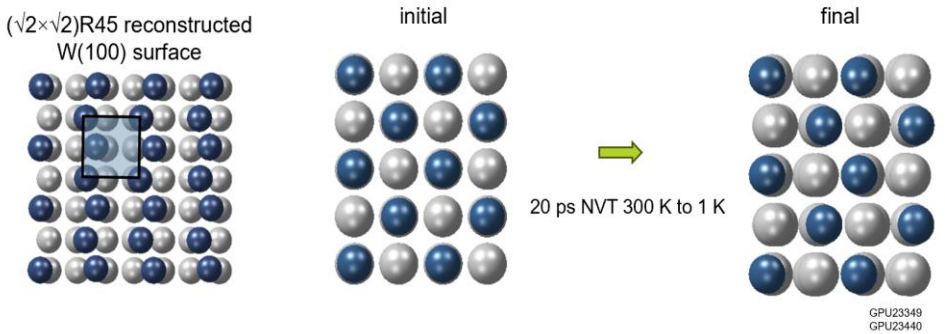




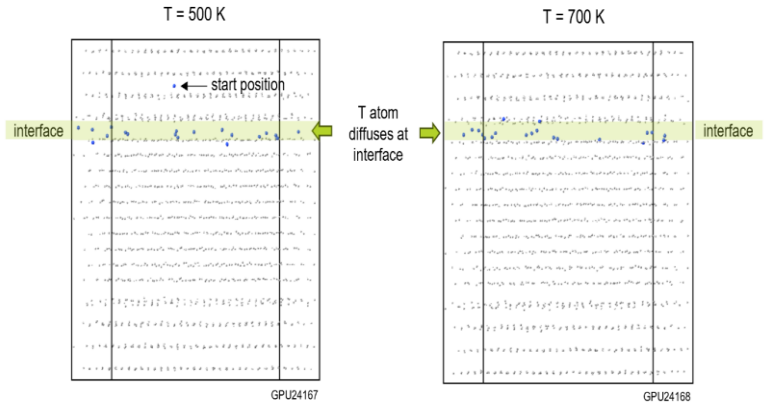
W/WO2 interface

MD simulations using MLPs of tritium diffusion in W



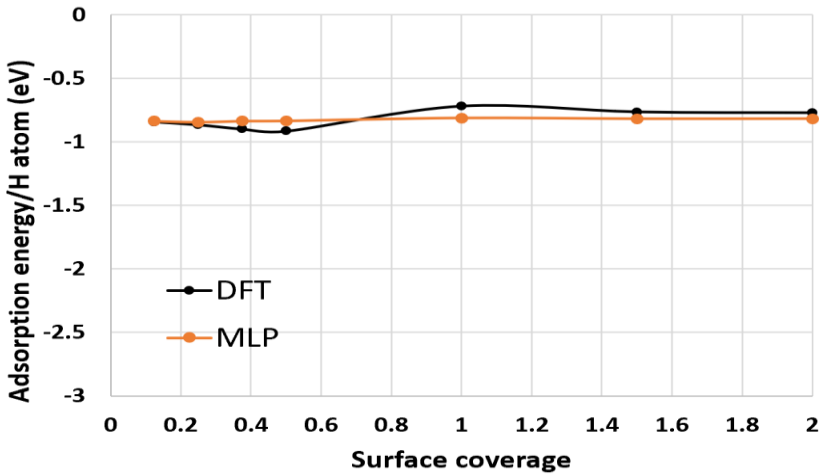


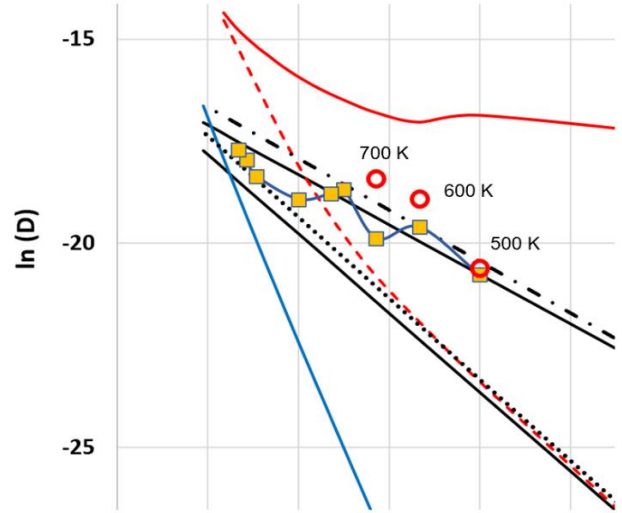
T diffusion at W(100)/W(110) grain boundary model in W



(Left) (√2×√2)R45 reconstructed W(100) surface. The square indicates the surface unit cell. Top surface W atoms are shown in dark blue. (Right) The surface reconstruction is obtained by a MD s in agreement with DFT

300 ps MD simulation at 700 K of 40 SIAs in a 16000 atom model. Many of the SIAs have formed clusters. A few SIAs are still isolated crowdions. The SIA interaction energy E_{SIA_SIA} = -3.4 eV.





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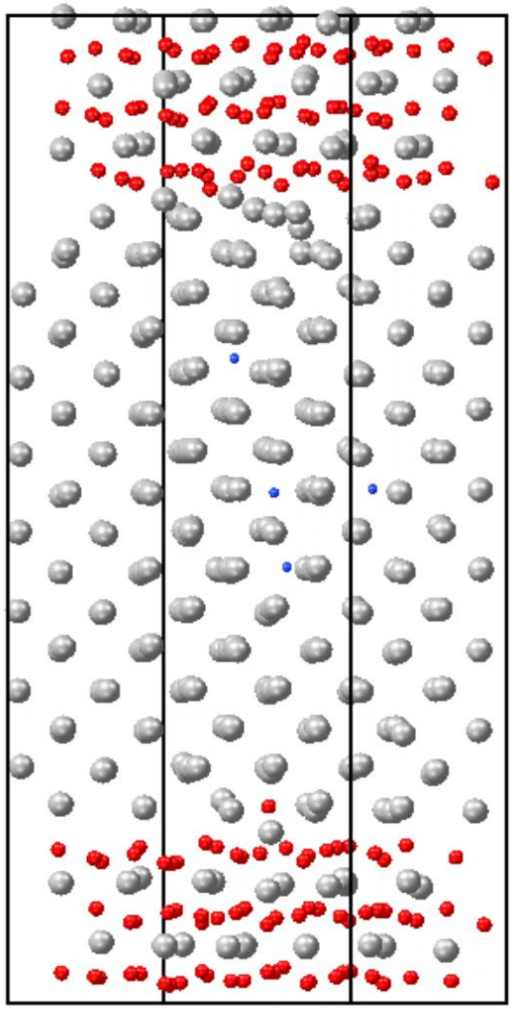
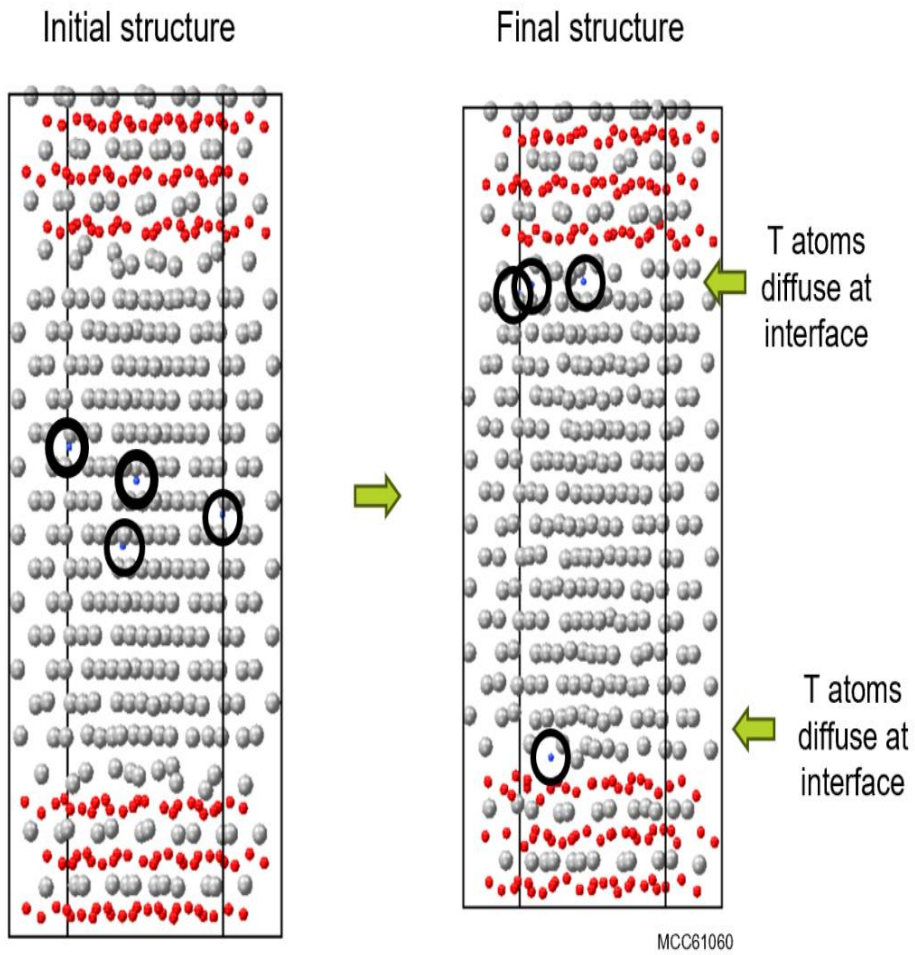
MLPs modelling of T diffusion at trapping at interfaces W/WO2

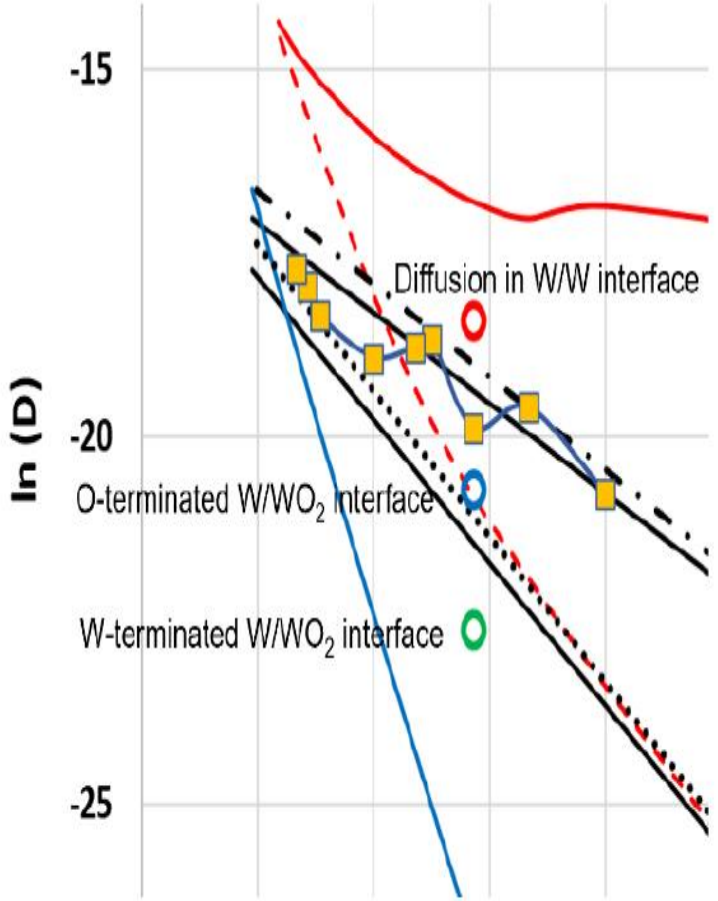
UK Atomic Energy Authority

W-terminated interface



MD simulations at T=700K





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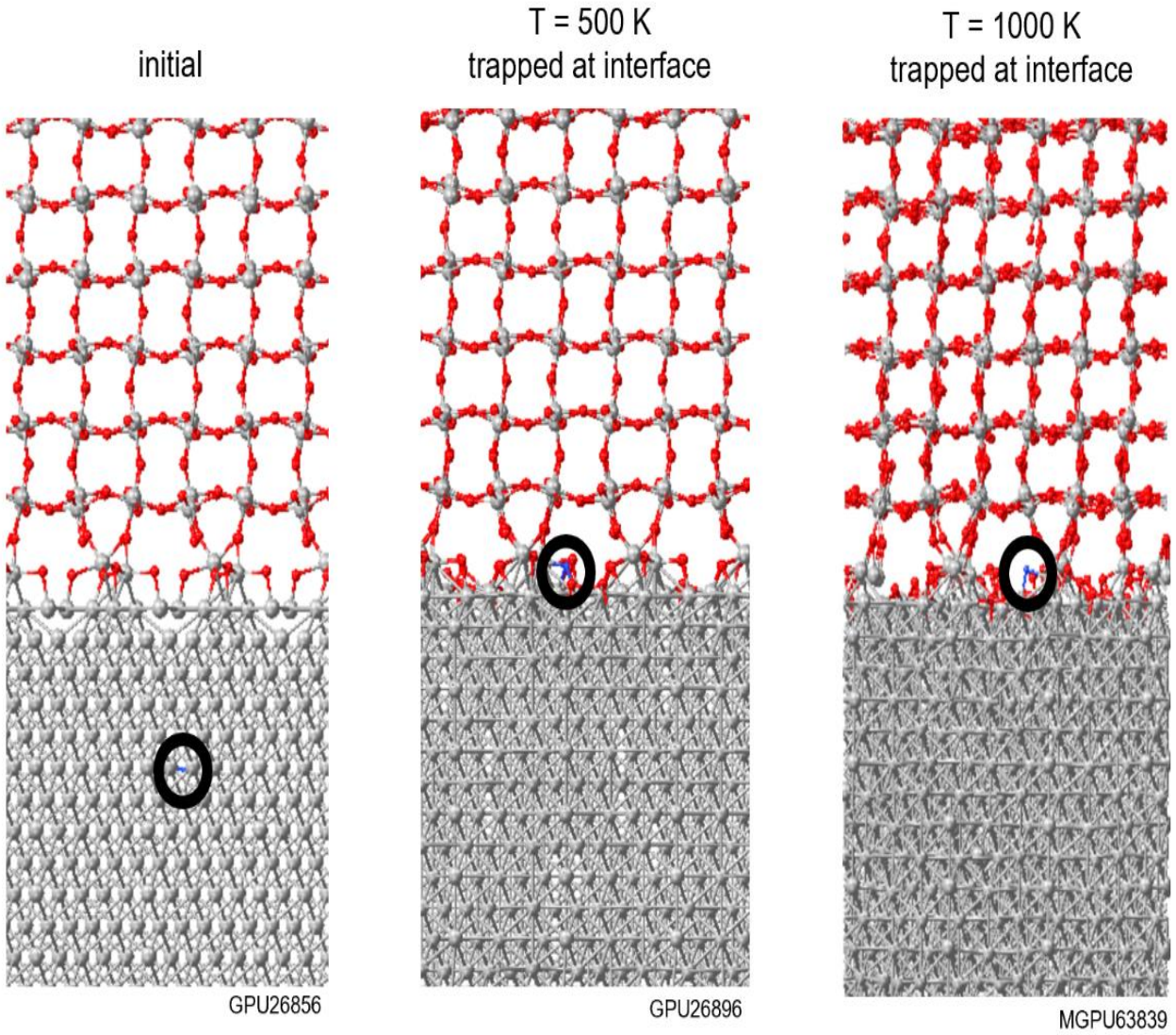
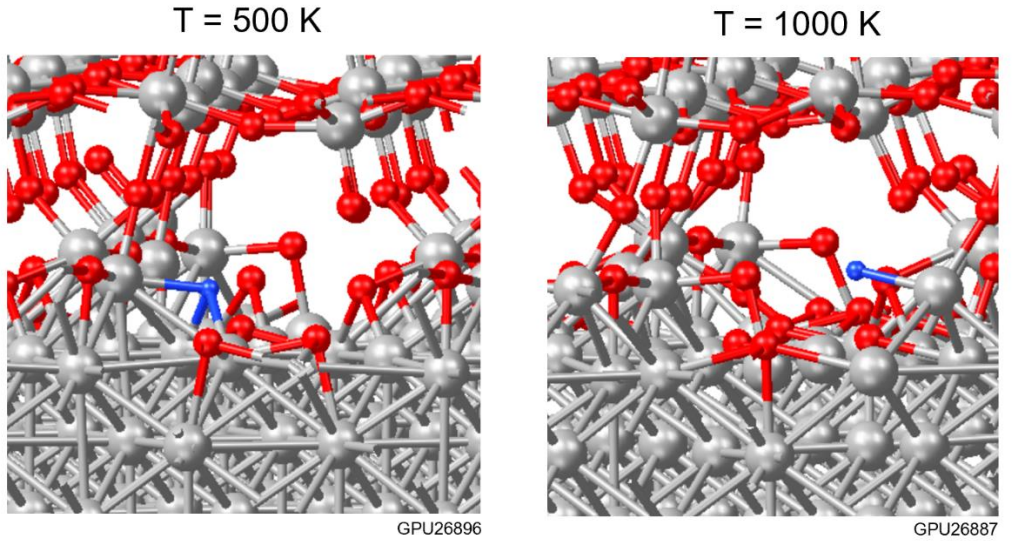
MLPs modelling of tritium diffusion and trapping at W/WO3 interface





Diffusion simulation of T at a W/WO_3 interface. The T atom diffuses from the bulk of the W phase to the W/WO_3 interface where it gets trapped. Ther trapping sites are similar for the T = 500 K and T = 1000 K simulations.

Oxidation and Detritiation from First-Principles Phase Field CM3D Modelling

The energy becomes a functional of the order parameters, concentration variables, and other fields

Driving forces

$$F = \int dV \left[f_{chemical} + f_{interface} + f_{elastic} + f_{nucleation} \right]$$

$$\frac{\partial c}{\partial t} = \nabla M(c, \eta, \boldsymbol{\sigma}, d) \nabla \frac{\delta F}{\delta c}$$

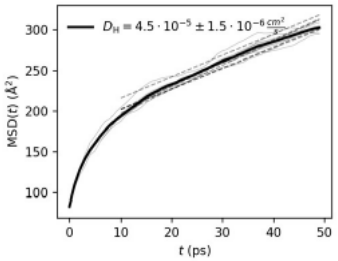
$$\frac{\partial \eta}{\partial t} = -L \nabla \frac{\delta F}{\delta \eta}$$

$$\nabla \cdot \boldsymbol{\sigma} = \mathbf{0}$$

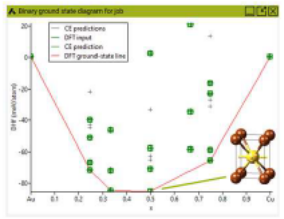
Update

Different PDEs are numerically solved, and fields are propagated in time to minimize the functional (e.g., Fick's diffusion equation, Allen-Cahn equation, etc):

Diffusion

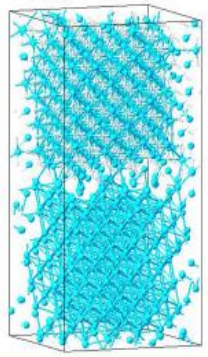


Free energy

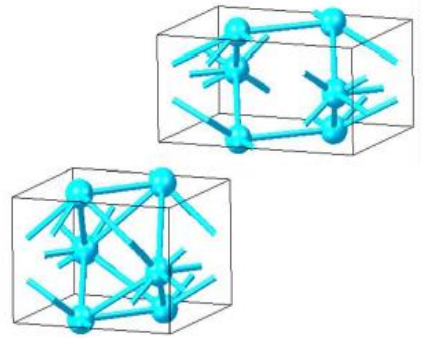


$$E = N \sum_{F} d_F \Pi_F(\mathbf{s})$$

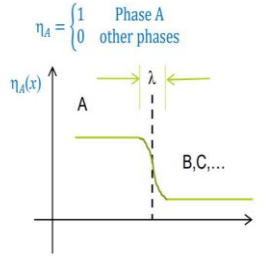
Interfaces



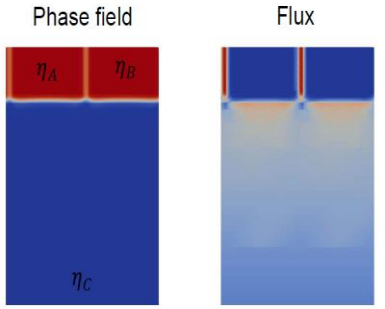
Elastic energy



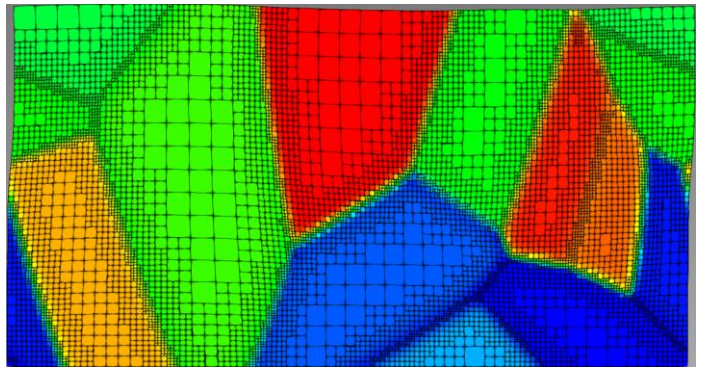
To move further up length and timescales, we must coarse-grain away information about atom positions and move towards a continuum approach where phases are represented as fields



Order parameters (η_A) are used to delineate different **phases**/grains → Phase field



From phase field equations to adaptive mesh using finite element method (FEM)



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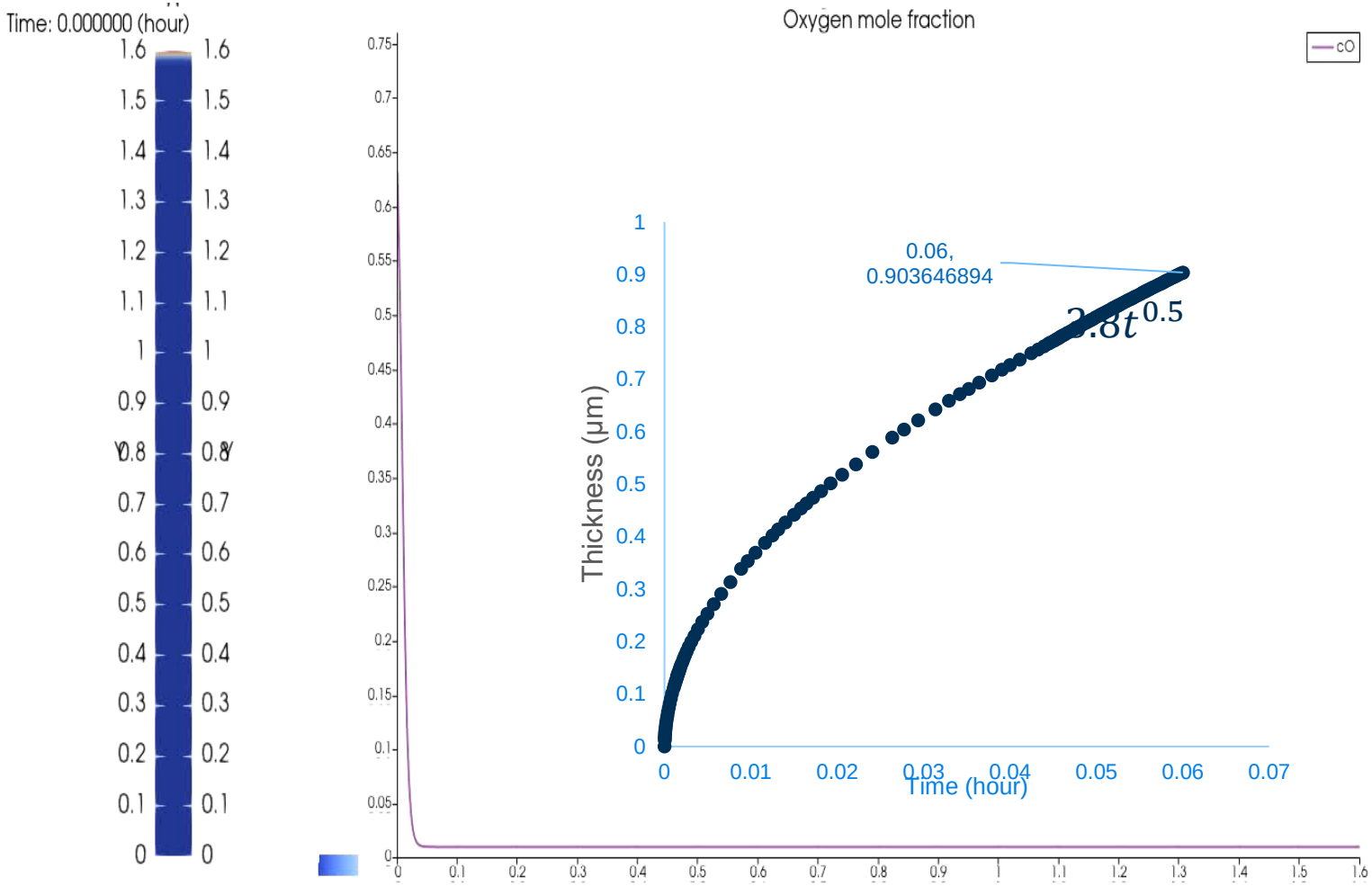
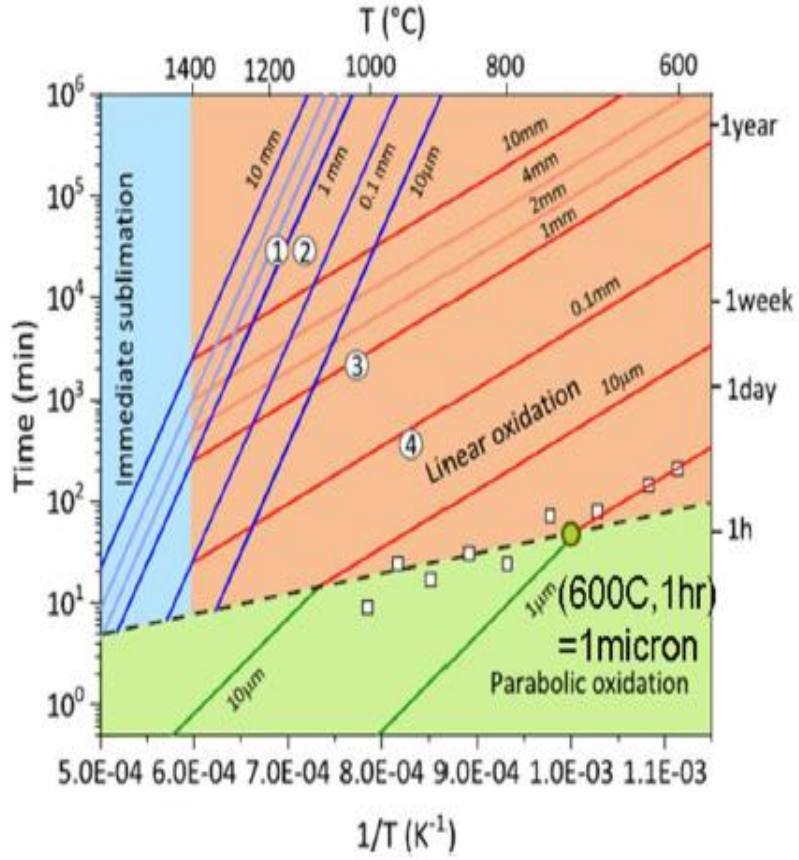
Oxidation kinetics and WO3 growth from W at 600^{0}C





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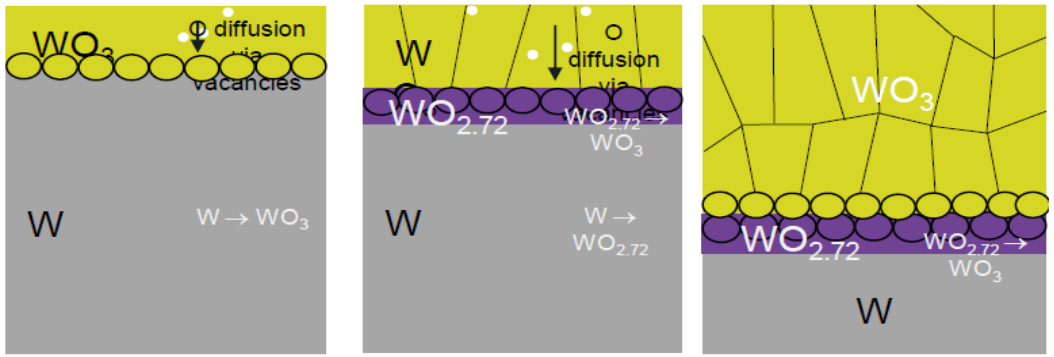
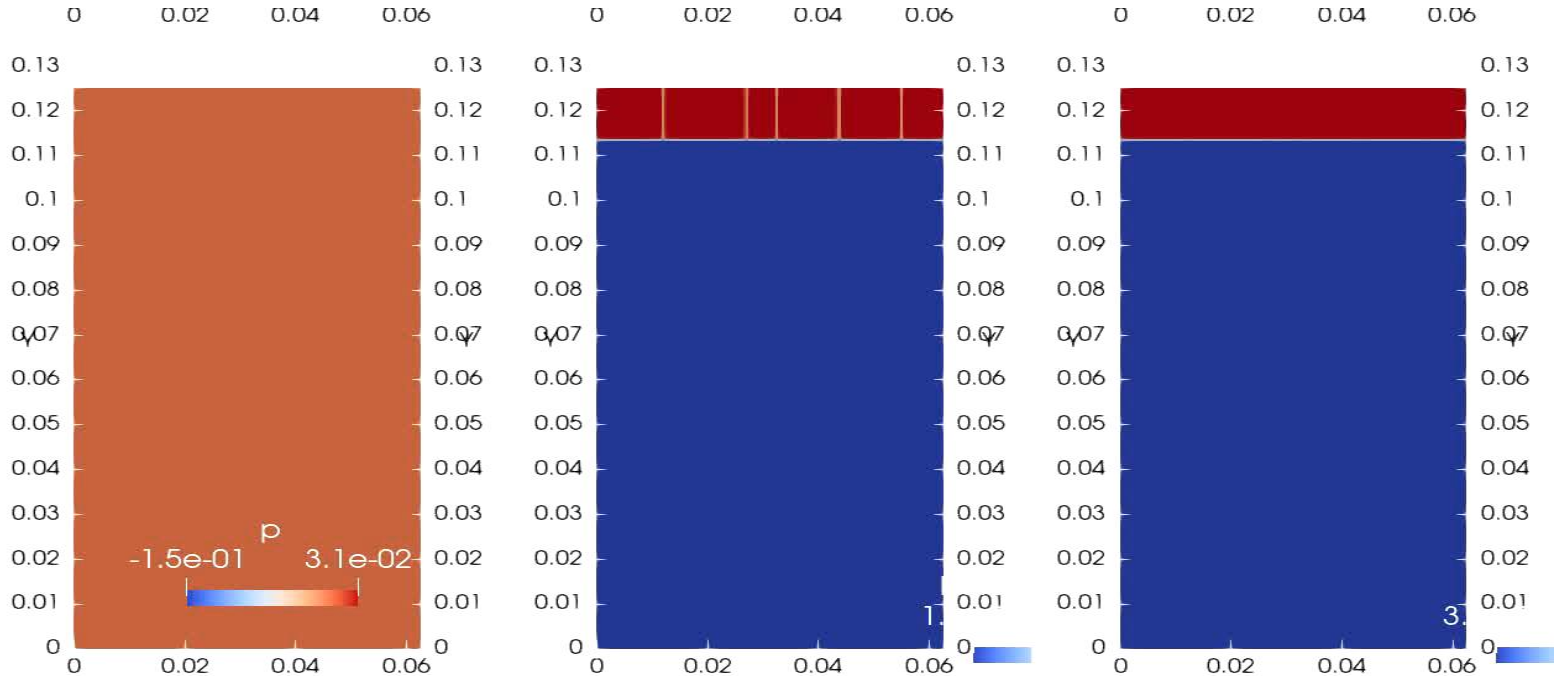
Heterogenous growth of WO_3 phase at W/WO3 interface: Effects of grains and nucleation of $W_{18}O_{49}$ phase

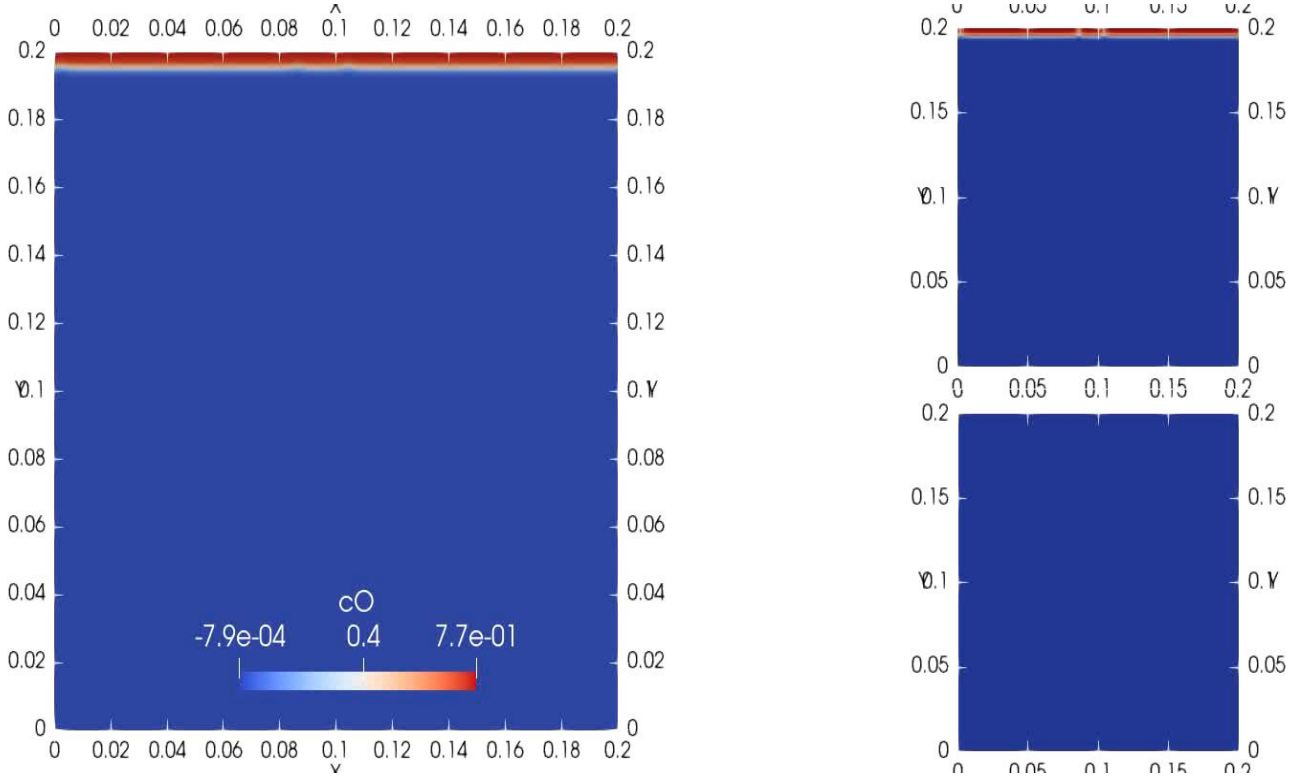


- Heterogeneous nucleation of WO_3 at the W/WO_3 interface is responsible for WO_3 grains
- Followed by nucleation of $W_{18}O_{49}$ at the W/WO_3 interface
- There is a potential to nucleate $W_{18}O_{49}$ grains at the W/ $W_{18}O_{49}$ interface
- WO_3 grains continue to nucleate at $W_{18}O_{49}$ /WO_3 interface as oxide grows

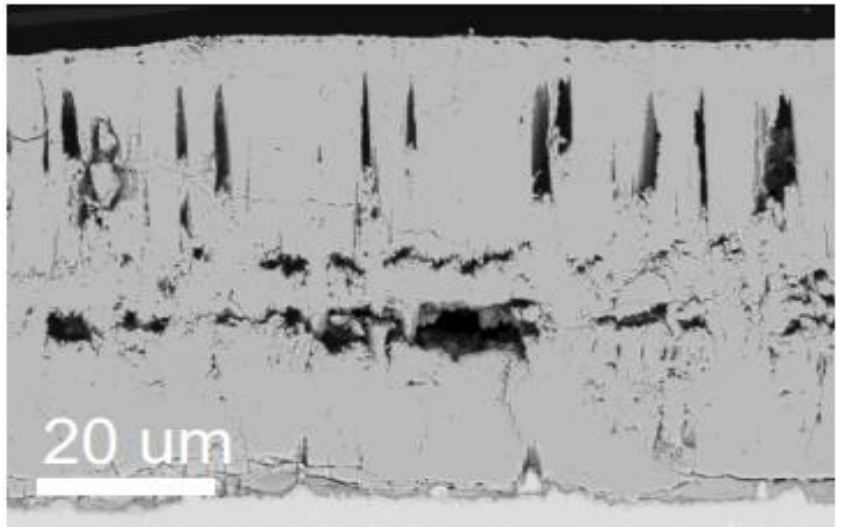
1) Pressure
2) Grain/Void distribution
3) Phase distribution



Crack modelling at W/W oxide interfaces with different Pilling-Bedworth ratios



$$PBR = \frac{V_{oxide}}{V_{metal}}$$



Regions near cracks show high concentrations of oxygen

From the experimental samples, it seems like one of the most probable nucleation sights for voids is at the WO_3 / WO_x interface

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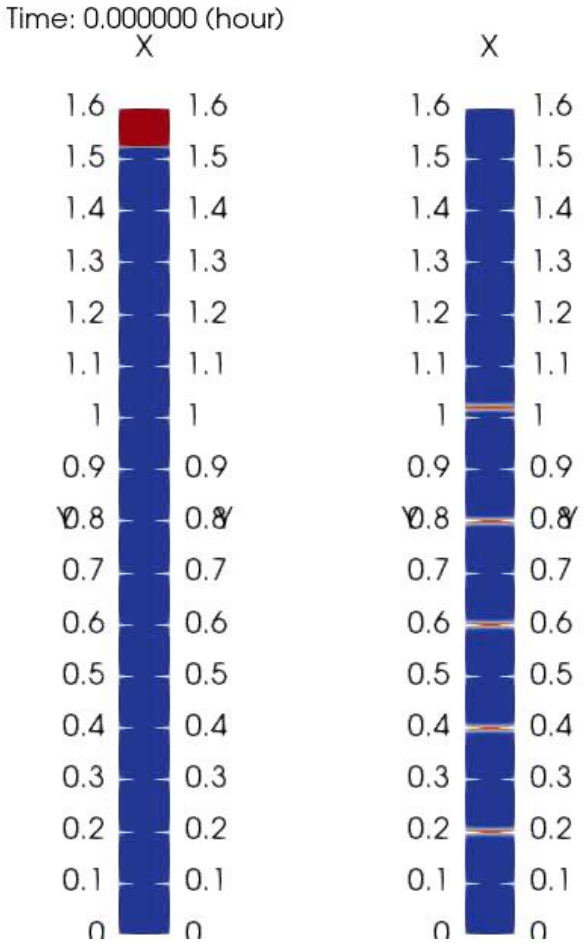
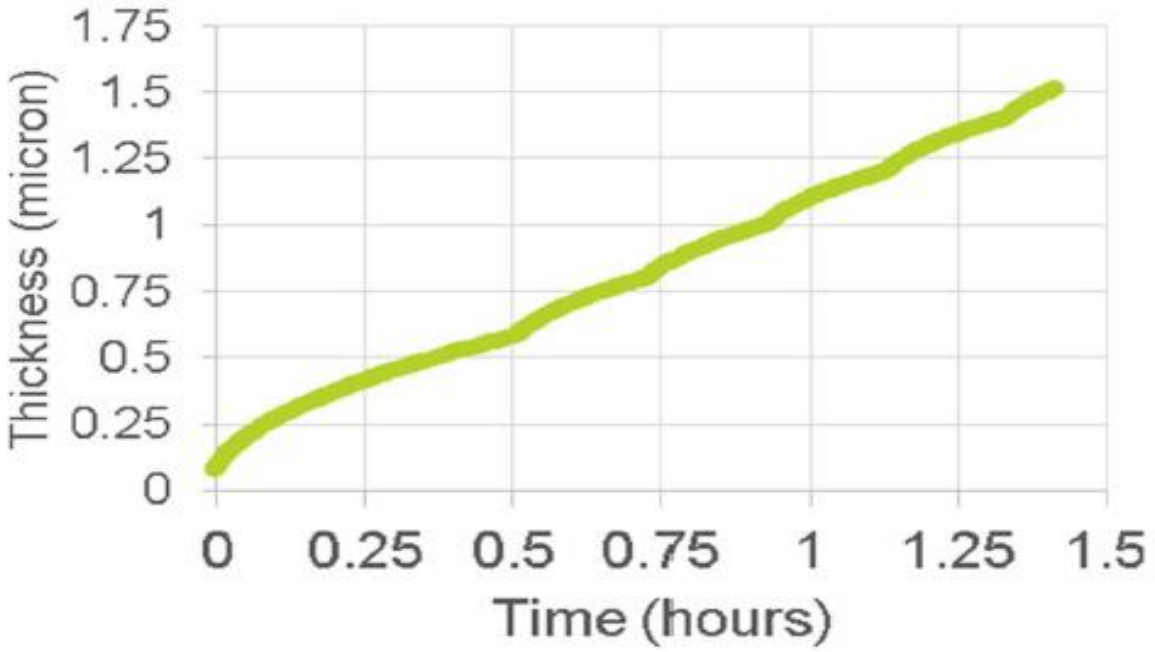
Role of crack on oxidation grows from parabolic to linear transition regime





To decrease computation time, we artificially introduced cracks spaced 0.2 microns apart. The cracks only act as sources once the oxide grows over them.

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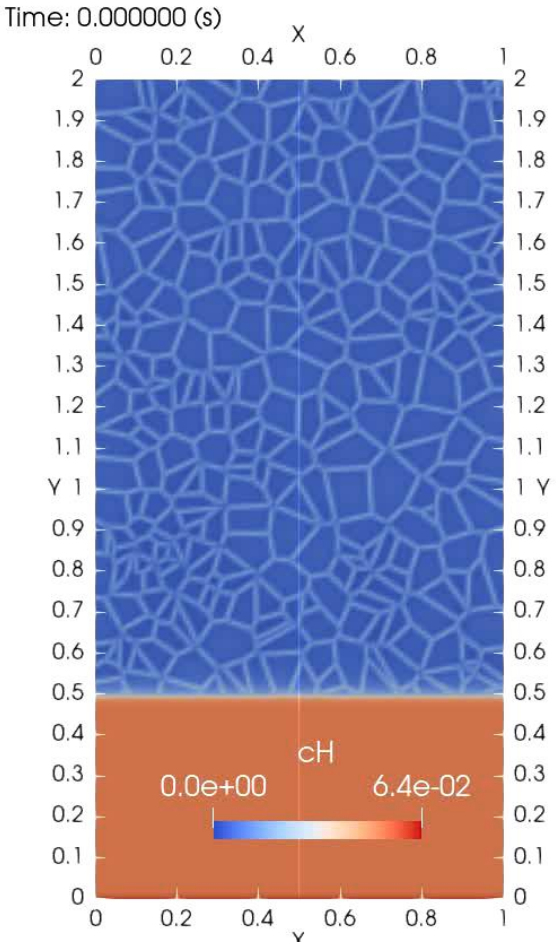
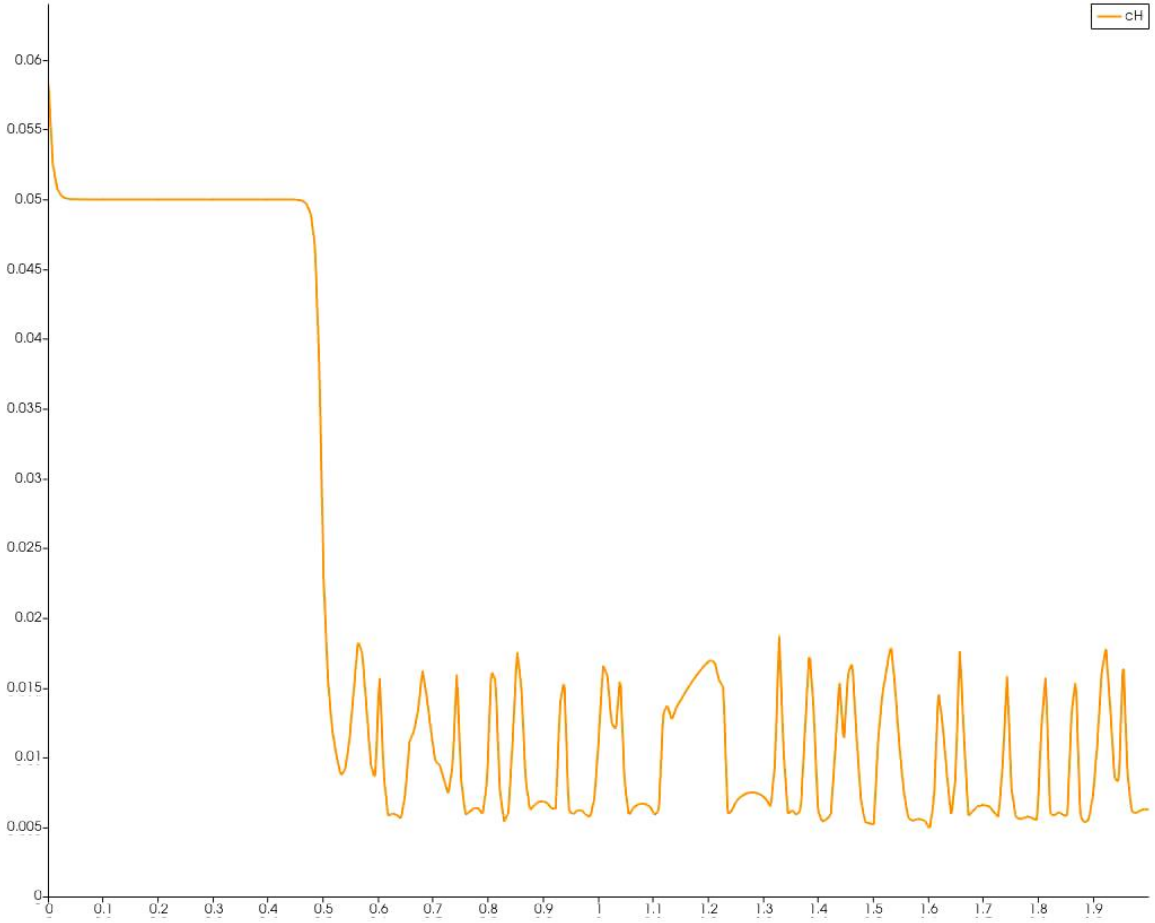
Tritium transport modelling at W/WO3 interface





- The oxide grains act as a significant trap for tritium.
- The amount of tritium that is stored scales with the surface area density of the trioxide grains
- Trapping at tungsten vacancies may also be a source of significant trapping in the tungsten & oxide grains, but this effect has not yet been included in the model.

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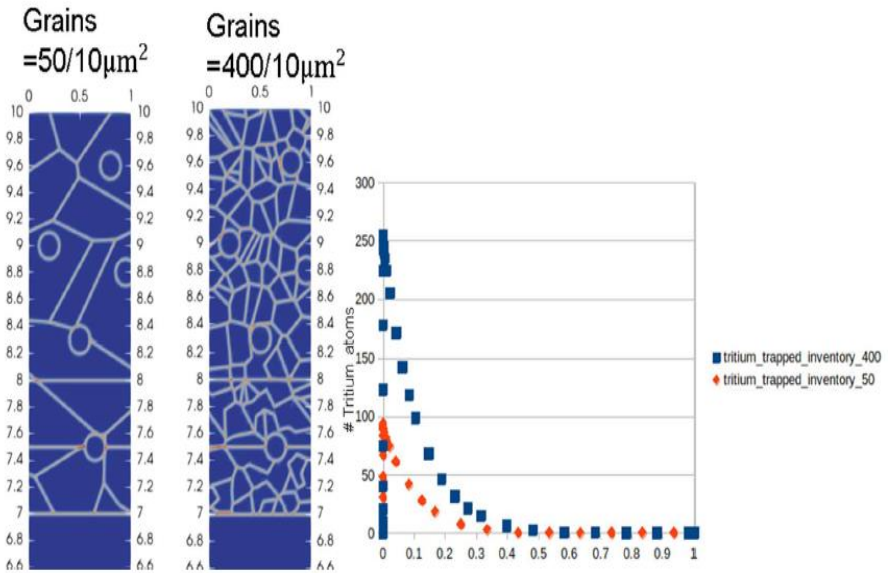
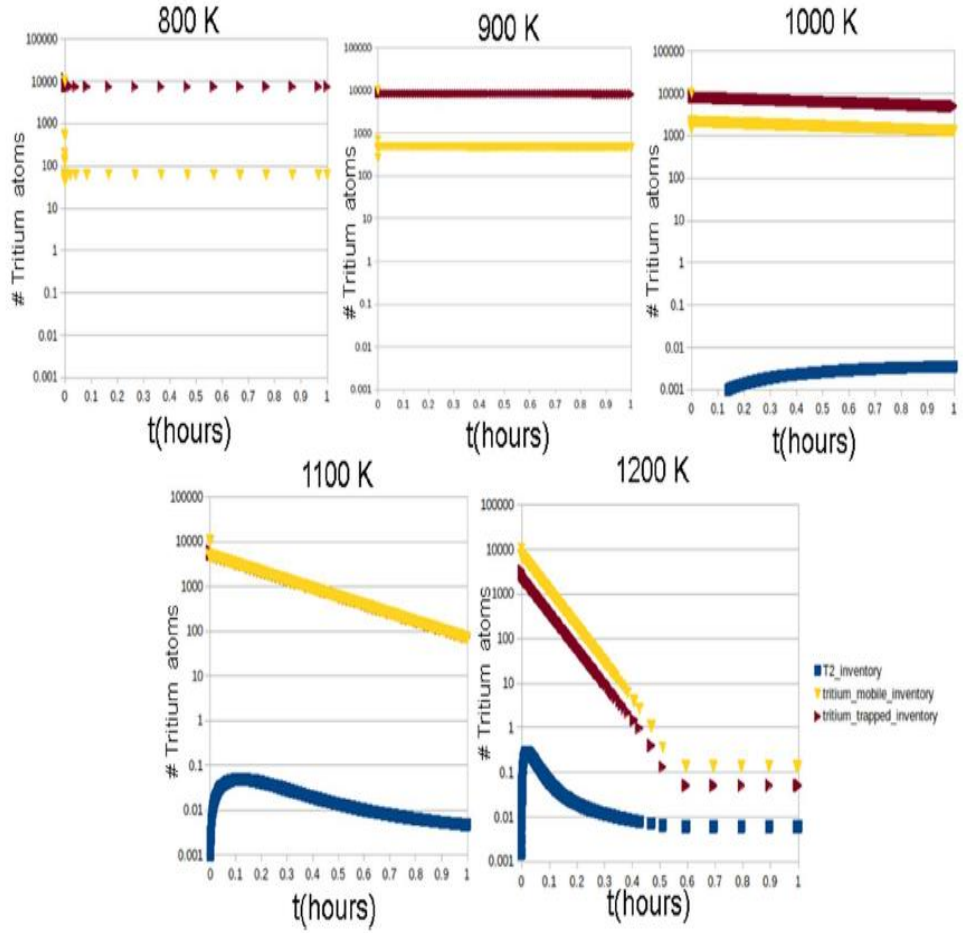
HI gases (H, H2) retention model in presence of microstructure of W/W oxide interfaces

$$\frac{dc_m}{dt} = \nabla \cdot (D_c \nabla c_m) - \frac{dc_t}{dt} + 2\left(k_{gs} c_2 (1-\theta)^2 - k_{sg} c_m^2\right) h_s$$

$$\frac{dc_t}{dt} = \frac{\alpha_t c_m (n - c_t)}{n} - \alpha_{dt} c_t + \sum_{ij} h_{S_{ij}} k_{S_{ij}}^{t} c_m \left(1 - \theta_{gb}\right) - h_{S_{ij}} k_{S_{ij}}^{dt} c_t$$

$$\frac{dc_2}{dt} = \nabla \cdot \left(D_{c_2} \nabla c_2\right) - \left(k_{gs} c_2 (1-\theta)^2 - k_{sg} c_m^2\right) h_s.$$





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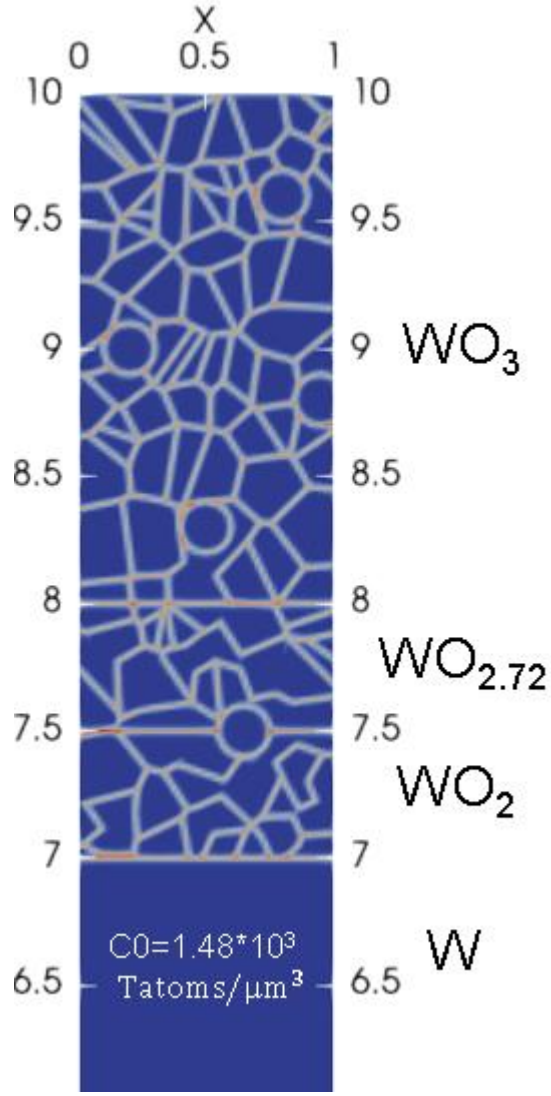
Summary

- This work discusses simulations relating to **microstructural evolution and T transport in the W-WO_x** system, with the objective of enhancing our understanding of, and our ability to control detritiation of W-based first-wall fusion reactor materials.
- Major progress towards this objective has been accomplished using a **multiscale, multiphysics approach synergising first principles, atomistic and phase field methods, and culminating in the development of a chemo-mechanical microstructural evolution code called CM3D**.
- **This code couples thermodynamic, mass transport, elastic, and interfacial properties** in the simulations. First-principles and atomistic computations both gave insight into microstructural evolution and T transport mechanism and provided quantitative input to the microstructure simulations.
- **Heterogeneous nucleation of WO_3 at the W/WO_3 interface**, driven by grain boundary diffusion of O, is primarily responsible for the evolving WO_x microstructure of W oxidation films.
- Additional **$WO_{2.72}$ grains** may nucleate at W/$WO_{2.72}$ interfaces, as pre-existing $WO_{2.72}$ grains transform to WO_3 at $WO_{2.72}$/WO_3 interfaces.
- **At 1200K, > 95% of the tritium is removed from the sample** containing a 3 micron thick oxide in approximately 30 minutes.
- **At 900 K, > 95% of the tritium absorbed in a W substrate will exit if no impermeable surface oxide** is present to impede the process. Gas storage only seems to be relevant at elevated temperatures (T>1000K)

Outlook: Role of WO_2 phase on detritiation

- Assuming there are no trapping, the presence of a dense, adherent WO_2 oxide layer on W substrate surfaces could act to retain T within the substrate and could impede T extraction. On the other hand, a purely WO_3 surface oxide with no underlying WO_2 stratum likely would present fewer difficulties. These facts suggest **that a strategy to create an oxidising environment favouring WO_3 formation over WO_2 may facilitate efficient T extraction**.
- Conversely, if a dense (without transverse cracks or large voids) and adherent **WO_2 surface oxide were in place prior to T exposure, it could serve to limit T uptake by W components**. Subsequently, components could be heated in an oxidising atmosphere to convert the pre-existing WO_2 layer into WO_3, in order to facilitate T extraction.
- If W surface oxides formed during preceding service cycles are not removed from W system components between service cycles, **high-energy neutron fluxes likely will produce high W and O vacancy and interstitial concentrations within them. Such point defects in WO_x are capacious T traps with predicted strong free binding energies**



D. Nguyen-Manh et al., Microstructure impact on tritium retention and permeation in tungsten/oxide interface, 7th International workshop on MoD-PMI, Vienna, May 2025