# Hydrogenic retention of high-Z refractory metals exposed to ITER divertor relevant plasma conditions

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The fluence dependence of hydrogenic retention in tungsten and molybdenum was measured under ITER divertor relevant plasma conditions. Plasma exposures were performed in the linear plasma generator Pilot-PSI (~$10^{24}$ D/$m^2$·s, $T_e$ ~ 2 eV, 1 cm full-width-half-maximum beam, 4-160 s exposure duration). The exposed targets were analyzed post mortem with nuclear reaction analysis and thermal desorption spectroscopy. The highest retention levels were measured at 6 mm off-center of the target (1-4·$10^{15}$ D/$cm^2$), at the center the levels were a factor of 10 lower. This was interpreted as an effect of decreasing surface temperature with increasing radial distance from the center of the target. The surface temperature was measured with pyrometry to be ~1600 K at the center and decreasing to~1000 K at the edge. No clear dependence of retention on incident plasma fluence is seen for the W targets. For the Mo targets, boron (B) and carbon (C) deposits were detected on the surface by NRA and XPS (not seen on "clean" W targets). The Mo targets also showed higher D retention than the W targets at low fluences but the D retention in Mo appears to decrease with increasing fluence. It is suspected that the high retention in Mo and decreasing retention with fluence is connected to D co-deposition with B and C deposits.

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## 1. Introduction

Hydrogenic retention in the walls of ITER affects density control and fuelling rates. Also, during deuterium(D)-tritium(T) operation, there is a safety issue as only 700 g of mobilizable T are allowed to be stored in the ITER wall. Tungsten (W), a high-Z refractory metal, is marked for use as a plasma-facing components (PFC) material in the ITER divertor. The thermal properties of W allow it to survive the expected heat loads at the ITER strike points but, perhaps more importantly, W also has low hydrogenic solubility and, in the absence of a strong hydrogenic trap production mechanism, is expected to have low hydrogenic retention levels. Molybdenum (Mo) shares many of the same properties as W including low hydrogenic solubility, high thermal conductance, and high hydrogenic diffusion rates. Although Mo can not be used in a burning fusion device, such as ITER due to activation concerns, it is used in many current tokamaks (e.g. Alcator C-Mod, FTU, TRIAM, etc.) and fusion studies. Numerous laboratory studies have confirmed low hydrogenic retention in W [1-4] and Mo [5,6]. From this it has been assumed that W and Mo have an advantage over carbon-based materials (i.e. graphite, CFCs) with respect to trapped fuel inventory in fusion applications. However, it should be noted that these laboratory studies are performed at ion flux densities that are orders of magnitude lower than what is measured in current tokamaks and what is expected in ITER.

Recent studies have identified a mechanism for trap production in refractory metals that may be linked to high plasma flux densities. It has been postulated that exposure of refractory metals (W and Mo) to a high flux of low energy (≤200 eV) ions leads to a build-up of stresses in the material lattice due to the low hydrogenic solubility of these metals [3,4]. These stresses are relieved through deformation of the lattice and the creation of vacancies, dislocations or voids, which then represent hydrogen trapping sites. There are indications that this trap production mechanism is dependent on the incident ion flux density [3], but the relationship and how it extrapolates to ITER-relevant flux densities is not clear.

A campaign in Alcator C-Mod was performed with bare Mo PFC (10-15 at% B on the surface of most tiles). During this campaign 10 plasma discharges were specifically devoted to deuterium (D) retention with care taken to avoid disruptions and having similar discharge characteristics. For those dedicated discharges, the D retention increased linearly at roughly 1% of incident fluence depending on how the retained and incident fluences are calculated [7]. Both the rate of this D retention and the lack of saturation in the Mo PFCs are unexpected. It was also clear that the retention was not due to co-deposition with B [7]. The amount of retention was measured by gas balance calculations and exceeds any level of retention measured in W in laboratory experiments. This raises the question of whether or not W and Mo truly have similar retention properties, especially in a high plasma flux environment, such as a tokamak divertor.

The purpose of this study is to expose poly-crystalline tungsten and molybdenum samples to plasma flux densities and energies that are expected at or near the ITER divertor strikepoints. This allows the hydrogenic retention at these high flux densities ($\sim 10^{24}$ D/m$^2$·s) to be measured experimentally rather than relying on extrapolations from ion beam or low-density plasma experiments. This also can demonstrate any differences in the retention properties of these two refractory metals at high plasma flux densities, which would allow for a better understanding and comparison of laboratory and tokamak retention results found in literature.

## 2. Experiment

W and Mo targets were exposed to ITER divertor-relevant deuterium plasmas in the linear plasma device Pilot-PSI. The cascaded arc plasma source used in Pilot-PSI produces high plasma densities ($\leq 10^{21}$ m$^{-3}$) at low electron temperatures ($T_e \leq 5$ eV) [8]. The plasma is magnetically confined with an axial B-field to a narrow column (FWHM ~ 1cm) with the highest densities and temperatures located at the center of the column. The plasma electron density and temperatures are measured with Thomson scattering [9]. A 1-D spatial scan of the electron density and temperature across the column width for a typical plasma exposure can be seen for both the W and Mo exposures in Fig. 1. Each plasma shot ran for a maximum of 20 s and the $n_e$ and $T_e$ values are repeatable to within 10 % for each shot. For targets with exposure times >20 s, multiple, sequential 20 s shots were used. All W targets were electrically grounded for the exposures.

The W and Mo targets are mechanically clamped to an actively-cooled copper heat sink. A Mo clamping ring is used to secure the target to the heat sink. The surface temperature for the W exposures was measured with a vis-IR spectrometer (600-950 nm) and a single-colour pyrometer. The surface temperature for the Mo exposures was measured with a near-IR (900-

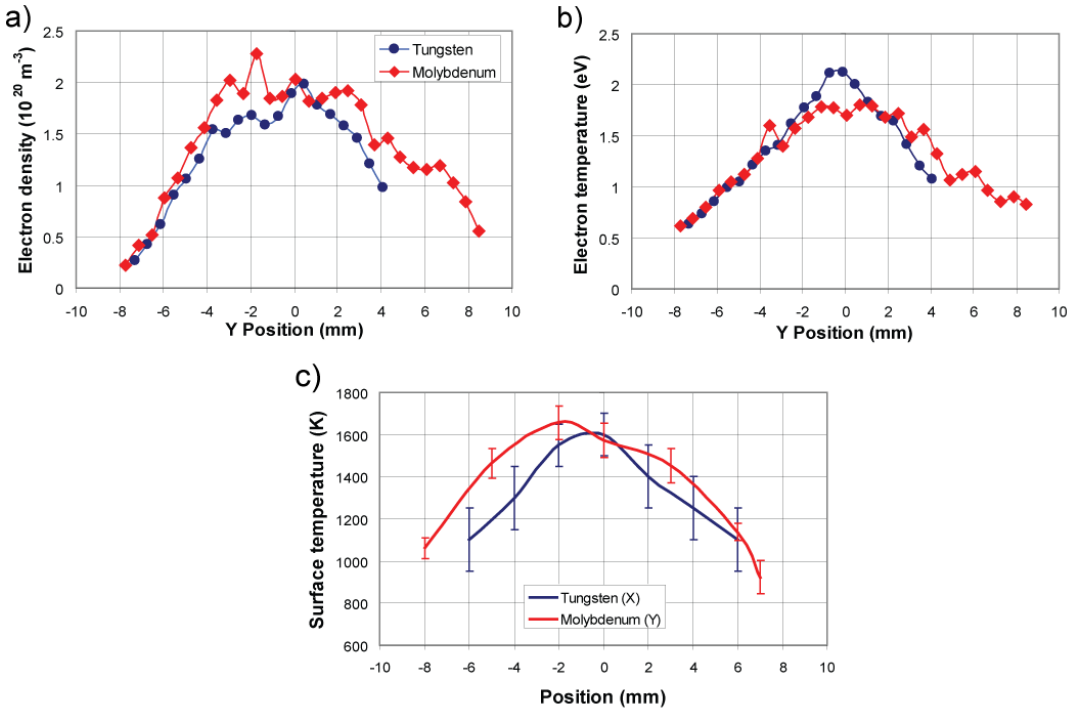


*Fig. 1: a) Electron density and b) electron temperature from a typical Thomson scattering profile in the vertical (Y) direction for the Pilot-PSI plasma column. c) The surface temperature of the W and Mo targets as a function of radial position (may be an over-estimation, see section 3).*

1700 nm) multi-wavelength spectropyrometer. 1-D surface temperature profiles were obtained by shifting the analysis area across the target for sequential plasma discharges and can be seen for W and Mo in Figure 1c. Typical central surface temperatures are ~1600 K and decreasing to ~1000 K near the edges of the target. It should be mentioned that there are indications that these pyrometery measurements significantly over-estimate the true target temperature. This will be discussed in more detail in section 3. All targets are disks of 20 mm diameter (16 mm diameter exposed area) and 1 mm thickness. All targets are exposed in the "as received" condition (rough surface, unannealed). Both Mo and W were purchased from Plansee and had an atomic purity content of 99.9 % and 99.97 % respectively.

The hydrogenic retention was determined with ex-situ nuclear reaction analysis (NRA) using the $D(^3He,p)\alpha$ reaction. For the W targets, 2.0 MeV $^3He$ ions incident to the surface yield a probing depth of ~3 μm. For the Mo targets, 2.5 MeV $^3He$ ions incident to the surface yield a probing depth of ~4 μm. B and C were detected using the $^{10}B(^3He,p_1)^{12}C$ and $^{12}C(^3He,p_1)^{14}N$ reactions at 2.5 MeV. The NRA technique has the advantage of measuring the local concentration of D within the beam spot (~1 mm diameter) but only to the depth of the $^3He$ ion range. The hydrogenic retention of the W targets is also determined by thermal desorption spectroscopy (TDS). TDS has the advantage of determining the hydrogenic retention from the entire bulk of the W but it has not spatial resolution and so the retention is averaged over the entire surface. The TDS is performed by clamping the W target to a ceramic heater and linearly ramping the temperature to 1273 K at a ramp rate of ~1 K/s and monitoring the mass 3 (HD) and mass 4 ($D_2$) signals with a quadrupole mass spectrometer. These singals are calibrated with $D_2$ and $H_2$

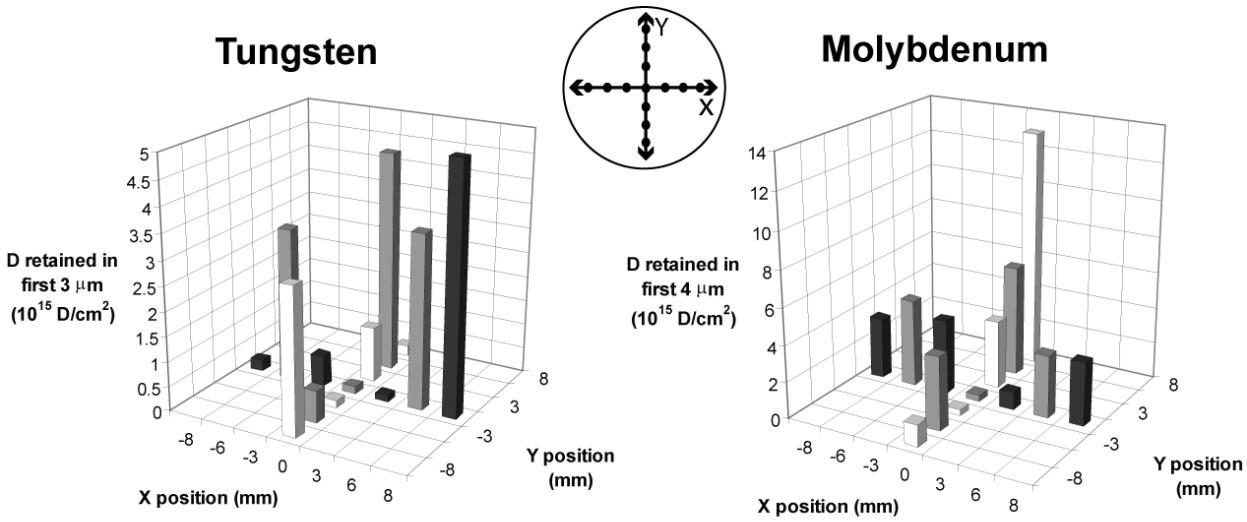


*Fig. 2: A 2-D NRA spatial scan of the W and Mo target with 80 s plasma exposure time.*

calibrated leaks. The mass 3 calibration is taken as the average of the mass 4 and mass 2 calibrations.

## 3. Results and Discussion

The NRA results were taken from various points on the target surface and each point corresponds to a different set of plasma parameters and surface temperature (see Fig. 1). The different analysis points on the surface correspond to different D retention rates. A 2-D NRA scan (see Fig. 2) of W and Mo targets with 80 s of plasma exposure reveals that the D retention increases with radial distance from the center in all directions. It should be noted that measurements at 8 mm off-center are at the point where the molybdenum clamping ring overlaps with the W target, so shadowing effects from the molybdenum ring could be responsible for the low retention measurements at some of the 8 mm off-center points. It is well known that surface temperature plays a role in the hydrogenic retention properties of W and Mo [1,2,5], and there is a large difference between the measured temperature at the center of the target (~1600 K) and at the edge (~1000 K, see Fig. 1c). Thus it is likely that the lower surface temperatures in the off-center regions are responsible for the higher D retention measured there despite this being a region of lower plasma flux and fluence.

The D retention is also measured as a function of plasma exposure time, which can be converted to fluence with the use of the Bohm sheath criterion and the Thomson scattering profile. In Fig. 3 the areal D retention (D/cm$^2$) in the first 3 μm of the W surface and 4 μm of the Mo surface is plotted as a function of plasma exposure time for the center of the target (0 mm) and a point 6 mm off center. The measured retention at the center point is typically very low (D concentrations $\leq 4 \cdot 10^{14}$ D/cm$^2$) for both W and Mo despite the high plasma flux density (~$10^{24}$ D/m$^2$·s) received in that region. The 6 mm off-center point has an order of magnitude or more higher retention than the center point for all targets despite being in a region exposed to lower flux densities (~$10^{23}$ D/m$^2$·s) and fluences.

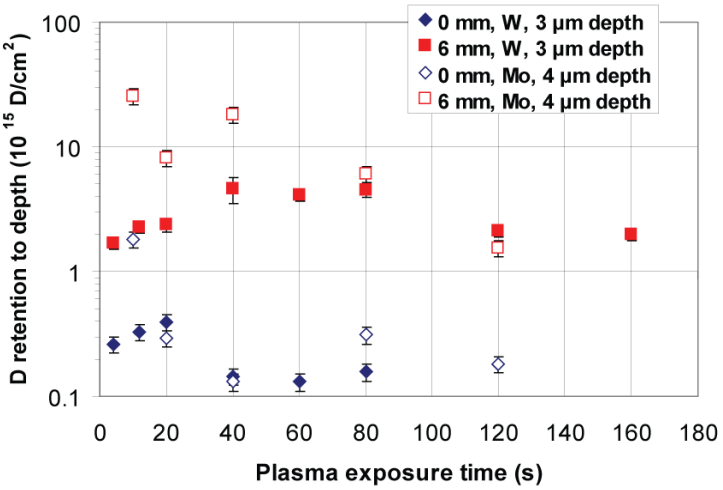


*Fig. 3: D retention in W and Mo as determined by NRA as a function of plasma exposure time for the center of the target ($T_{surf}$ ~ 1600 K, ~$10^{24}$ D/m$^2$·s) and a point 6 mm off-center ($T_{surf}$ ~ 1100 K, ~$10^{23}$ D/m$^2$·s). Total fluence can be calculated using the appropriate plasma flux density and exposure time*

Another observation from Fig. 3 is that, for the 6 mm off center spot, the retention in Mo is significantly higher than in W for the lower fluences/exposure times. However at the higher fluences the retention in W and Mo are very close in value. In fact, the retention in Mo appears to be decreasing with increasing plasma fluence. The Mo target with 10 s of plasma exposure had a measured surface temperature of ~200 K less than all other Mo targets. This helps explain why particularly high retention and deposition is seen in this target, especially for the 0 mm position. However, all other targets had measured central (0 mm) surface temperatures within 50 K of those shown in Fig. 1c. Another likely influence is surface contamination. For the Mo targets there is a layer of deposited boron (as measured by XPS and NRA) that likely originates from boron nitride spacers that are used in the plasma source. An unusually high content of carbon is also detected in the off-center spots analysed by XPS and NRA. The source of this carbon contamination is less obvious, but there are certainly many surfaces inside Pilot-PSI that have

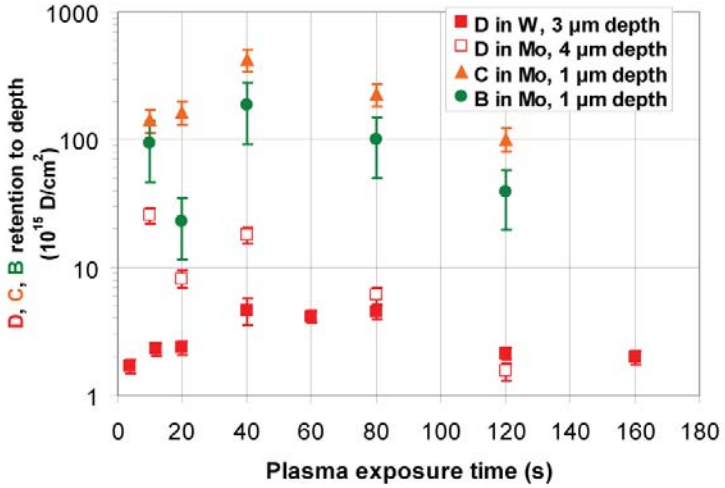


*Fig. 4: The D concentration for a position 6 mm off-center for W and Mo targets. The boron and carbon content for the Mo targets as measured by $^3$He NRA is also shown. The W target showed no signs of boron or significant carbon deposition on the surface.*

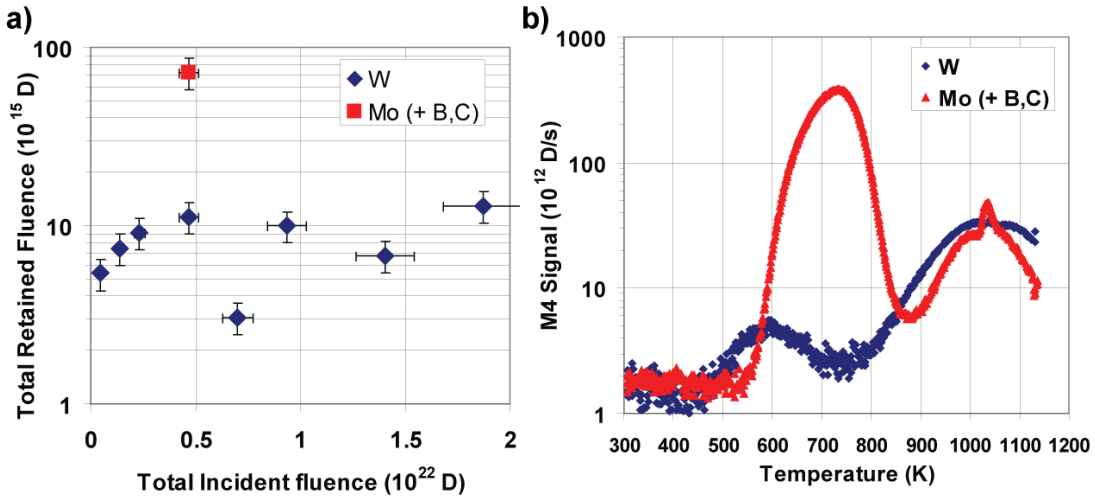


*Fig. 5: a) The retained D in W and Mo targets as a function of incident D ion fluence and b) the mass 4 ($D_2$) desorption spectra as a function of desorption temperature for W and Mo targets with 40 s plasma exposure (~4.5 · $10^{21}$ D total fluence).*

carbon coatings from previous carbon erosion and methane puff experiments. However, these layers of boron and carbon were not detected on the previously exposed W targets, so it is deduced that the surface deposition is likely due to the use of an unconditioned plasma source. A plot of the D, B, and C content for the Mo target (as well as the D content for the W target for comparison) is shown in Fig. 4. There is some correlation between the D content and the B and C content, however the D content decreases by approximately an order of magnitude as the fluence increases while the B and C content only decreases by a factor of ≤2, if at all.

The TDS results in Figure 5a show the total retained D in the W targets as a function of total incident D fluence. The incident fluence is calculated based on an integration of the local flux density (assuming Bohm sheath criterion) as determined by the Thomson scattering profiles (Figure 1). The Mo target with 40 s of plasma exposure is also included in the plot. In figure 5b, the mass 4 ($D_2$) desorption signal is plotted as a function of temperature for the Mo and W targets with 40 s of plasma exposure.

Much like the NRA results, the TDS results show the D retention in W has no apparent dependence on the incident plasma fluence as seen by the scatter in measured retention values in Figure 5a. The total D content in the Mo target is a factor of ~6 greater than the corresponding W target. This is similar to what was seen with NRA at 6 mm off center where the Mo target had a D content a factor of ~4 greater than the W target (for 40 s, see Fig. 2). The absolute value of the D retention in the W and Mo is low when compared to the incident D fluence (retained fraction $10^{-7}$-$10^{-5}$). The mass 4 signal from the thermal desorptions of the W and Mo targets with 40 s plasma exposure is plotted in Fig. 4b. From the clean W target there are desorption peaks at ~600 K and ~1050 K with the higher temperature peak dominating the retention. For the Mo target with B and C deposition there are desorption peaks at ~730 K and ~1050 K (note the spike in the 1050 K peak was due to momentary loss of temperature control) with the lower temperature peak dominating retention.

The high temperature peaks for both W and Mo have similar magnitudes and occur at similar temperatures, likely indicating that this peak corresponds to a trapping mechanism that is occurring in both materials, which is thought to be the trapping of D in voids and vacancy clusters. The lower temperature desorption peaks are the origin of the differences in retention properties between these two targets. For the Mo target the lower desorption peak occurs at ~730 K where as, for the W target, the lower desorption peak is at ~600 K. The different temperatures of these peaks suggest a different trap mechanism is occurring in the Mo target as in the W target. It is postulated that for the clean W target, the lower temperature peak corresponds to D trapping in lower energy trap sites such as monovacancies in the lattice. For the Mo target it is postulated that the lower desorption peak corresponds to D co-deposition with B and C. Since the lower temperature peak is ~100 times greater in magnitude for the Mo target than the W target this would also suggest that the presence of B and C deposits on the surface is the main factor for the difference in retention between the W and Mo targets.

It is interesting to note that the low temperature desorption peak for Mo and W occur at temperatures that are lower than the measured surface temperature of the targets during the exposures. If the measured surface temperatures are accurate, then how does this peak exist? If the peak was small, such as the lower temperature peak for the W target, this might be explained by small amounts of D implanted and trapped in empty trap sites after the plasma exposure is over or as the target cools down, but this explanation can not explain a large peak that is thought to be due to co-deposition processes occurring through out the plasma exposure. More likely this is an indication that the pyrometry measurements of the surface are significantly over-estimating the true temperature. With pyrometry this can occur if a small fraction of the measured surface area is at a heightened temperature (hotspots) since the total emission scales as $T^4$. This hypothesis is also supported by the fact that we have measured high temperatures even with low total signal strengths. These micro-hotspots, if they exist, are likely formed due to some special surface morphology of the targets although they have undergone no special surface preparation before plasma exposure. Perhaps when thermal desorptions of the other Mo targets are performed a more satisfactory explanation can be formed.

So while the enhanced retention in Mo is connected to co-deposition with B and C surface impurities, the explanation of why the D retention in Mo decreases with increasing plasma fluence remains incomplete. There are other possible effects such as bursting blisters that could be playing a role and this may become clearer as the Mo targets at higher fluence are thermally desorbed. The co-deposition of D with B was also concluded to not be a contributing factor in Alcator C-Mod [7] but that does not appear to be the case in Pilot-PSI. Exposures of clean Mo targets would also help clarify many of the questions raised in this investigation and is marked for future work.

## 4. Conclusions

The main indication from these results is that W and Mo targets retain very little D when compared to the amount of D incident to the surface ($D_{retained}/D_{incident} \sim 10^{-7}$-$10^{-5}$) for these plasma and surface conditions. The W results show no clear dependence of retention on incident fluence. It is concluded that the plasma exposure itself has little influence on the trap concentration in the W and the scatter in retention data for W seen in Figures 3 and 5a is due to scatter in the population of natural or inherent defects and trap sites present in the W due to fabrication and

machining. It is concluded that the high surface temperature of the W during plasma exposure has eliminated or neutralized the stresses formed in the high-Z lattice due to the implantation of a high flux of low energy D ions into the surface.

The retention in the Mo targets is higher than in W for lower fluences but at higher fluences the two materials have comparable D retention rates. NRA and TDS analysis indicate that the enhanced retention seen in Mo is due to the boron and carbon deposits detected on the surface that were not present for the W targets. The explanation for the decreasing retention with increasing plasma fluence remains incomplete. It is suspected that D is co-deposited with B and C on the Mo surface which results in a desorption peak at ~730 K in the TDS spectrum but it is not understood how this process can occur if the surface temperatures of the Mo targets were measured to be 1000-1600 K during the plasma exposure are accurate.

There are indications that the retention behaviors for W and Mo are similar but exposures with clean Mo targets are needed to confirm this. Overall the trends of retention with plasma fluence observed in combination with the absolute amount of D retained when compared to the incident fluence are encouraging in terms of tritium retention in ITER. However, it should be noted that PFC irradiation and lower surface temperatures could both significantly increase the retention in W and Mo and further work is needed in these areas.

## 5. Acknowledgements

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