

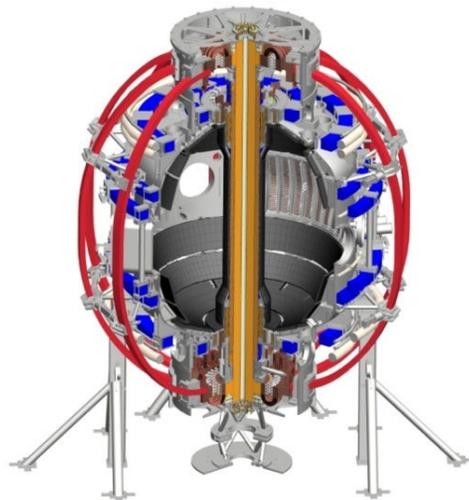
# Compositional changes of lithium coatings on TZM molybdenum during plasma bombardment

**Tyler Abrams**

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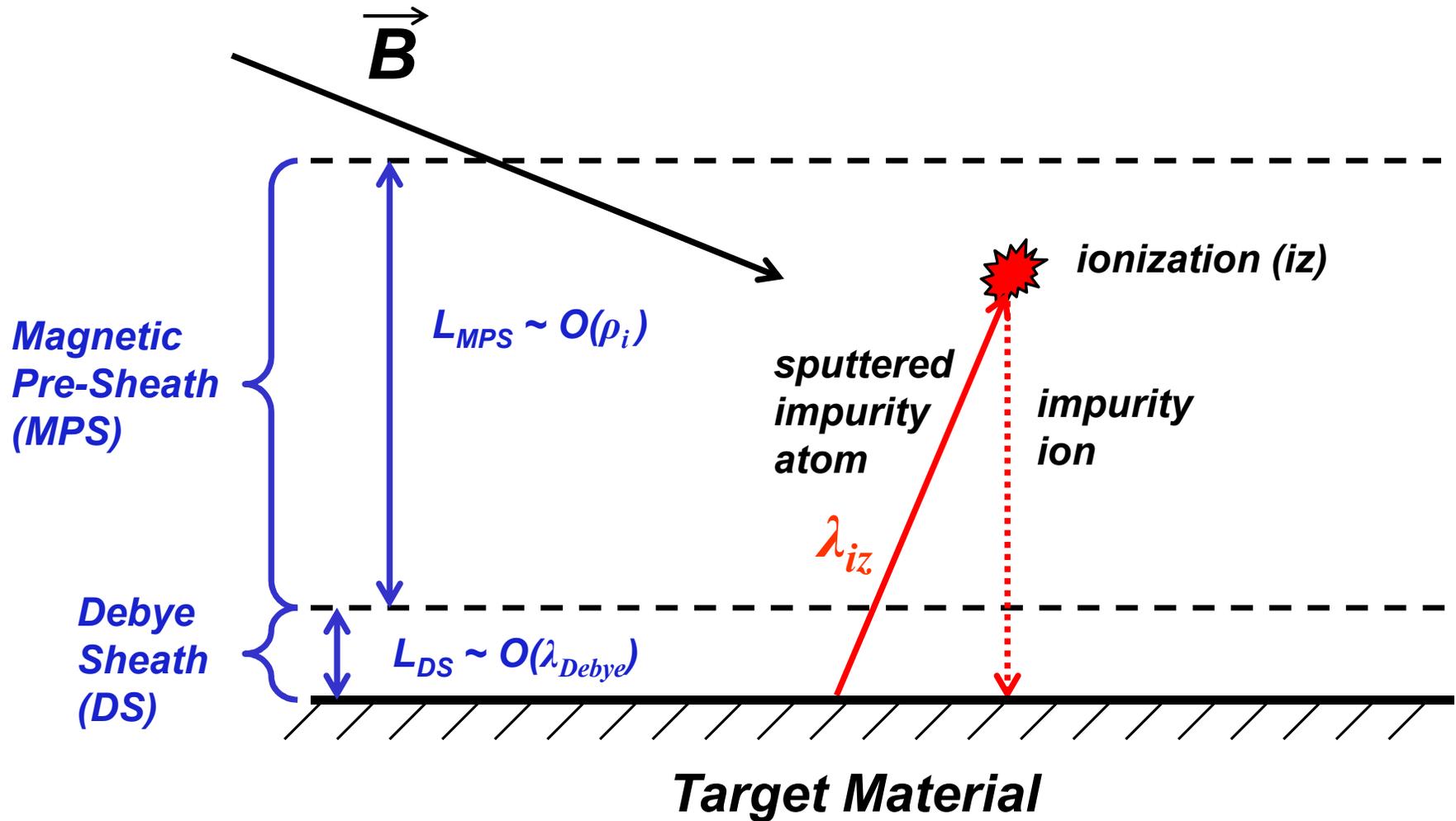


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## Abstract

The Titanium-Zirconium-Molybdenum alloy TZM has previously been used as a metallic plasma-facing component in Alcator C-Mod is being considered for use in NSTX-Upgrade. The time evolution of lithium (Li) coatings on TZM are studied in Magnum-PSI, a linear plasma device capable of ion fluxes up to  $10^{25} \text{ m}^{-2}\text{s}^{-1}$  at electron temperatures  $< 5 \text{ eV}$ . A series of 5 s exposures to a  $\text{D}^+$  plasma were run on a bare TZM sample then repeated after an evaporation of 100 nm of Li. The temporal and spatial variation of neutral Li and oxygen (O) radiation were monitored using optical emission spectroscopy (OES) and a fast camera with a Li-I (671 nm) filter. The O-I (777 nm) line intensity decreased during discharges while the Li-I line intensity increased. The ionization mean free path (MFP) of Li was calculated and validations against the ADAS collisional-radiative model (CRM) will be reported. Separate measurements of physical sputtering rates with a 100-1000 eV  $\text{D}^+$  ion beam incident on Li-coated TZM were also obtained and compared with theoretical predictions.

# Local material migration in the divertor occurs at fast gross rate but slower *net* rate



Adapted from P. Stangeby, PSI 2012

## Net erosion rates have been explored over a limited parameter range

Experiment	Ion Flux (m <sup>-2</sup> s <sup>-1</sup> )	Magnetic Incidence	Ion species	Target Material	Result
PISCES-B	8*10 <sup>21</sup>	normal (90°)	D <sup>+</sup> , He <sup>+</sup>	Li/O mixed material	Complete removal of O layer after ~400s (unknown thickness) <sup>1</sup>
DIII-D (DiMES)	6*10 <sup>23</sup>	grazing angle	D <sup>+</sup> , C <sup>+</sup>	Mo	~0.8 nm/s net (1.4 nm/s gross) erosion rate <sup>2</sup>
ASDEX-U ( <sup>13</sup> C Injection)	1-5*10 <sup>23</sup>	grazing angle	D <sup>+</sup>	Carbon	Re-deposition fraction ~0.28 (forward field), ~0.14 (reverse) <sup>3</sup>

1. R. Doerner et al., JNM 2001
2. P. Stangeby et al., APS 2012
3. L. Aho-Mantila et al., JNM 2011

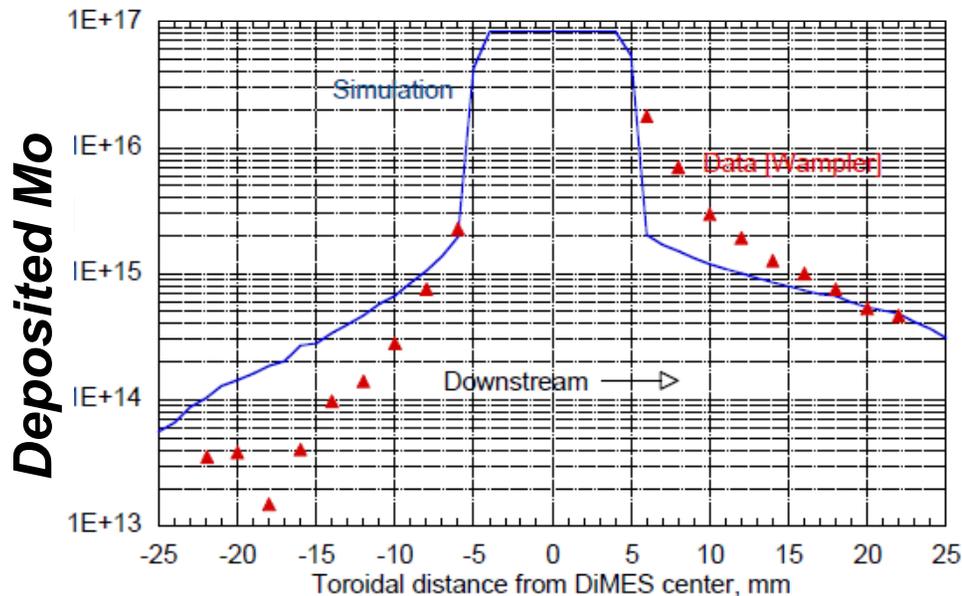
# 3D Monte Carlo codes have had limited success verifying *net* erosion rates in tokamaks

## WBC/REDEP

Net Mo erosion in C-Mod: **10x higher than simulation**

(J.N. Brooks, JNM 2011)

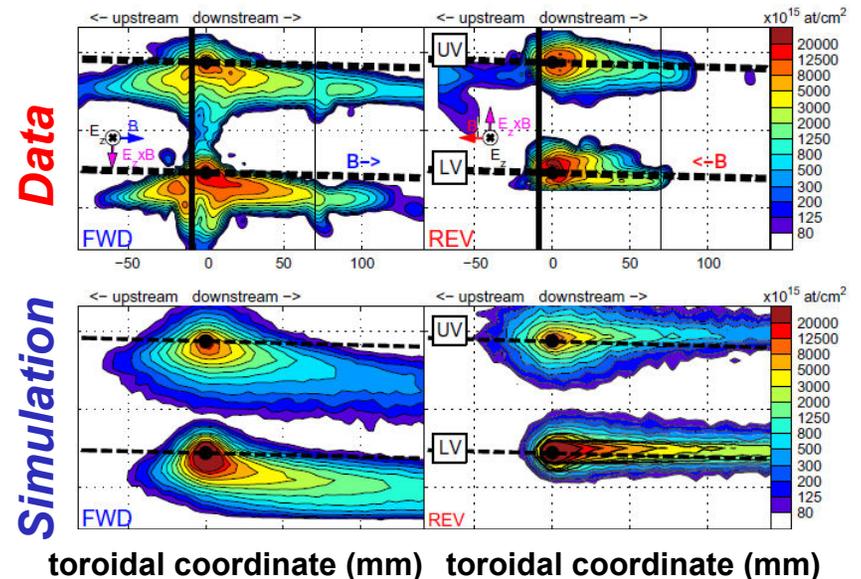
### Mo deposition profile in DIII-D



P. Stangeby, PSI 2012

## ERO/SOLPS

$^{13}\text{C}$  deposition profile in ASDEX-U



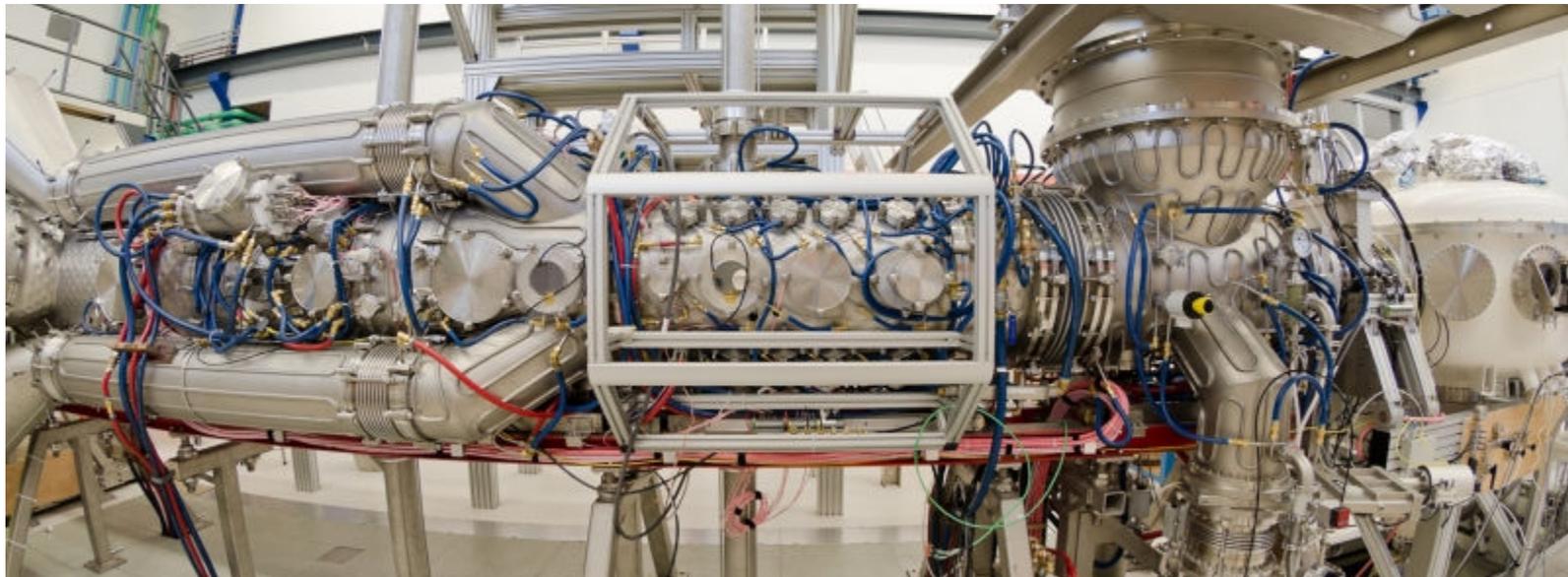
L. Aho-Mantila, JNM 2011

(downstream is relative to B field direction)

# Motivates experiments with divertor plasma simulators with better diagnostic access

- **Magnum-PSI**

- $\Gamma < 10^{24} \text{ m}^{-2}\text{s}^{-1} \text{ D}^+$ ,  $T_e < 2 \text{ eV}$ ,  $n_e < 5 \cdot 10^{20} \text{ m}^{-3}$
- 5 s pulses,  $B \sim 1 \text{ T}$  (**> 60 s, 2.5T superconducting- coming 2013**)
- Normal incidence: **no magnetic pre-sheath**
- Evaporative Li coatings applied in-situ, calibrated with quartz crystal microblanace (QCM)

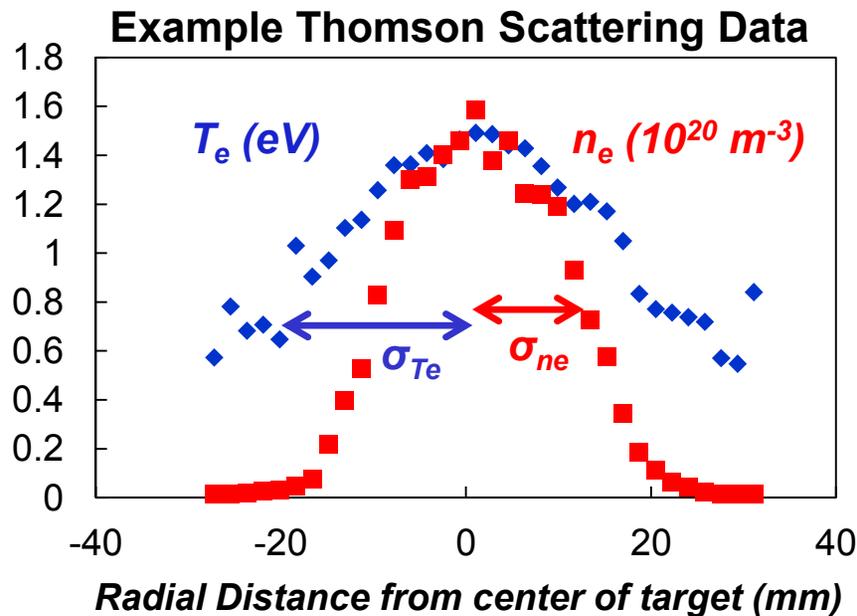


[http://www.differ.nl/en/magnum\\_plasma\\_en](http://www.differ.nl/en/magnum_plasma_en)

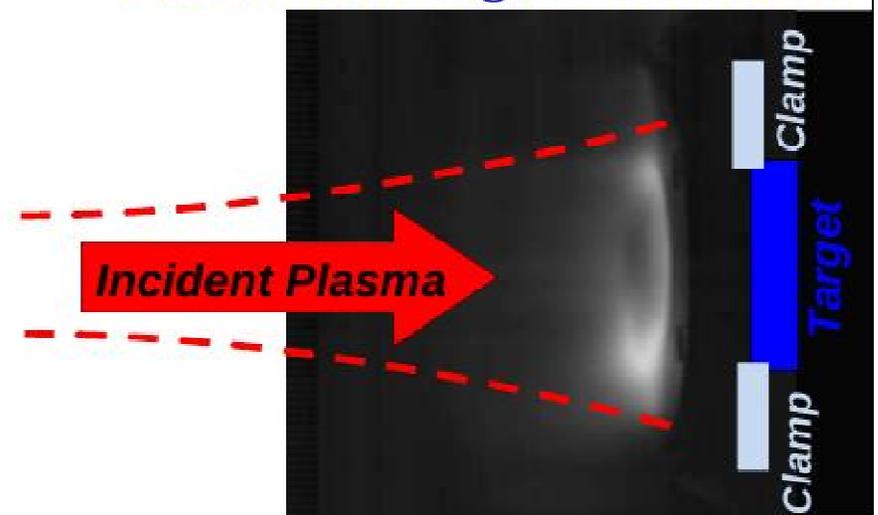
# Diagnostic suite provides *spatially comprehensive, in-situ, real-time re-deposition data*

- Thomson Scattering provides  $n_e(r)$ ,  $T_e(r)$ 
  - Single chord 2 cm from target, 1.8 mm resolution
- Visible Spectroscopy gives  $I_{\text{Li}}(t)$ ,  $I_{\text{Oxygen}}(t)$ ,  $I_{\text{H}}(t)$ 
  - $350 \text{ nm} < \lambda < 800 \text{ nm}$ , 0.2 nm, 5-10 Hz resolution
- Fast camera w/ Li-I (671 nm) filter gives  $I_{\text{Li}}(r,t)$ 
  - $0.285 \text{ mm} \times 0.285 \text{ m}$ ,  $\sim 2 \text{ kHz}$  resolution

**Measure ionization (re-deposition) rates  $S_{iz,\text{Li}}(r,t)$  and  $S_{iz,\text{O}}(t)$**



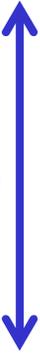
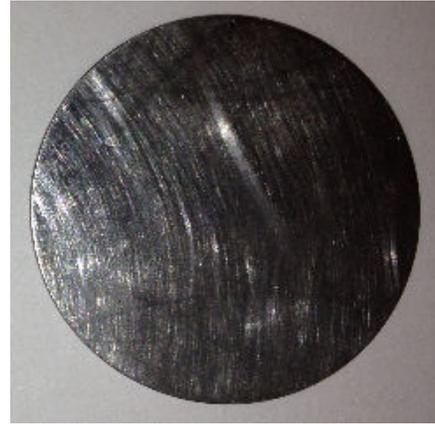
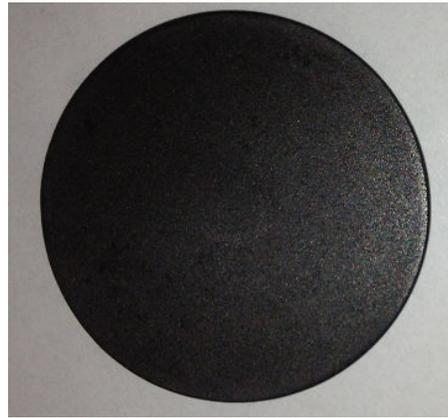
**Fast-camera Image Li-I Emission**



M.A. Jaworski

# ADAS Collisional-Radiative Model (CRM) predicts substantial *local* re-deposition of Li, negligible re-deposition of O

3 cm

	ATJ Graphite	TZM Molybdenum	Tungsten
$T_e$ (eV)	0.7 ↔ 1.7	0.6 ↔ 1.7	0.6 ↔ 1.7
$n_e$ ( $10^{20} \text{ m}^{-3}$ )	1.0 ↔ 3.8	1.0 ↔ 4.0	0.8 ↔ 3.8
$\Gamma_D$ ( $10^{23} \text{ m}^{-2}\text{s}^{-1}$ )	0.6 ↔ 3.4	0.5 ↔ 3.6	0.4 ↔ 3.4
Li MFP (mm)*	31 ↔ 0.22	94 ↔ 0.21	137 ↔ 0.22
O MFP (mm)*	5.6e6 ↔ 250	7.0e7 ↔ 230	8.3e7 ↔ 250
# discharges	5 (bare) 3 (100 nm Li)	5 (bare) 8 (100 nm Li)	6 (bare) 6 (100 nm Li)

\*calculated from ADAS Data Set (ADF11/SCD-96), [www.adas.ac.uk](http://www.adas.ac.uk), assuming  $E_{\text{ejected}}=1 \text{ eV}$

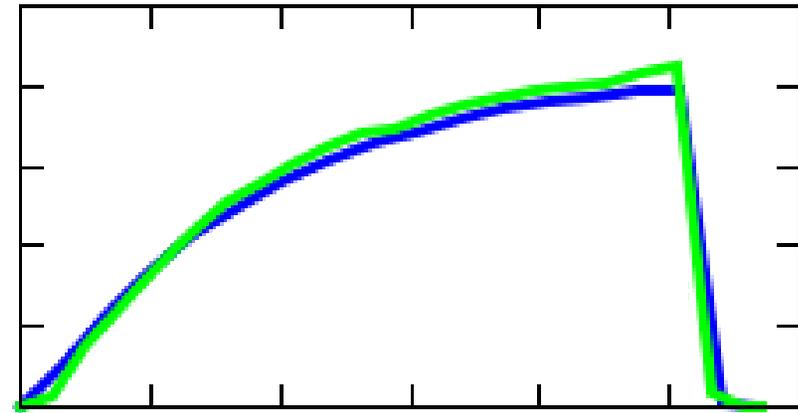
# Li-I intensity continuously increased throughout discharge, while O-I intensity decays exponentially

$T_e = 1.5 \text{ eV}$   
 $n_e = 1.5 \cdot 10^{20} \text{ m}^{-3}$   
 $t_0$   
Li-coated TZM Mo

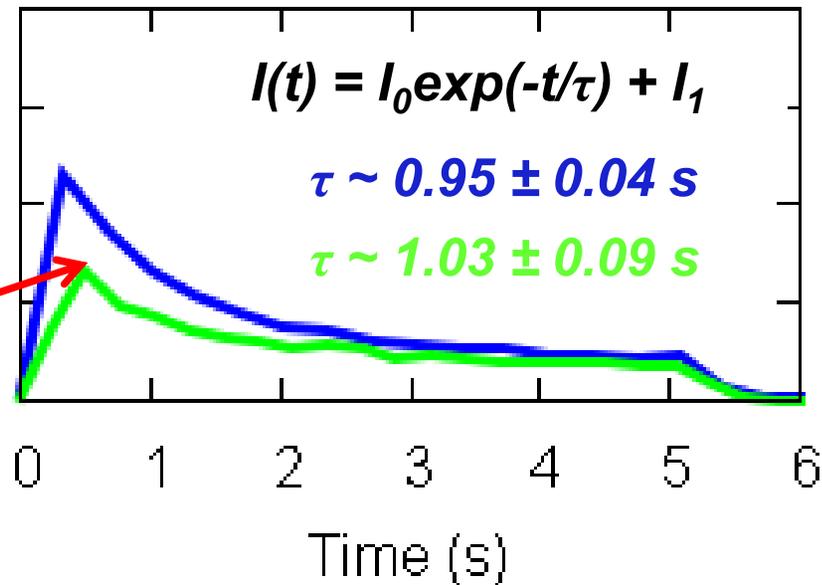
$T_e = 1.6 \text{ eV}$   
 $n_e = 1.9 \cdot 10^{20} \text{ m}^{-3}$   
 $t_0 + 9 \text{ min}$   
Li-coated TZM Mo

O-I intensity also decreases by ~40% in second discharge

Li-I Intensity (AU)



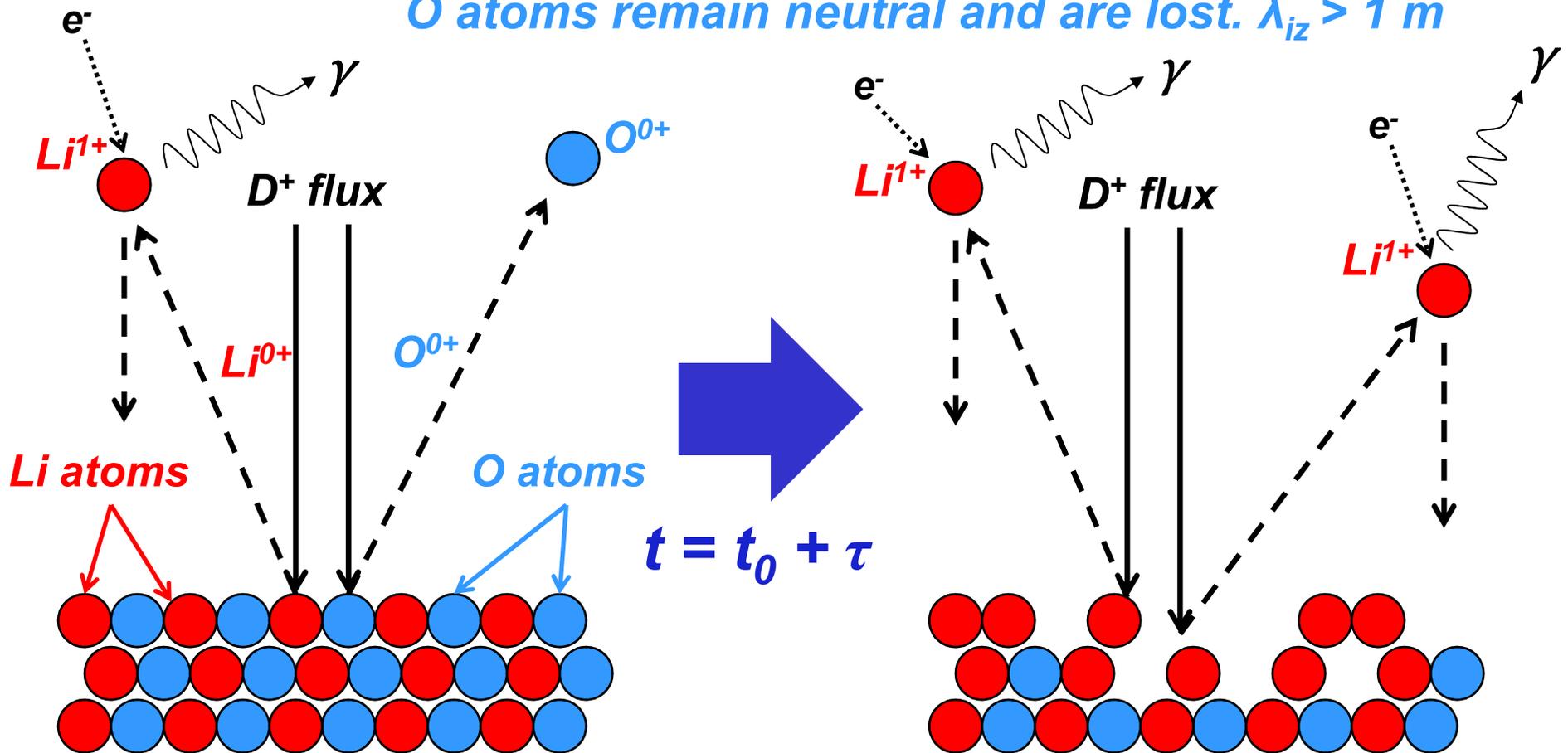
O-I Intensity (AU)



# Physical Interpretation: Difference in local re-deposition increases relative concentration of Li over time

*Li atoms are ionized by plasma and re-deposit locally.  $\lambda_{iz} \sim O(1 \text{ mm})$*

*O atoms remain neutral and are lost.  $\lambda_{iz} > 1 \text{ m}$*



# Predict *net erosion* rates from *local re-deposition* with 1-D analytic/numerical model

- Areal impurity density  $n(r,t)$

- Gross erosion rate  $R_{ero}(r,n)$

- Assume sputtering  $\sim \cos\theta$ , yield  $Y_0 = 0.1$
- Ejection energy assumed to be  $1 \text{ eV}$

- From a point source:

- Sputtered distribution  $f_{sputter}(r',t')$
- Ionization distribution  $f_{iz}(r',t')$

$$R_{ero}(r,t) = \begin{cases} Y_0 0.6 n_e \left( \frac{T_e + \gamma T_i}{m_i} \right)^{1/2}, & n > 0 \\ 0, & n = 0 \end{cases}$$

$$f_{sputter}(r',t') = \frac{1}{vt'} \Big|_{r' < vt'}$$

$$f_{iz}(r',t') = \frac{v}{\lambda_{iz}} \exp\left(-\frac{vt'}{\lambda_{iz}}\right) \Big|_{r' < vt'}$$

$v$  = ejected velocity  
 $\lambda_{iz}$  = ionization MFP

## Predict *net erosion* rates from *local re-deposition* with 1-D analytic/numerical model (continued)

- Re-deposition distribution  $f_{redep}(r')$ :

$$f_{redep}(r') = \int_{r'/v}^{\infty} f_{sputter}(r', t') f_{iz}(r', t') dt' = \frac{1}{\lambda_{iz}} \Gamma\left(0, \frac{r'}{\lambda_{iz}}\right)$$

- Total re-deposition rate  $R_{redep}(r, t)$ :

$$R_{redep}(r, t) = \int_0^{\infty} f_{redep}(r - r') R_{ero}(r', t) dr'$$

Incomplete  
Gamma  
function  $\Gamma(0, x)$



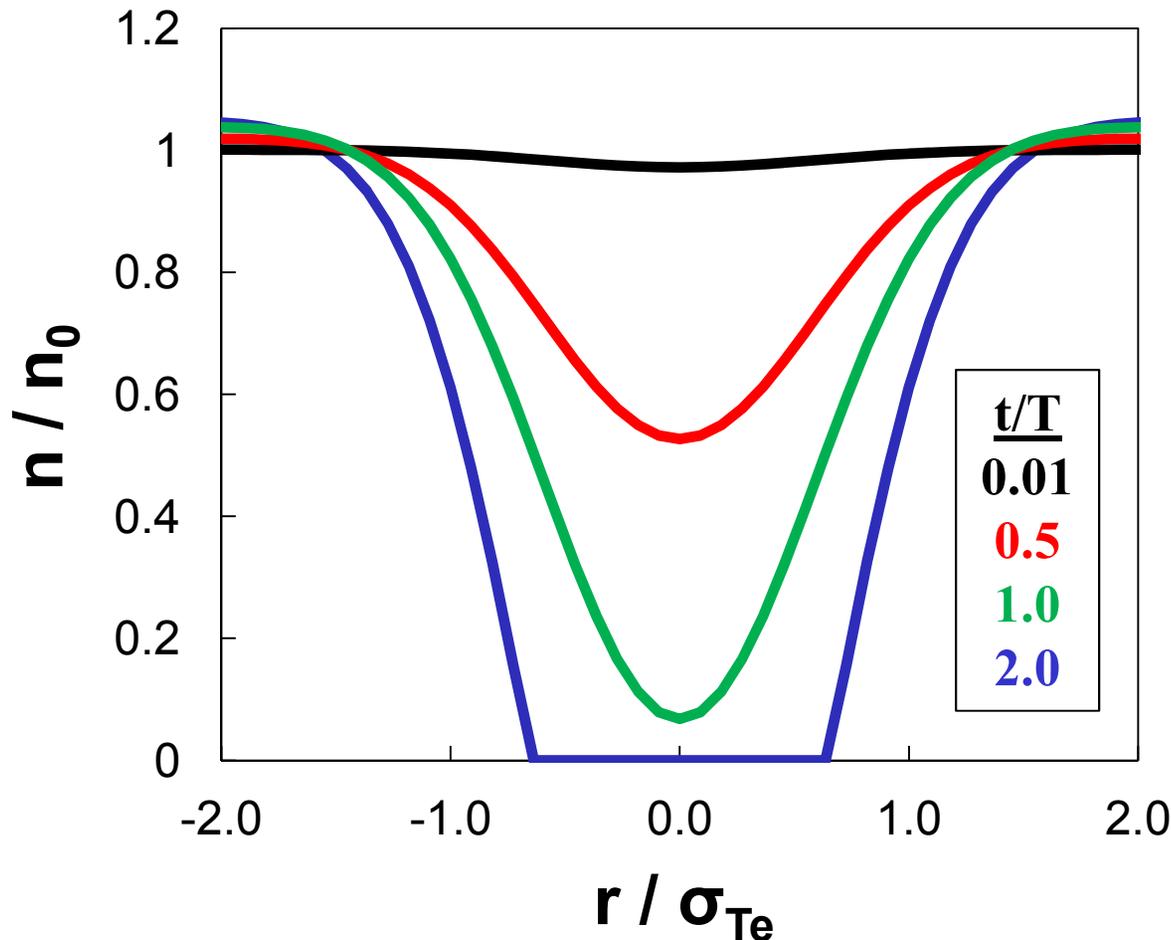
- Differential equation for  $n(r, t)$ :

$$\frac{dn(r, t)}{dt} = \underbrace{R_{redep}(r, t) - R_{ero}(r, t)}_{R_{ero, net}(r, t)} = R_{ero} [1 - F_{redep}]$$

$F_{redep}$  = re-deposition  
fraction

## Surface impurity density evolves quickly for high $\lambda_{iz}/\sigma_{Te}$

- $\lambda_{iz}/\sigma_{Te} = 185$  (typical for O in Magnum)
  - High escape probability



Initial condition: **flat areal density profile**  $n(r,t=0) = n_0$

Normalize time:

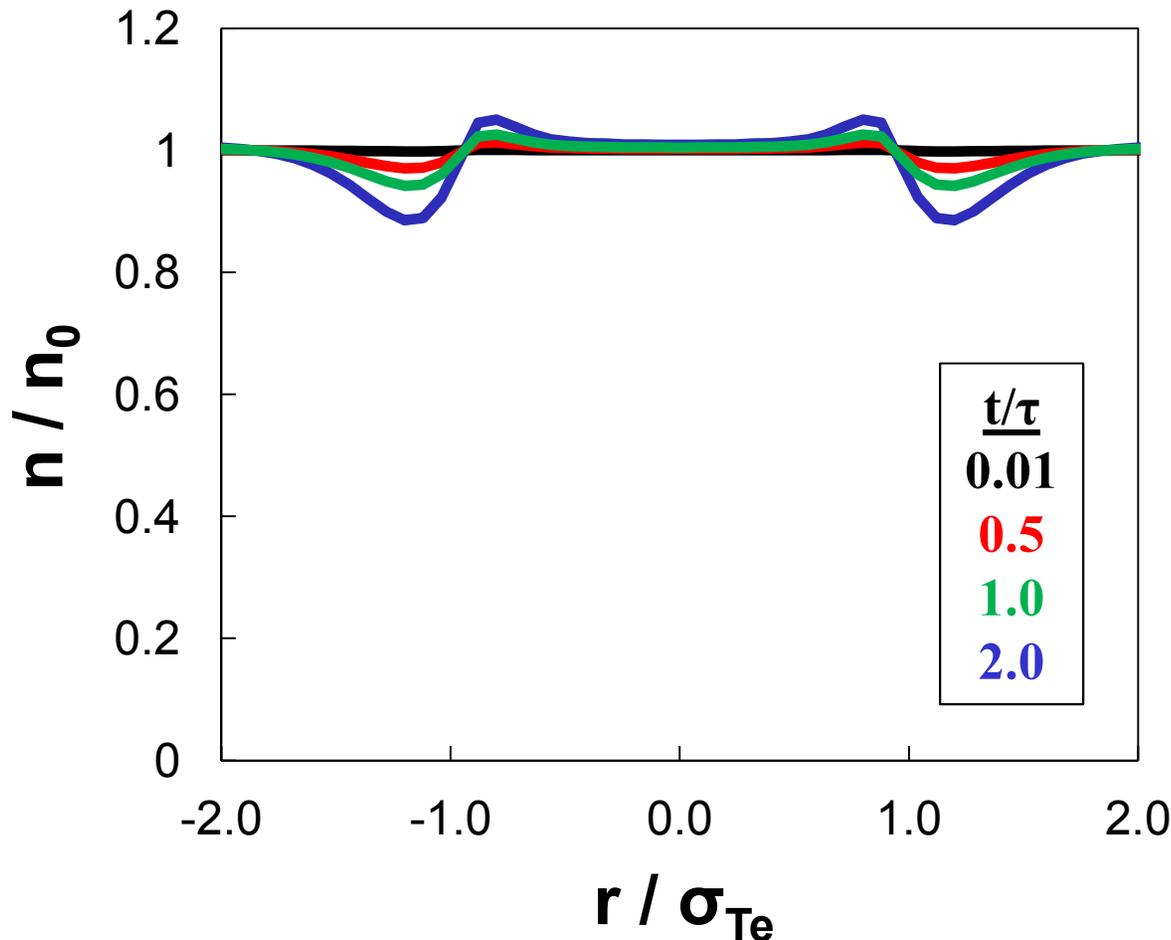
$$T = \frac{n_0}{R_{ero}(r=0, t=0)}$$

$n$  = areal impurity density  
 $r$  = radial distance from axis of plasma column  
 $\sigma_{Te}$  = HWHM of  $T_e$  profile

**Note:** choice of  $\sigma_{Te}$  as normalization for  $r$  is arbitrary.

## Surface impurity density evolves slowly for low $\lambda_{iz}/\sigma_{Te}$

- $\lambda_{iz}/\sigma_{Te} = 0.04$  (typical for Li in Magnum)
  - Low escape probability



Initial condition: **flat areal density profile**  $n(r,t=0) = n_0$

Normalize time:

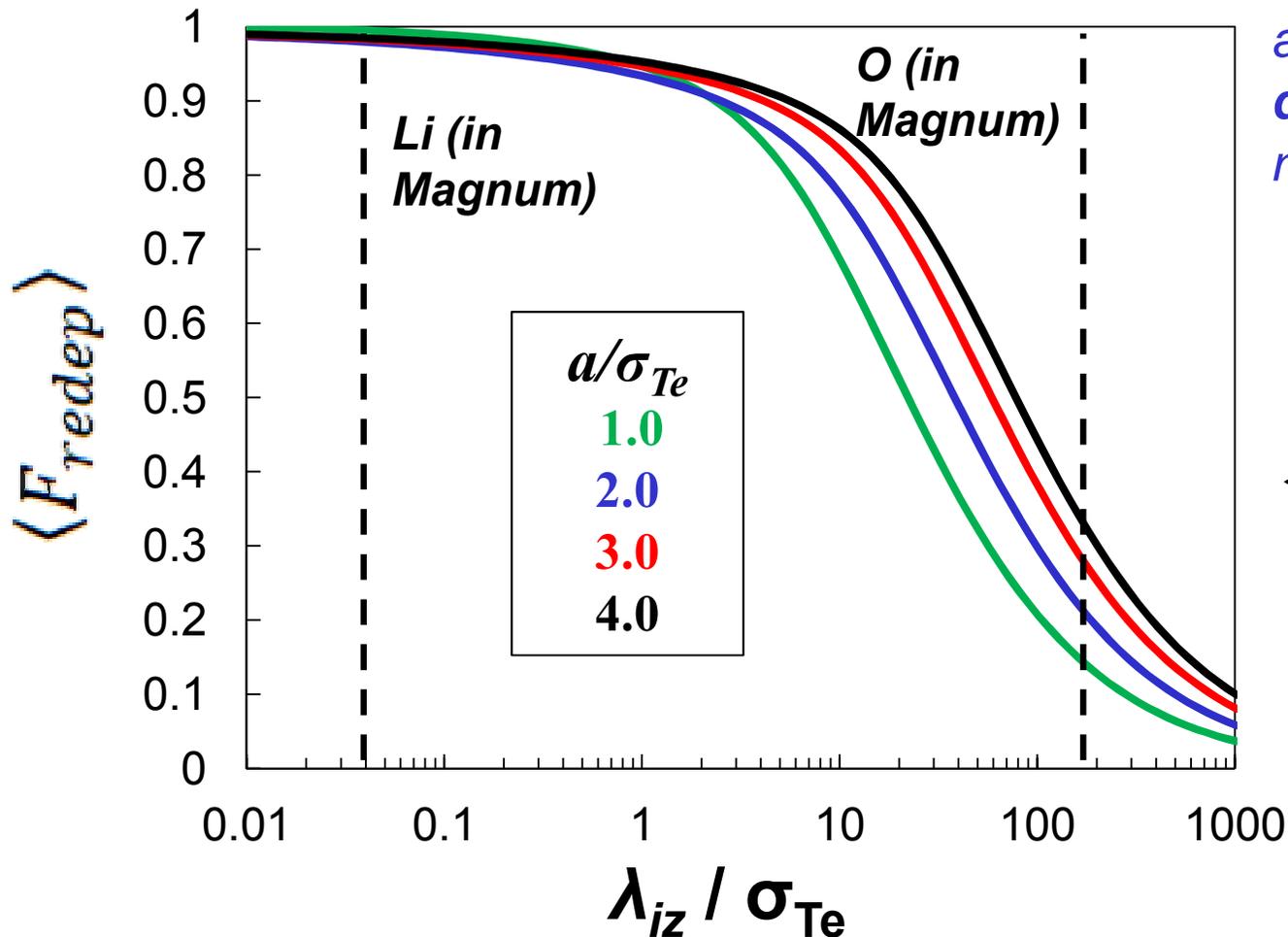
$$T = \frac{n_0}{R_{ero}(r=0, t=0)}$$

$n$  = areal impurity density  
 $r$  = radial distance from axis of plasma column  
 $\sigma_{Te}$  = HWHM of  $T_e$  profile

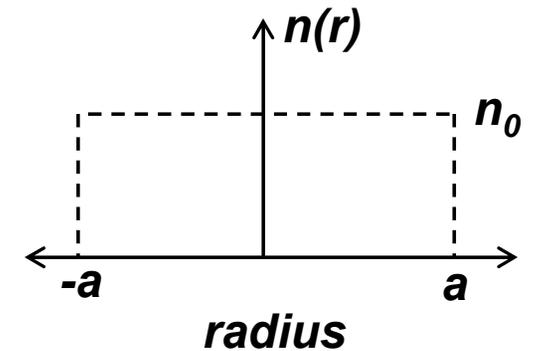
**Note:** choice of  $\sigma_{Te}$  as normalization for  $r$  is arbitrary.

# Average re-deposition fraction changes drastically between $5 < \lambda_{iz}/\sigma_{Te} < 100$

- Define  $\langle F_{redep} \rangle = \frac{1}{a} \int_0^a F_{redep}(r, t=0) dr$



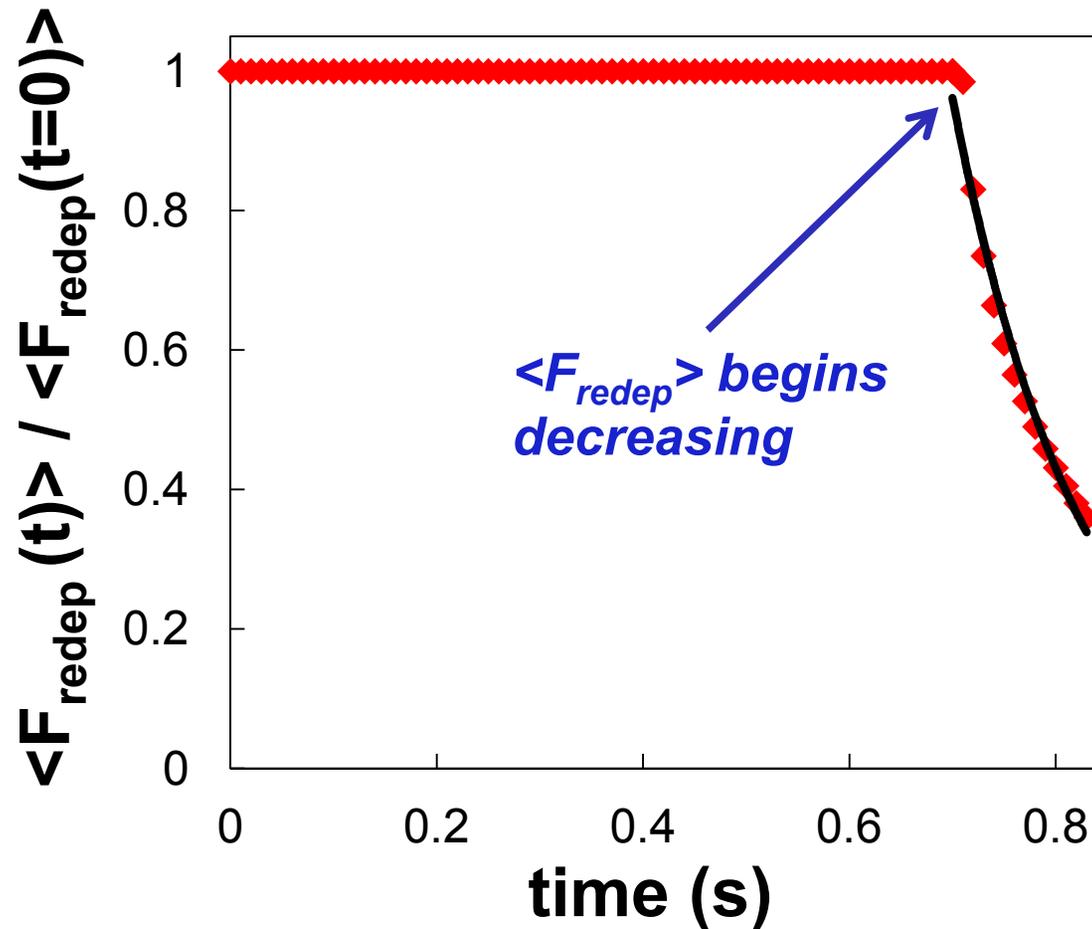
assume flat areal density profile  
 $n(r, t=0) = n_0$  for  $|r| < a$



Future work:  
 compare to data!

## Compare coating lifetime in model with experimental data

- Assume emission intensity  $\sim$  re-deposition rate
  - Fit an exponential curve to  $\langle F_{\text{redep}}(t) \rangle$  when it begins decreasing

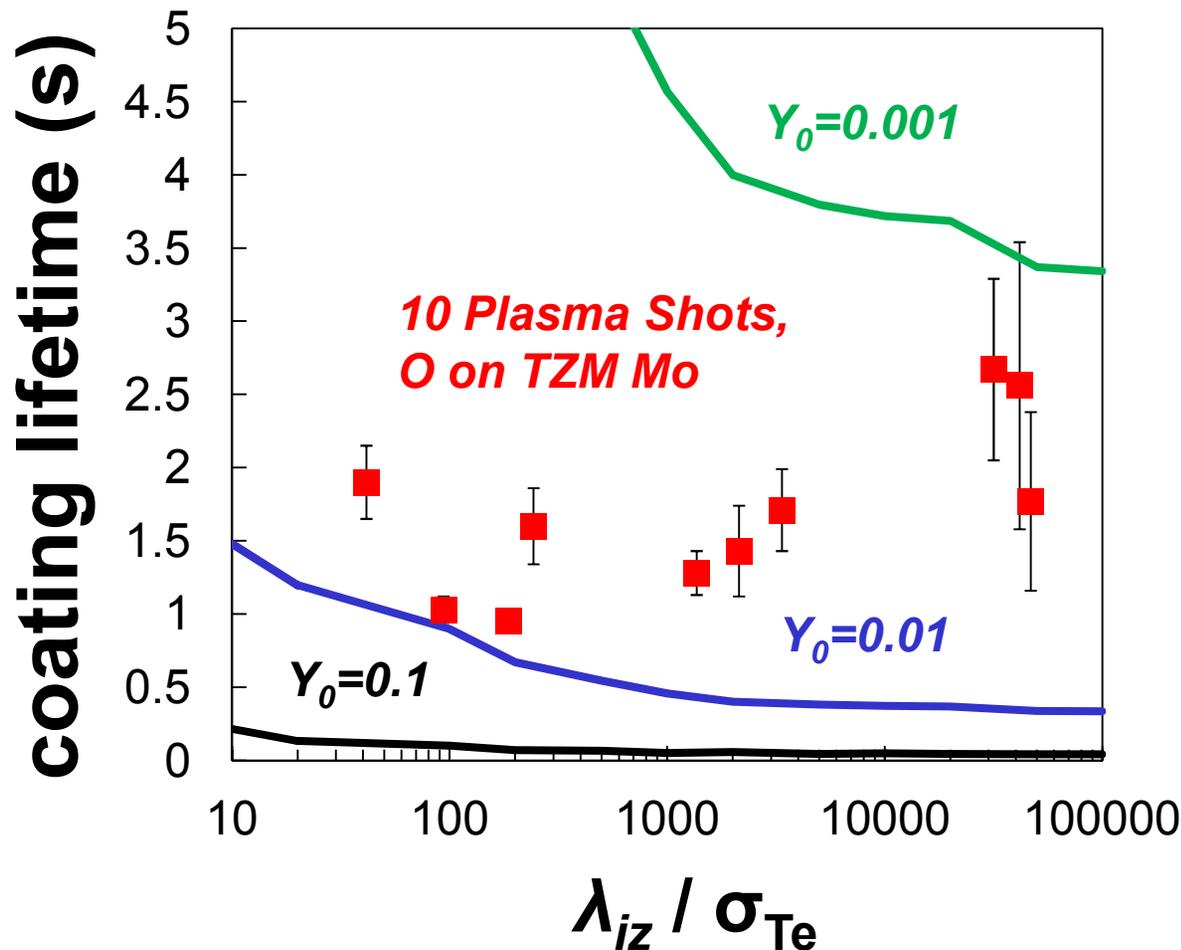


# Initial comparison with data indicates importance of absolute sputter yield determination

- TRIM gives  $Y_0=2e-4$  for 20 eV  $D^+$  on O
  - Does not take into account surface temperature

*$\tau$  calculated from spectroscopy data*

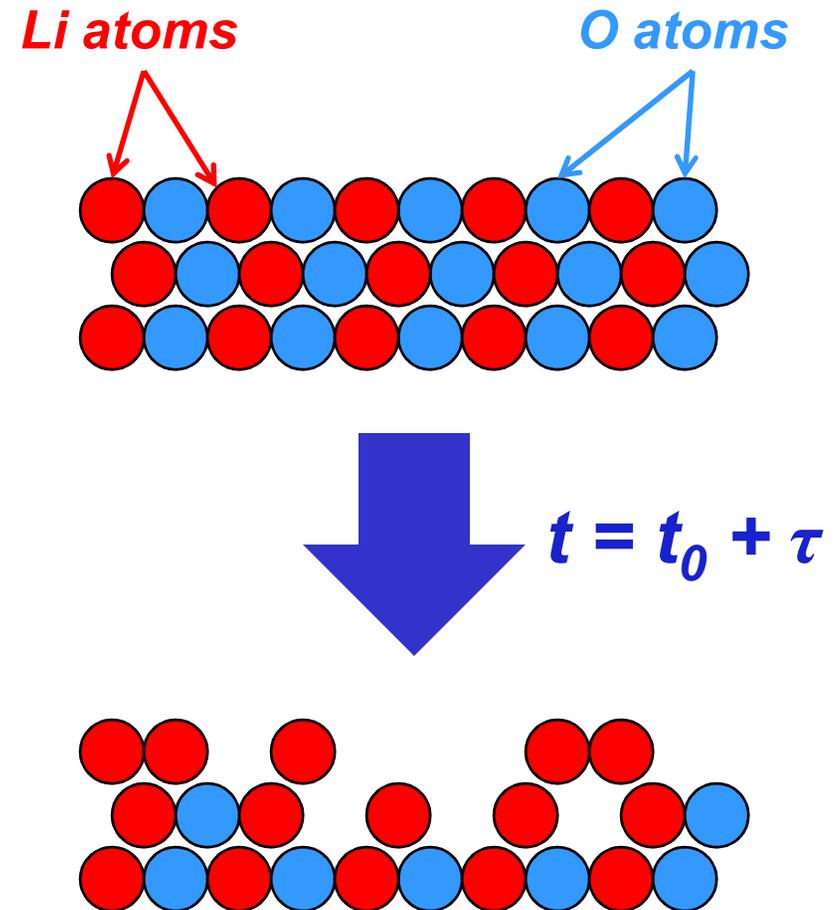
$$I(t) = I_0 \exp(-t/\tau) + I_1$$



$n_e$ ( $10^{20} \text{ m}^{-3}$ )	$T_e$ (eV)	$\lambda_{iz} / \sigma_{Te}$
1.50	1.50	190
1.90	1.60	94
0.70	0.90	4.2e4
0.60	0.90	4.7e4
1.80	1.05	3400
2.70	1.05	2100
1.00	0.90	3.1e4
2.70	1.70	41
3.50	1.30	240
4.00	1.05	1400

## Initial comparison with data indicates importance of absolute sputter yield determination (continued)

- **Mixed-material surface (D, O, Li)**
- Sputtering only occurs off **first few monolayers**
  - Bulk  $n_{\text{Li}}$ ,  $n_{\text{O}}$  unimportant
- Why does Li-I radiation increase continually?
  - Even after O-I intensity has saturated
  - If initially LiOH, should increase by factor of  $\sim 2$  and stop



## Caveats

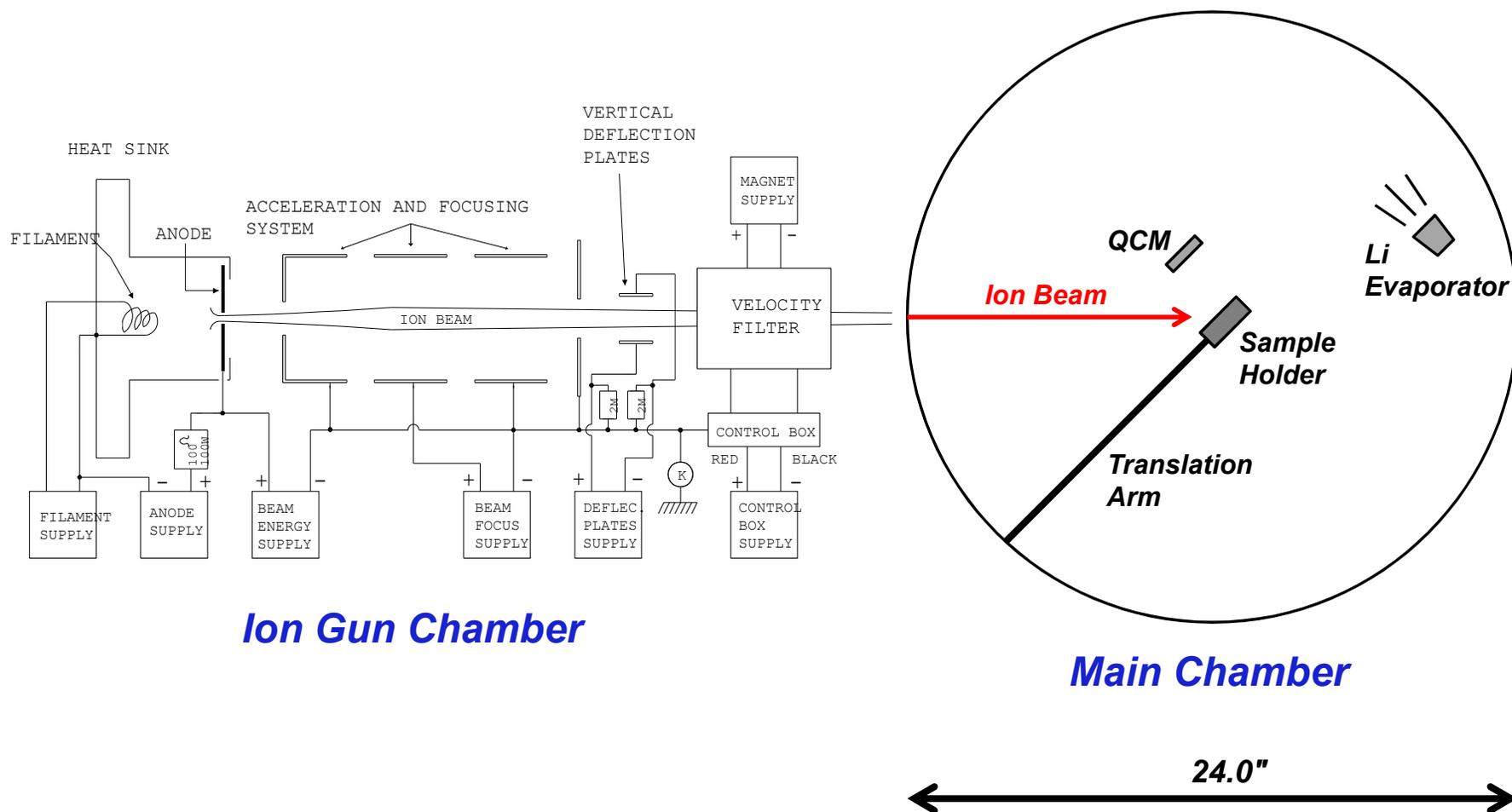
- $\lambda_{iz}$  will also vary with  $\sigma_{ne}$ 
  - But  $\sigma_{ne}$  usually scales with  $\sigma_{Te}$
- Other physics processes must be important
  - Adsorption/Desorption, Evaporation, etc.
  - Additional source/sink terms due to diffusion in the lithium material<sup>1</sup>
- Code assumes slow variation of  $\lambda_{iz}$  with  $r$
- ADAS data set contains limited resolution
  - Correct 2D interpolation between points is important

<sup>1</sup>R. Bastasz, J.A. Whaley, *Fus. Eng. Design* 2004

## Future Work

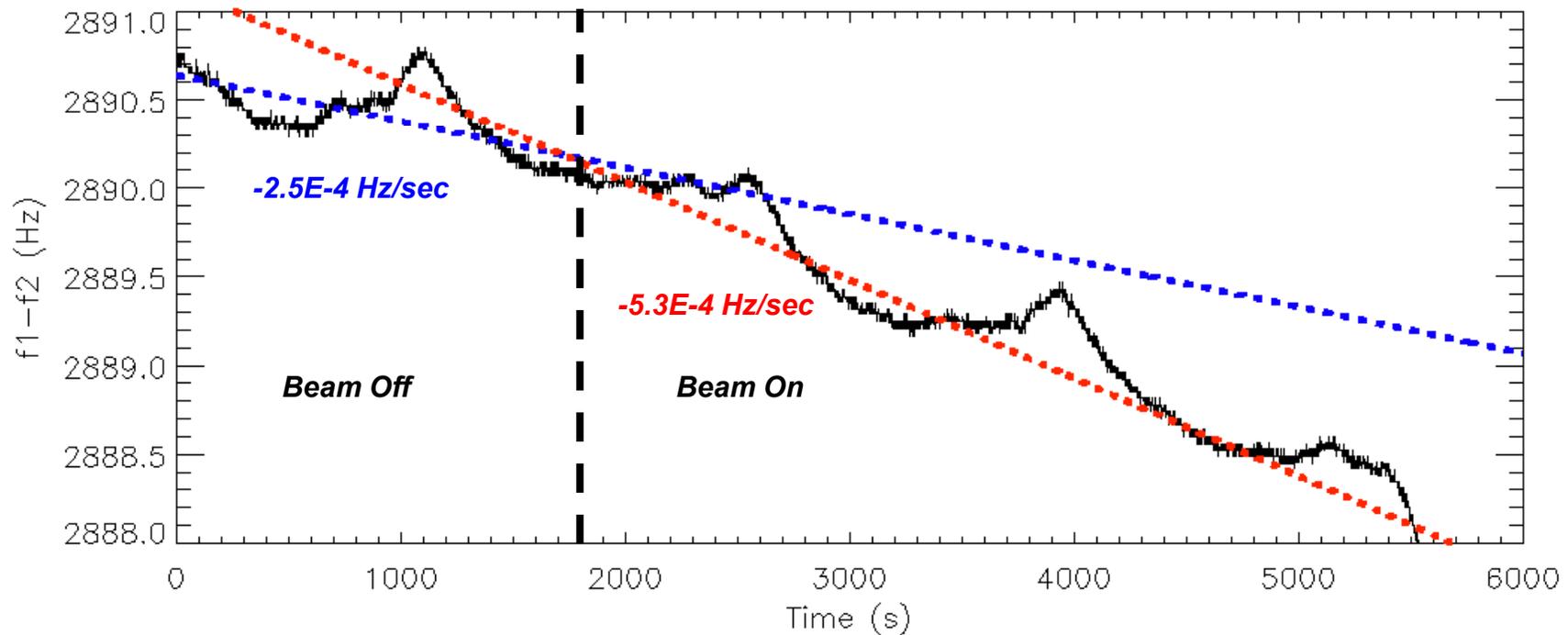
- **Refine analysis of spectroscopy data**
  - Apply spectrometer calibration to directly model the line emission and compare with absolute brightness
  - Incorporate geometric factors accounting for sight line of spectrometer
  - **Goal:** obtain **quantitative** agreement between simulations and measurements over wide range of  $\lambda_{iz} / \sigma_{Te}$ 
    - $f_{redep}$  values
    - "coating lifetime"  $\tau$
- **Improve accuracy of model:**
  - Add in additional source/sink terms for specific materials
  - Refine sputtering yields using Bodhansky/TRIM
  - Time-resolved  $T_e$  measurement from D line ratios
- **Longer term (new experiments):**
  - Heated (liquid) samples, non-zero impact angle
  - Additional coating materials (B, Sn, Sn-Li?)

# Obtained measurements of $D^+$ sputtering yield on Li-coated TZM at room temperature



## Obtained measurements of $D^+$ sputtering yield on Li-coated TZM at room temperature (continued)

- 2 keV  $D^+$  ions, beam current  $\approx 2.0 \mu A$
- Li thickness  $\approx 1.1 \mu m$
- Sputtered Li measured with dual-crystal QCM



# Obtained measurements of D<sup>+</sup> sputtering yield on Li-coated TZM at room temperature (continued)

- Data Analysis:

$$M \equiv \frac{\sigma_f}{\sigma_q} \quad F \equiv \frac{(f_q - f_c)}{f_q} = \frac{-\Delta f}{f_q} \quad M = F$$

- Sputter Yield (atoms/ion)<sup>1</sup>:  $Y_0 = \frac{N_A \dot{m}_{net}}{M f_{geo} i_{ion}} + \frac{N_A R Y_{ref}}{M}$ . Note: Different 'M'
- Simplifying assumptions:
  - All Li converted to Li<sub>2</sub>O (M=29.88 g/mol)
  - Reflection term is negligible
- Results in a sputter yield of **0.26 ± 0.10 for 2 keV D<sup>+</sup> on Li**
  - Previous work<sup>2</sup> finds  $Y_0 = 0.091 \pm 0.033$  for 700 eV D<sup>+</sup> incident on D-saturated Li
  - VFTRIM-3D simulation<sup>2</sup> gives  $Y_0 = 0.08$  at 1000 eV
  - This is a very preliminary data set that indicates higher erosion than previous studies. Further investigation is required.

1) M. Coventry, Ph.D. Thesis, 2007

2) J.P. Allain et. al, Nuclear Fusion, 2001

## Acknowledgements

- M.A. Jaworski (advisor) for experimental work & assistance with 1-D model
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  - UIUC CPMI (D.N. Ruzic et. al.)

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