# *Lithium Coatings and In-situ PMI (plasma-material interface) Diagnostic in NSTX*

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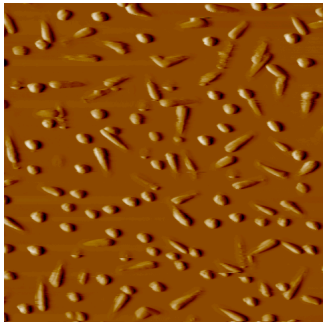
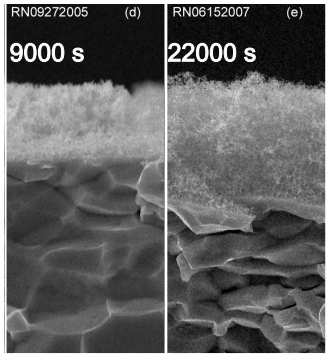
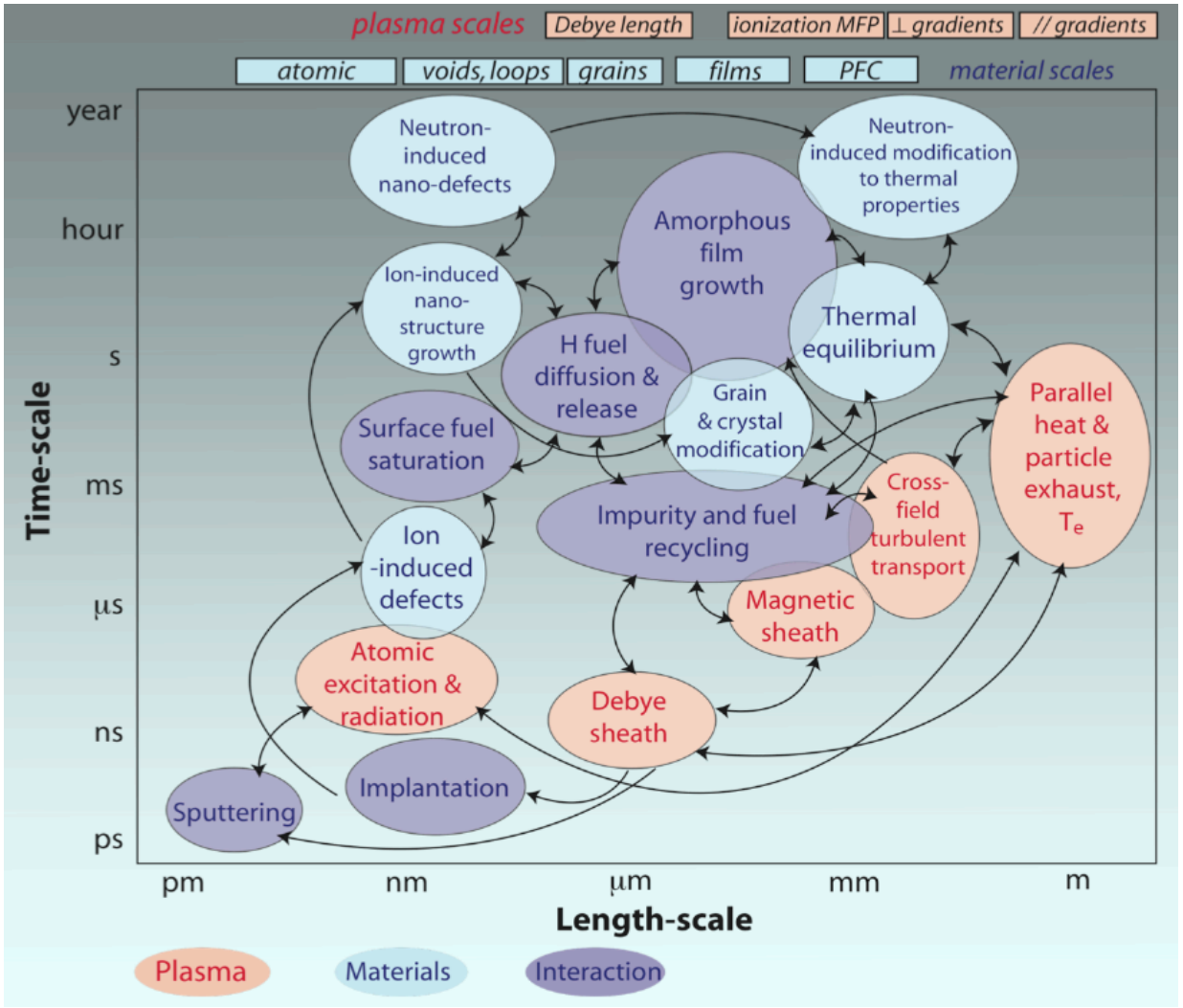
# *Outline*

- Plasma-material interface challenges
- Lithium-based surfaces and D retention
- Controlled studies of D-irradiated lithiated graphite
- PMI probe results from NSTX
- Summary and Future Work

# *Radiation-driven vs naturally-driven systems: instabilities and self-organization at the plasma-surface interface*

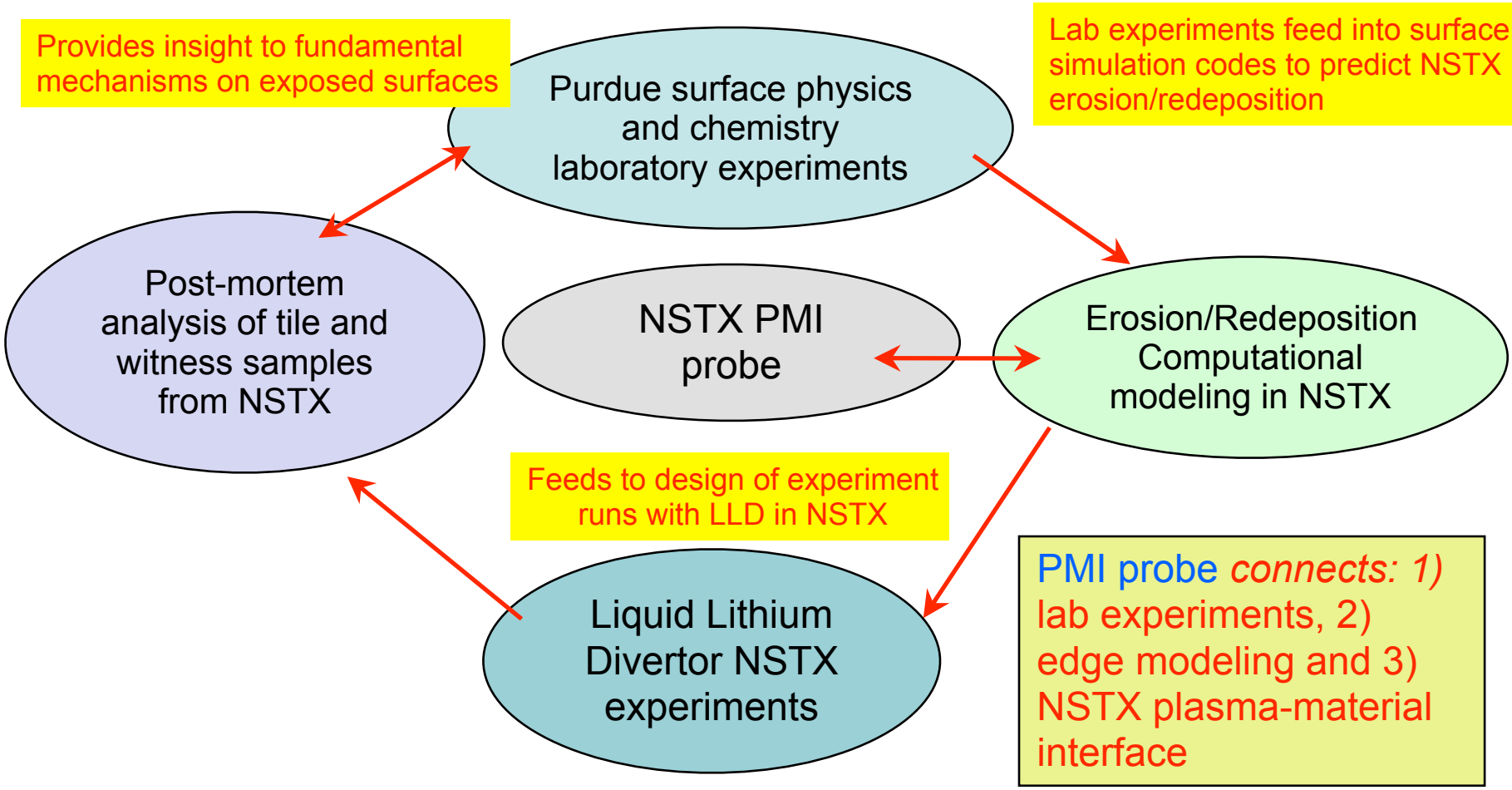





*Courtesy of: B. Wirth*

# *Summary of Li-based PMI work at Purdue*

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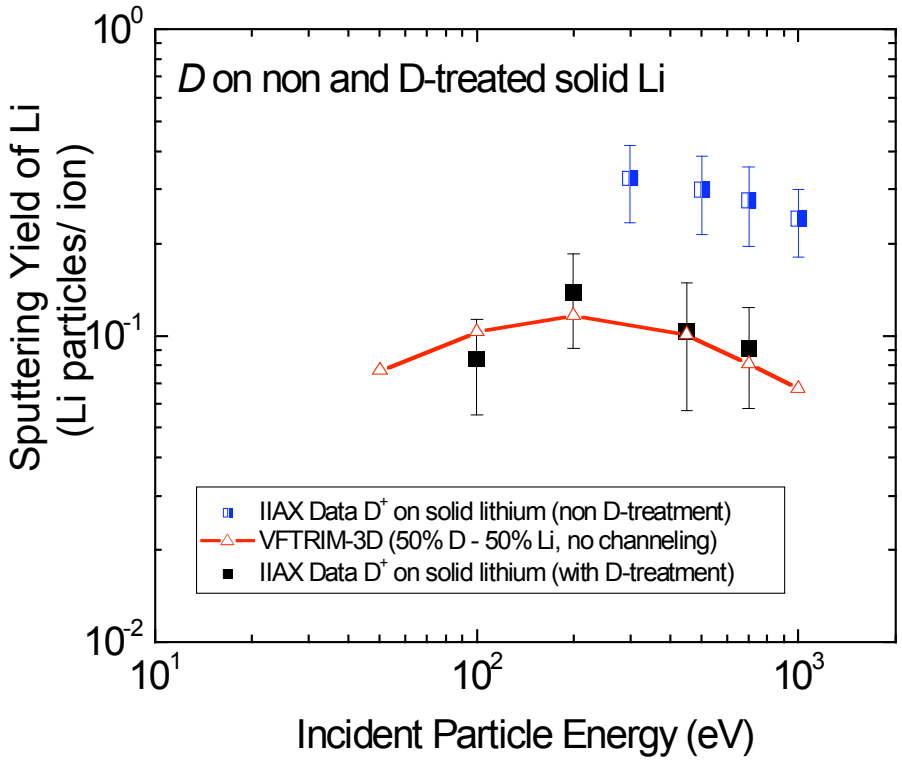
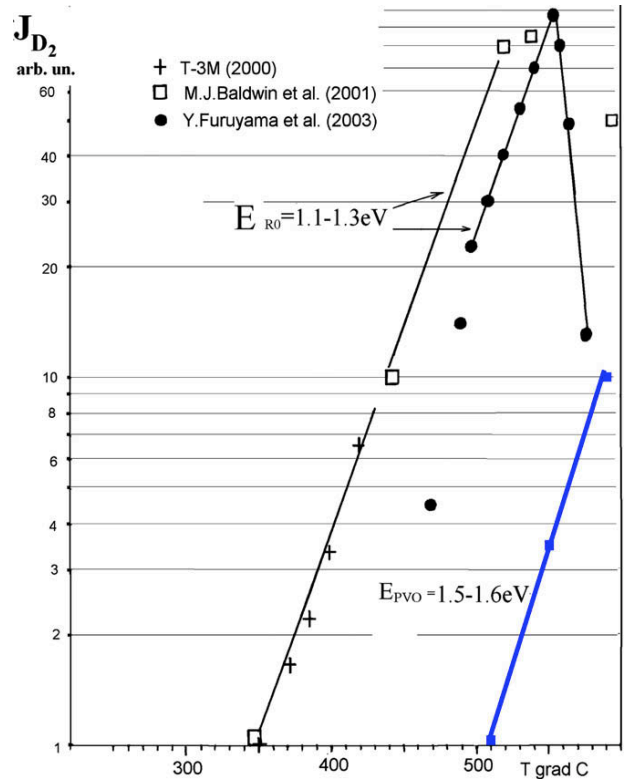
# *Lithium as a pump for hydrogen: the role of spatial scales*

- Critical to the recycling of D when using lithium as a PFS (plasma-facing surface) is the top layer of atoms
- Sputtered particles emanate from the first 2-3 ML of a metal surface (although the damage zone can be 10-100's nm below)
- Recombination of implanted D occurs at the first few layers at the surface-vacuum interface
- Diffusion and other mechanisms from surface-to-bulk and vice versa are obviously important, however we focus on the net condensed matter state *at* the surface
- Understanding the lithium surface properties (sputtering, D retention, ion yield, etc…) requires probing at these spatial scales

*J.N. Brooks and J.P. Allain, J. Nucl. Materials, 337-339 (2005) 1053*
*J.P. Allain, J.N. Brooks, Guojing Ho, J. Nucl. Mat. in preparation 2008*

# *Liquid lithium sputtering and D retention*




- D implanted at the lithium surface will lead to preferential sputtering of D atoms over Li leading to Li sputter yield reductions of ~ 40%[1]
- TDS measurements (Sugai, Baldwin, Evtikhin[2], Mirnov[3] and others) **show indirect evidence that D is implanted at the surface in solution with Li atoms based on their emission at temperatures (~ 400-500 C) lower than formation temp. for Li-D (T ~ 700 C)**

[1] J.P. Allain and D.N. Ruzic, Nucl. Fusion 42 (2002) 202.
[2] V.A. Evtikhin, et al. Plasma Phys. and Controlled Fusion, 44 (2002) 955.
[3] S. Mirnov, et al. J. Nucl. Mater. in press 2009

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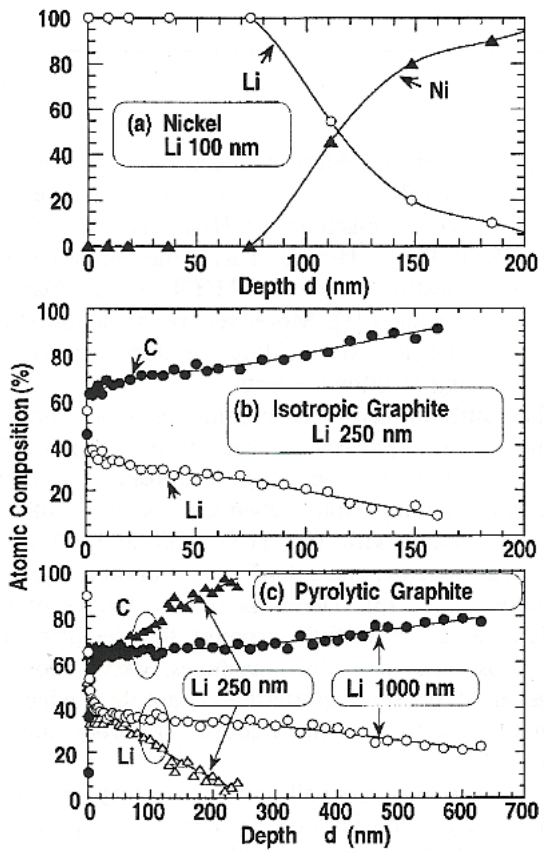
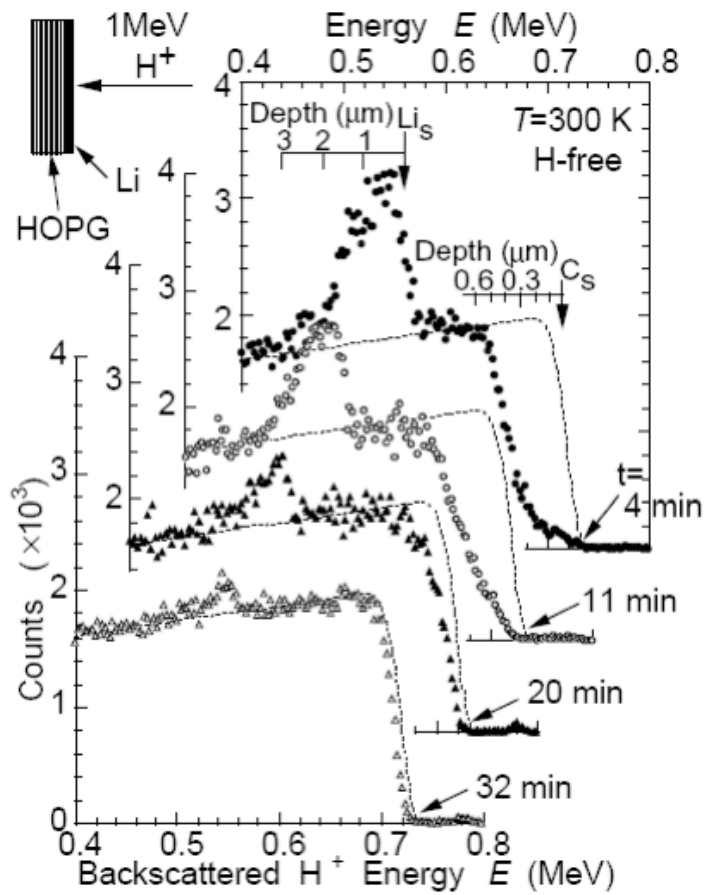
# *H. Sugai's work on lithium intercalation in graphite*




N. Itou, H. Toyoda, K. Morita, H. Sugai, J. Nucl. Mater. 290-293 (2001) 281.

Lithiated graphite: *lithium readily intercalates (diffuses) to bulk away from surface to depths of about 1-5 um (unless a barrier is made)*

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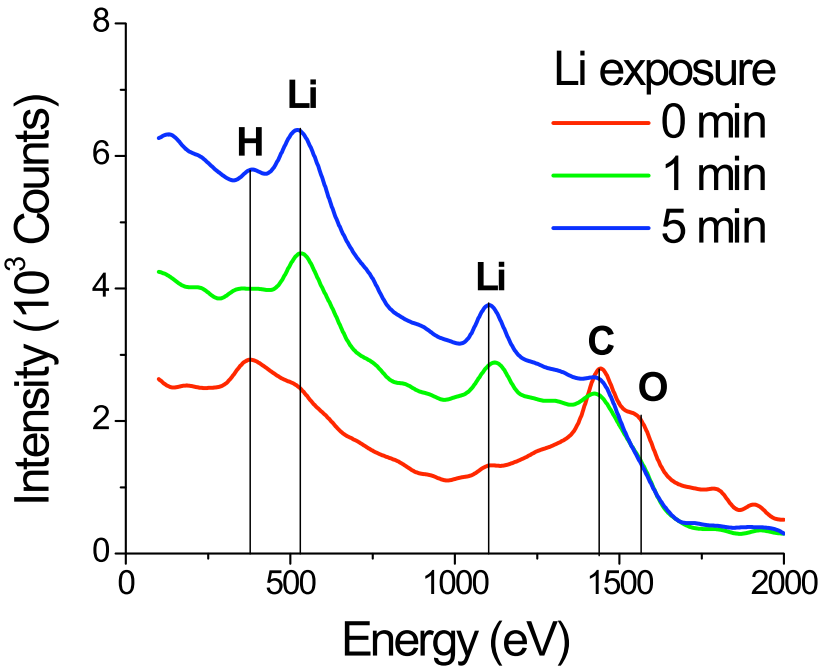
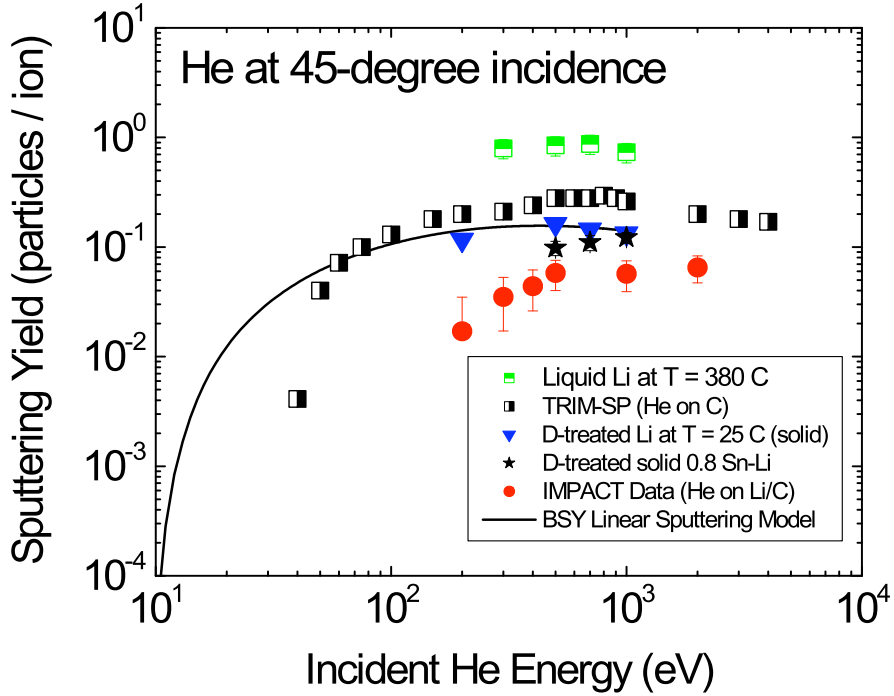
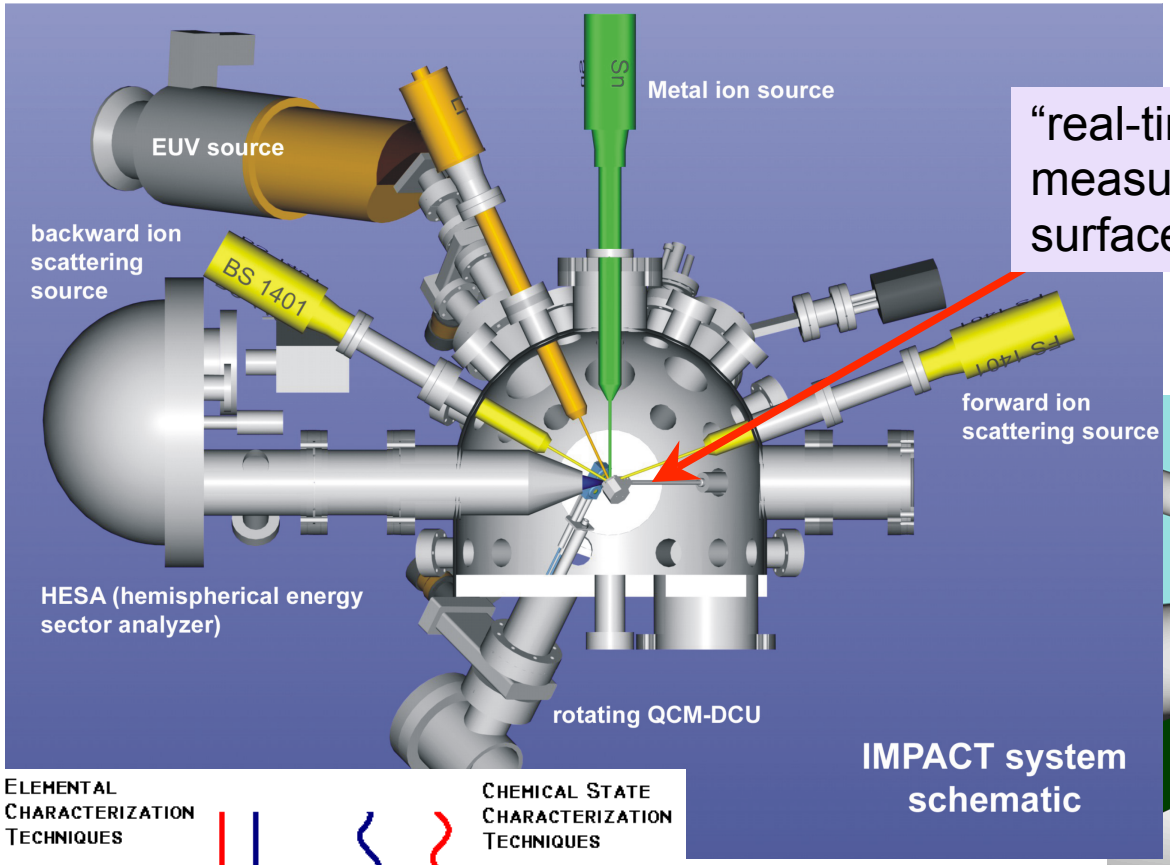
# *Lithium coatings on graphite: surface effects on erosion, particle retention*



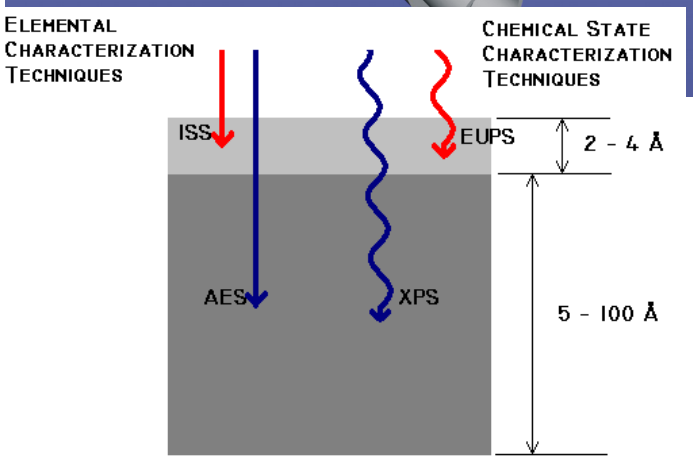



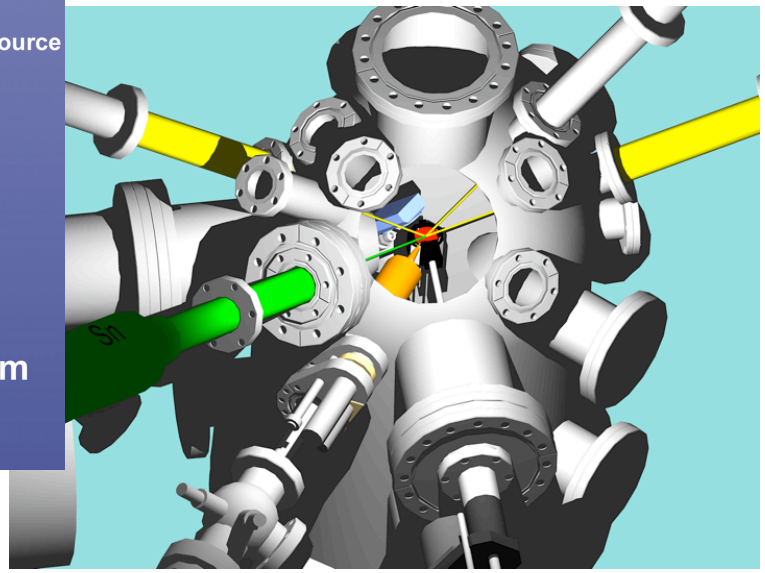

- *Nominally* lithium intercalates to the basal planes of graphite. Difficult to maintain 100% lithium layers on top few ML. Oxygen typically bound with lithium
- Substantial reduction of both *physical* and *chemical* sputtering by *D or He* bombardment when comparing lithiated graphite surfaces to either pure Li or C

*J.P. Allain, D.L. Rokusek, et al. J. Nucl. Mat. 390-391 (2009) 942*




"real-time" erosion rate measurement *during* analysis from surface with QCM-DCU system

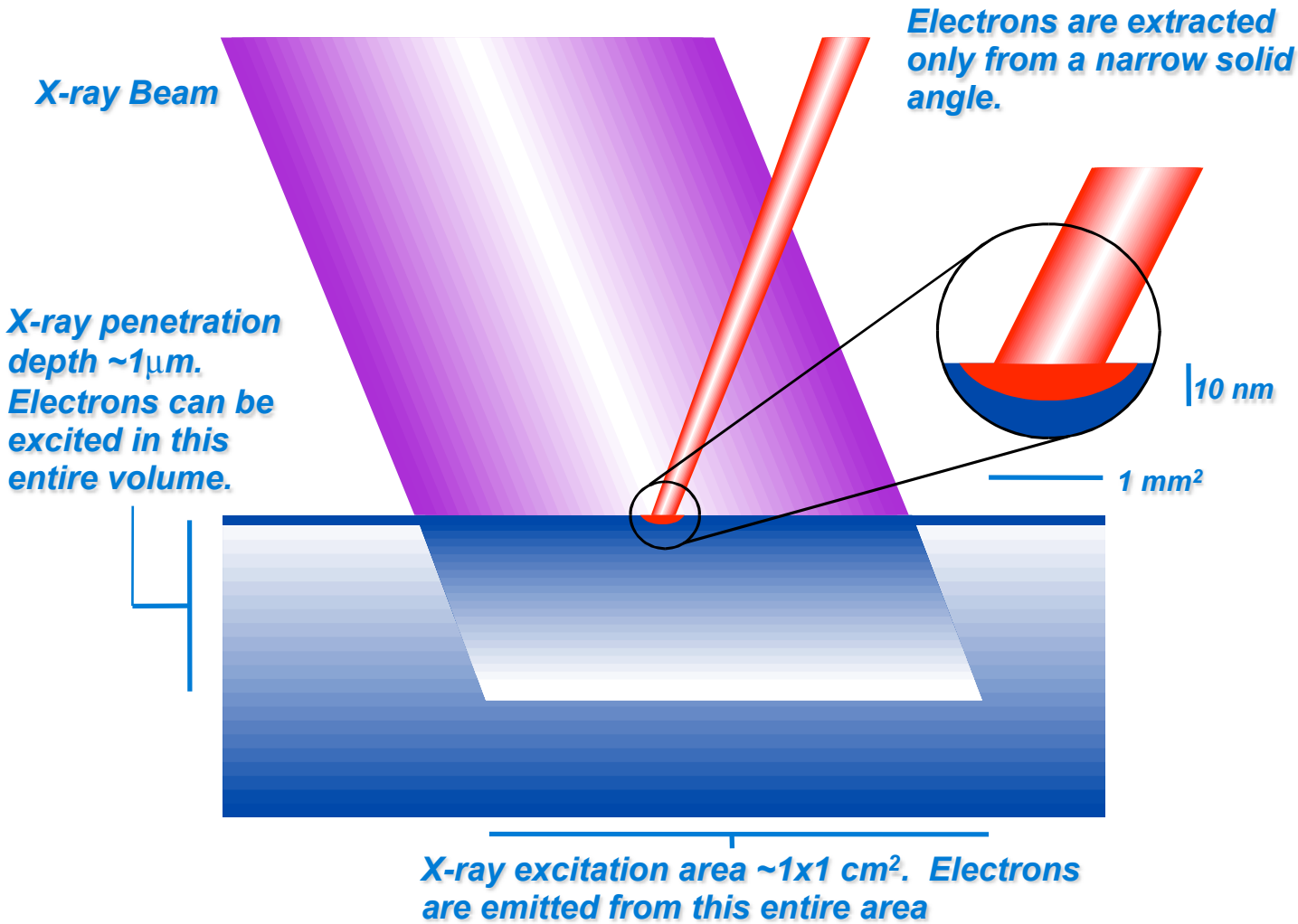


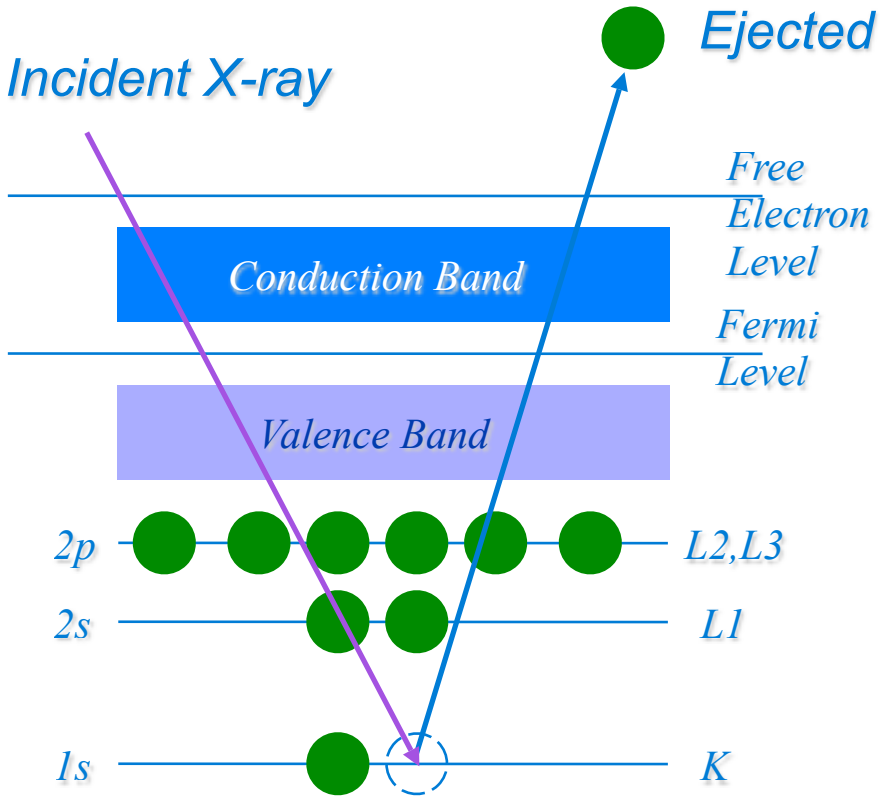
***IMPACT*** and ***PRIHSM*** use several electron spectroscopies for surface chemical analysis: XPS, UPS and ARPES with ion scattering spectroscopies: forward and backward scattering modes

# X-ray Photoelectron Spectroscopy

## Small Area Detection



# The Photoelectric Process




- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).
- The ejected photoelectron has kinetic energy:

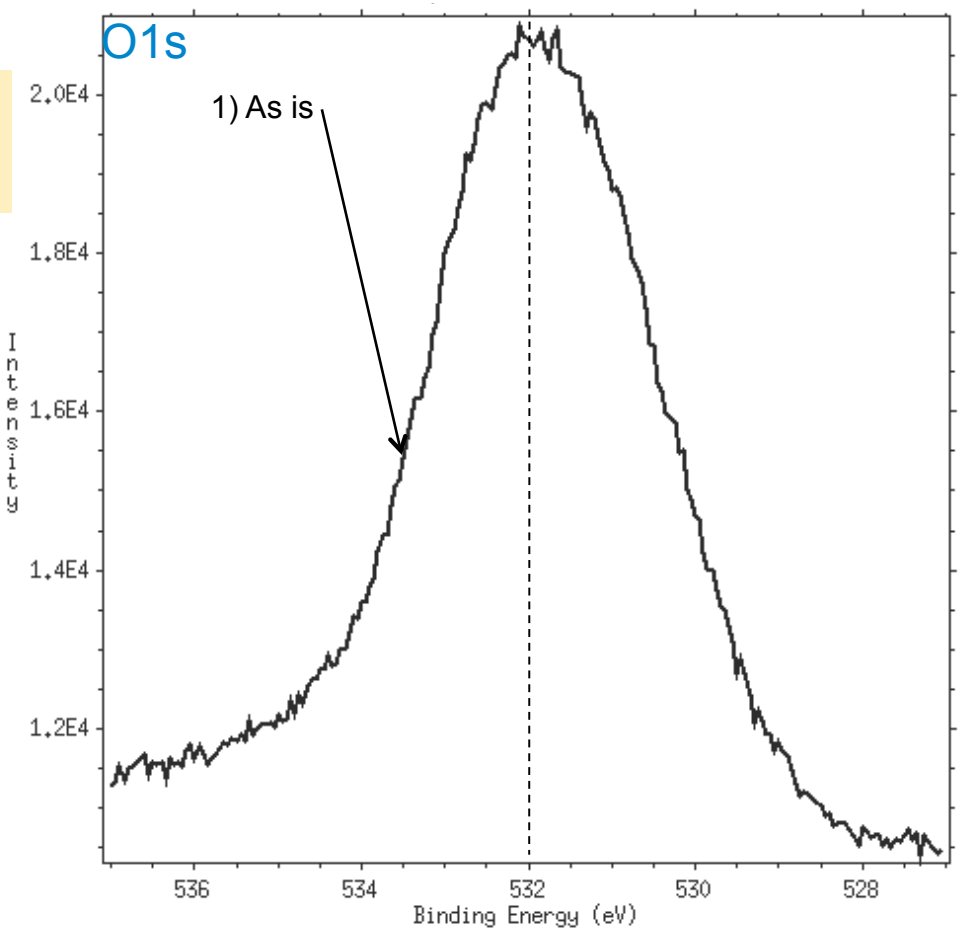
$$KE = h\nu - BE - \Phi$$

- Following this process, the atom will release energy by the emission of an Auger Electron (contributes to background at high binding energies).

# O 1s peak associated with C-O bonding:

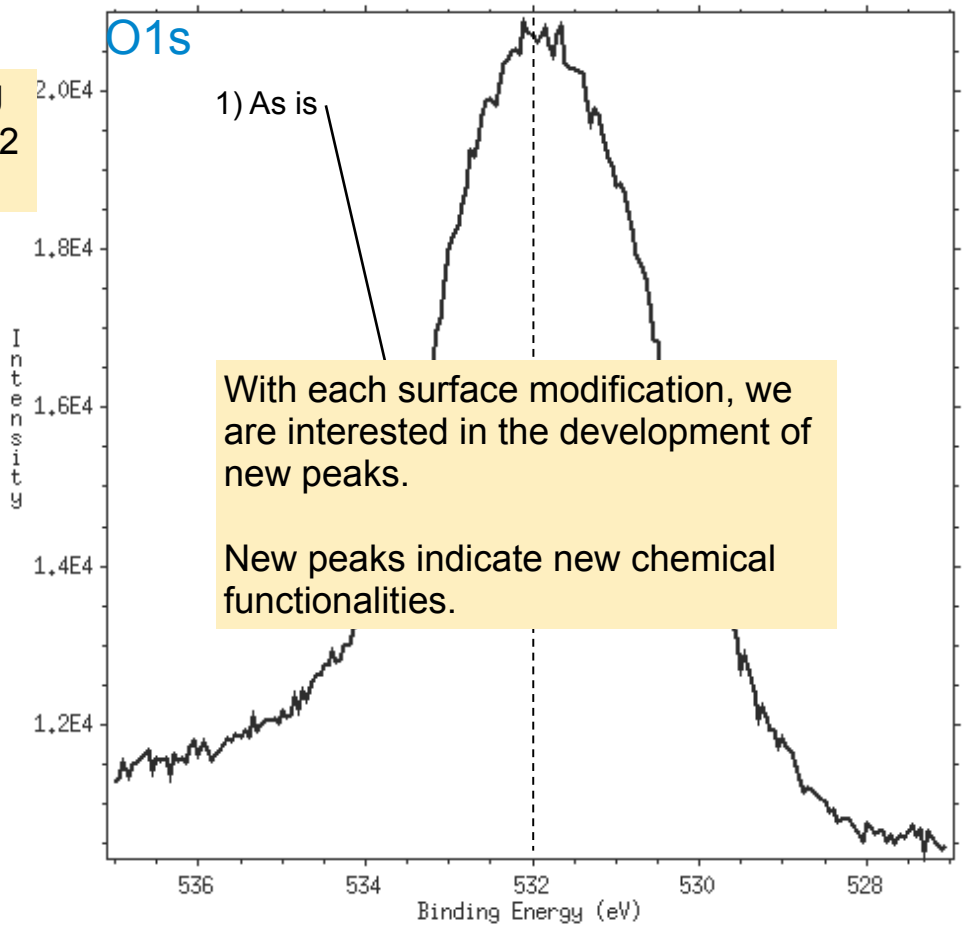
## No D irradiation and No Li deposition

1) The O1s peak on ATJ graphite is located at 532 eV



# *Examining the Li-D-O functionality from the O1s excitation peaks*

1) The O1s peak on ATJ graphite is located at 532 eV



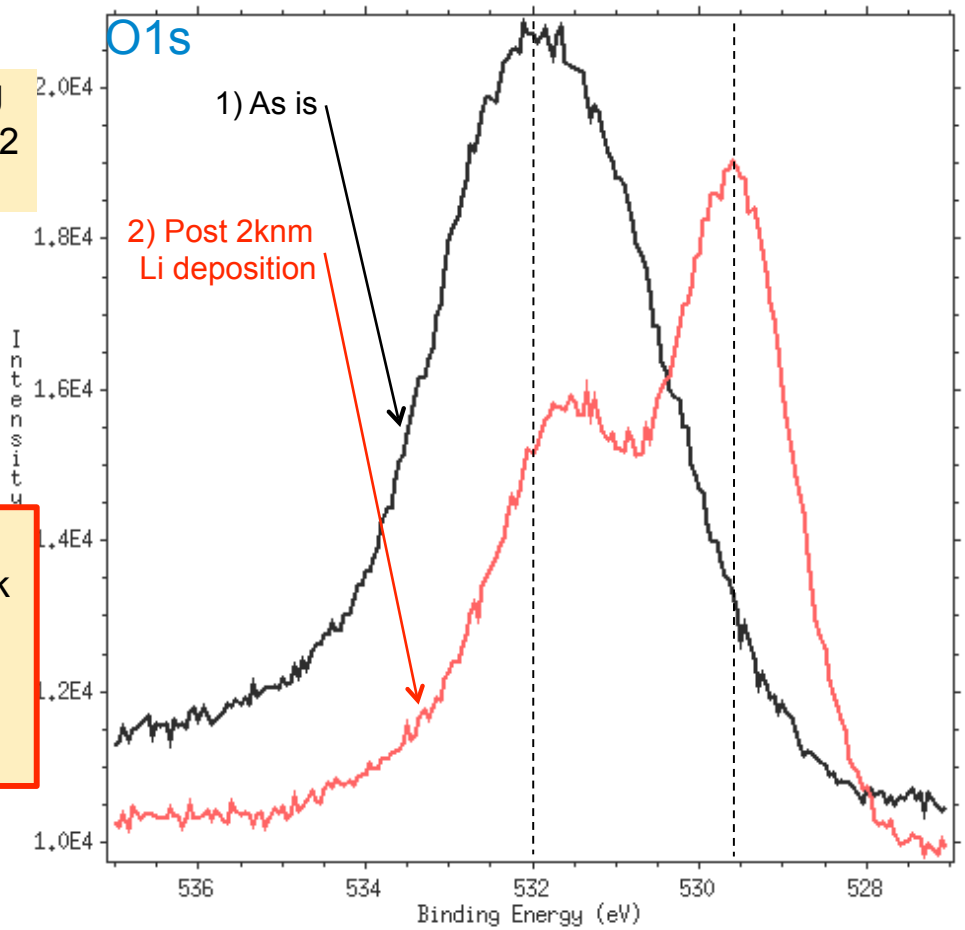

With each surface modification, we are interested in the development of new peaks.

New peaks indicate new chemical functionalities.

# *First: deposition of lithium on ATJ graphite surface:* ***note characteristic peaks***

1) The O1s peak on ATJ graphite is located at 532 eV

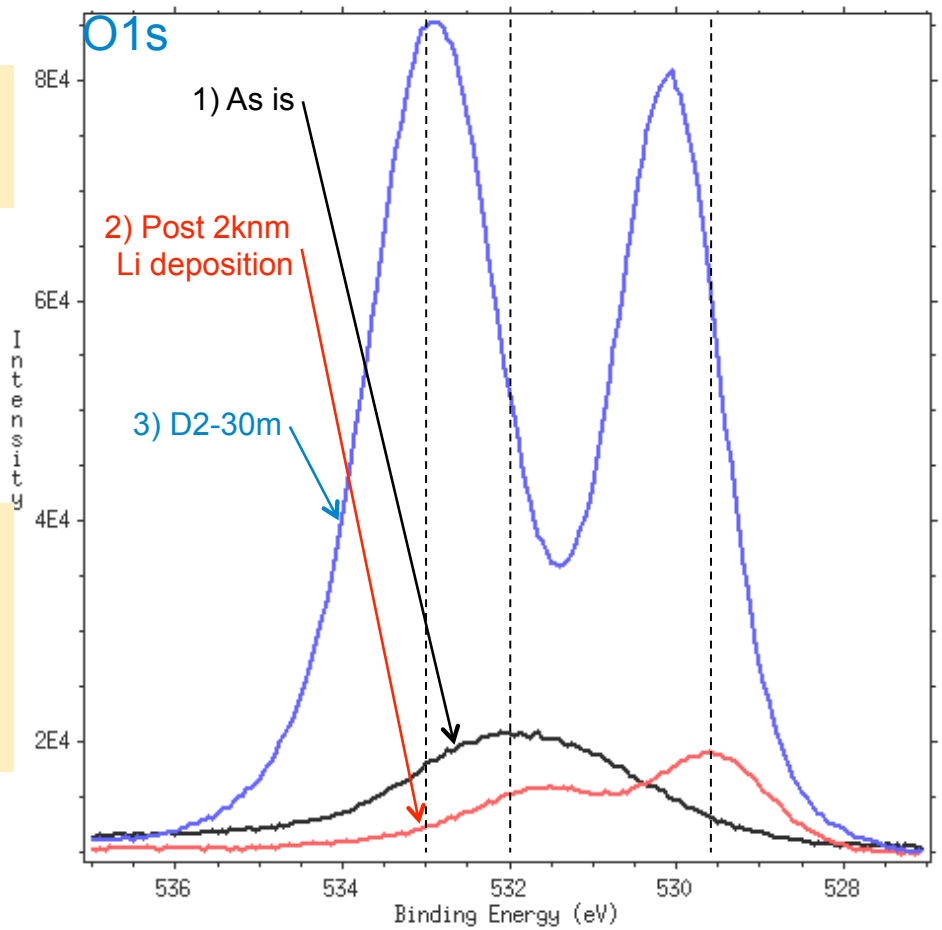
2) Lithium deposition results in a second peak at ~529.5 eV. A slight shift to lower binding energy in the 532 eV also occurs.



# *Irradiation with D leads to "shift" in O1s peaks:* ***Note peak at 533 eV***

1) The O1s peak on ATJ graphite is located at 532 eV

2) Lithium deposition results in a new second peak at ~529.5 ± .5 eV. A slight shift to lower binding energy in the 532 eV also occurs.

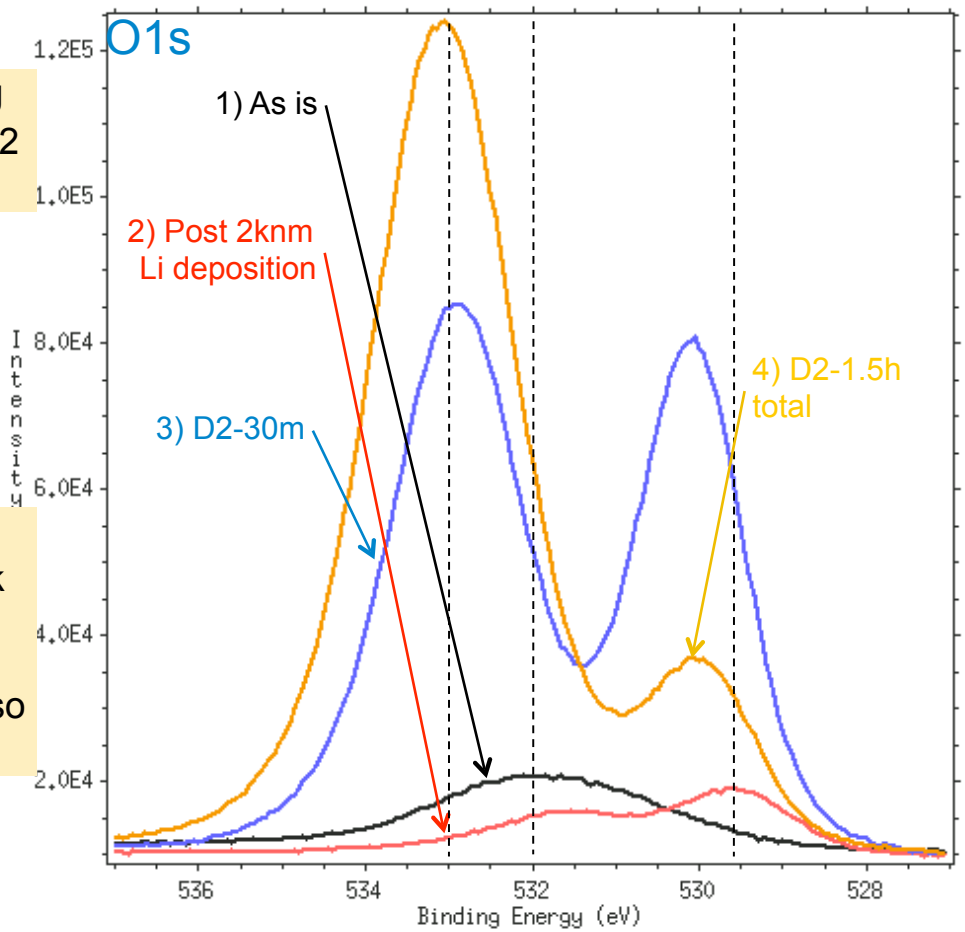



3) 30 minute deuterium irradiation (Γ ≈ 1.5 E15 $cm^{-2}$) causes a new peak to develop at 533 eV, and a slight shift to higher binding energy for the 529.5 eV peak.

# *Irradiation with D leads to "shift" in O1s peaks:* ***Note peak at 533 eV and correlation with dose***

1) The O1s peak on ATJ graphite is located at 532 eV

2) Lithium deposition results in a second peak at ~529.5 eV. A slight shift to lower binding energy in the 532 eV also occurs.




3) 30 minute deuterium irradiation (Γ ≈ 1.5 E15 $cm^{-2}$) causes a new peak to develop at 533 eV, and a slight shift to higher binding energy for the 529.5 eV peak.

4) The relative intensity of the 533 eV peak compared to the 529.5 eV peak increases with subsequent irradiations.

# *Irradiation with D leads to "shift" in O1s peaks:* ***Note peak at 533 eV and correlation with dose***

1) The O1s peak on ATJ graphite is located at 532 eV

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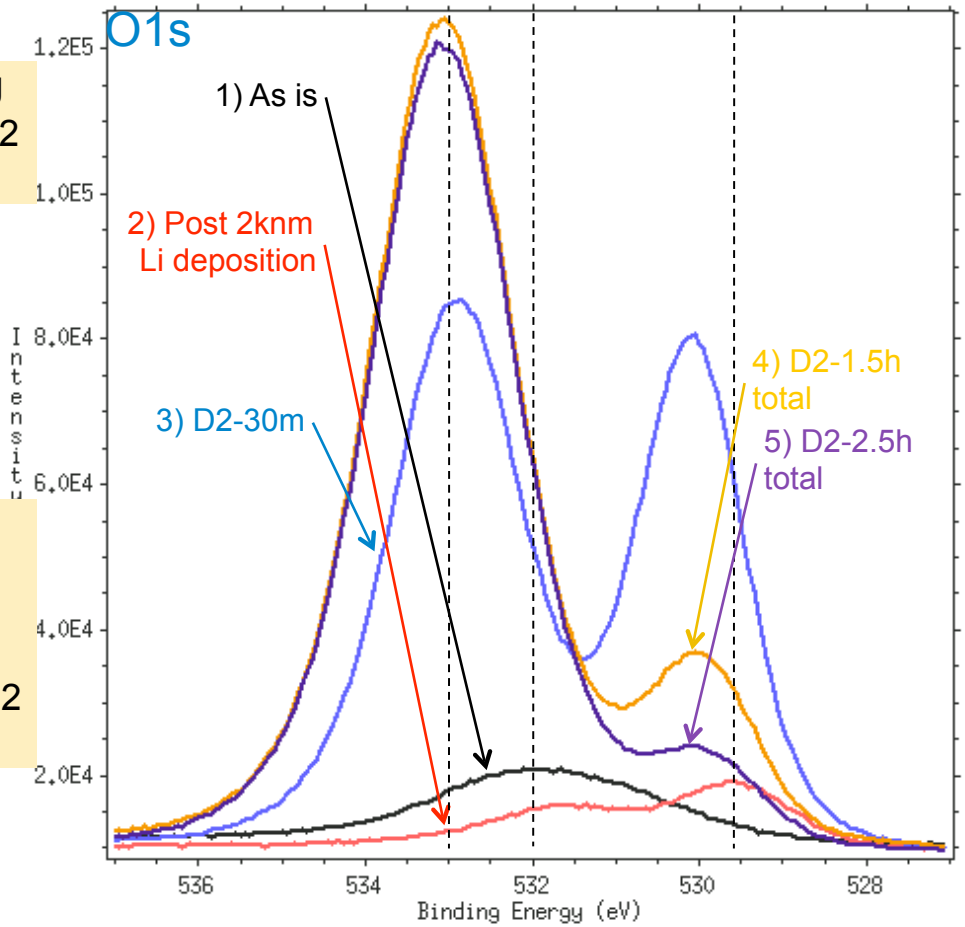


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4) The relative intensity of the 533 eV peak compared to the 529.5 eV peak increases with subsequent irradiations.

5) …and again...

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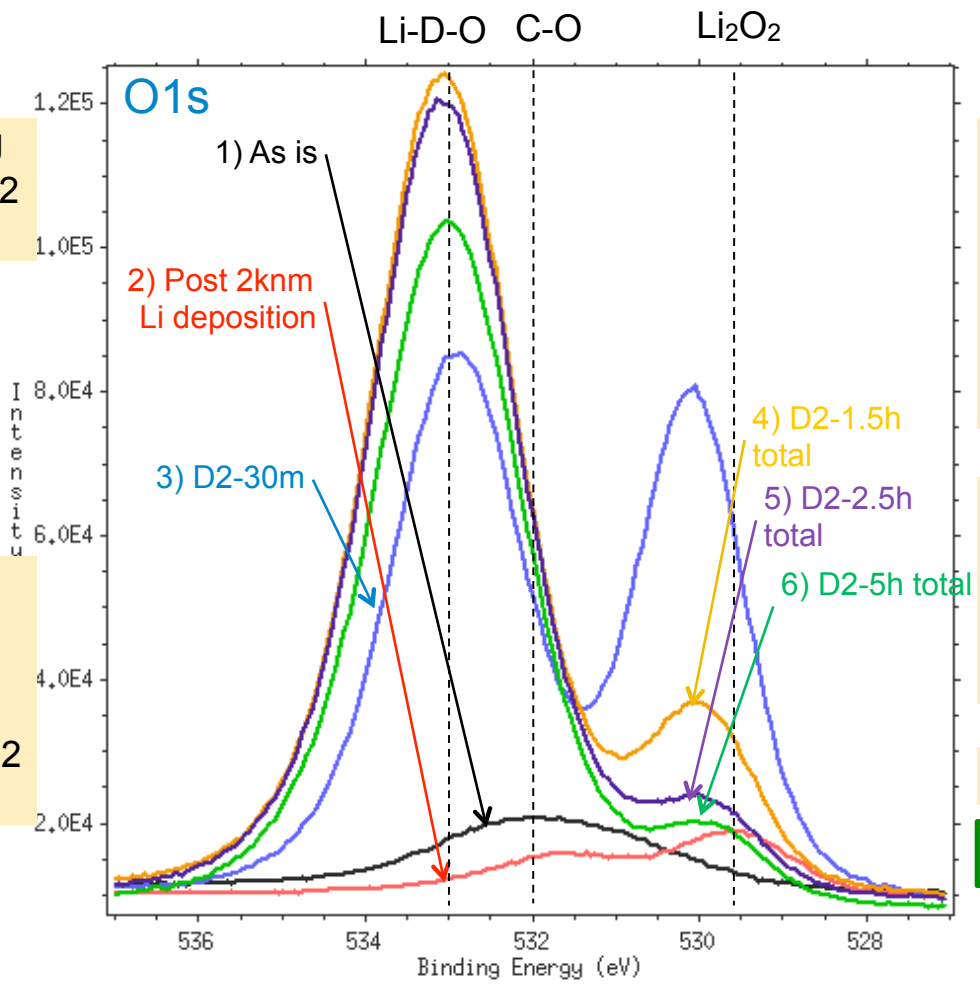



3) 30 minute deuterium irradiation (Γ ≈ 1.5 E15 $cm^{-2}$) causes a new peak to develop at 533 eV, and a slight shift to higher binding energy for the 529.5 eV peak.

4) The relative intensity of the 533 eV peak compared to the 529.5 eV peak increases with subsequent irradiations.

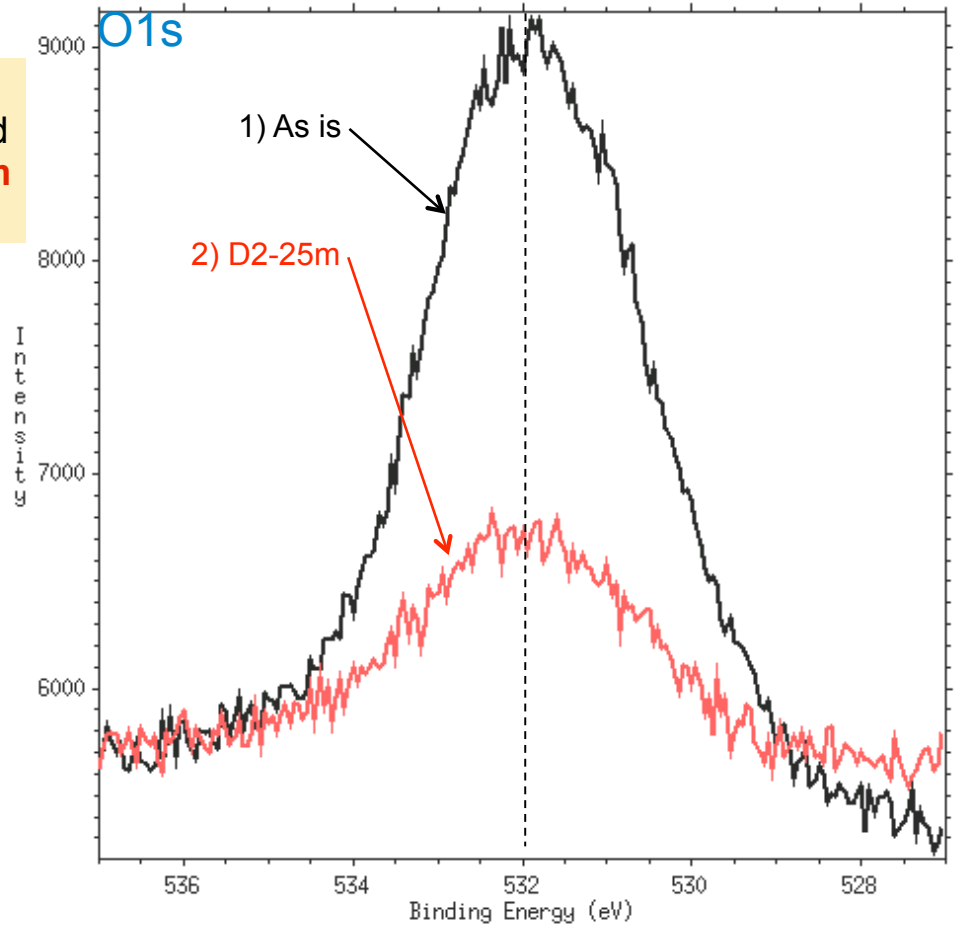
5) …and again...

6) …and again.

# *Control: Irradiate with D but no lithium*

Control experiment

**Procedure:**
ATJ graphite was irradiated with D ***without* any lithium conditioning**.




**Result:**
No shifts or new peaks were observed.

# *Control: Irradiate with D but no lithium*

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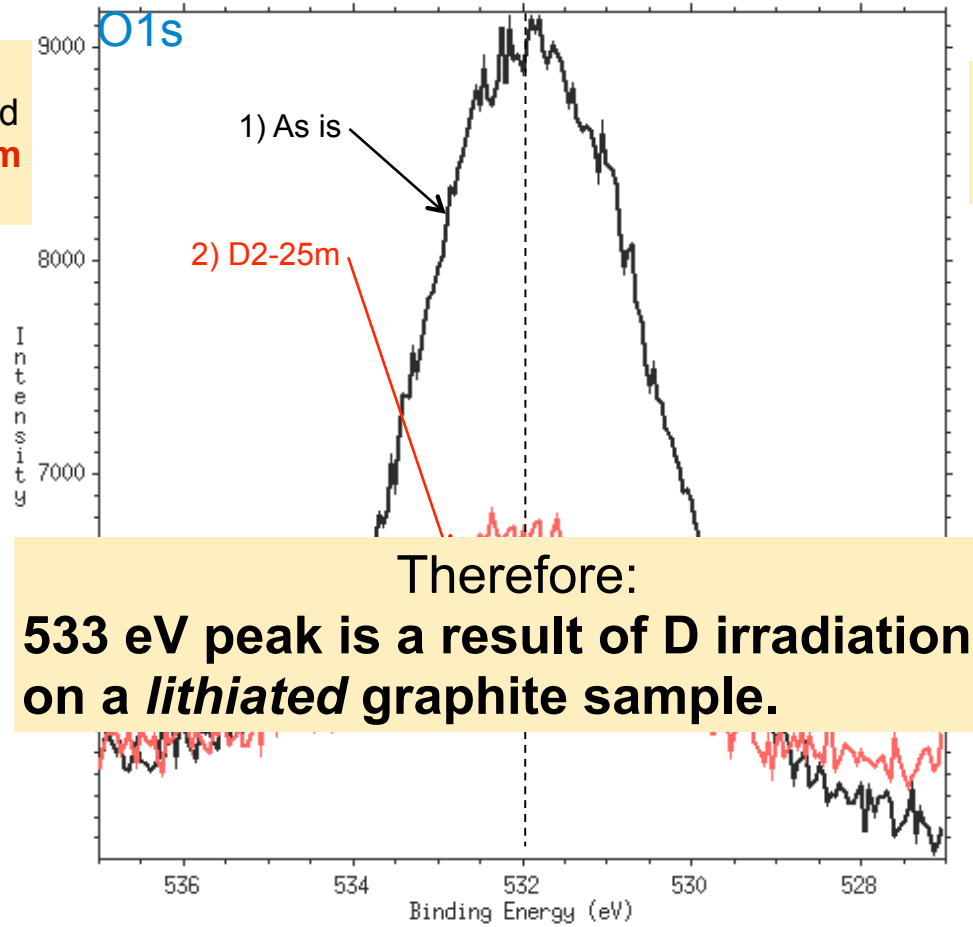
ATJ graphite was irradiated with D ***without* any lithium conditioning.**



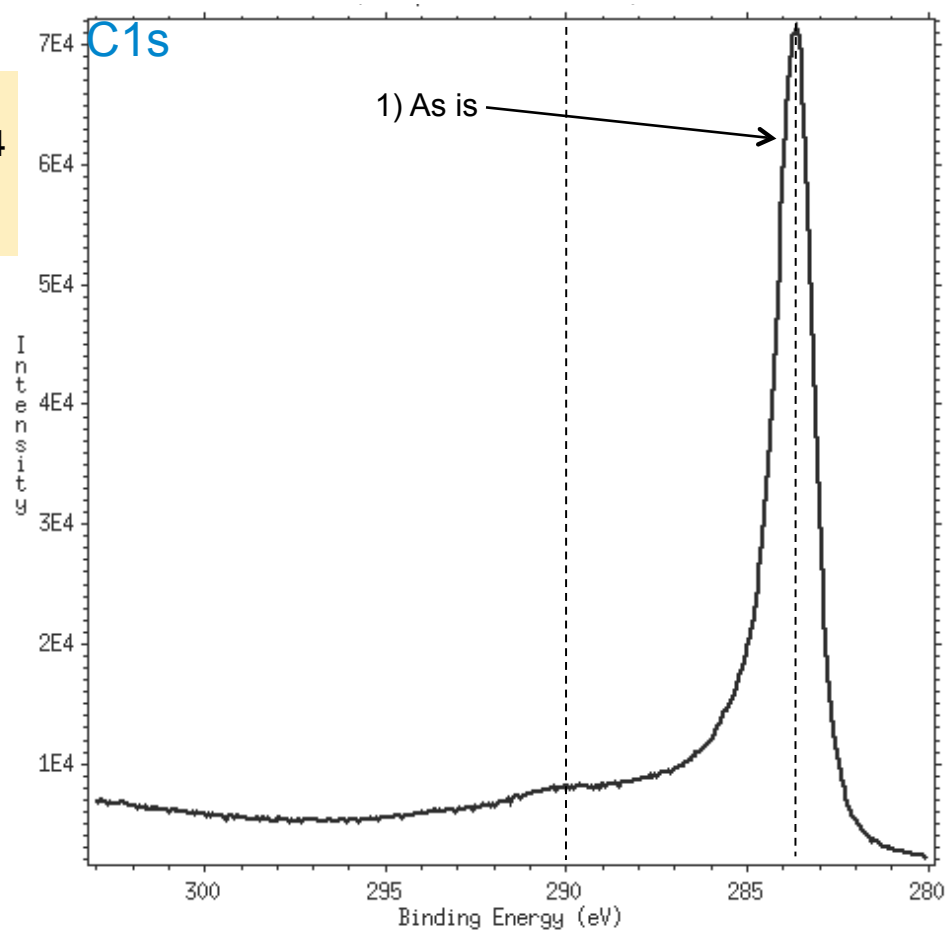

**Result:**
No shifts or new peaks were observed.

Therefore:
**533 eV peak is a result of D irradiation on a *lithiated* graphite sample.**

# *Effect of D irradiation on lithiated graphite also evident in C1s spectra; this case:*

## *No D irradiation and No Li deposition*

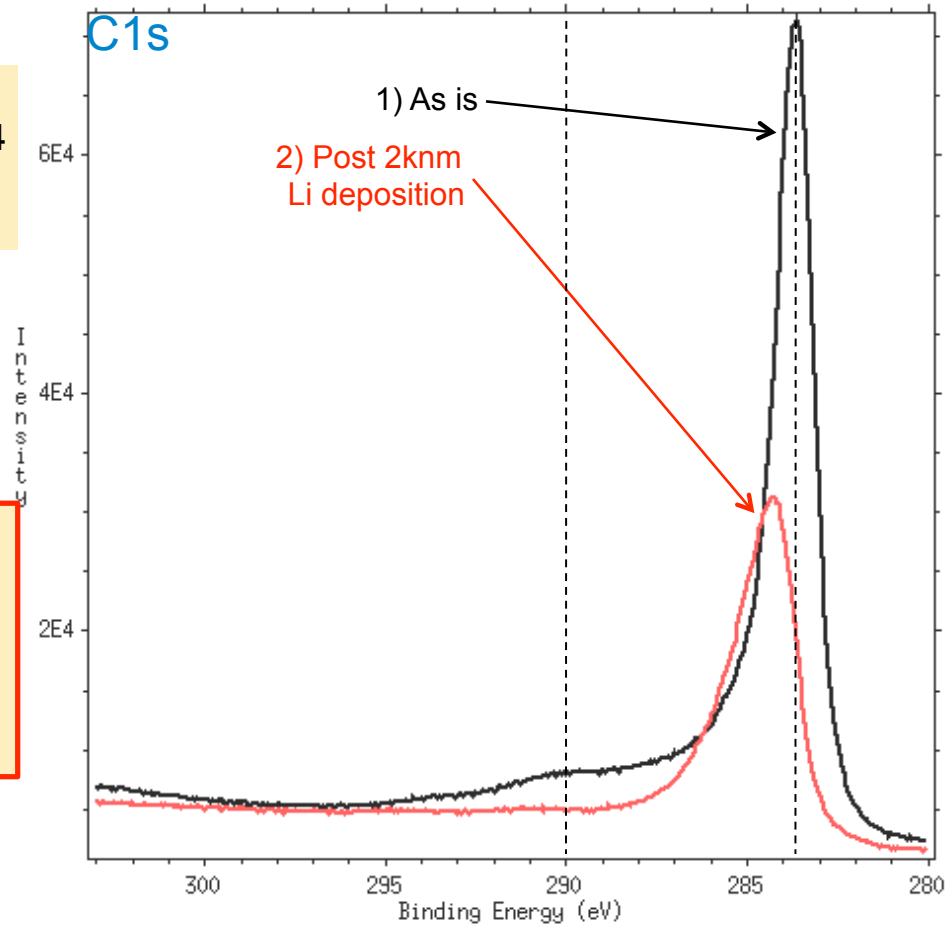
1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.



# *First: deposition of lithium on ATJ graphite surface: note characteristic peaks*

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

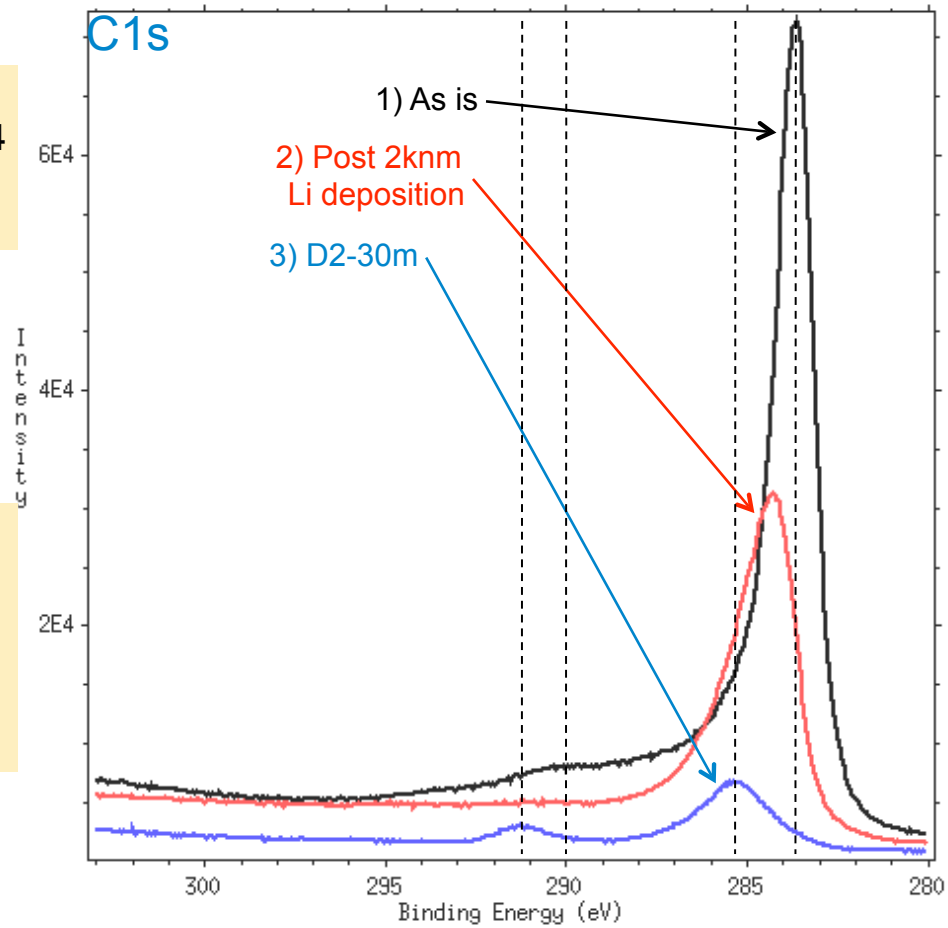
2) Lithium deposition results causes the FWHM of the primary peak to increase. Peak shifts ~1eV to higher binding energy.



# *Irradiation with D leads to "shift" in C1s peaks:* ***Note peak at 291 eV***

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results causes the FWHM of the primary peak to increase. Peak shifts ~1eV to higher binding energy.

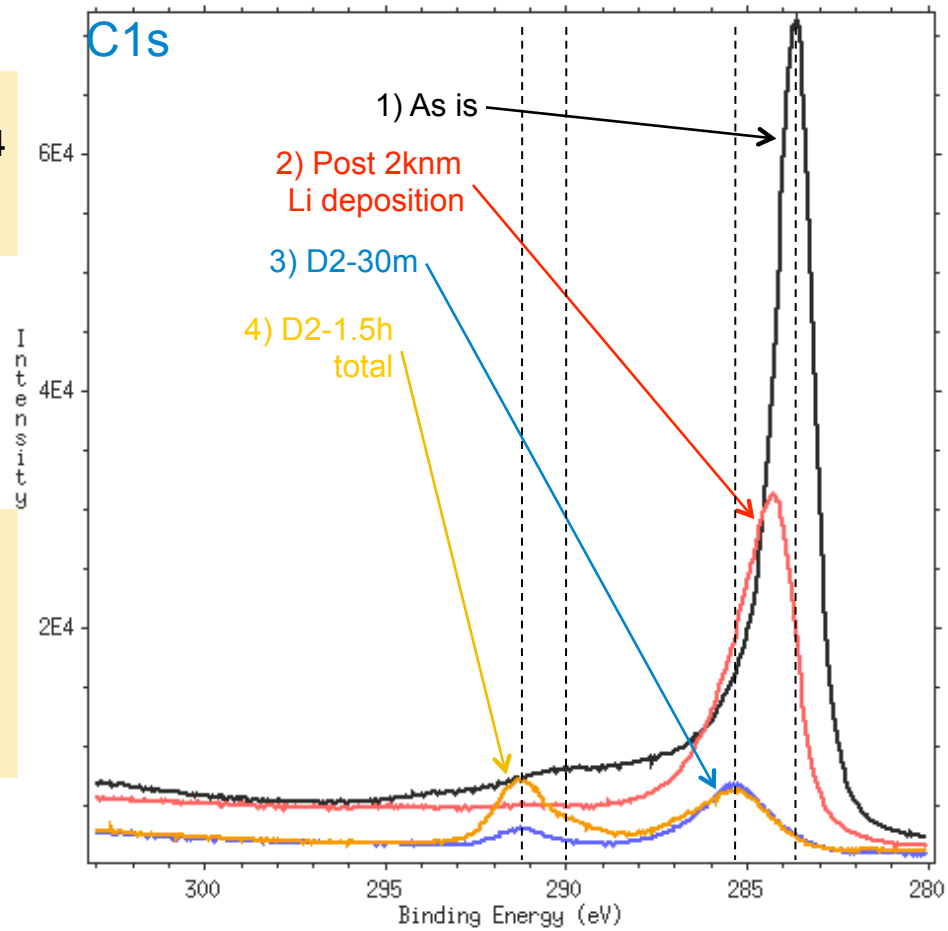



3) 30 minute deuterium irradiation (Γ ≈ 1.5 E15 $cm^{-2}$) causes a new peak to develop at 291 eV. The 284 eV peak shifts again to higher binding energy, now residing ~285 eV.

# *Irradiation with D leads to "shift" in C1s peaks:* ***Note peak at 291 eV and correlation with dose***

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results causes the FWHM of the primary peak to increase. Peak shifts ~1eV to higher binding energy.



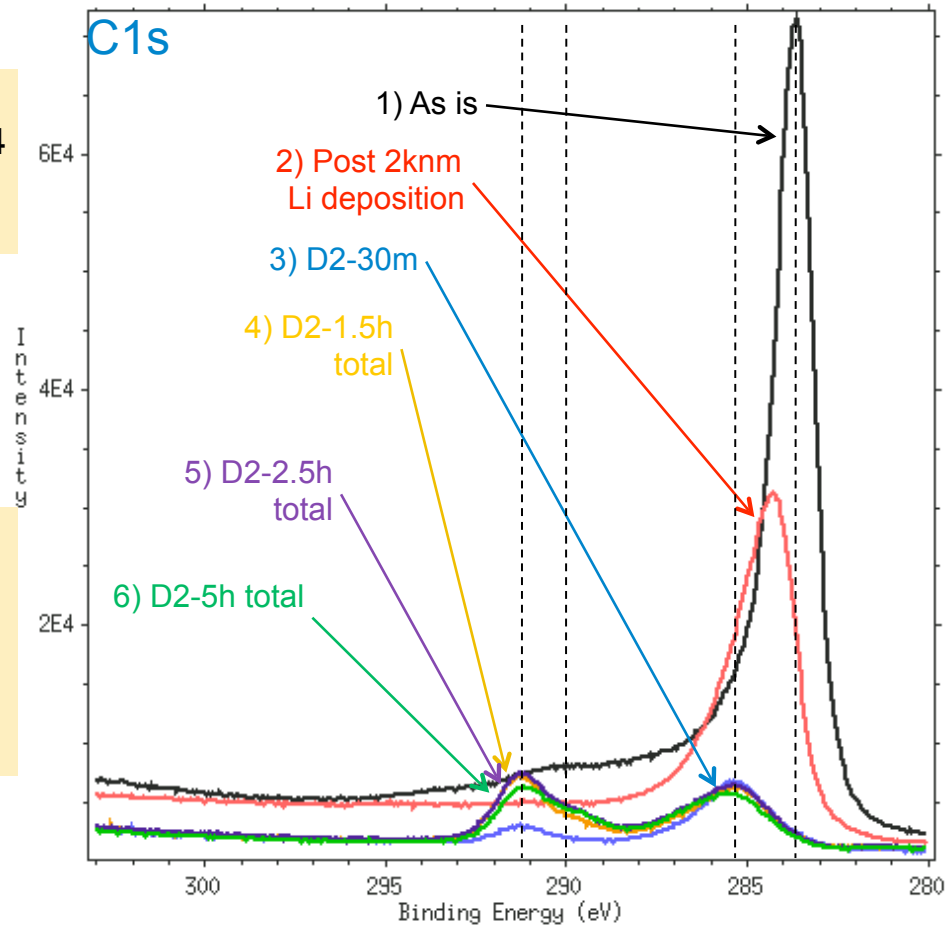

3) 30 minute deuterium irradiation (Γ ≈ 1.5 E15 $cm^{-2}$) causes a new peak to develop at 291 eV. The 284 eV peak shifts again to higher binding energy, now residing ~285 eV.

4) The relative intensity of the 291 eV peak compared to the 529.5 eV peak increases with subsequent irradiations. Peak at 285 eV ceases to change.

# *Irradiation with D leads to "shift" in O1s peaks:* ***Note peak at 291 eV and correlation with dose, reaching steady state***

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results causes the FWHM of the primary peak to increase. Peak shifts ~1eV to higher binding energy.

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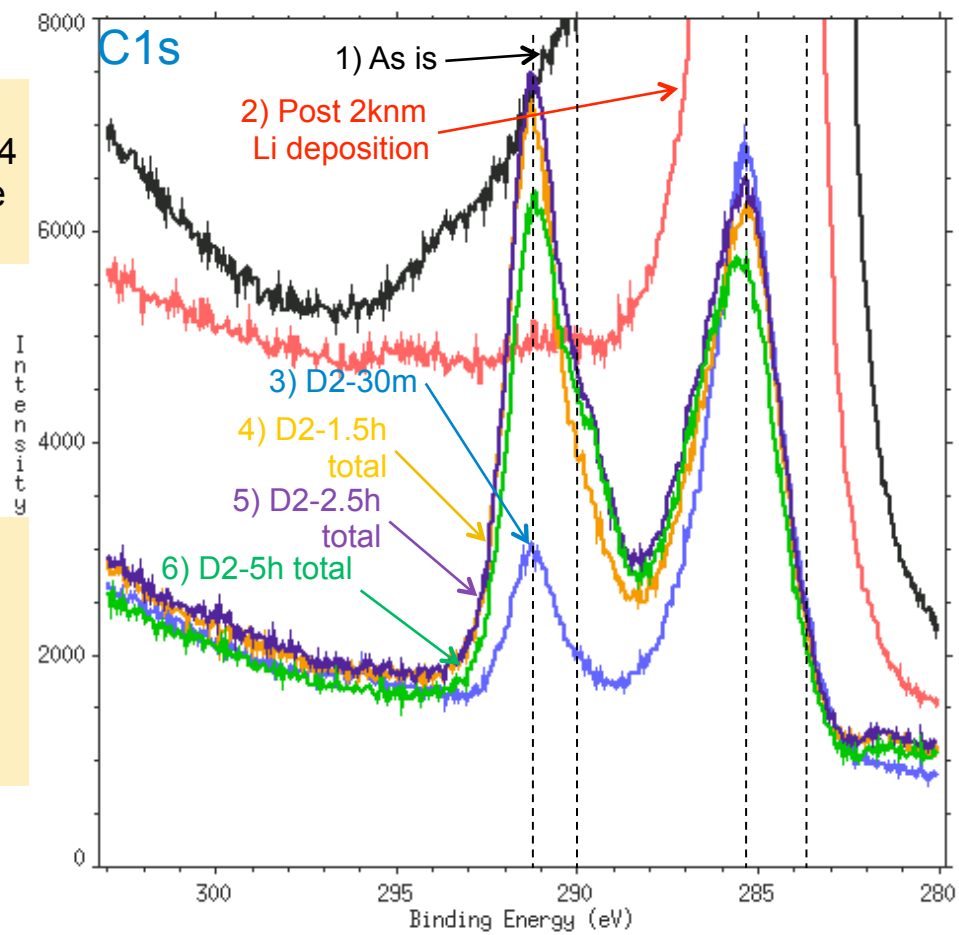
4) The relative intensity of the 291 eV peak compared to the 529.5 eV peak increases with subsequent irradiations. Peak at 285 eV ceases to change.

5,6) Change of relative intensity slows at some D fluence threshold.

# *Irradiation with D leads to "shift" in C1s peaks:* ***Note peak at 291 eV and correlation with dose***

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results causes the FWHM of the primary peak to increase. Peak shifts ~1eV to higher binding energy.

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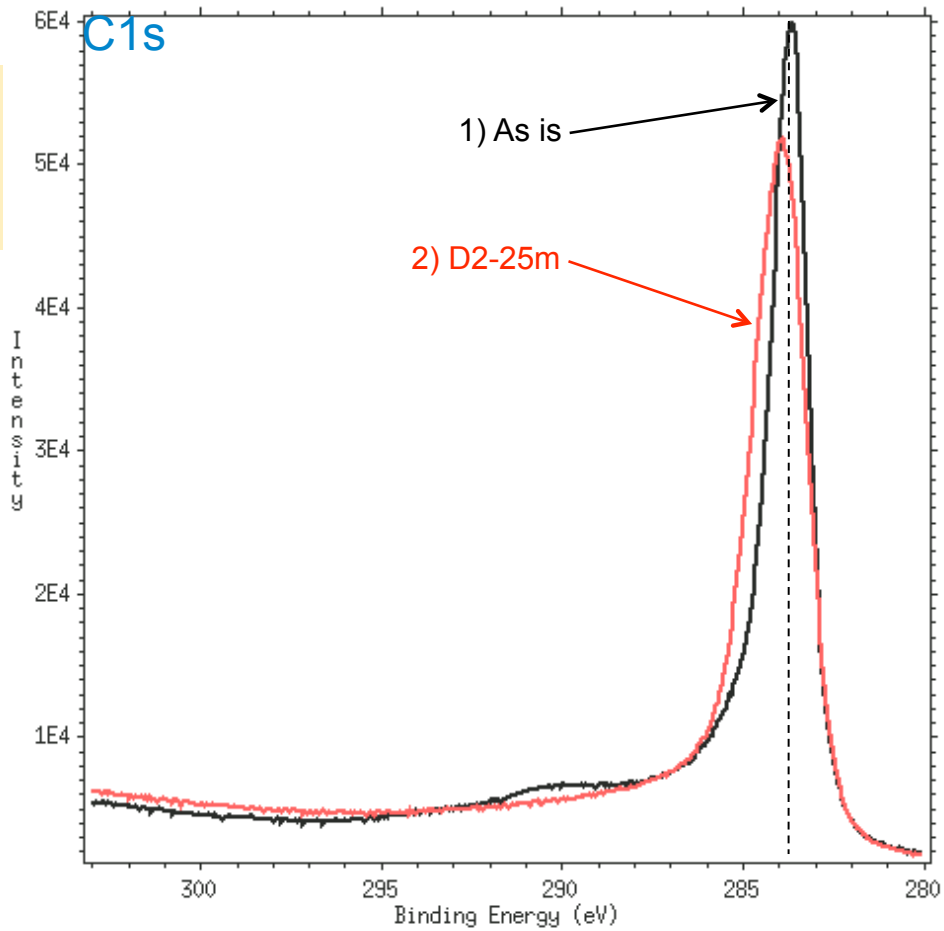
5,6) Change of relative intensity slows at some D fluence threshold.

# *Control: Irradiate with D but no lithium*

## Control experiments

**Procedure (repeat):**
ATJ graphite was irradiated with **D *without* any lithium conditioning.**




**Result:**
Graphitic peak (284 eV) shifted slightly to higher binding energy.

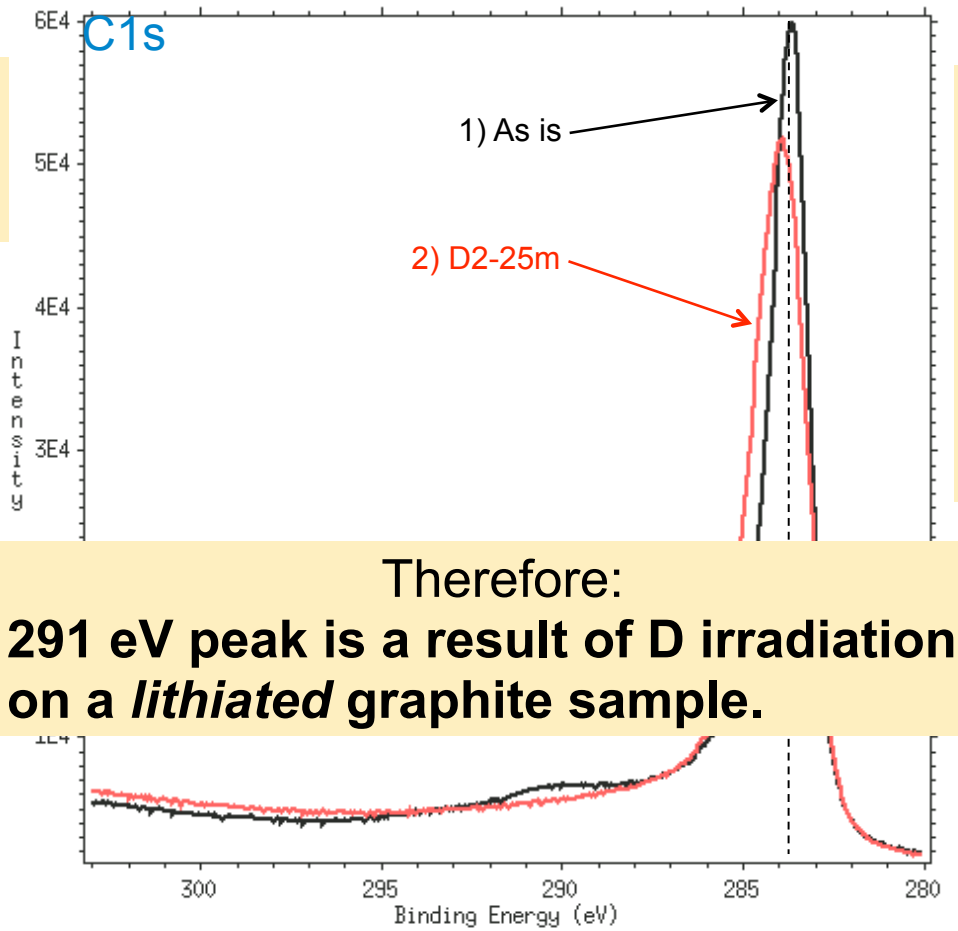
Carbonate peak (290 eV) diminished.

No new peaks were observed.

# *Control: Irradiate with D but no lithium*

Control experiments

**Procedure (repeat):**
ATJ graphite was irradiated with D ***without* any lithium conditioning.**



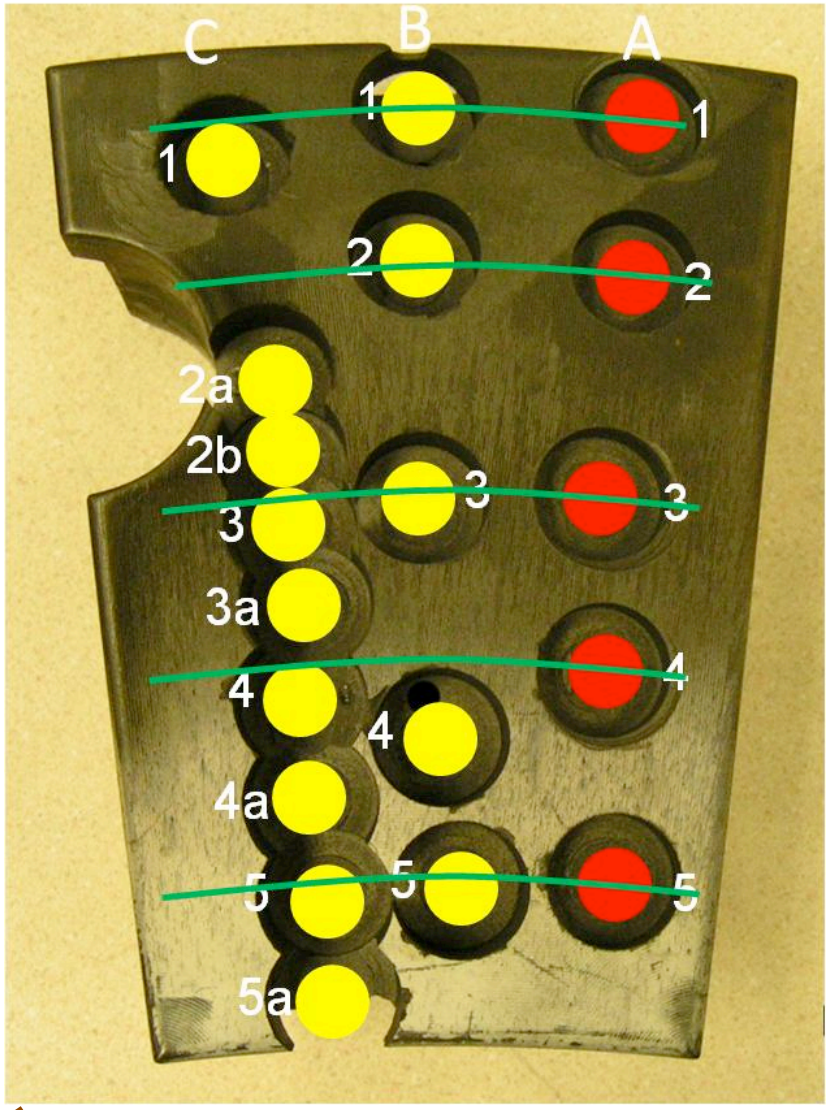

**Result:**
Graphitic peak (284 eV) shifted slightly to higher binding energy.

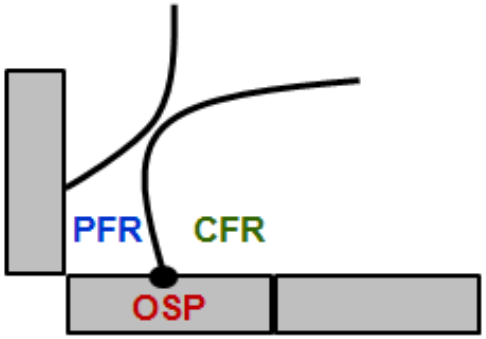
Carbonate peak (290 eV) diminished.

No new peaks were observed.

Therefore:
**291 eV peak is a result of D irradiation on a *lithiated* graphite sample.**

# *NSTX Tile A408-002*




Common Flux Region (CFR)

Outer Strike Point (OSP)

Private Flux Region (PFR)

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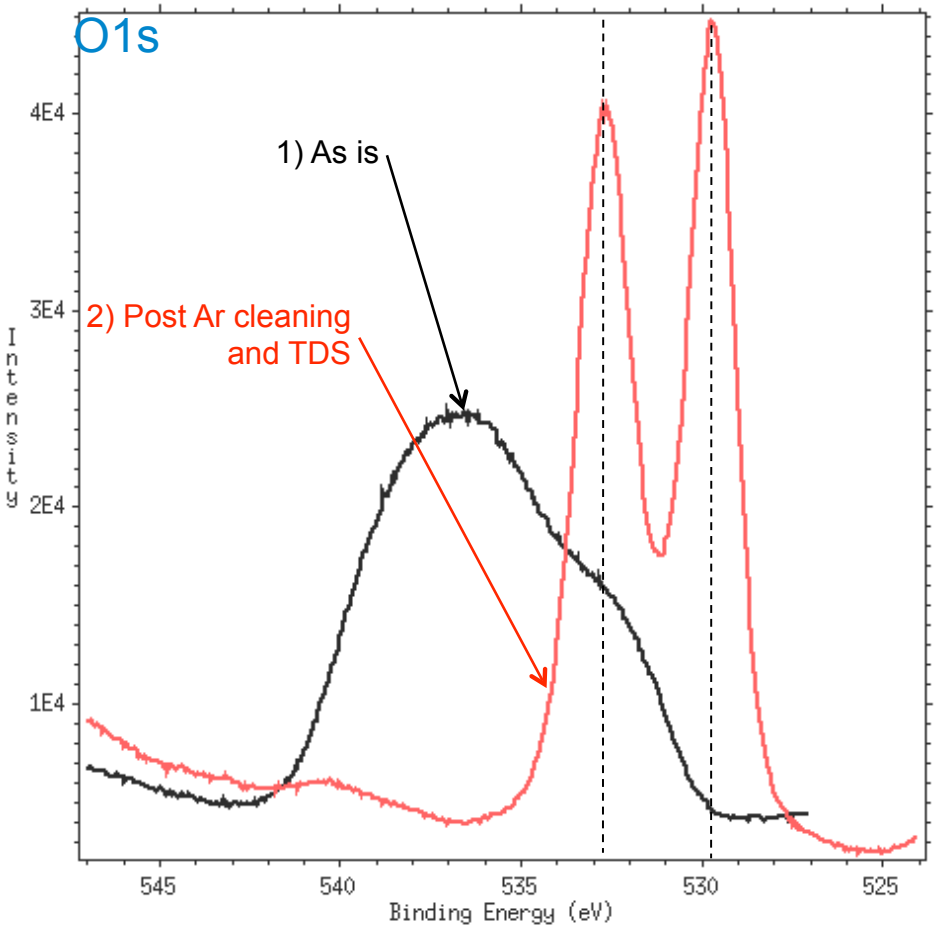
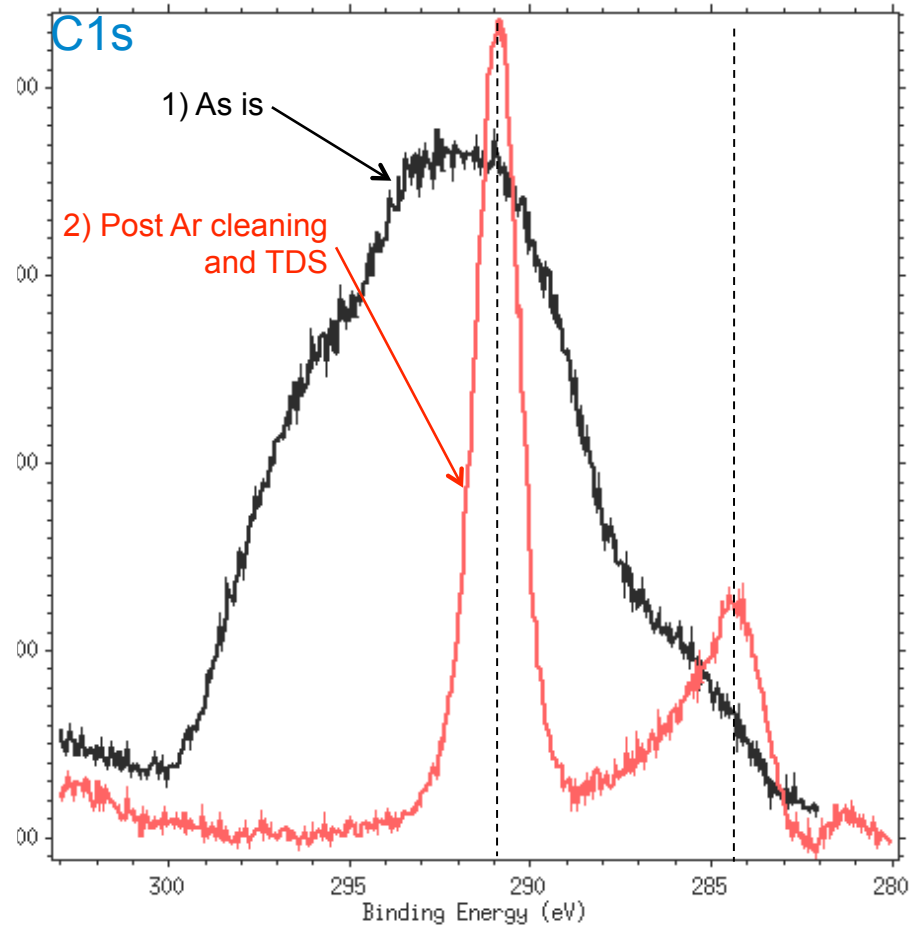
# Results – Post mortem NSTX FY08 tiles




Treatment procedure results in peaks at 529.5 and 533 eV.

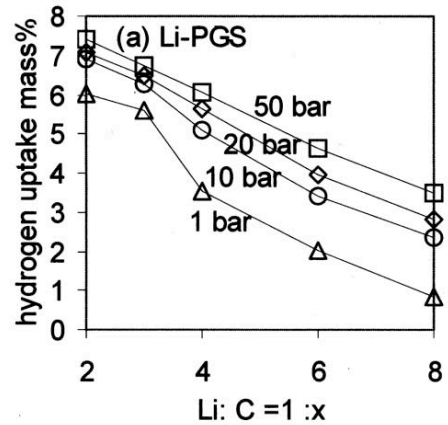


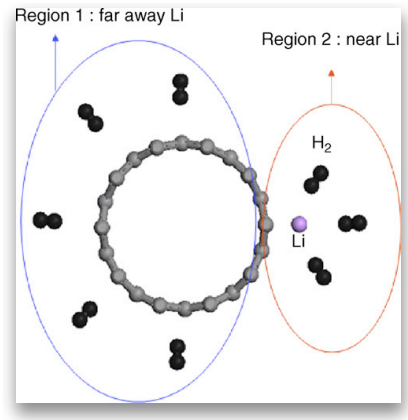

Treatment procedure results in peaks at 284 and 291 eV.

Before treatment procedure, passivated tiles exhibit **broad** peaks.
After cleaning, **tiles resemble peaks found in control experiments.**

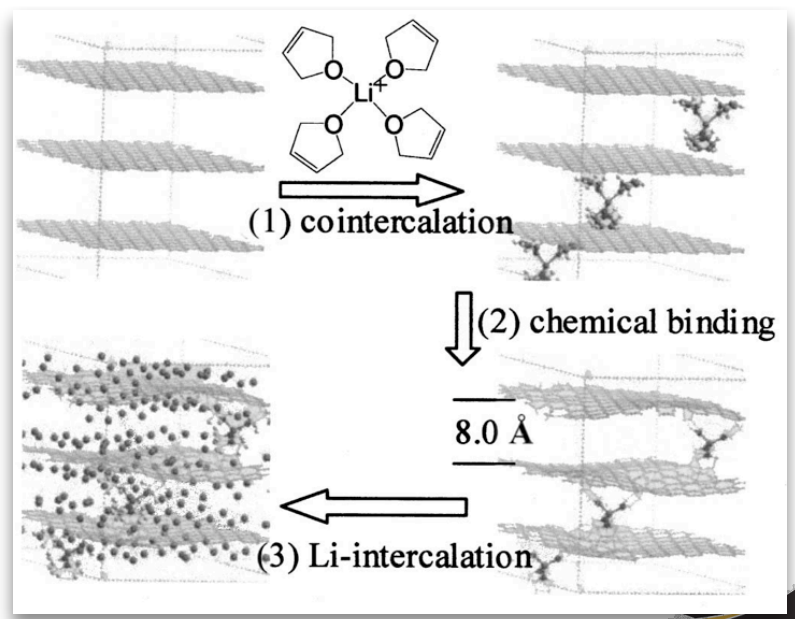
# Mechanisms for D retention in lithiated ATJ graphite surfaces

- Structural diversity in carbon leads to a number of “functionalities” or “preferred interactions” between hydrogen and Li in a carbon matrix
- Literature in the Li-C-H system is consistent with our observations
- Disorder in the carbon matrix can leave a large number of C valences unsaturated as dangling bonds
- H can also bind in the *vicinity* of Li atoms (similar for D)
- Electronic transfer from Li to C atoms can induce dipole interactions with D
- *More Li, more D interaction and effectively higher retention*



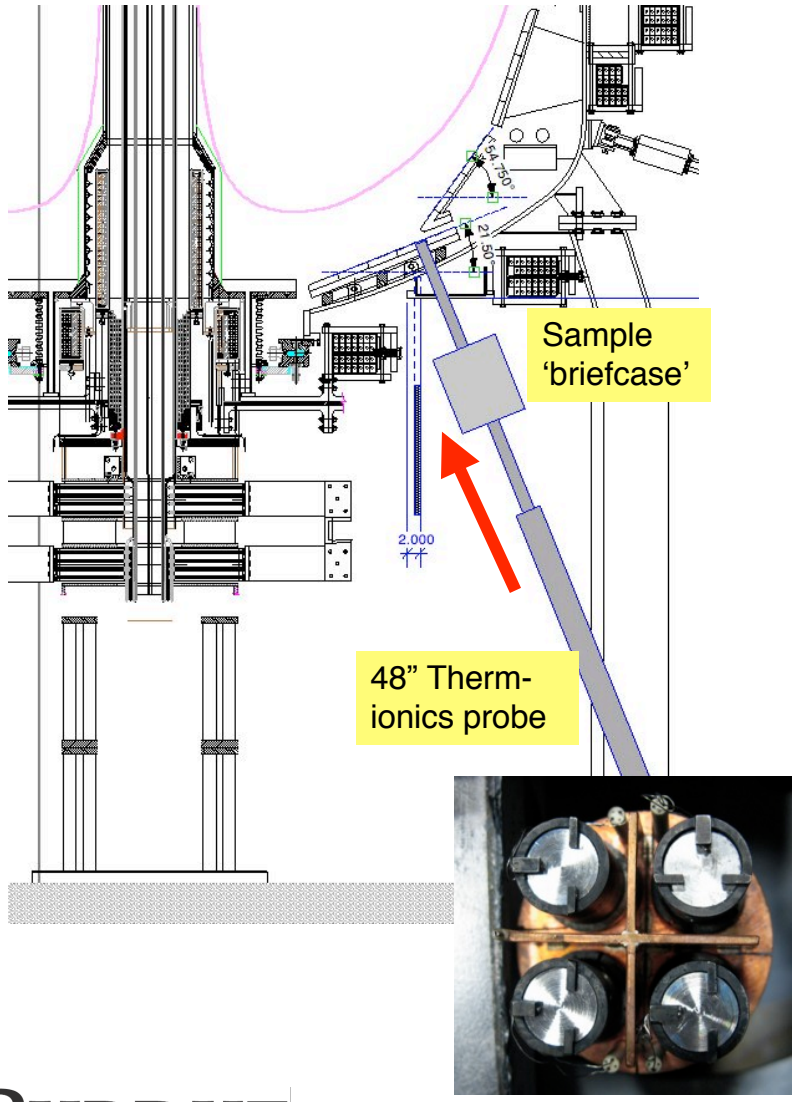

Lithium doping in nano-structured carbon surfaces using DFT and QMD modeling[2,3]

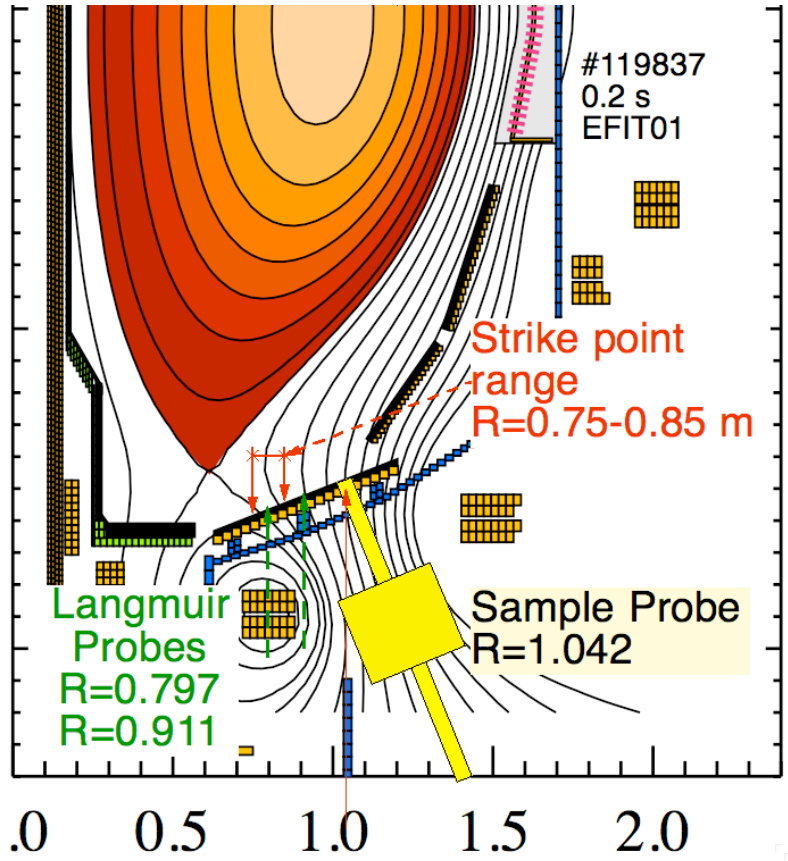




[1]J.R. Dahn et al. Science 270, October 1995, 590
[2]W.Q. Deng et al. Phys. Rev. Lett. 92, 2004, 166103
[3]J.H. Cho et al. Catalysis Today, 120, 2007, 407

# NSTX PMI Probe




Sample Probe aims to address: *"fundamental processes governing particle balance...using lithium surfaces in the divertor…"*
(Joule milestone language)

FY'09 Thermal Desorption Spectroscopy ex-vessel, promptly after plasma exposure (no air exposure).

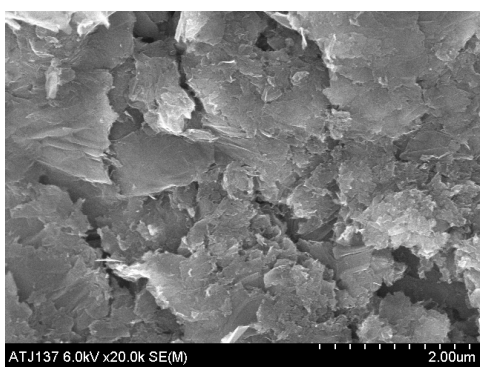
# Increased Li changes molecular state

Change in Li functionality of samples consistent with XPS tile spectra

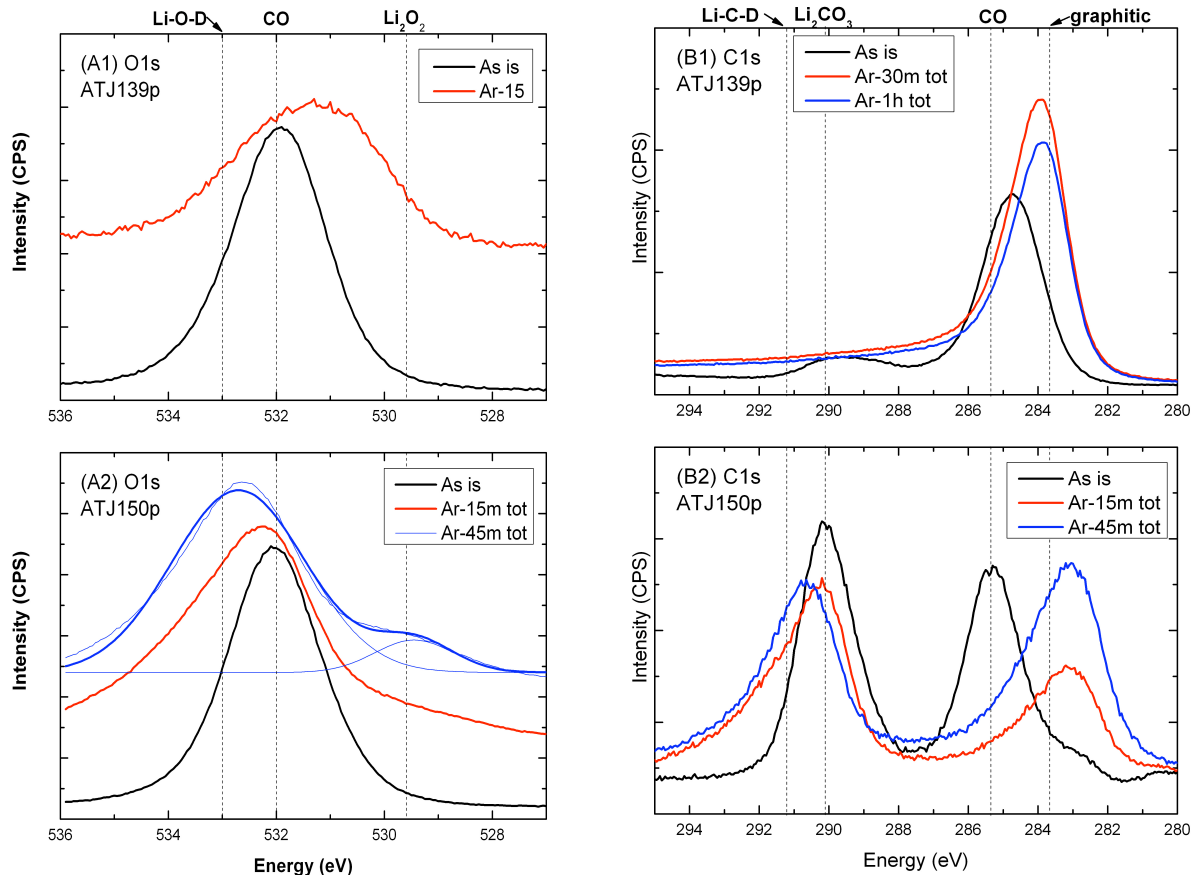
ATJ graphite exposed to 6 NB heated discharges with 0.75 g Li evaporation ~ 141 nm nominal Li 'thickness'

ATJ graphite exposed to 40 NB heated discharges with 9.8 g Li evaporation ~ 1842 nm nominal Li 'thickness'

NSTX exposed polished graphite surfaces modified by plasma.




XPS analysis of exposed samples shows molecular state changes with Li concentration.




After Ar cleaning removed passivated layer due to trace $O_2$.

Consistent with increased Li effect on retention with higher Li evaporation.

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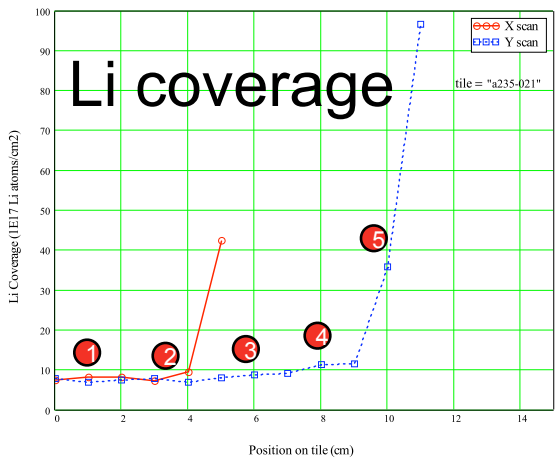
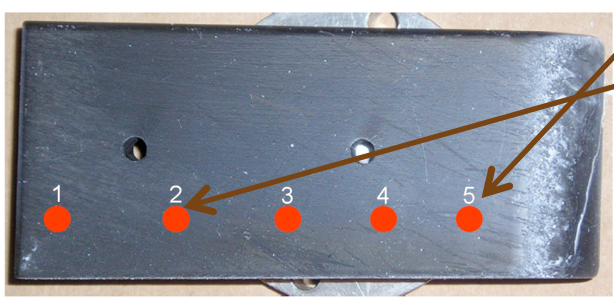
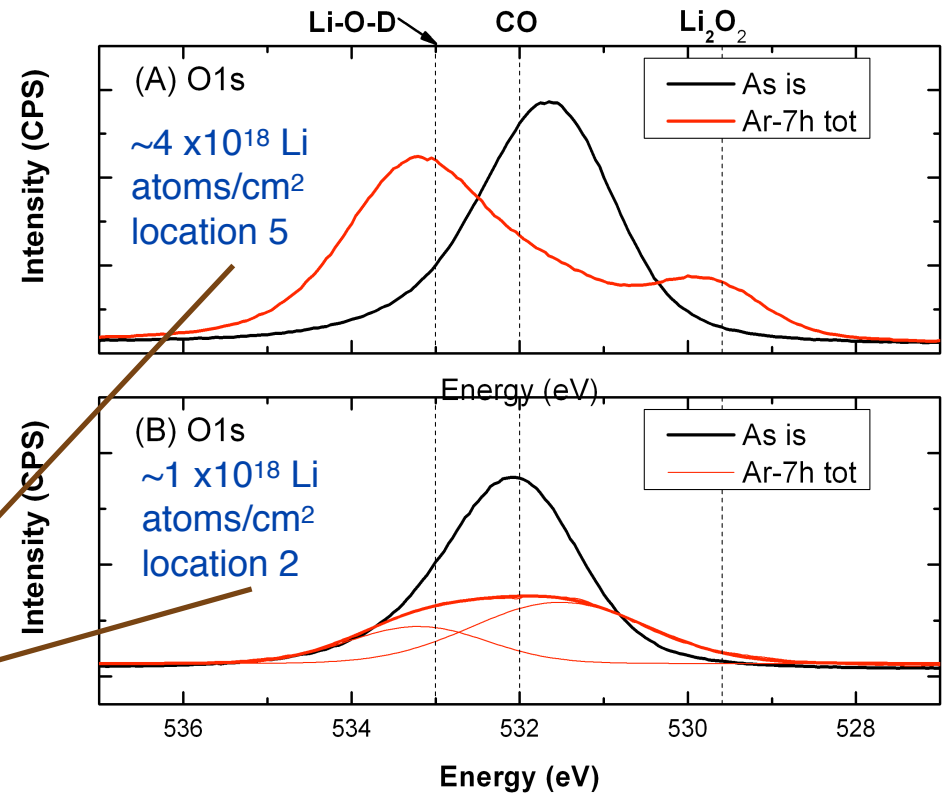
# Comparisons with post-mortem tile data

- Lithium dependence on surface chemistry




ATJ graphite tiles exposed to NSTX
XPS spectra after 7 h Ar cleaning removed passivated amorphous layer due to $O_2$ exposure.

Low Li concentration > no Li-O-D, or Li-D peaks
High Li concentration > yes, Li-O-D, or Li-D peaks

Ion Beam Analysis of Li and D on Tiles from NSTX, W. Wampler, 2006

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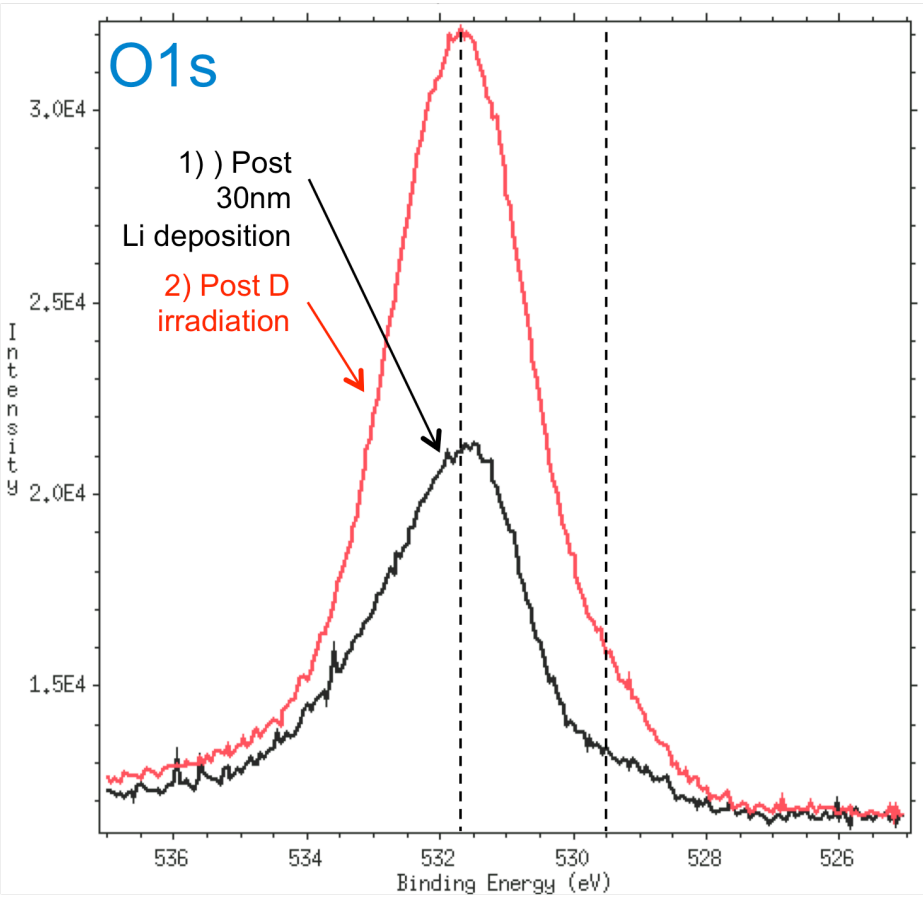
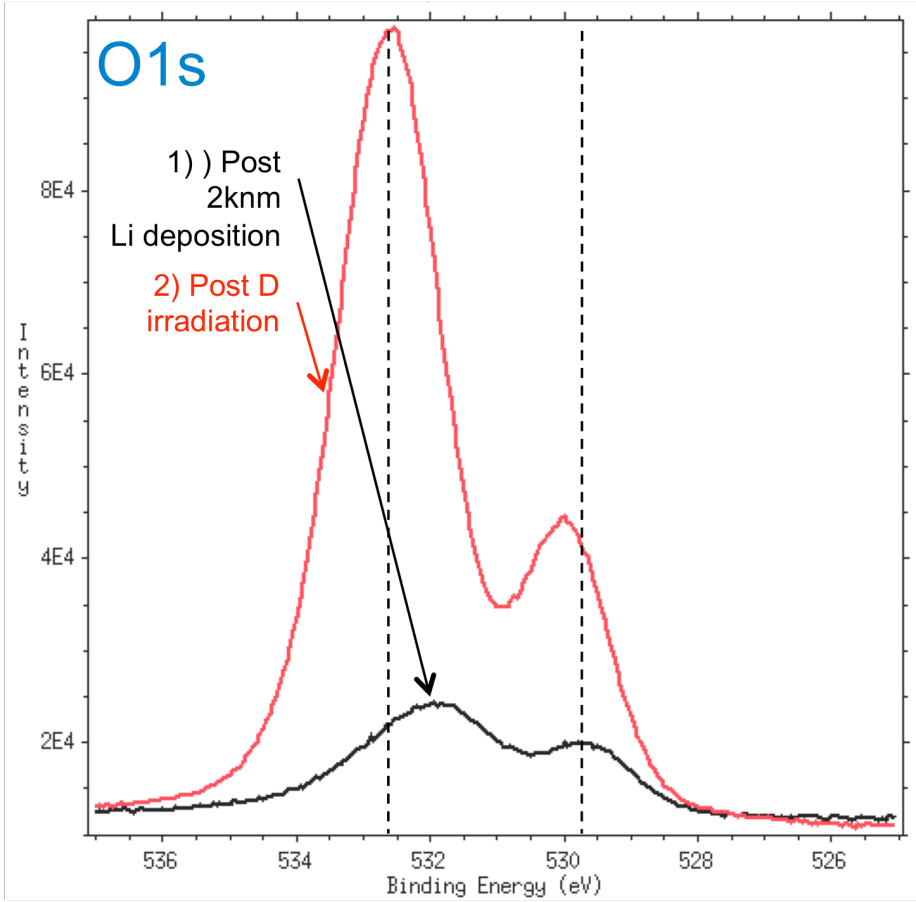
# Comparisons with controlled D ion-beam experiments




Li-30nm post deposition, post D irradiation

Li-2000 nm post deposition, post D irradiation

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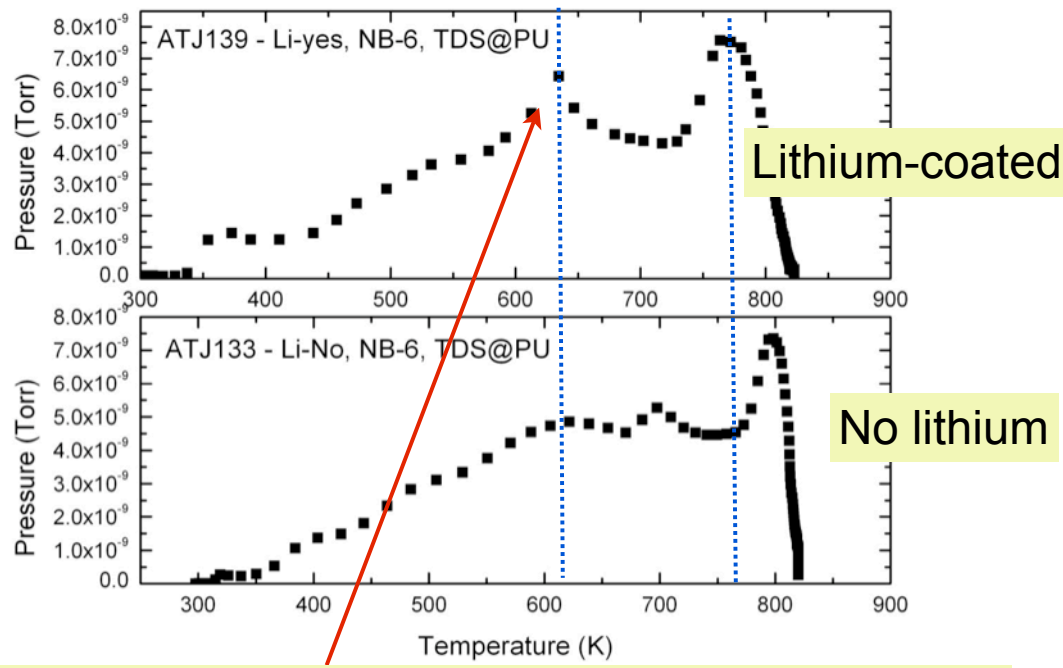
# *Thermal desorption spectra (TDS) of ATJ graphite samples exposed to ohmic discharges with and without Li conditioning*

- Two TDS peaks correspond to effective release of D.
- 800 K peak indicates covalent bonding of D to Li, O and/or C.
- 600 K peak with Li has weaker bonding of D 'in solution'.
- Consistent with prompt release of additional D after NSTX discharge in previous slide.




dominant low temperature peak associated with "weakly-bonded" deuterium atoms in lithiated graphite matrix

- Strong correlation between dose of lithium coatings and dynamic retention of deuterium (controlled beam experiments)
- We have identified a weakly-bonded state for deuterium atoms, similar to bond strengths for D atoms in solution with pure Li, except mechanism for binding is quite different due to presence of graphite matrix

# *Summary and Future Work*

- Controlled particle-surface interaction experiments at Purdue show importance of *in-situ, in-vacuo* characterization to study the role of Li-based systems on deuterium retention and recycling
- D retention in lithiated graphite is dictated by more than simple interactions between Li and D alone. The presence of carbon and oxygen plays a major role in dictating how D is bound in the lithiated graphite matrix (morphology could also play important role)
- Key Results from PMI Probe data
  - Strong correlation between dose of lithium coatings and dynamic retention of deuterium (controlled beam experiments)
  - Consistent with prompt release of additional D after NSTX discharge from gas balance results (C. Skinner)
- **Future Work**
  - Edge modeling coupling with experimental data (w/ J. Brooks)
  - Hybridization state of deuterium atoms in lithiated graphite (Raman spec.)
  - Understanding of metal impurities in NSTX
  - Further work on “weakly” bonding state of D

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# *Extra Slides*