Dynamic surface chemistry effects on lithium-coated graphite surfaces from deuterium irradiation

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NSTX Results/Theory Review,
Wednesday, 16 September, 2009

RSSEL

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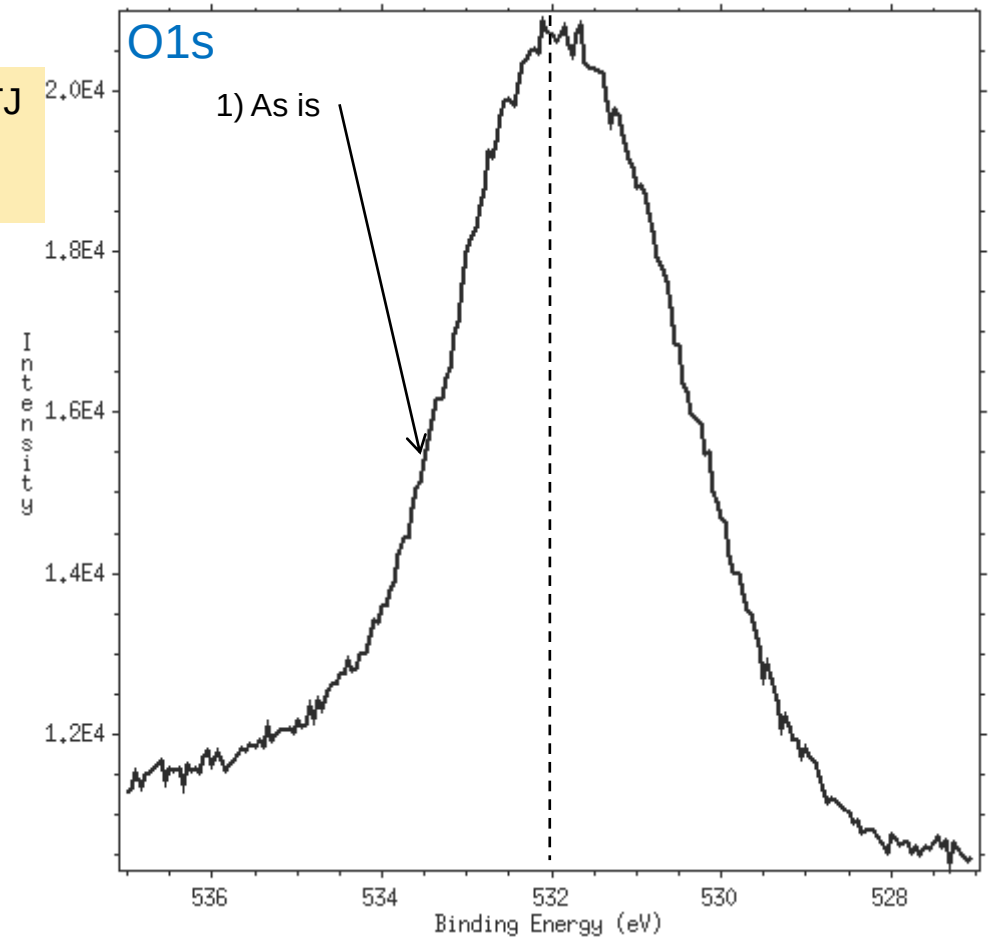
Results – Li-D-O functionality

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



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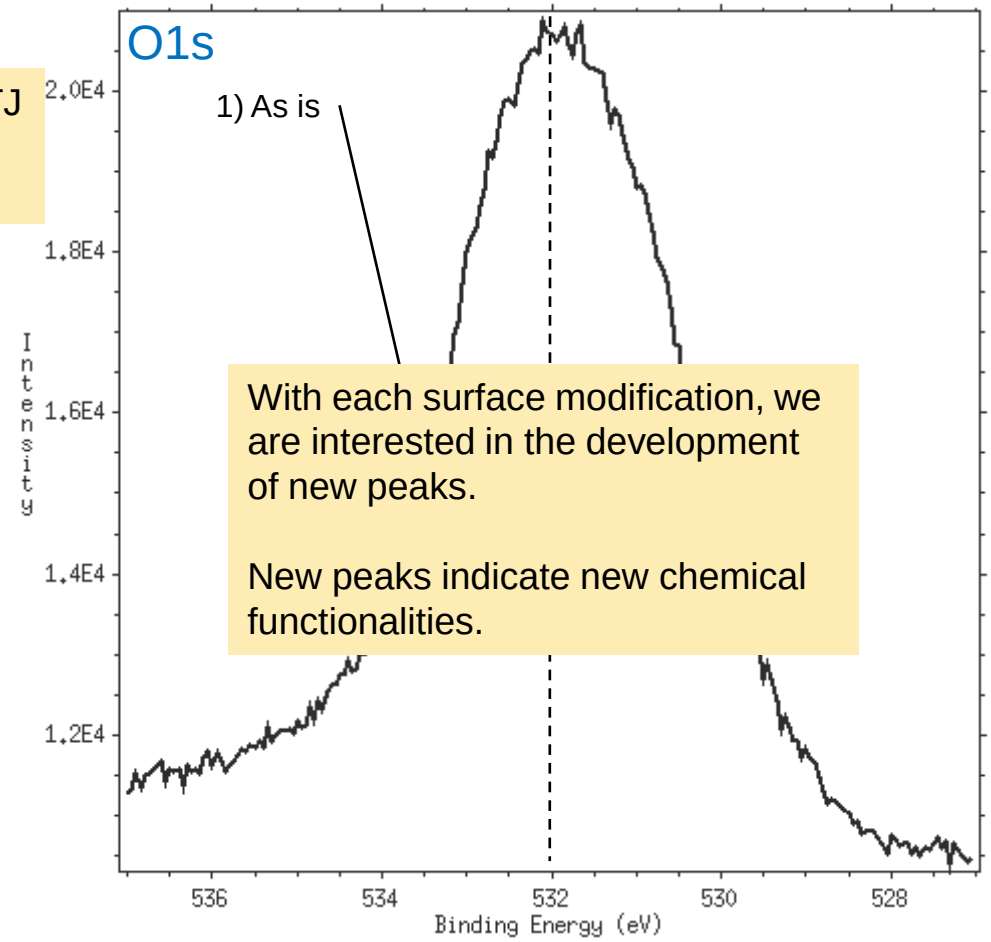


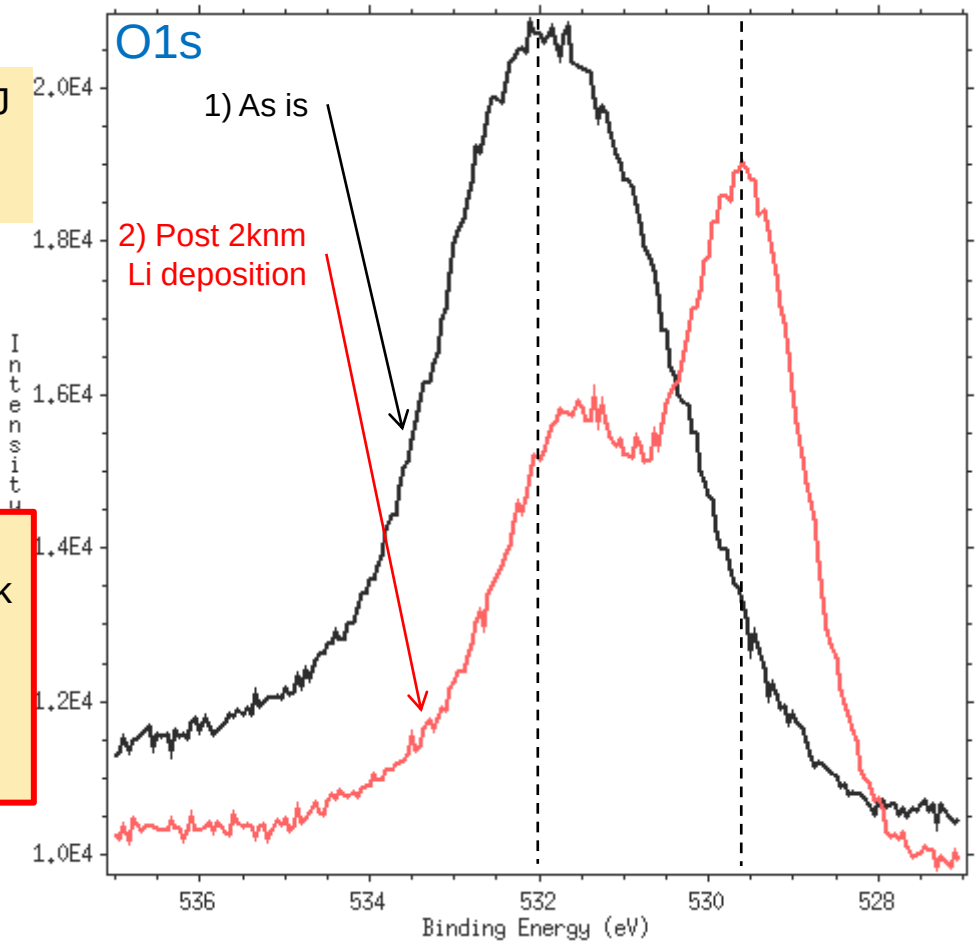
With each surface modification, we are interested in the development of new peaks.

New peaks indicate new chemical functionalities.

Results – Li-D-O functionality

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.



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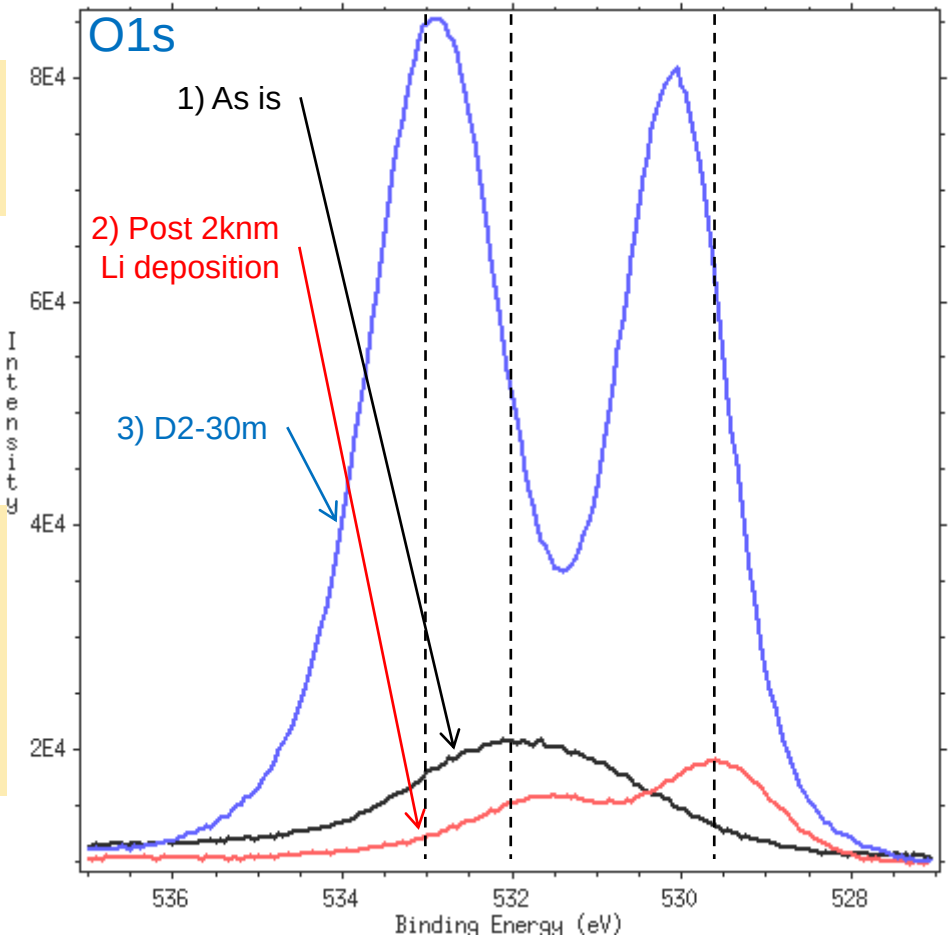

3) 30 minute deuterium irradiation ($\Gamma \approx 1.5$ E15 cm^{-2}) causes a new peak to develop at 533 eV, and a slight shift to higher binding energy for the 529.5 eV peak.

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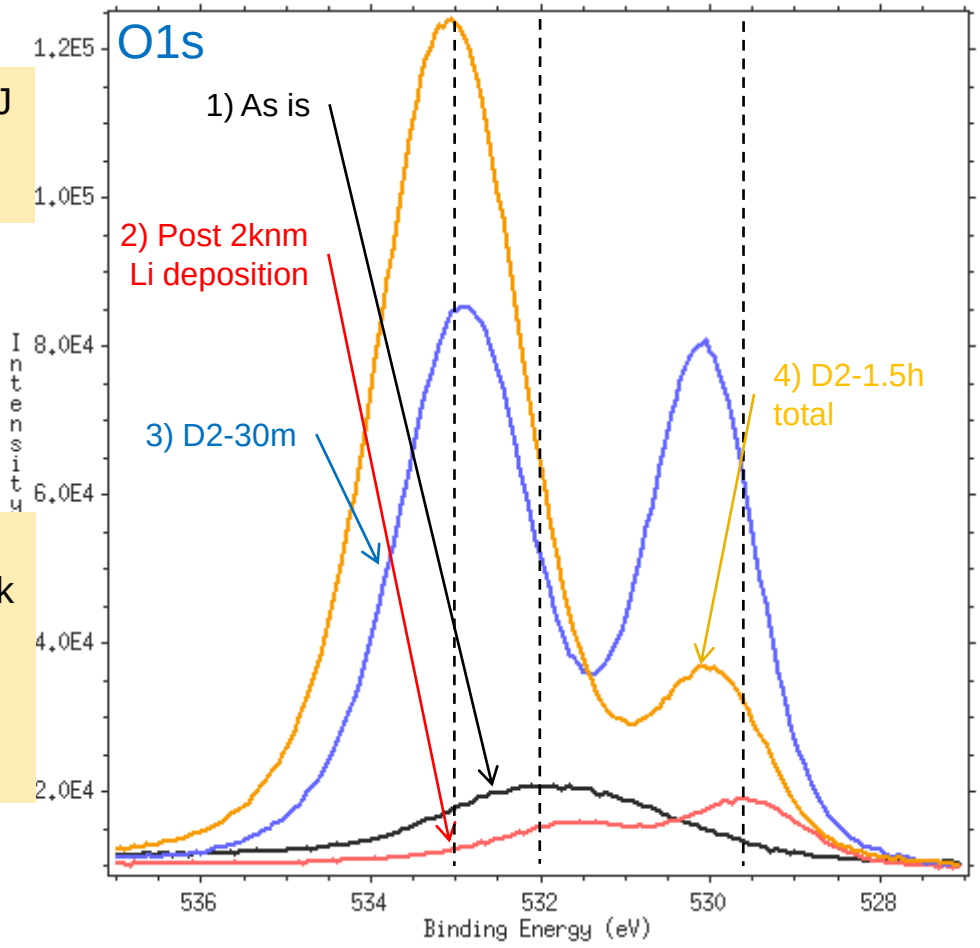

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4) The relative intensity of the 533 eV peak compared to the 529.5 eV peak increases with subsequent irradiations.

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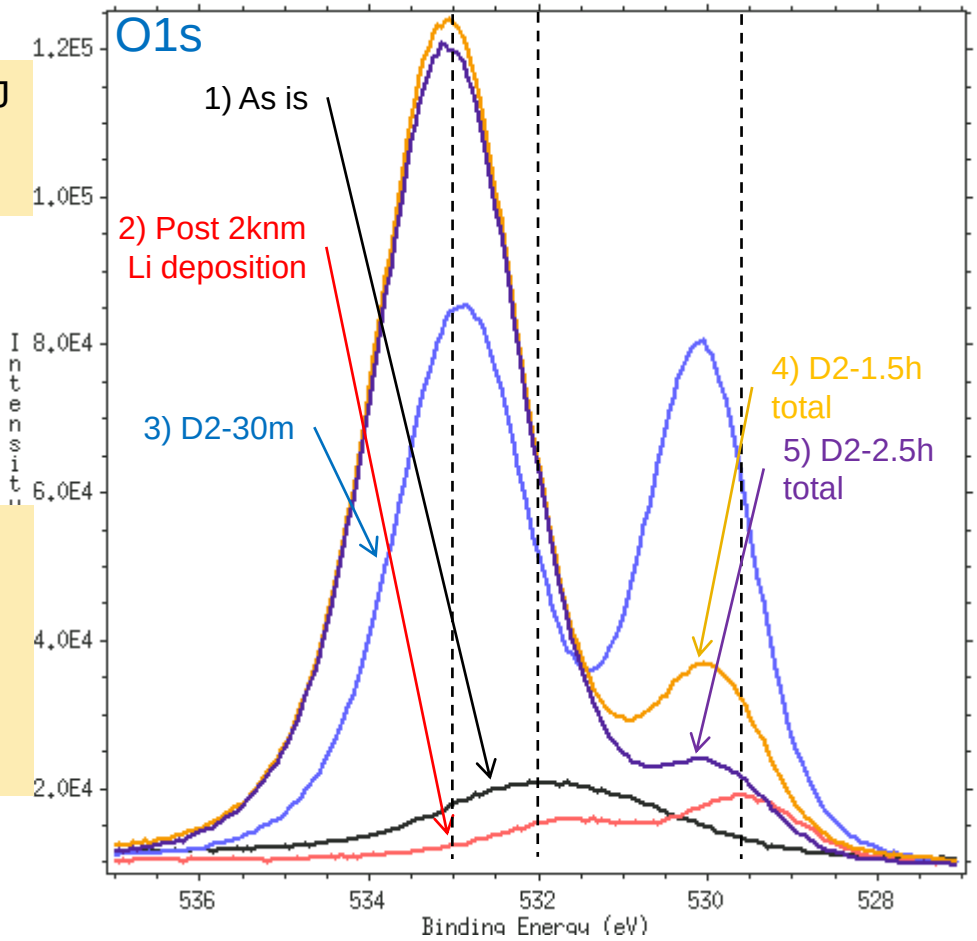

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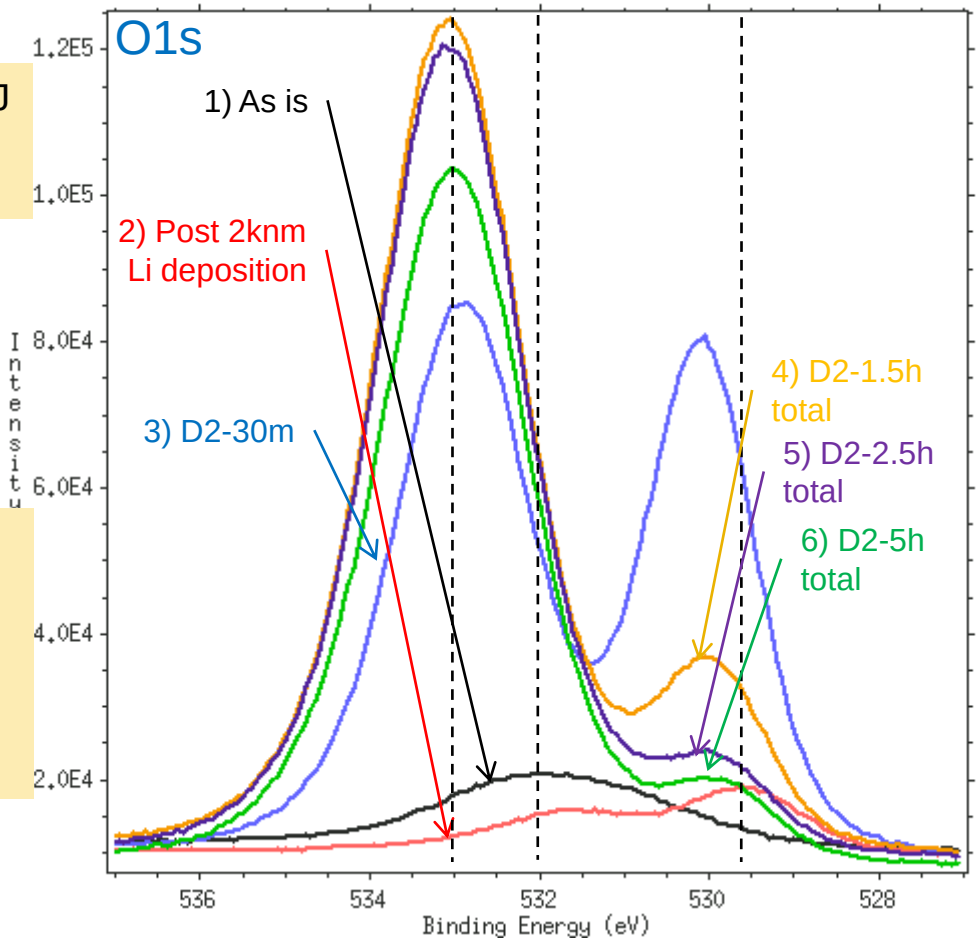

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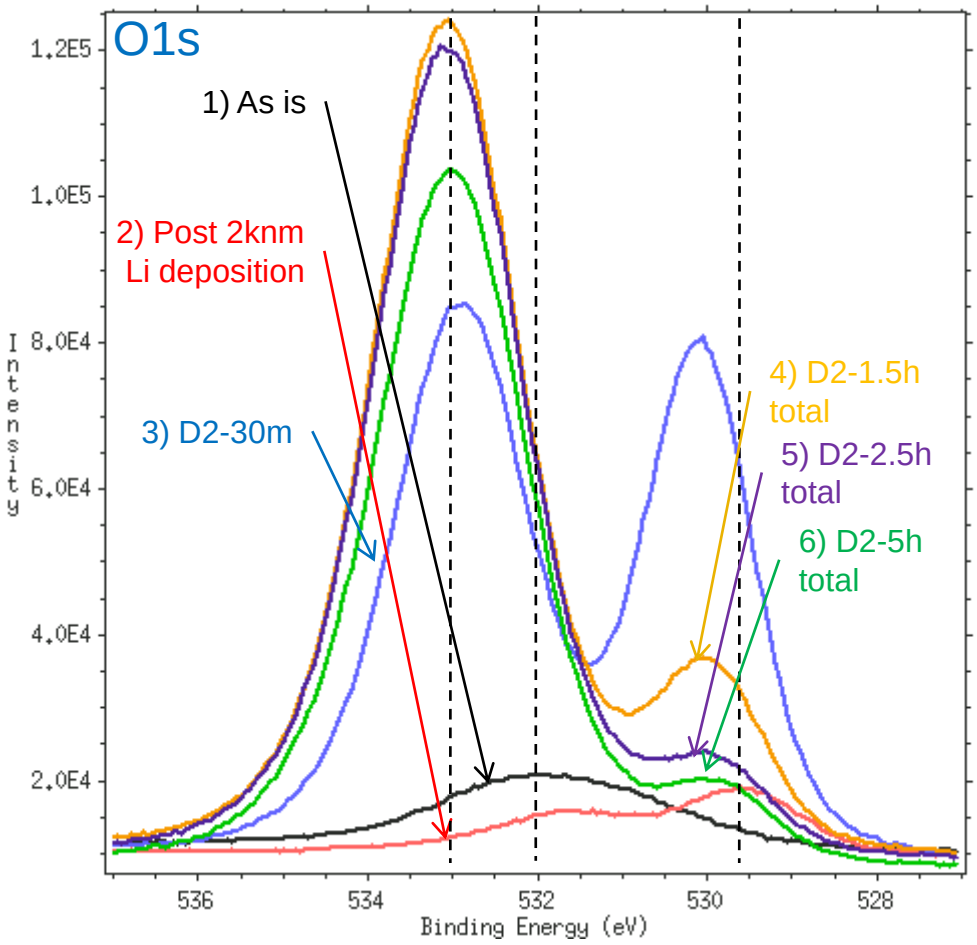
6) …and again.

Results – Li-D-O functionality

Observations

Based on these results and control experiments



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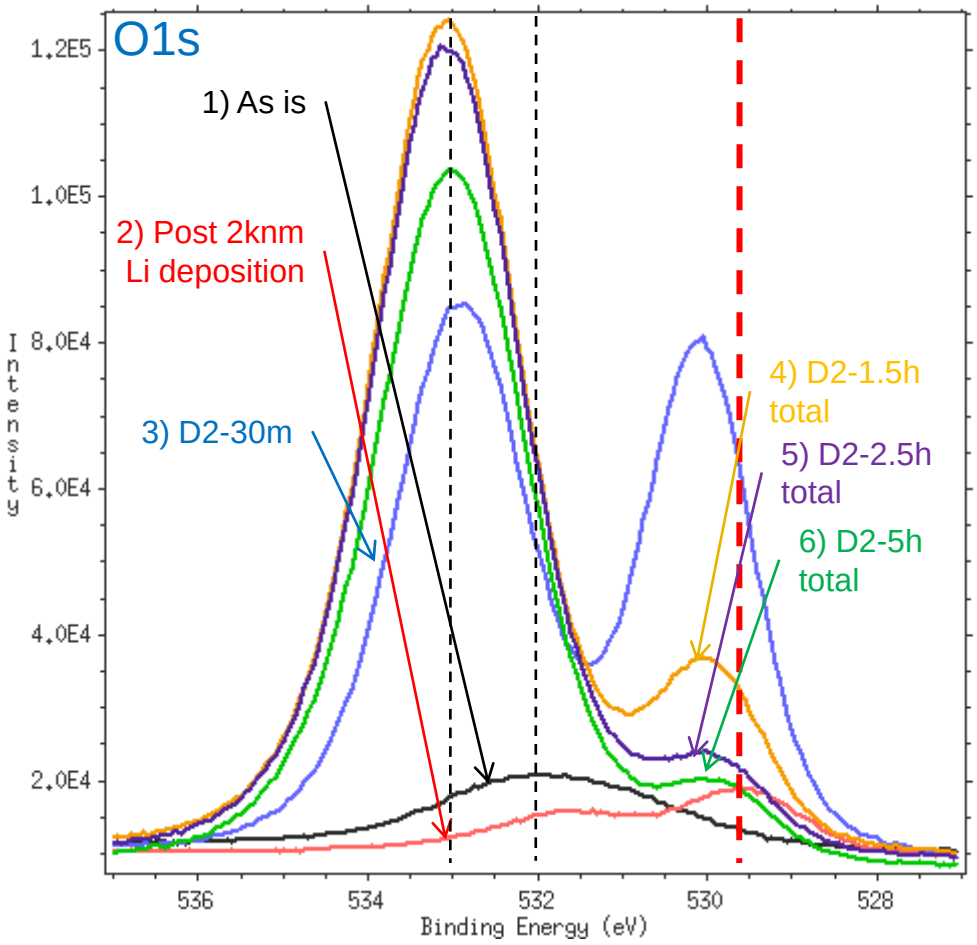


529 eV

- Only develops after Li deposition
- Shifts slightly (~.5 eV) after D2.
- Relative intensity decreases with higher D2 fuence

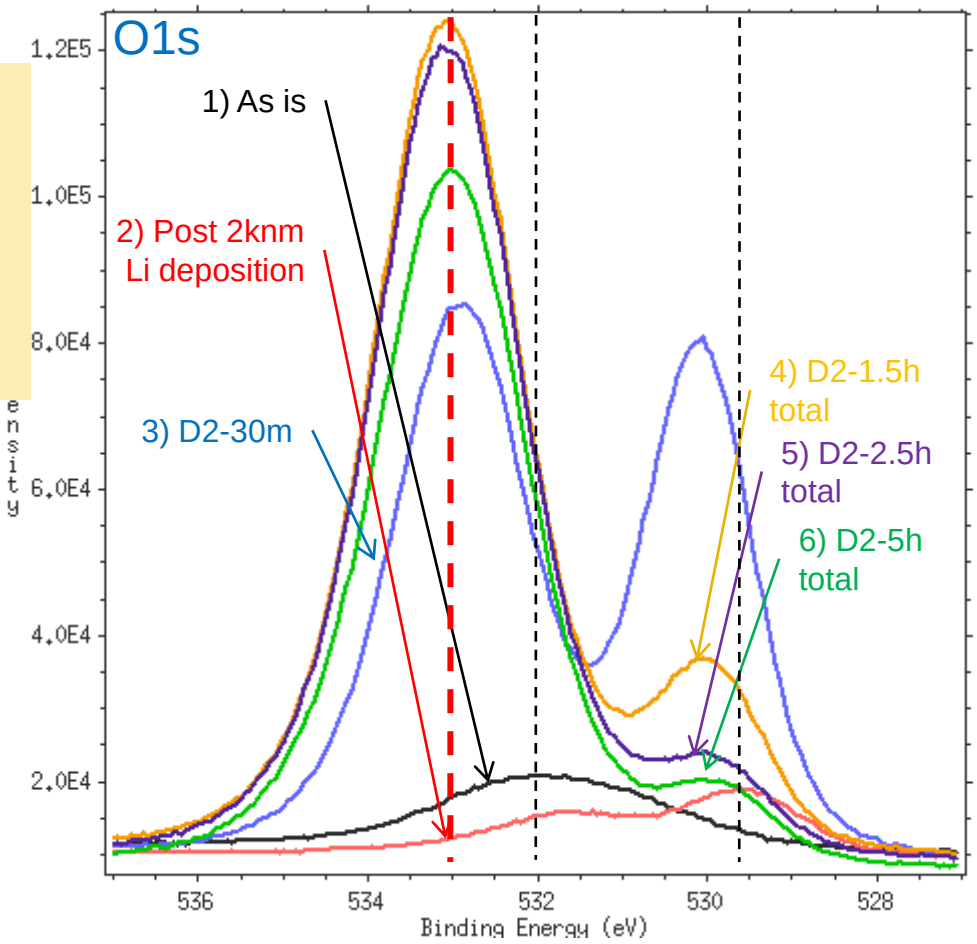
Results – Li-D-O functionality

Observations

Based on these results and control experiments

533 eV

- Only develops after irradiating a *lithiated* sample.
- Relative intensity increases with higher D2 fluence



529 eV

- Only develops after Li deposition
- Shifts slightly (~.5 eV) after D2.
- Relative intensity decreases with higher D2 fuence

Results – Li-D-O and C functionality

Observations

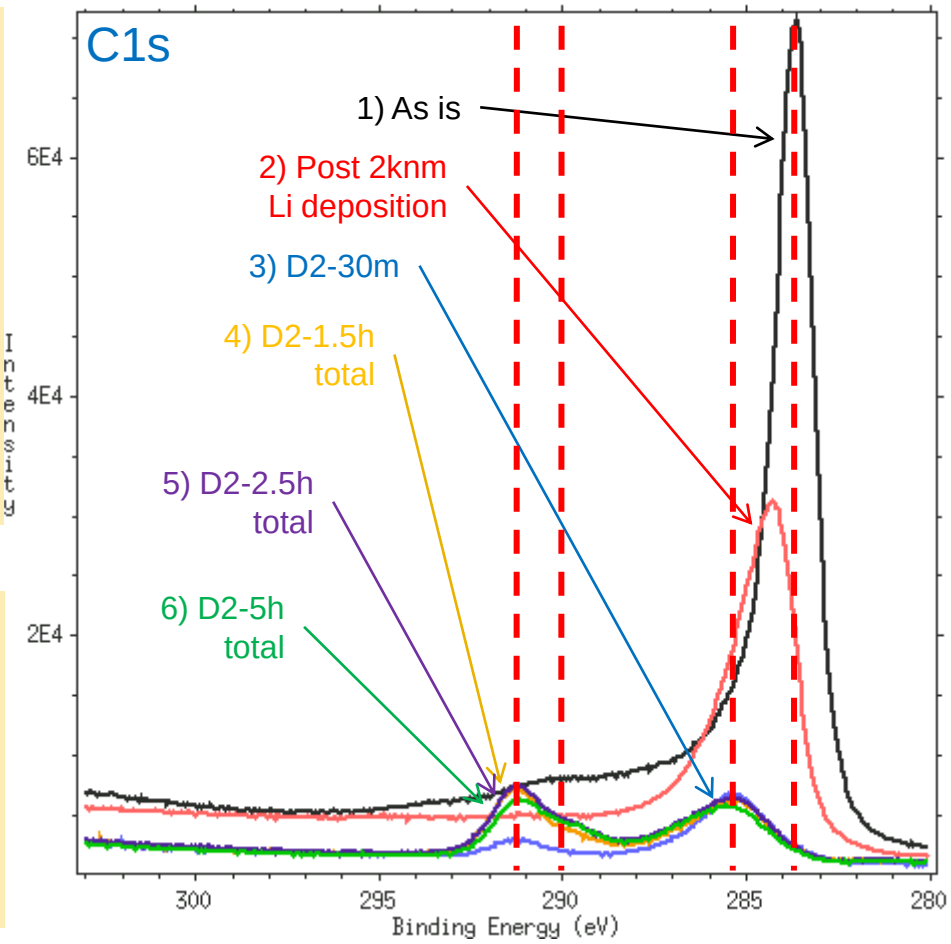
Based on these results and control experiments

291 eV

- Only develops after irradiating a *lithiated* sample.
- Relative intensity increases with higher D2 fluence.
- Eventually peak "saturates" and does not respond to increased D fluence.

290 eV

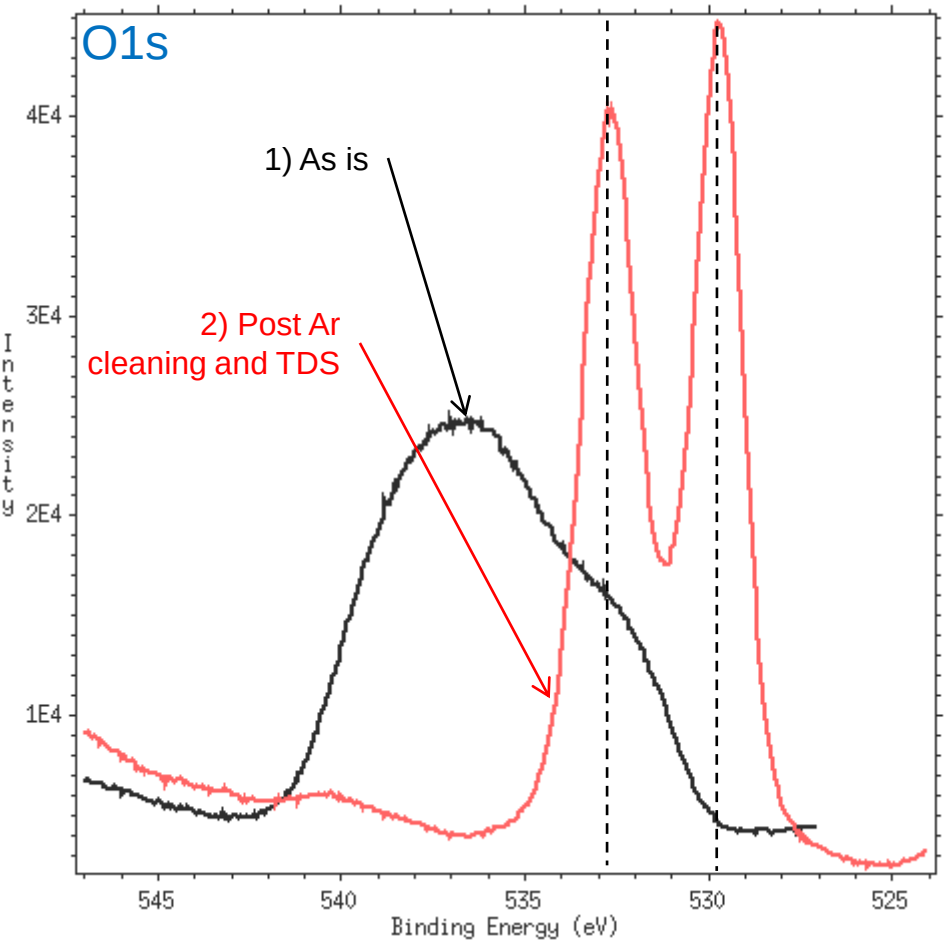
- Slight carbonate influence observed.
- Air exposure of a lithiated sample results in a carbonate peak (not shown).



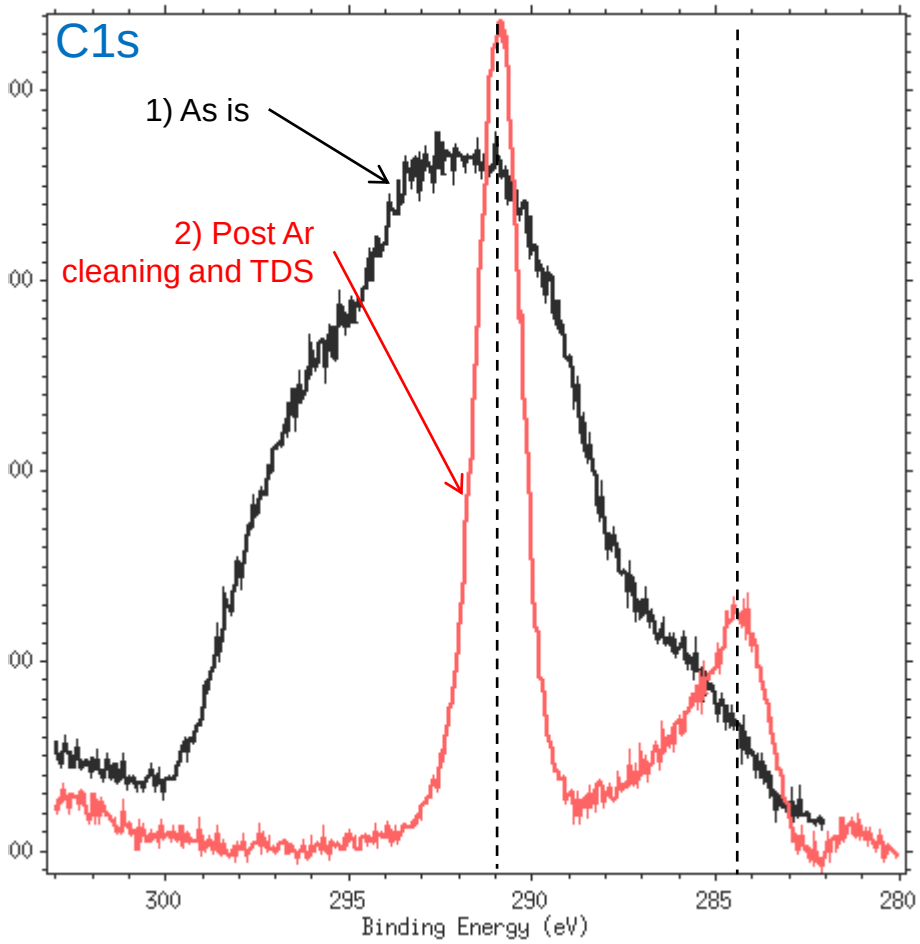
284-285 eV

- Control experiments have shown that 2 peaks momentarily coexist.
- Development of new peak indicates new bonding functionality.

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.**

Summary of controlled in-situ XPS studies

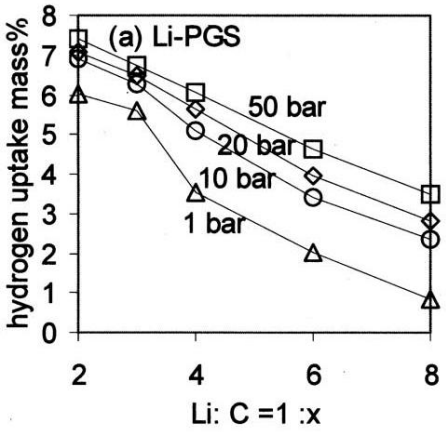
- Oxygen
  - *Li and O* interactions, on a graphite substrate, are manifest at *529.5 eV* in the XPS spectrum. Peak diminishes with larger D fluence.
  - *Li, O, and D interactions*, on a graphite substrate, are manifest at *533 eV*. Peak dominates with larger D fluence.

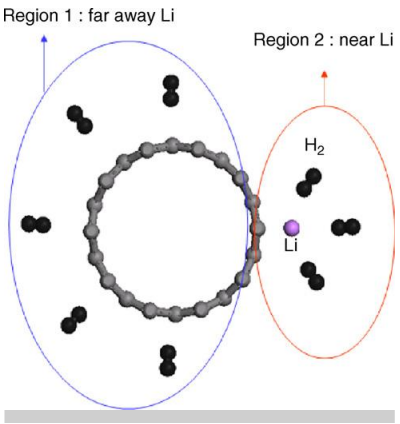
- Carbon
  - *Li, D, and C* interactions are manifest at *291 eV*. Relative peak energy increases with increased D fluence. Changes cease to occur at a yet to be discovered D fluence threshold.

- Post-mortem tiles
  - Treatment (Ar sputtering and heating) changes passivated, broad, inconsistent peaks to align with consistently produced peaks found in controlled experiments.
  - "Broad" peaks consistent with a highly porous and amorphous carbonaceous layer (in time-integrated PFR region)

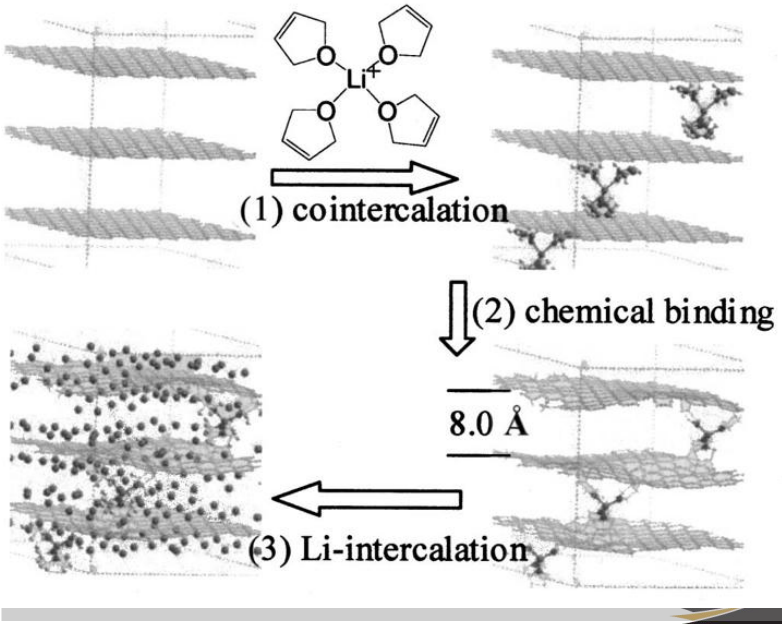
Mechanisms for D retention in lithiated ATJ graphite surfaces

- 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 (or D) can also bind in the *vicinity* of Li atoms
- Electronic transfer from Li to C atoms can induce dipole interactions with H
- More Li, more H interaction and effectively higher retention





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

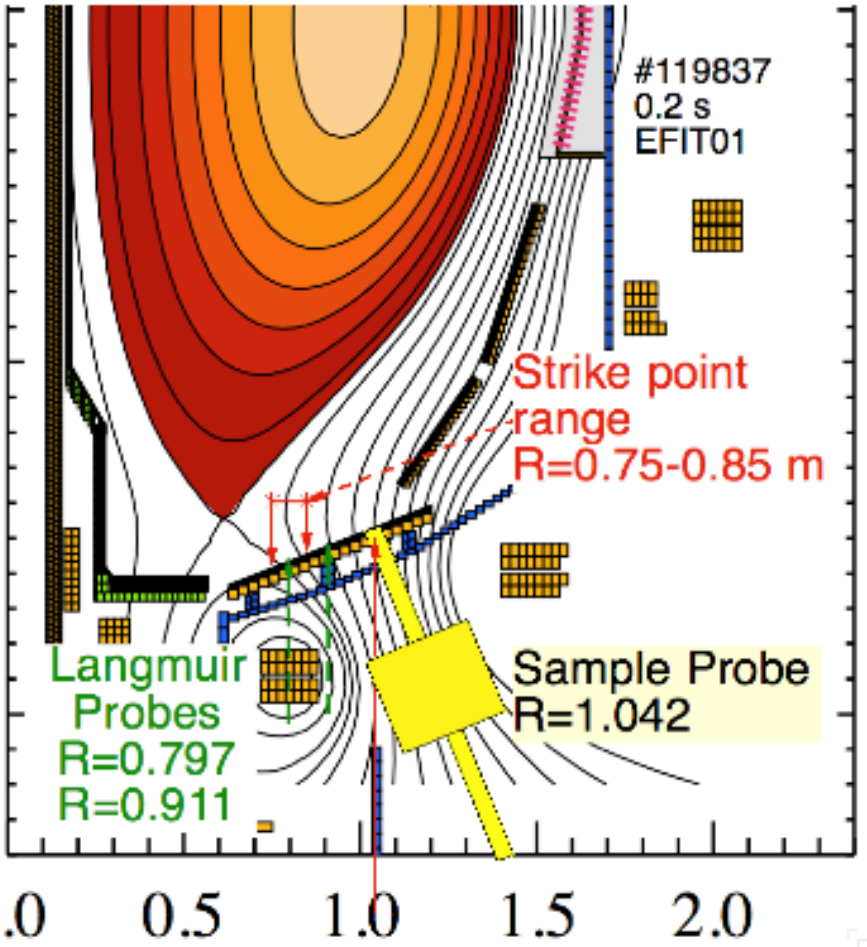


[1]J.R. Dahn et al. Science 270, October 1995, 590
[2]W.Q. Deng et al. Phys. Rev. Lett. 92, 2004, 166103
[3]J.H. Cho et al. Catalysis Today, 120, 2007, 407

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).



PMI Probe experiments (XP911) – Summary

No lithium conditioning

6 Neutral Beam Plasmas – 3 Apr 09

- ATJ132 – TDS at NSTX
- ATJ133 – TDS at Purdue
- Pd425 – XPS
- Si105

8 Ohmic Heated Plasmas – 6 Apr 09

- ATJ134 – TDS at NSTX
- ATJ135 – TDS at Purdue
- Rh sample
- Si112

With lithium conditioning

6 Neutral Beam Plasmas – 24 Apr 09

- ATJ138 – TDS at NSTX
- ATJ139 – TDS at Purdue
- Pd431 – XPS
- Si109

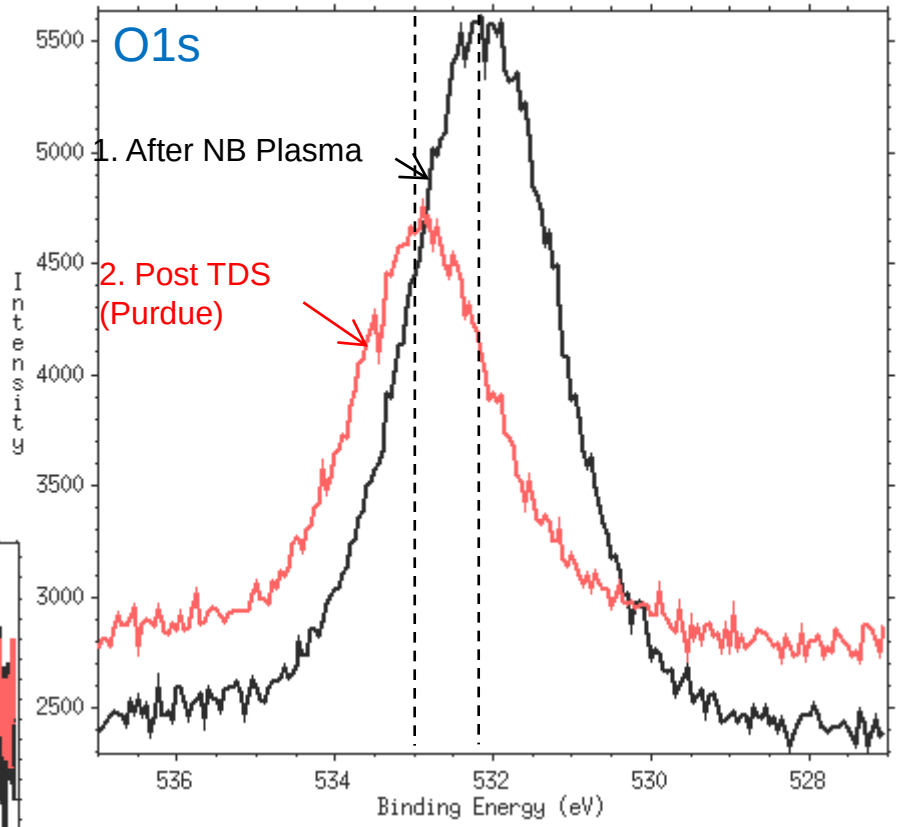
8 Ohmic Heated Plasmas – 22 Apr 09

- ATJ136 – TDS at Purdue
- ATJ137 – TDS at Purdue
- Pd422 – XPS
- Si108

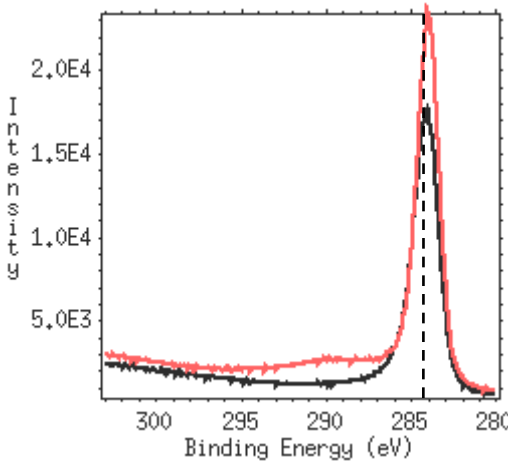
ATJ133 – Exposed to NB Plasma

Brief DoE

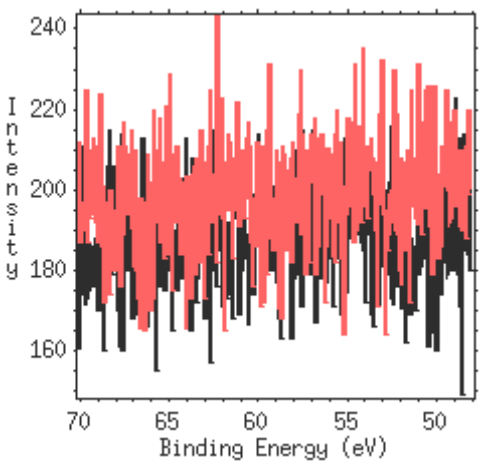
- No lithium conditioning
- 6 NSTX NB plasma shots
- Shipped to Purdue under Ar
- TDS at Purdue



C1s



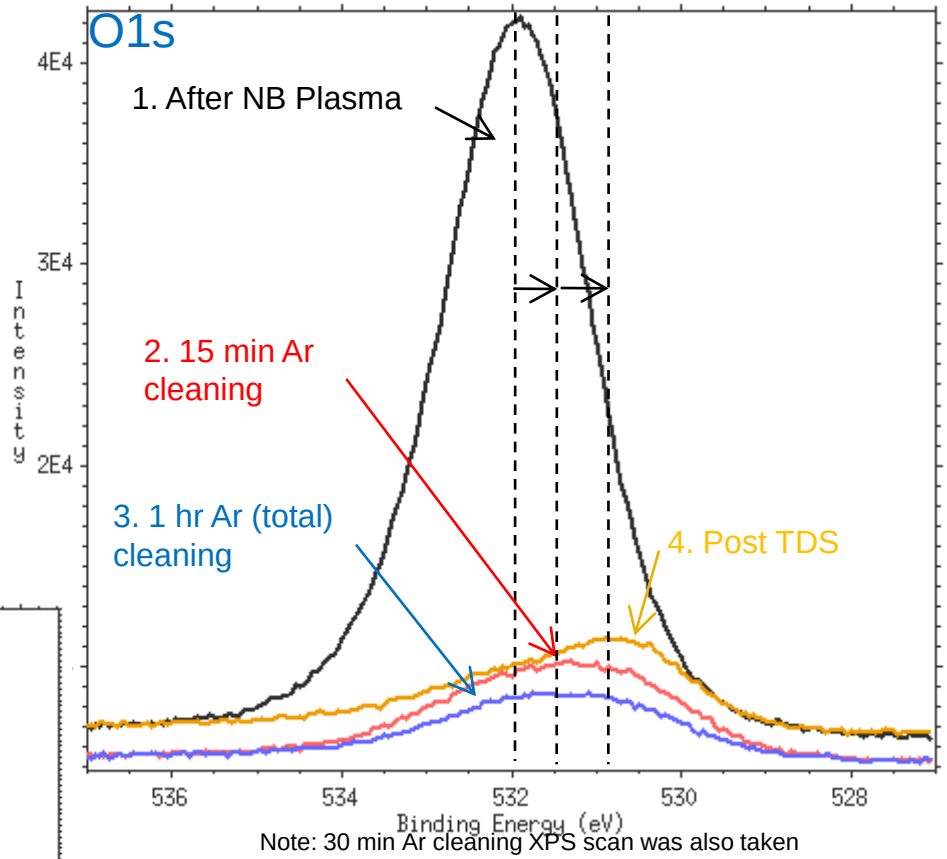
Li1s



ATJ139 – Exposed to NB Plasma

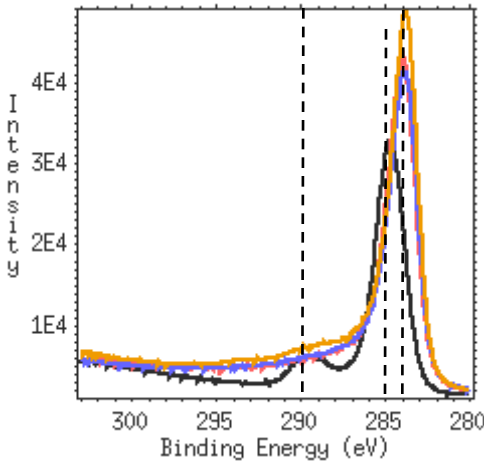
Brief DoE

- Lithium conditioning
- 6 NSTX NB plasma shots
- Ar cleaning
- TDS performed at Purdue
- XPS at Purdue

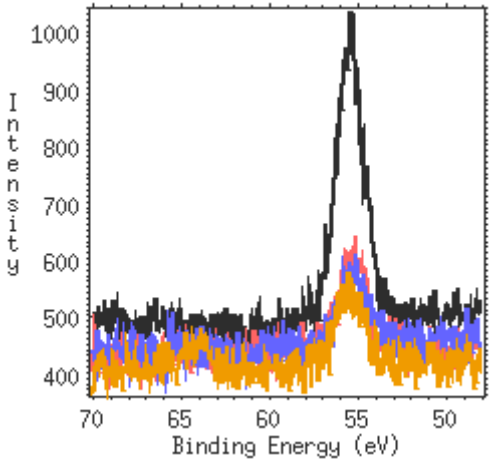


Note: 30 min Ar cleaning XPS scan was also taken

C1s

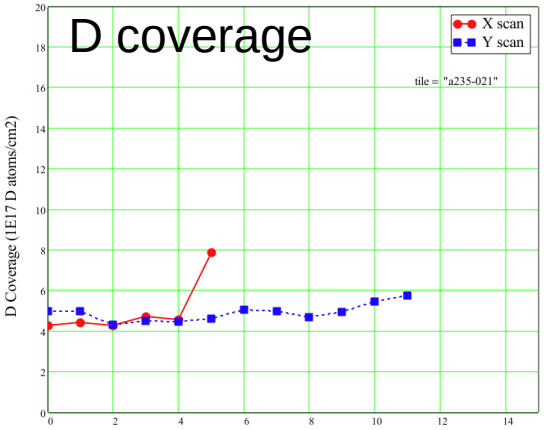


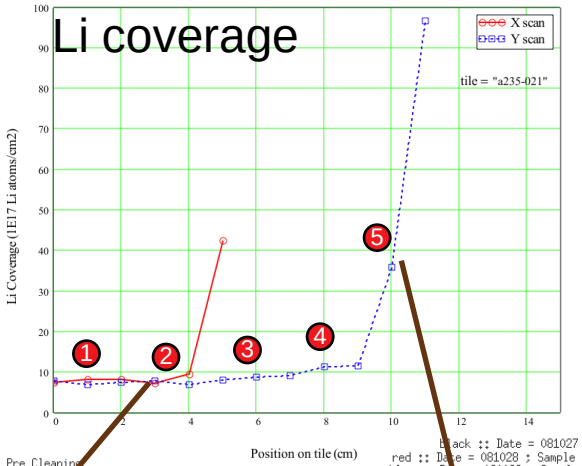
Li1s

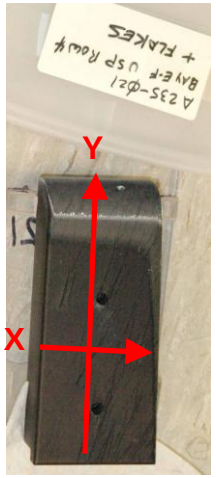


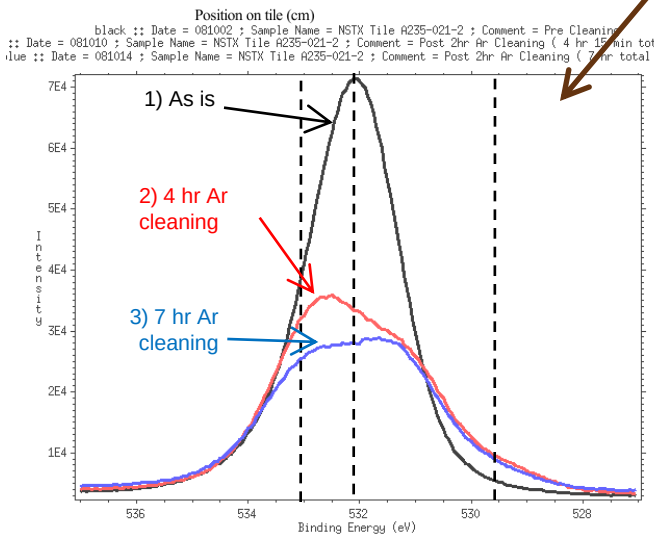
Comparisons of Ion Beam data with XPS

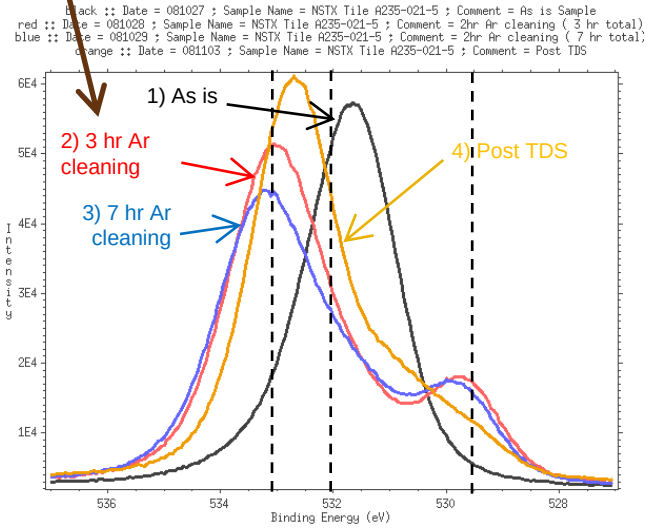
- Lithium dependence on surface chemistry











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

NSTX Tile A235-021

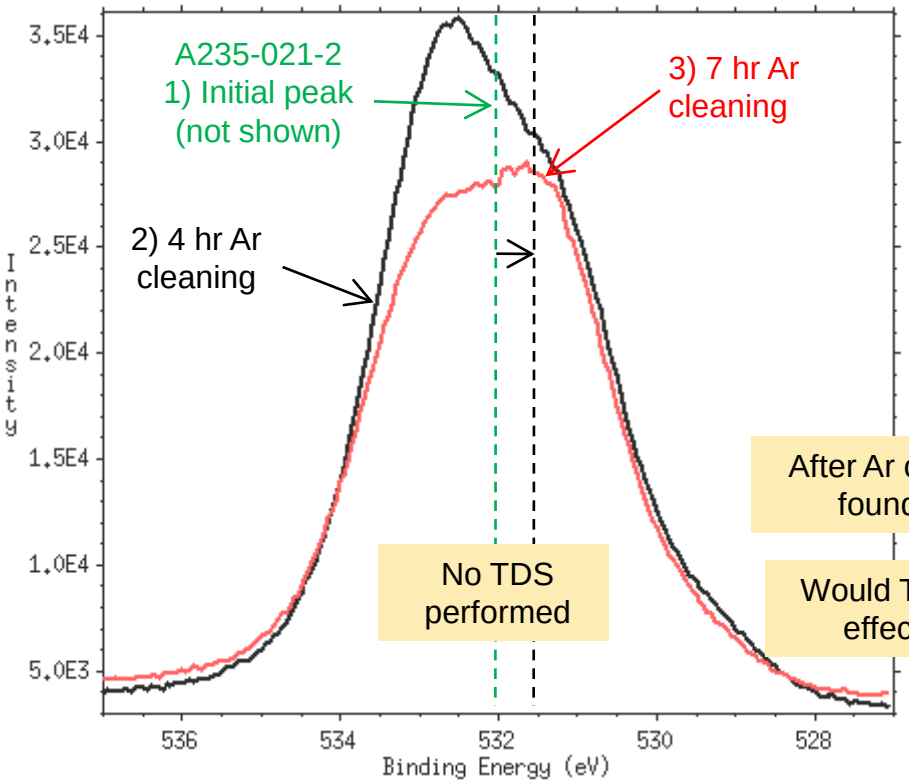
AJT139 vs. post-mortem tile near LITER

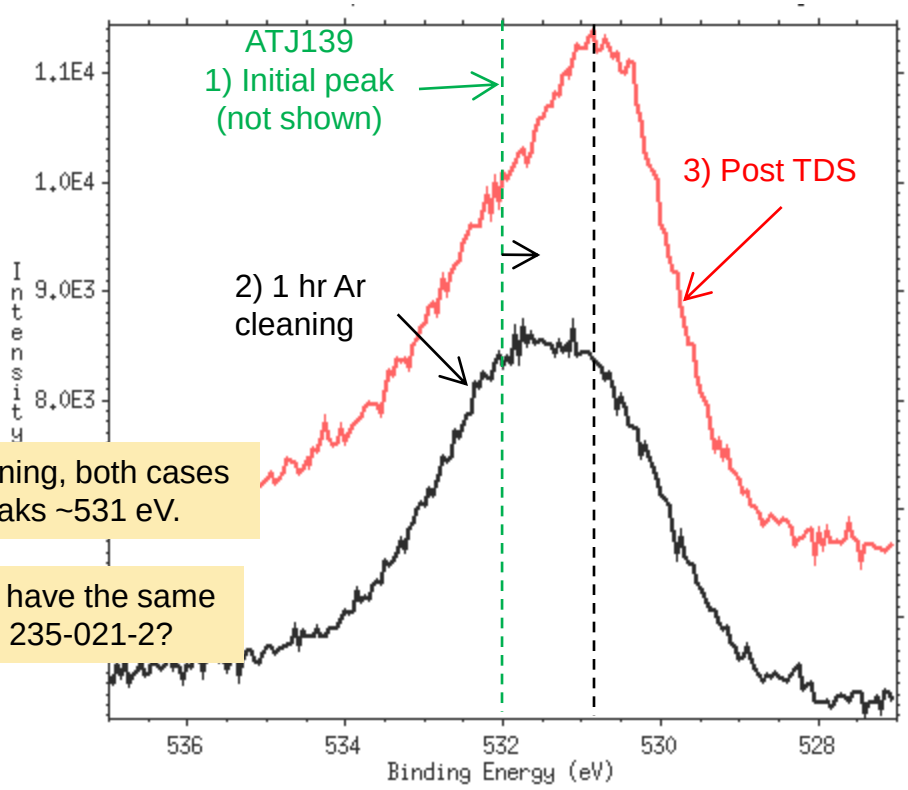
NSTX Tile A235-021-2

•Staged Ar cleaning

ATJ139

- Lithium conditioning
- 6 NSTX NB plasma shots
- Ar cleaning
- TDS performed at Purdue

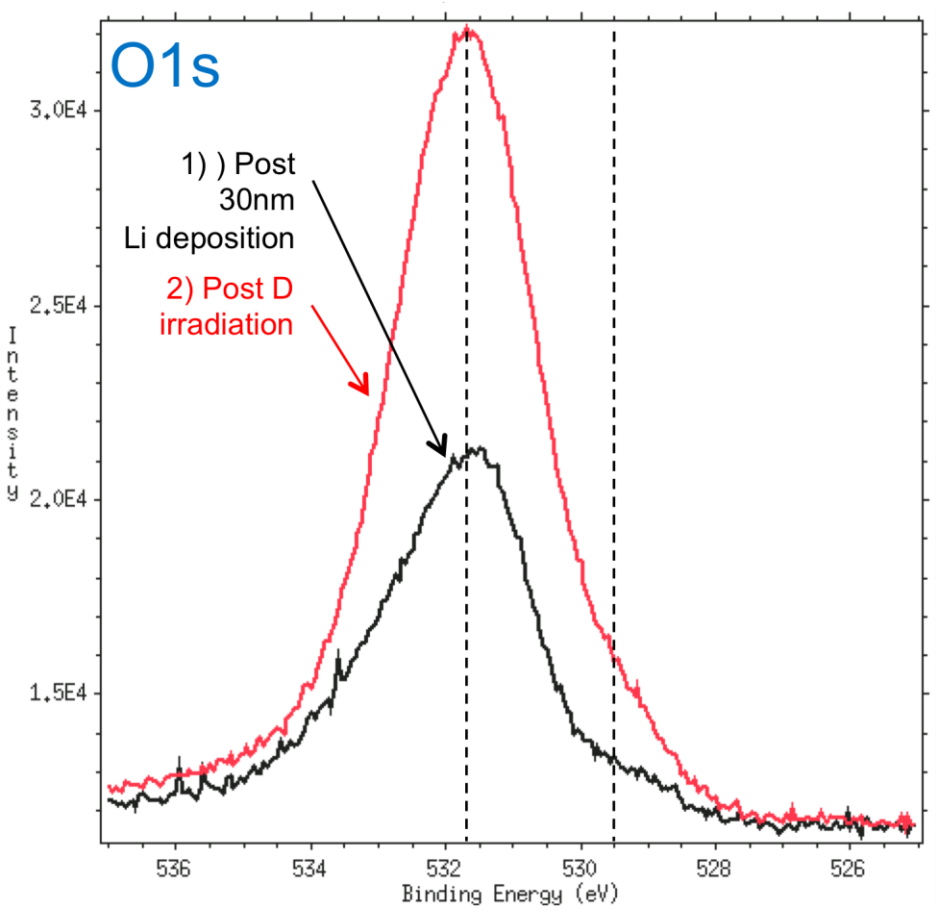


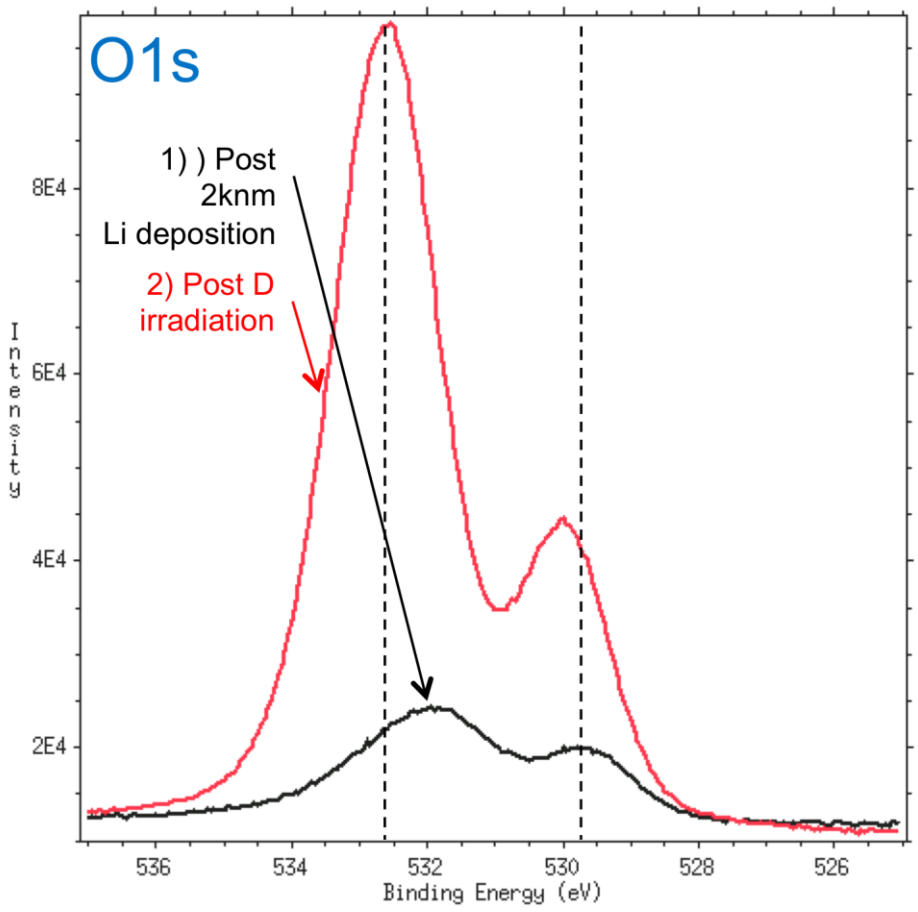


After Ar cleaning, both cases found peaks ~531 eV.

Would TDS have the same effect on 235-021-2?

Lithium dose affects Li-D-O-C functionality

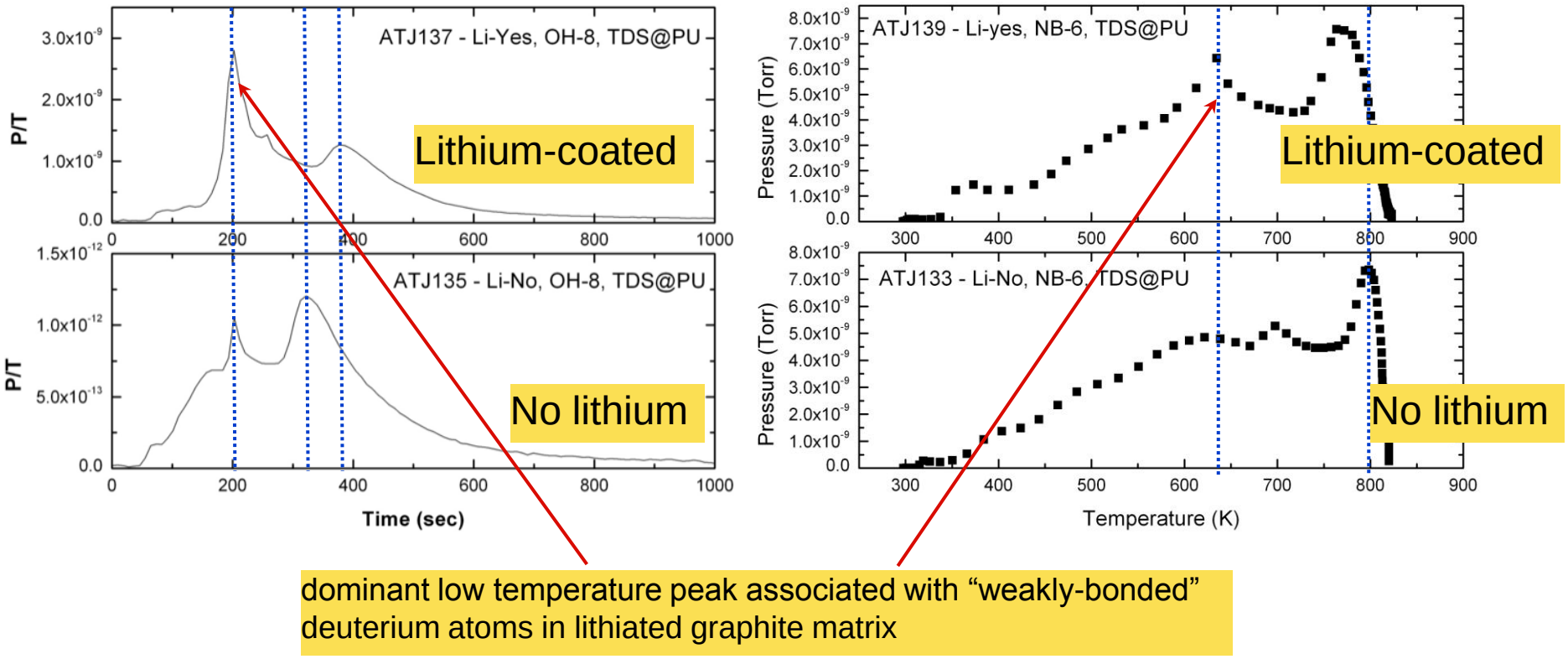




Li-30nm post deposition, post D irradiation

Li-2000 nm post deposition, post D irradiation

TDS of NSTX PMI probe exposed samples



- Strong correlation between dose of lithium coatings and dynamic retention of deuterium
- 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

PMI Probe sample examination

Si108

- April 22
  - Shots 132973-133018
  - XP911 occupied 8 Ohmic plasma shots
  - Assume Li coverage: 25% of 40m^2 area in vessel
  - In 8 shots, 343 mg deposited (64 nm)
- SEM of Si sample shows < 500-nm film
- Pd425
  - No Li conditioning
  - Exposed to 6 NB plasmas
  - Post analysis 4-point probe showed a D concentration of ~5.16 x 10^{20} m^{-2}
  - Pd sample was heated beyond 200 C emitting implanted D
  - Langmuir probes showed average deuterium flux of: ~3.34 x 10^{22} m^{-2}

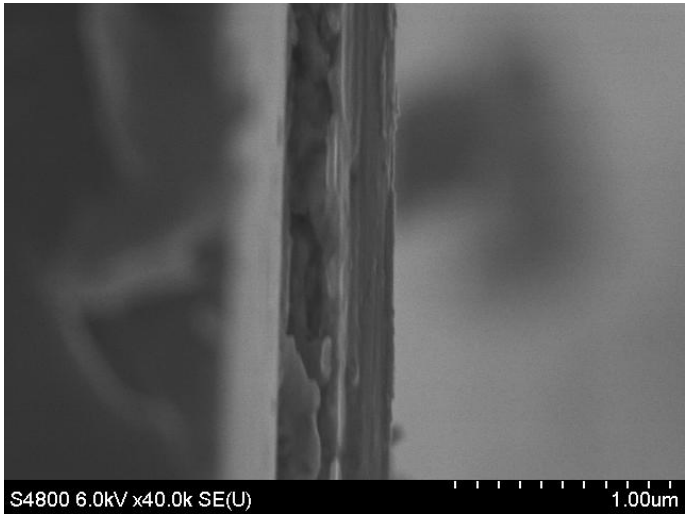
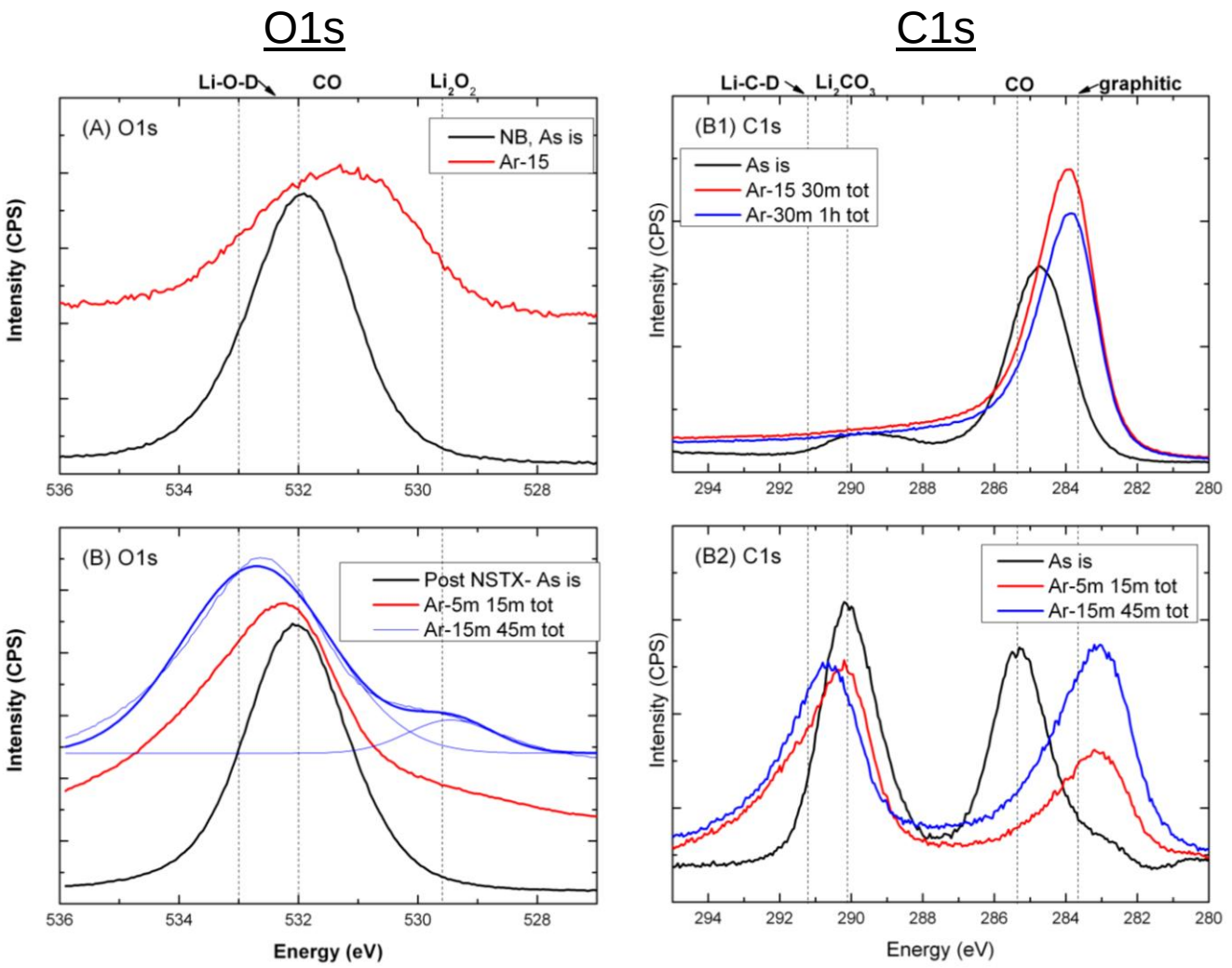


Fig. 1 Sample probe with ATJ graphite, Si and Pd samples

Probe experiments: round 2 – Piggyback

XP911: April 24
Low lithium: 213 nm

Piggyback: April 24
High lithium: 1,841 nm



Implications for LITER and LLD operation

- Controlled *in-situ* surface analysis of lithiated ATJ graphite surfaces show:
  - initially Li readily intercalates
  - Over time with large lithium dose (and with D) a diffusion barrier is created slowing intercalation to bulk
  - D irradiation and oxidation can also drive Li to surface
- It is obvious that "*the more lithium the better*"
  - Our work shows mechanism for D retention dependent on charge transfer mechanisms in Li:C:D and also on carbon structure (morphology)
  - Spreading more lithium on carbonaceous surfaces with thicknesses of at least 400-500 nm show signs of D retention (LLD will help with this)

Acknowledgements

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J.N. Brooks, Purdue University

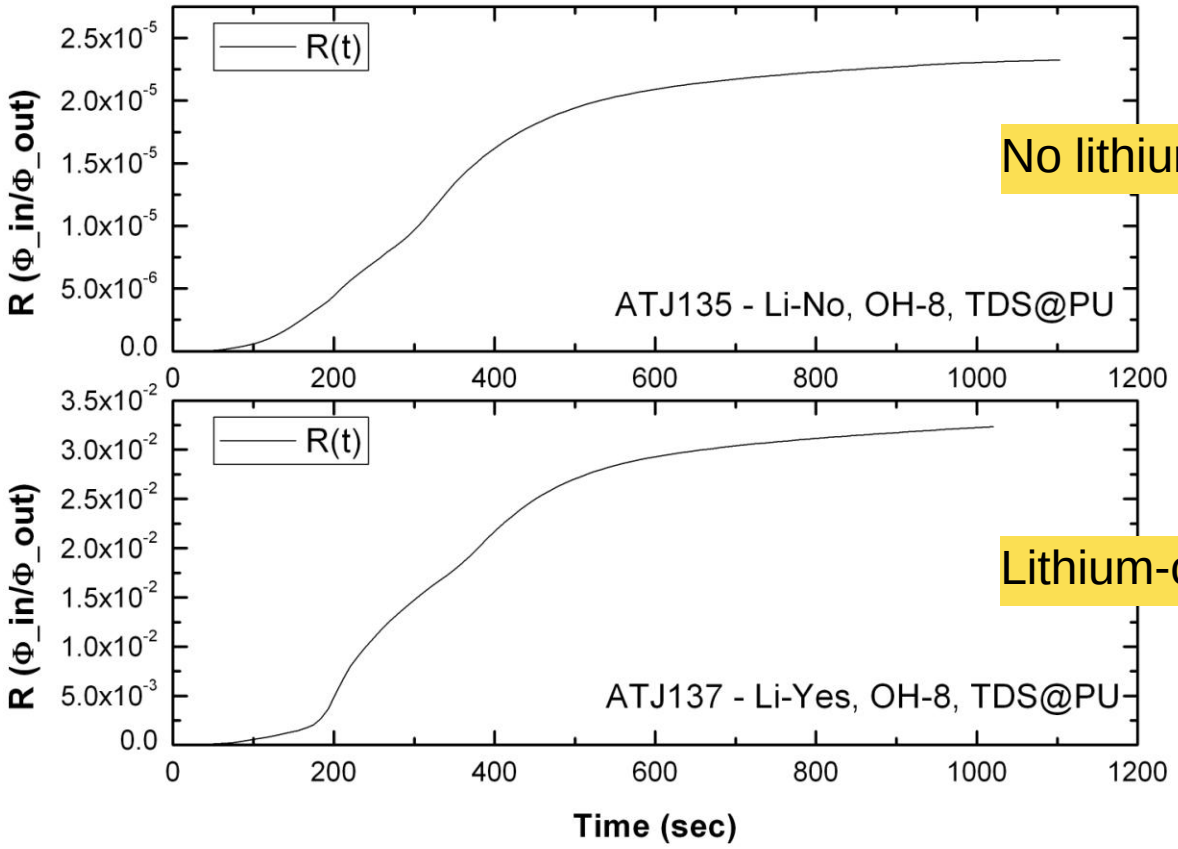
C. Skinner, H. Kugel, R. Majeski, R. Kaita
Princeton Plasma Physics Laboratory

•Purdue work under US-DOE Contract DE-FG02-08ER54990

EXTRAS

TDS – Deuterium retention

Retention for lithiated samples is ~3 orders of magnitude greater for lithiated samples



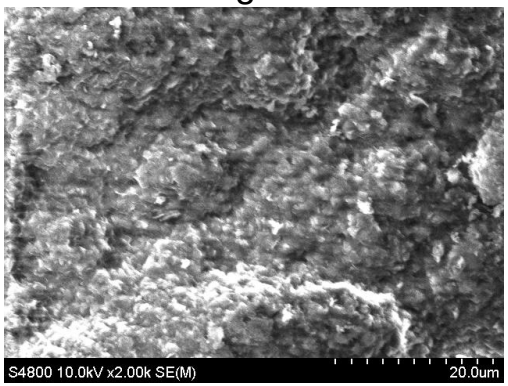
Surface morphology of ATJ graphite surfaces

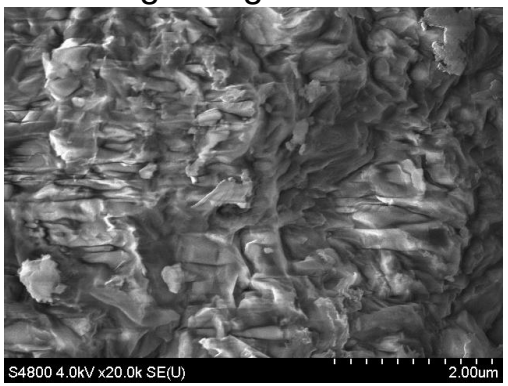
Low magnification

High magnification

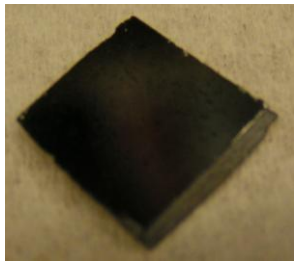
NSTX post mortem tile

Tile A408-002-C5
Removed after FY08 campaign

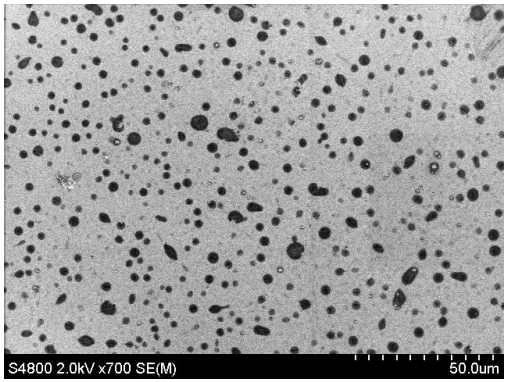


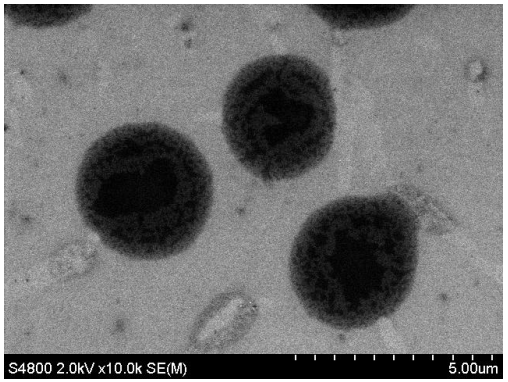


Si probe sample



Si108
Exposed to 8 NSTX Ohmic plasmas via sample probe





Control graphite sample

ATJ147a
2000 nm Li deposited, 1.5 hr D irradiation