Differentiating the role of lithium and oxygen in retaining deuterium on lithiated plasma-facing components

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Outline

- Motivation
- Methods

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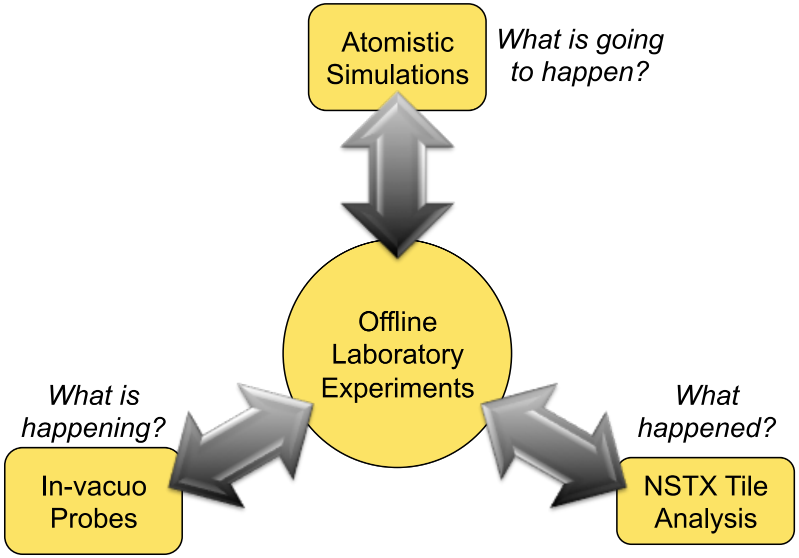
- Fundamental experiments
- Behavior of lithiated graphite
- Identify the role of oxygen
- Identify the role of lithium

- Summary



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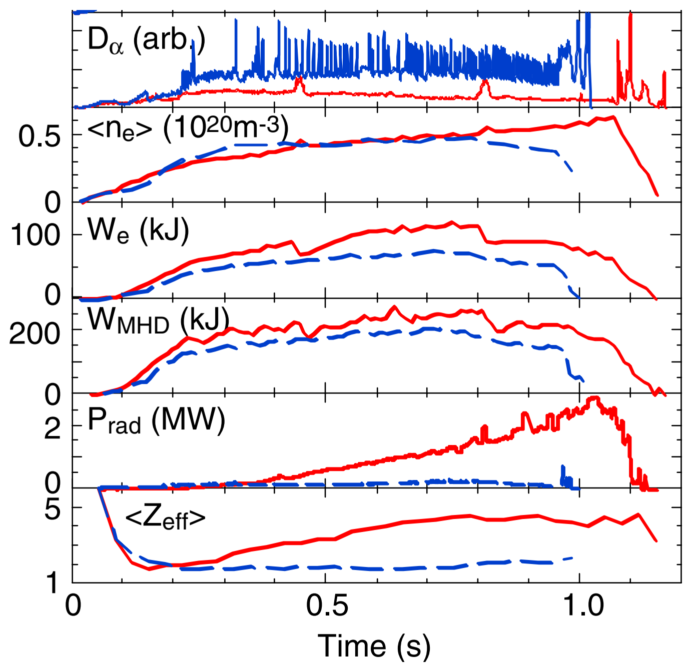
DE-FG02-08ER54990, DE-AC02-09CH11466, DE-AC07-05ID14517

Motivation

- Why study lithium as a plasma facing component?
  - Lithium improves plasma performance

NSTX



no lithium

260 mg lithium

- Improvement in energy confinement:
  - Total plasma stored energy
  - Electron stored energy
  - Decrease in ELMS while maintaining high performance
- Reduced recycling
- However, lithium deposition increases Z_{eff} and radiated power

M.G. Bell, et. al., Plasma Phys. Control. Fusion 51 (2009) 124054

Motivation

- We want to understand the fundamental mechanisms responsible for these benefits.

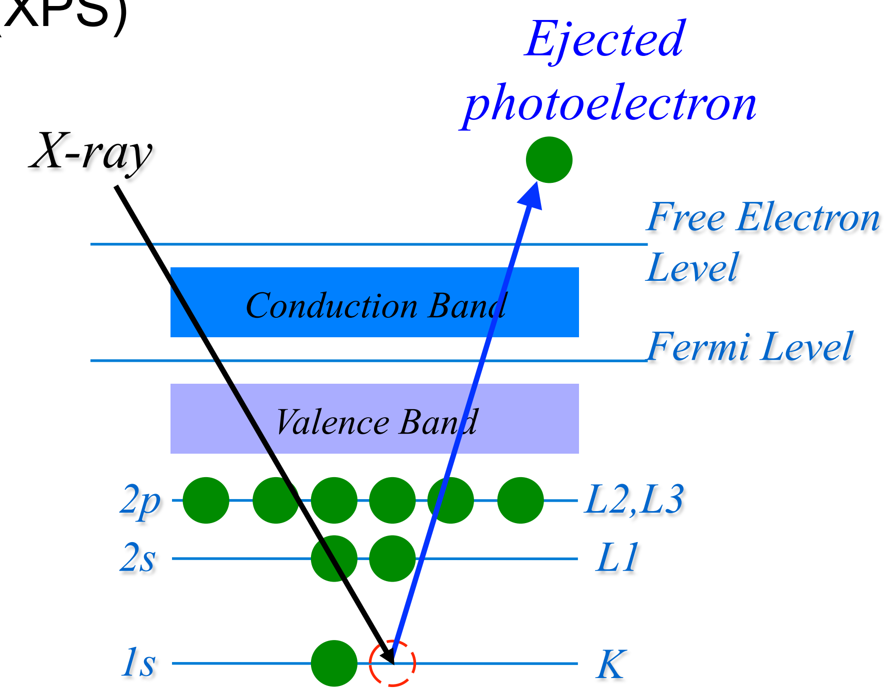
- Research outlook
  - Apply results to optimize lithium conditioning.
  - Understand how fundamental physics transfers to other systems.

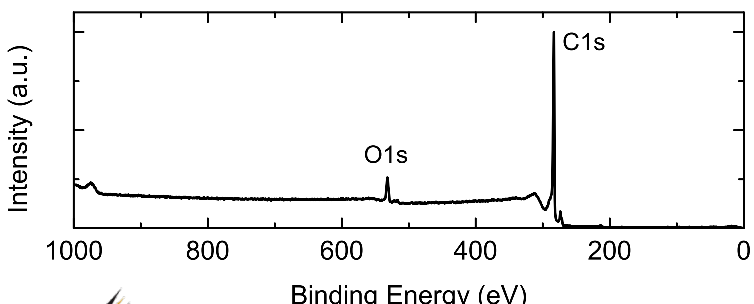
- Approach:
  - Surface chemistry: X-ray photoelectron spectroscopy (XPS)
  - Quantum-classical molecular dynamics (QCMD)

Methods

- X-ray photoelectron spectroscopy (XPS)
  - X-rays probe the near surface (~5 nm).
  - Core shell photoelectron is ejected and detected.
  - Photoelectron binding energy is characteristic of is binding chemistry.

$$KE = h\nu - BE - \text{Work Function}$$





XPS wide scan for virgin graphite

The formation of new peaks or a reproducible peak shift is an indication of a chemical change.

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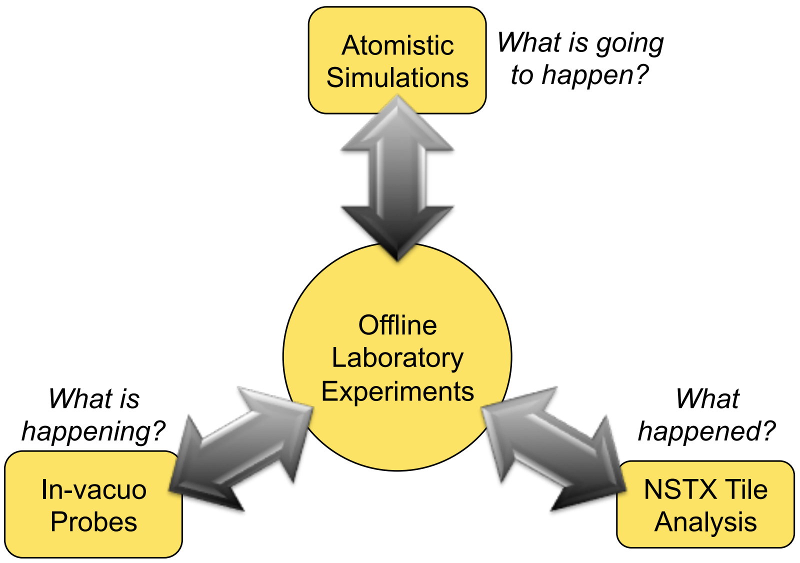
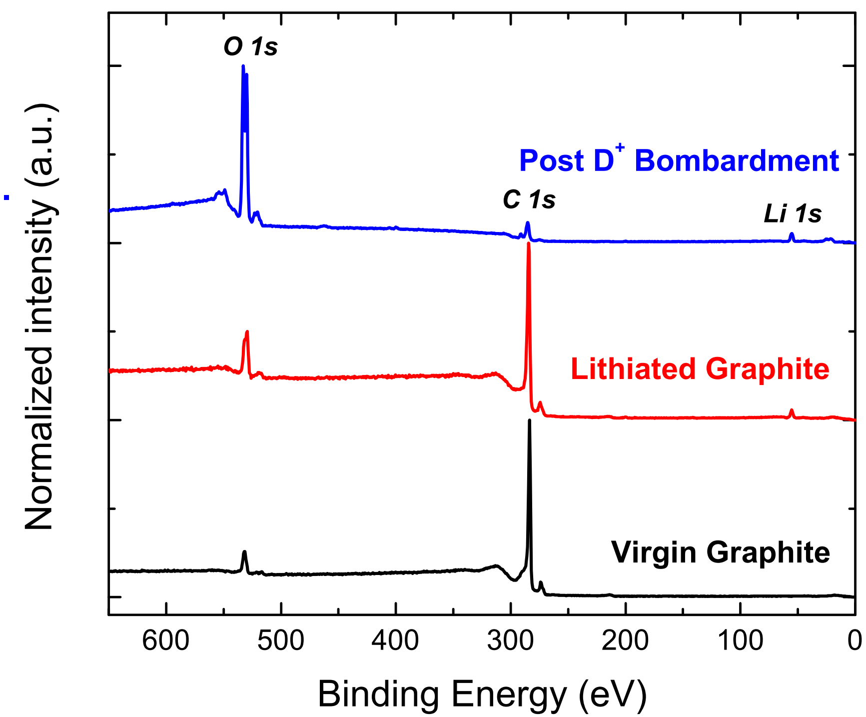


Typical XPS spectra for lithiated graphite

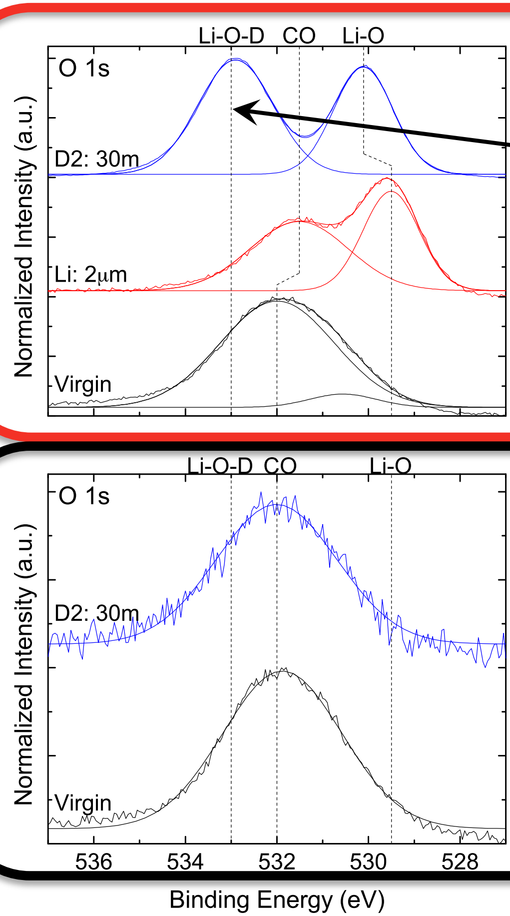
- The chemical bonds responsible for deuterium retention can be observed using X-ray photoelectron spectroscopy.
- Oxygen is found in ATJ graphite, lithiated graphite, and D irradiated Li-graphite.

3. After deuterium bombardment
   - Oxygen concentration increases to ~20-45%.
2. Lithiated graphite
   - Li 1s peak forms.
   - Oxygen concentration increases to ~10%.
1. Virgin graphite
   - Oxygen accounts for ~5% of surface concentration.



C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

Control experiments identify D-chemistry

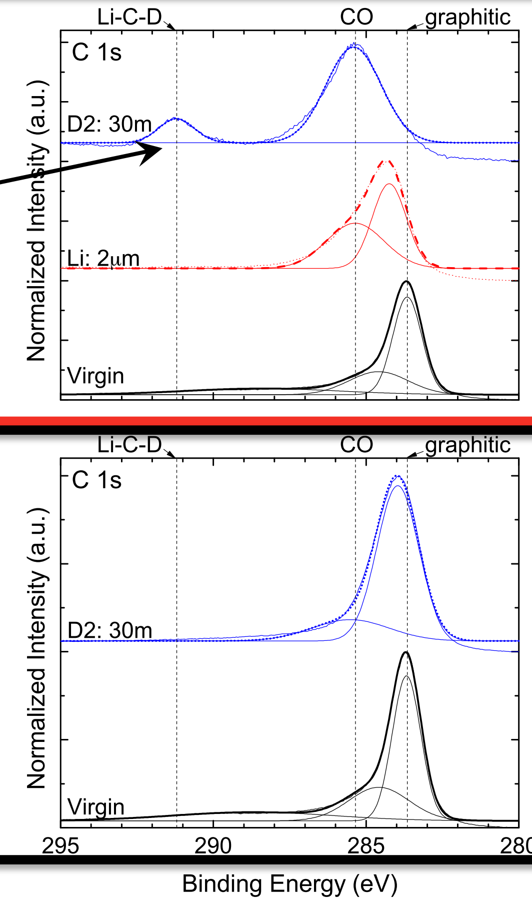


2µm lithium

Li-O-D peak forms in O1s
Li-C-D peak forms in C1s

No lithium

No new peaks form upon D-bombardment.

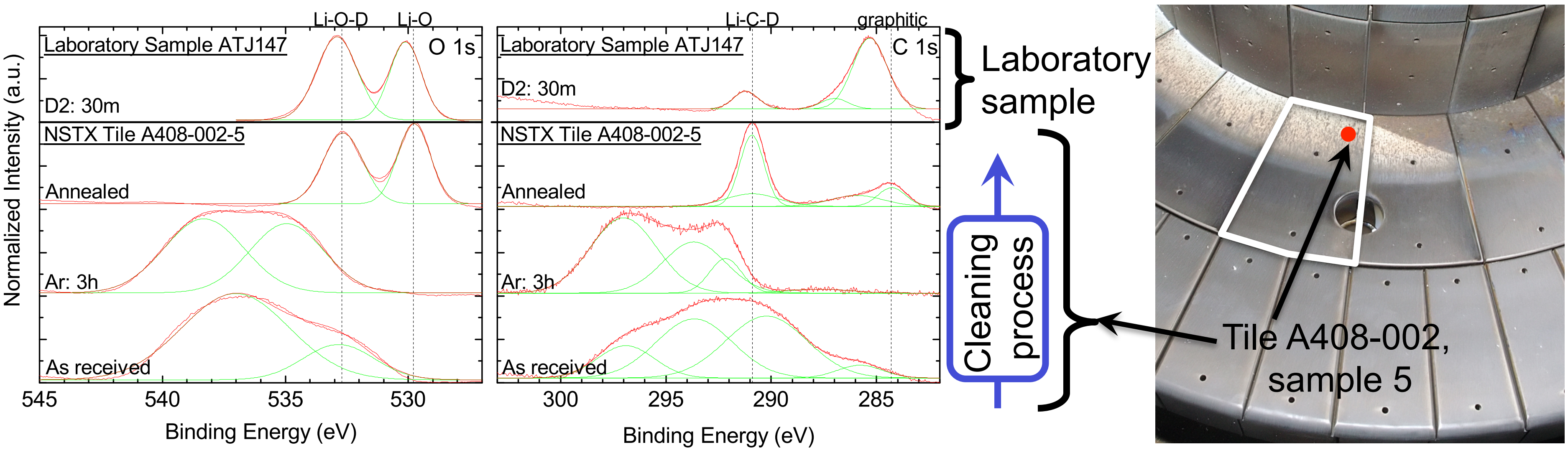


Deuterium related chemistry is observed indirectly in the O1s and C1s energy range. Li-O-D and Li-C-D interactions identified.

C.N. Taylor, et al., J. Appl. Phys. 109, 053306 (2011)

NSTX tile chemistry corroborates technique

- Lithiated graphite laboratory sample bombarded with D was analyzed.
- NSTX tile sample was removed, cleaned, and analyzed.
  - Li-O-D and Li-C-D chemistry from *NSTX tiles match chemistry* observed in laboratory samples.



Similarity in tile and laboratory spectra validates laboratory technique.

C.N. Taylor, et al., J. Appl. Phys. 109, 053306 (2011)
C.N. Taylor, et al., Fusion Eng. Des., in press (2013).

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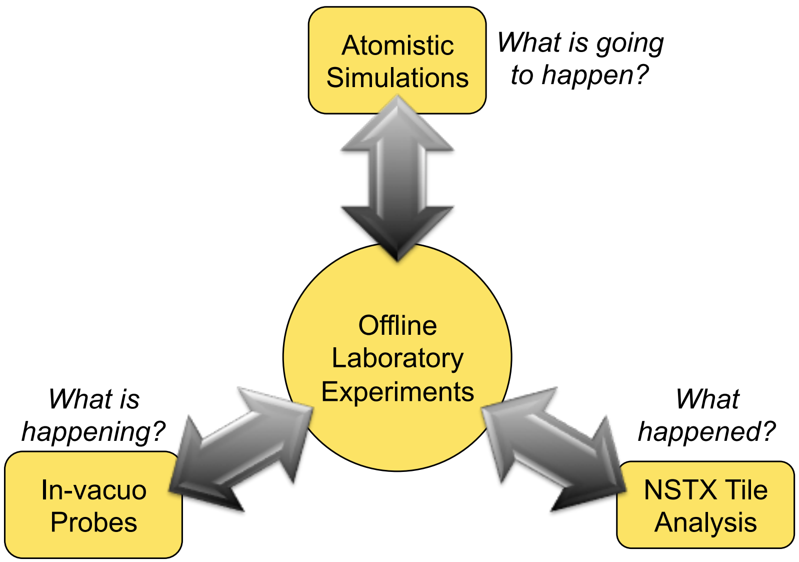
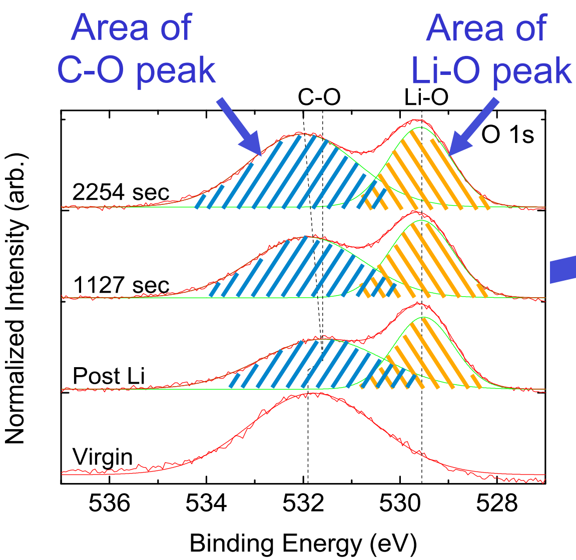
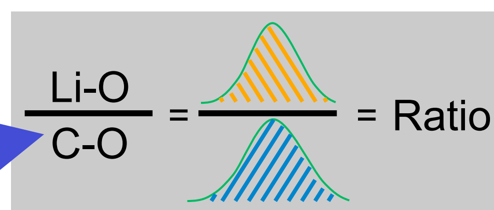
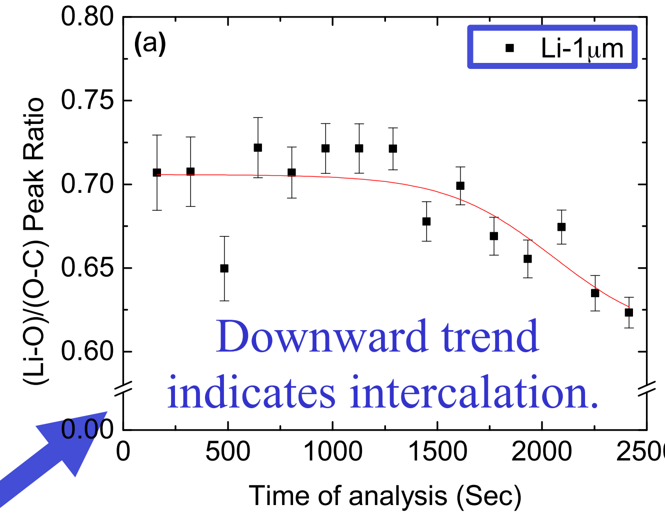


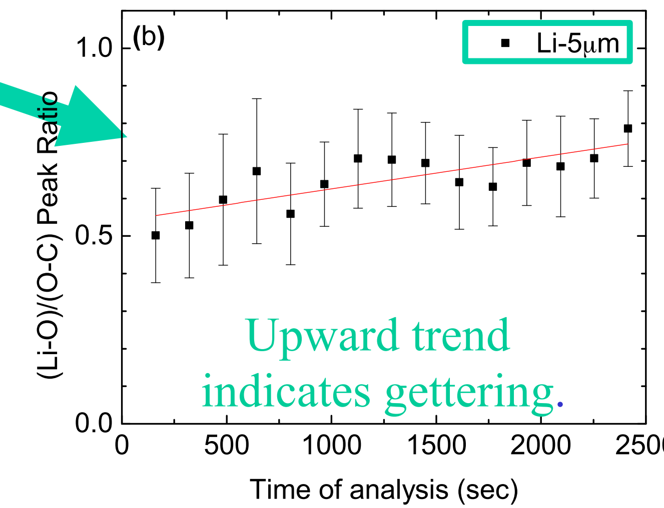
Intercalation and gettering observed in XPS

- Lithiated graphite chemistry changes with time.
  - Deposit lithium on laboratory sample.
    - 1 μm, 5μm
  - Wait in UHV (10^{-10} mbar).
  - Quantify surface concentrations with XPS.





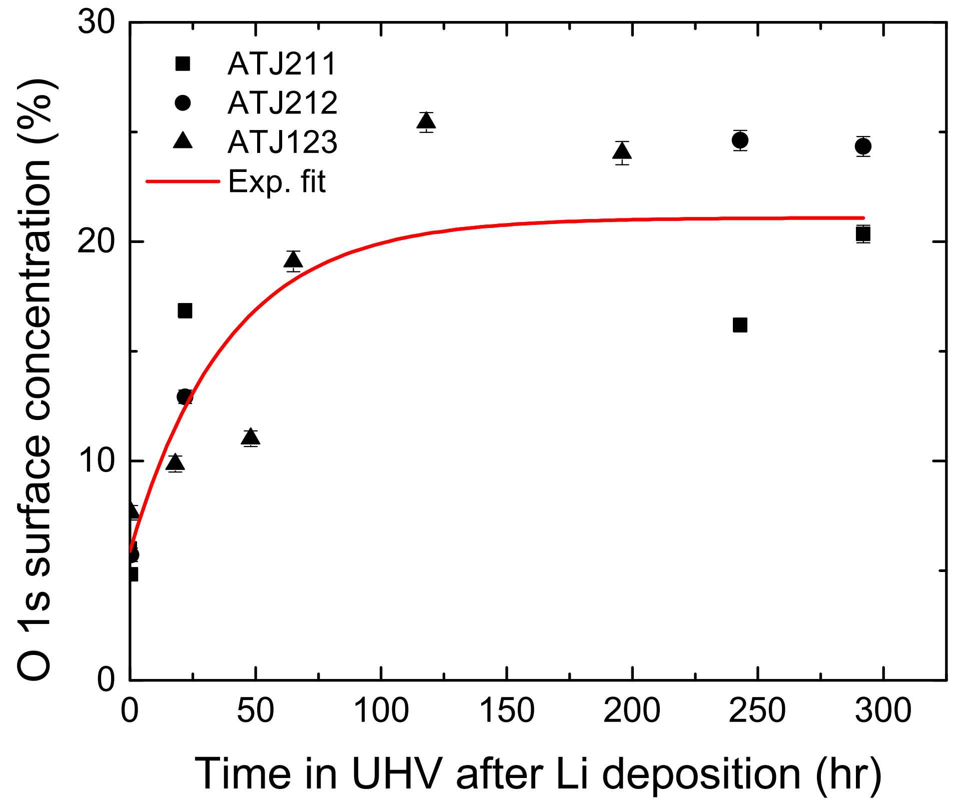




C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

Oxygen gettering active in UHV for 100+ hours

- Experiment
  - Deposit lithium.
  - Wait in UHV (10^{-10} mbar).
  - Quantify surface concentrations with XPS.
- Gettering is a slow, thermodynamic process (10-100s of hours).
- Curve fit suggests an ultimate oxygen surface concentration of ~20%.



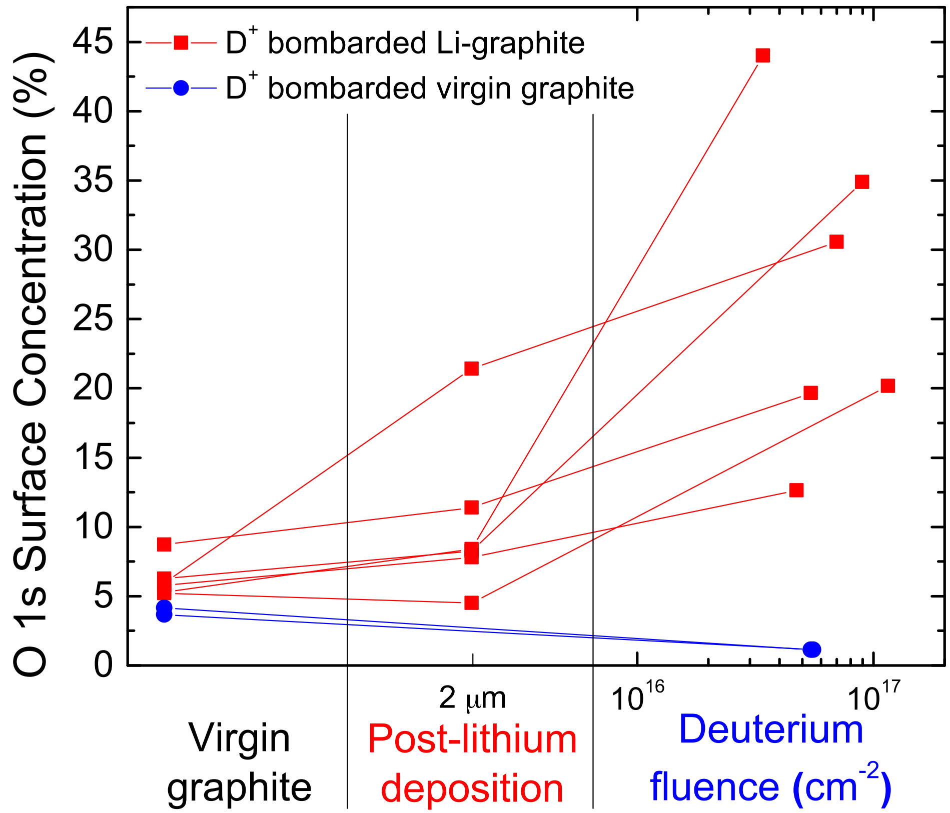
Over the course of ~100 hours in UHV (10^{-10} mbar), the oxygen concentration increases from ~8% to more than 20%.

C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

D bombardment increases O concentration to 20%

- Experiment
  - Deposit 2 μm lithium.
  - D^+ bombardment to ~$9x10^{16}$ cm^{-2}.
  - Quantify surface concentrations with XPS.

- Oxygen concentration increases dramatically upon D irradiation.
- Dramatic oxygen enhancement observed only when lithium is present.



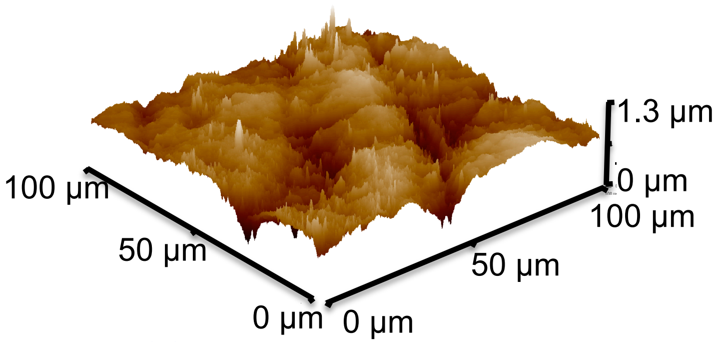
Large scatter in data suspected to be a consequence of surface morphology.

C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

Surface morphology effectively thins Li deposit

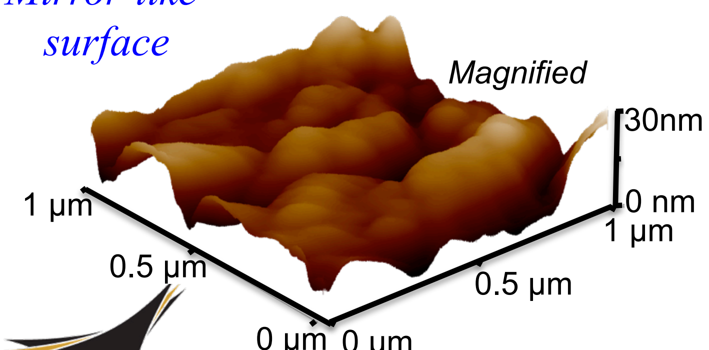
- Surface morphology results in larger effective surface area. Consequences:
  - Effectively thinner lithium coverage.
  - Faster intercalation into bulk graphite.
  - Faster oxygen gettering.

Polished ATJ graphite



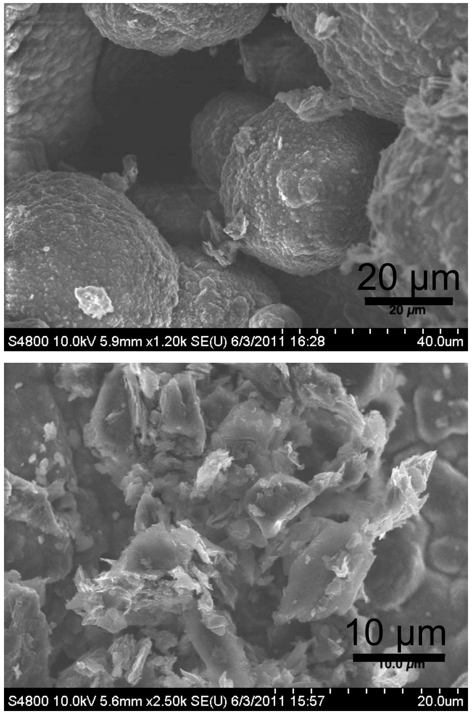
Atomic force microscopy (AFM) shows >1 μm peaks in 100 μm^2 domain.

"Mirror-like" surface



On 1 μm^2 domain, ~30 nm peaks observed.

NSTX tile sample



Clusters and flakes 10-40 μm.

C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

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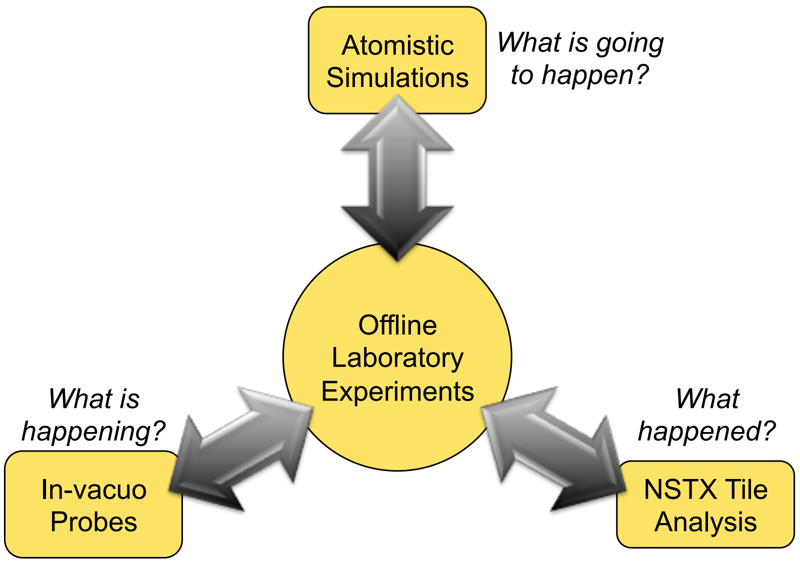
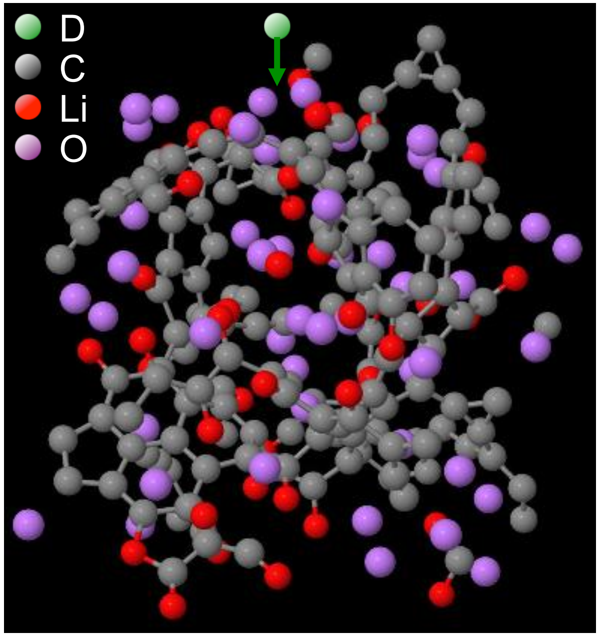


Atomistic simulations used to model D retention

- Quantum-classical molecular dynamics (QCMD) is used to model the C-Li-O-D system.
  - Quantum mechanical method.
  - Investigates electronic structure of many-body systems.
  - Cell: ~250 atoms, ~5000 D trajectories.
- Qualitative analyses:
  1. Partial charges
     - Assess charge state after D impact.
     - Binding pairs have opposite partial charges.
  2. Nearest neighbors
     - Assess rest position of implanted D^+.
     - Binding is more likely when atoms are close neighbors.

5000 independent random D trajectories (Monte Carlo approach)

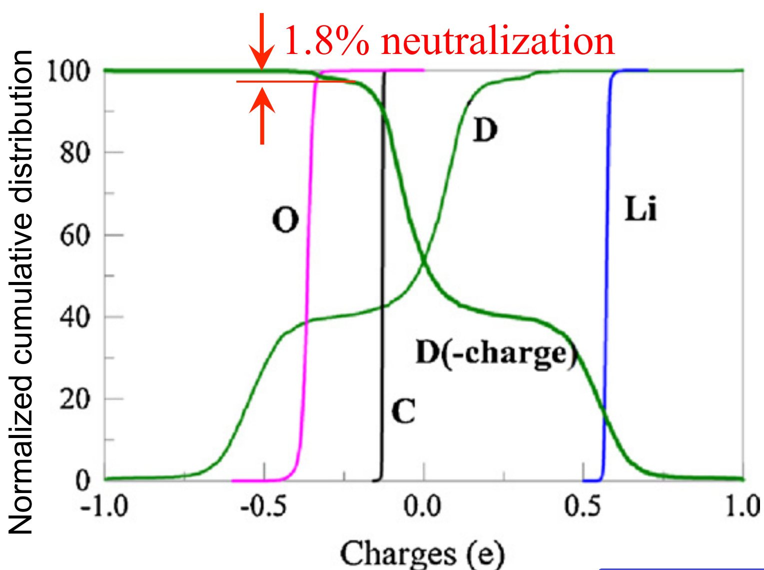


Krstic group at ORNL/UTK.

Simulations with 5% O indicate minimal retention

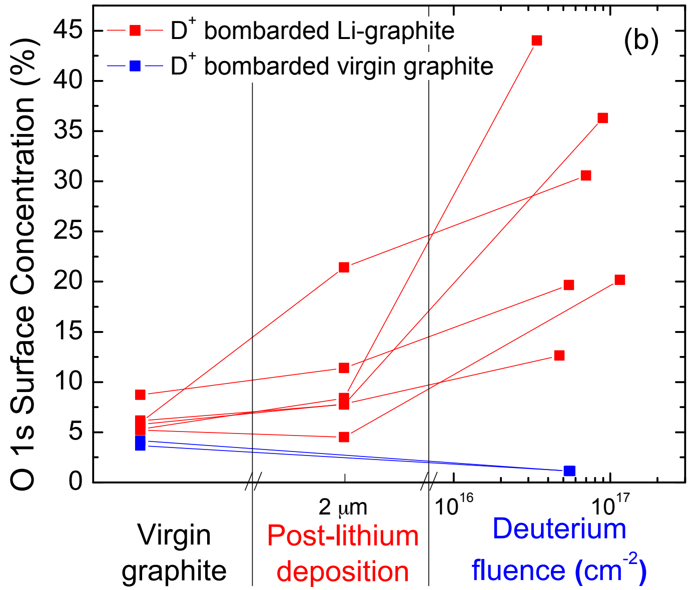
Initial atomistic simulations

- Matrix contained 5% oxygen.
  - Based on virgin graphite.
- Result:
  - <2% oxygen-deuterium neutralization.



Experiments

- Virgin graphite contains ~5% oxygen.
- After D bombardment, oxygen concentration increases to ~20%.



Repeat simulations with 20% oxygen concentration.

P.S. Krstic, et al., Fusion Engr. Des., 87 (2012) 1732–1736.
P.S. Krstic, et al., Phys. Rev. Letter, 110, 105001 (2013).

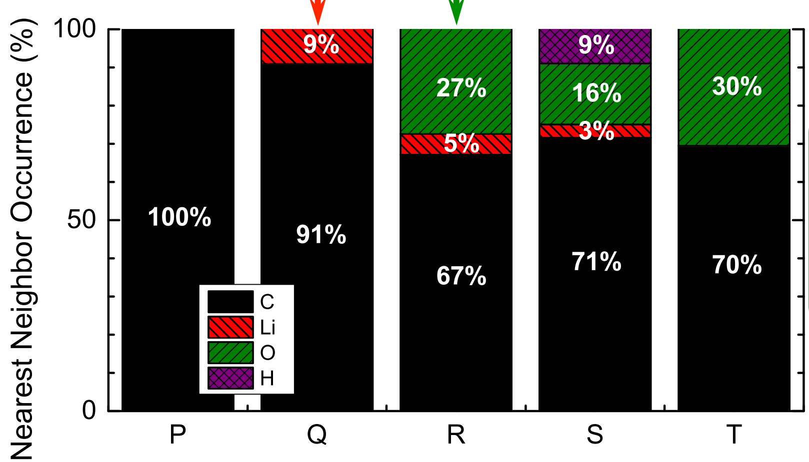
Simulations show D prefers O as its 'neighbor'

- Nearest neighbors analysis
  - The composition of the simulation matrix is shown in the table.
  - Percentage of deuterium's proximate neighbor after coming to rest shown in chart.

Matrix Composition

	P	Q	R	S	T
C	100%	80%	60%	52%	80%
Li		20%	20%	16%	
O			20%	16%	20%
H				16%	

20% lithium in carbon leads to *9% deuterium-lithium* nearest neighbors.



20% oxygen in carbon leads to *27% deuterium-oxygen* nearest neighbors.

When oxygen is present in the matrix, it becomes the predominant nearest neighbor, an indication of binding pairs, to deuterium.

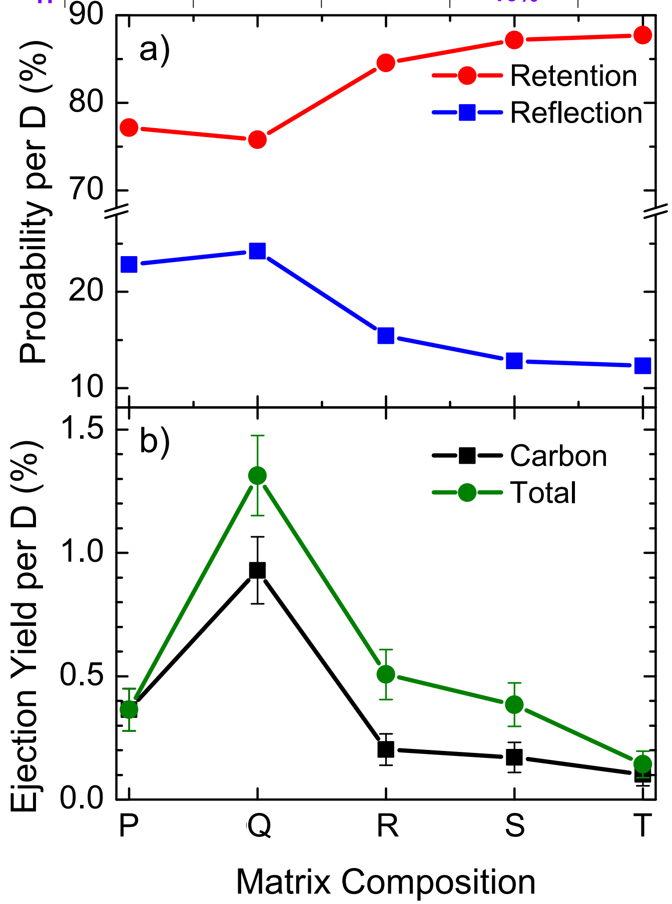
C.N. Taylor, et al., Journal of Applied Physics, submitted 2013.

Sputtering is lowest in matrix with 20% oxygen

- Simulations show:
  - Matrix prepared with 20% lithium has lowest retention.
  - Deuterium retention is highest in matrix with 20% oxygen and *no lithium*.
  - The ejection yield (sputtering) is at its highest in the case of 20% Li in carbon.
  - Sputtering is lowest in matrix with 20% oxygen.

Matrix Composition

	P	Q	R	S	T
C	**100%**	**80%**	**60%**	**52%**	**80%**
Li		**20%**	**20%**	**16%**	
O			**20%**	**16%**	**20%**
H				**16%**	



The presence of oxygen in the matrix reduces sputtering and enhances deuterium retention.

P.S. Krstic, et al., Phys. Rev. Letter, 110, 105001 (2013).

Differentiating the role of oxygen and lithium

- What is happening?!?
  - *Experiments* qualitatively find that oxygen plays a role in deuterium retention.
  - First Li-O-C-D *simulations* used 5% oxygen in carbon. Minute effect.
  - Return to *experiments*. Oxygen surface concentration increases to ~20% after D bombardment.
  - Repeat *simulations* with 20% oxygen. Significant effect.
  - Deuterium recycling suppressed in *NSTX* when using lithium.
  - *Simulations* shows poor retention with lithium only.

- What is the role of lithium?!?
  - Increase oxygen concentration in experiments without lithium.

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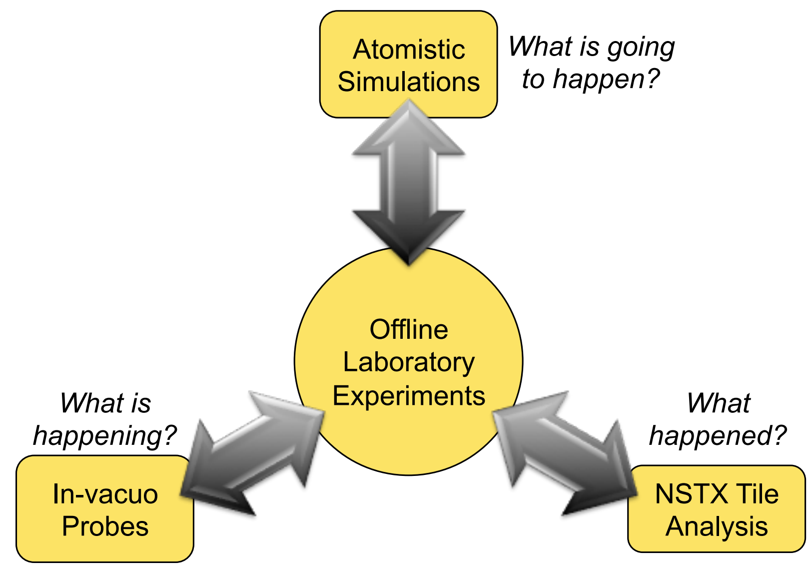
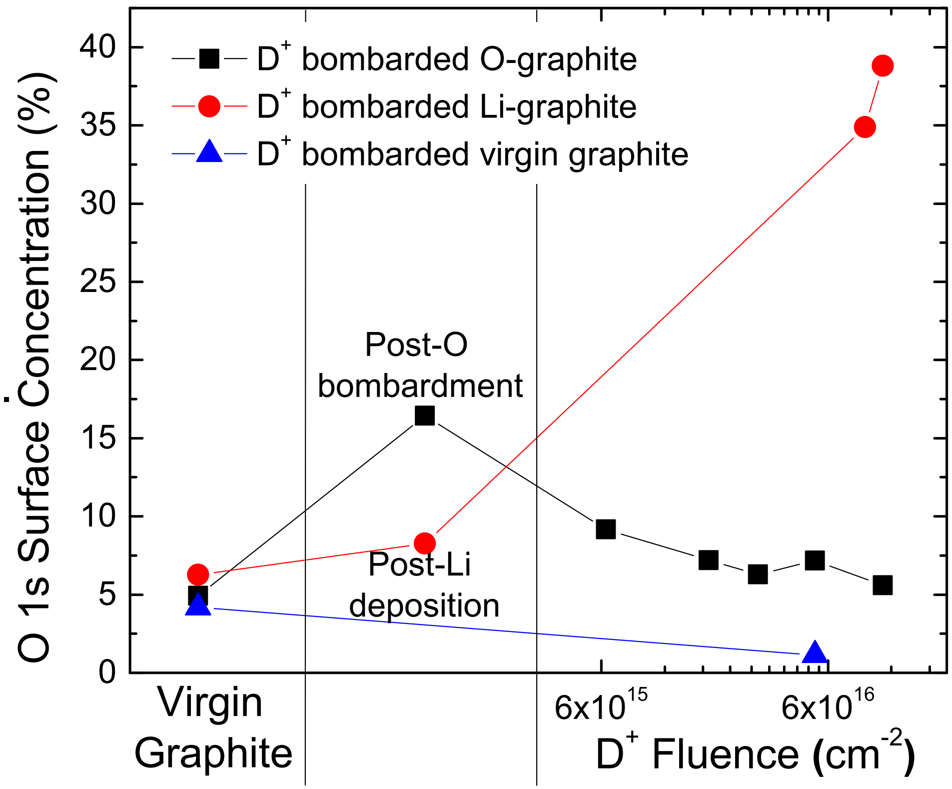


High O concentration not sustainable without Li

- Experimentally test case with 20% oxygen and no lithium.
  - Bombard with oxygen.
  - Bombard with dueterium.
  - Quantify concentrations.
  - Examine retention.
- Recall: D retention observed in XPS.
  - *D retention observed*
  - *No retention chemistry*
  - ***No retention chemistry***

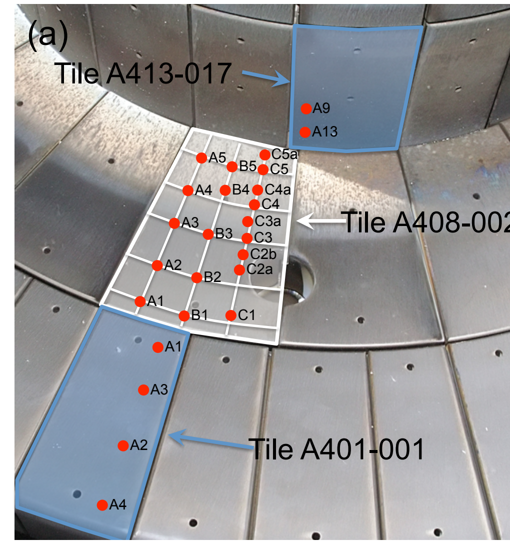


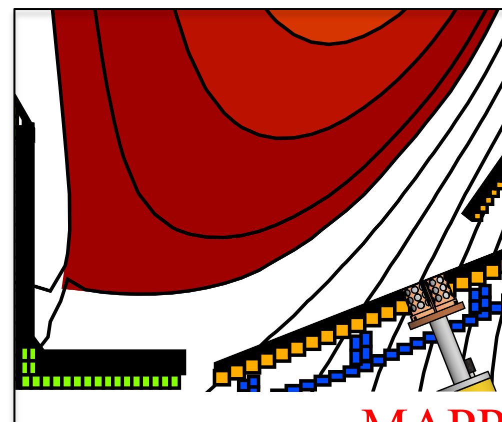
Oxygen concentration successfully increased, however cannot retain deuterium without lithium. Lithium not only getters oxygen, it retains the oxygen!

C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

XPS spectra reveal PSI behavior in NSTX tiles

- XPS analysis of NSTX tiles revealed the following[1]:
  - Procedure for quick recovery of passivated lithium surfaces.
  - Tile regions that require additional lithium conditioning.
  - A minimum lithium threshold for D retention is found between 50-500 nm.
- The Materials Analysis Particle Probe (MAPP)[2]
  - Provide shot-to-shot analysis of surface chemistry.
  - Operate during the between-shot window.
  - Investigate sputtering and redeposition.
- Applicability to other systems.
  - Currently researching lithium on metals.
  - Similar trends in oxygen behavior observed.





δ_1=0.7 (#121238 @ 0.3 sec)

[1]C.N. Taylor, et al., Fusion Eng. Des., in press (2013).
[2]C.N. Taylor, et al., Rev. Sci. Instrum. 83, 10D703 (2012).

Summary

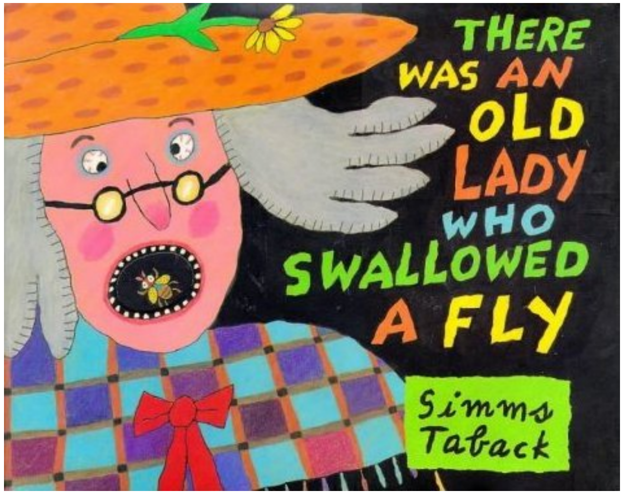
- Oxygen is the dominant channel for retaining deuterium in lithiated graphite.

- Lithium's primary role is that of bringing oxygen to the surface.

- Ion implanted oxygen in graphite is weakly bound compared to lithiated graphite.

- Lithium is necessary in order to retain oxygen in graphite.

Process of deuterium retention is reminiscent of children's story…



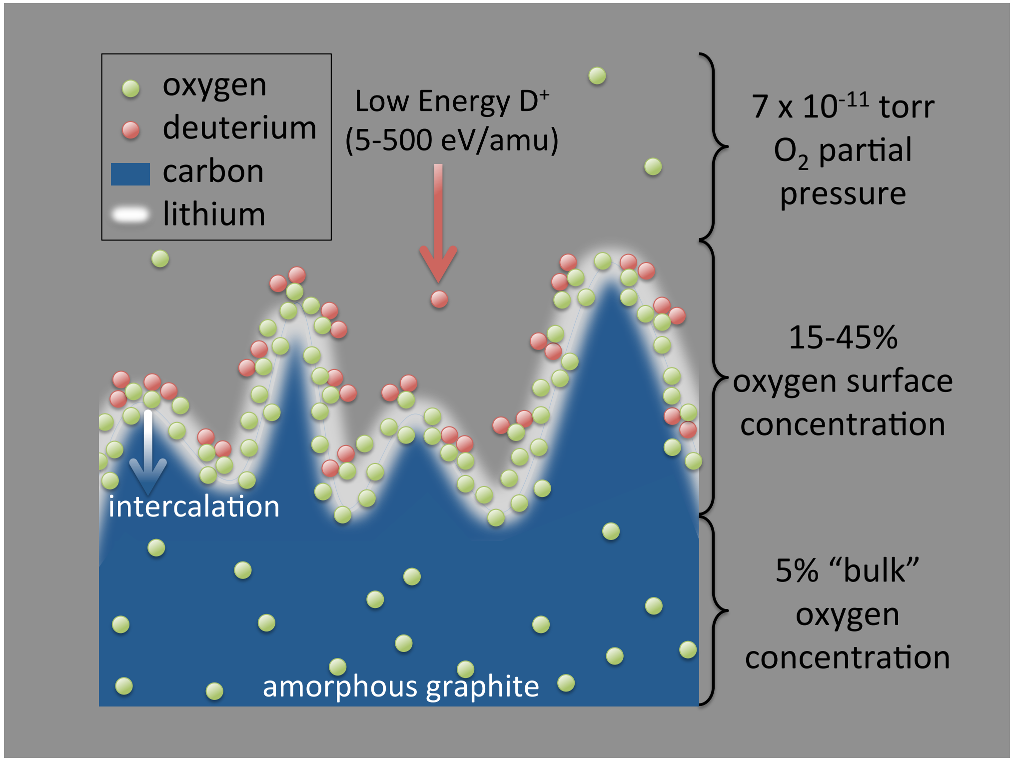
"fly"	*deuterium*
"spider"	*oxygen*
"bird"	*lithium*
.	.
.	.
.	.
"horse"	*carbon*

EXTRA SLIDES

Future work

Three possible sources of oxygen:

1. Bulk sample
2. Ambience
   - Chamber
   - Sources
3. Lithium deposit
   - Evaporator loading.
   - Inactive periods.
   - During and after evaporation.



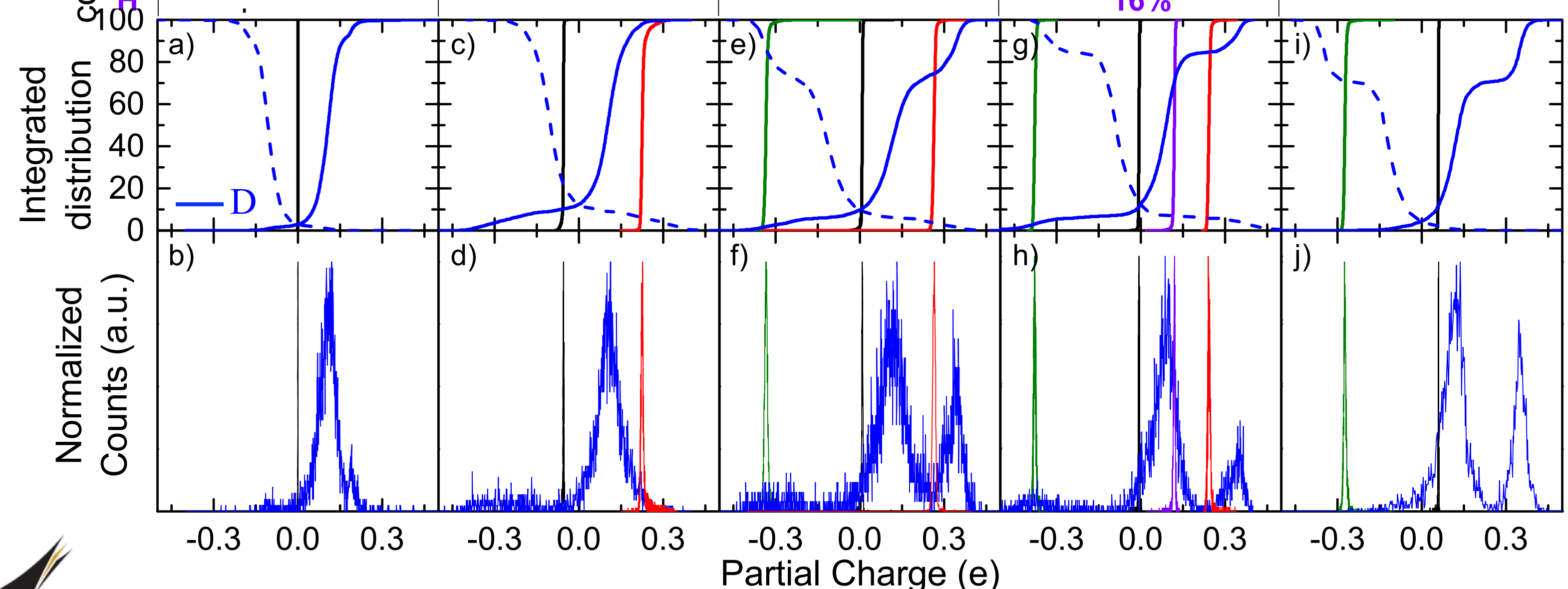
Hypothesis: ion bombardment breaks down oxygen containing species from within the lithium deposit and drives the oxygen to the surface.

C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

Simulation partial charges show D prefers O

- Interpreting "*partial charges*" data:
  - Matrix R: 0.33 e (oxygen) neutralizes -0.33 e (deuterium).

Matrix composition	P	Q	R	S	T
C	**100%**	**80%**	**60%**	**52%**	**80%**
Li		**20%**	**20%**	**16%**	
O			**20%**	**16%**	**20%**
H				**16%**	



C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

Simulation 'nearest neighbors' show D prefers O

- Interpreting "nearest neighbors" data.
  - Deuterium preferentially resides near oxygen.

Matrix composition	P	Q	R	S	T
C	100%	80%	60%	52%	80%
Li		20%	20%	16%	
O			20%	16%	20%
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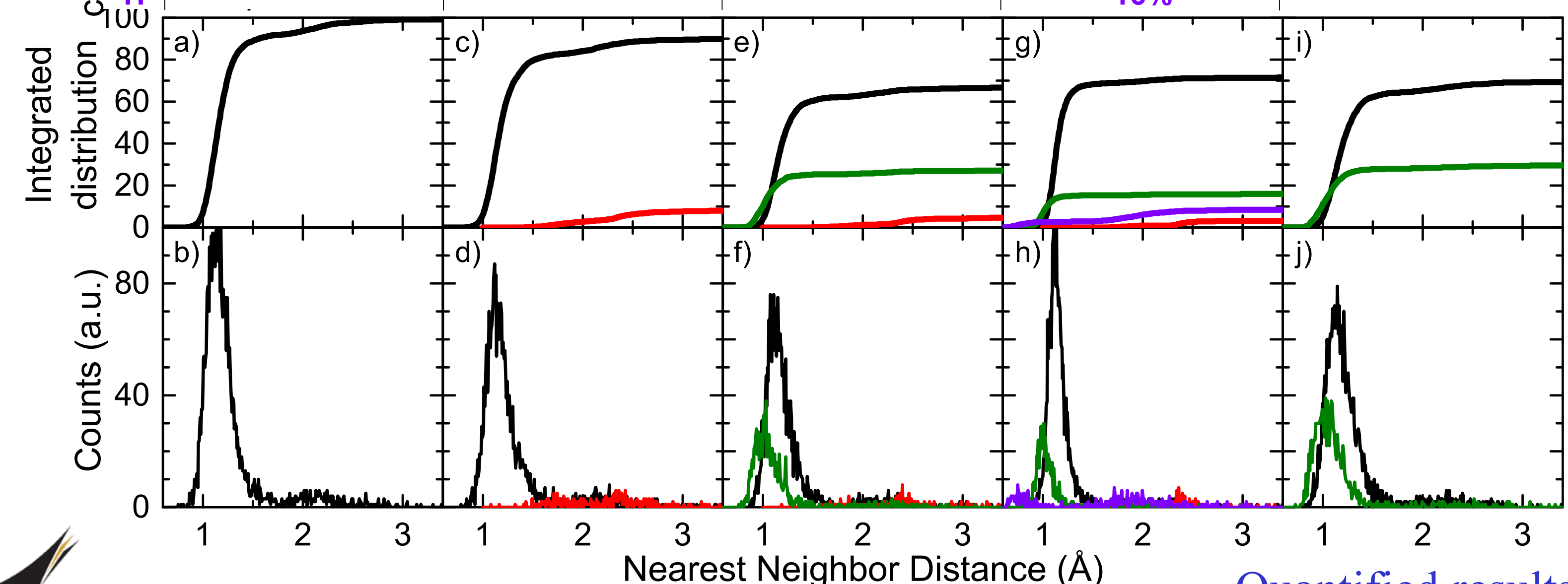
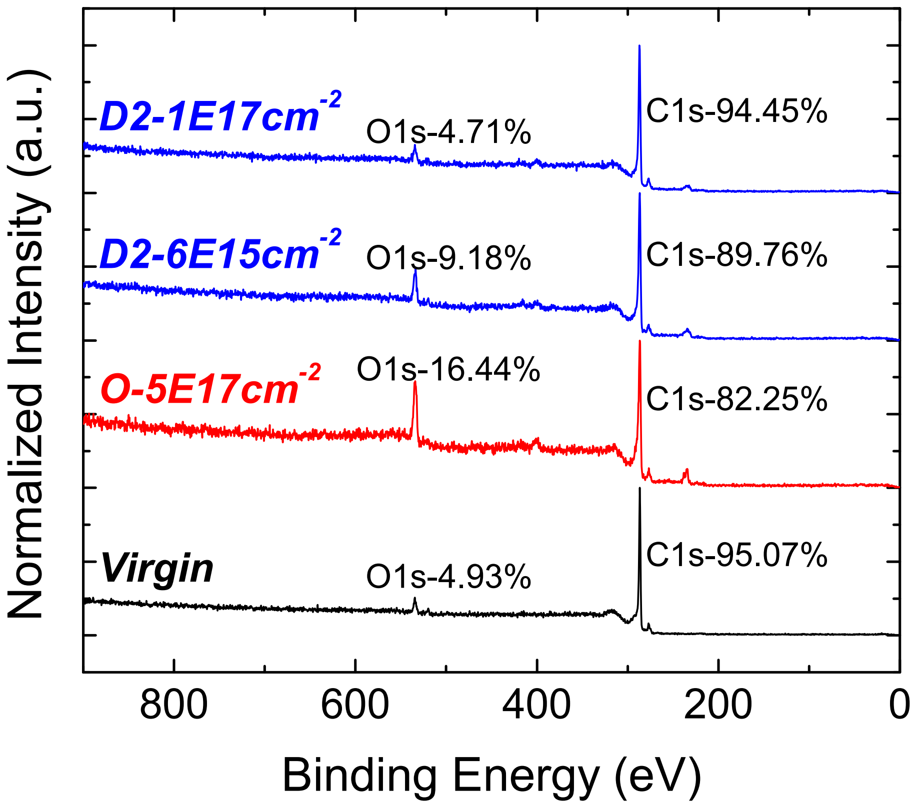


Quantified results next…

C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.

High O concentratoin not sustainable without Li

- Experimentally test case with 20% oxygen and no lithium.
  - Simulation time scale ~10^{-9} sec.
  - Experimental time scale ~10^{2} sec.
- Experiment:
  - Implant oxygen.
  - Bombard with D.
  - Quantify concentrations.
  - Examine retention.
- Oxygen is depleted during deuterium irradiation.



Localized heating effects that may release the oxygen in ~10^{2} sec are not resolvable in simulation time scale.

C.N. Taylor, et al., Journal of Applied Physics, Submitted 2013.