Lithium-based surfaces controlling fusion plasma behavior at the plasma-material interface

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2nd International Symposium on Lithium Applications for Fusion Devices
27-29 April, 2011
Princeton Plasma Physics Laboratory
Princeton, NJ

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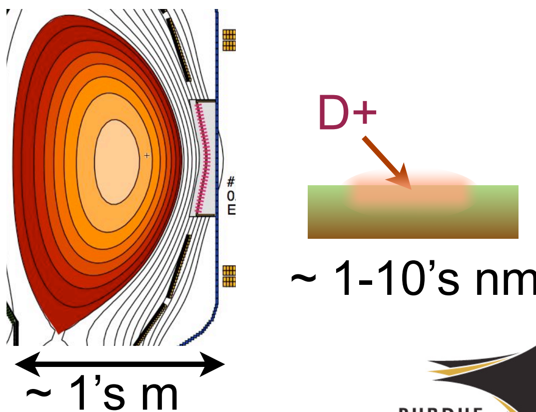
Outline

- Overview and evolution of particle and plasma-surface interactions on lithium-based systems
  - *Record of work on liquid lithium surfaces*
- Deciphering the lithium-plasma material interface
  - *Lithium-graphite system*
  - *Single-effect and in-situ particle-beam test stands*
  - *In-situ tokamak PMI diagnostics*
  - *Role of computational modeling*
- Summary

Unraveling the "black box" of the plasma-material interface in tokamak devices

- Fundamental interactions between the energetic particles from the plasma and its interface with the wall have for a long time been known to be important
- However, systematic understanding of this coupling has been challenged by the aggressive environment at the fusion plasma edge
- Wall material options were also driven in part by their influence on plasma performance (e.g. impurity erosion, particle recycling, etc...)
- In-vessel coatings deposition (e.g. boronization) led numerous efforts in manipulating plasma behavior with conditioning of the wall[1]
- however most of these efforts relied mostly on "trial and error" as the PMI (plasma-material interaction) empirical parameter space was developed over time
- spatio-temporal multi-scales became evidently important



[1]B. Lipschultz et al. Phys. Plasmas 13 (2006) 056117
[2]G. Federici et al. Nucl. Fusion 2001
[3]G.F. Councell et al. J. Nucl. Mater. 290 (2001) 255

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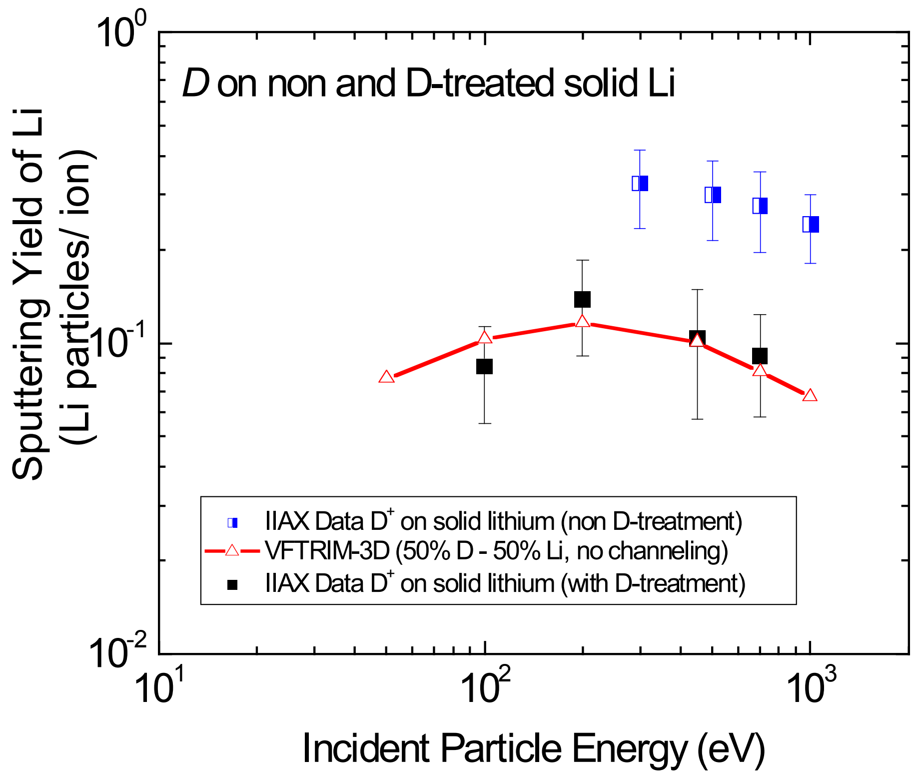
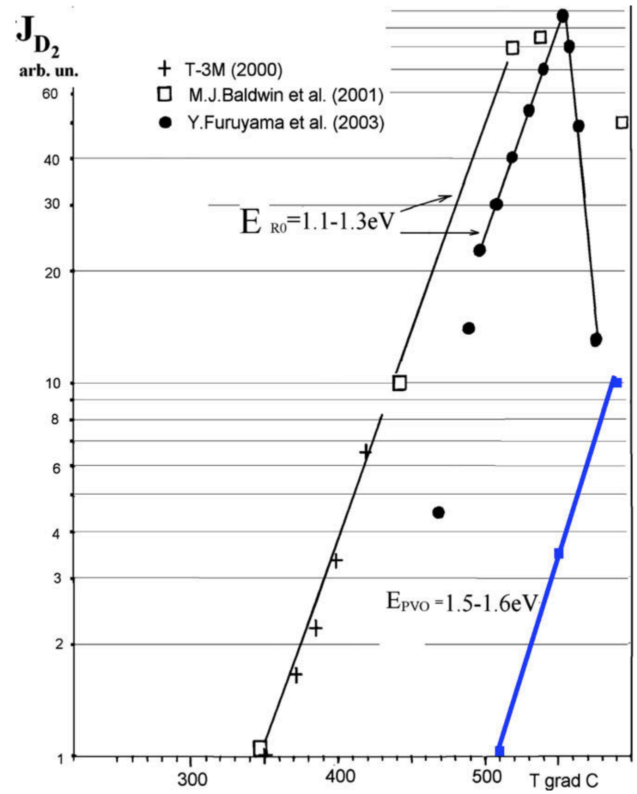
ALPS efforts in early lithium PSI research in the United States (1998-2003)*

- Close interaction between lab test stands and modeling of liquid Li surfaces
  - PISCES-B (R.P. Doerner and M.J. Baldwin)
  - ARIES (R. Bastasz, J. Whaley, R. Causey, D. Buchenauer)
  - IIAX (J.P. Allain, M.R. Hendricks, M.D. Coventry, D.N. Ruzic)
- PPPL introduces proof-of-principle strategy to study liquid lithium surfaces, opens opportunity for test stand efforts to link with confinement devices
  - CDX-U (preceded by Li coatings on TFTR limiter surfaces by Mansfield)
    - (R. Majeski and R. Kaita)
    - Various configurations: limiter, liquid Li divertor "pool"
  - Li DiMES effort (D.G. Whyte, J.P. Allain, J. Brooks and C. Wong)
  - FLIRE (M. Nieto, J.P. Allain and D.N. Ruzic)
    - Retention of D, He on flowing liquid Li surfaces
  - Beyond 2003: NSTX campaigns with Li coatings and recently with LLD

*Other work also with PFCs, liquid Li walls, MHD studies etc... in other projects

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)**
- Both solid and liquid Li surfaces can retain 1:1 D:Li; *solid surfaces however must be replenished*

[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. 290-291 (2009) 87.

The presence of oxygen on lithium surfaces

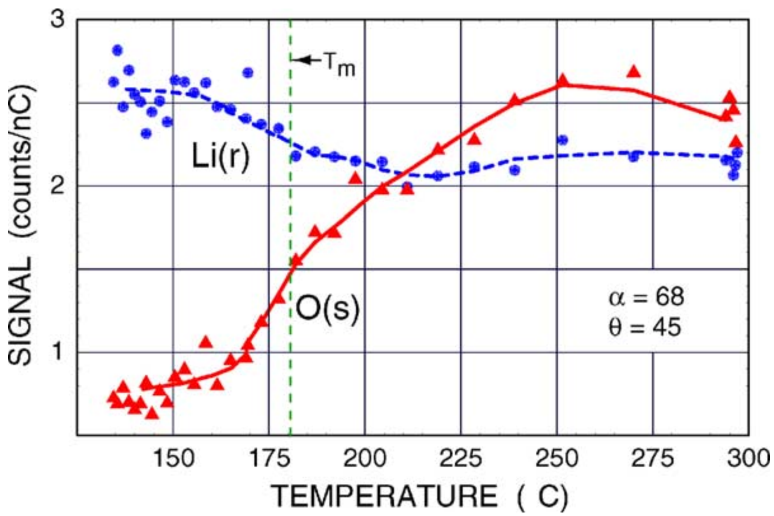


Fig. 3. Variation in oxygen signal intensity on a lithium surface as a function of temperature. The intensity of ion scattering from O and recoil emission from Li were monitored while the sample was bombarded with a 500 eV He^+ beam. Oxygen atoms appear more abundant on the liquid surface.

ARIES P_{base} ~ 10^{-10} Torr, P_{H2O} ~ 10^{-11}

- Detailed UHV surface analysis of lithium-based surfaces (solid and liquid) during ALPS program in U.S.
- Review issue: Vol 72 in 2004 (Fus. Eng. Des)

ELSEVIER

Fusion Engineering and Design 49–50 (2000) 127–134

Fusion Engineering and Design

www.elsevier.com/locate/fusengdes

ALPS–advanced limiter-divertor plasma-facing systems

R.F. Mattas [a,*,1], J.P. Allain [j], R. Bastasz [b], J.N. Brooks [a], T. Evans [l], A. Hassanein [a], S. Luckhardt [c], K. McCarthy [d], P. Mioduszewski [e], R. Maingi [e], E. Mogahed [f], R. Moir [g], S. Molokov [h], N. Morely [i], R. Nygren [b], T. Rognlien [g], C. Reed [a], D. Ruzic [j], I. Sviatoslavsky [f], D. Sze [a], M. Tillack [c], M. Ulrickson [b], P.M. Wade [e], R. Wooley [k], C. Wong [k]

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Available online at www.sciencedirect.com

SCIENCE DIRECT

Fusion Engineering and Design 72 (2004) 111–119

Fusion Engineering and Design

www.elsevier.com/locate/fusengdes

Surface composition of liquid metals and alloys

R. Bastasz*, J.A. Whaley

Sandia National Laboratories, Livermore, CA 94551–0969, USA

Available online 13 September 2004

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Available online at www.sciencedirect.com

SCIENCE DIRECT

Fusion Engineering and Design 72 (2004) 93–110

Fusion Engineering and Design

www.elsevier.com/locate/fusengdes

Studies of liquid-metal erosion and free surface flowing liquid lithium retention of helium at the University of Illinois

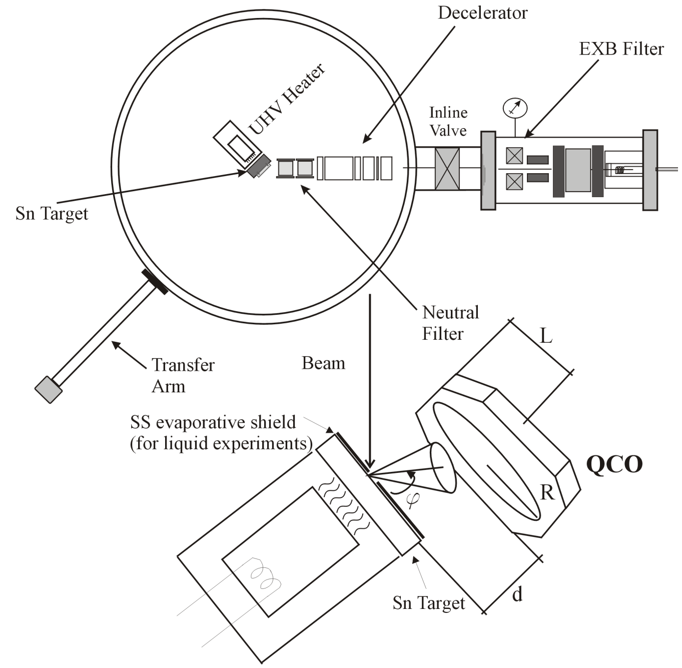
J.P. Allain[a,*], M. Nieto[b], M.D. Coventry[b], R. Stubbers[b], D.N. Ruzic[b,**]

[a] *Argonne National Laboratory, 9700 S Cass Ave, Argonne, IL 60439, USA*
[b] *University of Illinois, Urbana-Champaign, Urbana, IL, USA*

Available online 9 September 2004

Liquid Li and Sn-Li surface sputtering studies

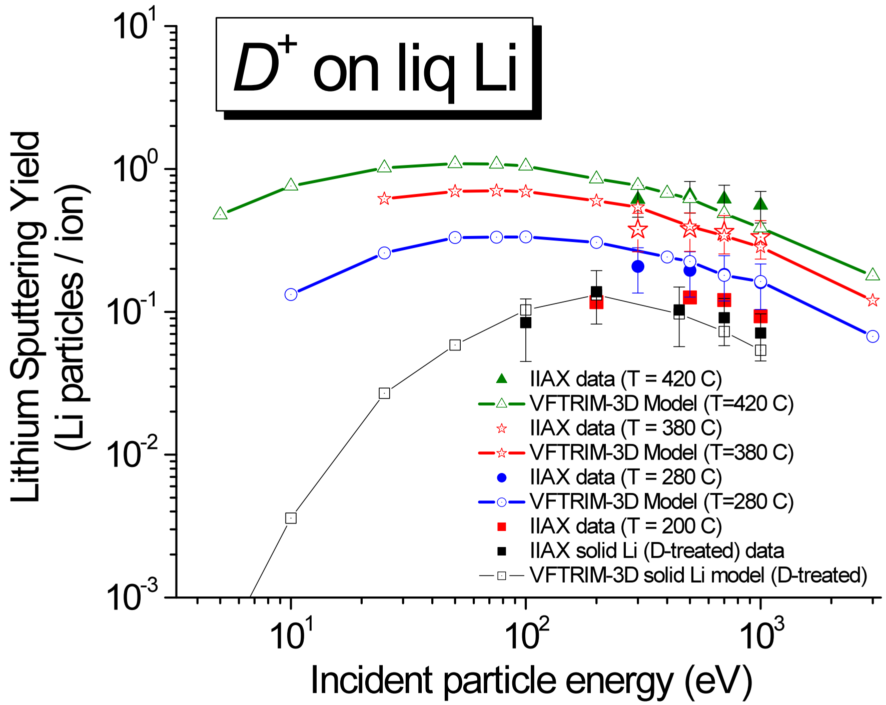
Liquid Lithium	Eo (eV) 200-1000	T (°C) 25-425	D-treated	Non D-treated
H^+	✓	✓	✓	
D^+	✓	✓	✓	✓
He^+	✓	✓	✓	✓
Li^+	✓	✓	✓	
Liquid Tin-lithium	**Eo (eV) 200-1000**	**T (°C) 25-425**	**D-treated**	**Non D-treated**
D^+	✓	✓	✓	
He^+	✓	✓	✓	✓
Li^+	✓		✓	
Liquid Tin	**Eo (eV) 200-1000**	**T (°C) 25-425**	**D-treated**	**Non D-treated**
H^+	✓	.		✓
D^+	✓	✓		✓
He^+	✓	✓		✓

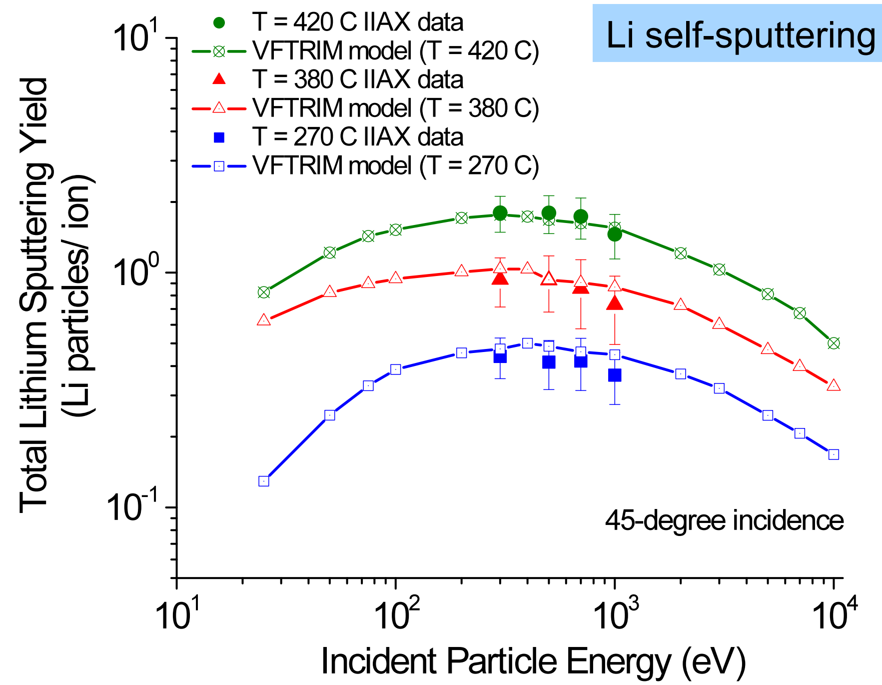


- Laboratory test stands consisted mainly of ion-beam facilities and PISCES-B (linear plasma device) studying liquid Li surface response under “simulated” conditions in the tokamak edge (e.g. 100-500 eV, 45-deg inc, D coverage)
- Numerous papers published incl. alternate liquid metals (e.g. Ga, Sn, etc...)

J.P. Allain, M.D. Coventry and D.N. Ruzic, Phys. Rev. B 13 (2007) 056117
J.P. Allain, M.R. Hendricks, and D.N. Ruzic, J. Nucl. Mater. 290-293 (2001) 180-184.

Temperature dependence of lithium sputtering

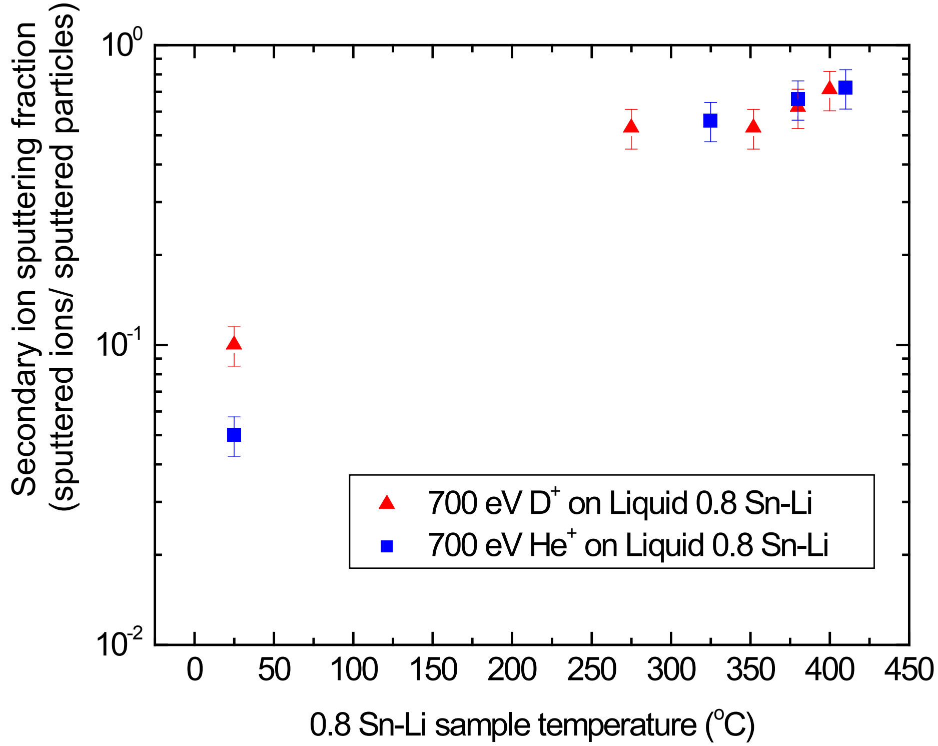


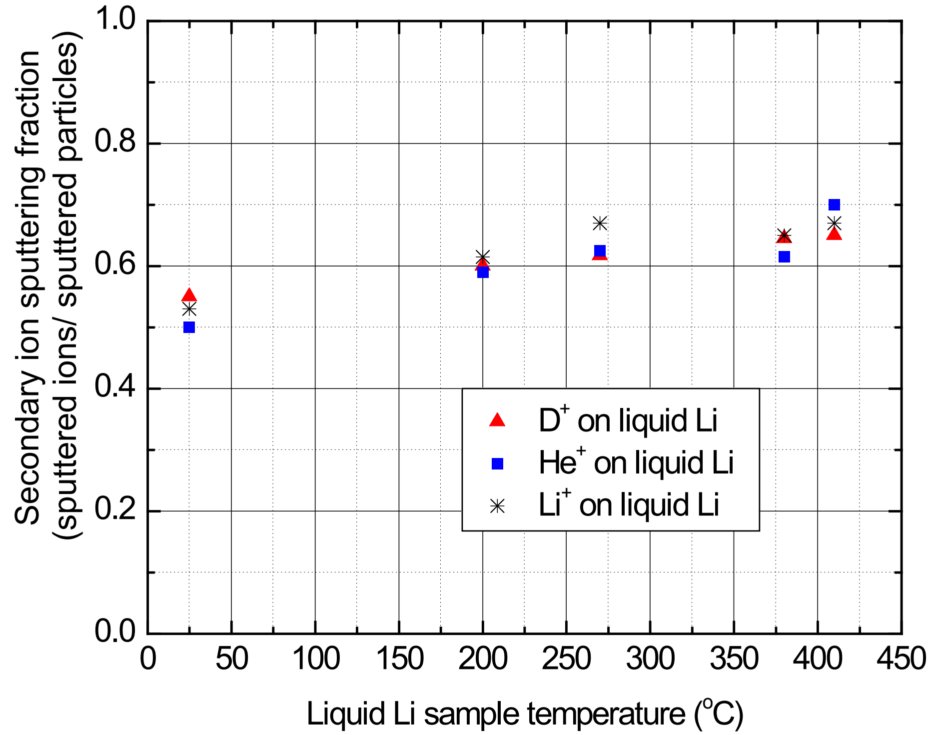


- Accounting for evaporation, ion-beam experiments identified temperature-dependent behavior of D and self-sputtering from liquid Li surfaces
- Experiments included: D saturation, oblique incidence, also He sputtering
- Many observed effects corroborated by linear plasma device experiments

J.P. Allain, M.D. Coventry and D.N. Ruzic, Phys. Rev. B 76 (2007) 205434
J.P. Allain et al. Fusion Engineering and Design, 72 (2004) 93

Secondary Li ion sputtering fraction



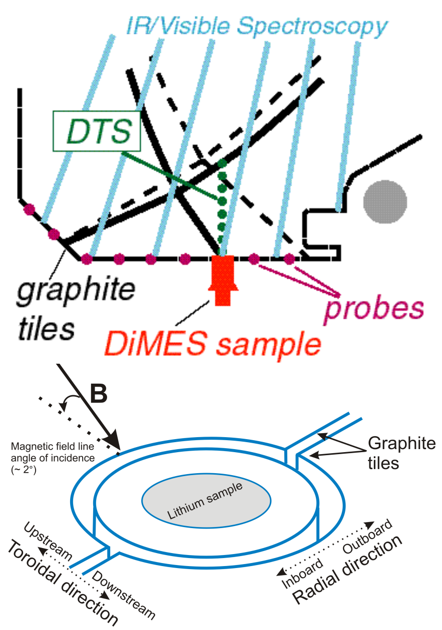


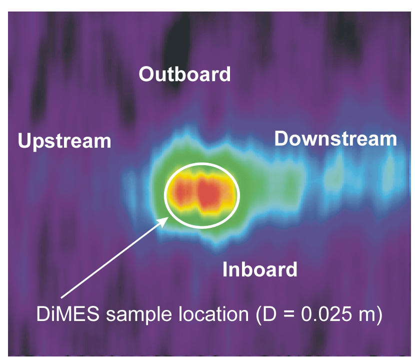
- The secondary sputtered ion fraction was measured first from solid Li surfaces and then systematic studies with temperature
- Sn-Li experiments revealed the segregation of a pure Li layer on the surface, consistent with LEISS data by Bastasz et al.

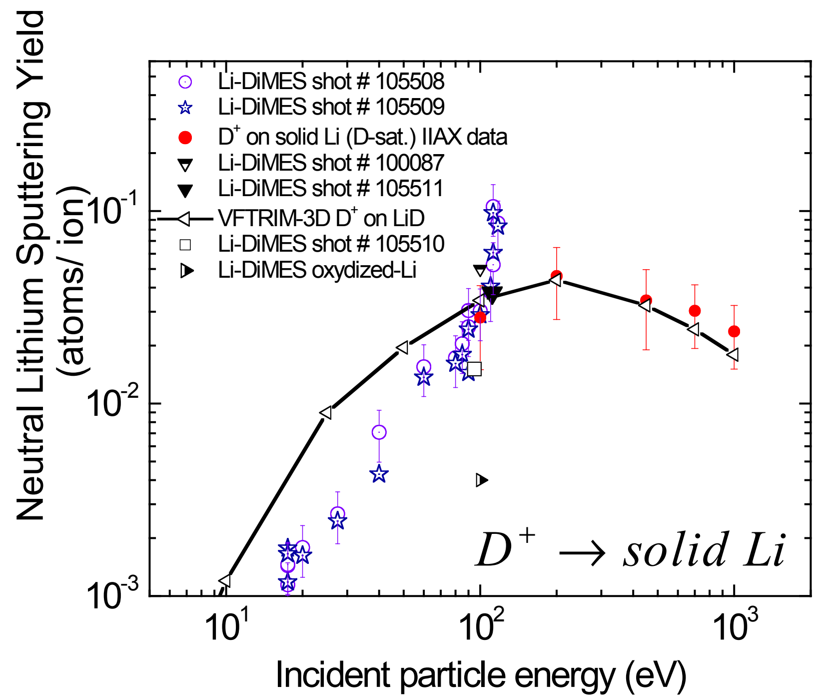
J.P. Allain, M.D. Coventry and D.N. Ruzic, Phys. Rev. B 13 (2007) 056117
R. Bastasz and W. Eckstein, 290-293 (2001) 19-24
J.P. Allain et al. NIMB 239 (2005) 347; paper included MD simul and stratifcation on liquid Li

Coupling surface response codes with edge plasma codes and in-situ experiments

- In-situ PMI diagnostics (e.g. DiMES probe in DIII-D) already demonstrated the advantage of coupling:
  - In-situ PMI probe data
  - Computational modeling codes (edge, surface)
  - Off-line single-effect experimental data







J.P. Allain, J.N. Brooks and D.G. Whyte, Nucl. Fusion, 44 (2004) 655
D.G. Whyte, J.P. Allain et al. Fusion Eng Des. 72 (2004) 133-147

What have we learned about liquid-lithium surfaces exposed to energetic D, He and Li bombardment?

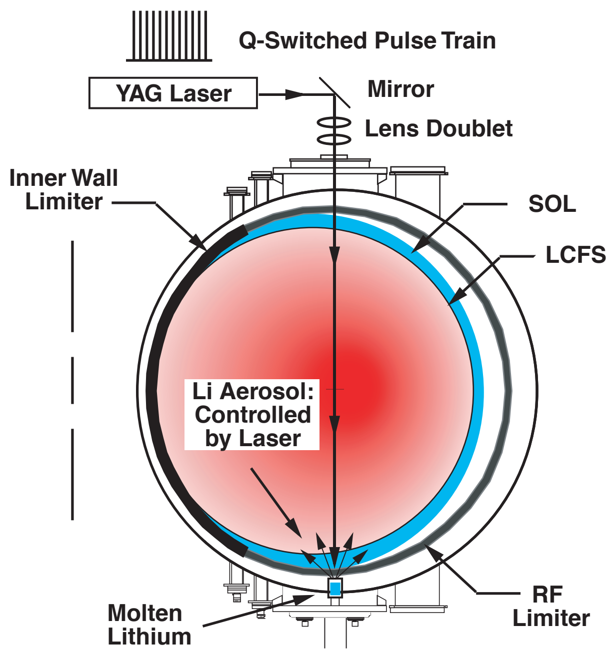
- No significant difference in sputtering from the solid to liquid state of lithium when temperature is near melting point
- Non-linear increase in sputtering from liquid-Li when temperature is about 50% higher than melting point (accounting for evaporation)
- Two-thirds of lithium sputtered particles are in the charged state
- Implanted hydrogen leads to a ~ 40% decrease in *lithium* sputtering
- So far: liquid Li, Sn-Li, Ga and Sn show signs of erosion enhancement (particularly lithium) *with* rise in temperature
- Li-DiMES data shows near-surface ionization of emitted Li particles within ~ 1cm[1]
- High retention of deuterium in liquid lithium (PISCES-B results by M. Baldwin et al.)[2]
- Critical to have 'stable' *flowing liquid lithium systems* due to: macro, micro and nano-scale oxide coverage; heat removal; etc...

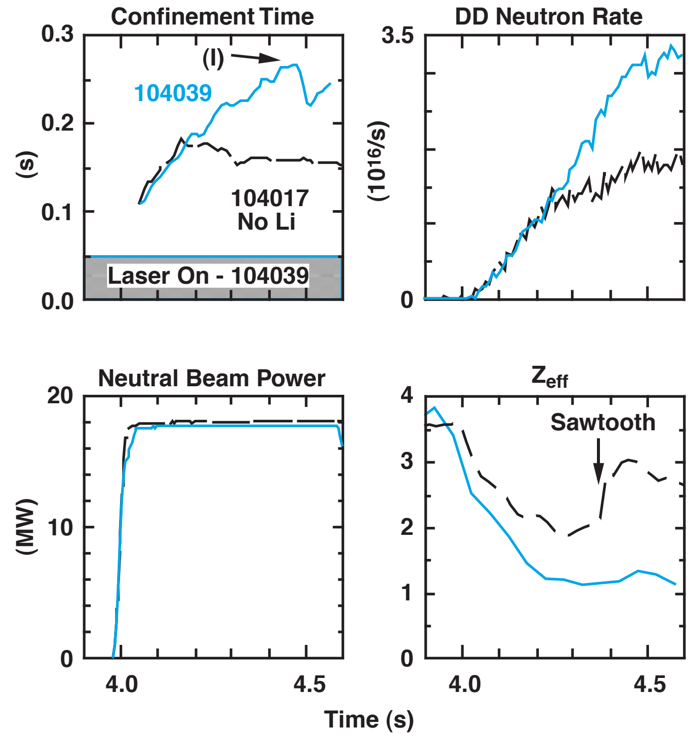
[1] J.P. Allain J.N. Brooks, and D.G. Whyte, Nucl Fusion, 44 (2004) 655.

[2] M. Baldwin, R.P. Doerner, R. Causey, et al. J. Nucl. Mater. 306 (2002) 15

Lithium on graphitic substrates

Lithium wall conditioning

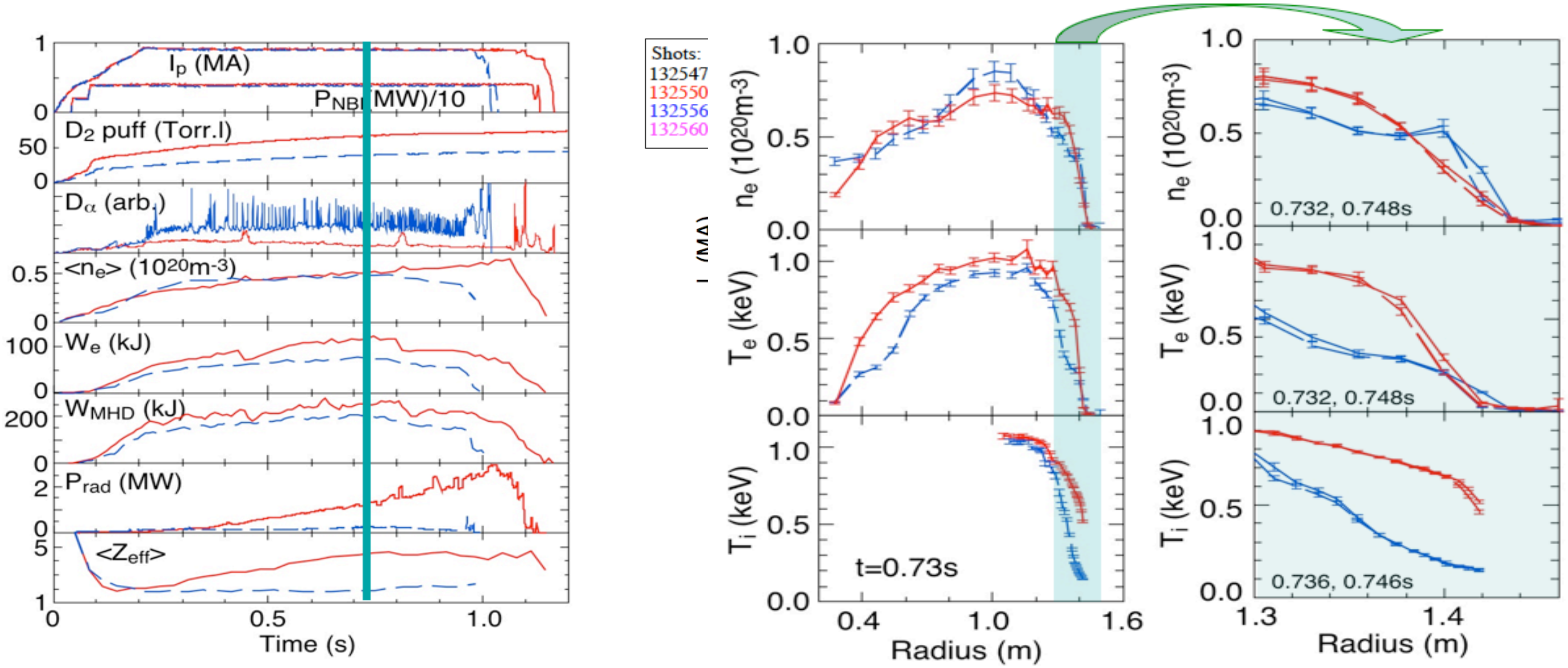




- Experiments in TFTR by D. Mansfield et al. led to one of the most successful campaign runs in a tokamak fusion experimental reactor[1]
- CDX-U conducts first experimental runs in a torus device with hot liquid Li divertor plate yielding *significant D pumping and low-recycling*[2,3]

[1]D. Mansfield, Nucl. Fusion 41, 1823 (2001)
[2]R. Majeski et al. PRL, 97 (2006) 075002
[3]R. Kaita et al. Phys. Plasmas, 14 (2007) 05611

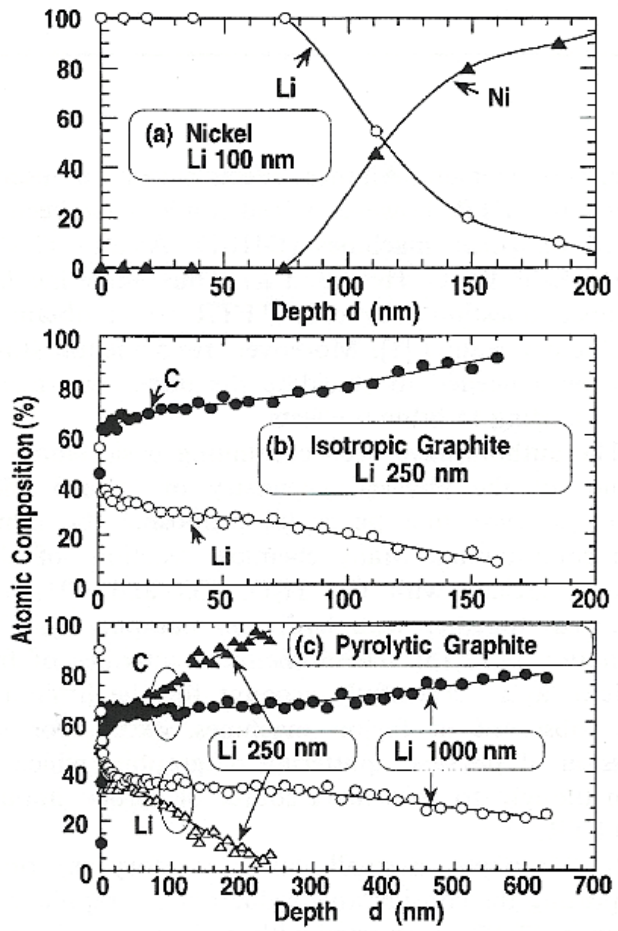
Lithium coating effects on NSTX performance

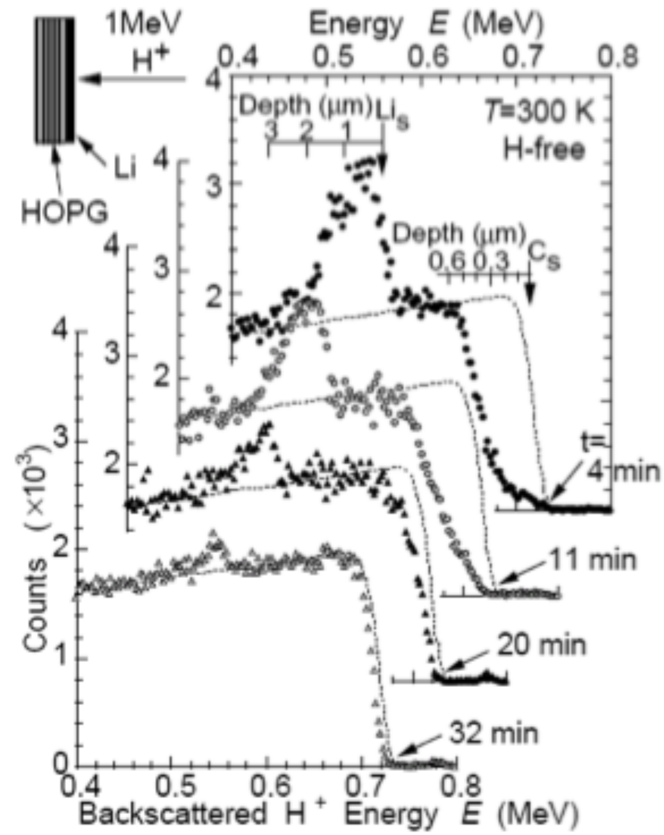


- Reference waveforms for relatively oxygen free pre lithium wall conditions (blue dashed line). After 260mg lithium deposition (red) deuterium recycling reduced, ELMs suppressed, stored energy increased, confinement improves. The vertical line at 0.72 s is the time reference for figure on the right.
- Improvements in plasma conditions were transient and performance reverted to the pre-lithium conditions by the following discharge unless evaporation resumed

H.W. Kugel et al. J. Nucl. Mater. 2010 In Press

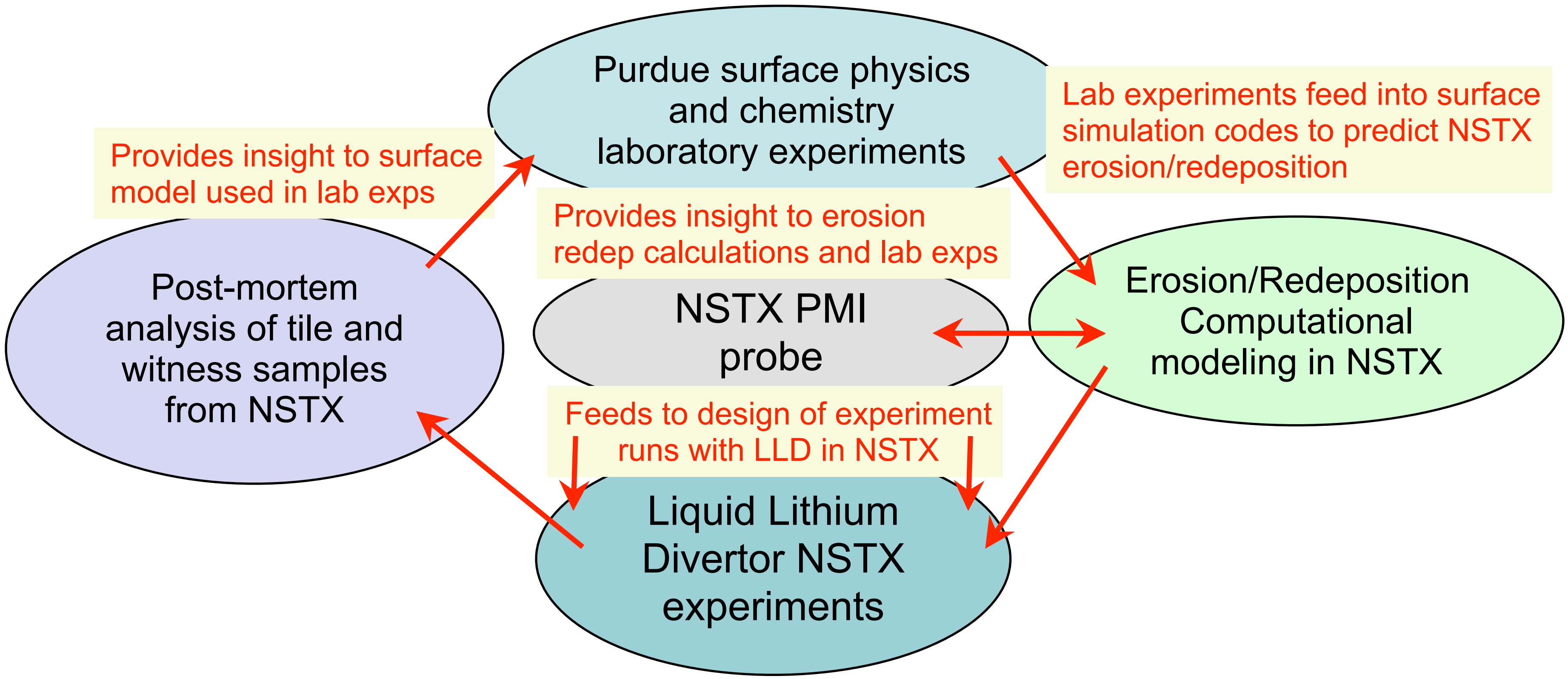
H. Sugai's work on lithium intercalation in various graphite allotropes





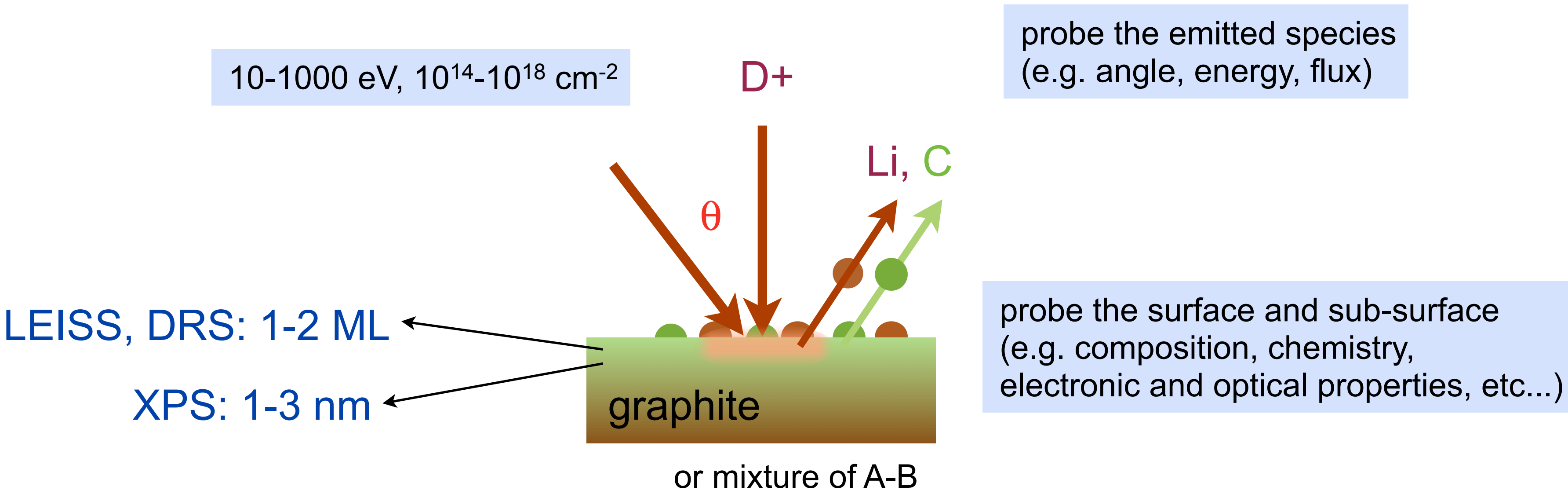
N. Itou, H. Toyoda, K. Morita, H. Sugai, J. Nucl. Mater. 290-293 (2001) 281.

Summary of Li-based PMI work at Purdue



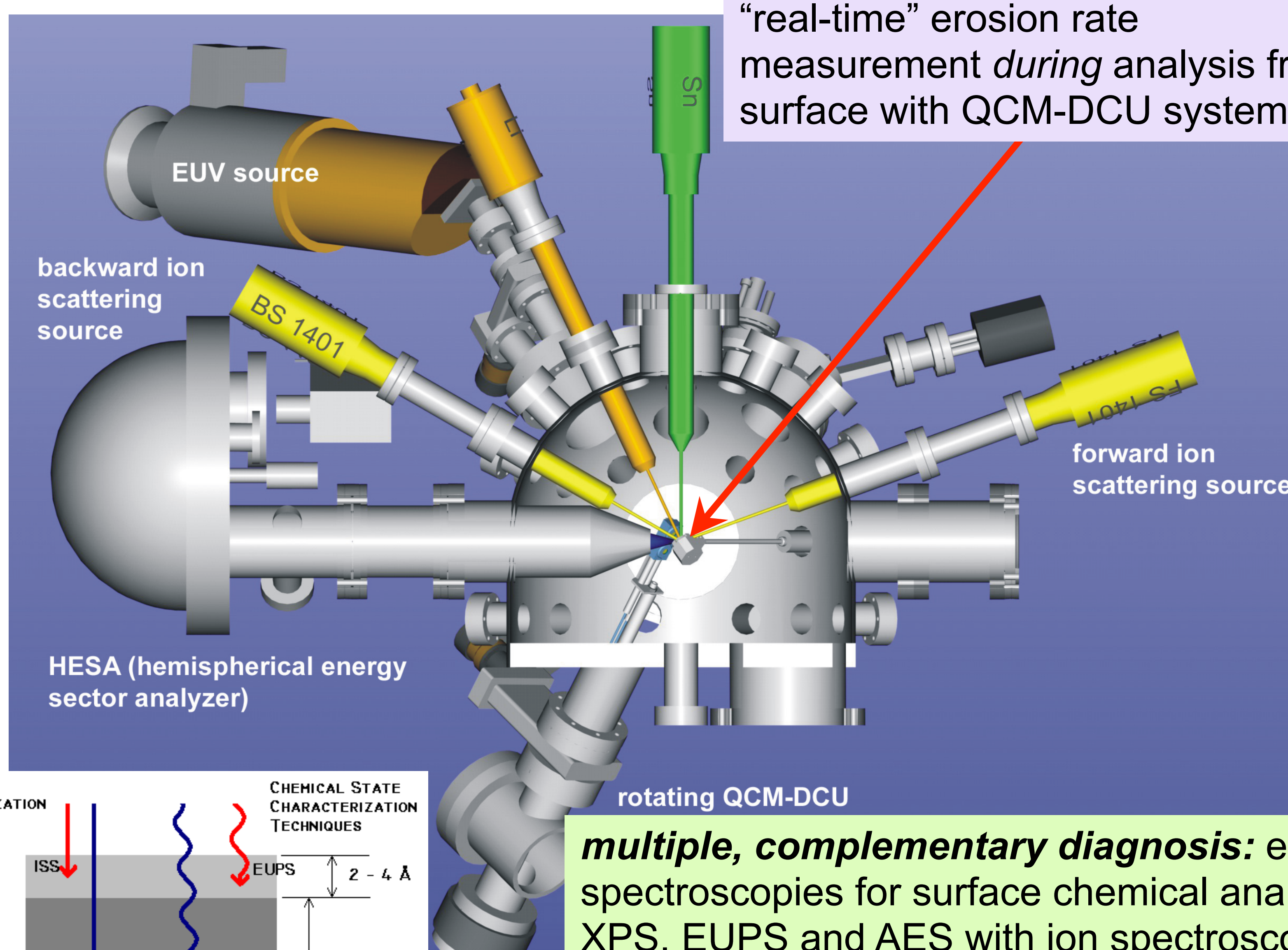
- At Purdue we're investigating the role lithium coatings on ATJ graphite has on deuterium pumping and recycling of hydrogen
- We systematically study lithiated graphite surface chemistry and ion-induced desorption to elucidate plasma-material interface interactions in NSTX
- Lab experiments also look at the effect of a lithiated graphite environment on the performance of NSTX plasma with the liquid lithium divertor (LLD)

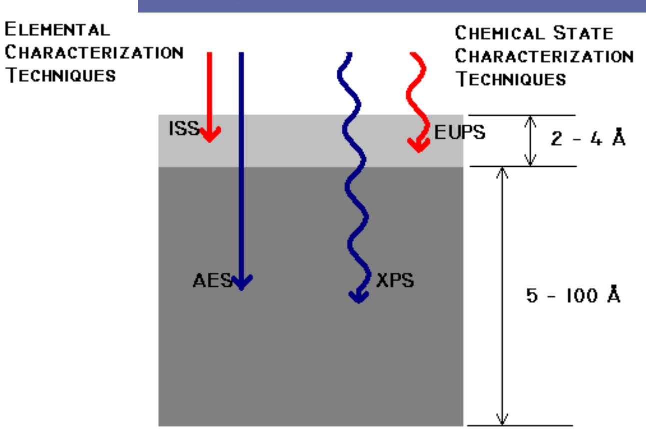
The Tool Set: In-situ characterization of an irradiation-driven surface



- amorphous layer: low-energy ion scattering spectroscopy (**LEISS**) in backscattering mode with 1.5-keV He ions; Forward and recoil scattering (**DRS**) to measure hydrogen content on the surface
- sub-surface layer (1-5 nm) with **XPS**
- We combine the two techniques *in-situ* during irradiation with various modification sources

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

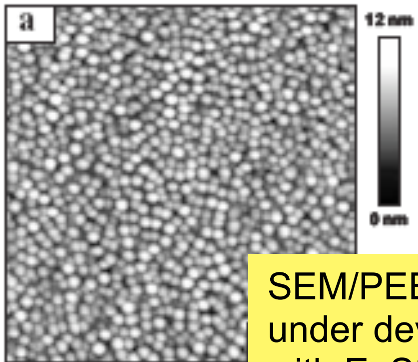


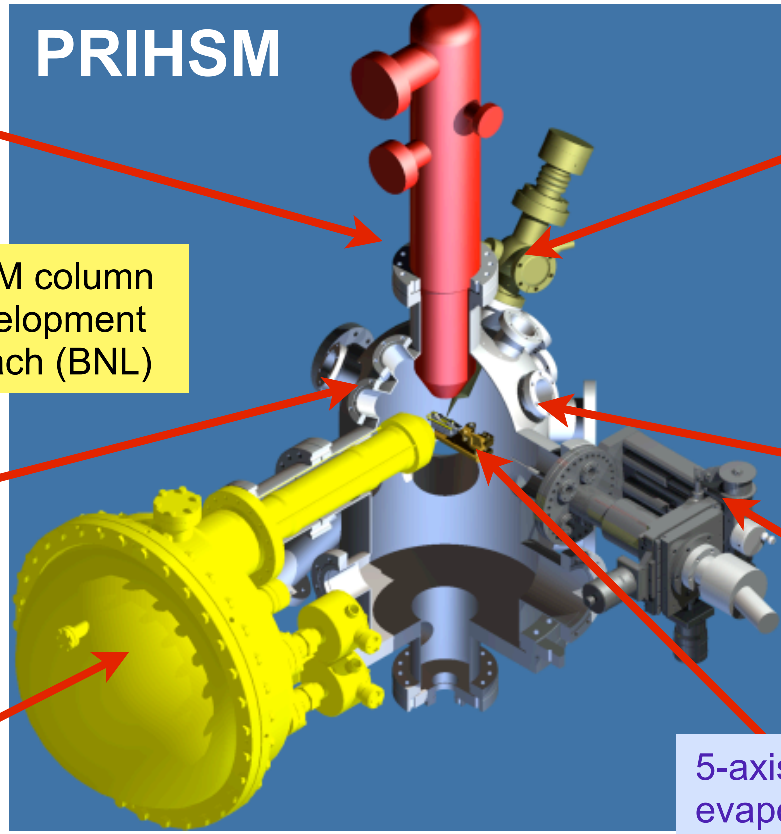


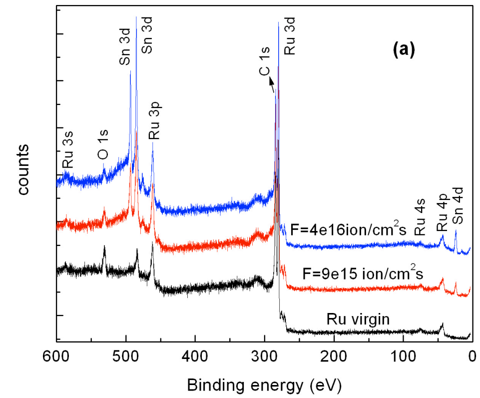
multiple, complementary diagnosis: electron spectroscopies for surface chemical analysis: XPS, EUPS and AES with ion spectroscopies: forward and backward scattering modes

J.P. Allain, et al. Rev. Sci. Instrum. 78 (2007) 113105

Modification ion sources with in-situ tool set







SEM/PEEM column under development with E. Stach (BNL)

Excitation sources for: **LEISS, DRS, XPD, XPS, UPS, ARPES**

2-D MCP/HESA detector/analyzer system dispersing energy and momentum

2 broad beam ion sources with 0.1-4 mA/ cm^2, 30-1000 eV

auto control on 2 degrees of freedom

5-axis manipulator with e-beam evaporator and liquid N2 (77K-1200K), tilt for variation of incident angle

- Conditions: Deposition of lithium coatings (under simulated conditions to NSTX) on ATJ graphite exposed to D and He irradiation at energies between 100-500 eV/ amu

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D.L. Rokusek and J.P. Allain, In prep. J.Vac. Sci. Tech. B, 2011

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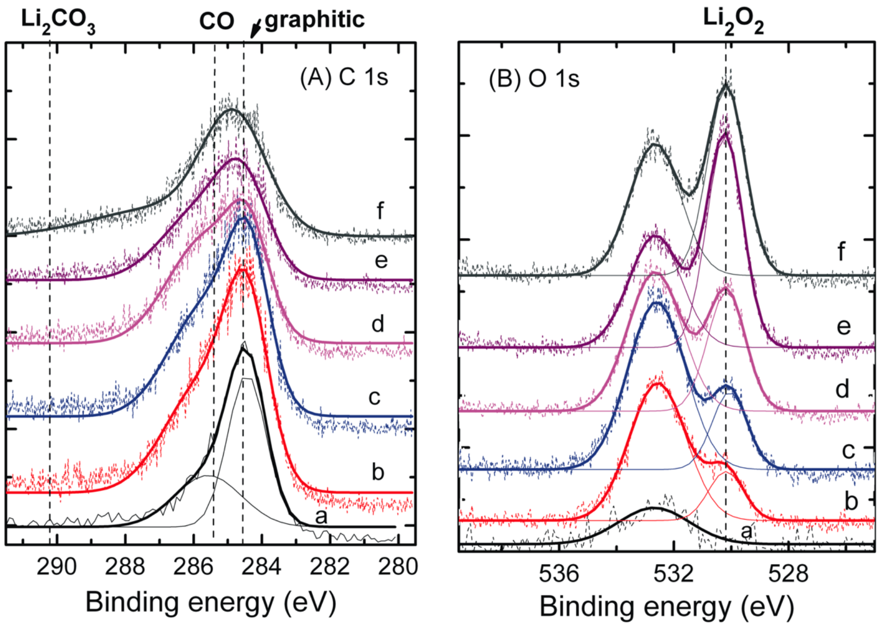
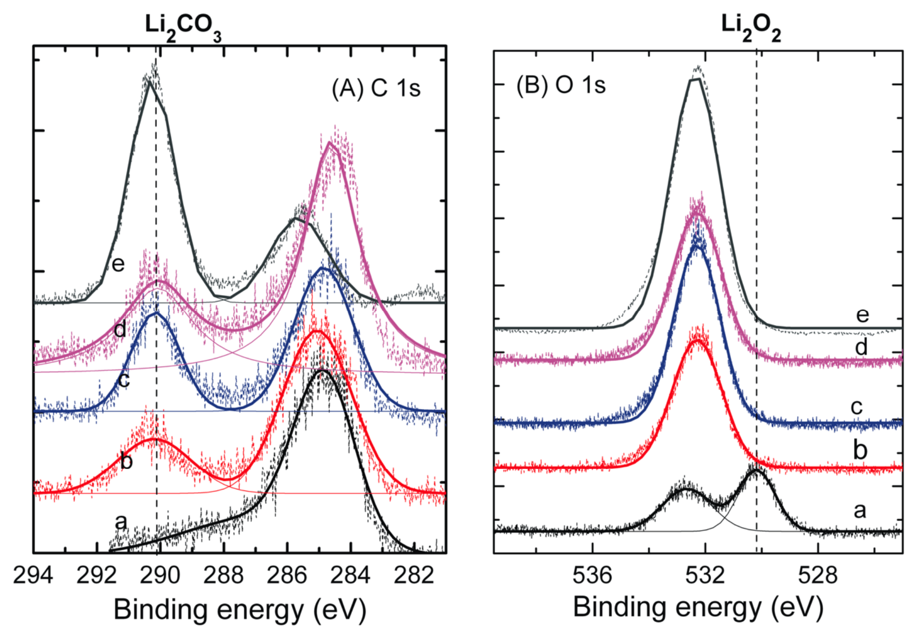
Controlled in-situ lithium deposition on ATJ graphite followed by air exposure



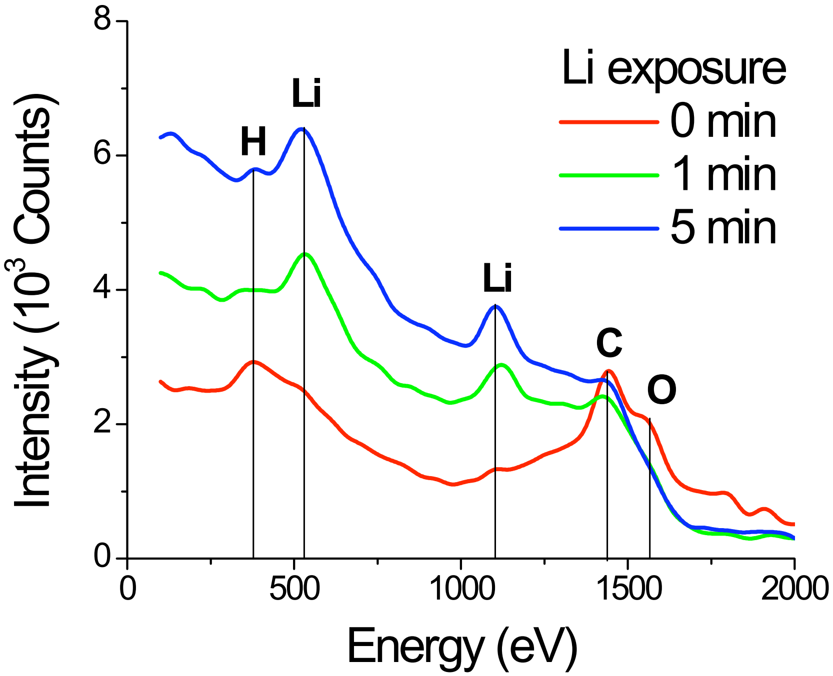


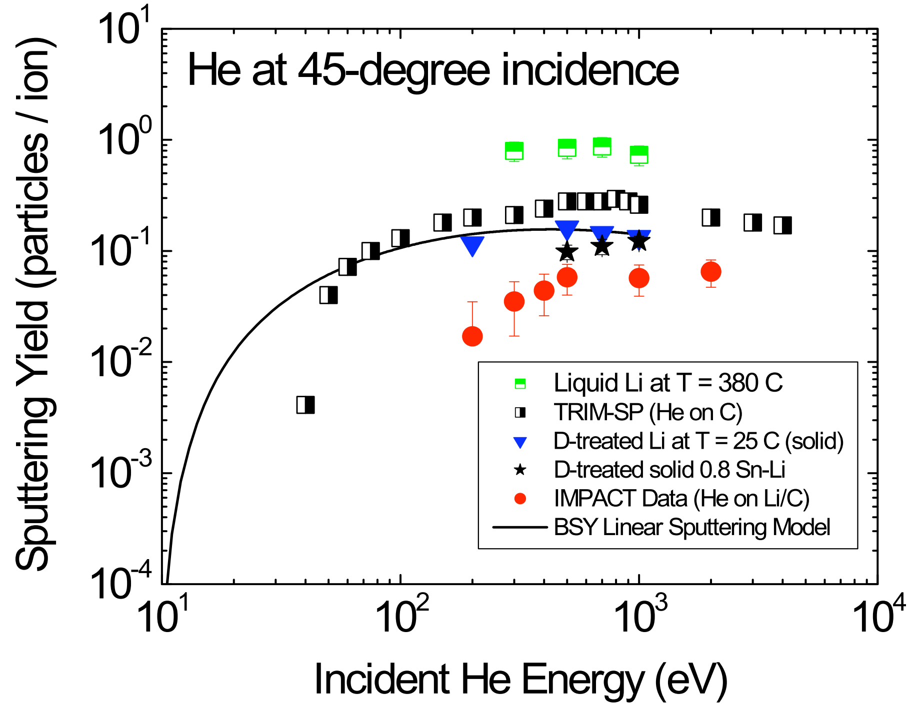
C1s | Li deposition | O1s | C1s | Exposure to air | O1s

- Lithium deposition yields peak at 529.5 eV ± 0.5 eV
- Exposure to air yields peak at 290 eV and 529 eV peak disappears

J.P. Allain, D. Rokusek, et al., J. Nucl. Mater. 390-391 (2009) 942
S.S. Harilal and J.P. Allain, Appl. Surface Sci. 255 (2009) 8539

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

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

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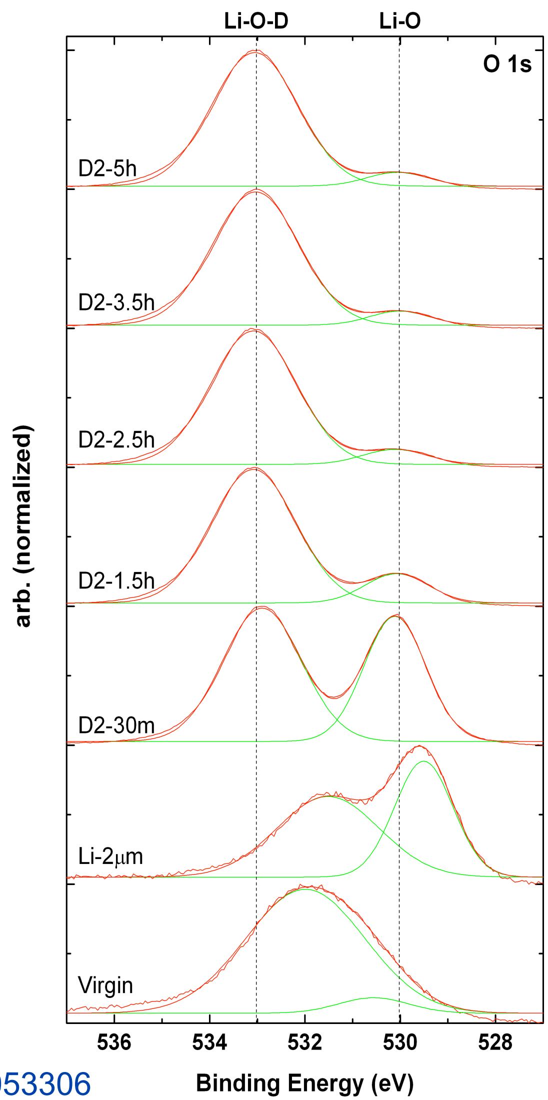
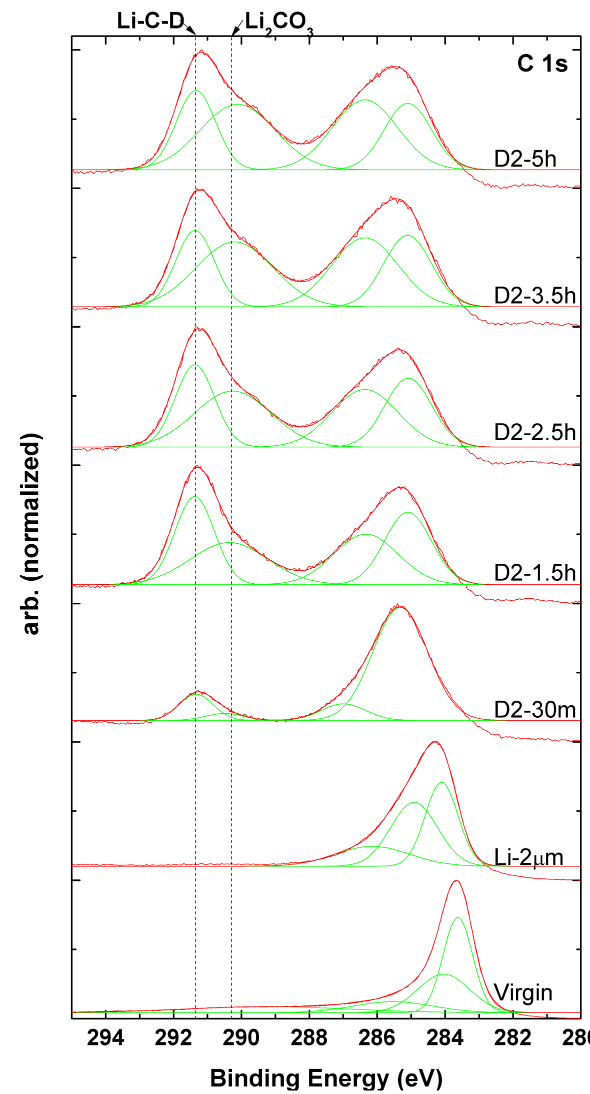
Lithiated graphite – Deuterium fluence

- Deuterium irradiation alters the surface chemistry of lithiated graphite.
- What happens as larger quantities of deuterium are introduced?
- Can lithium-deuterium saturation be observed indirectly?
- Peak "functionalities" associated uniquely to interactions between D, C, O and presence of Li





C.N. Taylor, et al. J. Appl. Phys. 109 (2011) 053306
C.N. Taylor, et al. J. Nucl. Mater. In press 2011

O1s peaks

C1s peaks

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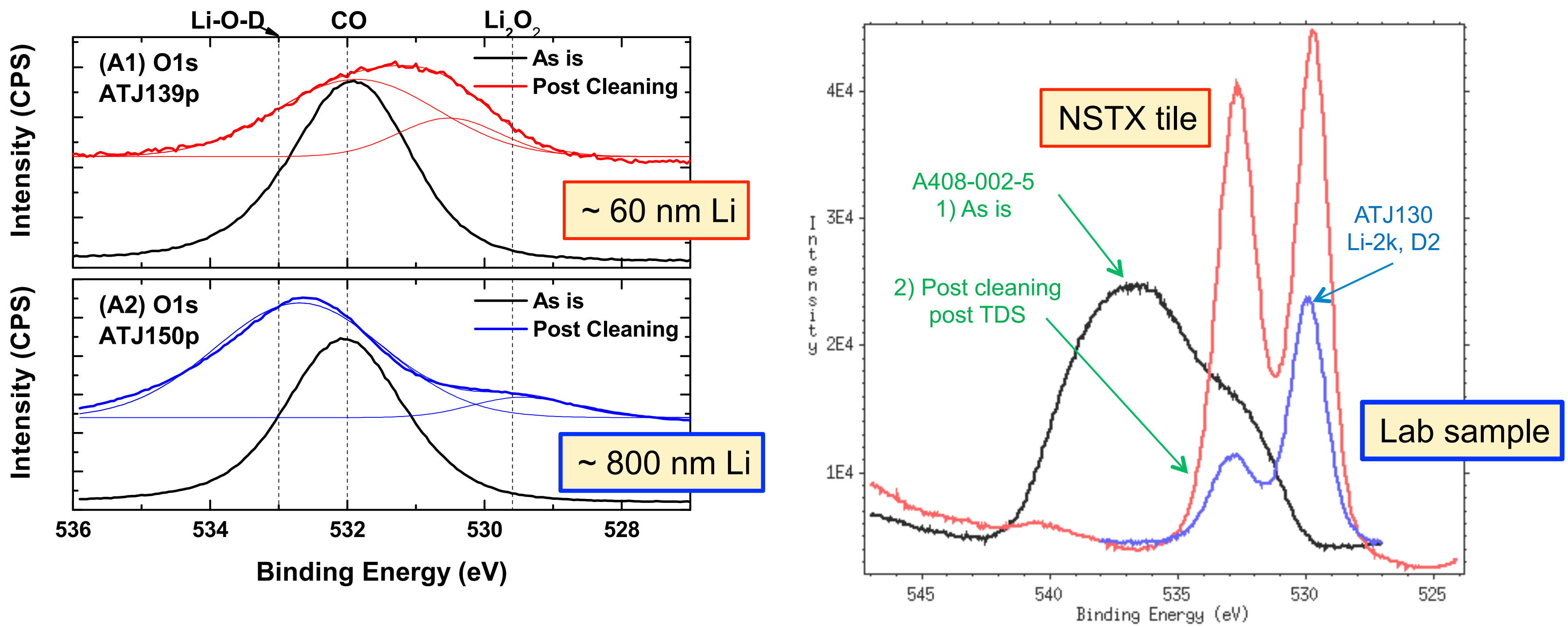
Laboratory experiments consistent with surface chemistry of NSTX tiles



- Connecting controlled “single-effect” studies in lab experiments to complex environment in NSTX by examining post-mortem surface chemistry “buried” under oxidized layer (left)
- Connect shot-to-shot NSTX plasma behavior with in-situ PMI diagnostics and connect back to lab data (right)

C.H. Skinner, J.P. Allain et al. in press 2011, J. Nucl. Mater.
C.N. Taylor, J.P. Allain et al. In press 2011, J. Nucl. Mater.

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Molecular Dynamics of Li–C–O–D Surfaces

See upcoming talk: P.S. Krstic in Session V

P.S. Krstic[1,2], Z. C. Yang[3], J. Dadras[2], P. R. C. Kent[4], A. Allouche[5], J. Jakowski[6], K. Morokuma[7], C.N. Taylor[3], J.P. Allain[3]

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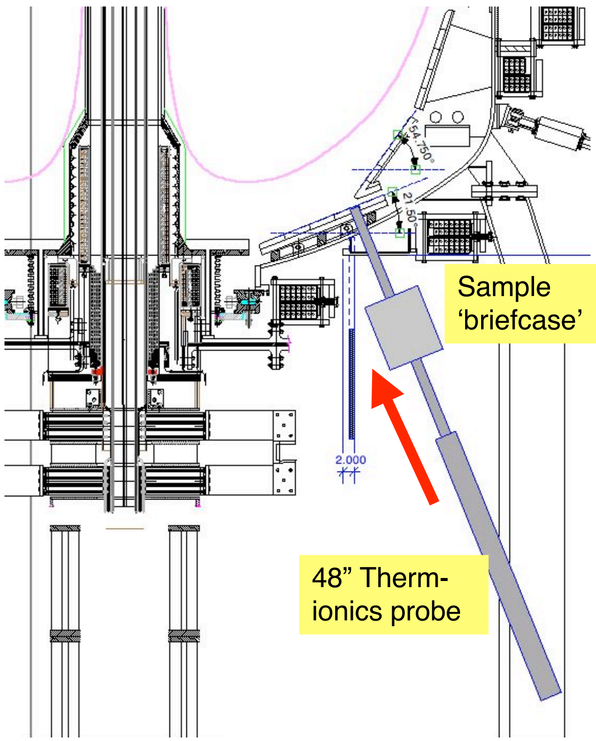
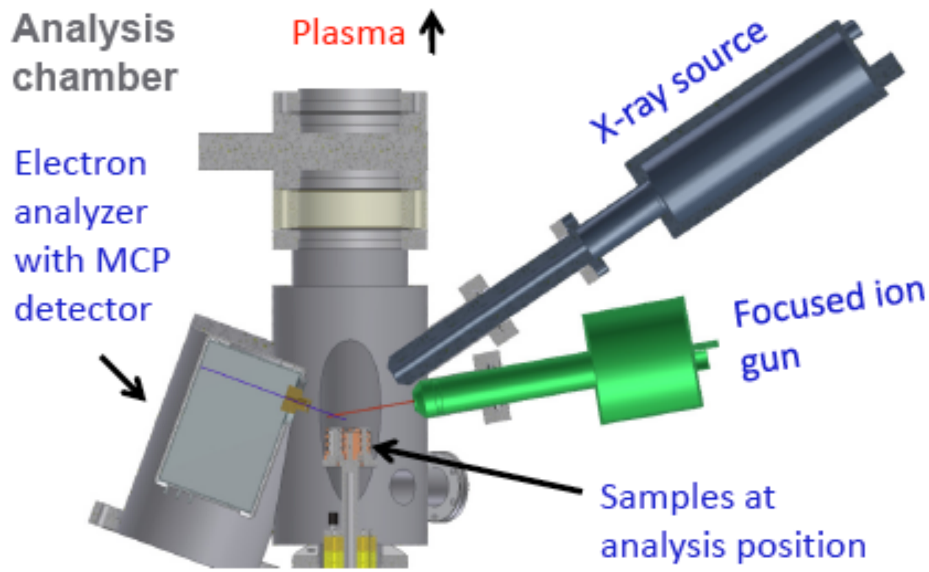
[2]Department of Physics & Astronomy, **University of Tennessee**, Knoxville TN, USA
[3]Department of Nuclear Engineering, **Purdue University**, West Lafayette IN, USA
[4]Center for Nanophase Materials Sciences, **Oak Ridge National Laboratory**, Oak Ridge TN, USA
[5]CNRS, **University of Provence**, Marseille, France
[6]National Institute for Computational Sciences, **Oak Ridge National Laboratory**, Oak Ridge TN, USA
[7] Fukui Institute for Fundamental Chemistry, **Kyoto University**, Kyoto, Japan

- The objectives of this research are two-fold:
  - To develop the realistic methods for computational simulation of the Li-C-H system, validated by experiments. The main difficulty and challenge consists of the high polarizability of lithium when interacting with other materials.
  - To explain the specifics of the chemistry of deuterium bonding in lithiated carbon. Experiments from Purdue indicate that bonded C-Li sites are preferable for H, D bonding due to lithium-induced dipole interactions with C, O.

Tokamak in-situ diagnosis of plasma-material interface: measurement of dynamic response

post-irradiation testing *will not* elucidate on *dynamic* effects





DRS (direct recoil spectroscopy)
TDS (measure H/D retention)
XPS (chemical bonding states)
LEISS (ion scattering spectroscopy)

NSTX Materials Analysis and Particle Probe (MAPP) with in-vacuo surface analysis: surface chemistry; To be installed for FY2011 and FY2012 NSTX experimental campaigns

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Example of in-situ diagnosis NSTX PMI research: what do we gain?

<u>Manufactured PFCs:</u>
Graphite
Moly tiles
Boron nitride …

→

<u>Tokamak environment:</u>
base vacuum, H_2O
Lithium evap.
Plasma, incl. ELMs, disruptions,
Erosion, redeposition, melting

→

<u>Mixed material surfaces,</u>
dust, with different composition and morphology to manufactured PFCs

→

Plasma Performance

Courtesy of C. Skinner

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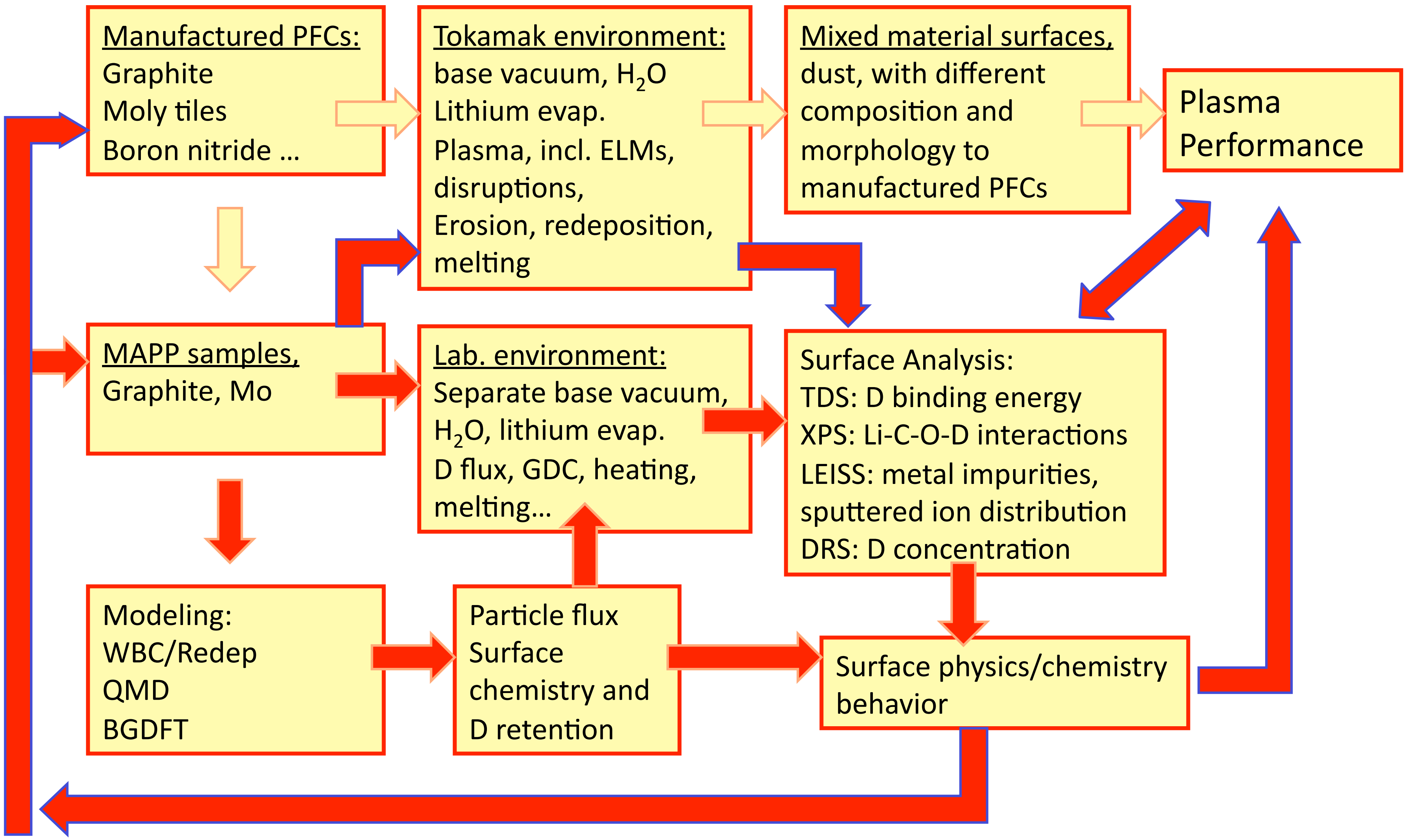


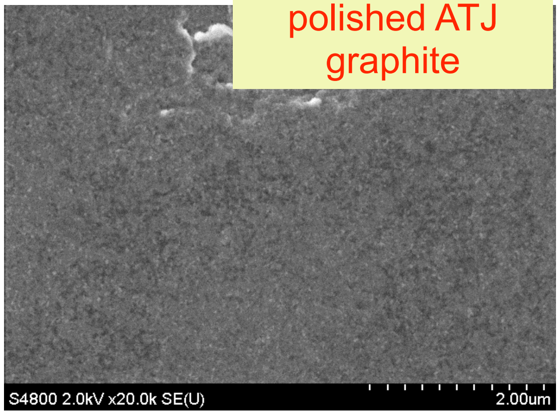
Courtesy of C. Skinner

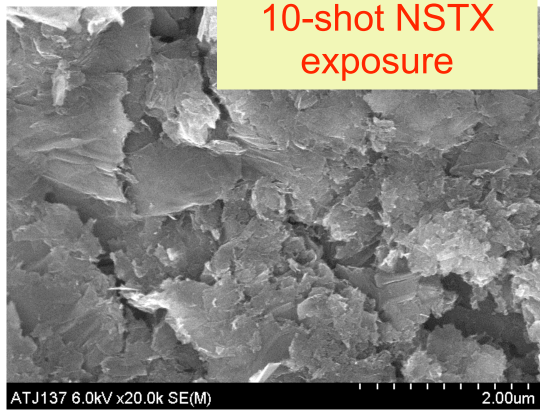
Challenges ahead...

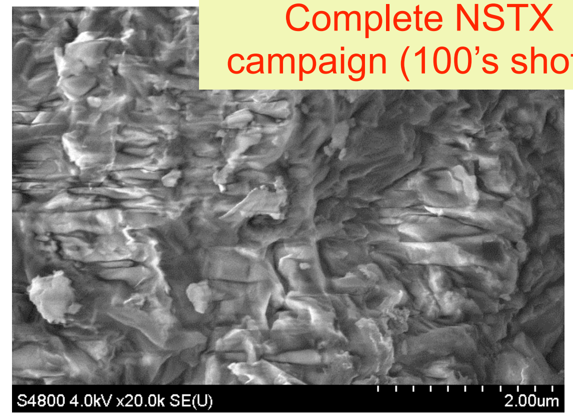
- Limits on in-situ PMI diagnostics
  - Access to PMI diagnostics in strategic regions of the plasma edge remain difficult
  - Limits on probing near-surface/surface spatial scales and relevant time scales
- Limits from off-line facilities
  - Simulating conditions in a tokamak remain complex
  - Learning to ask the right questions and connecting with modeling is also progressing
- Limits on computational modeling
  - Both temporal and spatial scales challenge available computational modeling (e.g. ballistics vs diffusion processes)
  - More importantly enabling the connection between off-line experiments and tokamak in-situ PMI diagnostics[1]

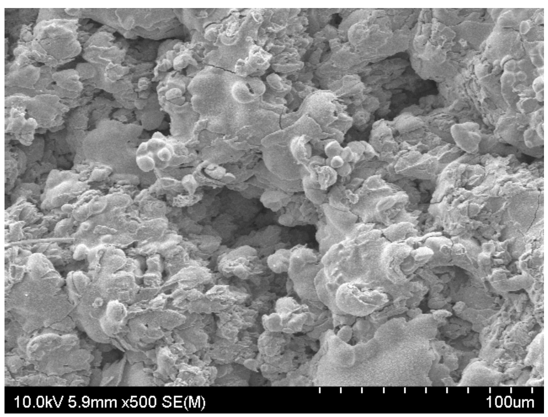
1. J.P. Allain and J.N. Brooks, Nucl. Fusion 51 (2011) 023002 **See: J. Brooks talk**

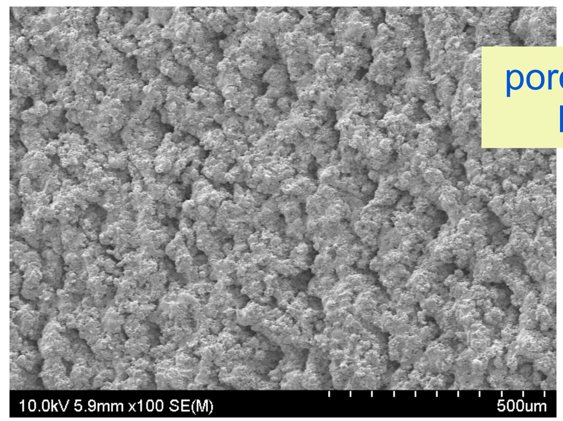
Role of surface morphology on hydrogen retention: aggressive environment











porous Mo substrate for LLD performance

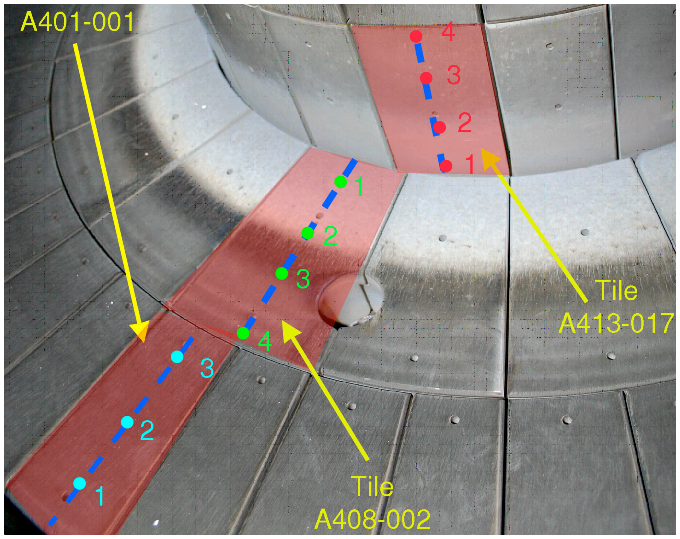
- Many questions on PMI performance (e.g. hydrogen pumping and recycling, erosion, etc...) will hinge on surface morphology and its evolution over plasma exposure dose

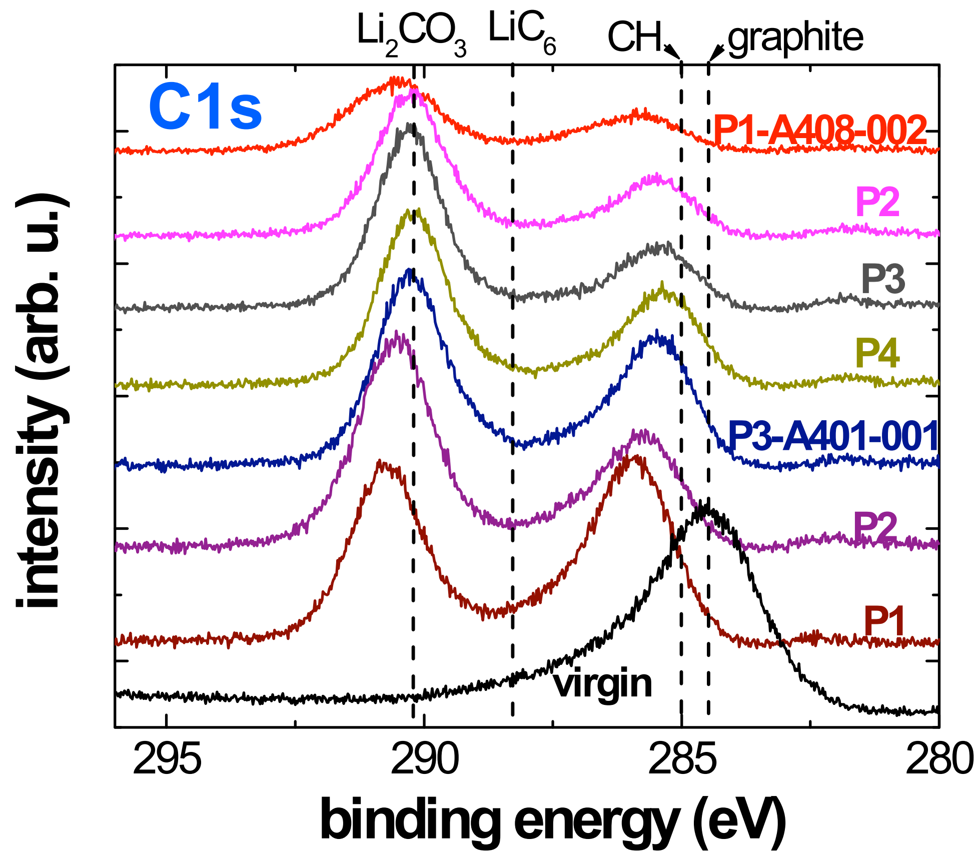
Summary and Outlook

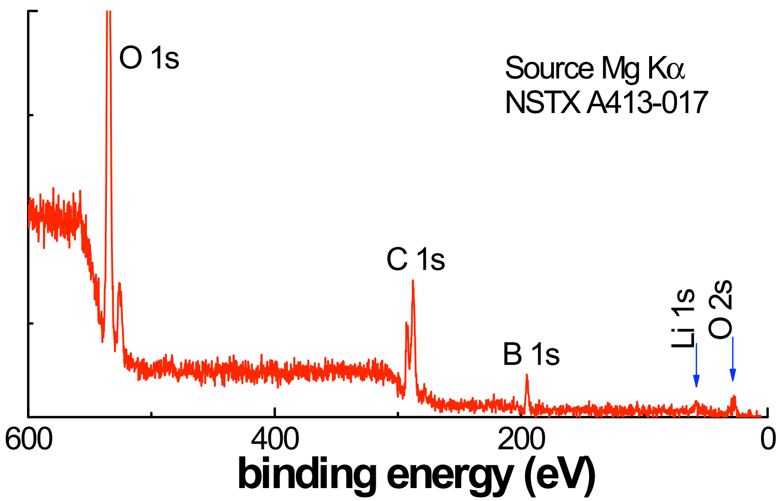
- *In-situ* surface characterization *during* particle irradiation can elucidate on relevant mechanisms of irradiation-driven self-organization
  - Well-diagnosed off-line facilities that properly simulate conditions in tokamak edge plasma-material interface is critical
- In-situ particle-surface interaction data coupled to computational modeling data suggest the potential of lithiated graphite as a legitimate candidate plasma-facing surface
- Critical questions still remain with the use of lithium-based surfaces
  - How is the dynamic evolving 10-100 nm lithium-based surface correlate with control of plasma behavior
  - Role of surface chemistry and morphology on hydrogen control
  - Need for additional lab test stand efforts and new additional surface science experts (e.g. Prof. Bruce Koel at Princeton University)

Extra Slides

NSTX tiles showed presence of Li_2CO_3





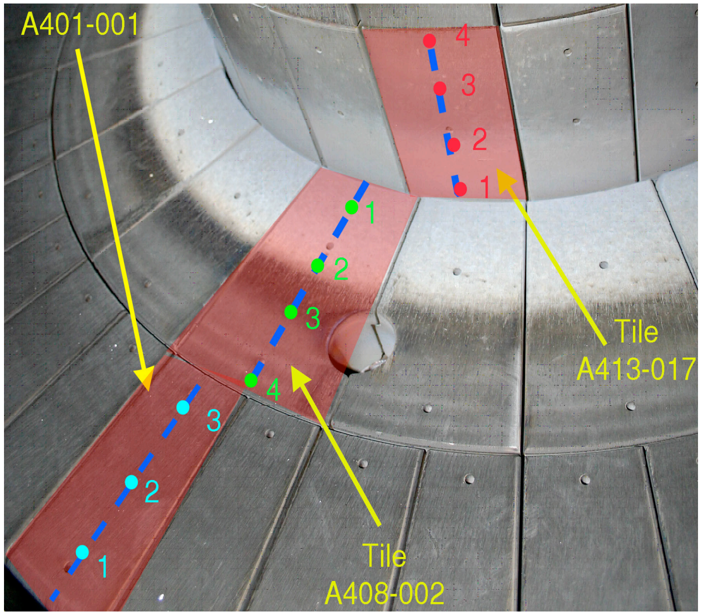


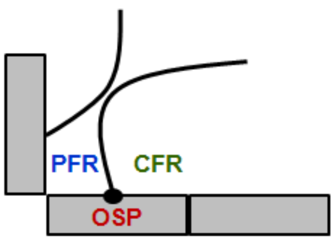
XPS spectra of NSTX tiles show presence of carbonate

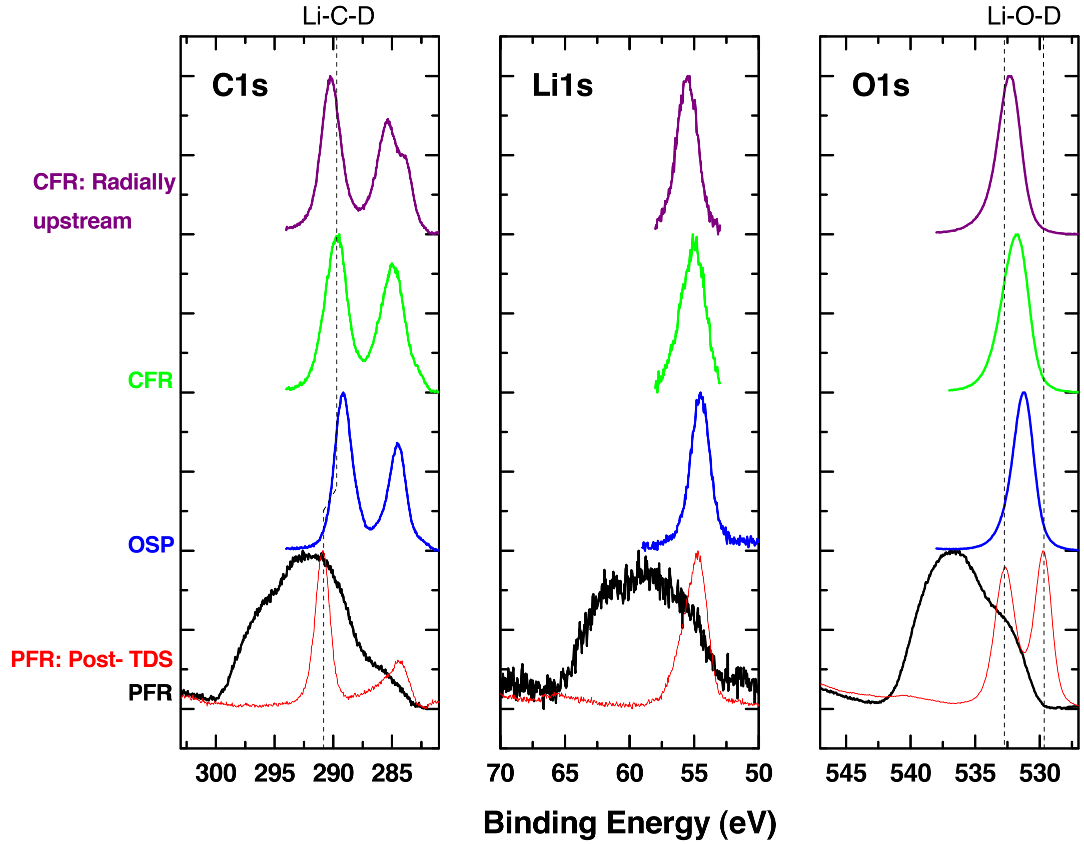
J.P. Allain et al. J. Nucl. Mater. 390-391 (2009) 942.

Typical XPS spectrum from a NSTX tile

Surface chemistry radially in NSTX





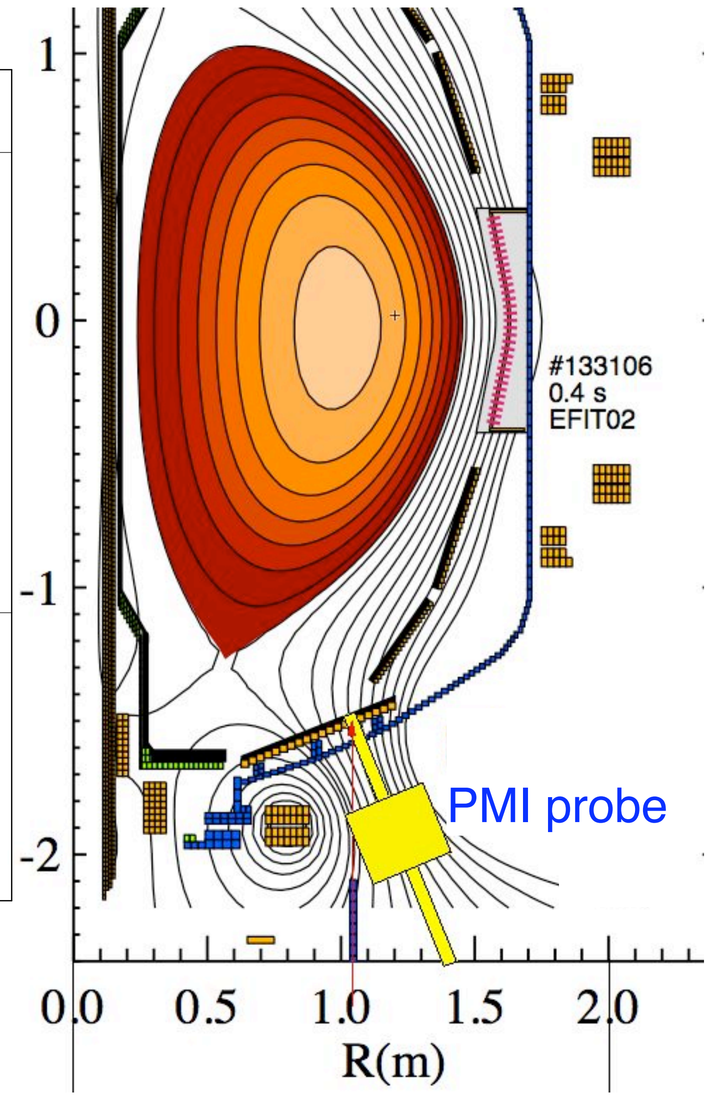


- Post-mortem analysis of core samples extracted from NSTX tiles elucidate on effect of lithium coatings on D recycling

Gas balance retention measurements correlate with in-situ PMI surface science measurements

DOE JRT milestone, PAC25-10,11

GAS BALANCE:	SURFACE ANALYSIS
Retention higher with Li, difference increases with Li concentration	X-ray Photo-electron Spectroscopy shows D atoms are weakly bound in regions near lithium atoms bound to either oxygen or the carbon matrix. Chemical bonding changes with Li concentration.
Additional D retained with Li is released promptly after discharge	Weak D bonding with Li conditioning observed in Thermal Desorption Spectroscopy.



C.H. Skinner and J.P. Allain 2009