

Lithium's Effects on the Chemical Sputtering of Carbon

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Background

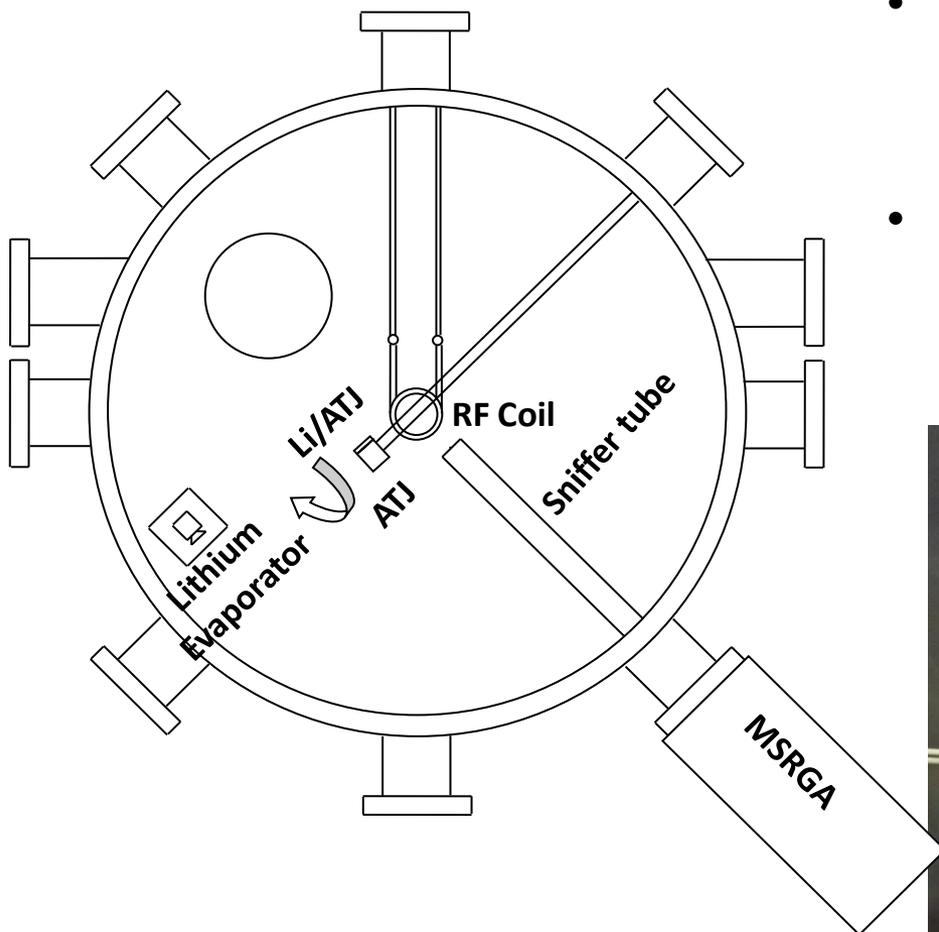
- Lithium evaporation treatments for ATJ graphite tiles of divertor regions in NSTX have shown a number of dramatic improvements in plasma performance
 - confinement time
 - low carbon impurity rate
 - low-hydrogen recycling
 - suppressing ELMs
- ATJ graphite tiles used in NSTX, how does lithium interact with ATJ graphite?
 - Previous studies have shown that Li intercalates into the graphite bulk region and might form a very thin layer on the surface.
 - Predicted that because of high diffusivity of Li in the graphite, Li atoms in the graphite bulk region segregate to the surface quickly forming a new layer after Li layer is sputtered off.
- To understand such complex interactions in Li-C system and in support of NSTX mission, laboratory studies are conducted in the Ion Surface Inter-Action (IIAX) facility at the University of Illinois.

Ion surface Inter-Action eXperiment (IIAX)

- To understand the complex system of lithiated with ATJ graphite, chemical sputtering measurements of plain and lithiated ATJ graphite
- IIAX-upgrade
 - RF plasma facility with a
 - differentially pumped Magnetic Sector Residual Gas Analyzer (MSRGA).
 - Everything is situated within one chamber – no need for breaking vacuum.
- Chemical sputtering of Graphite is dependent on the ion energy and substrate temperature,
 - hence the total effect of treating graphite with lithium in a hydrogen plasma is investigated in terms of different temperatures and bias voltages.
- The dominant chemical erosion product is CH_4
 - Consider only single carbon chains as it more likely than a double or triple carbon chain.
- Initial experiments show that lithium treatments have suppressed the chemical sputtering of ATJ Graphite.
- Also the wetting properties of Li on B-Mo have been carried out.
 - Boronized - moly tile from C-mod

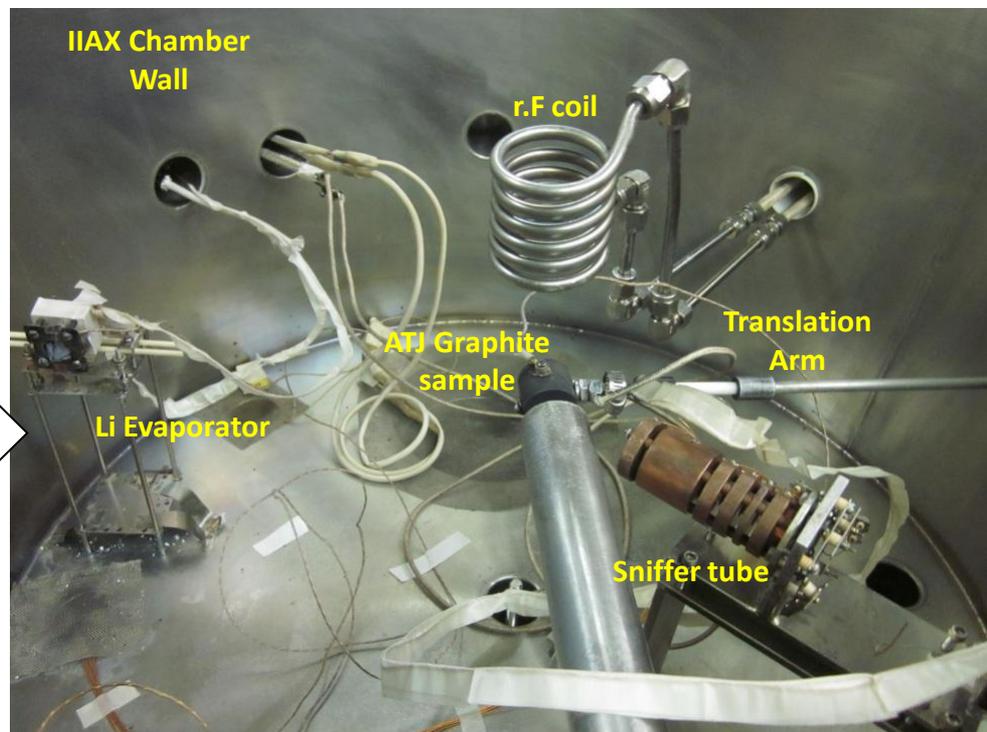
IIAX – cont.

- Experimental set-up consists of a cylindrical rotatable ATJ Graphite target and a lithium evaporator for in-situ evaporation of lithium.
- For this purpose, lithium is evaporated in-situ onto ATJ graphite and chemically sputtered species in hydrogen plasma is measured using MSRGA.



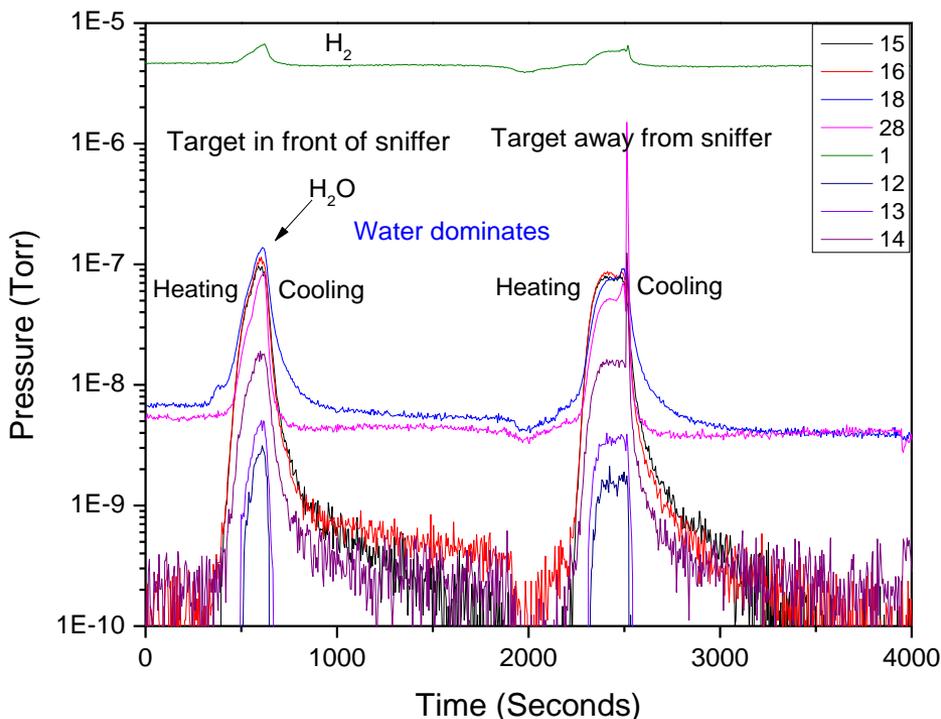
Above: Schematic of the IIAX-upgrade showing the relative position of the different components.

Right: Photo of the components inside the IIAX-upgrade chamber.



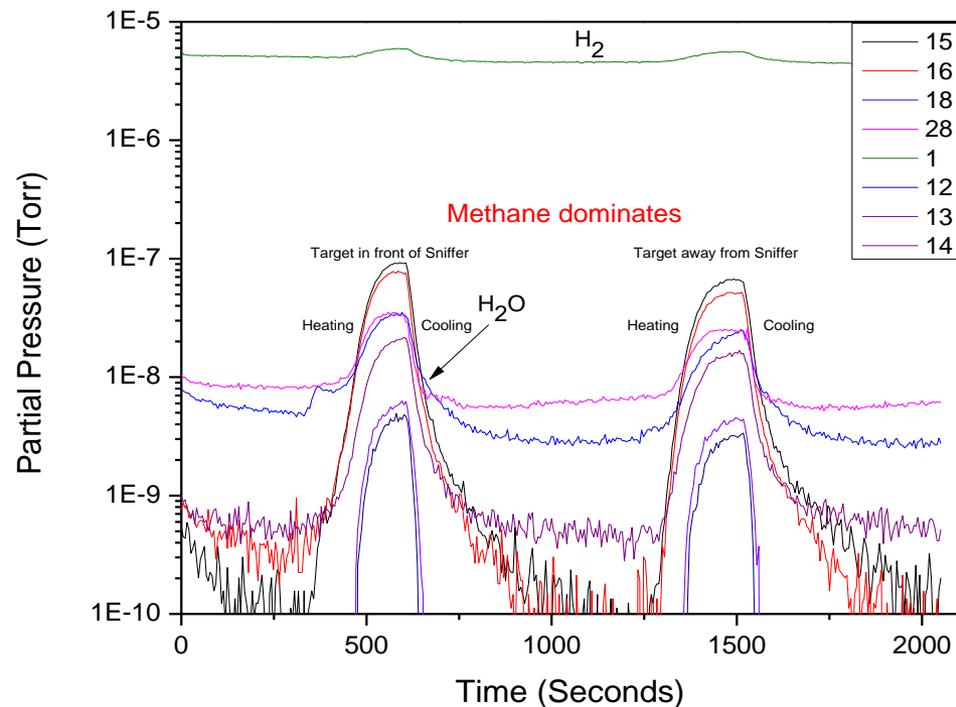
Importance of Baking Target Before Experiments

- Water from target dominated the methane signature peaks.
- Target was baked at $\sim 225^\circ\text{C}$ for 4 hours
- Water peak clearly went down and methane peaks are the dominant ones after baking.



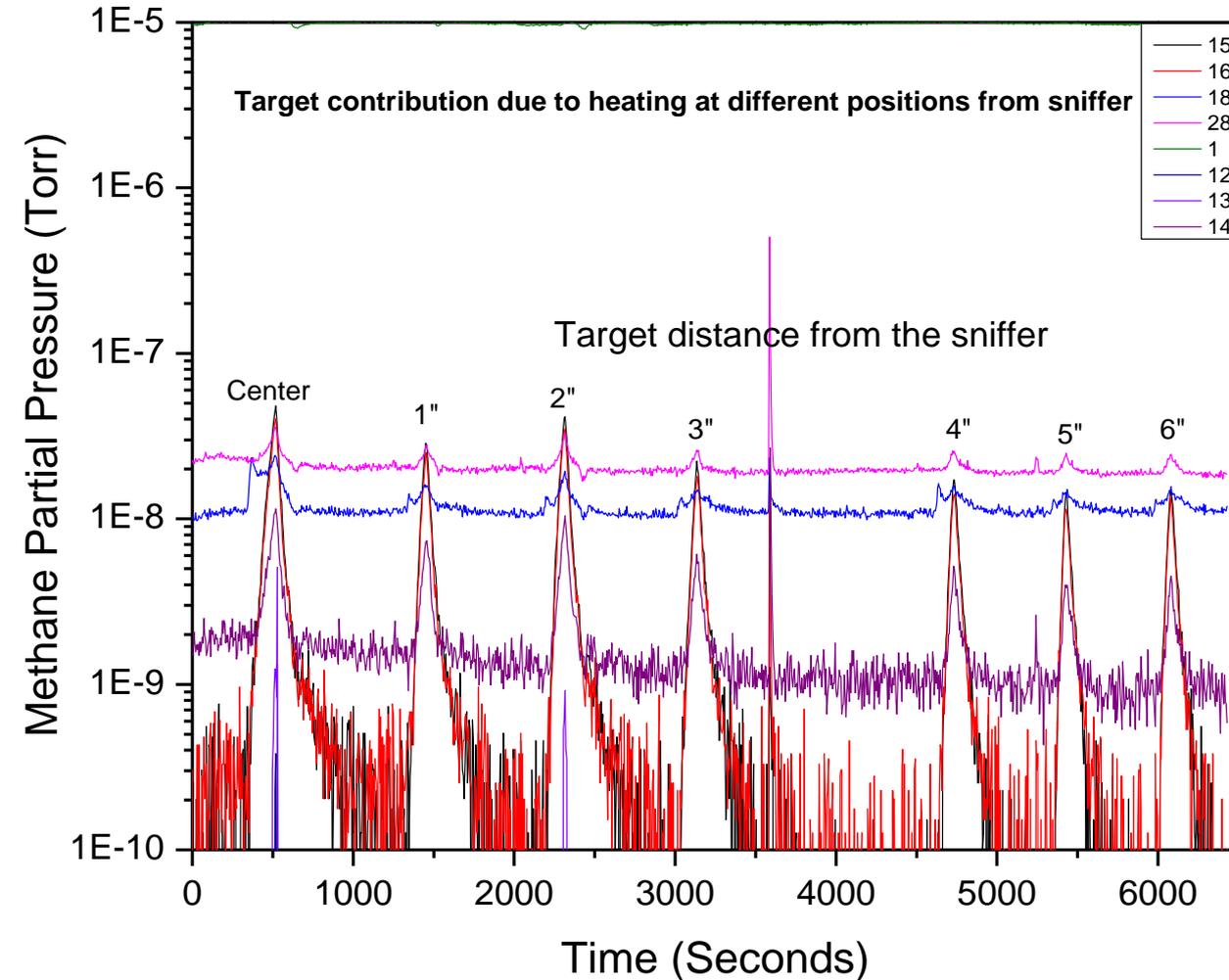
Above: Before baking. The water vapour peak dominates over the methane. This is seen both for when the target is at the sniffer and away from the sniffer

Right: After baking. Water vapour peak clearly goes down. This is seen both for the target in front of the sniffer and away from the sniffer.



Validation of signal origin

- Target was heated to 200° C and allowed to cool at different locations from the sniffer tube to understand the target contribution.
- It can be clearly seen that methane related peaks go down as we go away from the target clearly indicating target contribution.

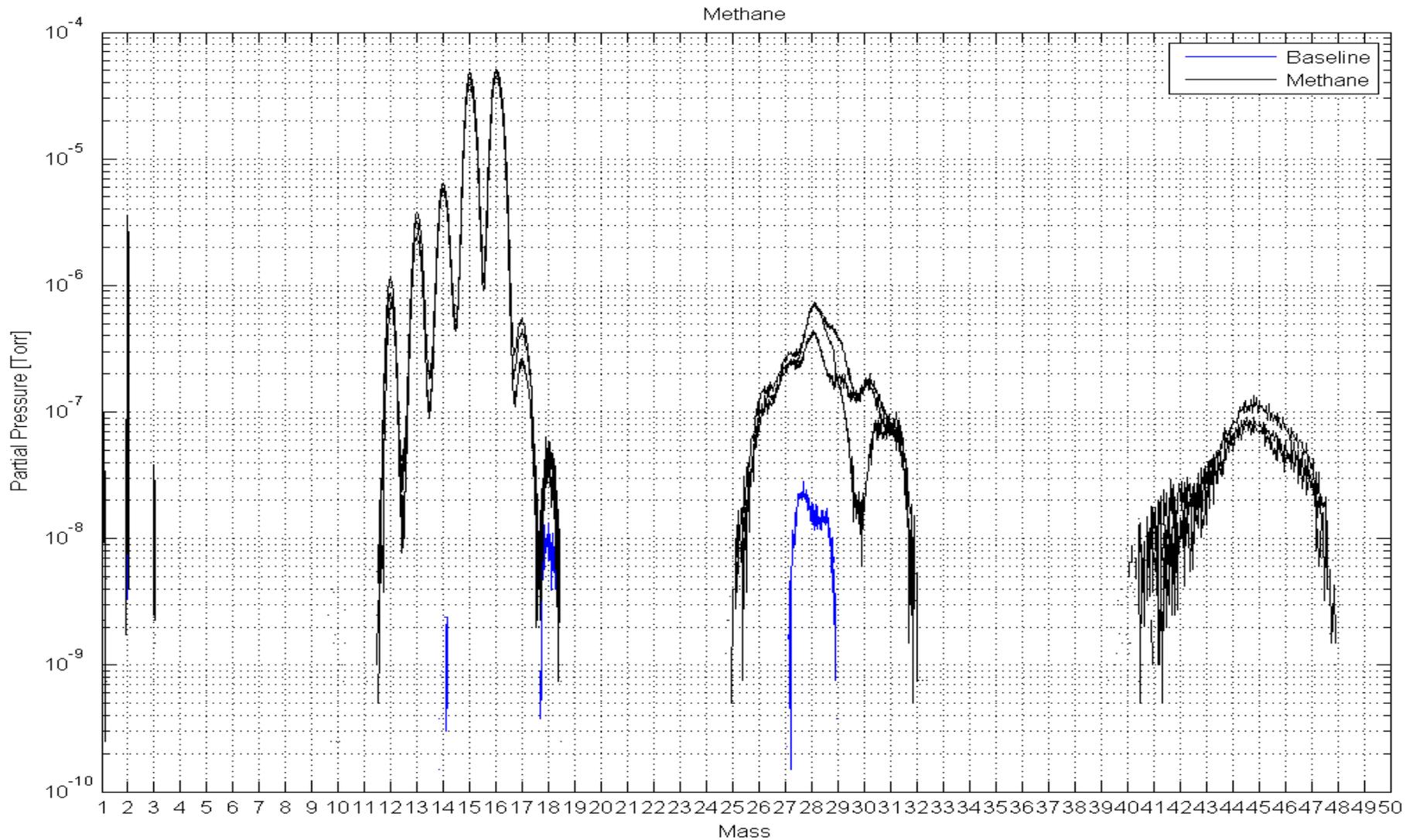


Left: Importance to determine the target contribution. The ATJ target is initially situated at the sniffer and gradually moved away. The water vapor peak stays the same while the methane peak goes down.

Results – Cracking Pattern Analysis

- Cracking patterns needed to be determined
 - Specific amounts of gas were flowed into IIAX using a mass flow controller
 - Magnetic sector RGA used to record the cracking ratios
- A matrix is formed from the cracking pattern ratios to determine the partial pressures for each species.
- Multiple experiments are performed to reduce errors
 - Standard deviations for each of the component coefficients were established.
 - Used in error propagation.
- Cracking patterns for:
 - Methane, water vapor, hydrogen, oxygen, argon, nitrogen and carbon dioxide

Cracking Pattern Analysis – Example



Matrix Analysis and Uncertainty Estimate

Mass Number	Possible Species
12	C ⁺
13	CH ⁺
14	N ⁺⁺ , CH ₂ ⁺
15	CH ₃ ⁺
16	CH ₄ ⁺ , O ₂ ⁺⁺ , O ⁺
28	N ₂ ⁺⁺ , CO ⁺
44	CO ₂ ⁺

Mass	CH ₄	H ₂ O	N ₂	O ₂	CO ₂	Ar	H ₂
1	0.18248	0.48632	0	0	0	0	0.087167
2	0.18221	0.48632	0	0	0	0	0.45642
3	0.007225						0.45642
12	0.013178	0	0	0	0.15221	0	0
13	0.025048	0	0	0	0	0	0
14	0.18277	0	0.13309	0	0	0	0
15	0.20354	0	0	0	0	0	0
16	0.20355	0	0	0.22964	0.24607	0	0
17	0	0.013678	0	0	0	0	0
18	0	0.013678	0	0	0	0	0
20	0	0	0	0	0	0.37948	0
22	0	0	0	0	0.017993	0	0
28	0	0	0.86691	0	0.092906	0	0
32	0	0	0	0.77036	0	0	0
40	0	0	0	0	0	0.62052	0
44	0	0	0	0	0.49082	0	0

- Known amounts of gases had their cracking ratios recorded by a Magnetic sector RGA. These were recorded multiple times and an uncertainty found for each coefficient. **For instance, $a_{15} = 0.204 \pm 0.0161$**
- The matrix formed from these cracking pattern was used to find the actual partial pressures of the species considered in the analysis.

Results – Data Analysis

- The RGA signals at specific masses from the wall case is subtracted from the target + wall cases. The desired partial pressures of the interested species can be calculated from the following equation. C is cracking pattern. S is the signals at desired masses and p is the partial pressures of the desired species.

$$C * p = S$$
$$p = C^{-1} * S$$

- The specific signals were multiplied with the inverse of the corresponding cracking pattern matrix to obtain the individual partial pressures.
- Five linear equations were used in this analysis.

$$S_{15} = 0.20354 P_{CH_4}$$

$$S_{16} = 0.20355 P_{CH_4} + 0.22964 P_{O_2} + 0.24607 P_{CO_2}$$

$$S_{18} = 0.006235 P_{H_2O}$$

$$S_{28} = 0.86691 P_{N_2} + 0.092906 P_{CO_2}$$

$$S_{44} = 0.49082 P_{CO_2}$$

Error Propagation

- The error in calculating the partial pressures of the species is determined by the classical McClintock Formula.
- An example the equation for calculating methane is given by

$$P_{CH_4} = S_{15} / a_{15}$$

$$\Delta P_{CH_4} = \sqrt{\left(\left(\frac{1}{a_{15}}\right)^2 (\Delta S_{15})^2 + \left(\frac{S_{15}}{a_{15}^2}\right)^2 (\Delta a_{15})^2\right)}$$

ATJ Case: $T = 180^\circ \text{ C}$, $V_B = -1000 \text{ V}$, $P_{CH_4} = 14.6 \text{ E-09 Torr}$

$$\Delta P_{CH_4} = \sqrt{\left(\left(\frac{1}{0.20354}\right)^2 (3.71\text{E-}10)^2 + \left(\frac{2.97\text{E-}09}{0.20354^2}\right)^2 (0.016085)^2\right)} = 2.13\text{E-}09 \text{ Torr}$$

Li ATJ Case: $T = 180^\circ \text{ C}$, $V_B = -1000 \text{ V}$, $P_{CH_4} = 9.04 \text{ E-09 Torr}$

$$\Delta P_{CH_4} = \sqrt{\left(\left(\frac{1}{0.20354}\right)^2 (3.71\text{E-}10)^2 + \left(\frac{1.84\text{E-}09}{0.20354^2}\right)^2 (0.016085)^2\right)} = 1.94\text{E-}09 \text{ Torr}$$

S_{15} is the mean value of signal at mass 15.

P_{CH_4} is the partial pressure of methane
 a_{15} is the mean cracking pattern ratio of methane at mass 15 which is obtained from the cracking pattern analysis.

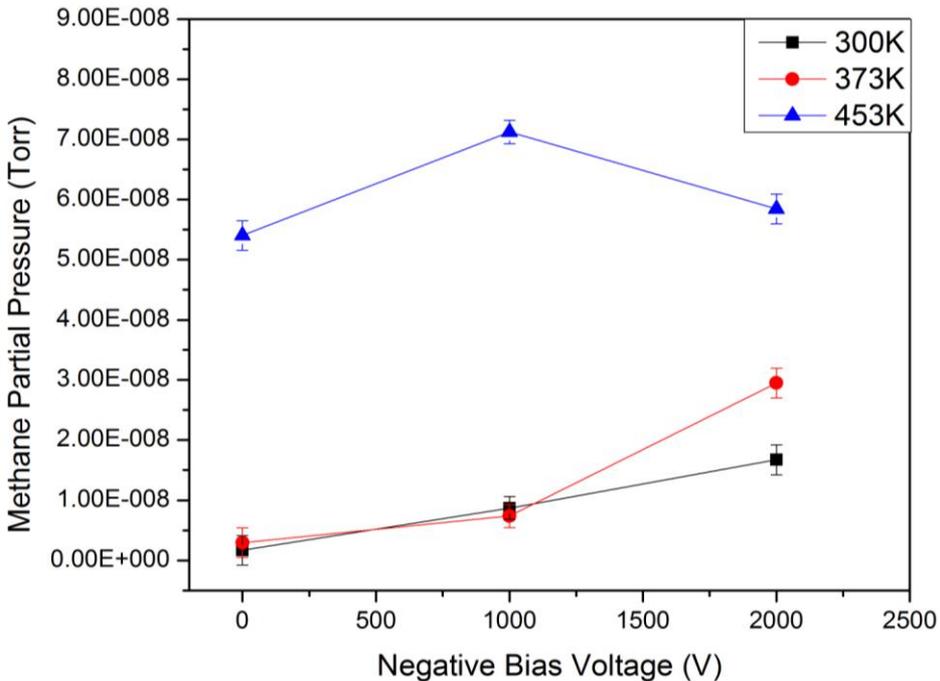
ΔS_{15} represents the standard deviation in of signal at mass 15.

Δa_{15} is the standard deviation of cracking pattern ratio of methane at mass 15.

ΔP_{CH_4} is the absolute error in calculating methane.

Signal at peak 15 was used in determining partial pressure of methane because of its high signal intensity at that mass which leads to lower error value.

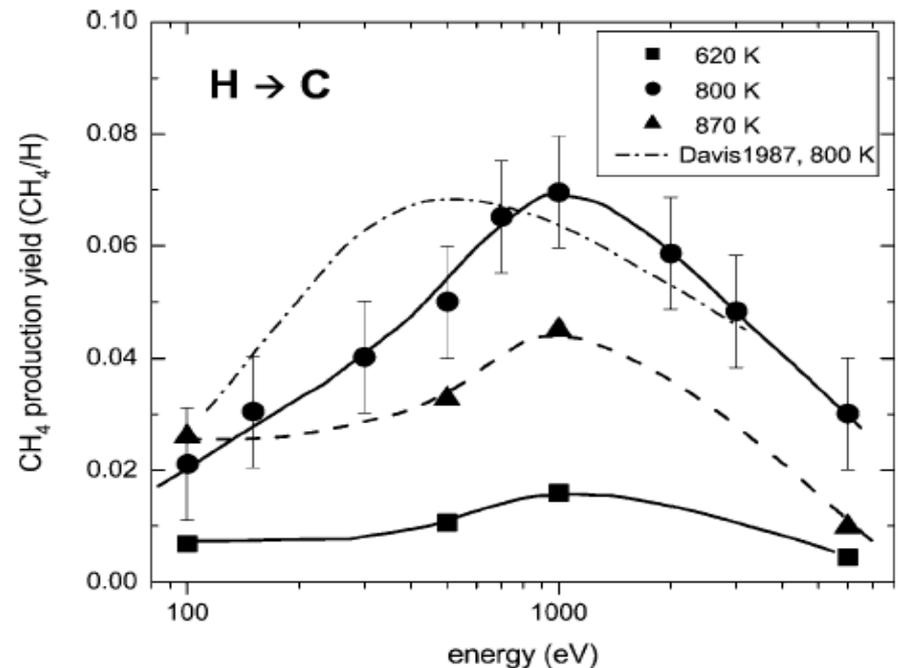
Results – Chemical sputtering during H plasma discharge



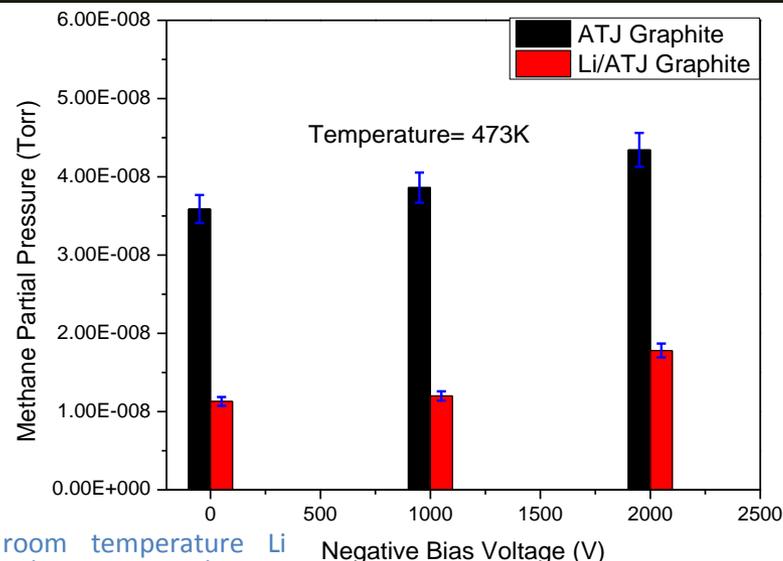
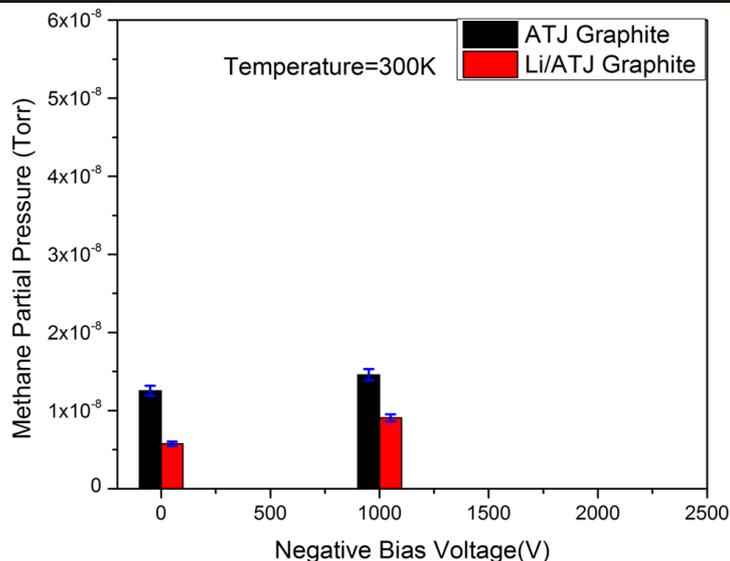
Left: Partial pressures of methane from ATJ target as a function of Hydrogen ion energy at different sample temperatures in pure non-Li environment.

Right: Methane production as a function of ion energy for hydrogen ions impinging on pyrolytic graphite measured at different sample temperatures¹.

1. **Wolfgang Jacob and Joachim Roth**
JR. Behrisch, W. Eckstein (Eds.): Sputtering by Particle Bombardment, Topics Appl. Physics 110, 329–400 (2007) Springer-Verlag Berlin Heidelberg 2007



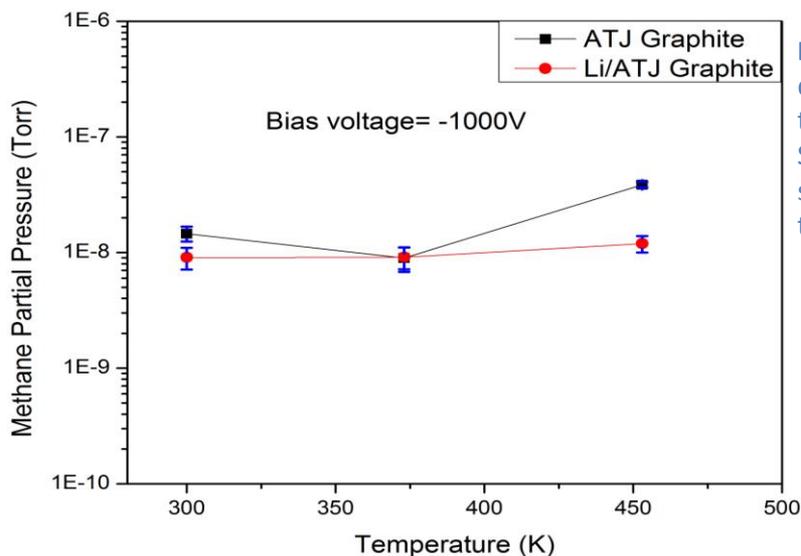
Results – ATJ vs. Li/ATJ Graphite



Above left: At room temperature Li suppresses Chemical sputtering, but at higher values of bias the effect is less pronounced.

Left: Chemical sputtering has a strong dependence on temperature. High temperature enhances Chemical Sputtering. We can see the chemical suppression effect at higher temperatures

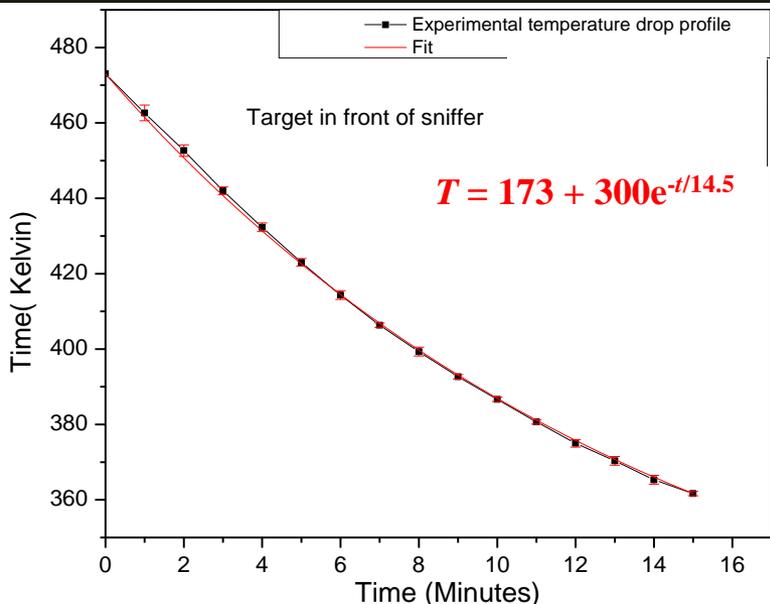
Above: Chemical sputtering and suppression effect can be clearly observed at 473 K



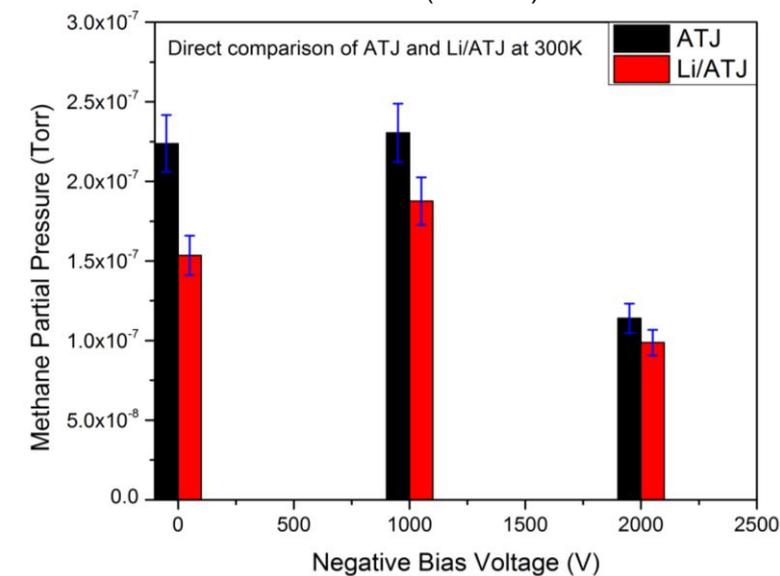
Bias Voltage (V)	Methane Partial Pressure (Torr)		Suppression
	ATJ	Li/ATJ	
0	3.6E-08	1.1E-08	68%
1000	3.9E-08	1.2E-08	69%
2000	4.3E-08	1.8E-08	59%

150 nm, Target Temperature: $T = 453$ K

Results – Heating and 5 min Li deposition



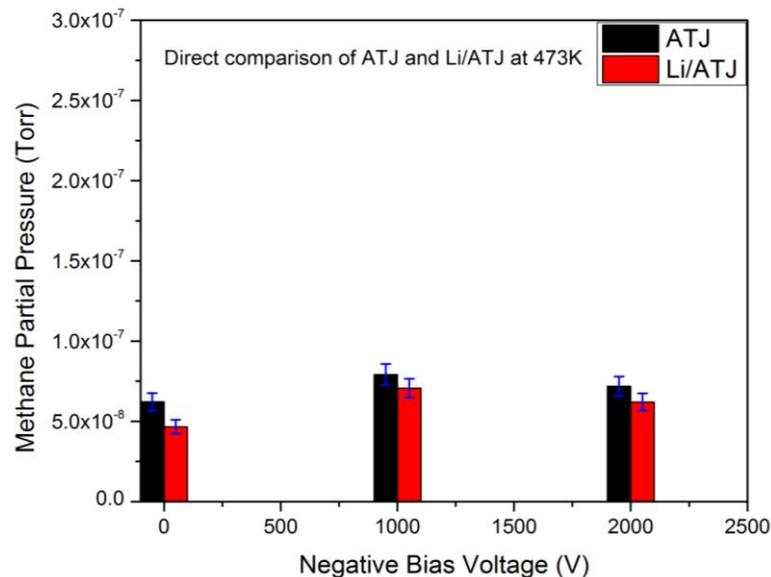
- 150 nm Li coating.
 - DEKTAK Profilometer
- Previous measurements, heating was performed through a heating lamp.
- Upgrade has joule heating of the target by passing a current through the target.
- Lithium suppression is still clearly seen
 - However, the amount of methane before lithization is lower at higher temperatures



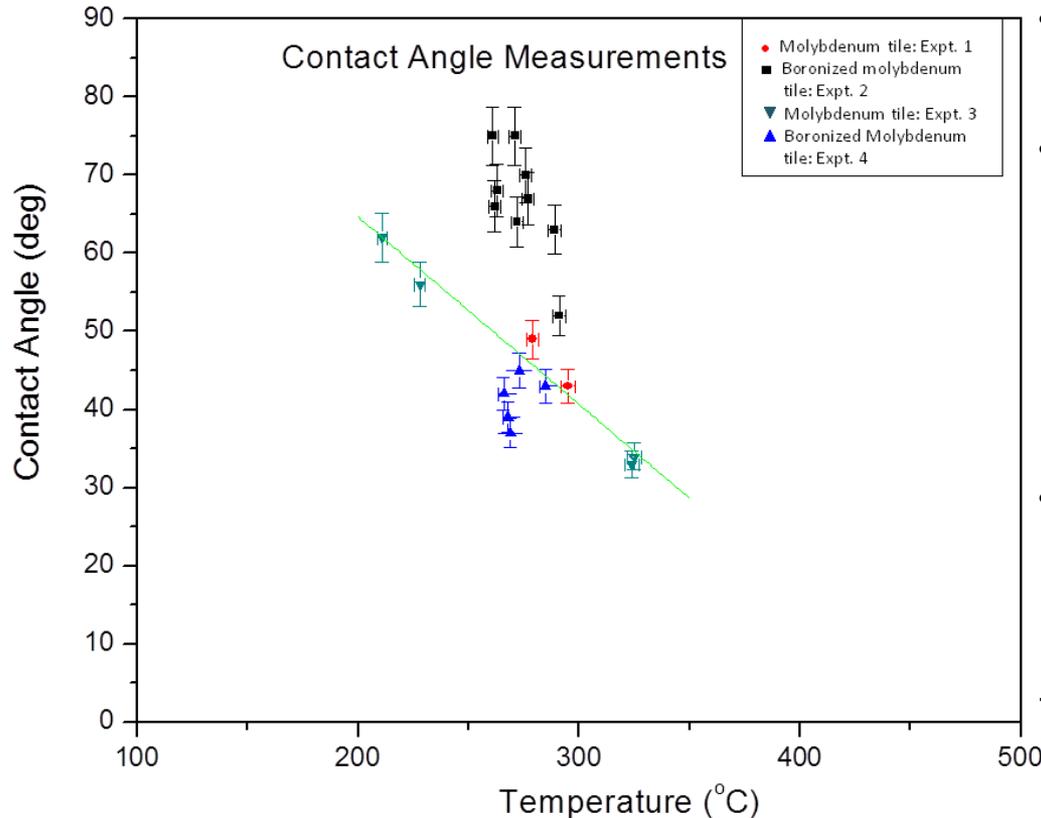
Top left: The cooling of the target after heating to 473 K.

Left: Methane suppression at 300 K due to Li/ATJ at different bias.

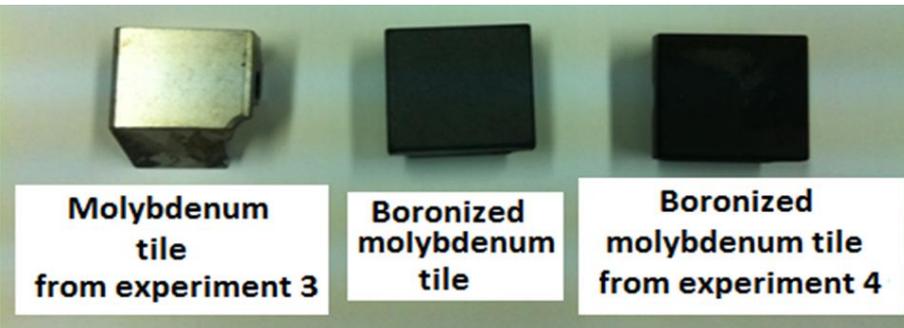
Right: Methane suppression at 473 K due to Li/ATJ at different bias.



Lithiated Boronized Molybdenum Tiles



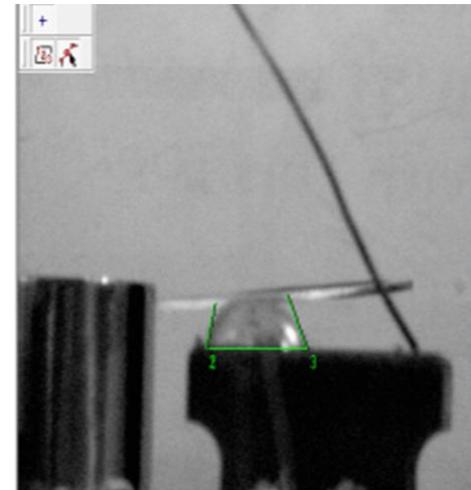
- Boronized tiles obtained from C-mod
 - Via Harold Barnard.
 - Porous Boronization on the surface
- Lithium was melted onto the surface and contact angle measured
 - Plain TZM
 - Contact angle $\theta = 65^\circ - 35^\circ$ over a 125° C range
 - Boronized TZM
 - Contact angle $\theta = 70^\circ$
 - Repeat Li on a previous Li B-TZM tile
 - Contact angle $\theta = 40^\circ$ at 275° C
 - Similar to a plain TZM tile.
- It was observed that after Li was melted on the tile the surface was change dramatically, a very smooth black surface.
 - When Li measurements repeated on the surface, wetting was dramatically improved.
- Is there formation on the surface of some new Li-B compound?



Above: Plots of the surface angle measurements at different temperatures for Mo, B-Mo and Li-B-Mo

Left: Three tiles showing the effects of Li on a boronized surface. Far left is a plain moly tile, middle is a boronized moly tile and right is a boronized moly tile after having Li exposed to it.

Right: Image from contact angle software of melted Li on a tile taken with a CCD camera.



Conclusions

- A simple mathematical approach that includes only single-carbon hydrocarbons is presented here. The species that were included in the analysis are CH_4 , H_2O , N_2 , O_2 and CO_2 .
- The ability to simply rotate the target in front of the “sniffer” tube from a bare graphite side to a lithium-coated graphite side allows direct comparison with the same background. In-situ lithium evaporation, a rf plasma source and a biasable target are critical experimental components.
- Lithium deposition on ATJ Graphite shows the suppression of methane from the initial set of experiments.
- The chemical erosion studies conducted in a plasma chamber, as opposed to beam experiments, provide a better understanding of the phenomenon taking place in tokamaks.

Future Work

- More experiments will be done to check for repeatability.
- Chemical sputtering measurements as a function of different lithium thickness are in progress.
- Experiments are planned to be carried out in deuterium environment as well as in hydrogen.
- Oxygen plasma cleaning will be carried out before each experiment to suppress the background contribution.
- Deuterium uptake of lithium on molybdenum and boronized molybdenum will be studied in the future.
- Erosion measurements of lithium on mixed materials (Li/Mo, Li/B/Mo) and ionization fraction measurements of the sputtered lithium in the IIAX facility is planned.