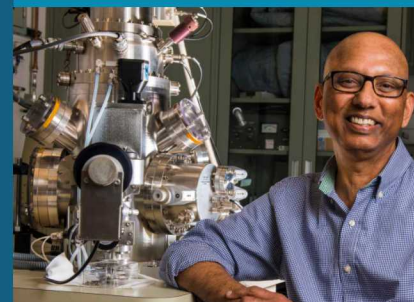


# Formation Mechanisms of in situ generated DLC-Like Tribofilms



**John F. Curry<sup>1</sup>**, Morgan Jones<sup>1</sup>, Tomas F. Babuska<sup>1,2</sup>,  
Brendan Nation<sup>1</sup>, Brandon A. Krick<sup>2</sup>, Michael T. Dugger<sup>1</sup>,  
Michael Chandross<sup>1</sup>, Nic Argibay<sup>1</sup>

<sup>1</sup>Material, Physical, and Chemical Sciences Center  
Sandia National Laboratories  
Albuquerque, NM

<sup>2</sup>Mechanical Engineering & Mechanics  
Lehigh University  
Bethlehem, PA



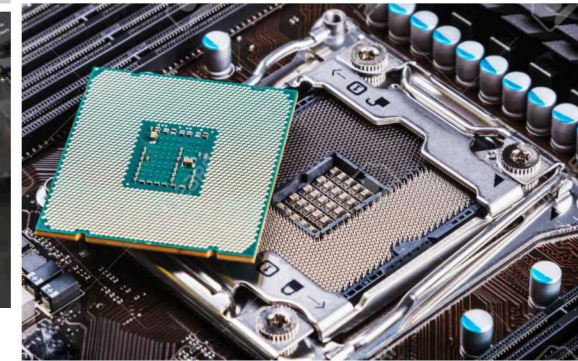
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

# Motivation for Metals Tribology Research

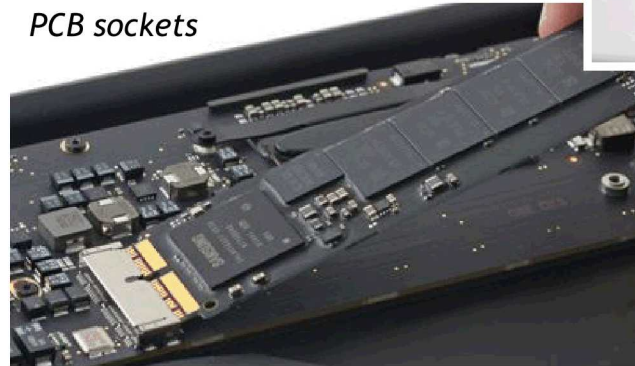
cell phones



CPU sockets



PCB sockets



wind turbine slip-rings  
(sensors and blade pitch motors)



**Estimated 150 Metric Tons (\$6.9B) of Au  
used in Electrical Contacts per Year:**

*Refs: Gold Survey, Gold Fields Mineral Survey Ltd, 2011  
Gold Bulletin 2010, Vol. 43-3, C. Hagelüken and C.W. Corti,  
Gold Bulletin 1986, Vol. 19-3, T.D. Cooke*

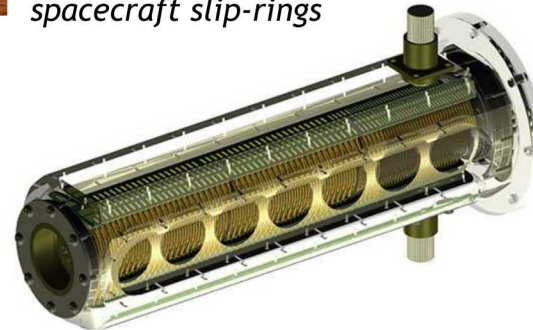
45 connectors



EV charging

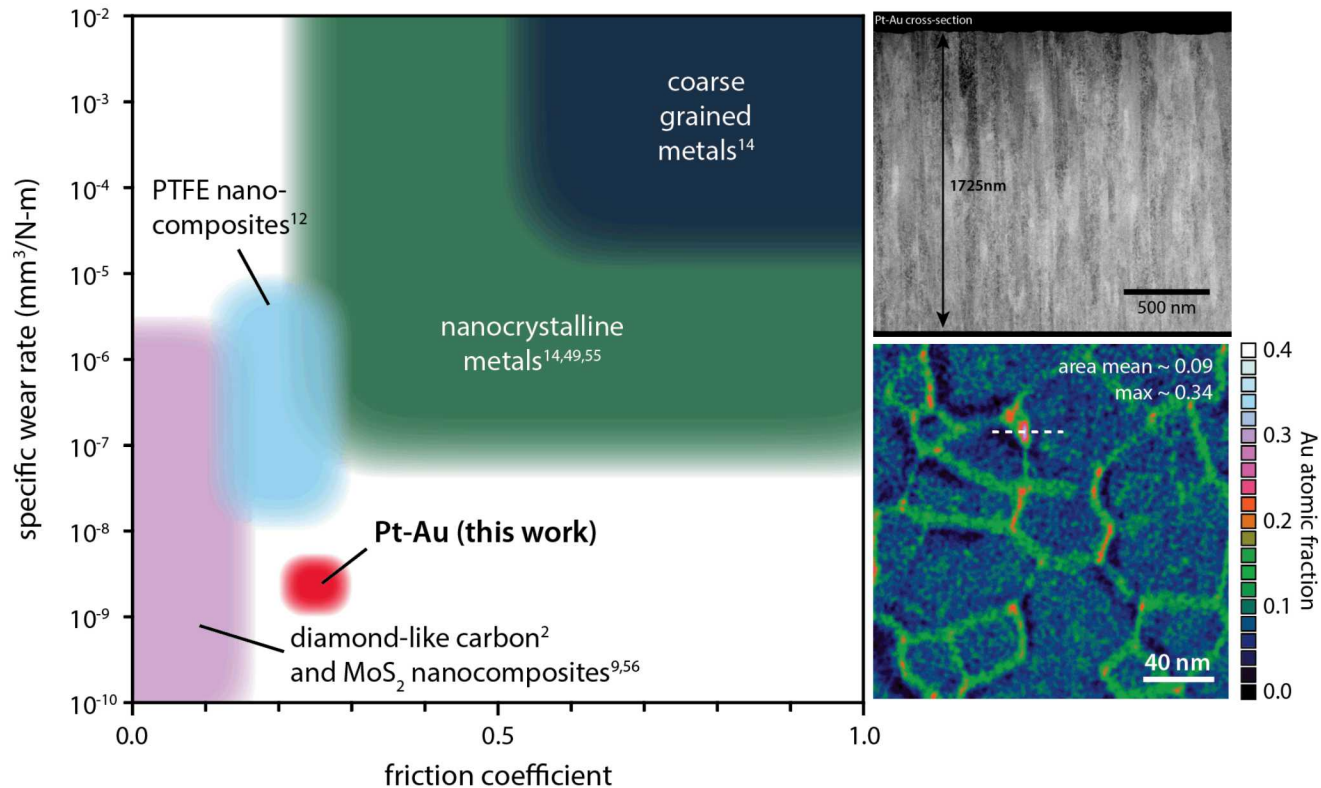


spacecraft slip-rings



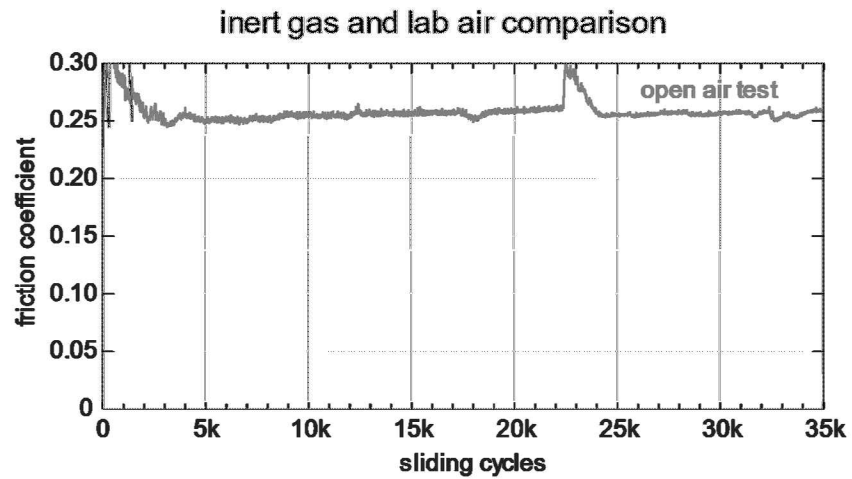


## Discovery: Ultra-Low Wear Pt-Au



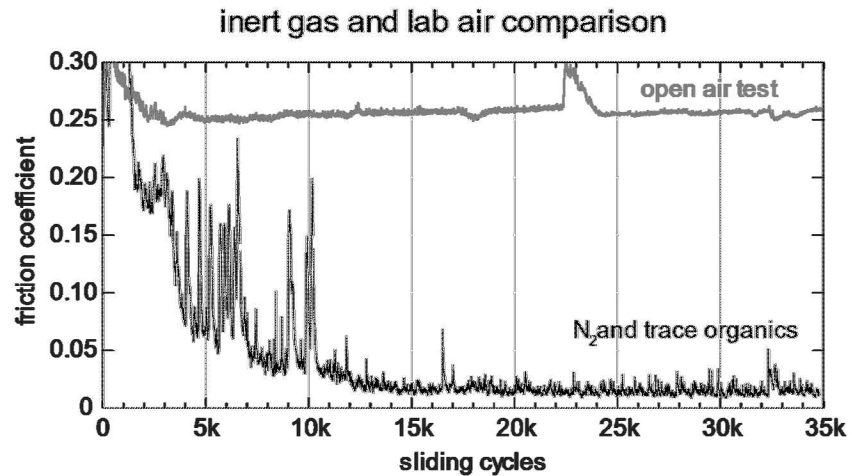
- Development of stable, ultra-nanocrystalline alloys with high fatigue resistance, helping shut down delamination driven wear

## 4 Environmental Sensitivity



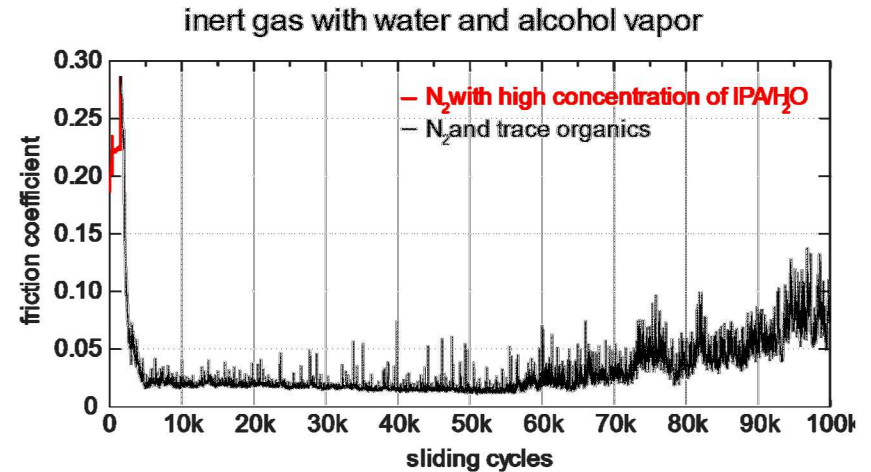
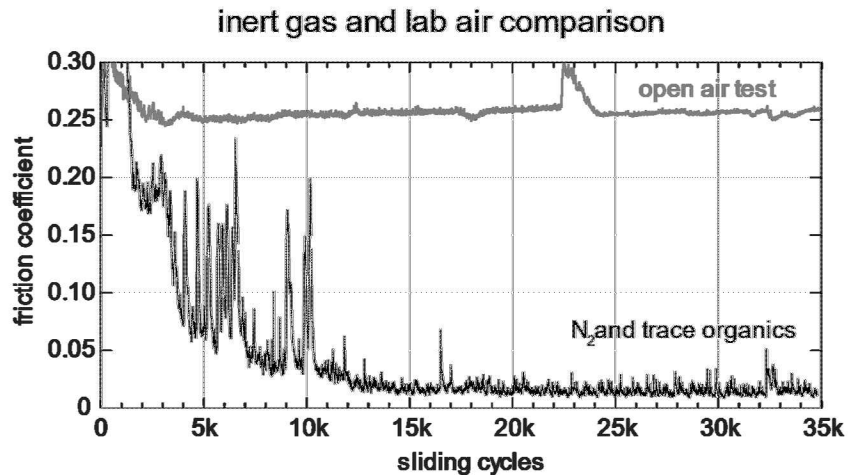
- Great friction performance in lab air ( $\mu \sim 0.25$ )...

## 5 Environmental Sensitivity



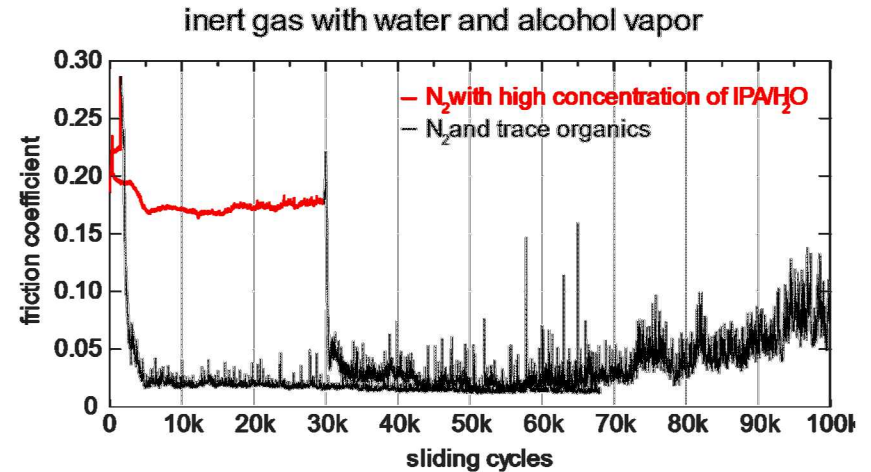
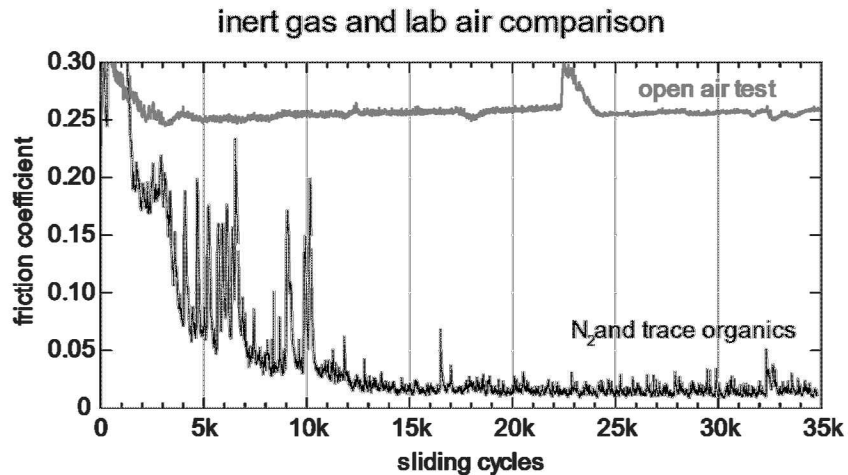
- Great friction performance in lab air ( $\mu \sim 0.25$ )...
- Testing in inert environments lowers friction?

## 6 Environmental Sensitivity

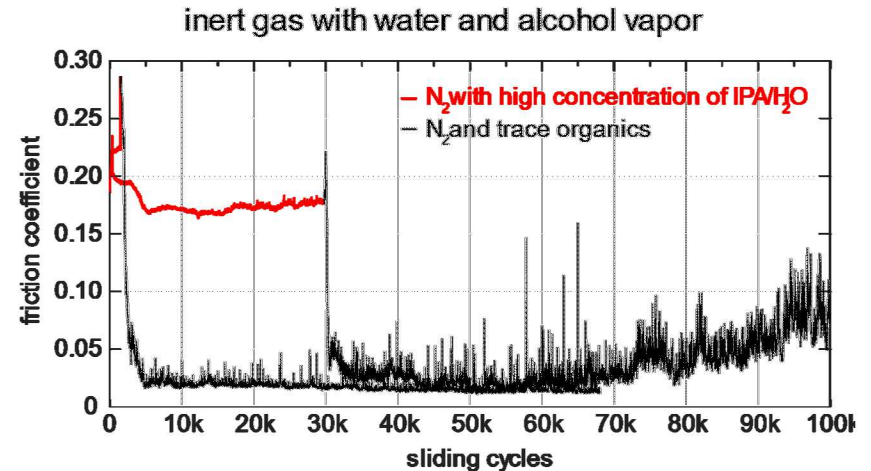
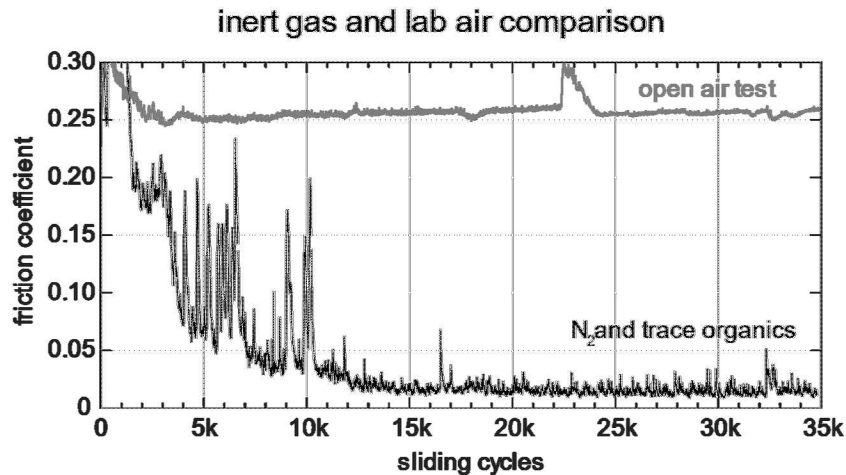


- Great friction performance in lab air ( $\mu \sim 0.25$ )...
- Testing in inert environments lowers friction?
- Priming the enclosure with hydrated IPA accelerates drop...

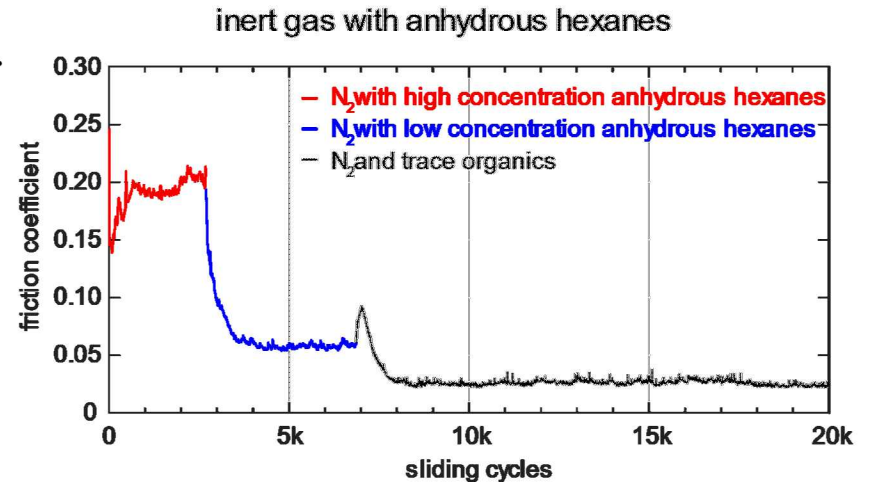
## 7 Environmental Sensitivity



- Great friction performance in lab air ( $\mu \sim 0.25$ )...
- Testing in inert environments lowers friction?
- Priming the enclosure with hydrated IPA accelerates drop... and prolongs it

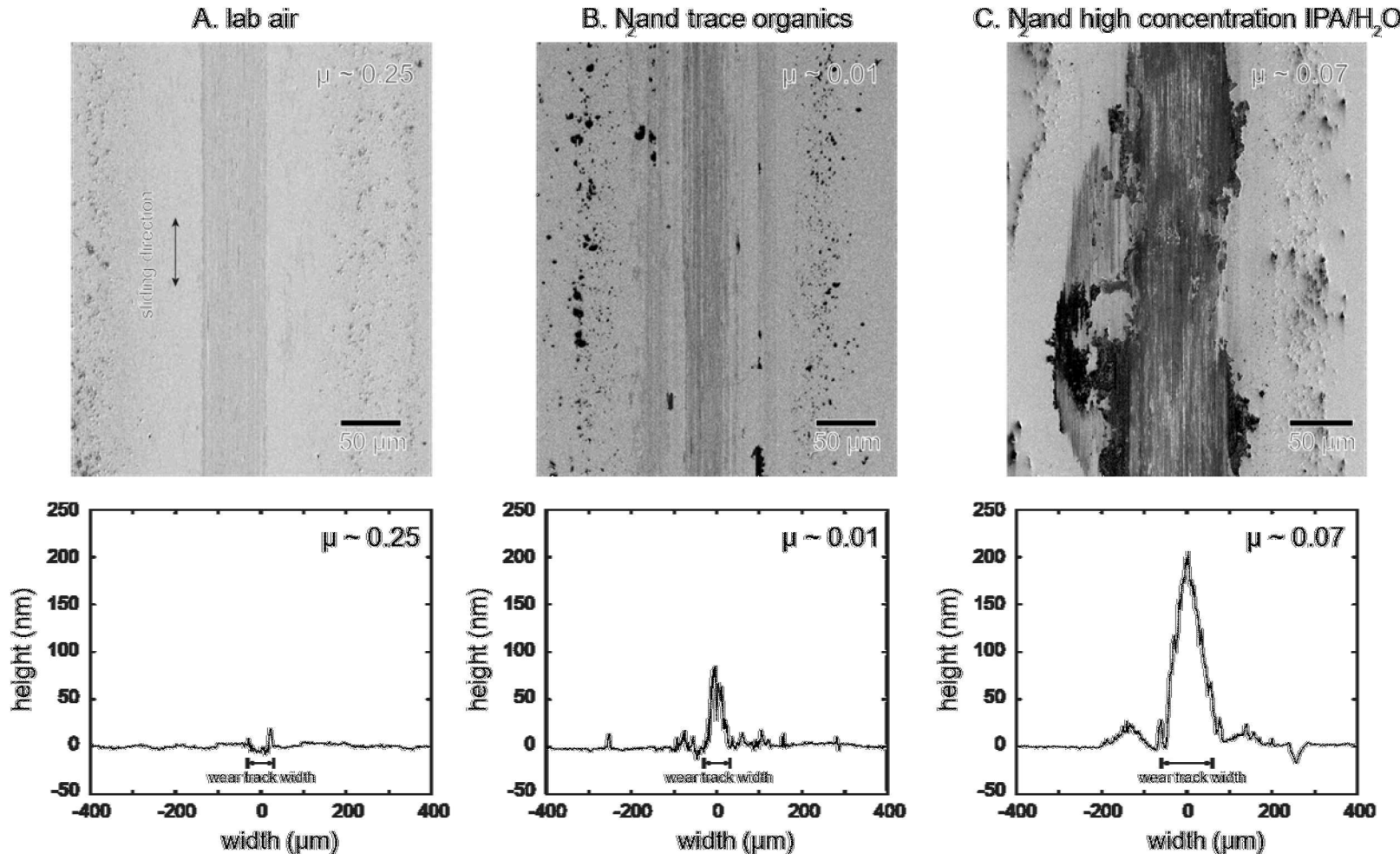


- Great friction performance in lab air ( $\mu \sim 0.25$ )...
- Testing in inert environments lowers friction?
- Priming the enclosure with hydrated IPA accelerates drop... and prolongs it
- Any amount of anhydrous hexanes increased friction, with higher/lower friction at higher/lower concentrations
- Unclear what role water/oxygen play





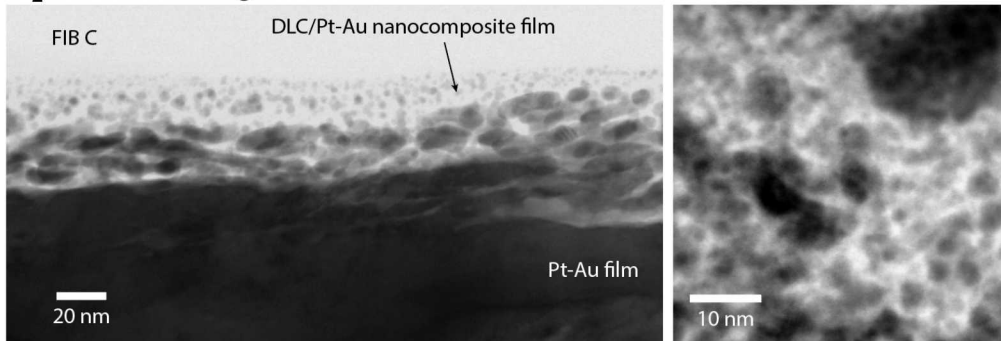
# Accumulation is Key



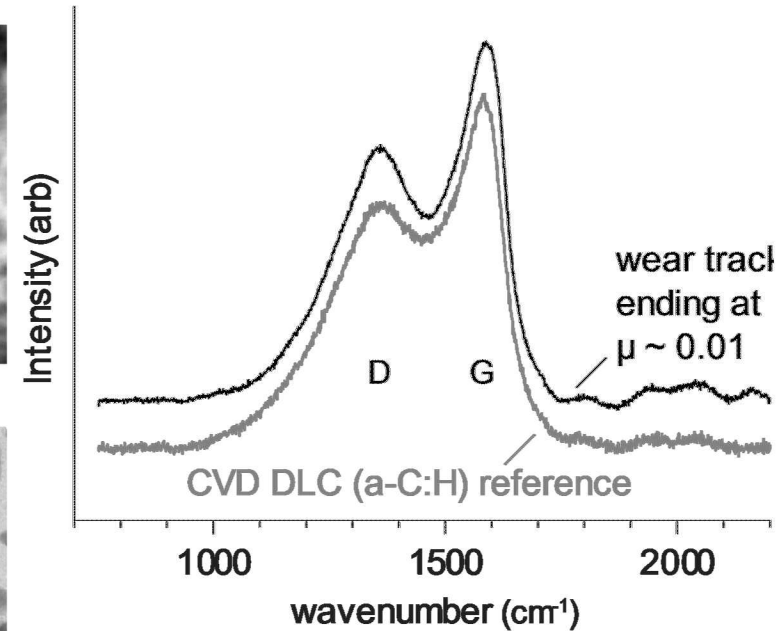
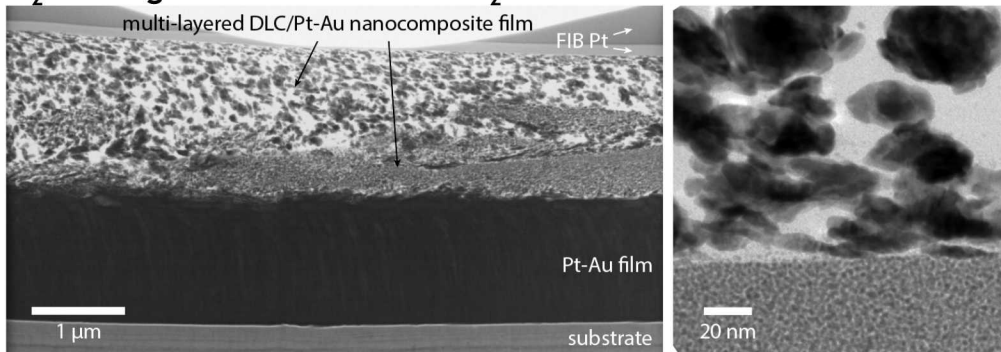
- Concentration also affects film growth in wear scar
- Highest concentrations produces thick films unable to reach low friction state

# Diamond-like carbon nanocomposite

## N<sub>2</sub> and trace organics



## N<sub>2</sub> and high concentration IPA/H<sub>2</sub>O



- Films are actually composite of Pt-Au nanoparticles and DLC, confirmed by TEM & Raman
- High concentrations exhibit phases of larger, less mixed/layered particles, possibly limiting mixing & Pt interaction at surface

# Literature Comparison

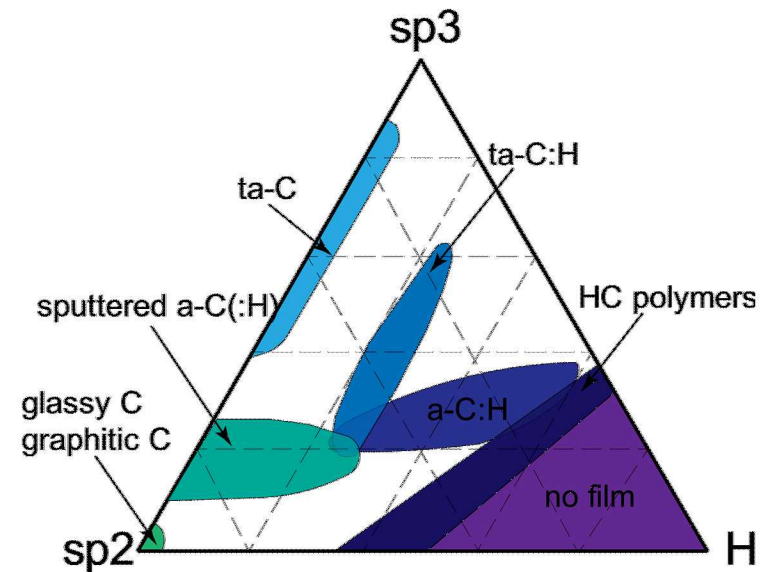
| solid lubricant                                      | deposition methods                    | $\mu_{ss}$         | $F_n$     | environment             |
|------------------------------------------------------|---------------------------------------|--------------------|-----------|-------------------------|
| graphite (sp <sup>2</sup> bonding)                   | evaporation, pyrolysis of HC polymers | 0.2 - 0.5          | 0.5 - 1 N | dry N <sub>2</sub> /UHV |
|                                                      |                                       | 0.1 - 0.2          | 0.5 - 1 N | humid air               |
| DLC (mixed sp <sup>2</sup> /sp <sup>3</sup> bonding) | rf and dc sputtering, ion beam, CVD   | 0.6 - 0.7 a-C      | 10 N      | dry N <sub>2</sub> /UHV |
|                                                      |                                       | 0.001 - 0.05 a-C:H | 10 N      | dry N <sub>2</sub> /UHV |
|                                                      |                                       | 0.1 - 0.2 a-C      | 10 N      | humid air               |
|                                                      |                                       | 0.2 - 0.3 a-C:H    | 10 N      | humid air               |

\* hydrogen content in a-C:H DLC can vary between 20-60 at %

\*\* sp<sup>3</sup> bonding in a-C:H DLC can vary between 20-65%

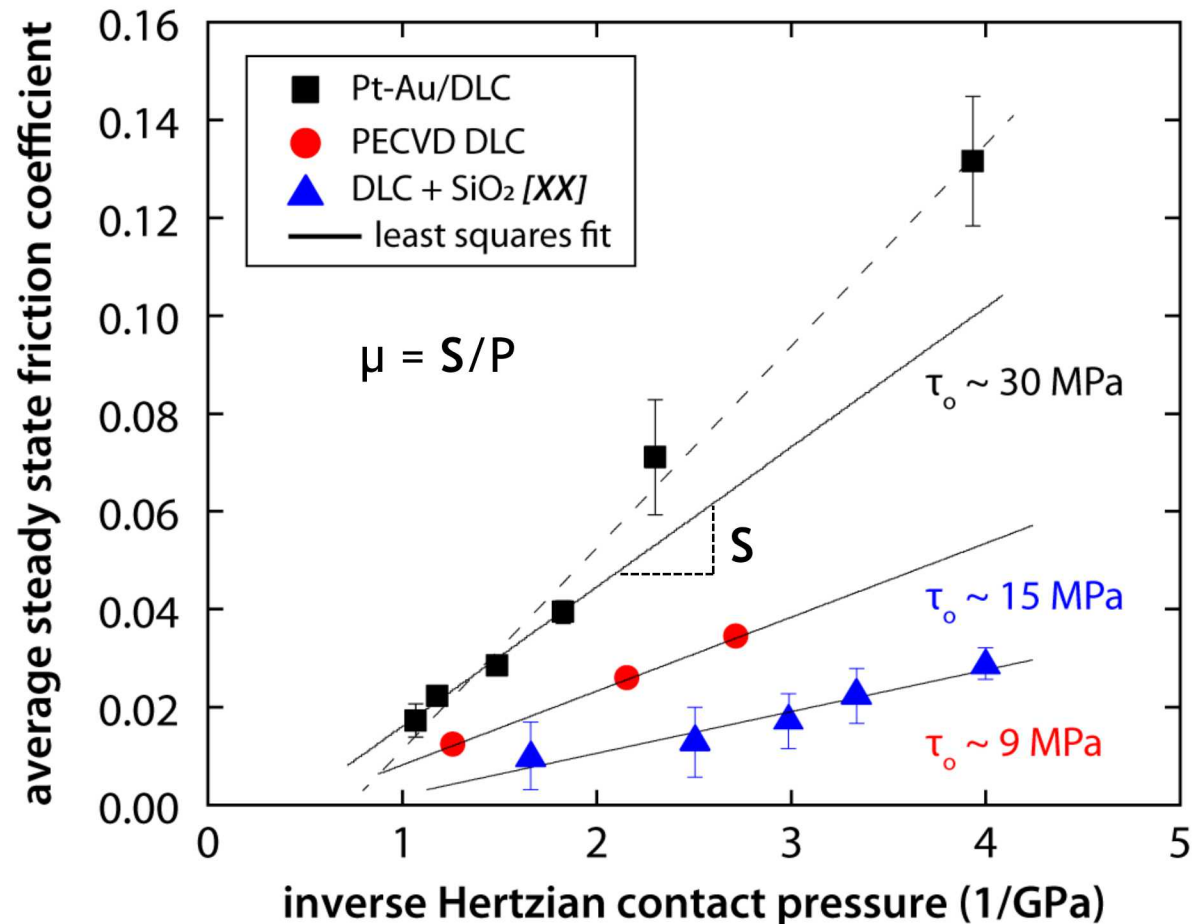
- Find similar behaviors for tribofilms generated on Pt-Au to DLC in literature

- Likely similar to polymeric tribofilms observed by McClimon et al (Trib Lett 2019)

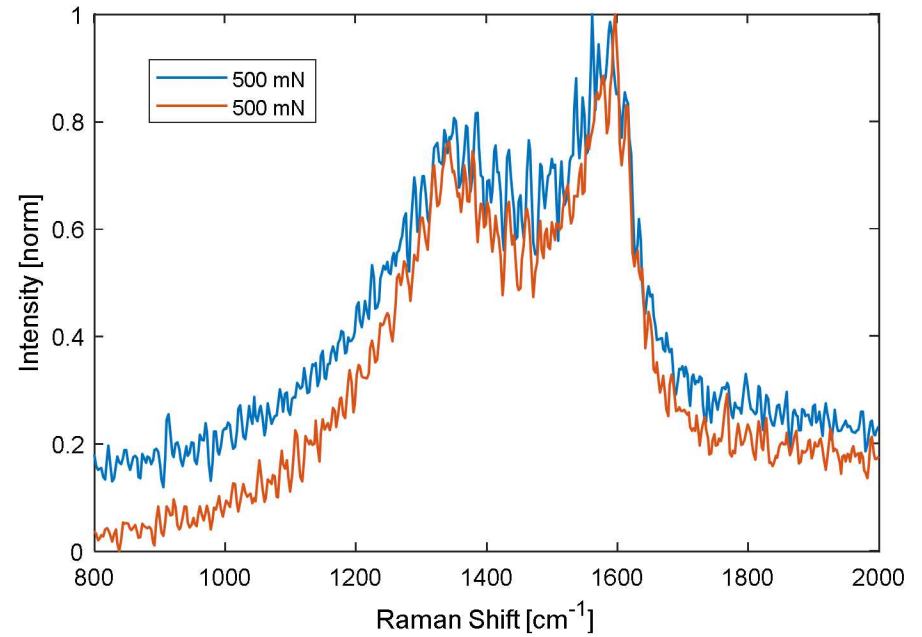
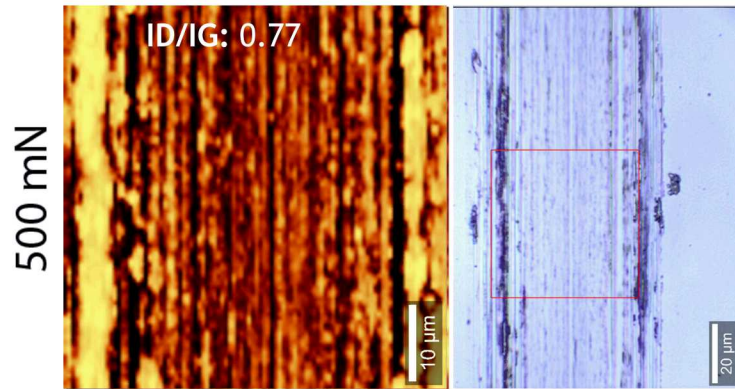


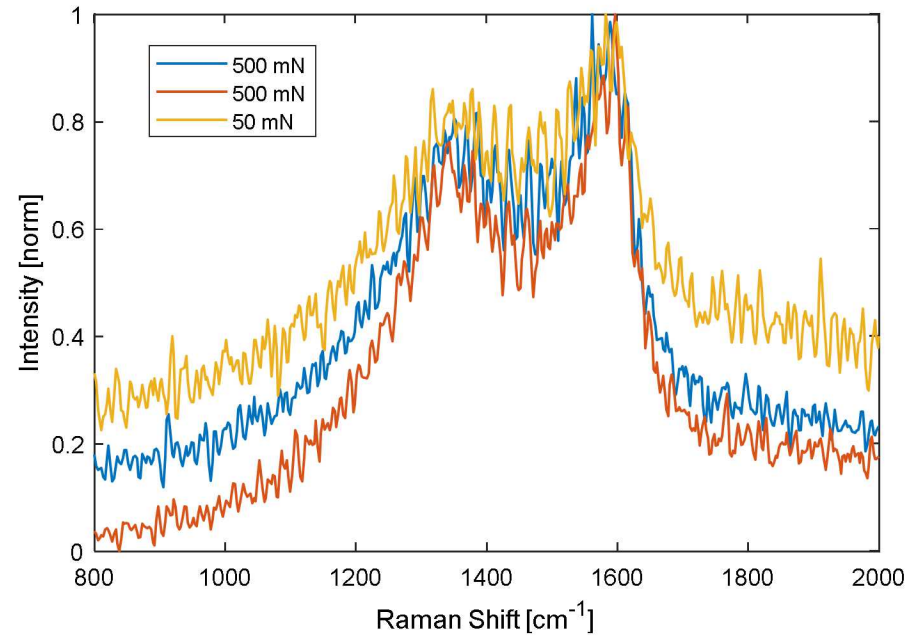
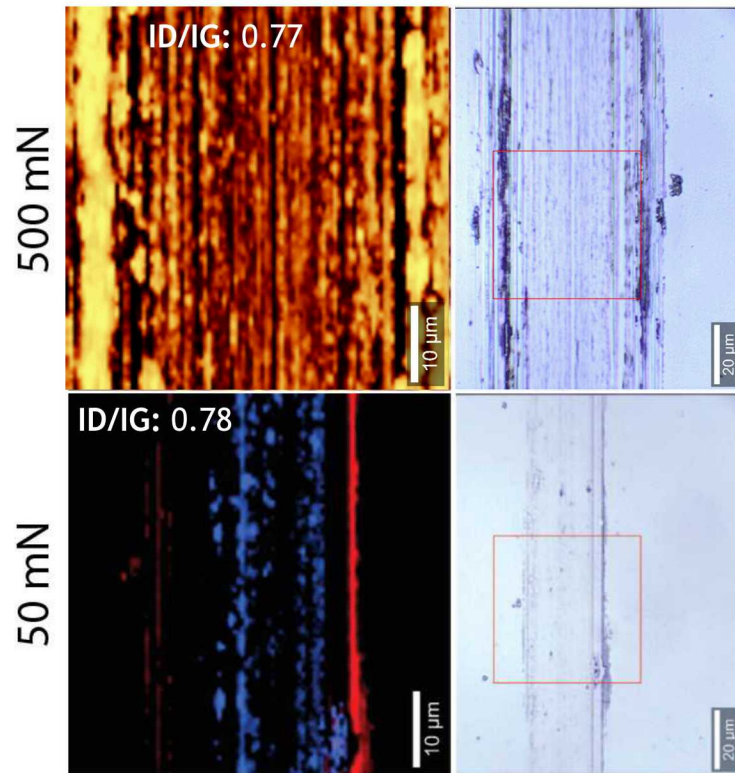
## Another Way to Qualify the “DLC” Tribofilm

- Can derive shear strengths from Hertzian contact model
- Shear strength comparable to commercially available
- Discrepancies may be due to composite nature of film and lower hydrogenation (20 vs 40%)



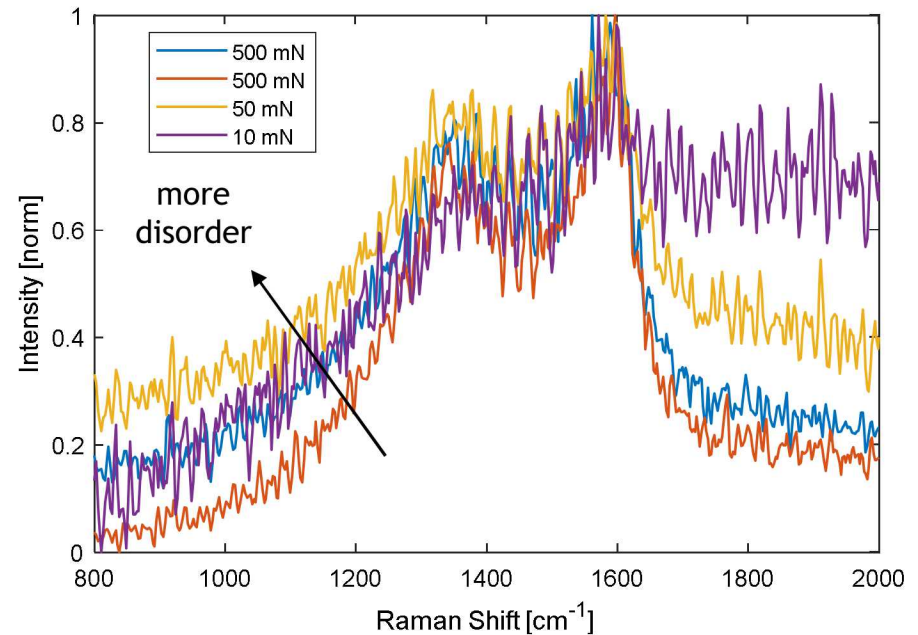
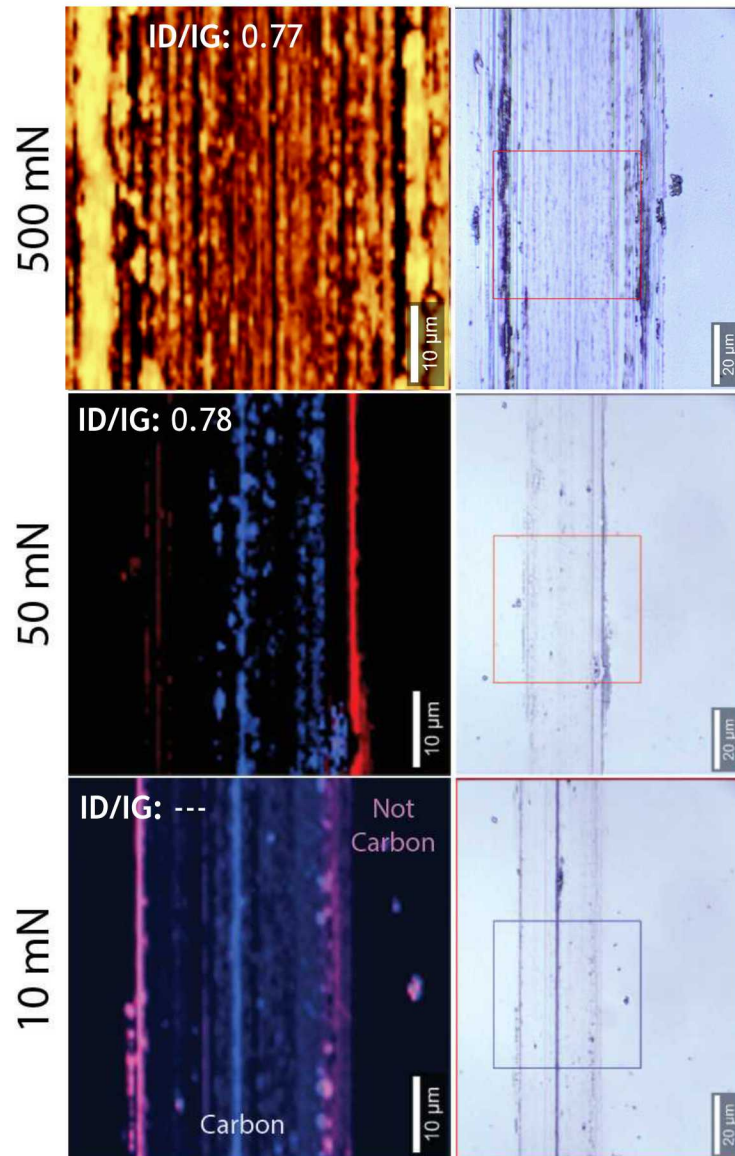






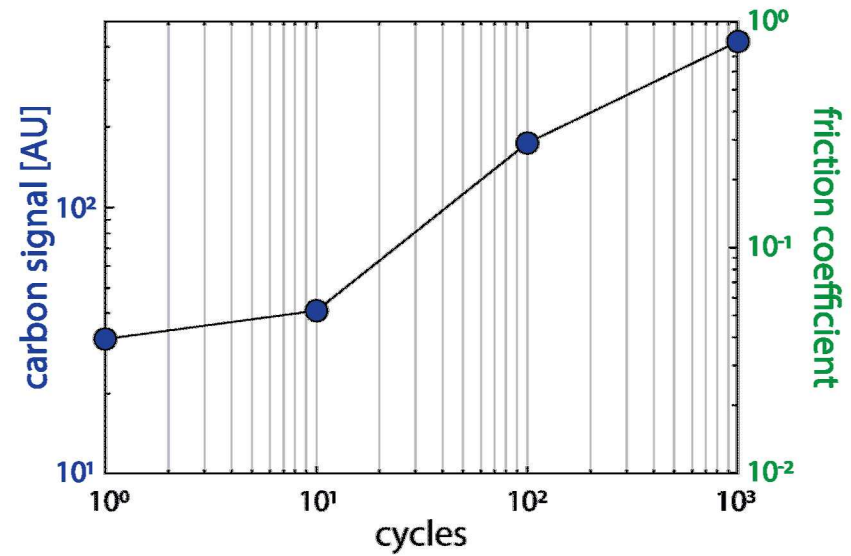
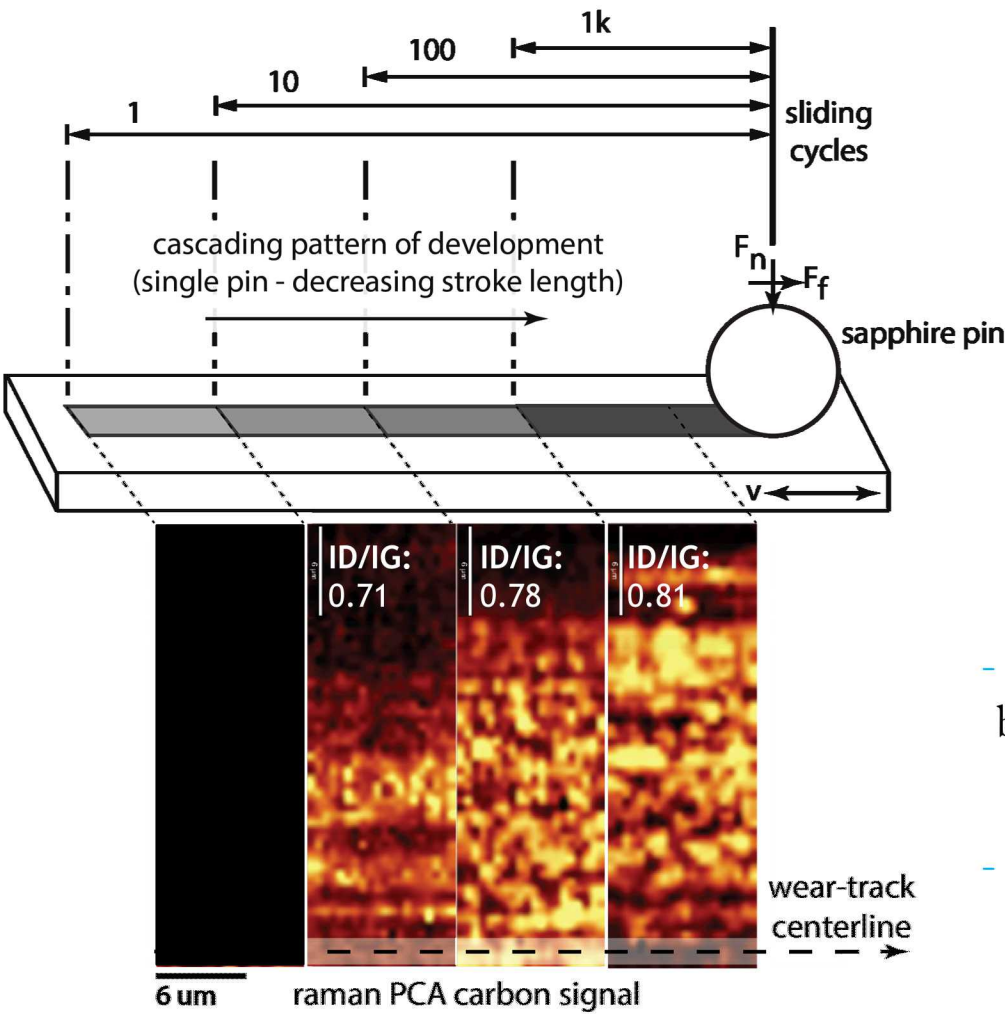
- Decreasing load leads to decreasing amounts of carbon coverage & lower signal to background

# Stress Dependent Formation



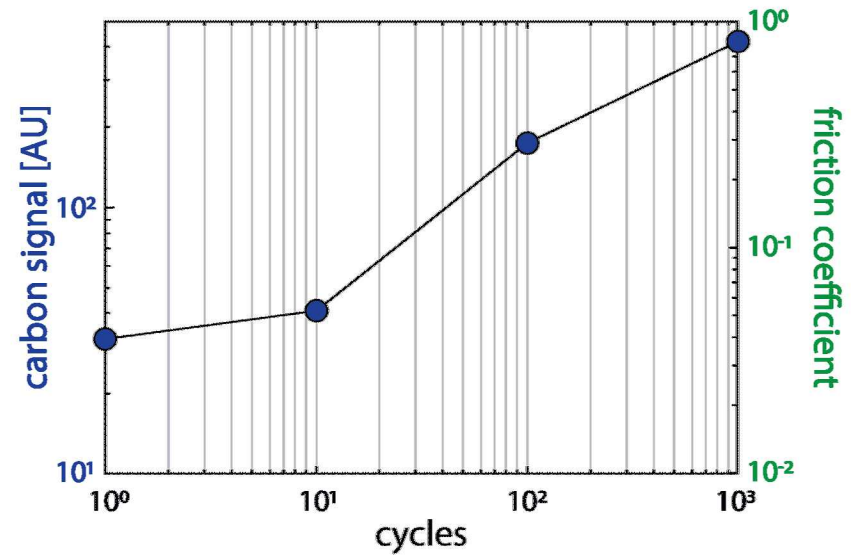
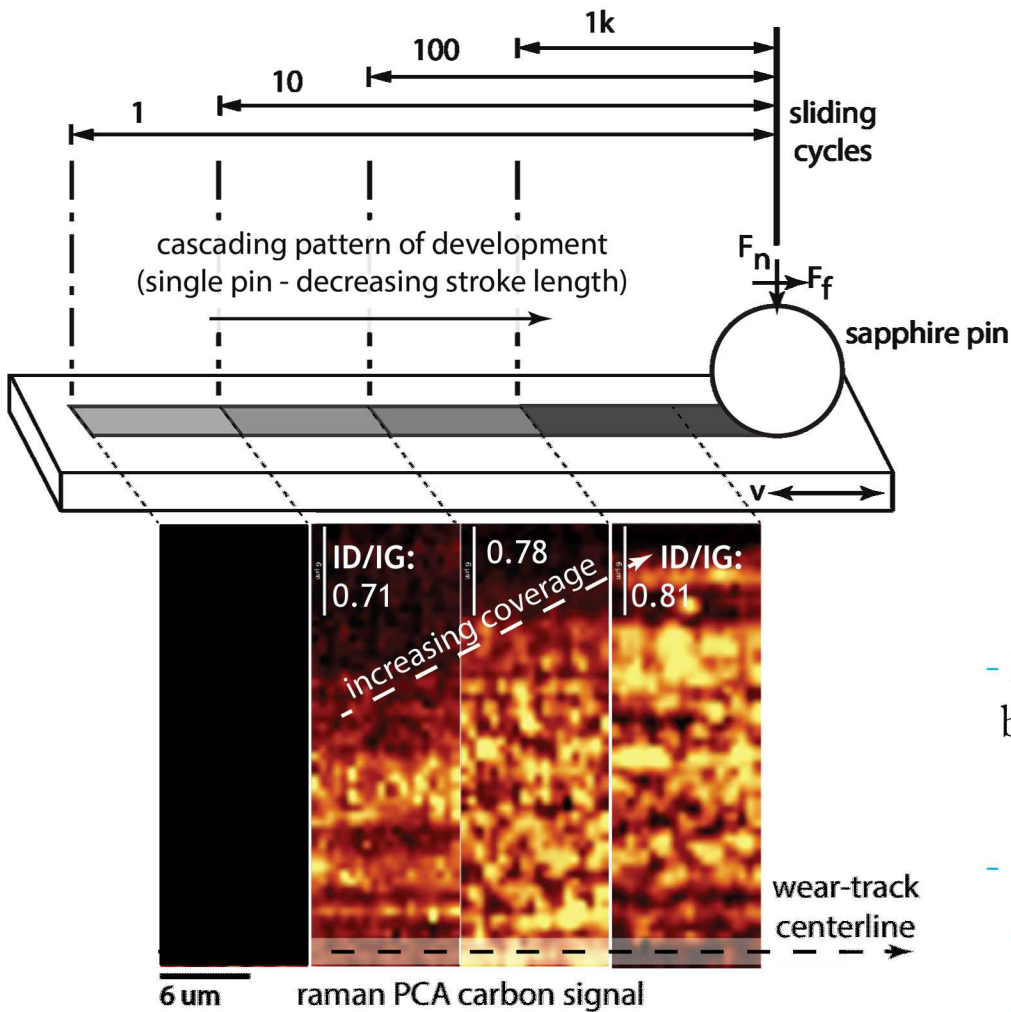
- Decreasing load leads to decreasing amounts of carbon coverage & lower signal to background

- Changes are small, but noticeable between differing lines w.r.t. greater disorder with decreasing load in spectrum

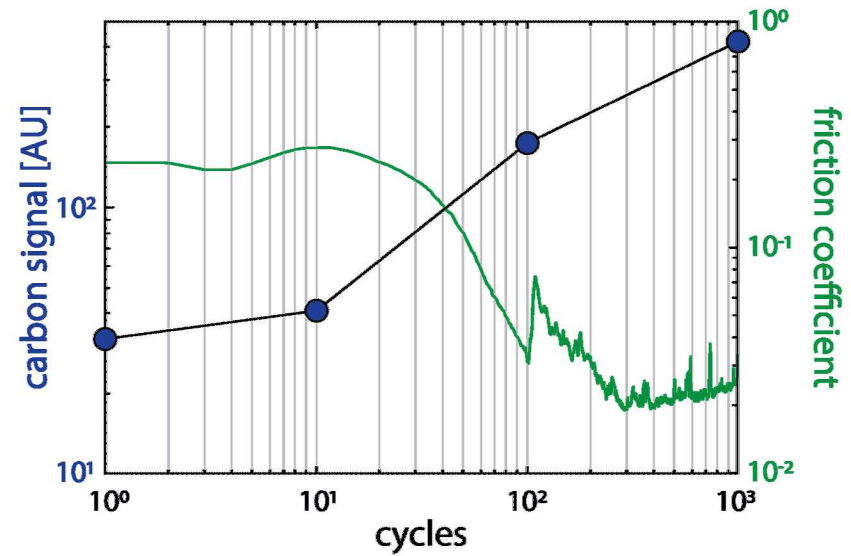
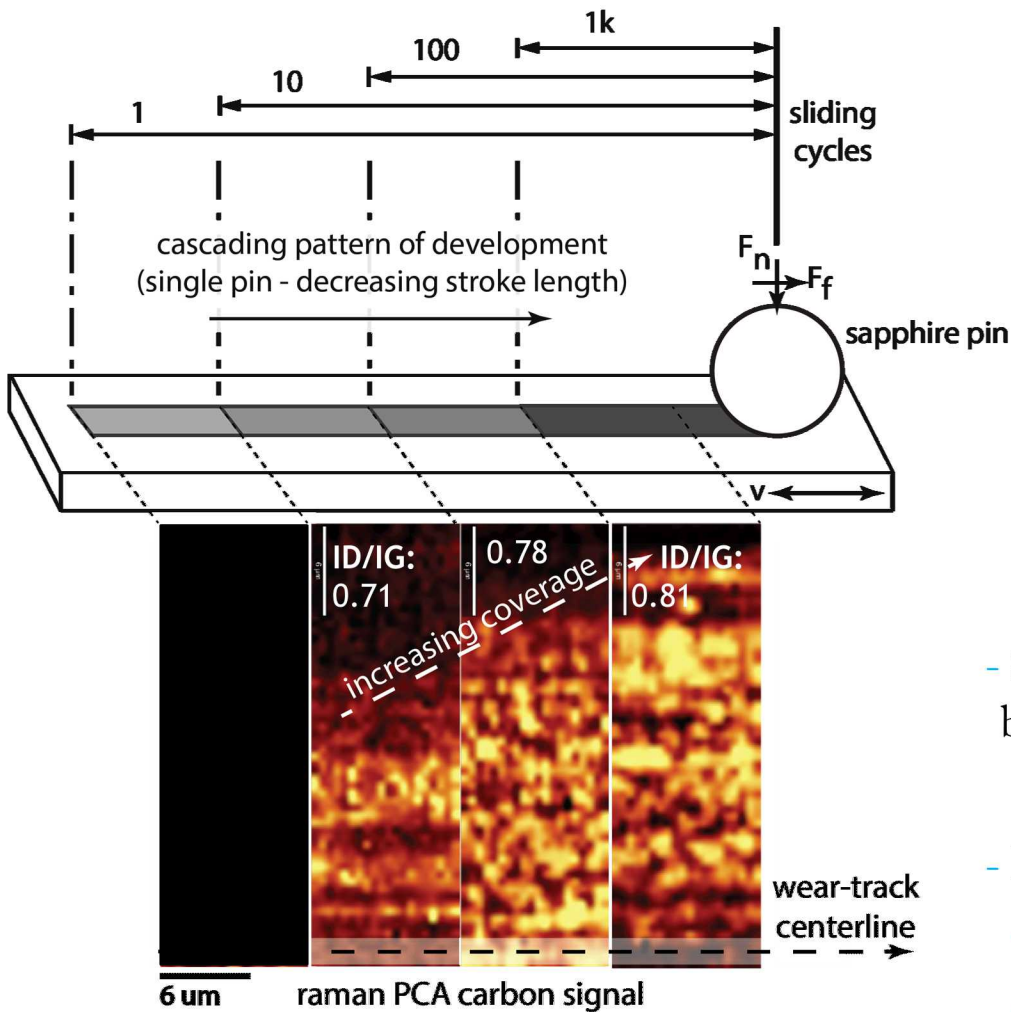


- Stripe tests elucidate time dependent behaviors
- Increasing cycle count leads to:
  - Stronger carbon signals in wear track



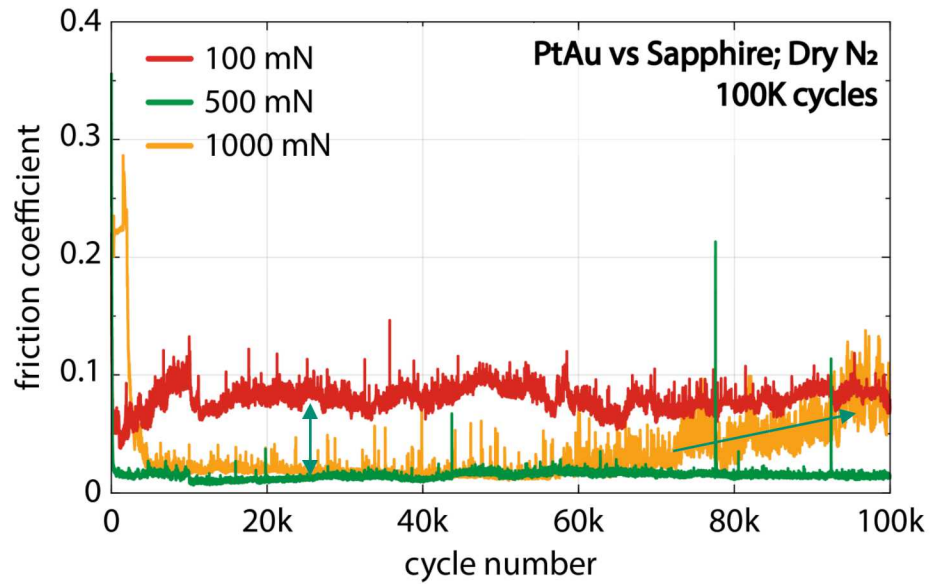


- Stripe tests elucidate time dependent behaviors
- Increasing cycle count leads to:
  - Stronger carbon signals in wear track
  - Higher coverage in wear scar



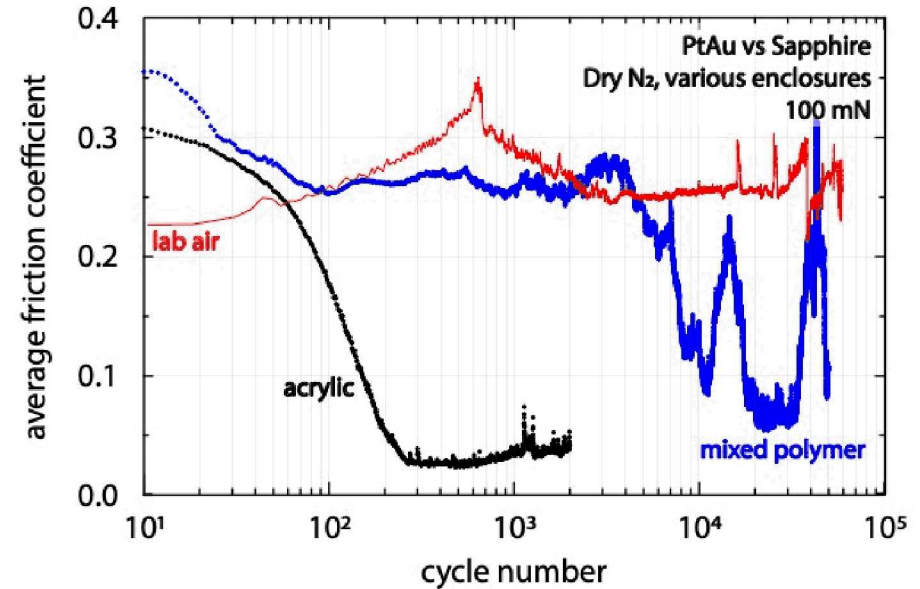
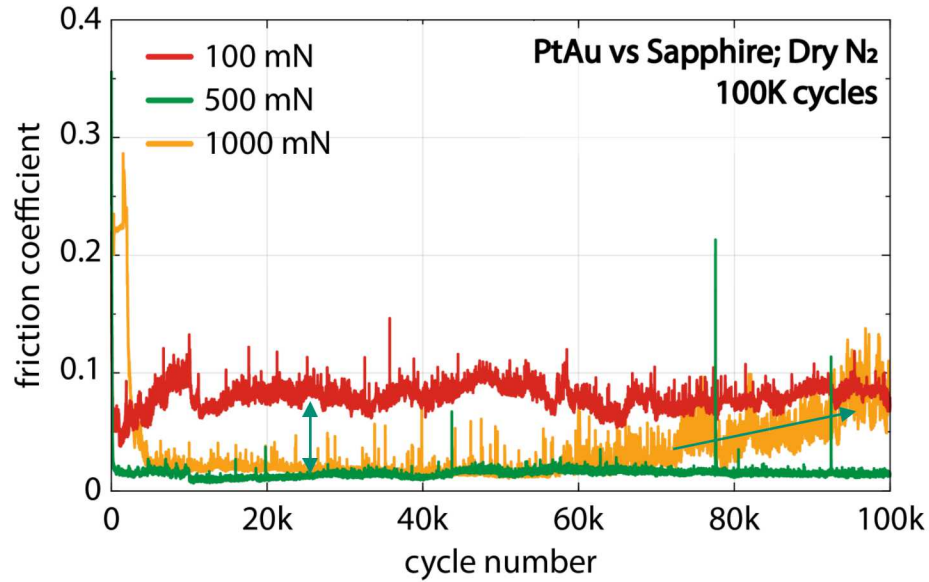
- Stripe tests elucidate time dependent behaviors
- Increasing cycle count leads to:
  - Stronger carbon signals in wear track
  - Higher coverage in wear scar
  - Decreasing friction coefficient

## Thresholds: Load



- Long cycle (100k) studies reveal changing behavior for each load; apparent threshold between 0.1-1N

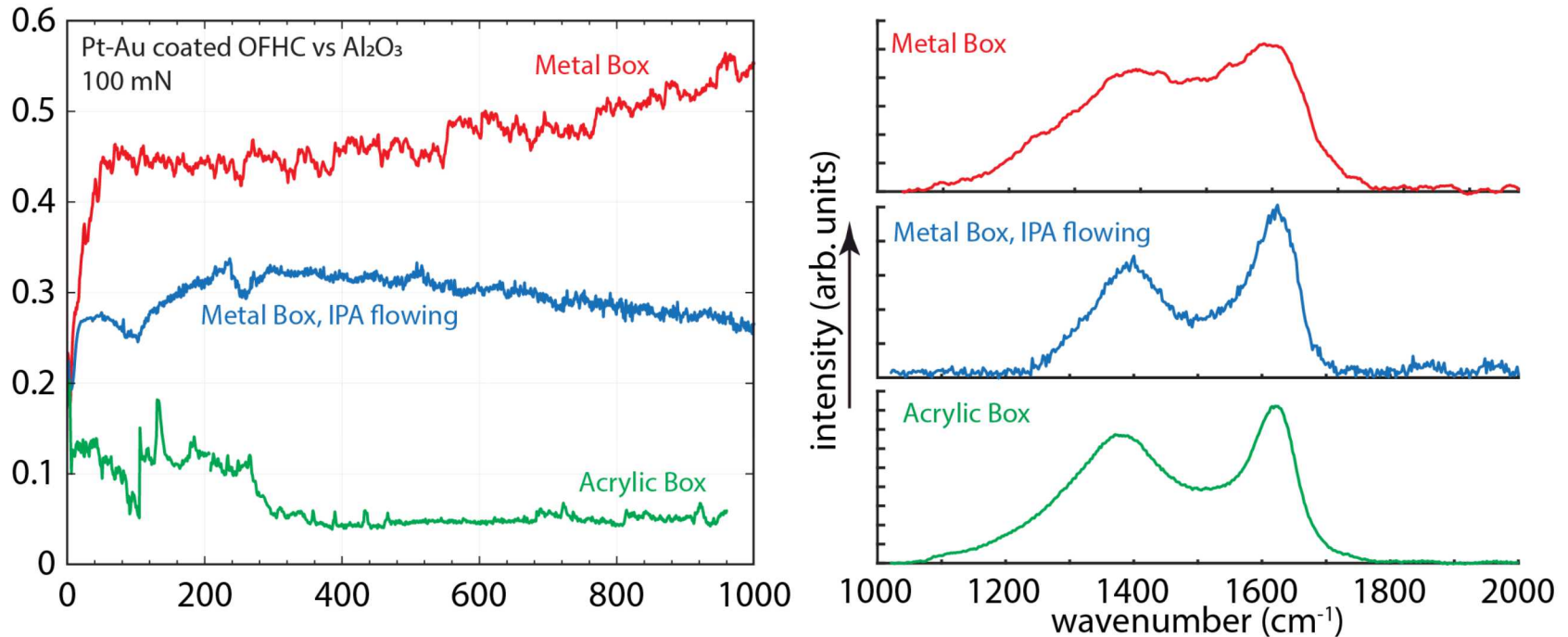
## Thresholds: Load & Composition



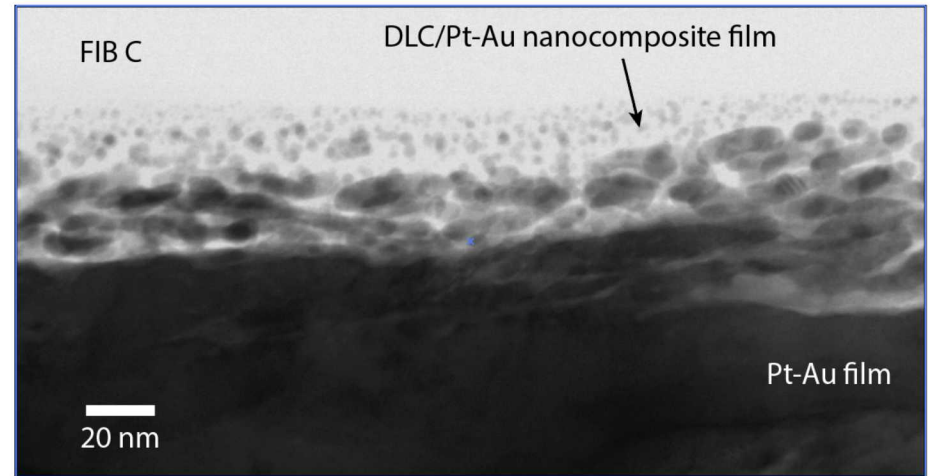
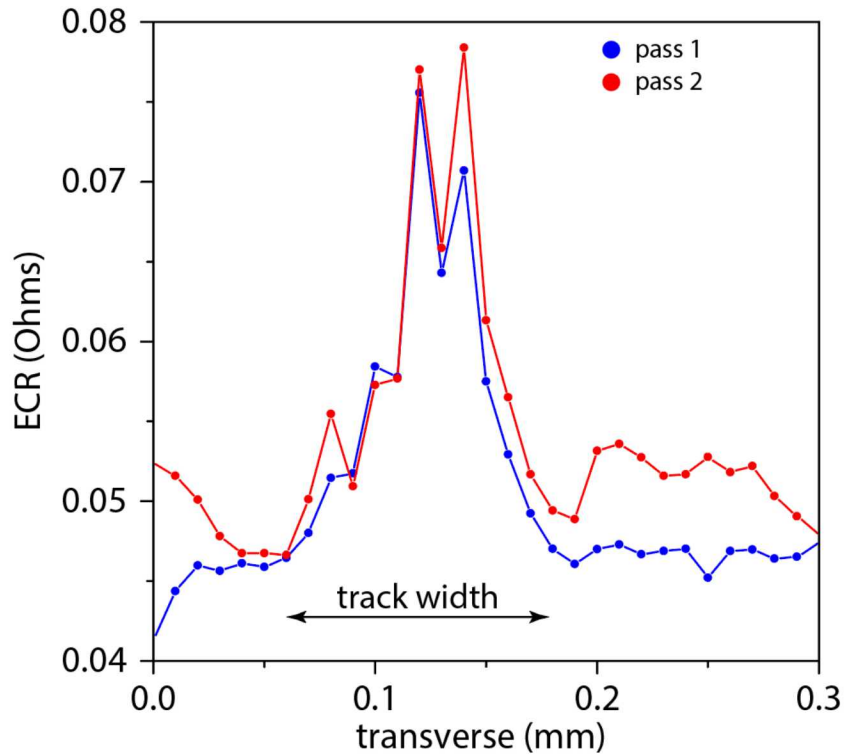
- Long cycle (100k) studies reveal changing behavior for each load; apparent threshold between 0.1-1N
- Even in other plasticized enclosures, formation can be prolonged and in some cases not form



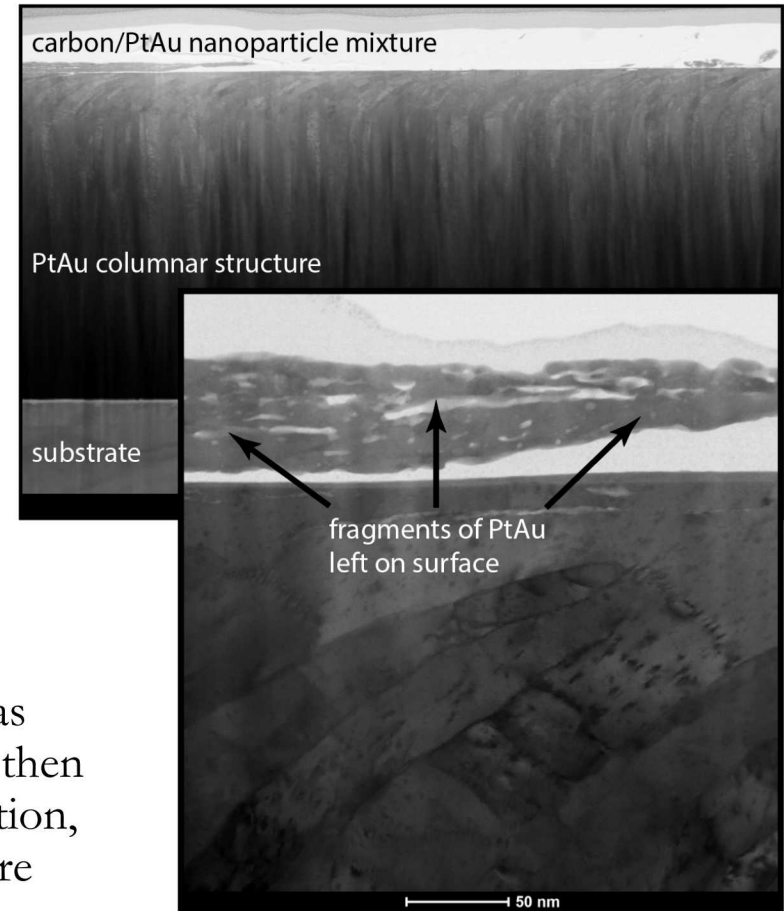
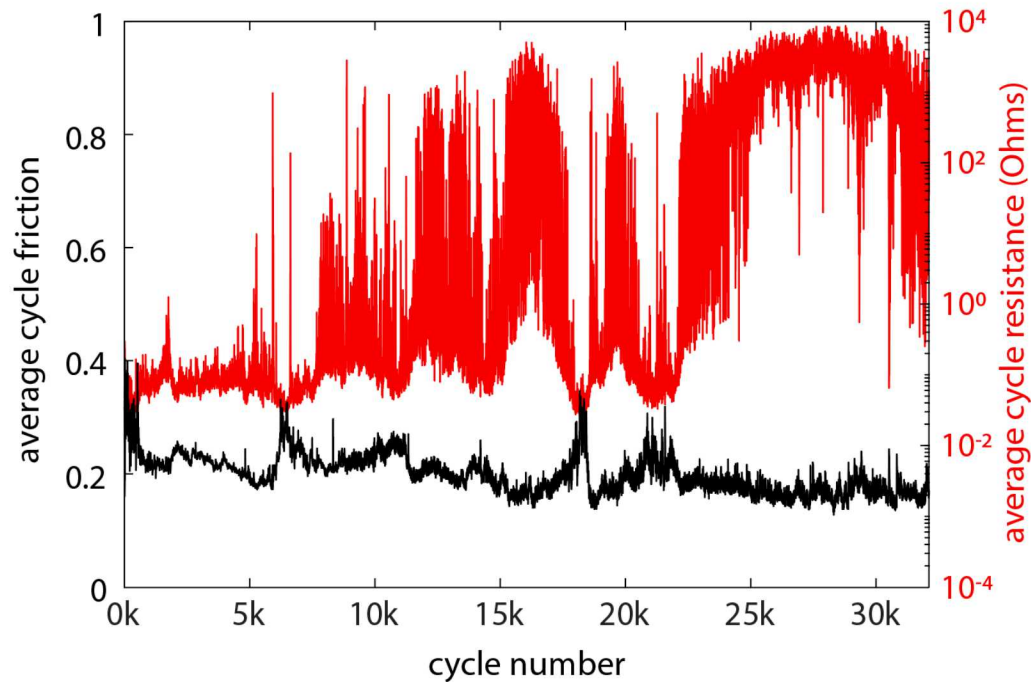
## Separate Lab Formation Study (Lehigh U)



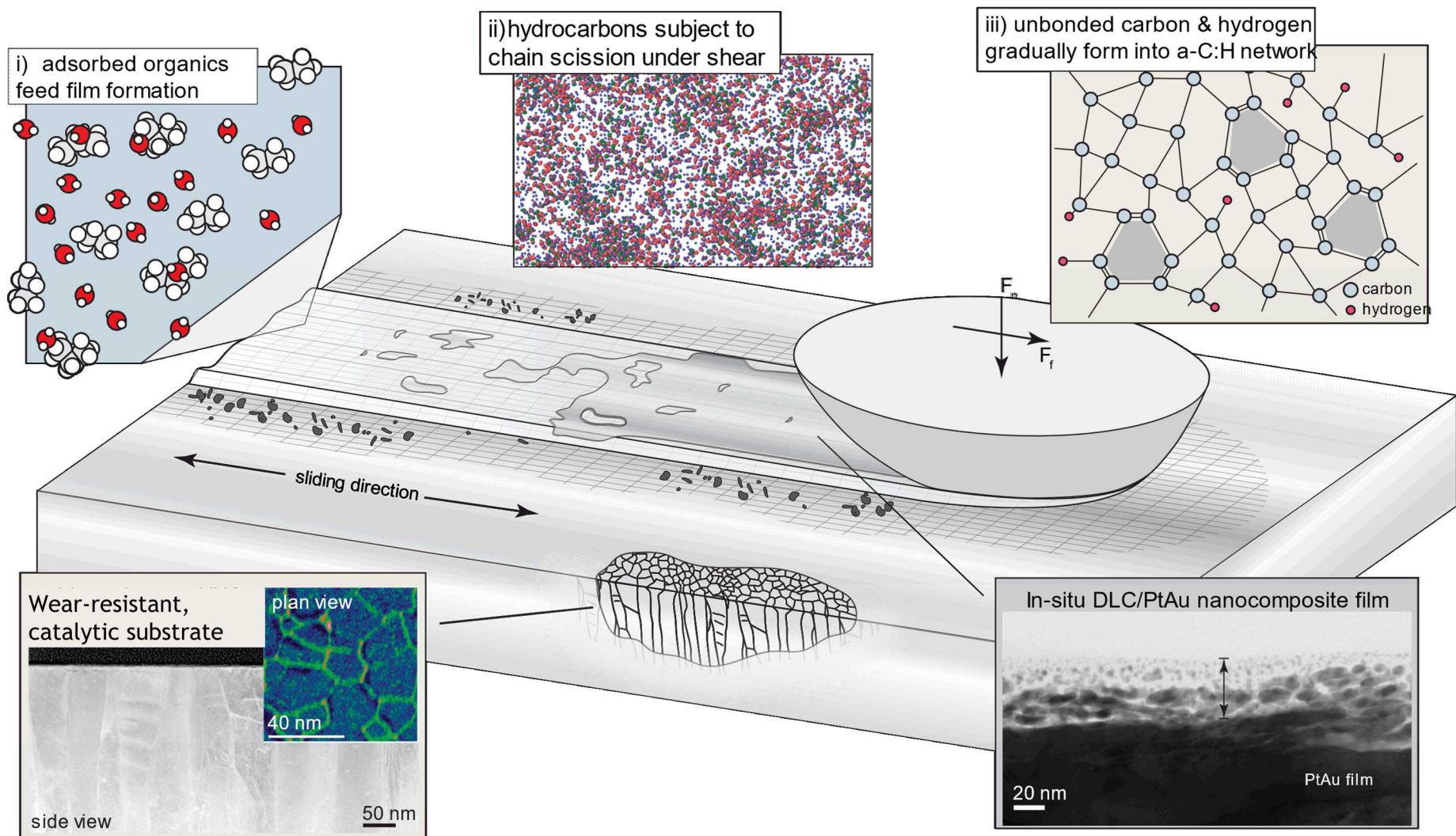
- Lehigh U Tribology laboratory able to form films only in acrylic enclosures
- Metallic enclosures still formed carbonaceous deposits and mixed lubrication when flowing IPA



*Low friction tracks ( $\mu < 0.05$ ) formed vs sapphire are conductive!*

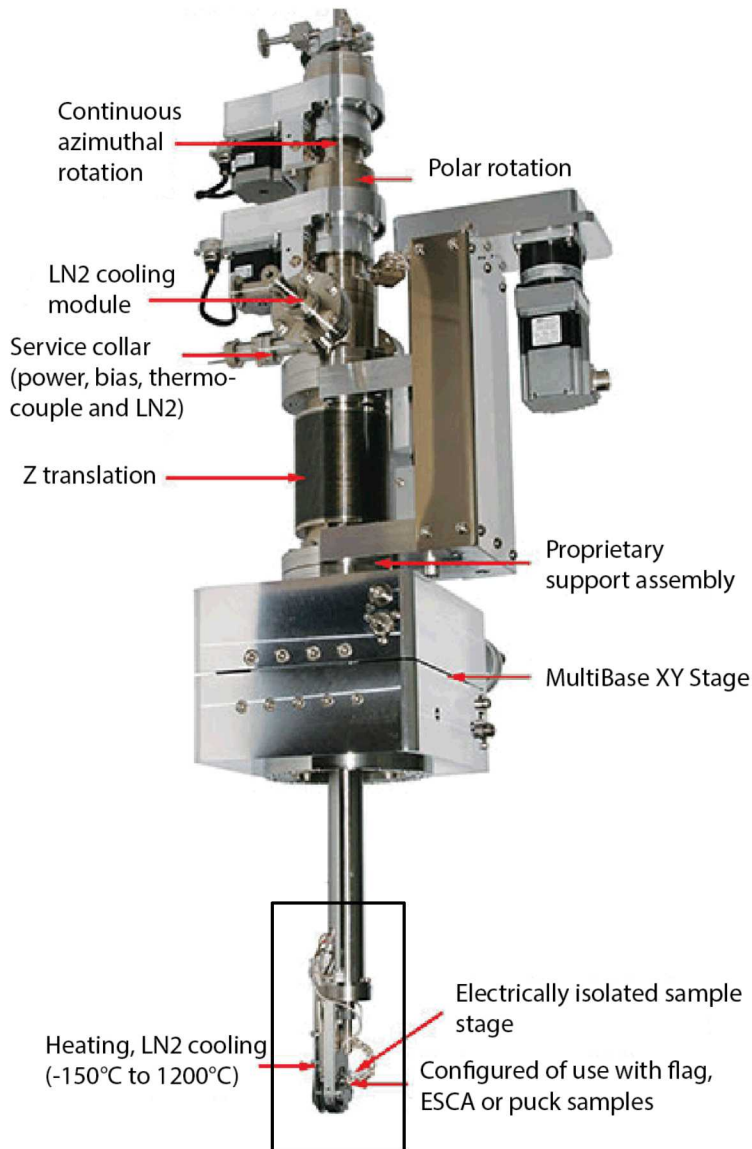


hard gold alloy vs. PtAu showed increased resistivity as carbon film grew over 30k cycles. Starts at  $\sim 20 \text{ m}\Omega$ , then experiences drastic increase at  $\sim 7\text{k}$  cycles. TEM, friction, and ECR shows much different behavior than sapphire on PtAu.





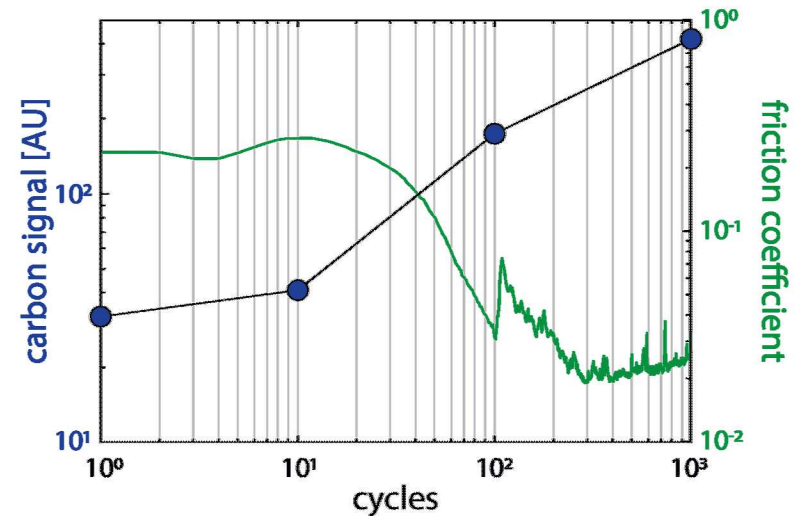
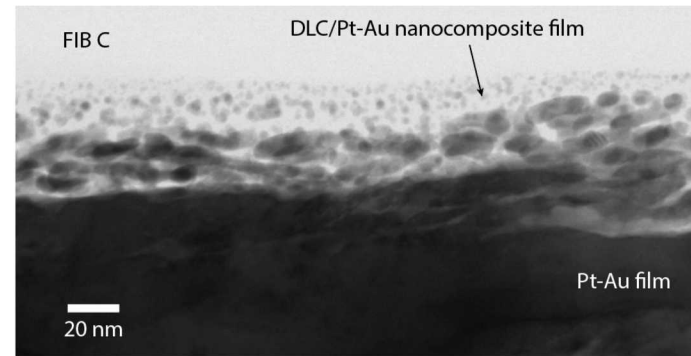
## Next Steps: In Situ Characterization



- 5-axis vacuum manipulator with analytical stage
- Designed to fit under various probes (and beamlines)
- Developed mini tribometer to fit underneath
  - Piezo flexure loading; Si strain gages for force sensing
  - Flag style sample grips; rotatable head for multiple tests
  - Modular design with adaptable stiffness flexures
  - **Enable novel in-situ experiments; portable system**

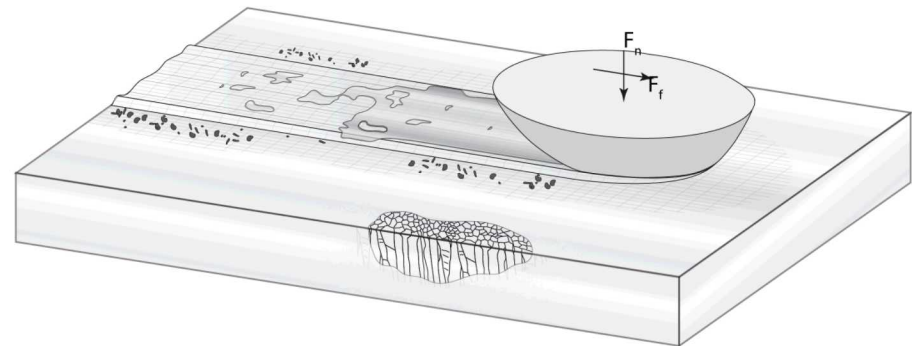
## Outcomes

- DLC-like tribofilms with Pt-Au nanoparticles observed in TEM
- Raman, ERDA & friction behavior suggest formation of DLC-like tribofilm
- Observable shear strengths similar to H-DLC & load/sliding history dependent formation mechanisms



## Future Work

- Understand the chemistry: In situ studies to observe formation processes, ideal loads, species for formation
- Assess relationship between growth rate, temperature for activation energies and reaction rates



# Thanks!

